Influence of Geology and Anthropogenic Activity on the Geochemistry of Urban Soils

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ABSTRACT

The concentrations of twenty two elements have been determined in urban soils from two locations: the London Borough of Richmond-upon-Thames, a non-industrial, mainly residential area of approximately 56km^2, and Wolverhampton an industrial city in the West Midlands of 70km^2. Soil samples were taken on a grid basis at a density of four per km^2 and analysis for elements was carried out by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). GIS based mapping techniques used in conjunction with statistical analysis of the data have highlighted the influence of land-use on the concentrations of a suite of elements in both study areas. Concentrations of Pb, Zn, Cu, Ni, Na, Be, Ca, Sr, Ba, Al, V, Cr, Co and P are observed at significantly higher concentrations in garden soils compared with soils from areas of open space in Richmond-upon-Thames. These elements have several anthropogenic sources in towns and cities. In Wolverhampton, soils from industrial areas have significantly higher concentrations of Pb, Zn, Cu, Cd, Ni, Mg, Ca, Cr and Fe than soils associated with the other land-uses in the city. It is postulated that this is the result of processes using these metals in industrial areas and the composition of the made ground which underlies much of the industrial area.

Normalisation of data from Richmond and Wolverhampton, as designated by parent material, land-use and sample depth, to data published in the Soil Geochemical Atlas of England and Wales (McGrath and Loveland, 1992) has shown the importance of parent material as a factor influencing concentrations of a number of elements in urban soils. In Richmond, low ratios are observed for clay-associated elements such as K, Mg, Al and Mn, irrespective of land-use or parent material, probably due to the dominance of the sand fraction in soils. However, soils overlying alluvium in Richmond have significantly higher concentrations of Na, V, Mn and Fe than soils overlying London Clay and the high level terraces. This may be a result of differences in the natural geochemical signatures for soils developed on these deposits, or greater anthropogenic additions to soils overlying deposits of alluvium. Normalisation has also shown that garden soils generally have concentrations of Zn and Cu two times higher than those reported as median concentrations for the soils of England and Wales (McGrath and Loveland, 1992). Concentrations of Pb in urban gardens from Richmond can be as much as twelve times higher than those reported as median concentrations for the soils of England and Wales (McGrath and Loveland, 1992).

Soils overlying the Triassic sandstones which outcrop in the west of Wolverhampton generally have lower concentrations of a suite of elements than soils overlying the clay-rich glacial-till. This is probably the result of the geochemical signature for the sandstones, with naturally low concentrations of elements and the location of these soils in the west of the city, several kilometres from the industrial base. For soils overlying glacial-till, concentrations of K, Mg, Al and Mn are very consistent, irrespective of land-use, with concentrations of Na, K, Mg and Al consistently higher at depths of 30-45cm compared to 0-15cm for this parent material, again irrespective of land-use. On average, soils in industrial areas overlying glacial-till have concentrations of Pb, Zn and Cu 3, 3 and 6 times higher, respectively than median concentrations reported for the soils of England and Wales (McGrath and Loveland, 1992). In industrial areas overlying made ground, these ratios are 4, 5 and 10, respectively.

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Libraries gave us power

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LIST OF ABBREVIATIONS AND UNITS

Li	lithium	Na	sodium	K	potassium
Rb	rubidium	Be	beryllium	Mg	magnesium
Ca	calcium	Sr	strontium	Ba	barium
Al	aluminium	La	lanthanum	Ti	titanium
V	vanadium	Cr	chromium	Mo	molybdenum
Mn	manganese	Fe	iron	Co	cobalt
Ni	nickel	Cu	copper	Ag	silver
Zn	zinc	Cd	cadmium	Pb	lead
P	phosphorus	As	arsenic	Hg	mercury

AM	Arithmetic Mean
ANOVA	Analysis of Variance
CEC	Cation Exchange Capacity
DIW	Deionised Water
GM	Geometric Mean
HRM	In-house Reference Material
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectrometry
LOI	Loss-on-Ignition
MAFF	Ministry of Agriculture, Fisheries and Food
N	Sample Number
SD	Standard Deviation
USDA	United States Department of Agriculture
WHO	World Health Organisation
cm	centimetre
km	kilometre
m	metre
ppm	parts per million (= μg/g, μg/g^{-1} and mg/kg)
μg/g	microgram per gram (= ppm, μg/g^{-1} and mg/kg)

CHAPTER ONE INTRODUCTION TO THE RESEARCH AND OBJECTIVES

1.1 Introduction

Urban environments, through a wide variety of anthropogenic activities, constitute sources of contamination by many elements. These activities generally result in waste substances which may reach soils, and result in increased concentrations of a number of elements in the surface environment (see chapter 3). The urban environment thus provides a complex and fascinating area of research. Each town or city has a specific economic, social and industrial history which is strongly influenced by geographical location, topography and proximity to mineral deposits. These factors are integral to the industrial development of a town or city, and hence the anthropogenic processes that occur there, which probably date back, at least, to the industrial revolution.

Mining and smelting processes, and metallurgical industries are the sources of many metals (MAFF, 1986) through the emission of aerosols and dusts, liquid effluent and the creation of waste dumps (Alloway, 1995). The combustion of fossil fuel, both in association with industrial activity and in domestic fires, results in the dispersion of a wide range of metals, whilst the use of leaded petrol is an important, although declining, source of Pb in the urban environment. Other industrial sources include the manufacture, use and disposal of electronics equipment, batteries, pigments and paints, and printing and medical equipment (see chapter three). Site specific sources of metals occur in urban areas, which again depend on the industrial nature of the area (various chemical industries) and the practices of the individual householder (with the application of fertilisers and the disposal of ash).

Investigations of trace metal concentrations in urban soils have a history of approximately thirty years. These are reviewed in detail in chapter three. Most of these studies have concentrated on measuring heavy metal contamination in specific locations such as roadside soils (Yassoglou *et al.,* 1987 and Ndiokwere, 1984) and urban garden soils (Purves, 1967; Purves and Mackenzie, 1969; Warren *et al.,* 1971 and Davies, 1978). The most detailed study of metals in urban dusts and soils in Britain, to date, was undertaken in the early 1980's. The study was commissioned by the Department of the Environment and involved an investigation of 100 towns and cities in Britain, with soil samples taken from the top 2cm of exposed garden beds (Culbard *et al.*, 1983; Thornton *et al.*, 1985; Culbard *et al.*, 1988 and Thornton 1989 - see section 3.5.3 for details and results).

This multi-element study of soils in Richmond-upon-Thames and Wolverhampton is probably the most detailed urban study of its kind in Britain, although similar studies have been undertaken in Warsaw (PIG, 1992) and Berlin (Birke and Rauche, 1994), as it involves sampling soils, on a grid basis (see section 5.3.1), across the entire area of these towns and cities. Such a sampling scheme allowed an investigation of the different land-uses in the two study areas as well a number of different parent materials. These are two important factors which influence concentrations of many elements in soils.

Two contrasting study areas were selected because they varied greatly in terms of land-use and industrial history. Richmond-upon-Thames has a very limited industrial history, with very few industries existing historically or today, a large residential population and a large amount of open space. In contrast, Wolverhampton has an extensive history of industrial activity, particularly metal processing works, with a large residential population and very little open space. Wolverhampton has undergone a great deal of change during the latter part of this century, fuelled by the industrial decline of the city and redevelopment of many of the industrial areas for housing and leisure facilities (Kelly *et al.*, 1996). Despite this, some industry remains in Wolverhampton today. The geology of the two areas also differs (see sections 4.5 and 4.7) facilitating an interesting comparison.

1.2 Objectives of the Research:

1. To investigate the spatial distribution of 21 elements in topsoils (0-15cm) in Richmond-upon-Thames and Wolverhampton.

2. To assess the influence of anthropogenic factors, particularly land-use, on the

distribution of 21 elements in the study areas.

3. To investigate if the underlying geology exerts an influence on the distribution of elements in soils in the study areas.

4. To compare and contrast multi-element data for soils in the study areas with the large data set for soils in England and Wales (McGrath and Loveland, 1992).

5. To compare and contrast multi-element data for two very different urban areas in England.

1.3 Thesis layout.

Chapters two and three comprise a review of the literature. Chapter two examines the natural sources of metals in rocks and soils, the factors which influence soil development and the characteristics of urban soils. Chapter three is a review of the uses of metals and other elements, trace metal emissions and deposition rates, reported concentrations of metals in soils in relation to various anthropogenic activities, and reported concentrations of metals in urban dusts and soils around the world. In chapter four, the sample areas are described in detail, particularly their industrial history, land-use and geology. In chapter five the sampling and analytical procedures are described with a very detailed examination of the data quality; robust ANOVA is applied to estimate the amount of sampling and analytical error.

Chapters six and seven present and discuss results for data from Richmond-upon-Thames. In chapter 6 the spatial distributions of 21 elements in topsoils are described, with an examination of the influence of land-use on metal concentrations and a comparison with other results reported for urban areas. In chapter seven a comparison is made between the Richmond data and those published for soils in the Soil Geochemical Atlas of England and Wales (McGrath and Loveland, 1992), in relation to land-use and parent material. A statistical analysis is undertaken to see if parent material is a significant factor influencing the concentrations of elements in soils from Richmond. The influence of house-age in

Richmond as a factor influencing the concentration of elements is also examined and comparisons are made with data from the National Reconnaissance Survey of metals in urban dusts and soils.

In chapter 8 the spatial distribution of 21 elements in topsoils from Wolverhampton is described. The spatial distribution of Pb, Zn, Cu and Cd is also examined in subsurface soils (30-45cm). An examination is made of the influence of land-use, and a comparison is made with the data from Richmond and other published urban data sets. In chapter nine a comparison is made with the data set for soils in England and Wales (McGrath and Loveland, 1992) to investigate the influence of geology and land-use on multi-element concentrations. House-age is also examined to see if this is a significant factor influencing the concentration of elements in soils from Wolverhampton, and comparisons are made with data from the National Reconnaissance Survey of metals in urban dusts and soils (Culbard *et al.,* 1983; Thornton *et al.,* 1985; Culbard *et al.,* 1988 and Thornton *et al.,* 1989).

In chapter ten the conclusions from the research are listed along with the recommendations for future work.

CHAPTER TWO NATURAL SOURCES OF ELEMENTS IN ROCKS AND SOILS

2.1 Metals in rocks and soils: isomorphous substitution

Trace metals occur as minor constituents of primary minerals in igneous rocks and they become incorporated into minerals by means of isomorphous substitution (Alloway, 1990b). This is very similar to isomorphism which is the crystallation of different compounds in the same structural type on the basis of similar size lattice constituents (Wedepohl, 1971). The same effect allows the mutual substitution of two or more atomic species in a crystal lattice. These substitutions are governed largely by valency and ionic radii, although electronegativity and, in the case of the first row transition elements, crystal field stabilisation energies are also important (Plant and Raiswell, 1983). Elements do not need to exhibit an identical ionic charge or radius to permit substitution and Krauskopf (1967) states that a substitution can occur when the charges differ by 1 and the radii of the constituent ion and substituting element differ by less than 15%. However, Golschmidt presented two empirical rules that reflect the size and charge controlled substitution of atoms and ions:

1. If ions of equal charge and similar size compete for the same lattice site, the one with the smaller radius will be preferred.

2. With ions of the same size the one with the higher charge will be preferentially substituted into the crystal. The excess charge can be balanced by substitution of an ion with a lower charge in a different lattice position, although exceptions do occur such as with feldspars where substitution is limited to certain positions producing a super-structure (Wedepohl, 1971).

Table 2.1 shows some ionic properties for both major and trace elements and from this it is possible to see why certain substitutions occur (Jenkins and Jones, 1980). Major elements are shown in bold, and the association of Pb^{2+} with K^{2+} and Zn and to a lesser extent Cu with Mg/Fe^{2+} are clearly shown.

2.2 Specific rock types and elements

Although igneous rocks account for 95% of the earth's crust, they are generated at high temperature and pressure which are the antithesis of conditions at the surface of the earth. Weathering results, with changes in conditions on exposure and the resulting sediments are converted to sedimentary rocks through biological action, ion exchange, recrystallization and cementation (Sposito and Page, 1981). Table 2.2 shows the concentrations of selected elements in abundant rock species and continental crust (Wedepohl, 1991). Igneous rock types include granite, granodiorite, basalt, gabbro and quartz diorite, and the element content of these is dependent on the composition of the melt from which the rock crystallises. In the group classified as igneous rocks two major divisions exist: the basic igneous rock known as basalt and the acid igneous group termed granite. The fundamental differences between these two groups is that the acid granite rocks are enriched with Be, Pb, Li, Th and U whilst the basic rocks have higher concentrations of Fe, Cd, Cr, Co, Cu, Mn, Ni, V and Zn (Sposito and Page, 1981 - see Table 2.2).

Sedimentary rocks account for approximately 75% of rocks that outcrop at the surface of the earth, illustrating their importance as soil parent material (Alloway, 1990b). These rocks are formed primarily by hydrological and glacial weathering of igneous rocks, and in essence, therefore, the element content should be similar to that of the parent igneous rock because of the same mineral composition (West, 1981). However, the common rock forming minerals can vary considerably in their susceptibility to weathering, with minerals such as olivine and hornblende easily weathered, albite and garnet being moderately stable and quartz very resistant to weathering (Mitchell, 1964). As a result the first sedimentary rocks to form are rich in secondary minerals and bioessential elements from basic rocks, with weathering breaking down the original lattice and the bioessential elements deposited in the hydrolysate matrices of elements of high ionic potential such as Si, Al and P.

Shales and clays account for 80% of all sedimentary rocks and these tend to have relatively high concentrations of many elements due to their large specific surfaces which have high cation exchange capacities. Although secondary minerals such as illite and kaolinite substitute Zn, Cr and Mn into their layer lattices these elements are more readily available than the corresponding lattice held ions, so, despite the fact that values for shales and clays may not be greatly different from those of rocks such as granite, (see Table 2.2) the increased availability of the elements in clays and shales is reflected in soils associated with these parent materials. A very specific type of shale is black shale which has naturally high concentrations of metals due to its mode of formation. In certain cases acid seepages from peat swamps into shallow seas just after sedimentation produced acid conditions conducive for the retention of molybdenum by marine or terrestrial organic matter. The organic matter acts as both an adsorbent for metals and also as a substrate for microorganisms. In other circumstances submarine hot springs, basinal brines, or modern groundwater, plus the action of modern supergene processes may have fixed metals in association with black shales (Kim, 1993).

Other sedimentary rocks include sandstones and limestones, and these in general have lower concentrations of metals, the former as a result of being formed from more resistant igneous rocks and minerals, which have low concentrations of most elements and very little capacity to adsorb metals (West, 1981; Alloway, 1990b).

Alteration of sedimentary rocks in conditions of high temperature and high pressure produces metamorphic rocks, in which, with the possible exception of a few elements such as Rb and B which are depleted at high temperatures, the element content reflects that of their sedimentary or igneous precursors (Plant and Raiswell, 1983). The data presented in Table 2.2 compares favourably to similar data from a wide variety of sources (Turekian and Wedepohl, 1961; Krauskopf, 1967; Rose *et al.*, 1979; Bowen, 1979 and Mason and Moore, 1980).

2.3 The weathering of rocks

2.3.1 Introduction

The weathering of rocks is basically the first stage of soil development, with formation of the regolith and the synthesis of a soil from the upper layers of this heterogeneous mass (Brady, 1990). Weathering occurs at the transitional contact between the lithosphere and the atmosphere in which physical, mineralogical and chemical properties of fresh bedrock are progressively modified. Weathering causes rocks that are coherent, dense and composed of anhydrous or weakly hydrated minerals to alter progressively, at rates which vary according to lithology and climate from 5-50 mm per 1000 years, to a more friable material (Trescases, 1989).

2.3.2 Factors influencing weathering

Several factors influence the rate of weathering of rocks and hence soil formation; these can be summarised as:

1). Climatic conditions - This is possibly the most influential factor in all stages of soil formation, directly as a consequence of weathering and indirectly through vegetation. Figure 2.1 illustrates the influence of climate with tropical areas having deep well-weathered soils in response to high temperatures and high annual rainfall that have remained uninterrupted by the glacial periods. This is in contrast to higher latitudes.

2). Physical properties of rocks - These include factors such as grain size, texture, and the nature and degree of cementation.

3). Chemical and crystal composition - The stability of rock-forming minerals depends on climatic conditions, but in general those formed in conditions most akin to those at the earth's surface are the most stable (e.g. quartz).

4). Permeability - Water infiltration greatly enhances weathering, with coarser grained rocks more susceptible to decomposition as a result of micro-channels.

5). Drainage - Chemical weathering is most active where the water table is at a maximum beneath the surface, compared to swamp areas and mountainous areas where material is removed quicker than it can be chemically weathered.

2.3.3 Physical weathering

In general this process results in the particle size decrease of rocks and minerals without affecting the chemical composition, which may be an integral part of the initial weathering system in some locations. This disintegration technique is an important aid to chemical weathering because it increases the surface area exposed to rainfall and solar radiation which are the main agents of chemical weathering (Plant and Raiswell, 1983). Temperature is an important agent in the process of physical weathering, and in areas where large differences exist in day and night temperatures some minerals may expand and contract more than others so setting up differential stresses and cracks. This phenomena is most pronounced at the surface thanks to the slow conduction of heat leading to exfoliation/flaking, which may be accelerated by the freezing of any included water. Water, ice and wind are other agents in physical weathering in a more abrasive manner through the action of rivers, glaciers and dust storms respectively. To a lesser degree the physical action of roots and animals is another aspect of this weathering process, with the movement of worms and termites increasing the access of air and water and thus facilitating chemical action.

2.3.4 Chemical weathering

With the onset of physical weathering, chemical decomposition also proceeds, particularly in warm and wet climates, the two most important elements of this process. Water, in combination with dissolved material, O_2 and various acids from plant residues, reacts with minerals to break them down further to soluble material or resistant end products. This constitutes a much more powerful attack on rocks, often radically changing the nature of the parent material (Rose *et al.,* 1979). The major types of chemical weathering can be listed as:

1). Dissolution - The most basic weathering technique, affecting in general minerals with a high solubility product (i.e. gypsum and calcite) and dissociating them into their constituent ions.

2). Oxidation - Some elements have several oxidation states in primary minerals (i.e. Fe and Mn), with the lowest oxidation state the general rule for the unaltered primary state. On weathering the introduction of percolating waters oxidises ferrous iron (2^+) to ferric iron (3^+).

3). Hydrolysis - In most weathered environments in which the pH is between 5 and 9 the usual reaction to the addition of water is hydrolysis, particularly for the silicates. On hydrolysis silicates produce hydroxyl anions, cations, dissolved silica, and possibly secondary minerals. In contrast to oxidation reactions, hydrolysis reactions consume H^+ ions and produce OH^- ions, so increasing the pH of the solution.

4). Hydration - This involves the adsorption of water into the crystal structure of the mineral, such as with hydrated aluminium oxide.

Other types of chemical weathering include acid hydrolysis, which differs from the hydrolysis process described above by the presence of a hydrogen ion, and various types of biological weathering, which occur from plant and bacteria activity. Both are addressed along with factors which influence the rate of weathering such as climate and individual properties of the rocks.is covered in much more detail in a number of texts and it is not the aim of this thesis to provide a detailed consideration of such activity. As with soil profile development (see section 2.5), the discussion limits itself to those processes that occur in Britain, making it directly relevant to this urban study.

Table 2.1 Some ionic properties of selected major and trace elements (after Jenkins and Jones, 1980)

Z	Ionic charge
IR(A)	Ionic radii for the coordination (C) indicated. (N.B. for Fe and for Co high (H) and low (L) - spin values given).
C	Observed coordination with respect to O_2
E	Electronegativity (Pauling)
IP	Ionic potential(Z/IR)
EHID(A)	Effective diameter of hydrated ion in aqueous solution

	Z	IR	C	E	IP	EHID
Cs	+	1.96-1.89	12-10	0.7	0.5	2.5
Rb	+	1.81-1.74	12-10	0.8	0.6	2.5
K	+	1.68-1.59	12-8	0.8	0.6	3.0
Ba	+2	1.68-1.59	12-8	0.9	1.3	5.0
Pb	+2	1.57-1.37		1.8	1.4	4.5
Sr	+2	1.40-1.33	10-8	1.0	1.5	5.0
Na	+	1.24-1.10	8-6	0.9	0.9	4.5
Ca	+2	1.20-1.08	8.6	1.0	1.8	6.0
Mn	+2	1.01-0.75	8.6	1.5	2.0	6.0
Cu	+	0.96		1.9	1.0	
Fe	+2	0.86/0.69	6	1.8	2.6	6.0
Zn	+2	0.83	6	1.7	2.4	6.0
Co	+2	0.83/0.73	6	1.7	2.6	6.0
Li	+	0.82	6	1.0	1.2	6.0
Cu	+2	0.82	6	2.0	2.5	6.0
Ni	+2	0.77	6	1.7	2.6	6.0
Mg	+2	0.80	6	1.2	2.5	8.0
Fe	+3	0.73/0.63	6	1.9	4.4	9.0
Cr	+3	0.7	6	1.6	4.3	9.0
Ti	+4	0.69	6	1.5	5.8	
Mn	+4	0.62	8-6		6.5	
Al	+3	0.61-0.47	6-4	1.5	5.6	9.0
V	+5	0.44	4		11	
Cr	+6	0.38	4		16	
Si	+4	0.34	4	1.8	12	
P	+5	0.25	4	2.1	20	

* Major elements in bold   Blank space denotes no data.

Table 2.2 Concentrations of selected elements in the continental earths crust and in abundant rock species (μg/g) - Adapted from Wedepohl (1991)

	Be	Mg	Ti	V	Cr	Mn
Shales	3	16000	46000	130	90	850
Greywackes	3	13000	3800	67	50	750
Limestone	0.5	26000	400	20	11	700
Granitic	5.5	6000	3000	94	12	325
Gneisses mica schists	3.8	13000	3870	60	76	600
Basaltic and gabbroic	0.6	37000	9700	251	168	1390
Granulites	2.1	14000	3520	73	88	895
Continental crust	2.9	16000	4680	109	88	800

	Fe	Ni	Cu	Zn	Cd	Pb
Shales	48000	68	45	95	0.13	22
Greywackes	38000	40	45	105	0.09	14
Limestone	15000	15	4	23	0.16	5
Granitic	20000	7	13	50	0.09	32
Gneisses mica schists	33000	26	23	65	0.10	16
Basaltic and gabbroic	86000	134	90	100	0.10	3.5
Granulites	38000	33	27	65	0.10	9.8
Continental crust	42000	45	35	69	0.10	15

2.4 Factors of soil formation

2.4.1 Introduction

In section 2.2 the importance of soil parent material and how this can influence the trace element content of soils was addressed. Parent material is however, only one factor, although a highly significant one, in the process of soil formation. The eminent Russian soil scientist Dokuchaiev put forward five soil factors to explain soil formation:

1). Parent material
2). Climate.
3). Age of land.
4). Plant and animal organisms.
5). Topography.

Jenny (1941) expanded upon this to develop an equation for soil formation :

$$s = f(Cl, O, R, P, T)$$

where s is a soil property as a function of (f) the factors climate (Cl), organisms (O), relief (R), parent material (P) and time (T).

2.4.2 Climate

The importance of temperature and rainfall to chemical reactivity and the weathering of rocks in particular was illustrated in section 2.3, and its role in soil formation is a continuation of that. Climate is composed of a number of factors which include temperature, humidity and evapotranspiration, in addition to rainfall and temperature. On a global scale these factors vary greatly, with rainfall varying from less than 250 mm to as much as 12 500 mm per annum whilst temperatures in certain areas can vary by as much as 43 °C and by as little as 0.5 or 1.0 °c (Bridges, 1978). The modest soil profiles of cold climates vividly contrast with the deep, well weathered profiles of the humid tropics (Brady, 1990). Climate also influences soils indirectly via vegetation and organisms. Certain organisms are sensitive to temperature, whilst even more significantly they influence the indigenous vegetation.

Soils can be classified on a zonal basis relating to environmental uniformity for a climatic/latitudinal zone (Bridges, 1978). This involves making some generalisations for the individual zones to give the most typical soils for each climatic belt. Figure 2.1 illustrates the climatic zonation of soils with vigorous and long-term weathering in tropical and equatorial regions producing deep mature soils, with the more resistant products of chemical weathering (Al and Fe oxides) dominating soil profiles. This study is more concerned with temperate conditions in which British soils have developed. The Pleistocene Glaciations drastically changed the climate in recent times and this coupled with the lower temperatures and lower annual rainfall has resulted in soil profiles which are not as deep as those in tropical and equatorial regions (see Figure 2.1).

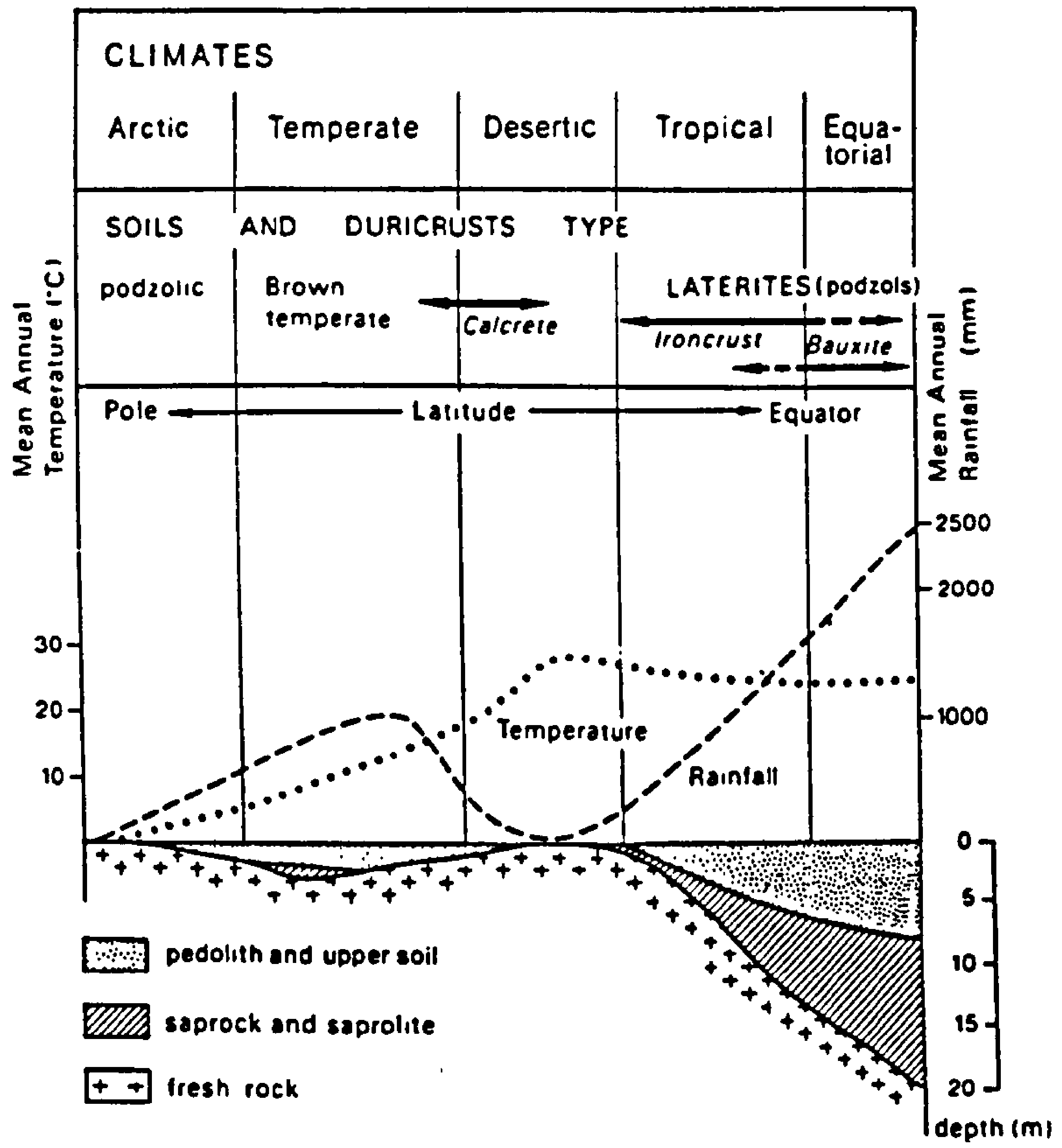


Figure 2.1 Soils and thickness of weathering zone and their relationship with climate (mean annual temperature and mean annual rainfall - after Pedro, 1985)

2.4.3 Organisms

Soil organisms play a vital role in soil profile development (Jenny, 1941). Initially bacteria and fungi are responsible for breakdown of the leaf-litter layer, whilst the leaf-litter protects the soil from natural erosion. Further breakdown of organic matter occurs in the soil with the eating of plant remains by mites and springtails, whilst earthworms and termites are vital for incorporating the organic matter into the mineral soil (Bridges, 1978). Organisms also exert a major influence on profile mixing and differentiation, nutrient cycling and structural stability (Brady, 1990).

Although, the importance of vegetation was discussed briefly in relation to climate (see section 2.4.2), it also exerts an independent influence upon soil formation and processes. Soil organic matter content under grassland vegetation is generally higher than that under forest, particularly in subsurface horizons, with improved soil structure and cation-exchange capacity associated with the higher organic matter. The nature of the vegetation is also vital with coniferous trees (acidophiles) low in metallic cations such as calcium, magnesium and potassium, and hence the cycling of nutrients will be low compared to that of deciduous trees which are rich in metallic cations. Acidity is therefore often associated will soils beneath coniferous trees (Brady, 1990).

2.4.4 Topography

As with many of the other factors of soil formation discussed in this section, topography can exert an influence in several ways, particularly through the reduction of temperature and increase in rainfall associated with high elevation. Cloud cover at altitude is also generally increased so reducing solar warming and encouraging the development of thick organic layers (Bridges, 1978). The physical nature of the landscape also exerts a control, with soils in flat or gently sloping areas generally being thicker than soils on steep slopes. In gently sloping areas there is a tendency for material to remain in place and soils are more likely to have a high percentage of clay minerals, whilst on steeper slopes the shallow soils are usually stony and contain many primary minerals. The exception to this may occur where steep slopes are well vegetated and a thick soil may develop (FitzPatrick, 1971).

2.4.5 Parent material

The metal content of parent material greatly influences the metal content of the soils that develop over them. This is discussed in more detail in section 2.2 and illustrated in Table 2.1. Soil parent material also greatly influences the soil texture, which influences a large number of soil processes. A geographical difference of soil type which is strongly influenced by geology can be seen in Scotland with brown earths forming on basic igneous rocks and podzols over acid igneous rocks, and in Wales more clearly, where outcrops of limestone give rise to brown earths at elevations and levels of rainfall which would produce peaty gleys and peaty gley podzols on non-calcareous parent material. In the Peak District of Derbyshire, brown earths developed on limestones are observed adjacent to peaty gleys and peaty gley podzols soils on sandstones and shales (Bridges, 1978). Mature soil profiles are achieved where sandy parent materials exist because this texture permits the movement of materials in solution, and hence the formation of acid brown soils, brown podzolic soils or podzols. This is common on the coarse-textured glacio-fluvial sands and gravels of the tertiary formations in the London basin, which is relative to soils in Richmond-upon-Thames (see section 6.4). In contrast, a clay texture may impede drainage, resulting in gleying, as seen in the lowlands of England. Alluvial material, a parent material observed close to the Thames in parts of Richmond (see Fig. 4.2), is often well sorted, silty and possess organic material to greater depths than other soils.

2.4.6 Time

Soil formation is a very slow process taking thousands of years and this process is further complicated by periodic changes in climate and vegetation, and therefore any discussion of time as a soil forming factor is part speculation (FitzPatrick, 1971). Not all soils have been developing for the same length of time; most started their development during the last 100 million years (FitzPatrick, 1971). The length of time that material has been exposed to weathering plays a vital role in soil formation and this can be seen by comparing soils of a glaciated region to those of a comparable unglaciated area. The influence of time is very apparent in soils of glaciated regions where insufficient time has passed to permit the full development of many soils (Brady, 1990). Soils on alluvial material are also generally not as mature as those of surrounding upland areas. Some soil horizons differentiate before others, especially those at the surface which only take a few decades to form on unconsolidated deposits. At greater depths horizons develop more slowly, a process limited by the amount of translocation or weathering that is necessary (FitzPatrick, 1971).

As briefly discussed in the first part of this section, soils have often developed under a succession of different climates which have given rise to various changes and soil genesis. This renders explanations of soil conditions in concordance with prevailing environmental conditions erroneous (FitzPatrick, 1971). King (1967) suggests that the oldest land surfaces date from the early part of the Tertiary Period, although most of the early surfaces developed in the mid-Tertiary Period, and these are located in Africa and Australia. These soils are probably younger than the land surfaces and evidence provided by plant remains shows that full tropical conditions existed in many of the same areas as today as well as in many of the present subtropical and arid areas. These conditions result in deep weathering in these areas as such conditions were maintained throughout most of the Tertiary Period. Interestingly in Britain, the flora from the late Cretaceous to the Miocene Period suggests much warmer climates with the remains of palms discovered (FitzPatrick, 1971).

2.5 Soil profile development

2.5.1 Introduction

The examination of a soil pit reveals a soil profile with distinctive horizontal layers, something which would not be revealed by a similar pit into unconsolidated material (Brady, 1990). Soil genesis, or soil profile formation, occurs because of three (general) processes:

1). Weathering and organic matter breakdown - by which some soil constituents are modified or destroyed and others are synthesised.

2). Translocation of inorganic and organic materials up and down the soil profile, the materials being moved mostly by water but also by soil organisms.

3). Accumulation of soil materials in horizontal layers either as a result of movement from above or below (generally above in Britain) or from in situ formation.

The weathering of parent material has been covered in detail in section 2.3, whilst the role of organisms in decaying plant material and then distributing of this further down the soil was briefly introduced in section 2.4.3. Both of these activities are central to the production of the first horizon, different in colour and composition to the parent material (Brady, 1990). The soil forming processes outlined below are those which would be expected to occur in a humid environment such as Britain producing soils such as the podzols, brown soils, argillic brown soils and the grey soils (Figure 2.1 shows thickness of the weathering zone in relation to climatic zones and the associated soil types).

2.5.2 Leaching

In a humid environment such as Britain most of the soil solution normally migrates in response to gravity by moving vertically down through the soil, and eventually into underground waters and then river systems (FitzPatrick, 1971). Leaching occurs where rainfall exceeds evaporation and soluble soil constituents are removed from the soil. Readily soluble salts are dissolved by percolating waters, with the most soluble materials such as carbonates, sulphates and nitrates often completely lost from the soil system. The process of leaching also attacks bases held as exchangeable ions by the clay-humus complex (i.e. Ca, K and Mg), replacing them with hydrogen, increasing acidity and producing a weathered B horizon.

2.5.3 Eluviation

Eluviation refers to the removal of material in suspension from upper or eluvial horizons. Humus and clay particles can move in colloidal suspensions from eluvial to illuvial horizons. This results in the formation of a B horizon, considerably enriched in clay compared to the amount remaining in the E horizon, which is characterised by its pale colour (Bridges, 1978).

2.5.4 Podzolisation

This process can be distinguished from eluviation which is strictly a mechanical process, whilst podzolisation involves the breakdown of clay particles. This soil process is associated with heath or coniferous vegetation and the formation of the characteristic acidic mor humus due to the slow decomposition of the plant debris. As plant residues decay organic acids are formed which are carried by percolating waters through to the mineral soil where clay minerals are chemically altered and Fe, Al and silica form complexes with organic substances and are removed from the surface horizons (Bridges, 1978). Diagnostic of a podzol is a bleached subsurface horizon (Ea) from which many constituents have been removed and some silica accumulated. The Fe oxides which are mobilised from an eluvial horizon together with Al or organic matter are deposited in an illuvial B horizon further down the profile. This deposition may occur in the B horizon as a result of changes in pH or moisture conditions, bacterial attack or the presence of flocculating ions (Bridges, 1978).

2.5.5 Gleying

Gleying can occur in a number of environments where water is allowed to accumulate such as on plateaus or where drainage is impeded, due to factors such as the formation of an iron-pan in some podzolic soils. This can occur in a number of environments and these soils are considered to be intrazonal in their distribution (Bridges, 1978). With the anaerobic conditions that prevail with water accumulation, bacterial activity brings about a deficiency of oxygen which results in the reduction of iron compounds. Exposure of the soil will allow re-oxygenation and colour changes result, giving a typical mottled pattern compared to a blue/grey colour where oxygen is absent.

2.6 Urban soils

2.6.1 Introduction

Having briefly examined the factors and processes which play an integral role in the development of a soil profile, the special properties of soils found in urban environments needs to be addressed. Of the approximate 1.7 million hectares of urban land in Britain approximately 12% is open space, a definition which includes allotments, parkland and derelict land (Best, 1991). Some soils in urban areas have been well maintained, particularly in parks and allotments, but many others are contaminated, compacted with poor drainage, and have a high stone content (Bullock and Gregory, 1991). With regard to contaminated land, the industrial revolution and subsequent decades has bequeathed a number of contaminated sites in towns and cities. This is exacerbated by industrial evolution or a complete change of land-use which may confuse patterns of contamination. Conversely, a change of land-use from a polluting industry to a non-polluting industry may bring the re-working of a site and hence the masking of contamination. The House of Commons report on Contaminated Land (1990) focuses on the lack of knowledge regarding the extent, nature and location of contaminated land in Britain.

2.6.2 Classifying urban soils

Urban soils are unique in many aspects and this makes them difficult to classify within the confines of classical schemes. Several attempts have been made specifically to define urban soils, and one such by Bockheim (1974) suggests that this is soil material having a non-agricultural, man-made surface layer more than 50cm thick, that has been produced by mixing, filling, or by contamination in urban or suburban areas. Some disturbance of the profile is inferred and this may not always be the case for urban soils as briefly discussed in section 2.6.1. Hollis (1991) summarises several features of urban soils as follows:

1). The extensive presence of man-made materials, as either physical components or extra chemical inputs such as salts or heavy metals.

2). Other physical properties, such as compact topsoils, subsoils and surface crusts on bare soils. These may restrict aeration and the downward movement of water, and hence the soil moisture regime.

3). Interrupted nutrient cycling and modified soil organism activity.

4). Greater and less predictable vertical and spatial variation of properties because of human activities. This occurs either directly, because of disturbances such as the removal or replacement of soil, or indirectly, as a result of local physical and chemical alteration of the upper few centimetres of soil.

In an urban context it is important to distinguish between disturbed and undisturbed soils preferably at the highest level of a hierarchical scheme. The soil classification scheme for England and Wales includes a group for man-made soils with two diagnostic properties, the second of which describes a dark `man-made' A-horizon at least 40cm thick that contains at least 0.6 % organic carbon throughout, with the organic matter intimately mixed with the mineral fraction and which usually contains artefacts such as brick or pottery fragments. Alternatively, there is a disturbed subsurface layer that extends below 40cm depth that consists wholly or partly of materials derived from pedogenic horizons of pre-existing soils (Avery, 1980 and Hollis, 1991). These are important definitions for urban soils and reflect the disturbance that many soils will undergo in the urban environment, and illustrates their often unique nature. In general however, soil classification schemes from around the world define anthropogenic activity as resulting from agricultural activity or the addition of manures. If urban soils are to be successfully classified then a number of features from several schemes needs to be incorporated into a single scheme, including those from the classification of derelict land (Hollis, 1991). Soil surveyors have usually avoided the problems associated with working in urban areas by simply defining these as `built-up' (Bridges, 1991).

2.6.3 Building material in soils

One of the most common anthropogenic materials introduced into urban soils is rubble from building material (see section 2.6.2). The use of the bulldozer since the 1950's has brought an introduction of cut and fill techniques, with houses being built on the resulting platform. This greatly disturbs natural soils and buried profiles may result. Building waste in suburban soils is generally restricted to broken brick, tile and glass, with fragments of timber, piping, cable and insulation material, and clumps of concrete, cement and plaster. In general such material does not give rise to contamination itself, although it affects the structure of the soil. Urban garden soil may consist of a subsoil containing scattered patches of rubble, all of which has been run over and compacted by heavy machinery, on top of which is placed a layer of `topsoil' of approximately 0.2-0.5m (Mullins, 1991). Industrial sites may have the added complication of contaminated material mixed with soil.

A study of `clearance sites' in Liverpool (Bradshaw and Chadwick, 1980) found pH values to be generally greater than 7.0 and Ca concentrations of over 8000 μg/g, probably due to the concrete, plaster and cement in these soils, whilst domestic gardens are subject to the application of fertilisers, lime, pesticides, fossil fuel residues, cinders, ash, soot and other household wastes. A review of the potential contamination of soils from various sources is presented in chapter 3, and it only remains very briefly to cite some specific cases associated with urban soils. Gasworks have been present in most towns over the last century and have been subject to a number of spillages and waste material disposal within the premises, particularly the spent oxides which are particularly rich in organic material and heavy metals. Land released from Beckton Gasworks was so contaminated that it had to be covered by 1.2m of London Clay and 0.3m topsoil, with a 22.5cm thick layer of gravel beneath the London Clay and above the waste to act as a drainage and venting channel (Bridges, 1991). Residential areas subsequently built on land previously used by this particular gasworks are currently under investigation as health problems persist with local residents.

Chemical works may also cause problems in urban areas, and in the Netherlands, at Lekerkerke, houses were built over the waste tip of a dyestuffs factory. In addition to the extensive organic contamination waste material was found to be rich in Pb, Zn and Cd (Schuuring, 1981). Redevelopment of the old Woolwich Arsenal at Thamesmead, a munitions factory, exposed a legacy of metallic contamination with Cu, Ni, Co, Sr, Ba and Hg salts present in soils and slags in the area (Lowe, 1980).

Areas that are or have been extensively mined may directly or indirectly affect urban soils. In areas disturbed by opencast mining, the restored landscape is often avoided as a residential area because of engineering problems and hence such sites are often redeveloped as sports fields or golf courses, as is the case in Wolverhampton. In addition a great deal of colliery waste is used throughout Britain in a number of amenity projects, with unburnt shale forming the subsoil of many re-landscaped areas (Bridges, 1991).

2.6.4 Physical properties of urban soils

The use of a soil in an urban area, coupled with the soil texture, is probably the biggest influence on the physical properties of urban soils, such as porosity and structural stability (Mullins, 1991). Continuous use of playing fields in wet conditions results in compaction and an increase in waterlogging, so rendering their use less frequent and altering the soil chemistry (Mullins, 1991).

In residential soils the mixture of material left after demolition outlined in section 2.6.2 is generally defined as gravel and stones > 2mm in diameter. It is erroneous merely to treat `stones' as material that reduces the overall soil volume accessible to plant roots. This material may exert an influence on the chemical and physical properties of the soil via the available water capacity and cation exchange-capacity of the material (Mullins, 1991).

2.6.5 Summary

In sections 2.1 and 2.2 isomorphous substitution of trace metals into minerals and the trace metal content of different parent material are discussed, respectively. Factors which influence the weathering of rocks along with the processes of physical and chemical weathering were briefly discussed in section 2.3, whilst in section 2.4 the factors which influence soil formation were introduced. In section 2.5 the development of the soil profile by processes which are common in temperate climates was reviewed. In section 2.6 urban soils were discussed in terms of their classification and physical properties, with a brief discussion of building materials (a common component of urban soils).

2.7 Baseline or average concentrations of metals in soils

2.7.1 Introduction

Before an assessment can be made of metal contamination in soils, baseline concentrations, baseline concentration ranges and average concentrations for these metals have to considered. In Table 2.2, the metal concentrations pertaining to specific parent materials are reported (Wedepohl, 1991), and in general these concentrations can be expected to relate to concentrations found in soils that develop on such parent materials. A number of studies have involved the systematic collection of a large number of samples from a country or region to estimate the range and average concentrations of a number of elements. The results from such surveys are summarised in Table 2.3, although these are only a few of the many similar studies that report average values for uncontaminated soil or a specific region. This includes the most extensive soil survey carried out in Britain to date, which was published as the Soil Geochemical Atlas of England and Wales (McGrath and Loveland, 1992). In total over 5000 topsoil samples were taken (0-15cm) at an interval of 1 composite sample per $5km^2$. In general the aim was to sample the non-urban environment, although large public open spaces and parks in urban areas were sampled, so the median values quoted in Table 2.3 are a fair estimation of the element concentrations found in uncontaminated soil. Tables 2.4-2.8 summarise reported mean concentrations of Pb, Zn, Cu, Cd and Ni for studies from around the world. These metals are environmentally important, and their data are examined before that of the other 17 elements analysed in soils from Richmond and Wolverhampton.

2.7.2 Lead

Most of the surveys listed in Table 2.3 relate to Britain in general, and a good estimation of a Pb concentration for uncontaminated topsoils in Britain is < 50 μg/g. The results from extensive surveys by Archer and Hodgson (1987) and McGrath and Loveland (1992 - see Table 2.3) are very similar reporting mean and median concentrations of Pb, respectively of approximately 40 μg/g, whilst Davies (1983) gave a graphical estimation of Pb concentrations in uncontaminated soils as 42 μg/g using percentage cumulative frequency distribution diagrams. With a ubiquitous trace element such as Pb one has to make the distinction between remote regions and areas exposed to low level contamination. Davies (1990) does this (see Table 2.3) reporting a concentration range of 10-30 μg/g for remote areas whilst a concentration range of 30-100 μg/g can be expected for topsoils that have been exposed to low-level contamination. A concentration range is reported for remote regions because even areas unexposed to anthropogenic sources will have natural variation of the geochemical signature.

In Britain the history of industrial activity coupled with extensive urbanisation has meant that most areas have Pb concentrations greater than might be expected for very remote regions (Davies, 1990; Moir, 1992). A mean value of 56 μg/g reported for 850 topsoils in Wales (McGrath *et al.*, 1985) reflects some of the lead mineralisation in this country and compares to other values for Welsh soils of 73 μg/g reported by Davies and Paveley (1985) and 41 μg/g by Bradley (1980). Berrow and Reaves (1984) report a mean Pb concentration of 14 μg/g for 896 samples from Scotland which compares to a median Pb concentration of 20 μg/g for Scottish soils reported by Jones and Johnston (1991), reflecting the lack of mineralisation in this country. Zimdahl and Skogerboe (1977) state that the terrestrial abundance of Pb in soils varies from 1-200 μg/g with a mean of 15 μg/g, whilst Lagerwerff (1972) reports a Pb baseline concentration of 50 μg/g for soils which compares to Aubert and Pinta (1977) and Vingradov (1959) who report world averages for Pb in soils of 15-25 μg/g and 10 μg/g, respectively (see Table 2.3).

Table 2.3 Concentrations of selected elements reported as averages or as concentration ranges for soils ($\mu g/g$)

	1	2.	3	4	5	6
Ba		121		100-3000		
Cr	41	39.3	≤ 60	5-1000	42.4	100
Mn	50-7000	577	500-1000	850		850
Fe		**2.67**				**3.8**
Co	10-15	9.8	10-15	1-40	7.9	8
Ni	25	22.6	20-30	5-500	22.6	40
Cu	20-30	18.1	15-40	2-100	19	20
Zn	50	82	50-100	20	78.1	50
Cd	< 1	0.7		1	0.6	0.5
Pb	10-30-100	40	15-25	2-200	39.8	10
P		756				

1. Values reported in specific chapters from `Heavy Metals in Soils' ed. B.J. Alloway (1990).

2.. Median concentrations of elements reported in the `Soil Geochemical Atlas of England and Wales (McGrath and Loveland, 1992).

3. Values reported by Auberta and Pinta (1977) for world soils.

4. Values reported by Levinson (1980) for world soils.

5. Values reported by Archer and Hodgson (1987) for soils in England and Wales.

6. Values reported by Vinogradov (1959) for world soils.

Values shown in bold are percentages rather than $\mu g/g$

For the United States of America a number of surveys show that metal concentrations of soils, and those from agricultural areas in particular, tend to be lower than that for Britain. An extensive survey by Holmgren *et al.* (1993) involved the sampling of over 3000 soils from 32 states on sites at least 8km away from any stack emission, 200m from a highway, 100m away from any building site and 50m from a field boundary, and this gave an overall geometric mean of 10.6 μg/g for Pb in topsoils (see Table 2.4). This survey was biased towards sampling areas that may be deemed remote in comparison with similar large scale geochemical surveys in Britain (e.g. McGrath and Loveland, 1992) and this is reflected in such a low geometric mean for a number of states in North America. Pierce *et al.* (1982) also reports a low mean value for Pb, < 25 μg/g, for Minnesota soils which compares with data from Ohio and Ontario - 19 μg/g and 14.1 respectively (Logan and Miller, 1983 and Frank *et al.*, 1976 respectively - see Table 2.4).

Data also exists for other parts of the world for estimating the background concentration of Pb in soil. Andersen *et al.* (1980) reported concentrations of 30 μg/g for rural areas outside Copenhagen, whilst Romero *et al.* (1987) quote 25 μg/g as an estimate of uncontaminated soil from rural areas of Spain (see Table 2.4). Minimum values of 16.8 μg/g Pb were found in allotment soils in Upper Silesia, although this value is not representative of other Pb concentrations from the area (Gzyl, 1990), whilst Kabata-Pendias and Dudka (1991) suggest that 18.3 μg/g is a good estimate of the baseline concentration for Polish soils. Chen *et al.* (1991) sampled nearly 4000 soils in mainland China finding a Pb geometric mean of 24 μg/g and the same paper quotes a geometric mean of 28 μg/g for Pb in soils from Tibet and 12 μg/g for Alaska (see Table 2.4). Literature for African studies is rarer, although Nwankwo and Elinder (1979) reported an average Pb concentration of 16 μg/g for Lusaka (see Table 2.4).

Table 2.4 Summary table of average or baseline concentrations of Pb in topsoils of specific locations

Location	Mean μg/g	Range μg/g	Reference
Wales	56		McGrath *et al.* (1985)
Wales	73		Davies and Paveley (1983)
Wales	41		Bradley (1980)
Scotland	14		Berrow and Reaves (1984)
Scotland	20		Jones and Johnston (1991)
World	15	1-200	Zimdahl and Skogerboe (1977)
World	50		Lagerwerff (1972)
USA	10.6		Holgren *et al.* (1993)
Minnesota		< 25	Pierce *et al.* 1982
Ohio	19		Logan and Miller (1983)
Ontario	14.1		Frank *et al.* (1976)
Copenhagen	30		Andersen *et al.* (1980)
Spain	25		Romero *et al.* (1987)
Poland	18.3		Kabata-Pendias and Dudka (1991)
China	24		Chen *et al.* (1991)
Tibet	28		Chen *et al.* (1991)
Alaska	14		Chen *et al.* (1991)
Africa	16		Nwankwo and Elinder (1979)

2.7.3 Zinc

Table 2.5 shows that average or baseline concentrations of Zn in soil tends to exceed those of Pb. The Aubert and Pinta (1977) estimate of 50-100 μg/g seems to be a good summary of the values listed. For British soils specific surveys have produced mean Zn concentrations of approximately 78 μg/g and 82 μg/g for England and Wales (Archer and Hodgson, 1987 and McGrath and Loveland, 1992 respectively - see Table 2.3). For Welsh soils McGrath *et al.* (1985) reported a mean value of 84 μg/g, whilst Bradley (1980) found a mean Zn concentration of 73 μg/g for soils in Dyfed. In the United States the large scale survey conducted by Holmgren *et al.* (1993), and described in more detail in section 2.7.2, found an overall geometric mean of approximately 43 μg/g (approximately 4 times greater than the Pb mean - see Tables 2.4 and 2.5) for north American agricultural soils, and this compares to mean concentrations of 75 μg/g, 53 μg/g and 53.5 μg/g for Ohio, Minnesota and Ontario respectively (Logan and Miller, 1983;

Pierce *et al.,* 1982 and Frank *et al.,* 1976 respectively - see Table 2.5).

For other parts of Europe, average Zn concentrations of 36 μg/g are reported for rural areas of Copenhagen (Andersen *et al.,* 1980), whilst Steinnes *et al.* (1989) reports that the average Zn concentration for soils in southern Norway is approximately 30 μg/g and Romero *et al.* (1987) quotes 65 μg/g as the mean Zn concentration for unpolluted soils in Spain (see Table 2.5). Chen et al (1991) reported a geometric mean of 67 μg/g for mainland China, whilst the same paper records geometric means of 71 μg/g and 70 μg/g for Tibet and Alaska respectively (see Table 2.5). In Africa, the average concentration of Zn in soils in Lusaka was 35 μg/g (Nwankwo and Elinder, 1979 - see Table 2.5).

Table 2.5 Summary table of average or baseline concentrations of Zn in topsoils of specific locations

Location	Mean μg/g	Reference
Wales	84	McGrath *et al.* (1985)
Wales	73	Bradley (1980)
USA	49.2	Holgren *et al.* (1993)
Minnesota	75	Pierce *et al.* 1982
Ohio	53	Logan and Miller (1983)
Ontario	53.5	Frank *et al.* (1976)
Denmark	36	Andersen *et al.* (1980)
Spain	65	Romero *et al.* (1987)
Norway	30	Steinnes *et al.* (1989)
China	67	Chen *et al.* (1991)
Tibet	71	Chen *et al.* (1991)
Alaska	70	Chen *et al.* (1991)
Africa	35	Nwankwo and Elinder (1979)

2.7.4 Copper

With copper an examination of Table 2.3 shows that a mean Cu concentration of 20 μg/g is fairly representative of a background concentration of this metal in British soils. The extensive soil surveys of England and wales conducted by Archer and Hodgson (1987) and McGrath and Loveland (1992) found mean and median topsoil concentrations of 19 μg/g and 18.1 μg/g, respectively (see Table 2.3). In Wales McGrath *et al.* (1985) also reported a mean Cu concentration of 19 μg/g, whilst Bradley (1980) reports a mean of 11 μg/g for Dyfed, Wales (see Table 2.6). Andersen *et al.* (1980) measured a mean Cu concentration of 6.5 μg/g for rural areas of Copenhagen, Steinnes *et al.* (1989) suggests 10 μg/g as a baseline concentration for southern Norway, and Romero *et al.* (1987) suggests 25 μg/g as a mean concentration for unpolluted soils in Spain (see Table 2.6). In the United States, Holmgren *et al.* (1993) reports a geometric mean concentration of 18 μg/g for agricultural soils in north America and this compares with 26 μg/g, 19 μg/g and 15.9 μg/g for soils in Minnesota, Ohio and Ontario respectively (Pierce *et al.*, 1982; Logan and Miller, 1983 and Frank *et al.*, 1976 -see Table 2.6). For mainland China, Chen *et al.* (1991) quote a Cu geometric mean of 20 μg/g, in addition to geometric means of 20 μg/g and 24 μg/g for Tibet and Alaska respectively (see Table 2.6).

Table 2.6 Summary table of average or baseline concentrations of Cu in topsoils of specific locations

Location	Mean μg/g	Reference
Wales	19	McGrath *et al.* (1985)
Wales	11	Bradley (1980)
USA	18	Holgren *et al.* (1993)
Minnesota	26	Pierce *et al.* (1982)
Ohio	19	Logan and Miller (1983)
Ontario	15.9	Frank *et al.* (1976)
Denmark	6.5	Andersen *et al.* (1980)
Spain	25	Romero *et al.* (1987)
Norway	10	Steinnes *et al.* (1989)
China	20	Chen *et al.* (1991)
Tibet	20	Chen *et al.* (1991)
Alaska	24	Chen *et al.* (1991)

2.7.5 Cadmium

The estimate for the Cd content of unpolluted soils given by Alloway (1990c) of < 1 μg/g (see Table 2.3) is a good indicator of the natural or background concentration for this metal, and this is echoed by all the other surveys listed in Table 2.3 with the highest concentration being 0.7 μg/g (McGrath and Loveland, 1992). This is also confirmed by McGrath *et al.* (1985) with their study of Welsh topsoils where a mean of 0.56 μg/g is reported, although Bradley (1980) found a mean Cd concentration just exceeding this threshold in Dyfed of 1.1 μg/g (see Table 2.7). In the United States, Holmgren *et al.* (1993) found a geometric mean of 0.175 μg/g for agricultural soils in north America, which compares to Cd concentrations of 0.31 μg/g, 0.2 μg/g and 0.56 μg/g for Minnesota, Ohio and Ontario respectively (Pierce *et al.*, 1982; Logan and Miller, 1983; and Frank *et al.*, 1976 - see Table 2.7).

In other parts of Europe, baseline concentrations of Cd in southern Norway are given as 0.2 μg/g (Steinnes *et al.*, 1989), whilst Romero *et al.* (1987) quote 1 μg/g as the mean concentration of unpolluted soils in Spain (see Table 2.7). Gzyl (1990) found the lowest concentrations of Cd in a polluted area of Upper Silesia to be 1.2 μg/g, although Kabata-Pendias and Dudka (1991) report that 0.41 μg/g is a good estimation of baseline Cd concentrations in Polish soils (see Table 2.7). Chen *et al.* (1991) report a geometric mean of 0.074 μg/g for mainland China and the same paper reports a geometric mean for Tibet of 0.08 μg/g. In Lusaka, Africa, Nwankwo and Elinder (1979) found an average Cd concentration of 0.16 μg/g (see Table 2.7).

Table 2.7 Summary table of average or baseline concentrations of Cd in topsoils of specific locations

Location	Mean μg/g	Reference
Wales	0.56	McGrath *et al.* (1985)
Wales	1.1	Bradley (1980)
USA	0.18	Holgren *et al.* (1993)
Minnesota	0.31	Pierce *et al.* (1982)
Ohio	0.2	Logan and Miller (1983)
Ontario	0.56	Frank *et al.* (1976)
Poland	0.41	Kabata-Pendias and Dudka (1991)
Spain	1.0	Romero *et al.* (1987)
Norway	0.2	Steinnes *et al.* (1989)
China	0.07	Chen *et al.* (1991)
Tibet	0.8	Chen *et al.* (1991)
Africa	0.16	Nwankwo and Elinder (1979)

2.7.6 Nickel

Nickel baseline concentrations are very similar to those of copper and this is confirmed by Table 2.3 with the extensive British surveys measuring mean and median concentrations, respectively of approximately 20 μg/g (Archer and Hodgson, 1987 and McGrath and Loveland, 1992 - see Table 2.3). In Wales McGrath *et al.* (1985) report an identical Cu and Ni mean topsoil concentration of 19 μg/g, whilst Bradley (1980) presents a mean Ni concentration of 20 μg/g for soils in Dyfed (see Table 2.8). In Scotland, Berrow and Reaves (1986) reported a derived mean of 27 μg/g for Ni and found that this compared favourably with data from Japan. Romero *et al.* (1987) quotes 10 μg/g as the mean Ni concentration for unpolluted soils in Spain, whilst in America Holmgren *et al.* (1993) found a Ni geometric mean of 16.5 μg/g (compared to 18 μg/g for Cu) and this compares to 21 μg/g, 18 μg/g and 15.9 μg/g for Minnesota, Ohio and Ontario respectively (Pierce *et al.*, 1982; Logan and Miller, 1983; and Frank *et al.*, 1976 - see Table 2.8). For mainland China, Chen *et al.* (1991) reported a geometric mean of 23 μg/g and compare it to geometric means of 29 μg/g and 24 μg/g for Tibet and Alaska respectively (see Table 2.8).

Table 2.8 Summary table of average or baseline concentrations of Ni in topsoils of specific locations

Location	Mean μg/g	Reference
Wales	19	McGrath *et al.* (1985)
Wales	20	Bradley (1980)
Scotland	27	Berrow and Reaves (1984)
USA	16.3	Holgren *et al.* (1993)
Minnesota	21	Pierce *et al.* (1982)
Ohio	18	Logan and Miller (1983)
Ontario	15.9	Frank *et al.* (1976)
Spain	10	Romero *et al.* (1987)
China	23	Chen *et al.* (1991)
Tibet	29	Chen *et al.* (1991)
Alaska	24	Chen *et al.* (1991)

2.7.7 Summary

As a guide to assessing metal contamination in soils, average or baseline concentrations for several metals from a number of countries are reviewed. In general, soils in England and Wales have naturally higher concentrations of metals, particularly Pb, than soils in Scotland and north America. This is because of the greater degree of mineralisation in England and Wales. These data are summarised in a number of tables (see Tables 2.3-2.8).

CHAPTER THREE ANTHROPOGENIC SOURCES OF METALS IN THE ENVIRONMENT

3.1 Uses of metals

3.1.1 Lead

Lead has a long history of anthropogenic use, dating back to Roman times when silver was extracted from it (Waldron, 1980). In general both mining and smelting activities were occurring on a fairly significant scale even at this early stage of history, the smelting process aided by leads' low melting point. In Britain the major areas of lead mineralisation are around north Wales, the Pennines and in parts of south-west England, these areas being sites of both mining and smelting activity. Peak production of lead occurred in the late nineteenth century when Britain was producing the bulk of the world's lead, copper and tin (Maskell and Thornton, 1993).

Lead has a low melting-point and is very soft, which allows it to be readily cut and shaped. These features account for its widespread use as pipes or on roofs, lead pipes being common until recent times (Davies, 1990). Today, lead is more important as an anti-knock agent in petrol in the form of lead alkyl compounds (see Table 3.1), although this will be discussed in more detail in section 3.4.6. Lead is also used in batteries both as an alloy with Sb for battery plates and as lead metal combined with PbO_2 to fabricate lead-acid accumulator batteries (Davies, 1990 - see Table 3.1). This application, along with leaded petrol, is the most important use of the metal. Lead is also used in paint (see section 3.4.5) with the yellow chromate used for road markings and Pb oxides or Pb soaps used in house paints to promote polymerisation (Davies, 1990). Lead is also an important constituent of liquid and vapour wastes from coal burning, lead arsenate pesticides and phosphate fertilisers (Lagerwerff, 1967). The uses of Pb are summarised in Table 3.1

3.1.2 Zinc

The major use of zinc is in the car industry, approximately one third of commercial

Zn in the USA is used by the car industry, thanks to the metals' versatility. It is chemically active, alloys easily, and its high position in the electromotive series largely accounts for its extensive use to protect iron and steel against corrosion (Cammarota, 1980 - also see section 4.6.3). The element has the fourth highest annual consumption of any metal, behind steel, aluminium and copper. Other uses include as a chemical compound in rubber and paints (Cammarota, 1980). Many household implements contain Zn, products which range from kitchen utensils to ointments and antiseptics (Adriano, 1986). Zinc is also an important constituent of agricultural produce such as fertilisers and pesticides, and is a minor constituent of building materials such as concrete. The uses of Zn are summarised in Table 3.1.

3.1.3 Copper

Copper is principally used in the production of wire and the alloys, brass and bronze (Baker, 1990). Because of its high thermal conductance and relative inertness the metal is used extensively in containers such as boilers, steam pipes, automobile radiators and cooking utensils (Adriano, 1986). It has a fairly extensive use in agriculture in the form of fertilisers, bactericides and fungicides, with Bordeaux mixture used as a foliage spray to combat exanthema and bluestone a common fertiliser (see Table 3.1). Significant quantities of Cu can be emitted from the smelting not just of Cu but Zn and Pb as well, in addition to the incineration of municipal waste and the application of sewage sludge (see section 3.4.3). The uses of Cu are summarised in Table 3.1.

3.1.4 Cadmium

Cadmium has only very recently become widely used with the development of electroplating at the end of the first world war (Fassett, 1980). Cadmium is geochemically very similar to zinc (in terms of ionic radius and electronegativity - see Table 2.1) and hence has always been present as an impurity in many Zn compounds, leading to the elevation of Cd as a result of mining and smelting activities and from the application of phosphatic fertilisers (Alloway, 1990c). Cadmium has also been extensively used in dry cell batteries, and the growth of the plastics industry has been accompanied by the use of

Cd stabilisers and Cd pigments (see Table 3.1). It is also used as a protective plating on steel and several authors have reported an association of Cd with roadside soils, suggesting a vehicle source, again most likely as a result of its presence as an impurity with other trace metals (Lagerwerff and Specht, 1970; Ward *et al.,* 1977 and Warren and Birch, 1987- see section 3.4.6). Data presented by Fassett (1980) for Cd use in the U.S.A. in the late 1960's showed that electroplating accounted for 45 % of Cd used in north America whilst pigments and plastics accounted for 21 % and 15% respectively. The uses of Cd are summarised in Table 3.1.

3.1.5 Nickel

As with Cr the biggest single use of Ni is in stainless steel and it is commonly associated with alloys that are strong and resistant to corrosion. It is therefore found in such diverse commodities as cars, batteries and coins (Sevin, 1980). More specifically, other major uses of Ni are in electroplating, in Ni-Cd batteries, various electrical components, and as a catalyst (McGrath and Smith, 1990). The uses of Ni are summarised in Table 3.1.

3.1.6 Chromium

The largest uses of Cr are in the metallurgical refractory and chemical industries (Langard, 1980). Of the total chromium produced annually (10^7t), 60-70% is used in alloys such as stainless steel along with Fe and Ni with the Cr content varying from 10-26 %. The production of refractory bricks uses approximately 15% of the chromate ore whilst a similar percentage is used in general chemical industries such as those which involve tanning leather, pigments and wood preservatives (McGrath and Smith, 1990). Chromates are also used in photography and as antiknock agents. The uses of Cr are summarised in Table 3.1.

This study involves a multi-element investigation of urban soils, so a summary of the major sources of other elements discussed is an important aid to the interpretation of the data. This is presented in Table 3.2.

Table 3.1 Major uses of selected metals

Metal	uses
Pb	leaded petrol, pipes and roofing, batteries, paint, coal burning and pesticides.
Zn	galvanising as a protector for iron/steel, in cars, rubber and paints, coal burning, utensils, fertilisers and building materials.
Cd	Present as an impurity in many Zn compounds, in phosphate fertilisers, dry cell batteries, plastics (stabilisers and pigments) and for plating steel.
Cu	Wire, alloys (brass and bronze), thermal conductors, utensils, agricultural materials (fertilisers, bactericides and fungicides).
Cr	Alloys, especially stainless steel, refractory bricks, tanning leather, pigments, wood preservatives, photography, leaded petrol and plating of car parts
Ni	Alloys, especially stainless steel, cars, batteries and coins, electroplating and electrical components and catalysts.

Table 3.2 Major sources and uses of selected elements (various sources - see text)

Element	uses
Li	in nuclear technology and ceramics, in alloys, in lubricants and as batteries in cameras.
K	in potassium fertilisers.
Be	Major source is from the burning of coal, although also used in alloys with Cu for military purposes, whilst the oxide is a good electrical insulator.
Mg	Approximately 57% of Mg is used in Al alloys for airplane components and cans. Also used as an additive to fertilisers and feed.
Ca	limestone is used in blast furnaces in the iron-steel industry. Calcium is also a component of several building materials such as gypsum, plaster and concrete and used in ceramics.
Sr	Mainly used in the nuclear industry.
Ba	used as both a filler and pigment in paints, it is a component of coal, an additive to diesel fuel, used in the manufacture of alloys, in cement and as an insecticide.
V	A component of all fossil fuels; mainly used in the manufacture of steel.
Mn	90% is processed into ferro-manganese in blast furnaces and used for alloying with Al, Mg and Cu; used in fertilisers and wood preservatives.
Fe	Ore used in the production of steel and its alloys for use in construction, transportation and machine manufacture.
Co	used as a pigment in ceramics, glass and paint, as a catalyst and as a component of super alloys, magnetic steels and in the steel making process.
Al	has a large use in engineering and in the packaging of food and liquids.
P	Mainly used in phosphatic fertilisers

3.2 Emissions of metals

3.2.1 Introduction

An examination of metal concentrations in air is an integral part of any investigation of anthropogenic influence on soils. The atmospheric pathway is one of the most important ways that metals emitted from anthropogenic processes reach soils, although by no means the exclusive pathway. More direct pathways will be discussed in section 3.4. Various metallurgical industries, particularly non-ferrous metal production, emit fumes into the atmosphere which will eventually reach soils. The same industries may also make a significant contribution of metals to the environment via a number of other pathways, with the production of effluent and the creation of waste tips.

3.2.2 Global emissions of metals

As with metals in soil, the atmosphere is supplied with both natural and anthropogenic sources of these particulates. The natural sources are terrestrial (continental dust), marine, volcanic and biogenic (Puxbaum, 1991; Lantzy and Mackenzie, 1979). It is well documented that for a number of metals, particularly Cd, Cu, Ni, Pb, Cr, As and Zn, the anthropogenic inputs greatly exceed those from natural processes (Pacyna, 1986; Nriagu, 1988; Peirson *et al.,* 1974; Bowen, 1979; Lantzy and Mackenzie, 1979). On a global scale a number of inventories exist for metal emissions in particular, although these generally omit values for developing countries which often have less stringent legislation regarding permissible emission values, so the values presented in Tables3.3a and 3.3b are very possibly an underestimation (Nriagu and Pacyna, 1988). The emission factors presented are also subject to a further source of error with the authors suggesting that the values presented in Tables 3.3a and 3.3b fall within an accuracy range of 2-10 owing to the varying concentration of metals in a particular raw material, the applied technology, and the efficiency of pollution-control installations. Table 3.4 shows how the use of metals has evolved globally over the last 55 years up until the mid 1980's. The use of Zn, Cd, Cu, Ni and Fe has steadily increased over this period. The production of Pb has decreased over the last 15 years, although levels are likely to have fallen even more due to the reduction in the Pb content of petrol (see section 3.4.6.1). A more contemporary study carried out in the Rhine basin (Stiglliani *et al.* 1993) has shown a significant decrease in the atmospheric emissions of Pb, Zn and Cd from the mid 1960's to 1988. Lead emissions decreased from 16.5Kt to 4.5Kt, Zn from 15.3Kt to 2.6Kt, and Cd from 238t to 33t.

Table 3.3a Emission factors for the release of metals to the atmosphere (after Nriagu and Pacyna, 1988)

Source category	unit	Cd	Cr	Cu	Mn
Coal combustion					
electrical	$\mu g/MJ^{-1}$	5-25	800-500	60-200	70-450
industry/domestic	gt^{1}	0.1-0.5	1.7-12	1.4-5	1.5-12
Oil combustion					
electrical	$\mu g/MJ^{-1}$	4-30	15-100	60-400	10-100
industry/domestic	gt^{1}	0.005-0.2	1-5	0.5-3	1-5
Pyrometallurgical non-ferrous metal production					
-mining	gt^{1} metal	0.1-0.5		20-100	50-100
-Pb production	gt^{1} metal	10-50		60-80	
-Cu-Ni production	produced	200-400		1700-3600	100-500
-Zn-Cd production		200-1000		50-150	
Secondary non-ferrous metal production	gt^{1} waste	2.5-4		50-150	
steel and iron manufacturing	gt^{1} steel	0.04-0.4	4-40	0.2-4	1.5-40
Refuse incineration					
-municipal	gt^{1}	0.4-10	0.7-7	7-14	1.8-9
-sewage sludge		1-12	50-150	10-60	50-100
Phosphate fertilisers	gt^{1} ferts	0.5-2		1-5	
Cement production	gt^{1} cement	0.01-0.6	1-2		
Wood combustion	gt^{1} wood	0.1-0.3		1-2	

A blank space denotes an insignificant contribution from a particular source

Table 3.3b Emission factors for the release of metals to the atmosphere (after Nriagu and Pacyna, 1988)

Source category	unit	Ni	Pb	Zn
Coal combustion				
electrical	$\mu g/MJ^{-1}$	90-600	50-300	70-500
industry/domestic	gt^{-1}	2-15	1-10	1.5-12
Oil combustion				
electrical	$\mu g/MJ^{-1}$	60-2500	40-300	30-200
industry/domestic	gt^{-1}	20-80	2-6	1-7
Pyrometallurgical non-ferrous metal production				
-mining	gt^{-1} metal	100	500-1000	50-100
-Pb production	gt^{-1} metal	85	3000-8000	50-120
-Cu-Ni production	produced	900	1300-2600	500-1000
-Zn-Cd production			1200-2500	100000-180000
Secondary non-ferrous metal production	gt^{-1} waste		50-800	300-1600
steel and iron manufacturing	gt^{-1} steel	0.05-10	1.5-20	10-45
Refuse incineration				
-municipal	gt^{-1}	0.7-3	10-20	20-60
-sewage sludge		10-50	80-100	50-150
Phosphate fertilisers	gt^{-1} ferts	1-5	0.4-2	10-50
Cement production	gt^{-1} cement	0.1-1	0.02-16	2-20
Wood combustion	gt^{-1} wood	1-3	2-5	2-10

A blank space denotes an insignificant contribution from a particular source

Table 3.4 Changes in the primary production of metals with time (10^3t/yr^{-1} - after Nriagu, 1988)

	1930	1950	1980	1985
Al	120	1500	15396	13690
Cd	1.3	6	15	19
Cr	560	2270	11248	9940
Cu	1611	2650	7660	8114
Fe	80180	189000	714490	715440
Pb	1696	1670	3096	3077
Mn	3491	5800	26720	
Ni	22	144	759	788
Zn	1394	1970	5229	6024

3.2.3 Fossil fuel combustion

The widespread combustion of fossil fuel, associated with a number of industries, is a particularly important source of metals in the atmosphere and relates to a number of the sources listed in tables 3.3a and 3.3b. Coal is a compacted mature form of peat which itself is an evolved stage in the accumulation of decomposing land plants. A number of suitable factors is necessary for the formation of coal, which include an anaerobic environment, rapid subsidence and a clastic sediment input. Most major coal deposits were formed either in the period between the Carboniferous to early Triassic era or between the late Jurassic and Palaeocene, periods of suitable climate and plant life (Woodcock, 1994). In section 2.2 the ability of organic matter to adsorb appreciable quantities of metals was briefly discussed, and in the early stage of its formation coal also accumulates significant concentrations of several metals. Table 3.5 shows the mean metal content of coal to be burned in E.C. countries by 1990 (Cernuschl and Giugliano, 1987).

On burning, not all of the metal content of coal will be emitted into the atmosphere and therefore potentially will reach soils. Some remains associated with the by-products of coal combustion, the bottom or the fly-ashes (Teixeira *et al.,* 1992). Fly-ash and bottom-ash, however, has to be disposed, representing another environmental pathway for metals. Despite this, the most important environmental impact of coal combustion is the gaseous and particulate emissions from point and diffuse sources, with the particulate matter emitted through the stack enriched with metals in comparison to bottom and fly ash, particularly with As, Cd, Pb, Sb, Se and Zn (Cernuschi and Giugliano, 1987). The second column in Table 3.5 shows the estimated emissions into the atmosphere that can be expected for the early part of the 1990's in E.C. countries. Cernuschi and Giugliano (1987) calculated these values using data from column one of Table 3.5, the total emission factor for a typical pulverised coal-fired power station equipped with an electrostatic precipitator, the mean coal/ash ratio, and values of a single-mode log-normal distribution pattern for a typical particulate emitted from a coal fire power plant, as well as constants from another study.

Table 3.5 The metal content of coal to be burned in E.C. countries by 1990 (after Cernuschl and Giugliano, 1987)

	Content (μg/g)	Amount mobilised into atmosphere t/yr^{-1}
Cd	0.4	4.3
Cr	34.2	91.2
Cu	23.4	61.2
Ni	40.4	107.7
Pb	44.3	295
Zn	80.9	934.4

3.2.4 Metal emissions in the United Kingdom

The present study of urban soils is based exclusively in the U.K. so, although a global perspective of metal emissions is important, an examination of emissions relating specifically to Britain is necessary. One of the most extensive inventories of such emissions was undertaken by Hutton and Symon (1986) who looked at Cd, Pb, Hg, and As from a variety of sources which is in contrast to a number of papers which deal with single elements or sources (Hutton *et al.,* 1988; Lester *et al.,* 1979 and DOE, 1985).

The non-ferrous metal industry involves the primary production of Pb, Zn, and Sn and the secondary production of Pb and Cu. The Pb-Zn smelter at Avonmouth is the largest source of Cd and Pb from this particular industry, the smelter emitted 27t yr^{-1} Pb and 3.5t yr^{-1} Cd into the atmosphere in 1982. Other significant contributions occur to landfill sites and marine systems such as the Bristol channel. Table 3.6 is a summary of the emissions of Pb and Cd from a number of sources in Britain.

Table 3.6 Estimated atmospheric metal emissions in the U.K. (after Hutton and Symon, 1986)

Source	Atmospheric emission (t/yr^{-1})	
	Pb	Cd
Non-ferrous metal Production	51	3.7
Miscellaneous production and use	6802	
Iron and steel production	478	2.3
Fossil fuel combustion	80	1.9
Cement manufacture	36	1.0
Municipal waste incineration	142	5.0
Sewage sludge incineration	1.2	0.2
Total	7590	14.0

A blank space denotes an insignificant contribution from a particular source

The use of alkyl Pb compounds in petrol and the manufacture and disposal of Pb-acid batteries are believed to result in the largest environmental discharges of this metal. This is accounted for by the source entitled `miscellaneous production and use' of which Pb in petrol accounts for 6790t yr^{-1} of the 6802t yr^{-1} emitted in the United Kingdom atmosphere each year (Hutton and Symon, 1986). A Department of the Environment report (1985) stated that 70 % of the Pb contained in petrol is emitted into the atmosphere, with the rest being retained in the exhaust and oil. Cadmium, as discussed in section 3.1.4, is mainly used as a protective plating for steel, as Ni-Cd batteries, and in pigments and stabilisers used in plastics. As a consequence the waste material from these uses has a different environmental pathway (via sewage) and hence no value is listed in Table 3.6.

Of the 29 million tons of municipal solid waste (MSW) produced each year in the United Kingdom approximately 8 % is currently incinerated, although this is likely to increase owing to restrictions on the availability of landfill space for bulky raw MSW

(Mitchell *et al.*, 1992). As with the emission from the burning of fossil fuel, Wadge and Hutton (1987) found a three-fold enrichment of Pb-Cd in suspended particulate matter from the stack compared to that of incinerator fly-ash, similar to other results found in Europe. From this study it was estimated that incineration in the U.K. results in atmospheric discharges of 6 tons Cd yr^{-1} and 115 tons Pb yr^{-1}. A detailed study of anthropogenic inputs of selected metals into the atmosphere showed that incineration is largest single source of airborne Cd in the U.K. and the third largest of Pb (Hutton and Symon, 1986).

Despite the introduction of appreciable amounts of metals into the atmosphere, a study of the environment close to an incinerator in north London showed that although Cd concentrations in dust decreased in distance away from the incinerator, the values close to the incinerator were no higher than other values in London. It is believed that the 100m high stack of the Enfield incinerator provides effective dispersal and dilution of the plume (Hutton *et al.*, 1988). However, it is argued that the disposal of MSW is more problematic than coal fly-ash owing to the higher concentrations of metals in MSW and their greater availability (Mitchell *et al.*, 1992).

3.2.5 Atmospheric concentrations of metals

All the data in this section are summarised in Tables 3.7a and 3.7b. In this section specific examples will be given of how metal concentrations vary in ambient air between cities and within countries for urban and rural environments. In Britain a comprehensive study by Lee *et al.* (1994) examined the metal content of air in several locations in England which were defined as rural, residential and industrial. In general, the study was carried out from the early to mid 1970's until the late 1980's. In the residential areas the mean concentration of Pb varied from 0.3-1.3 μg/m^{-3}, the highest concentration occurring at the Walsall site which was close to a smelter. This compares to 0.05 μg/m^{-3} and 0.1 μg/m^{-3} at the two rural sites (see Table 3.7a). For Zn, the mean residential concentrations varied from 0.1-0.3 μg/m^{-3} compared to 0.04-0.08 μg/m^{-3} in rural areas (see Table 3.7b), the major sources being fossil fuel combustion and the wear of tyres (Lagerwerff and Specht, 1970). Other metals were reported at concentrations in the order Ni = Cr > Cd. These compare favourably to results reported for Coventry, Bolton, Brent and a separate study in Port Talbot (Pattenden, 1974) which all have mean Pb concentrations which fall within the range found in the more detailed British study (Lee *et al.,* 1994), with the highest concentration found in Brent (0.94 μg/m^{-3}) which probably reflects the higher traffic density associated with this area (Pattenden, 1974 and McInnes, 1979 - see Table 3.7a).

In general most studies of urban air report metal concentrations in the order Pb > Zn > Cu > Ni > Cd. In rural locations, Zn concentrations in air samples are often similar to those of Pb, probably due to a decrease in the traffic density in such areas, with the same order for the other metals, although at decreased concentrations (Pierson *et al.*, 1973). Several studies undertaken in Britain have examined the Pb content of air in the roadside environment. Duggan (1984) measured the Pb in air concentrations in several busy roads in London where a range of 0.28-1.90 μg/m^{-3} was found (see Table 3.7a), the highest values generally being associated with busy roads in central London, whilst Harrop *et al.* (1990a) lists the background urban concentration of Pb as 0.1 μg/m^{-3} based on a study in Harringay, London, where kerbside Pb concentrations of 0.5 μg/m^{-3} occur (see Table 3.7a).

Saltzman *et al.* (1985) investigated the trace metal content of air in eight cities in America, and found a range of geometric means of 0.30-3.40 μg/m^{-3} for Pb, the highest concentration found in Los Angeles (see Table 3.7a). The geometric means for Zn were reported to vary from 0.02-0.62 μg/m^{-3}, Ni from 0.015-0.042 μg/m^{-3} and Cd from 0.001-0.006 μg/m^{-3} (see Table 3.7b). A later study based in remote areas of the United States (Eldred and Cahill, 1994) which involved the measurement of very fine particles (0-2.5 μm) reported very low Pb concentrations ranging from 0.001-0.002 μg/m^{-3} and Zn concentrations generally of a similar magnitude. A study of Pb air concentrations at six sites in Brisbane, Australia, (Simpson and Hongchang, 1994 - see Table 3.7a) found that all sites had experienced a decrease in average Pb concentrations from the mid 1980's until the most recent measurements in 1991, with most sites now having Pb air concentrations of between 0.2-0.4 μg/m^{-3}. The decrease of Pb from 1986 coincides with the introduction of unleaded petrol in a city where cars were a source of between 83-97% of the atmospheric lead. This compares with a similar study undertaken in Canada from 1981 to

1992, which found concentrations of Pb in air at three sites in 1992 ranging from 0.079-0.225 $\mu g/m^{-3}$, which represents a substantial decrease from the early 1980's (Loranger and Zayed, 1994 - see Table 3.7a).

A study of an industrial and a residential site in Genoa, Italy, found a marked difference in the Pb air concentrations, although this is likely to be as result of the locations of the samplers rather than any empirical differences between the two sites (i.e. in this case one air sampler was higher and further away from main roads). Geometric means for the two sites were 1.037 $\mu g/g^{-3}$ and 0.476 $\mu g/m^{-3}$ respectively, both within the air quality standards proposed by the USA of a monthly average of 1.5 $\mu g/m^{-3}$ (Valerio *et al.,* 1992 - see Table 3.7a). A multi-element study of the air quality in two parts of Rio de Janeiro, Brazil, reported low concentrations of trace metals. A Pb concentration of approximately 0.5 $\mu g/m^{-3}$ was observed in both locations, with Zn ranging from 0.145-0.298 $\mu g/m^{-3}$, Cu concentrations of approximately 0.02 $\mu g/m^{-3}$ and Cd ranging from approximately 0.002-0.003 $\mu g/m^{-3}$ (Trindale *et al.,* 1981 - see Tables 3.7a and 3.7b). An average Pb concentration of 0.3 $\mu g/m^{-3}$ is reported for Varanasi in India, which is similar to results from other Indian cities such as Kanpur, Bombay and New Delhi (Tripathi, 1994).

Table 3.7a Atmospheric concentrations of Pb in rural and urban environments

Location	reported range or mean $\mu g/m^{-3}$	Reference
Walsall	1.3	Lee *et al.* (1994)
2 British rural locations	0.05 and 0.1	Lee *et al.* (1994)
Brent	0.94	McInnes (1979)
London roadside	0.28-1.90	Duggan (1984)
Harringay background	0.1	Harrop (1990a)
Harringay roadside	0.5	Harrop (1990a)
8 USA cities	0.3-3.4	Saltzman (1985)
Remote USA	$1x10^{-3}$-$2x10^{-3}$	Eldred and Cahill (1994)
Brisbane	0.2-0.4	Simpson and Hongchang (1994)
Canada	0.079-0.225	Loranger and Zayed (1994)
Genoa	1.037 and 0.476	Valerio *et al.* (1992)
Rio	0.5	Trindale *et al.* (1981)
India	0.3	Tripathi *et al.* (1981)

Table 3.7b Atmospheric concentrations of other metals in cities

Location	Reported range or mean		Reference
	$\mu g/m^{-3}$	metal	
British towns	0.1-0.3	Zn	Lee *et al.* (1994)
British rural	0.04-0.08	Zn	Lee *et al.* (1994)
8 USA cities	0.02-0.62	Zn	Saltzman (1985)
8 USA cities	0.015-0.42	Ni	Saltzman (1985)
8 USA cities	$1x10^{-3}$-$6x10^{-3}$	Cd	Saltzman (1985)
Rio	0.145-0.298	Zn	Trindale *et al.* (1981)
Rio	0.02	Cu	Trindale *et al.* (1981)
Rio	$2x10^{-3}$-$3x10^{-3}$	Cd	Trindale *et al.* (1981)

3.3 Metal deposition

3.3.1 Introduction

Metals in the atmosphere mainly occur as aerosol particles with a typical size range of 0.1 to 10μm, and these reach the earths surface by two major processes: dry deposition and wet deposition. The size of the particulate matter is important in both these processes. With larger particles (> 10 μm) dry deposition is achieved rather quickly by sedimentation, whilst with smaller particles dry deposition results from impaction to surfaces and diffusion. With wet deposition, similarly, two distinct processes occur. Rainout takes place in the clouds with the metal particle acting as either a condensation nuclei or being captured by cloud particles. Washout is simply the removal of air particulate by raindrops and this process is only important for particles of > 5 μm (Cawse, 1981).

A number of studies examine the chemistry of atmospheric deposition, be it in the form of wet or dry deposition or `bulk' deposition. Recently research has concentrated on the acidity of deposition and the content of ammonia (Gatz, 1991; Matzner and Meiwes, 1994; Lee and Longhurst, 1992), although a number of papers do examine the metal content in particular. An extensive review of the literature was undertaken by Galloway *et al.*(1982) and it is necessary at this stage to distinguish between researchers who have measured deposition rates (generally kg/ha^{-1}y^{-1}) and those which examine metal concentrations in rainwater measured in μg/l^{-1}.

3.3.2 Deposition rates

The data from this section is summarised in Table 3.8. A number of studies have investigated the deposition rate of trace metals in a particular urban or industrial region of the world. In rural locations in Britain Cawse (1978) reports a deposition rate range of 0.16-0.45 kg/ha^{-1}y^{-1} for Pb, 0.49-1.2 kg/ha^{-1}y^{-1} for Zn, 0.098-0.48 kg/ha^{-1}y^{-1} for Cu and < 0.1 kg/ha^{-1}y^{-1} for Cd (see Table 3.8). Results reported for Tennessee (Anden *et al.*, 1975) for the same metals generally lie closer to the lower end of these ranges, a trend also found for other studies in rural America (Lazrus *et al.*, 1970 and Schlesinger *et al.*, 1974). In Britain the generally higher concentrations of metals is reflected in higher background concentrations of these metals in soils as discussed in section 2.6.

In urban locations the deposition rate of metals is higher, as a consequence of increased traffic density and industrial activity. Cawse (1978) reports results from surveys conducted in New York, Swansea and Gottingen with the Pb deposition rate varying from 0.23-0.79 kg/h^{-1}y^{-1}, Zn from 0.47-1.0 kg/h^{-1}y^{-1}, Cu from 0.11-0.36 kg/h^{-1}y^{-1} and Cd from 0.004-< 0.2 kg/h^{-1}y^{-1}. Sposito and Page (1981) suggest a deposition rate range for Europe of 0.087-0.536 kg/h^{-1}y^{-1} Pb, 0.02-25.23 kg/h^{-1}y^{-1} Zn, 0.013-7.73 kg/h^{-1}y^{-1} Cu and less < 0.1 kg/h^{-1}y^{-1} for Cd (see Table 3.8).

In industrial areas deposition rates have been measured by a number of researchers. Beavington (1973) investigated the deposition of trace metals at varying distances around a smelting complex (copper and a steelworks) in Australia. At sites within 100m of the smelter deposition rates of 30.7 kg/h^{-1}y^{-1} Cu, 8.4 kg/h^{-1}y^{-1} Zn, 4.7 kg/h^{-1}y^{-1} Pb and 0.19 kg/h^{-1}y^{-1} Cd (see Table 3.8) were measured which decrease by factors of approximately 6, 3, 4 and 2.5 respectively at a distance of 600m. Hallet *et al.* (1982) report a similar trend with deposition rapidly decreasing as a function of distance from an industrial centre in Belgium, but never quite dropping to zero.

3.3.3 Metal content of bulk deposition

The studies presented in this section examine the deposition of metals as concentrations in bulk deposition or in rainwater rather than as deposition rates. Harrison *et al.*(1975) carried out a study of Pb and Cd in bulk deposition in London and the measured Pb concentration of 190 $\mu g/l^{-1}$ is considerably higher (generally five times higher) than the measured values for a number of other cities, particularly in America, such as Seattle, Los Angeles and Pittsburgh (Galloway *et al.,* 1982 - see Table 3.9). Only New York has a similar value, with a bulk deposition reading of 147 $\mu g/l^{-1}$ Pb. The corresponding Cd measurement for the London study was also much higher than those found in similar urban studies elsewhere in America and Europe. In America, peak Pb consumption as an additive to petrol occurred in 1978 and since then it has decreased rapidly with pre-1943 values reached by 1988 (Miller and Friedland, 1994). Reduction of the Pb content of petrol did not occur until in Britain until the mid-1980's (see section 3.4.6.1), which may account for, generally, higher concentrations of Pb in British studies. A seven year study in the Delta area of the Netherlands found average concentrations of metals in bulk deposition to be in the order Zn > Pb > Cu > Ni > Cd > Co, and land-use, as an influence on metal concentrations, in the order industrial > urban > rural. The peak concentrations for these elements in the industrial zone are 1318 $\mu g/l^{-1}$ Zn, 284 $\mu g/l^{-1}$ Pb and 90.4 $\mu g/l^{-1}$ Cu (Nguyen *et al.*, 1990 - see Table 3.9).

Table 3.8 Deposition rates of selected metals in cities

Location	Reported range or mean kg/ha^{-1} y^{1}	metal	Reference
Rural Britain	0.16-0.45	Pb	Cawse (1978)
Rural Britain	0.49-1.2	Zn	Cawse (1978)
Rural Britain	0.098-0.48	Cu	Cawse (1978)
Rural Britain	< 0.1	Cd	Cawse (1978)
Europe	0.087-0.536	Pb	Sposito and Page (1981)
Europe	0.025-25.23	Zn	Sposito and Page (1981)
Europe	0.013-7.73	Cu	Sposito and Page (1981)
Europe	< 0.1	Cd	Sposito and Page (1981)
smelter, Australia	4.7*	Pb	Beavington (1973)
smelter, Australia	8.4*	Zn	Beavington (1973)
smelter, Australia	30.7*	Cu	Beavington (1973)
smelter, Australia	0.19*	Cd	Beavington (1973)

* refers to sites less than 100m from the smelter

Table 3.9 The metal content of bulk deposition in the urban environment

Location	Reported range or mean $\mu g/l^{-1}$	 metal	Reference
London	190	Pb	Harrison *et al.*(1975)
New York	147	Pb	Galloway (1982)
Netherlands	peak of 284	Pb	Nguyen *et al.* (1990)
Netherlands	peak of 1318	Zn	Nguyen *et al.* (1990)
Netherlands	peak of 90.4	Cu	Nguyen *et al.* (1990)

3.4. Metals in soils

3.4.1 Introduction

In sections 3.2-3.3.3, the pathways by which metals from both natural and anthropogenic sources enter the atmosphere and are then deposited in a number of different environments (i.e. rural, urban and industrial) are reviewed. For the purpose of this study a review of anthropogenic additions of metals to soils is necessary. A number of these sources correspond to those outlined in sections 3.2-3.2.5 as, their emissions enter the atmosphere before reaching soils. Others sources, such as the use of fertilisers, pesticides, sewage sludge (not including the incineration of this particular source) and the disposal of waste material represent more direct inputs to soils.

3.4.2 Industrial activity

The mining and smelting of non-ferrous metals in Britain has a long history (see section 3.1.1) and Thornton (1980) suggests that such activity has contaminated in excess of 4000 km^2 of agricultural land in Britain. The nature of the industrial techniques, together with a general lack of statutory controls regarding smelter emissions and the disposal of wastes and effluent, has led to considerable environmental contamination with Pb, Zn and Cd (Davies, 1977). A study of soil in the near vicinity (0.2 miles) of the Pb-

Zn smelter at Avonmouth was undertaken by Burkitt *et al.*(1972), which reported concentrations of Pb, Zn and Cd of 600 μg/g, 5000 μg/g and 32 μg/g respectively (see Tables 3.10 and 3.11). In comparison soils 7.9 miles from the smelter were found to have metal concentrations of 60 μg/g Pb, 90 μg/g Zn and 1.1 μg/g Cd. Griffiths and Wadsworth (1980) also investigated the smelter at Avonmouth by examining the metal content of soils on farms close to an industrial complex which includes the smelter. Farms closest to the complex (1km) were found to have a mean Pb concentrations of 154 μg/g, 780 μg/g Zn and 11.1 Cd (see Tables 3.10 and 3.11).

An example of mining and metal contamination of soils in Britain is provided by Shipham in Somerset where Zn was mined in the 18th and 19th century. Median concentrations of metals calculated from 329 soil samples were 2340 μg/g Pb, 7600 μg/g Zn and 91 μg/g Cd (Sims and Morgan, 1988; Alloway, 1990c - see Tables 3.10 and 3.11). Alloway and Davies (1971) investigated soils potentially contaminated by mining activity, and found a mean Pb concentration of 1419 μg/g in alluvial soils of the Ystwyth river valley.

The formation of waste tips from mining activity also constitutes an environmental problem and a source of metals to soils. Davies (1977) reports that past mining techniques were very inefficient and at Ceredigion 15-38 tonnes of waste material were produced to enable the concentration of one tonne of Pb ore and hence this led to the formation of spoil tips. At Ceredigion the < 2mm fraction typically had 0.8% Pb and 0.1% Zn (see Tables 3.10 and 3.11). The same author reports approximately 0.4% Pb and 1.1% Zn in soils 20m from a spoil tip in Castleton, Derbyshire. Harper *et al.* (1987) investigated the influence of waste tips on metal concentrations in garden soils in the Lower Swansea Valley. Median values of Cu and Cd in Swansea were both twice as high as those found in London (from the National Reconnaissance Survey), with the median concentration of Zn also higher than the geometric mean found for London in the earlier survey (see Tables 3.17 and 3.22).

Examples of metal contamination from mining in America are provided by soils near Leadville, a historic mining community in Colorado, where Pb concentrations reached nearly 5% in places, Zn 1.2 % and Cd up to 110 μg/g (Levy *et al.,* 1992 - see Tables 3.10 and 3.11). In Butte, Montana, a soil representative of a mine waste site had a Pb concentration of 3900 μg/g (Davis *et al.,* 1992 - see Table 3.10). A great deal of research has also been carried out in the vicinity of smelters in the United States (Buchauer, 1973; Ragaini *et al.,* 1977 and Beyer *et al.,* 1984). Two of these studies relate to Zn smelters, with the earlier of these undertaken in Palmerton and reporting that the O_2 horizons of soils within 1 km of the smelter have Zn concentrations of 135 000 μg/g, 1750 μg/g Cd, 2000 μg/g Cu and 2000 μg/g Pb (Buchauer, 1973 - see Tables 3.10 and 3.11). These compare to peak concentrations of 35 000 μg/g Zn, 1300 μg/g Cd, 3200 μg/g Pb and 280 μg/g Cu also found in the O_2 horizons of soils around zinc smelters in Palmerton in a later study (Beyer *et al.,* 1984 - see Tables 3.10 and 3.11). This later study suggests that the estimation of the background concentrations of metals reported in the earlier study (12-16 km west and 19-39 km east of the smelter) were too high and hence underestimated the extent of contamination from the smelter. Ragaini *et al.* (1977) sampled soils close to a lead smelter in Kellogg, Idaho, and found metal concentrations of up to 7900 μg/g Pb, 29 000 μg/g Zn and 140 μg/g Cd (see Tables 3.10 and 3.11).

Studies have also been carried out involving smelters other than Zn and Pb. For Ni two such studies are by Hutchinson and Whitby (1974) and Davis (1987). The former was based in Sudbury, USA, and recorded Ni concentrations of up to 5104 μg/g in soils 1.1 km from the smelter (see Table 3.11). Beavington (1975) reported Cu concentrations of 847 μg/g in garden soils close to a Cu smelter in Australia and 229 μg/g Zn (see Table 3.11).

In Poland an investigation by Gzyl (1990) which involved sampling soil from allotments in the highly industrialised area of Silesia found a mean Pb concentration of 221.4 μg/g reaching a maximum of 1640.8 μg/g and a mean and maximum concentration of 8.3 μg/g and 51.7 μg/g, respectively, for Cd (see Tables 3.10 and 3.11). This compares to peak concentrations for soils around smelters in Poland of 290 μg/g Cd, 1200 μg/g Cu, 4650 μg/g Pb and 10 000 μg/g Zn (Pawlowski, 1990 - see Tables 3.10 and 3.11). Some similar studies have been carried out in the third world and Nriago (1992) reports that soils 5 km northeast of a Pb-Zn smelter in Kabwe, Africa had metal concentrations of up to

3500 μg/g Pb, 2580 μg/g Zn, and 46 μg/g Cd (see Tables 3.10 and 3.11).

Table 3.10 A summary of the Pb content of soils associated with industrial activity

Location	concentration μg/g	Reference
Avonmouth[1]	600	Burkitt *et al.* (1972)
Avonmouth[2]	60	Burkitt *et al.* (1972)
Avonmouth[3]	154	Griffiths and Wadsworth (1980)
Shipham	2340	Sims and Morgan (1988)
Wales	1419	Alloway and Davies (1971)
Ceredigion	8000	Davies (1977)
Leadville	up to 50000	Levy *et al.* (1992)
Montana	3900	Davis *et al.* (1992)
Palmerton	2000	Buchauer (1973)
Palmerton	3200	Beyer *et al.* (1984)
Idaho	up to 7900	Ragaini *et al.* (1977)
Poland	mean 221.4 peak 1640.8	Gzyl (1990)
Poland	up to 4650	Pawlowski (1990)
Africa[4]	up to 3500	Nriagu (1992)

[1] Samples 0.2 miles from the Pb-Zn smelter

[2] Samples 7.9 miles from the Pb-Zn smelter

[3] Samples 1km from the Pb-Zn smelter

[4] Samples 5km northeast of a Pb-Zn smelter

Table 3.11 A summary of the metal content of soils associated with industrial activity

Location	reported concentration µg/g	metal	reference
Avonmouth[1]	5000	Zn	Burkitt *et al.* (1972)
Avonmouth[1]	32	Cd	Burkitt *et al.* (1972)
Avonmouth[2]	90	Zn	Burkitt *et al.* (1972)
Avonmouth[2]	1.1	Cd	Burkitt *et al.* (1972)
Avonmouth[3]	780[3]	Zn	Griffith and Wadsworth (1977)
Avonmouth[3]	11.1[3]	Cd	Griffith and Wadsworth (1977)
Shipham	7600	Zn	Sims and Morgan (1988)
Shipham	91	Cd	Sims and Morgan (1988)
Ceredigion	1000	Zn	Davies (1977)
Leadville	up to 12000	Zn	Levy *et al.* (1992)
Leadville	up to 110	Cd	Levy *et al.* (1992)
Palmerton	up to 135000	Zn	Buchauer (1973)
Palmerton	2000	Cu	Buchauer (1973)
Palmerton	1750	Cd	Buchauer (1973)
Palmerton	35000	Zn	Beyer *et al.* (1984)
Palmerton	280	Cu	Beyer *et al.* (1984)
Palmerton	1300	Cd	Beyer *et al.* (1984)
Idaho	up to 29000	Zn	Ragaini *et al.* (1977)
Idaho	up to 140	Cd	Ragaini *et al.* (1977)
Sudbury	up to 5104	Ni	Hutchinson and Whitby (1974)
Australia	847	Cu	Beavington (1975)
Australia	229	Zn	Beavington (1975)
Poland	8.3	Cd	Gzyl (1990)
Poland	up to 10000	Zn	Pawlowski (1990)
Poland	up to 1200	Cu	Pawlowski (1990)
Poland	up to 290	Cd	Pawlowski (1990)
Africa[4]	up to 2580	Zn	Nriagu (1992)
Africa[4]	up to 46	Cd	Nriagu (1992)

1 Samples 0.2 miles from the Pb-Zn smelter

2 Samples 7.9 miles from the Pb-Zn smelter

3 Samples 1km from the Pb-Zn smelter

4 Samples 5km northeast of a Pb-Zn smelter

3.4.3 Sewage sludge

Sewage sludge is the organic residue derived from the sewage of towns and cities and this is applied to soils for a number of reasons. It may be used as a fertiliser and organic soil conditioner, but most importantly sludge is added to soil as a means of disposal (Alloway, 1990b). However, not all sewage sludge is added to soil and other methods of disposal include incineration, disposal at sea or through landfill. Sludge is not usually applied to urban land and therefore not a major source of metals in towns and cities, but the application to agricultural land is a well established practice (Boswell, 1975). In Britain alone the application affects approximately 10% of arable land (Alloway, 1990b). The agricultural use of sewage sludge has been favoured increasingly as a means of both disposal and as an additional source of phosphorus and nitrogen for crop requirements (Yingming and Corey, 1993). However, it is the elevated concentrations of metals associated with the sewage sludge that has been a cause for concern and a great deal of research (Boswell, 1975; Miles and Parker, 1979; Baxter *et al.*, 1983; Chang *et al.*, 1984 and Yingming and Corey, 1993). Alloway (1990b) presents data which listed typical ranges of metals in sewage sludge as 29-3600 μg/g Pb, 91-49000 μg/g Zn, 50-8000 μg/g Cu, < 1-3410 μg/g Cd, 6-5300 μg/g and 8-40600 μg/g Cr.

3.4.4 Agricultural materials

Fertilisers and phosphatic fertilisers in particular constitute a significant source of several metals to soils, particularly agricultural soils, although not exclusively. Fertilisers are often applied to domestic gardens and may therefore be a source of metals in the urban environment. Hutton and Symon (1986) reported that in 1980 1324t x 10^3 rock phosphate was imported into Britain, the majority of which was used to produce fertilisers, and this had a Cd and Pb burden of 42.8t and 3.9t respectively. In general, phosphate fertilisers are not a significant source of Pb to soil (Jones *et al.*, 1987). All fertilisers contain some Zn most usually in the form of an impurity, and inorganic fertilisers have a Zn concentration range of 50-1450 μg/g. Phosphate deposits usually contain approximately 30 μg/g Ni, although some deposits have as much as 1000 μg/g Ni. Chromium, however, is generally more enriched in fertilisers with a concentration range of 30-3000 μg/g reported for Canadian fertilisers (McGrath and Smith, 1990).

A wide variety of agricultural materials and compounds can be used to supply Cu to soils, although the usual source of Cu is via bluestone ($CuSO_4.5H_20$) which contains approximately 25% Cu (Baker, 1990). Jones *et al.* (1987) carried out controlled experiments of archived soil to investigate the anthropogenic addition to soils from a number of sources. The soils originate from the 1800's and some have undergone additions of phosphate fertilisers and organic manures. It was found that the soils which had undergone additions of phosphate fertilisers did not have any significant increases in the concentrations of Zn, Cu or Pb. However, soils that had experienced additions of organic manures had 70 μg/g Pb, 142 μg/g Zn and 37 μg/g Cu, compared to concentrations of 40 μg/g Pb, 83 μg/g Zn and 28 μg/g Cu for unmanured soils. Goodroad and Caldwell (1979) also found that applications of phosphatic fertilisers did not result in any significant increases of Pb and Cr in soils. However, contrary to these findings, several authors report an increase in metal concentrations in soils on additions of fertilisers, particularly in relation to Cd (Mulla *et al.*, 1980; Tjell and Christensen, 1985).

Metals are also present in other agricultural applications such as certain pesticides, fungicides and insecticides. Copper, is contained in Bordeaux mixture, a fungicidal spray and soils which support crops that have been treated with it have been found to have Cu concentrations ranging from 110-1500 μg/g (Baker, 1990). Copper and Zn are also present in agricultural pesticides although Cr and Ni are generally not.

3.4.5 Paint

Section 3.1 in general examines the uses of selected metals, and the presence of certain metals in paint was very briefly touched upon. Lead in particular is a metal strongly associated with paint, or, perhaps more accurately, which was associated with paint. Paint manufactured pre-1914 possibly had a Pb content of up to 50% in the dry film. Post-1945 the use of lead pigments in paints decreased, being restricted to primers (Rundle and Duggan, 1986). Despite this, Pb paints were still produced and utilised after this period by more affluent people as they were believed to be of a good quality. Even today in Britain, particularly with the older housing, a great deal of paintwork exists which contains a high percentage of Pb, usually between 5-50 %. A study conducted by Schwar and Alexander (1988), looking at the lead-in-dust content of school playgrounds in relation to redecoration, found that the highest Pb values in dust were associated with older schools. The highest mean value of 74000 μg/g Pb associated with schools aged at pre-1914 and between 1914-1939, with the highest values occurring within 2.5m of the building.

3.4.6 Vehicles

The issue of Pb in petrol and its' dispersion into soils is an important influence on urban geochemistry. Lead is added to petrol to increase the octane quality of a gasoline which in turn allows resistance to spontaneous ignition or `knock'. Increasing octane quality allows the use of engines with higher compression ratios and consequently reduced fuel consumption. Lead alkyl additives, tetraethyl lead and tetramethyl lead, remain the least energy-demanding and cheapest way of raising octane quality. In addition to considerations of octane quality, the use of leaded petrol prevents damage to the engine via high valve seat wear (Shell International Petroleum Company Limited PAC/3 July 1985).

There are a great number of studies which deal specifically with the Pb content of roadside soils, and these date from the 1960's. A review of such works is vital to urban geochemistry because so many soils both in areas of open space and residential areas are greatly influenced by busy roads. A number of central themes are shared by the great majority of these reports, and in particular the relationship between the metal soil burden and factors such as distance from the road and traffic density.

Cannon and Bowles (1962) demonstrated that grass sampled within 25 feet of the road contained up to 4 times as much Pb as grass collected 500 feet away, whilst Kloke and Riebartsch (1964) reported that an increase in traffic density by a factor of 2 or 3 caused an increase in the Pb content of roadside grass by a similar factor. Lagerwerff and Specht (1970) investigated the contamination of roadside soils and vegetables with Pb, Cd, Zn and Ni at four sites with a high traffic density in North America. Soils were found to be contaminated in the order Pb > Zn > Ni > Cd. It is a misconception that Pb is the only metal associated with roadside soils, but this is certainly not the case and is reiterated by several studies in this area. Lagerwerff and Specht (1970) explained their findings by stressing that Pb is the most abundant metal through its' association with leaded petrol whilst Zn and Cd are contained in tyres. Nickel is, or was, used on a limited basis in nickelled petrol. These metals are also therefore deposited in the roadside environment (Ward *et al.,* 1977). Table 3.12 summarises the sources of metals from automobiles, not only from the paper by Lagerwerff and Specht (1970) but from several reports cited in this review.

Table 3.12 Vehicles as a source of metals

Metal	Source
Pb	Petrol, Motor Oil
Zn	Tyres, Motor Oil
Cu	Brake Lining, Motor Oil
Ni	Limited-Use Ni Gasoline, Motor Oil
Cd	Tyres, Motor Oil

Page and Ganje (1970) compared areas of low and high traffic densities in California. All of the sample sites were more than one mile from major highways, and it was found that areas with a traffic density of < 30 cars/km^2 showed no significant accumulation of Pb over 40 years. This is in rich contrast to areas where vehicle densities exceeded 223/km^2 and surface soils have increased from 16 μg/g to 32 μg/g accordingly over the same period (see Table 3.13). This indicates that even over large distances Pb fumes from petrol can influence surface soils in areas of high traffic density. In areas closer to major roads, concentrations of Pb in topsoil were found to range from 100-300 μg/g (see Table 3.13). Ward *et al.* (1977) investigated the potential contamination of soils with several metals close to a major motorway in New Zealand and found that traffic density greatly influenced the metal content of soils with Pb concentrations in excess of 2000 μg/g and the soil concentrations of Zn, Cu, Ni, Cr and Cd all greatly increased above background values (see Table 3.13).

Work by Ward *et al.* (1975) and Rodriguez-Florez and Rodriguez-Castellon (1982) also investigated the principle of traffic density/volume. Ward *et al.* (1975) took an uninhabited area of New Zealand, 20km from the nearest town, through which a single highway passed with a low traffic volume of 1200 vehicles per day. Soil Pb burden was investigated as a lateral and vertical function, with samples taken at regular intervals of 5 or 10m and at depths down to 10cm. No significant Pb elevation was found below a depth of 5cm in the soil, and at a depth of 1cm the mean Pb content of the soil varied from 160 μg/g at 10m away from the highway to 90 μg/g at 30m and 60 μg/g at 100m (see Table 3.13), clearly illustrating the distance-decay principle. A more detailed examination of the data involved calculating the volume increments of excess Pb in the soil cores, and plotting this as a function of distance to find an integrable function which fits the decay closely. Results showed that up until 50m away from the highway an exponential decrease of Pb with distance was evident. However, at distances of greater than 50m the decrease in soil Pb content is less than would be predicted by an exponential plot. This gradual decrease could well be due to the influence of secondary dispersal processes such as surface soil mobilisation by wind.

Rodriguez-Florez and Rodriguez-Castellon (1982) expanded on this theme, looking at Pb and Cd concentrations in the top 5cm of soils in Puerto Rico. Again an exponential decrease was found with increasing distance from the road, as well as excellent correlations between traffic density and the relative `area' of Pb burden in soils ($R = 0.9941$, $P < 0.001$) for distance and Pb concentrations. Davies (1990), states that most authors agree that this distance decline relationship is curvi-linear, with background levels reached by 30-50m from the road.

Wheeler and Rolfe (1979) modelled the deposition of Pb by a double exponential function:

$$Pb = A1 \exp(-KD) + A2 \exp(K'D)$$

Where A1 + A2 are linear functions of average daily traffic volumes and the two exponents are assumed to represent two families of particles of different size. The larger particles were deposited within 5m of the road and the smaller particles within 100m.

A number of other studies have been carried out in Europe to investigate the relationship between metal contamination, Pb in particular, and major roads. Such studies include Muskett and Jones (1990) in Oxford, Albasel and Cottenie (1985) in Brussels, Harrison and Johnston (1985) in North West England, Yassoglou *et al.* (1987) in Athens, Majdi and Persson (1989) in Sweden and Warren and Birch (1987) and Harrop *et al.* (1990), both of which are based in London.

Muskett and Jones (1990) measured levels of Pb, Cd and Ni in the vicinity of the A40 both in the air, soil and invertebrate macrofauna at intervals of 1m, 10m, 30m and 100m away from the A40. Concentrations of metals in the air were found to be in the order Pb > Cd > Ni, whilst the concentrations in soil were found to be in the order Pb > Ni > Cd. The similarity exhibited by the metals (especially Pb + Ni) in their dispersion patterns, a sharp decrease in air at distances greater than 10m from the road, suggests a common source. Particle sizes and the wind direction are both important considerations when interpreting metal concentrations in roadside soil.

The particle size of Pb from traffic emissions has been reported as being very small, approximately 0.2 μm (Habibi, 1970 and Little and Wiffen 1978). Both Ni and Pb are subjected to high thermal conditions, whilst an element such as Cd which has been reported as a constituent of tyres (see Table 3.12) may not be subjected to such high temperatures and therefore probably has a different particle size, and different dispersion pattern. With two London-based studies, the earlier study investigated the roadside environment of the A13 in east London finding a distance decay principle for Pb, Zn, Cu and Cd. Nearly 1000 μg/g Pb was reported for soils 6m from the busy road with 70000 vehicles a day, (Warren and Birch, 1987 - see Table 3.13) whilst Harrop *et al.* (1990b) reported slightly lower concentrations in roadside dusts of the London Borough of Harringay, which no doubt reflect the lower traffic densities in the later study.

Several studies have also taken place close to the M25, the London orbital, with Ward (1990a and 1990b) carrying out two studies. The first of these was a multi-element analysis of soil, dust vegetation and airborne material which found extensive enhancement of V, Cr, Mn, Co, Ni, Cu, Zn, Br, Mo, Cd and Ce in relation to increasing traffic density (Pb not analysed). It was postulated that this was due to a combination of tyre and brake wear and the combustion of petrol and lubricating oil. The second study looked at Pb contamination near a section of the M25 that had been monitored since its opening in 1986. The Pb concentration here was reported to increase from 20.4 μg/g before its opening to 446.9 μg/g 24 months later (see Table 3.13). This can be compared to a study by Milberg *et al.* (1980) which conducted a similar study in Beltsville over two years, finding a Pb increase from 16.8 μg/g to 130 μg/g in soils on the west side of the road compared to an increase from 12.8 μg/g to 246 μg/g on the east side (see Table 3.13).

In a study by Albasel and Cottenie (1984) the impact of highways, and urban/industrial areas on concentrations of elements in soils was assessed with elevated levels of Mn, Cu, Zn, and Pb found in roadside soils. Again a decrease in element concentration was recorded away from the major highways, and in addition elevated levels were found in urban gardens in Brussels. The variations that can occur in the deposition rates of metals on a temporal scale are investigated in a paper by Harrison and Johnston (1985), who studied verges around the M6. The study was carried out between late 1981 and 1983, and the metal deposition patterns exhibit a great deal of temporal variation which relates very closely to the changes in traffic density. This study also found a critical distance of some 20m away from the M6, after which the concentrations of Pb, Cu and Cd remained fairly constant.

Majdi and Persson (1989) investigated the accumulation of Pb and Cd in the FH-layer of forest soil close to a road and compared this to accumulation in the mineral layer. Results showed greater accumulation in the FH-layer than in the mineral soil, and accordingly greater accumulation in the soils closer to the road than those further into the forest. Yassoglou *et al.* (1987) in their study of roadside soils in Athens also found a number of trends which bear a close resemblance to those relationships already encountered in this report. Total surface Pb was found to have an excellent correlation with distance from the road (varying from R = 0.73 to 0.81 in relation to traffic density). The concentration of Pb in topsoils was also found to have a good correlation with the number of vehicles per day (R = 0.76 and 0.90 in relation to different distances from the road). Cadmium and Zn were also found to show an exponential decrease with distance, although Ni exhibited no such relationship. Similar studies have taken place in less developed countries and these have included papers by Ndiokwere (1984) and Burguera and Burguera (1988). The former study was carried out along a busy highway in Nigeria, a road which carries 34,000 vehicles a day which is also 20km from the nearest urban centre. This isolated the road as the primary source of metals. The topsoils (depth 2cm) displayed a decrease in the levels of Pb, Zn, Cr, Ni, Cu, and Cd to a greater or lesser extent at sites 1.5m from the edge of the road to sites 50m away from the highway. Burguera and Burguera (1988) concentrated on the Pb content of roadside soils in Venezuela with different traffic volumes. Where the volume exceeded 5,000 vehicles per day the surface soil (0-2cm) showed very little evidence of Pb accumulation, with a concentration varying from 11.7 $\mu g/g$ to 19 $\mu g/g$. However, at sites where traffic density reached over 10,000 vehicles a day Pb accumulation varied from 42.4 $\mu g/g$ to 177 $\mu g/g$ (see Table 3.13). A study of roadside dust in a number of locations in Lagos by Ogunsola *et al.* (1994) found the highest mean concentrations of Pb to be from major highways and then from industrial regions with the lowest concentrations from residential areas. A similar pattern was expressed for a number of metals.

An interesting addition to the literature on the impact of vehicles in general on soil geochemistry is a paper by Vazquez-Duhalt (1989). This deals with the environmental impact of used motor oil which contains considerable quantities of Pb, Zn, Cu, Cr, Ni, Cd, and Ba. Motor oil which is in use has properties which allow it to accumulate metals. This oil can then be dispersed in to the soil in 5 different ways:

1). Escape and loss of oil during engine operation.
2). Applications on rural roads for dust control.
3). As a constituent of asphalting (using waste crankcase oil).
4). Placement in landfill sites.
5). Burning as auxiliary fuel in special burners.

Table 3.13 A summary of the influence of roads on the Pb content of soils

Location	details and reported value	Reference
California	increase from 16-32 μg/g at sites over 1 mile from major roads in the space of 40 years	Page and Ganje (1970)
California	100-300 μg/g close to major roads	Page and Ganje (1970)
New Zealand	160 μg/g 10m from road 90 μg/g 30m from road 60m μg/g 100m from road	Ward *et al.* (1975)
New Zealand	2000 μg/g close to a major motorway	Ward *et al.* (1977)
London	approximately 1000 μg/g 6m from A13	Warren and Birch (1987)
London	in roadside dusts	Harrop *et al.* (1990b)
London	Increase from 20.4 μg/g to 446.9 μg/g of a roadside soil in 2 years.	Ward (1990a)
USA	Increase from 16.8 μg/g to 130 μg/g on west of road and from 12.8 μg/g to 246 μg/g on east.	Milberg *et al.* (1980)
Venezuela	11.7-19 μg/g - low traffic density and 42.4-177 μg/g high traffic density	Burguera and Burguera (1988)

3.4.6.1 Lead in petrol legislation

A major issue regarding the impact of lead from automobile sources is how legislation concerning the acceptable level of Pb in petrol has evolved. Since 1986, in accordance with EC policy, the lead alkyl content of petrol has been set at 0.15 g/l for member countries. A number of studies have since been undertaken to investigate how this new ruling has effected the Pb content of both air and soils. Page *et al.* (1988) in a study on six sites in Wales from 1984-1986 found that the recent decrease in lead alkyl levels in petrol had resulted in a corresponding 52-61 % decrease in air Pb at both the urban and sub-urban sites. Two similar studies conducted outside the EC include those by O'Conner *et al.* (1990) in Western Australia and Fu *et al.* (1989) in Honolulu. The first of these investigated the impact of unleaded petrol and the variation of Pb in leaded petrol on the air quality in Perth. This involved the use of atmospheric Pb concentrations and petrol Pb consumption from 1982-1987 (unleaded petrol was introduced in 1985). It was found that a close correlation existed between total Pb consumption and mean annual atmospheric Pb levels, and also that temporal variations in petrol Pb concentrations need to be considered when investigating the impact of unleaded petrol on air quality. This is illustrated by the fact that, even for premium grade petrol, in September 1986 Pb lead levels varied from 0.39 g/l to 0.8 g/l (O'Conner et al., 1990).

The paper by Fu *et al.* (1989) examined the variation in soil Pb content in a major Honolulu park from 1972 to 1987, a period over which local Pb emissions decreased by 80% due to an increase in the use of unleaded petrol. Results showed that in the exposed part of the park where the largest Pb accumulation occurred, total soil Pb content decreased by 53% (3500 μg/g to 1650 μg/g). However, the weighted mean Pb levels for the entire transect only decreased by 21%, probably a reflection of the fact that the sites further inside the park are less effected by vehicle emissions. Ho (1990) in a study in Hong Kong looked at metal concentrations in kerbside dust. Lead in petrol was decreased stepwise from 1981 in Hong Kong, and this gave a Pb reduction similar to that found by Page *et al.* (1988 - 60% in this case) in dust from 1977-78 to 1987. This reduction was not reflected in the same comparison for Zn, Cu and Mn and this indicates the importance of automobile sources other than petrol for Cu and Zn, whilst Mn is believed to be derived from the soil. Both Fergusson (1986) and Nriagu (1990) present extensive reviews of petrol lead in the environment and how this has evolved.

3.4.6.2 Urban patterns and driving cycles

Perth was also used as an example to examine the relationship between urban structure and vehicle emissions by Lyons *et al.* (1990). Much of this study was based on work by Kenworth *et al.* (1983) who employed an urban ecology approach, treating the city as an integrated system to obtain representative driving cycles across Perth. The

Metropolitan area was divided into 6 regions characterised by socio-economic status and the intensity of traffic activity. Most importantly movement away from the CBD resulted in fewer traffic events, higher speeds, longer cruise periods, and shorter stops. As a result a reduction occurs in the root mean square acceleration and most significantly in vehicle emission factors. Although this paper concentrates on carbon monoxide, hydrocarbons, and nitrous oxides emissions, the increase in Co/No x` ratio in the CBD due to vehicle congestion and an increase in root mean square acceleration has important implications for the dispersal of vehicular Pb in the urban environment, particularly an area like Richmond. Two later studies which investigated aspects of driving patterns and emission parameters are by Andre *et al.* (1994) and Tonkelaar (1994). The former study of privately-owned cars in six European cities found that cars were frequently used for short distances creating unfavourable thermal conditions which coupled with urban traffic conditions account for excessive fuel consumption which increase pollution. Tonkelaar (1994) found that the introduction of a new system of speed limits on Dutch motorways initially decreased emissions and fuel consumption but these rose again slowly in the following year. Lead emissions have, however, steadily decreased since the new regulations were implemented in 1986.

3.4.7 Other sources of metals

A number of other sources exist which do not really fit any of the other categories. Moseholm *et al.* (1992) investigated soil around a car battery factory north of Copenhagen believed to be a major source of Pb dust in the area. Soils closest to the factory were found to have a Pb concentration of 360 μg/g (see Table 3.14). Blake *et al.* (1987) investigated metal contamination around scrap metal yards, which mainly handled ferrous metals, and car breaker yards where the waste Cu, Pb, Zn and various alloys were collected and sold. For the scrap yard, the dusts which showed the greatest contamination were those associated with the scrap yard that broke Pb batteries. Dusts at the entrance to this site had concentrations of Pb of nearly 3.3%, with control samples from nearby major roads ruling out the possibility of this being as a result of Pb in petrol (see Table 3.14). This site also yielded metal concentrations of up to 34200 μg/g Cu, 12000 μg/g Zn and 19.4 μg/g Cd (see Table 3.14). In general, the extent of metal contamination at the breakers yard was less, although higher than the results published from an earlier survey at the same site (Blake *et al.*, 1987). Peak concentrations in dusts were 3% Pb, 230 μg/g Cd, 8500 μg/g Zn and 2900 μg/g Cu (Blake *et al.*, 1987 - see Table 3.14).

Soils close to transmission towers and high tension lines have exhibited high concentrations of certain metals. A study conducted in Holland (Kraal and Ernst, 1976) looked at soils in the vicinity of Cu high tension wires and found that samples close to wires had higher concentrations of Cu, whilst Jones *et al.* (1988) investigated corn plants growing near electrical transmission towers and found Zn concentrations in soils near to a 30 year old tower of 1425 μg/g (see Table 3.14). This high value of Zn results from the corrosion of Zn as soon as galvanised metal is exposed to the environment. This compares to Zn concentrations of 10431 μg/g in soils 1m from towers (Jones and Burgess, 1984 - see Table 3.14). Another very specific source of metal, Pb in this case, occurs around printworks in central London with concentrations in excess of 20% found at the entrance to the works, with a close association between the Pb and Sn. Tin is a constituent of the Pb alloy used in printing (Jensen and Laxen, 1985 - see Table 3.14)

Table 3.14 Miscellaneous sources of metals in urban areas

Source	Reported concentration	metal	Reference
Car Battery Factory	Soils closest to factory (360 μg/g)	Pb	Moseholm *et al.* (1992)
Scrap metal	dusts at entrance of works:		Blake *et al.* (1987)
	3.30%	Pb	
	3.42%	Zn	
	1.20%	Cu	
	19.4 μg/g	Cd	
Breakers yard	3%	Pb	Blake *et al.* (1987)
	8,500	Zn	
	2,900	Cu	
	230 μg/g	Cd	
Copper high tension wires	Increased Cu concentrations in soils below the wires		Kraal and Ernst (1976)
Transmission towers	30 years old tower: 1425 μg/g in soils	Zn	Jones *et al.* (1984)
Transmission towers	soils 1m from tower 10,431 μg/g	Zn	Jones and Burgess (1984)
Printworks	Dust close to printworks 20% Pb close association of Sn and Pb	Pb	Jensen and Laxen (1985)

3.5 Urban geochemistry

3.5.1 Lead levels in British dusts and soils

The earliest work regarding metal contamination and urban areas stems from a report by the Departmental Committee on Ethyl Petrol (1930). This report was produced because of fears regarding the potential risk to city dwellers from Pb in street dust. This report presented high Pb levels in London street dusts and in many ways this started a trend that continues today with studies of this kind. Later reports by Turner (1973) and

Duggan and Williams (1977) also concentrated on London with the latter employing a more detailed approach and investigating areas of London that were classified as central, mid-urban and outer urban. Results showed a decrease in the Pb content of dust from central London to outer London. The results summarised in Table 3.15 represent, in general, the overall average Pb content for dusts at all locations within the individual studies. The exception to this is the mean value reported for Lancaster which relates purely to residential sites within the urban area. This is of course an over simplified approach, and all of these studies to a certain extent were structured to enable the comparison between areas of differing traffic density. Despite this, an examination of Table 3.15 shows that with the possible exception of Birmingham the mean Pb content of urban street dusts is in fairly good agreement for all of the cities reported. An approximate value of 1000 μg/g appears to be a reasonably good estimate of the Pb content of urban dusts in large British cities in the late 1970's. Any differences that do exist in Pb dust content can possibly be explained, not only by any intrinsic differences between sampling locations, but also by variations in sample number and analytical techniques.

A closer examination of the individual reports listed in Table 3.15 confirms the trend found by Duggan and Williams (1977) in London with regard to Pb dispersion and road type/traffic density. Farmer and Lyon (1977) in their study of Glasgow found that the edges of several parks had significantly higher concentrations of Pb than their central sections, and also that Pb concentrations in soils fell with increasing distance from a major road (744 μg/g 2m from the Great Western Road compared to 230 μg/g at a distance of 50m).

Table 3.15 Lead concentrations in urban dusts

Location (year)	Number of samples	Arithmetic mean (μg/g)	Range (μg/g)
Manchester (1975)	350	970	
Birmingham (1976)	1,061	1,630	160-50,000
London (1977)	79	1200	
Glasgow (1977)	130	960	150-2,300
Lancaster (1979)	7	850	620-1,240

Archer and Barratt (1976) in their study of Pb levels in Birmingham dusts also reported substantial differences between Pb dust levels associated with `A' roads, `B' roads, and residential roads. These particular sites produced arithmetic mean Pb concentrations of 2,350 μg/g, 1,557 μg/g, and 1,050 μg/g, respectively. The study in Lancaster by Harrison (1979) took the investigation a step further by adopting a more detailed differentiation in traffic patterns. This involved an analysis of samples from car parks, the town centre, main roads, residential roads and rural roads. The pattern of results for Pb that emerged showed car parks displaying the highest means (46,300 μg/g) with a decrease down to rural roads (570 μg/g). This pattern can be explained by differences in the movement of traffic with higher Pb concentrations associated with areas such as car parks and town centres where traffic is subjected to a greater degree of stopping/starting and acceleration. Results reported by Day *et al.* (1975) show that concentrations of Pb in dusts from Manchester were of a similar magnitude throughout the city.

3.5.2 Urban soil geochemistry

The history of urban geochemistry which deals specifically with metal contamination of soils spans less than 30 years. The innovative work in this area was conducted by Purves (1966 and 1967) through the investigation of metal concentrations in garden soils in Edinburgh and Dundee. It was discovered in the earlier work by Purves that total Cu and water extractable B were significantly higher in urban garden soils than in arable areas. In further work the following year it was found, using a variety of extraction techniques, that city/small town gardens have significantly higher plant `available' Cu, B, and Pb than rural gardens. Purves and Mackenzie (1969) extended the study to examine the difference between the metal contamination of urban parks and rural parks. Using the same extractants as those employed out by Purves (1967), it was found that the trend of greater contamination in urban gardens was also observed for their analysis of samples from urban/rural parks. This paper also highlighted the confusion surrounding the sources of metals in the urban environment. It was suggested that it is difficult to do more than speculate about the relative contribution made by various kinds of human activity in view of the number of possible sources (Purves and Mackenzie, 1969).

Warren *et al.* (1971) examined metal contamination in urban and industrial environments both in Canada and England. Allotment gardens were selected as the sampling media in Liverpool, and this small-scale investigation (five samples) provided evidence of rich enhancement of Pb, Zn, and Cu. Fleming and Parle (1977) investigated soils in an industrial part of west Dublin, and found peak Pb concentrations of 540 μg/g, although most ranged from 70-150 μg/g (see Table 3.16). Some additional sources of metals in the urban environment were listed as abraded tyre material, plastics, insecticides and old car batteries. Davies (1978), investigated British garden soils in general and briefly discussed the difficulties of classifying gardens in suburban and village areas as either urban or rural locations. However, results of Pb analysis using EDTA as an extractant show that of the 87 gardens 63 % were contaminated with respect to rural arable norms (set at 65 μg/g in this paper), with the highest values derived from Pb mining areas and city gardens (see Table 3.16). Similar results were found for Zn and Cu, whilst Cd proved to exhibit difficulties with regard to the analytical techniques employed in the study.

Davies *et al.* (1979) examined soils in London and found that an urban ecological approach could be used to explain the pattern of Pb dispersal. This involved the separation of the city into 3 zones originating from the city centre and moving further out (0-4km, 4-10km, and 10-30km). A range of 42-1840 μg/g was reported with Pb means of 523 μg/g, 242 μg/g and 142 μg/g respectively for the 3 city zones listed (see Table 3.16).

Wilkins (1978) sampled over 500 sites in West Pembrokeshire and the highest values of lead were associated with the large towns of the area, especially Haverfordwest and Pembroke Dock (Pb > 69 μg/g - see Table 3.16). One of the largest individual studies of this kind was undertaken at the University of Liverpool to investigate the role of surveying metal concentrations in soils for local planning policy (Parry *et al.* 1981). Topsoil (0-5cm) samples were taken from a number of different land-uses, i.e. parks, gardens, and agricultural, on a grid basis across the 650km^2 which comprises the Merseyside Metropolitan County. Available Pb, Zn, and Cd were determined using 0.5 M acetic acid and results showed that concentrations of these metals tended to be greatest in the urban gardens, whilst mapping of the elements in general showed that the highest values occurred in the most densely-populated regions such as the city itself.

Table 3.16 A summary of the Pb content of urban soils

Location	Reported concentration	Reference
Dublin	up to 540 μg/g	Fleming and Parle (1977)
London	63% of urban gardens had Pb concentrations > 65 μg/g.	Davies (1978)
London	mean of 523 μg/g 0-4km from city centre mean of 242 μg/g 4-10km from city centre mean of 142 μg/g 10-30km from city centre	Davies (1979)
Pembrokeshire	> 69 μg/g for largest towns	Wilkins (1978)

3.5.3 National Reconnaissance Survey of metals in urban dusts and soils

The most extensive work to date regarding metals in British urban soils was undertaken at Imperial College in 1981, when the Department of the Environment commissioned a study to ascertain the usual concentration ranges of metals in British urban soils and dusts (Culbard *et al.,* 1983; Thornton *et al.,* 1985; Culbard *et al.,* 1988; Thornton, 1989). Between late 1981 and June 1982 fifty three towns and cities, selected by criteria such as population size, industrial activity and geographical location, were sampled for housedust, garden/allotment and park soil, and streetdust. Within each location 100 households were selected on a grid basis with dusts sampled from the internal environment and soils taken from exposed surfaces in the back garden. This soil sample was taken from the top 5cm, and was a composite made up of 25 sub-samples. This particular sample is comparable with a sample taken both in the Richmond and Wolverhampton projects (see section 5.3.1), hence allowing a direct comparison with results from the National Reconnaissance Survey.

Table 3.17 Reconnaissance survey results for topsoils in residential areas for London (*) as a whole

Element	Geometric mean (μg/g)	Range (μg/g)	Sample No.
Pb	654	60-13,700	578
Zn	427	58-13100	579
Cu	73	13-2320	579
Cd	1.3	< 1-40	579

* Table 3 is a summary of results from the London Boroughs of Brent, Croydon, Hammersmith and Fulham, Lewisham, Newham, Richmond-Upon-Thames, and Westminster

Table 3.18 Reconnaissance survey results for topsoils in residential areas in the London Borough of Richmond-upon-Thames

Element	Geometric mean (μg/g)	Range (μg/g)	Sample No.
Pb	516	80-2240	97
Zn	310	84-5620	97
Cu	57	16-752	97
Cd	1.2	< 1-6	97

Table 3.19 Reconnaissance survey results for topsoils in London parks

Element	Geometric mean ($\mu g/g$)	Range ($\mu g/g$)	Sample No.
Pb	294	28-1260	35
Zn	183	34-482	35
Cu	49	8-117	35
Cd	1	< 1-2	35

Table 3.20 Reconnaissance survey results for topsoils in all residential areas in Britain with the exception of the hotspots

Element	Geometric mean ($\mu g/g$)	Range ($\mu g/g$)	Sample No.
Pb	266	13-14100	4126
Zn	278	13-14600	4126
Cu	56	5-16800	4126
Cd	1.2	< 1-40	4126

Table 3.21 Reconnaissance survey results for topsoils in residential areas in hotspot regions excluding Derbyshire

Element	Geometric mean ($\mu g/g$)	Range ($\mu g/g$)	Sample No.
Pb	493	49-8340	433
Zn	671	104-8290	1044
Cu	63	14-724	424
Cd	2.7	< 1-75	1044

It is clear when comparing Tables 3.17 and 3.20 that soils from residential areas of London have significantly higher concentrations of metals than those of other residential areas in Britain (excluding the hotspots), particularly with regard to Pb and Zn. An examination of Table 3.19 which summarises results for soil samples taken from London parks shows that even areas of open space are affected by urbanisation in a large conurbation such as London. Geometric mean values of Pb are higher in London parks than for the residential areas of Britain as a whole (294 μg/g compared to 266 μg/g), whilst levels of Cu and Cd are comparable for the same areas (see Tables 3.19 and 3.20). A comparison of the concentration ranges for Pb in hotspot areas and London, shows that concentrations of Pb in London can exceed those found in areas of mineralisation; as predicted by Warren *et al.* (1971) - see Tables 3.17 and 3.21.) This is probably due to such factors as the high traffic density associated with London, the wealth of old housing, and a number of other practices, such as the disposal of spent fossil fuel, which have been carried out over the passage of time. If more information was provided regarding the proximity of roads to the sample sites in the parks, it would be possible to assess the influence of traffic on the concentrations of Pb and Zn in particular, rather than merely speculate.

3.5.4 British studies after the National Reconnaissance Survey

Other work in the field of urban geochemistry includes: Thornton and Jones, 1984; Gibson and Farmer, 1986; Davies and Thornton, 1987; Davies *et al.*, 1987; Harper *et al.*, 1987 and Schwar *et al.*, 1988. Thornton and Jones (1984) investigated both allotment soils and soils in residential areas in five different British cities/towns. Two contrasting sites were investigated within each sample area, and soils were found to be contaminated in the order Pb > Zn > Cu > Ni > Cd with the highest metal concentrations found in London (both sites had Pb topsoil concentrations > 2000 μg/g) followed by Newcastle Upon Tyne, Leeds, Stoke on Trent, and Scunthorpe (see Table 3.22).

Two studies that followed on from the National Reconnaissance Survey of metals were those by Davies and Thornton (1987) and Davies *et al.* (1987). The first of these was based in Brighton and aimed to investigate the very high levels of Pb in housedust discovered in the earlier survey. Sampling was organised so that an equal number of houses were chosen from the different age groups present in the town, as a means of testing the hypothesis that the national survey was biased towards older housing, so increasing the Pb content of housedust to a level which was not representative of Brighton as a whole. Results showed that concentrations of Pb in housedusts and garden soils were both lower than those found in the National Reconnaissance Survey, with a new Pb housedust mean of 705 μg/g compared to 1100 μg/g and a garden soil mean of 404 μg/g compared to a previous value of 485 μg/g (see Table 3.22). This highlights the importance of house age on Pb levels and illustrates the need to investigate the age of a property from which a particular sample is acquired.

The second study by Davies *et al.* (1987) was based in Birmingham, with the emphasis again placed on the age of the housing as well as additional locational features such as the proximity of major roads and industrial regions. Results showed that the geometric mean for Pb from 86 garden soils was 313 μg/g, very similar to the 278 μg/g from the national survey. An examination of the survey in more detail shows that soils associated with houses > 35 years old have a geometric mean of 342 μg/g compared to 176 μg/g for houses below this threshold age (see Table 3.22). Samples taken close to metal using industries were found to have a geometric mean of 342 μg/g compared to 248 μg/g for those that are not. Both the age of the housing and proximity to metal using industry were found to be statistically significant at the 0.01 and 0.001 levels of confidence, respectively.

A study which was part of the National Reconnaissance Survey, but also published separately, was that by Harper *et al.* (1987) based in lower Swansea. The results from garden samples produced a mean Pb concentration of 385 μg/g, 573 μg/g Zn, 152 μg/g Cu and 2.5 μg/g Cd (see Table 3.22). The concentrations of Zn, Cu and Cd were all higher than the overall mean for the survey as a whole and the mean values for London. The importance of waste tips produced by industrial activity in influencing the soil concentration of these metals is highlighted. A more contemporary study of Lower Swansea was undertaken by Bridges (1993), which examined the influence of land-use on the metal content of soils. The highest concentrations of Pb, Zn, Cu and Cd were associated with industrial land (mean concentrations of 2594 μg/g, 2757 μg/g, 408 μg/g and 16.7 μg/g, respectively - see Table 3.22) with the lowest concentrations found on common land or reclaimed land. The same study also showed that soils from gardens of older housing had a higher metal content than those associated with newer housing. This illustrates the importance of differences that exist within the same urban location regarding metal concentrations, and how this can be masked by the presentation of an overall mean value for a town or city.

Gibson and Farmer (1986) undertook a more detailed examination of Glasgow topsoils (0-5cm) by subjecting approximately 90 to a six step sequential extraction to investigate how various heavy metals differ in both their mobility and in their phase associations. In total 400 samples were taken across Glasgow and total analysis found that Pb and Zn were of a similar magnitude, mobility was of the order Cd > > Pb > Zn > Cu. However, the average concentration of Cd in topsoils (0.53 μg/g) is probably less than that which would necessitate environmental concern. The actual order of environmental concern was listed as Pb > Cd > Cu > Zn. Most of the Pb (51 %) was present in the moderately reducible phase, whilst most of the Cu and Zn was present in the strongly bound organic phase (41 % and 29 % respectively).

The study by Schwar *et al.* (1988) returned to the study of dusts rather than soils in London. Some 400 samples were collected on a grid basis across the city in an attempt to provide a representative selection of sample sites throughout the city. Geometric means were found of 370 μg/g Pb, 372 μg/g Zn, 80 μg/g Cu and 2.7 μg/g Cd (see Table 3.22). However, the study also highlighted geographical differences with elevated concentrations of metals in dust associated with the industrial areas of the Lee Valley, central London, and parts of east and west London.

Table 3.22 A summary of the data reported in urban studies

Location	Reported concentration	Element	Reference
5 British	2 London sites > 2000 μg/g	Pb	Thornton and Jones (1984)
Brighton	geometric mean garden soil concentration of 404 μg/g.	Pb	Davies and Thornton (1987)
Birmingham	313 μg/g overall mean for garden soils: 342 μg/g houses > 35 yrs 176 μg/g houses < 35 yrs	Pb	Davies *et al.* (1987)
	Means: garden soils		
Lower Swansea	385 μg/g	Pb	Harper *et al.* (1987)
	573 μg/g	Zn	
	152 μg/g	Cu	
	2.5 μg/g	Cd	
	Means: industrial areas		
Lower Swansea	2594 μg/g	Pb	Bridges (1993)
	2757 μg/g	Zn	
	408 μg/g	Cu	
	16.7 μg/g	Cd	
	GM for dusts		
London	370 μg/g	Pb	Schwar (1988)
	372 μg/g	Zn	
	80 μg/g	Cu	
	2.7 μg/g	Cd	

GM = geometric mean

3.5.5 Urban studies in the United States

A great deal of research has also occurred on a global scale, including an expanse of work in the United States: (Lepow *et al.*, 1975; Solomon and Hartford, 1976; Spittler and Feder, 1979; Francek, 1992; Francek *et al.*, 1994; Mielke, 1991; Schmitt *et al.*, 1988; Krueger and Duguay, 1989; Friedland *et al.*, 1986; Ritter and Rinefierd, 1983; Pierce *et al.*, 1982; Pouyat and McDonnell, 1991; Rice *et al.*, 1984; Tong and Marrell, 1991). The three earliest studies in America date from the 1970's, and the first of these reported a Pb concentration range of 700-1750 μg/g in the major parks of Hartford (Lepow *et al.,* 1973). Solomon and Hartford (1976) reported a soil Pb concentration range of 20-1060 μg/g in a small residential community, whilst a mean Pb concentration of 800 μg/g was reported for Boston, USA (Splitter and Feder, 1979).

As with the preliminary work in this field, most of the later studies were also very case-specific, dealing with very particular aspects of the urban environment. Francek (1992) reported a median Pb concentration of 460 μg/g for residential soils in Mont Pleasant which is very similar to the result reported by Preer *et al.* (1984) for garden soils in Washington (480 μg/g). Krueger and Duguay (1989) and Francek *et al.* (1994) expanded on this by investigating the difference in soil Pb content between residential soils associated with housing of a different age. Both studies found that the older the housing the higher the Pb concentration in garden soil, with 54% of houses built before 1950 reported as having a Pb soil concentration of > 1000 μg/g in the earlier study (Krueger and Duguay, 1989). The later study also concluded that houses located closer to roads had higher values than houses located further away. Although not statistically significant, both increased traffic volume and a greater amount of exposed soil increased household Pb levels (Francek *et al.,* 1994).

A paper by Mielke (1991) summaries a number of studies investigating Pb in residential soils, and refers back to some earlier work by the same author in Baltimore which showed that most of the highest occurrences of Pb were sited in a cluster towards the centre of the city where most of the houses were of brick construction rather than painted wood. As a consequence of this paint was not believed to be the major source of Pb, but one that was secondary to auto-emission factors. It was suggested that for such an explanation could be offered for other cities in the United States which showed the same pattern (Mielke, 1991). Statistical analysis of results showed that the Pb pattern within the community of the city was robust enough to allow only five samples per census (a sample area within a city) to produce a map of Pb distribution in a city. It was also concluded from a four-city study that the higher the population the greater the amount of Pb due to increased traffic flow, with the highest Pb levels in the inner city (Mielke, 1991).

Chaney *et al.* (1984) investigated variation in the measurement of soil Pb that can occur in a single back garden due to the number of sources. Three gardens were sampled over 50 times, producing a range of 100-2040 μg/g, 70-2440 μg/g, and 57-4080 μg/g. This illustrated the variability of Pb even over such a short distance as a back garden, and highlighted the negative effect that this may have on the interpretation of results. Two studies based within urban forests were those by Friedland *et al.* (1986) and Pouyat and McDonnell (1991). The earlier study found that a specific area of Zn smelting in New Jersey produced the highest values of Zn in the nearby forest (Friedland *et al.,* 1986) whilst the later study, set along the rural-urban gradient in south-east New York, found that mean Pb levels at the urban end of the gradient were four times the level of those at the rural end of the gradient. Copper and Ni were only twice as high at the urban end of the gradient (Pouyat and McDonnell, 1991).

3.5.6 Other European urban studies

An extensive amount of work has also taken place in other parts of Europe. In Italy Valerio *et al.* (1992) found that the highest values of Pb were observed in the urban areas of Genoa and La Spezia when compared to sub-urban areas, whilst Polemio *et al.* (1982) investigated industrial and rural areas of Bari, Italy, finding that both areas accumulate metals to a certain degree, the latter areas as a result of agrochemical components (As, Cu and Zn). Hernandel *et al.* (1987) investigated Pb and Cd levels in plants from an urban area of Madrid, Spain, and how this varied from season to season. Lead levels were found to correlate well with traffic density, with Pb concentrations highest in the winter. Sanchez-Camazano *et al.* (1994) investigated Pb and Cd in 16 garden soils in Salamanca, Spain, and found a Pb range of 20.1-92.6 μg/g and a Cd range of 0.21 - 0.95 μg/g, which is lower than that found for larger and more industrial centres both in Britain (Culbard *et al.,* 1988 and Davies *et al.,* 1987) and Madrid (the same paper reports a mean Pb concentration of 621 μg/g for the centre of Madrid). A study of soils from the Greek city of Thessaloniki (Cook *et al.,* 1994), which for the most part were located along three major roads found, concentration ranges of 1-620 μg/g Pb, 29-590 μg/g Zn and 25-210 μg/g Cu, with the three metals highly-correlated, suggesting a similar source.

An extensive geochemical investigation of Berlin has been undertaken by Birke and Rauche (1994) which looked at the different facets of land-use as well as the area surrounding the city. The geochemical background concentrations were calculated for several metals in the urban area, with Pb reported as 21 μg/g, Zn as 24 μg/g, Cu as 8 μg/g and Cd as 0.12 μg/g. The mean concentrations for metals were highest in the residential areas of the city centre and industrial areas with Pb approximately 6 times higher in the residential area than the background concentration, Zn approximately 9.5 times higher, Cu 6.5 times higher and Cd approximately 6 times higher.

Some studies have also been undertaken in the former Soviet Union and these were outlined by Lukashev (1988), who noted a study in Byelorussia which reported anomalous concentrations of Hg, W, and Bi which were found to be local in their distribution and confined to specific, easily delineated regions. It was also acknowledged that metals such as Zn, Pb and Cu are more widespread within modern environments.

3.5.7 Studies outside Europe and America

Urban geochemistry has also been studied extensively outside Europe in a series of small investigations, although only on a more recent basis in the developing world. Hewitt and Candy (1990) looked at Pb, Cd, and Zn concentrations in 10 soil samples from around the city of Cuenca, Ecuador. Mean values of 293 μg/g Pb, 509 μg/g Zn and 0.36 μg/g Cd were reported, compared to concentrations of 76 μg/g Pb, 70 μg/g Cu, and 0.28 μg/g Cd for a sub-urban area 5.5 km from the city. Xuelin and Ke (1988) investigated the level of Pb in four cities in China and compared them to baseline concentrations, calculated by taking a number of samples from sub-urban sites within the respective cities. Results showed that soil samples taken closer to the city centre had, in most cases, a Pb concentration two times higher than those estimated as background concentrations.

Three studies based in Hong Kong are those by Tam *et al.* (1987), Yim and Nau (1987) and Ho and Tai (1988). The first of these (Tam *et al.*, 1987) examined topsoils (1cm) from thirteen roadside parks in the city and found that levels of Pb, Cu, Mn, Zn and Fe were all significantly higher than levels in uncontaminated control soils. Lead, in particular, was significantly correlated with traffic volume, although so were Zn, Fe, and Cu to a lesser extent, which suggests that these are also related to vehicle emissions. Ho and Tai (1988) also investigated roadside soils in Hong Kong and found these contaminated in the order Pb > Zn > Cu > Cd. Table 3.23 compares the results from the two studies in the same city and the generally higher values found in the later study can be attributed to the fact that these samples were taken closer to the road. As with the earlier investigation in Hong Kong, the elevation of Fe in the roadside environment is illustrated, a metal not extensively examined in British studies, although Hoplee (1984) does report this element's elevated presence in roadside soils.

Table 3.23 Comparison of metal concentrations in topsoils from two different studies based in Hong Kong

Element	Mean (μg/g) 1987	Mean (μg/g) 1988
Pb	268	991
Zn	281	633
Cu	142	120
Fe	15070	22660
Mn	758	408
Cd		1.08

The third of these studies examined the metal content of dust in selected urban areas of Hong Kong and found mean concentrations for all sample areas of 1287 μg/g Pb, 2902 μg/g Zn, 635 μg/g Cu and 7.6 μg/g Cd (Yim and Nau, 1987). Highest concentrations of metals in general were associated with industrial/residential areas.

A study by Hinshery and Kumar (1992) of dust in a number of different locations in Tripoli, Libya, found that Pb concentrations were significantly higher in main street dusts than other locations in the city such as from outside petrol stations and playgrounds (a mean of 797 μg/g compared to 533 μg/g for both the other locations). This Pb concentration for main streets in Tripoli is much smaller than those reported for five urban areas in England, U.S.A., Canada, New Zealand and Jamaica (Fergusson and Ryan, 1984) and much smaller than those reported for street dust close to specific sources such as spray painters, a battery factory, a galvanizer and an electrolplater (Fergusson and Kim, 1991). The peak value for Tripoli is, however, similar to the mean found for Bahrain of 697.2 μg/g (Akhter and Madary, 1993).

3.6 Summary

This chapter has involved a detailed examination of the major uses of metals, particularly those of Pb, Zn, Cd, Cu, Cr and Ni. The major uses of the other elements studied are summarised in Table 3.2 (where data are available). Emissions of metals are reviewed on both a British and global scale, along with the emissions of metals from specific activities such as the burning of fossil fuels. As this study is concerned with concentrations of elements in soils, data of deposition rates and metal concentrations in bulk deposition are also presented. The concentrations of metals in soils associated with industrial activity, the application of sewage sludge and other agricultural materials, the use of leaded paint, and from vehicle emissions are presented. These activities are important sources of many elements in the urban environment and a review of such work is an important aid to the interpretation of data from this study.

The studies which have investigated concentrations of metals in urban dusts and soils have also been reviewed in detail, from the earliest work undertaken Purves (1966) in Edinburgh through to the present day. This covers the early work in British cities which investigated Pb concentrations in urban dusts (see Table 3.15) through to the National Reconnaissance Survey of metals in urban dusts and soils (results summarised in Tables 3.17-3.21), which is the largest study to date in Britain. Data from studies in other parts of Europe, the United States and the third world are also presented. This provides an extensive data base with which to compare data from this study.

CHAPTER FOUR INTRODUCTION TO THE STUDY AREAS

4.1 Sample site selection

4.1.1 Introduction

Urban sampling was carried out in two locations in England: Richmond-upon-Thames, a suburban borough of London, and Wolverhampton, a city in the west Midlands. Details of sampling techniques are presented in chapter five along with analytical procedures.

4.1.2 Richmond-upon-Thames

Richmond was selected as the pilot investigation area and sampled between January and April of 1992. Selection was based on the following criteria:

1). This London borough provides a unique example of a non-industrial urban environment with proximity to a very large city and a large residential population, but which has a large amount of open space. This allows a comprehensive investigation into the influence of land-use and other anthropogenic activity on multi-element concentrations in urban soils.

2). The abundance of open space in the borough also facilitates an investigation into the modification of the natural geochemical signature that has occurred due to anthropogenic activity.

3). Data were already available for Richmond from the nationwide reconnaissance survey of metals in urban dusts and soils, undertaken for the Department of the Environment. This allows a direct comparison of two studies separated by more than 10 years (see section 3.5.3 for details regarding the National Reconnaissance Survey).

4). The proximity of Richmond to Imperial College, where sample preparation and analysis was to be carried out, made it an ideal sampling location.

4.1.3 Wolverhampton

Wolverhampton was sampled during June of 1993 and was selected as a second sampling location for the following reasons:

1). As a city with very little open space and an extensive industrial history, particularly those relating to the metal processing industry, it provides a perfect contrast to the non-industrial suburban area of Richmond.

2). The opportunity to investigate extensively multi-element concentrations in soils from a city which has not been studied in the past.

3). Selection of Wolverhampton as a study location at a time when the BGS were conducting an extensive urban investigation programme in the city enabled sampling to be completed in two weeks representing a significant reduction in sampling time compared to Richmond.

4.2 The history of Richmond-upon-Thames

4.2.1 Introduction

The London Borough of Richmond-upon-Thames covers an area of 56 km^2 some 11 km from the city centre (measured to Marble Arch) and has a population of approximately 162 000. The borough enjoys historical links with royalty, both as a place to reside and through the royal parks and Kew Botanical Gardens. The river is a very prominent feature in Richmond with approximately 34 km of river frontage and this borough is the only one in London to lie both north and south of the Thames. Richmond-upon-Thames is shown in detail in Fig. 4.1.

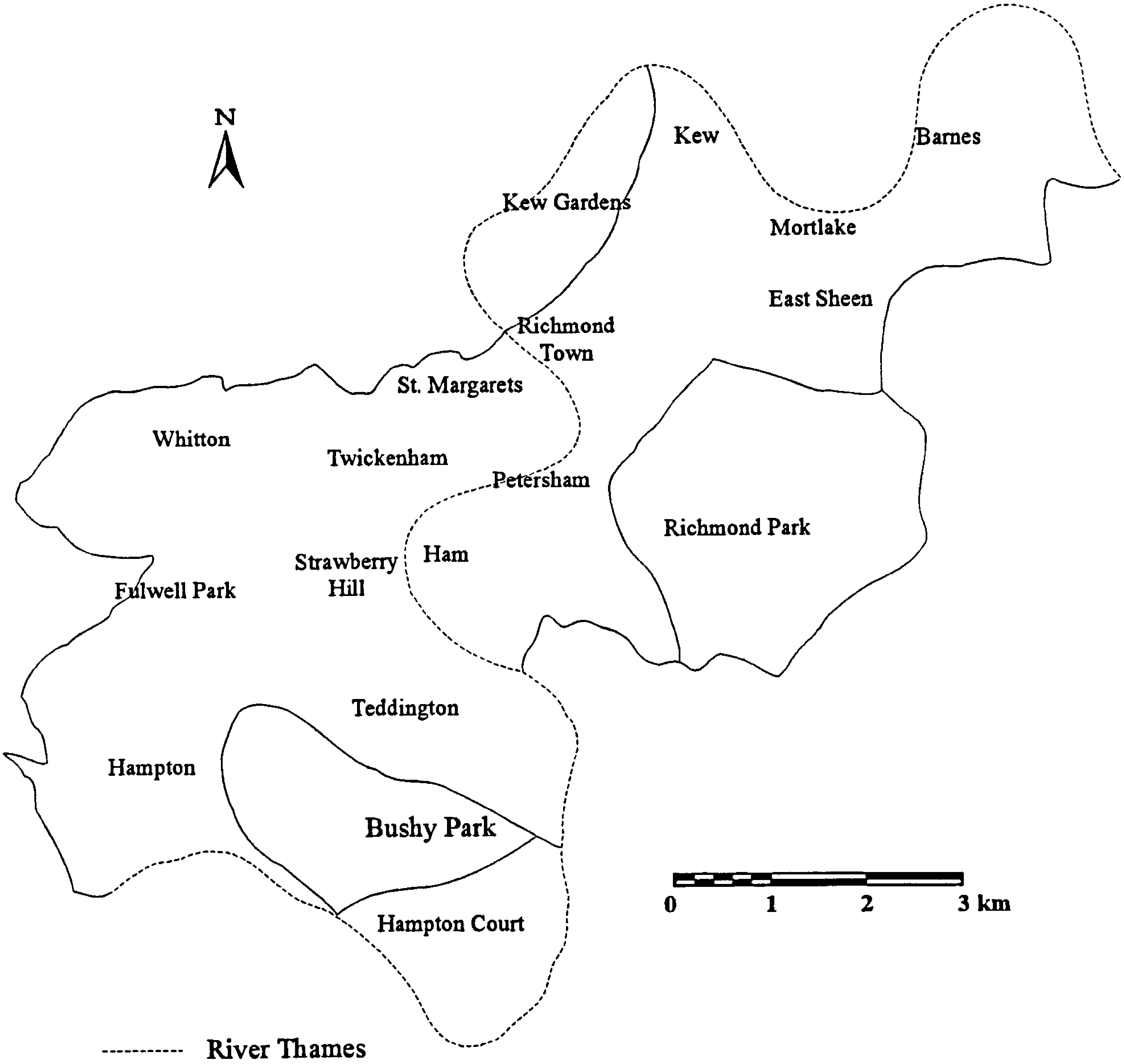


Figure 4.1 The London Borough of Richmond-upon-Thames.

4.2.2 Industrial history of Richmond

Some minor industry is present in the borough with an absence of metal works or what could be described as polluting industries. The brewery in Mortlake has been there since the early part of the eighteenth century and although industries associated with clothing, food and horticulture have resided in Richmond, few industries which use metals or emit fumes laden with metals have been located in Richmond. Possible exceptions to this are the foundry which was present in the Hampton Wick region until the middle of this century, and a gasworks south of this was also active until the middle of this century (see Supp. Fig. 6c).

The use of the river is an important consideration industrially and the contrast between the riverside use in Richmond and that in east and south-east London has implications for metal concentrations in Richmond soils. The east and south-east of London developed as industrial centres because of their proximity to the Metropolis; once polluting industries took up residence in the area this encouraged further settlement and the development of the infrastructure to support it. Even when bye-laws were introduced in 1885 (compared to 1844 in the Metropolis) regarding the location of polluting industries, the local authorities used their power very sparingly (Kelly, 1991). Conversely the local authorities in Richmond have always been strongly opposed to any industrial activity in the area, and as a consequence Richmond's riverside wharfs have only been employed for leisure activities.

4.2.3 Richmond Park

Richmond park covers an area of 1,000 hectares (2,500 acres) and has changed very little over the centuries, having never been encroached upon by an expanding London. There has been a park in Richmond since the early thirteenth century (Cloake, 1993). The park has enjoyed connections with royalty dating back to the time of Edward I (1272-1307) and during his reign, as with kings before and after, the park was utilised as a hunting ground. Charles I moved his court to Richmond in an effort to avoid the plague in 1625 and his aim was to make the park a home for red and fallow deer as well as creating ponds and installing railings to protect coppices. Charles II issued permits for the removal of 7,200 loads of gravel from 1673 to 1683 and the resulting 25 or so pits formed the ponds that still remain (Richmond Park, 1993). The mid eighteenth century brought the erection of gates at East Sheen and Ham whilst the early nineteenth century saw the planting of trees at Sheen Wood, Sheen Cross Plantation, Spankers Hill Plantation, Sidmouth Wood and Pond Plantation. Subsequent years in this century saw the introduction of most of the major plantations which still remain today e.g. Isabella Plantation. During World War I an army camp was set up and large areas of the park were put under plough; this represents the only major disturbance of the soil in the park over centuries of use. World War II gave rise to more military activity in the park (Archer and Curson, 1993).

4.2.4 Hampton Court and Bushy Park

Bushy Park, the area lying north of Hampton Court Palace, is the second largest Royal park in London (behind Richmond park) at 450 hectares (1,099 acres). Evidence of field boundaries and ridge and furrow ploughing suggests that large areas of the park were cultivated in medieval times. In 1514 work began on Hampton Court and after Cardinal Wolsey made a gift of Hampton Court Palace to Henry VIII in 1529 a similar development scheme to that of Richmond Park was adopted with the development of a deer park. Another characteristic shared with Richmond Park is the link with the military services, as Canadian troops were stationed here in World War I and more significant numbers of American soldiers based here during World War II (Bushy Park, 1993).

4.3 The soil characteristics of areas of open space in Richmond

4.3.1 Introduction

Richmond has large areas of grassland, mainly associated with the two royal parks, which have remained relatively undisturbed. Two thirds of this grassland (580 acres) is described as acidic which is defined in terms of the plant communities (such as sheeps fescue, heath grass) which have developed over acidic soils (Archer and Curson, 1993). Most of this acid grassland is located in the vicinity of Richmond, Home and Bushy Parks on gravels of the river terraces. These parent materials give rise to free draining, light soils, although the majority of Richmond Park is underlain with London Clay giving rise to soils which are not so freely drained and hence a vegetation develops which is suited to soils with a higher water content; this includes plants such as cleavers and pendulous sedge. Unmanaged acidic grassland often results in bracken dominating large areas which is the case in both Richmond and Bushy Parks (Archer and Curson, 1993).

4.3.2 Richmond Park

The most extensive areas of dry acidic grassland are found between Sidmouth Wood and Saw Pit Plantation, to the north and west of Sidmouth Wood, and further south around Thatched House Lodge. These are dominated by red and sheeps fescues and heath grass. Neutral grassland (developed on soils with a pH of 7) covers much of Petersham Park, to the west of Pembroke Lodge and also around Ham Bottom and in the valley of the north east bog (Archer and Curson, 1993).

4.3.3 Ham Common

Ham Common lies on river terrace gravels, laid down by the Thames when it followed a different course, giving rise to well drained slightly acidic soils. Up until 1933 the common was grazed by cattle maintaining a heathland and acidic grassland vegetation, but with cessation of grazing a woodland of birch and oak developed (Archer and Curson, 1993).

4.3.4 Sudbrook Park golf course and East Sheen Common

This lies on the northern edge of Richmond park over glacial gravels producing sandy acidic soils similar to those of Ham Common. Between the short grass of the fairway are narrow strips of acid grassland. The vast majority of the common is wooded, although a section of heather existed until very recently (Archer and Curson, 1993).

4.3.5 Petersham Common

This lies over deposits of London Clay in Richmond. The common slopes fairly steeply to the west, counteracting the drainage problems that could arise from this parent material. Woodland is therefore fairly abundant with the oldest wood at the top of the slope and rich in oak (Archer and Curson, 1993).

4.3.6 Ham Lands

This is an area of infilled gravel workings, with the gravel pits reaching their maximum extent in 1945. By this time, with the exception of a strip along the river margin north of the Young Mariners Base, the entire area had been excavated. After the second world war this area was infilled with rubbish and rubble from bombed sites. After tipping was completed in the 1960s, the land was at a higher level than prior to the commencement of excavations to prevent flooding. Sixty acres of the land were also developed for housing in the 1960s. Vegetation such as clover, conifers and ferns associated with a dry sandy soil is common (Ham Lands, 1987).

4.3.7 Bushy Park and Home Park

Bushy Park lies on the flood plain of the Thames on free draining river terrace deposits which again give rise to acidic soils. Unlike Richmond Park the topography and geology are uniform reducing the variety of flora (Archer and Curson, 1993).

4.3.8 Home Park/Hampton Court Park

This area also lies on river terrace gravels and as a result much of it is given over to acid grassland. Neutral grassland rich in herbs occurs along the eastern edge of the park on land overlying alluvial deposits not open to the public. Heather used to be more widespread on the common, but this has given way to acidic grassland (Archer and Curson, 1993).

4.3.9 Barnes Common

Barnes Common lies on the flood plain gravels laid down during the Pleistocene and recent periods, once again giving rise to freely drained acidic soils (Archer and Curson, 1993).

4.4 Residential development: Richmond-upon-Thames

Urban development in the area now known as Richmond-upon-Thames was stimulated by the arrival of the railway in the mid-nineteenth century in Richmond town. Until this period Richmond had maintained its rural character. Very minimal development did occur at the beginning of the nineteenth century along Lower Mortlake road in the 1820's for the working classes. The 1840's brought the development of the fields south of what is now the A305 on Friar Stile road, with the building of Villas and the development of Park Road and Queens Road (Archer and Curson, 1993). The advent of the railway brought with it the movement of middle class Londoners to the new country suburb and in the 50 years between 1801 and 1851 the population approximately doubled from 4628 to 9255, doubling again by 1881. In the last quarter of the nineteenth century the fields which made up Richmond began to disappear under the development of varying size villas, with Richmond Hill Road quickly becoming a residential location and accelerated development along Sheen Road and at both ends of Kew Road (Cloake, 1993). Kew Gardens station was also opened at this time and brought with it the development of the area to the east of Kew Gardens with houses and more roads. By the end of the century a great deal of Richmond fields had been developed and the next step was to redevelop many of the areas that were the home of large mansions, the roads taking on the name of the mansions such as Mount Ararat. By the end of the century the population of Richmond had increased to 25,000. During the same period, Richmond was also the first area in London to build a council estate in Manor Grove. The last quarter of the century also saw the development of the other areas which now make up the borough, with estates and terraced houses built in open countryside at Hampton Hill, near Fulwell station and around the stations of Strawberry Hill, Kew Gardens and St. Margarets (Archer and Curson, 1993).

By 1904 there was almost a continuous corridor of development from Barnes and Kew through Richmond and Twickenham to Hampton and Hampton Wick, following the course of the railways. Between the wars, new housing estates were built along the road between Petersham and Ham and in the North Sheen area, along with the initial destruction of the large old houses. The building of stations at Whitton and north Sheen (opened on the same day in 1930) continued the pattern of town development in response to an improvement in the infrastructure, with houses built over the open space between Richmond and Mortlake. Similar development occurred between Castlenau and Lonsdale roads and also between Teddington and Hampton Wick. The Chertsey road was opened in 1933, improving the access to London, increasing the through traffic to London and providing an east-west physical barrier (Archer and Curson, 1993).

During World War II Richmond suffered quite badly, as did London as a whole, and both the riverfront and the town centre had to be completely redeveloped. The layout of the road was retained along with many of the older buildings. Many new shops and offices were constructed. Ham and Petersham remained fairly isolated and retained many of their rural characteristics. The riverside land at Ham was farmed as recently 1924 and continued to be dug for gravel from 1900 to 1952. The 1960's, however, brought the development of riverside estates in the Ham area (Archer and Curson, 1993). Further development occurred in the 1970's with over 1700 houses built on nursery lands near Hampton. The present borough of Richmond-upon-Thames was created in 1965 with the merging of Richmond, Barnes and Twickenham. Richmond-upon-Thames is very unusual as a borough on the edge of a major city, having no agricultural land on its outer fringe and being no more built up at Barnes than land further from the centre of London. However, the existence of Richmond, Home and Bushy parks provide the borough with an unusually large amount of open space with several old village centres such as Barnes and Hampton. Today, after open spaces, housing represents the most important land use, with over 60000 dwellings of which three quarters are over 40 years old (Archer and Curson, 1993).

4.5 Geology of Richmond-upon-Thames

4.5.1 Solid geology

The use of boreholes in Richmond and surrounding regions has confirmed the presence of an entire chalk section at depths of approximately 50m below the surface down to approximately 250 m (BGS, 1981). This includes a sequence of Upper, Middle and Lower Chalk, the Upper Chalk being composed of soft white limestone with flints, whilst the Middle and Lower Chalk is white and in parts marly chalk. These are underlain in turn by Upper Greensands (glauconitic sandstone), Gault clays, thin Jurassic limestones and mudstones and Devonian of both marine and old sandstone facies (BGS, 1981). The Woolwich and Reading beds lie immediately over the chalk sequences, and this is a sedimentary complex composed of a basal bed made up of glauconitic sands, loams and pebbles with clays and sands above which vary laterally (BGS, 1981).

The London Clay rests with disconformity on the Woolwich and Reading Beds and was deposited during early Eocene times approximately 53 million years ago over a period of about 3 million years. It consists of dark grey pyritous silty clays, in parts sandy with common courses of claystones (nodular limestones) which weather to a brown or yellow-brown colour near the surface. The basal part of the formation is composed of glauconitic pebbly clayey sand and silt and contains a distinctive shallow water marine molluscan fauna. Both the lower and upper parts of this include more fine grained sand with the upper third in particular containing more glauconite and ripple marks where the sand is present (BGS, 1981). Figure 4.2 shows that outcrops of London clay occur in Richmond, particularly in Richmond Park (see Supp. Figs. 6b and 6d) and to the west of the Borough in very minor strips such as those around the Crane valley. In total, some 20 samples from Richmond were taken of soil developed on London Clay.

4.5.2 Drift deposits

Drift deposits cover the vast majority of Richmond and these vary in age from the older and higher terraces to the younger and lower terraces. These have been laid down

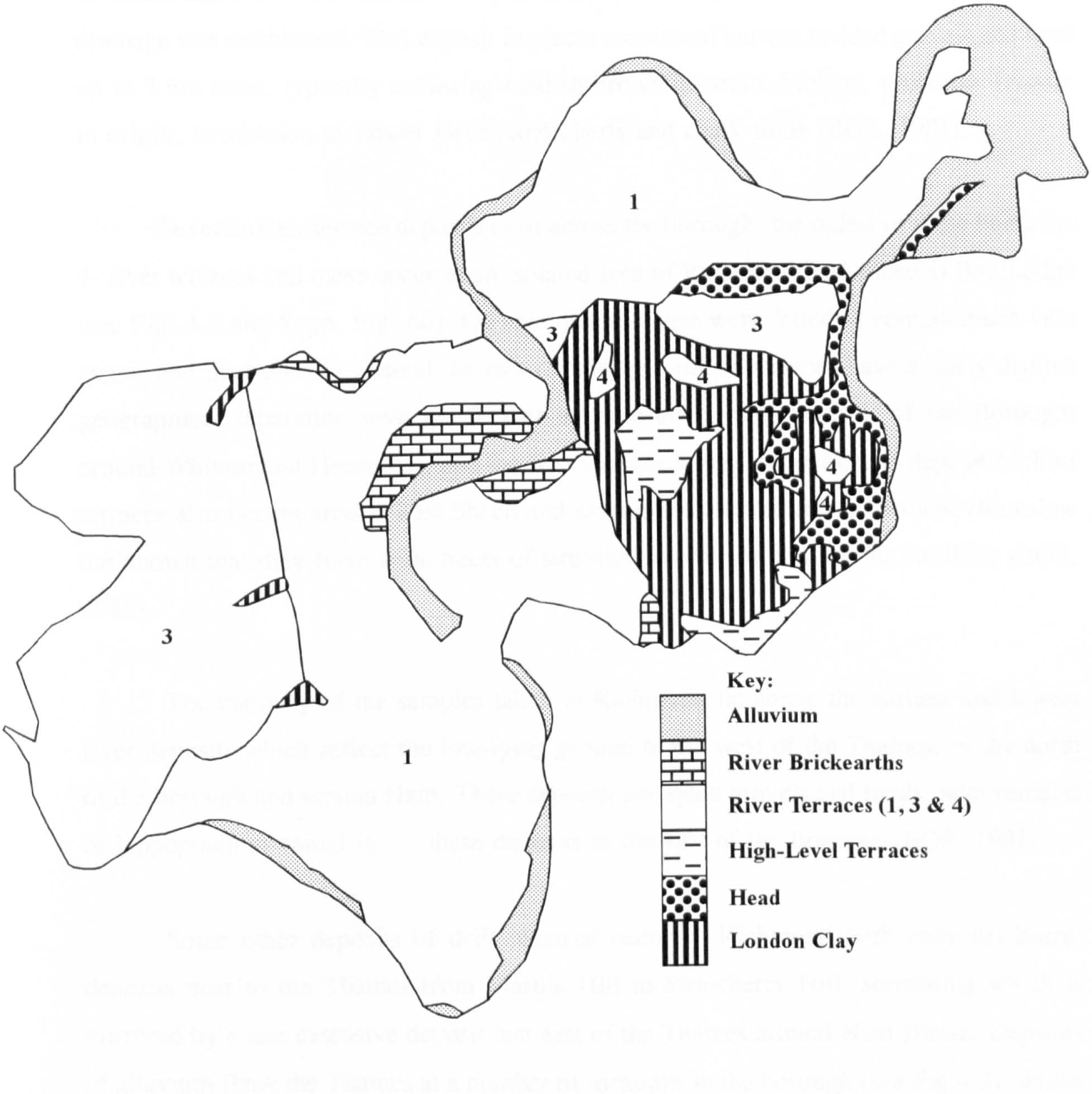


Figure 4.2 The solid and drift geology of Richmond-upon-Thames.

in Quaternary or recent times during times associated with sea level changes. The oldest and highest deposits are the high-level terraces which cover the higher ground in Richmond Park both to the south of the park and on the summit of Richmond Hill, a height of over 50m. The younger river terraces lie on top of the sands of the Claygate Beds, whilst both of these deposits were laid down by a braided river system before the main Thames drainage was established. This deposit in places consists of current bedded gravels and sand up to 7.6m thick, typically enclosing reddish brown quartzite pebbles, probably Triassic in origin, in addition to Lower Greensand cherts and chalk flints (BGS, 1981).

Several other terrace deposits exist across the borough, the oldest of these being the 4- river terraces and these occur in an isolated area of Richmond Park close to Bog Lodge (see Fig. 4.2 and Supp. Fig. 6d). On examination these were found to contain much vein quartz and quartzile. In general the two remaining types of terraces have a fairly distinct geographical separation with the 3-river terraces occupying the west of the Borough, around Whitton and Hounslow, and the first terraces lying further east. A deposit of third terraces also occurs around East Sheen and examination of the deposit around Hounslow has shown that they form wide tracts of stratified gravel and sand up to 8m thick (BGS, 1981).

The majority of the samples taken in Richmond lie above the earliest and lowest river deposits which reflect the low-lying ground to the west of the Thames, in the north of the borough and around Ham. These deposits are again gravels and sands, with remains of hippopotamus found in these deposits to the east of the Borough (BGS, 1981).

Some other deposits of drift material occur in Richmond with river brickearth deposits near to the Thames from Marble Hill to Strawberry Hill, something which is mirrored by a less extensive deposit just east of the Thames around Ham House. Deposits of alluvium flank the Thames at a number of locations in the borough (see Fig 4.2), whilst the Beverley Brook has also deposited a very narrow strip of alluvium. The widest expanse of alluvium occurs around Barnes Elms and at a number of sites where the Thames cuts a path from Barnes to Kew, past Ham and south towards Hampton Court (see Fig 4.2 and Supp. Fig. 6d). Such deposits consist mainly of silty and sandy clays containing numerous stones and some wood in the lower parts. Fine-grained sands and lenses of gravels also occur with interbedded peat which has been dated at 1800-3200 years old (BGS, 1981).

Along the eastern edge of the borough, the valley of the Beverley Brook contains Head deposits which are locally derived washes of London Clay material transported to the foot of the slope (see Fig 4.2).

4.6 The Industrial history of Wolverhampton

4.6.1 Introduction

Wolverhampton is located in the west Midlands approximately 45 miles from Birmingham, covering an area of 70 km^2 and with a population of 175 000. The city has a strong industrial history particularly that relating to the iron industry and more recently the iron and steel industry. This grew from the mid-eighteenth century up until the middle of the nineteenth century with the peak production being from 1850 to 1860. Since then the decline has proved to be even more rapid (Gale, 1979).

4.6.2 Industrial evolution

Wolverhampton's extensive industrial history is a direct consequence of the geological structure of the city and the surrounding area (Gale, 1979). This industrial activity is in contrast to the farming land which lies just outside the perimeter of the city, particularly the west side of the city. The city itself and the villages which make up the east side of the city such as Wednesfield, Heath Town and Monmore Green stand on the western edge of the south Staffordshire Coalfield (see Fig 4.3). With the abundance of coal and ironstone near by, the city specialised in the manufacture of ironmongery and hardware, notably in bolts, locks, and keys, tinned, galvanized and japanned goods. In later years the development of industries involved in the manufacture of bicycles and motor-cars occurred, the large Goodyear factory which remains today being an example of this trend.

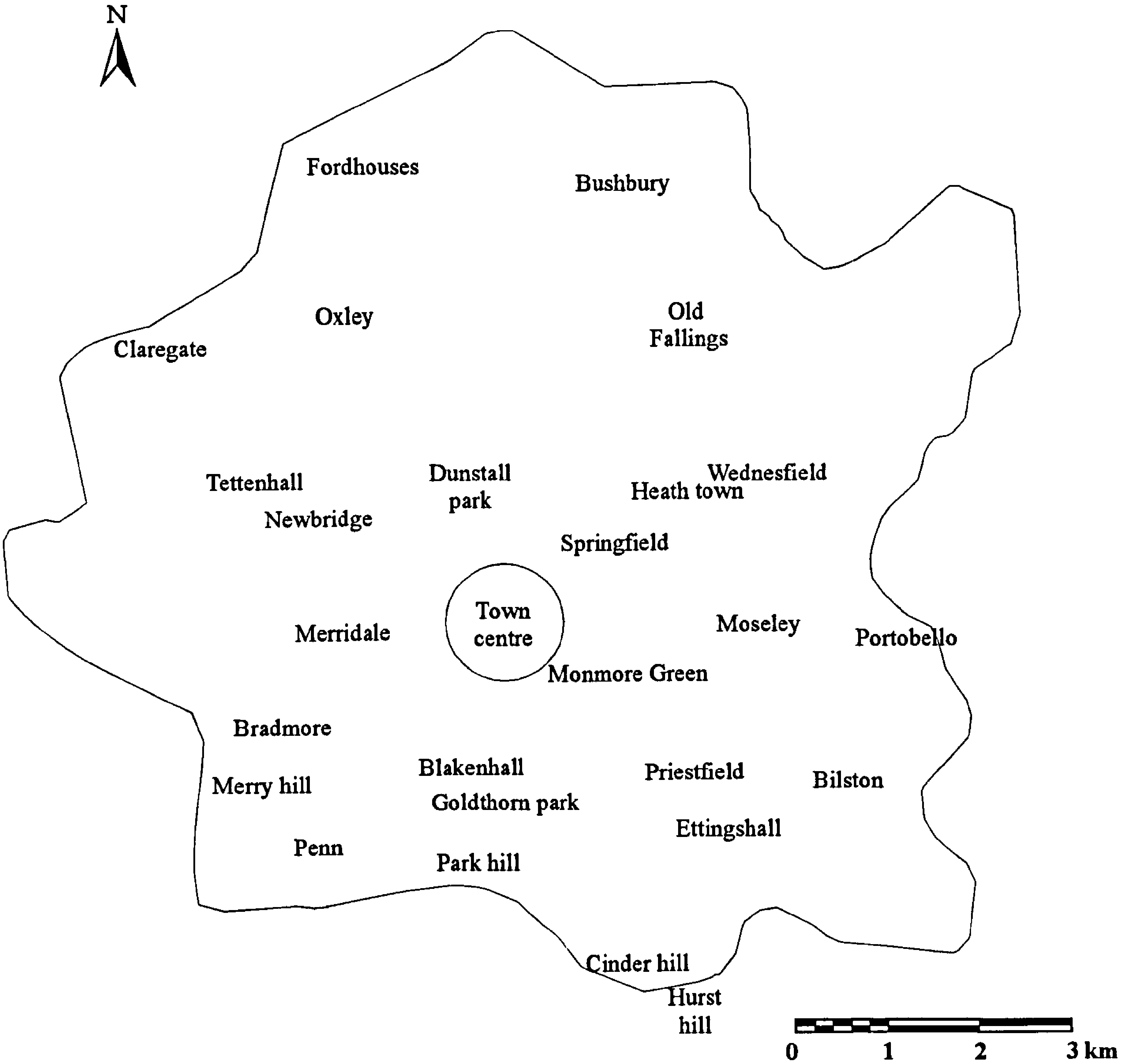


Figure 4.3 The Metropolitan area of Wolverhampton.

The proximity to farming land often resulted in Wolverhampton acting as a market town in the past for the assemblage and distribution of agricultural produce for the Black Country as a whole. The land in the east was used for mining and smelting activities which resulted in much of this area being covered with spoil-banks, slag-heaps, factories and squalid streets. The more rural borderlands provide a complete contrast to this grimy region, particularly the higher parts of Wolverhampton to the west, where Tettenhall allows a transition to the countryside (see Fig. 4.3).

In addition to the ideal geological conditions, good transport facilities aided the growth of Wolverhampton as an industrial city in the late eighteenth and early nineteenth centuries. Canal links with Birmingham were opened in 1770 and canals in general proved to be one of the most important factors in industrial location, because by the time railway links were improving industry was on the decline in Wolverhampton.

Wolverhampton's industrial history predates the eighteenth century going back to the time of Queen Elizabeth I when the wool trade was prevalent. Records suggest that although the south Staffordshire coal mines were exploited as early as AD 1315, it was not until the eighteenth century that coal became more widespread as a fuel both domestically and industrially. At this time Britain was being threatened with the loss of its trees due to the charcoal demand for iron smelters, something which was brought to the notice of parliament, placing the future of the iron industry in serious doubt. At the end of the seventeenth century 12-14 collieries were being worked in Wolverhampton, and by the late eighteenth century the black country had over 500 collieries and an annual yield of coal and slack of over 13 million tones. There was a great deal of early opposition to the use of coal as an industrial fuel, but by 1788 south Staffordshire did not have a single furnace making charcoal iron and 42 blast furnaces by 1802. This number decreased by the mid-nineteenth century, but at the end of the eighteenth century 700 000 tones of pig iron were being produced in the district (Gale, 1979).

The iron industry in Wolverhampton was, and still is to a certain extent, based in the east of the city with the main producers based around Monmore Green. The Chillington Iron Co. was one of the most important manufacturers, being established in

1822 and having 9 blast furnaces in total with 4 at Monmore Green and 3 at Mosely all blowing (see Fig. 4.3). The company employed 1000 workers at its peak in the mid nineteenth century and produced 300-500 tones of iron weekly before liquidation in 1885. Within a few metres walking distance were John Lysaght Ltd. and Sparrow, Jenkins and sons. John Lysaght owned several works in the area including Swan Garden ironworks and Osier Bed Ironworks with a number of blast furnaces. Swan Garden works was converted to a heavy foundry in 1904. A number of other iron works were located in this area, with works at Priestfield, Bilston and Monmore Green (see Fig. 4.3).

Several other industries related to the iron industry were also widespread in Wolverhampton in the mid eighteenth to nineteenth century. These included those making japanned and tinned wares which were introduced into Wolverhampton from south Wales in the 1750's. These industries were particularly prominent in Bilston where trays and snuff boxes were made in abundance, although a number of firms were also located in what is now the city centre. Wolverhampton was also renowned for the manufacture of locks and keys, being the centre of this industry in Britain along with Willenhall and Wednesfield. Most parts of these were made of iron and brass and in total the Black Country was home to 500 lock workshops in the late 1800's with an estimated 370 000 locks produced per week (Gale, 1979).

4.6.3 Galvanised ware

Galvanising, the technique of plating iron and steel with a protective cover such as Cr, Al or Zn, was developed in the 1840's for the manufacture of hollow-ware and galvanising sheets. Under most conditions, non-ferrous metals are more corrosion resistant than carbon-steels. Zinc has been used to coat steel articles for over one hundred years, although Zn is not used exclusively. Chromium plate is used for car trims and tin plate for food containers. The metals most commonly allied to impart corrosion resistance properties to constructional steelwork are Zn, Al and Cd, with Zn the most widely used of these. Zinc is generally applied to the steel via a hot-dipping technique favoured because of zincs low melting point (420 °C), although this is complicated slightly if a Zn-Al coated sheet is used, as aluminium has a melting pint of 660 °C. Basically the steel is placed in a bath of molten Zn (after a number of preparatory stages) at a temperature exceeding the melting point of either zinc or Al, depending on the galvanising substance. With pure Zn, a series of Fe-Zn alloys forms the coating with zinc at the surface.

It is believed that Edward Davies introduced the manufacture of galvanised articles into Wolverhampton in 1839. Buckets, bowls, baths, coal hods and later dustbins were the principal galvanised articles, with various utensils and containers for agricultural and industrial purposes made by the hollow-ware manufacturers. Demand for these articles continued to grow until 1914. Galvanised sheets were most usually corrugated and used for roofing, the domestic market provided by the railway companies for sheds and stations with eastern Europe and Asia overseas importers. By 1865 five large galvanising works were in operation in Wolverhampton employing four hundred workers. By the late nineteenth century with steel replacing wrought iron the domestic trade reduced and export became more important. Relocation therefore occurred with the industry moving to the west coast to locations such as Ellesmere Port and Newport. A rejuvenation of the domestic market was experienced after World War I with the construction of houses and the use of galvanised iron in petrol tanks and window-frames.

Wolverhampton was world famous for its iron output and at one time it was estimated that more galvanised iron was produced in and around Wolverhampton than in the rest of the world in total. When the heavy industries became depressed at the end of the nineteenth century this balance was redressed by the development of light industries. Between the wars the town became well known for the manufacture of motor-cars and motor-bikes; although no cars or motor-bikes are made today, component parts are still manufactured on a fairly large scale. Today Wolverhampton still has a strong link with engineering activities and the manufacture of items such as rubber tyres, tubes, soles and heels, conveyor belts, aircraft components and machine tools.

4.7 The geology of Wolverhampton

4.7.1 Introduction

The geology of Wolverhampton is represented in 2 maps shown in figures 4.4 and 4.5. Figure 4.4 shows the solid geology, figure 4.5 shows the surface geology in Wolverhampton, including the solid geology, the drift deposits and made ground. These will be referenced along with figure 4.3 which is a map of the towns in Wolverhampton. The account of the geology in this section is a summary of the work carried out by the British Geological survey in Wolverhampton during the urban programme with text by Bridges *et al.* (1995). It concentrates on the geological outcrops, and drift geology on which the soils of Wolverhampton have developed.

4.7.2 Solid geological outcrops

The Metropolitan Borough of Wolverhampton is underlain by rocks varying from Silurian to early Devonian in age, although most of these do not outcrop within the borough boundary (see figures 4.4 and 4.5). One of the exceptions to this is the prominent north-north-west trending ridge that includes Park Hill, Cinder Hill and Hurst Hill at the southern end of the borough (see figures 4.3 and 4.5). The exposed succession is described as undivided Silurian on Fig. 4.5, is approximately 265m thick and consists of 5 formations:

1). Whitcliffe formation - Flaggy silty shales and thin sandstones exposed between Cinder Hill and Goldthorn Park (12m thick).

2). Aymestry Limestone - Nodular limestone with greenish grey shaly mudstone exposed in a northward-plunging anticline on Park Hill (10m thick).

3). Elton Formation - Greenish grey, buff-weathering shales and sandy mudstones with thin beds of limestone nodules, exposed on Hurst Hill (150m thick).

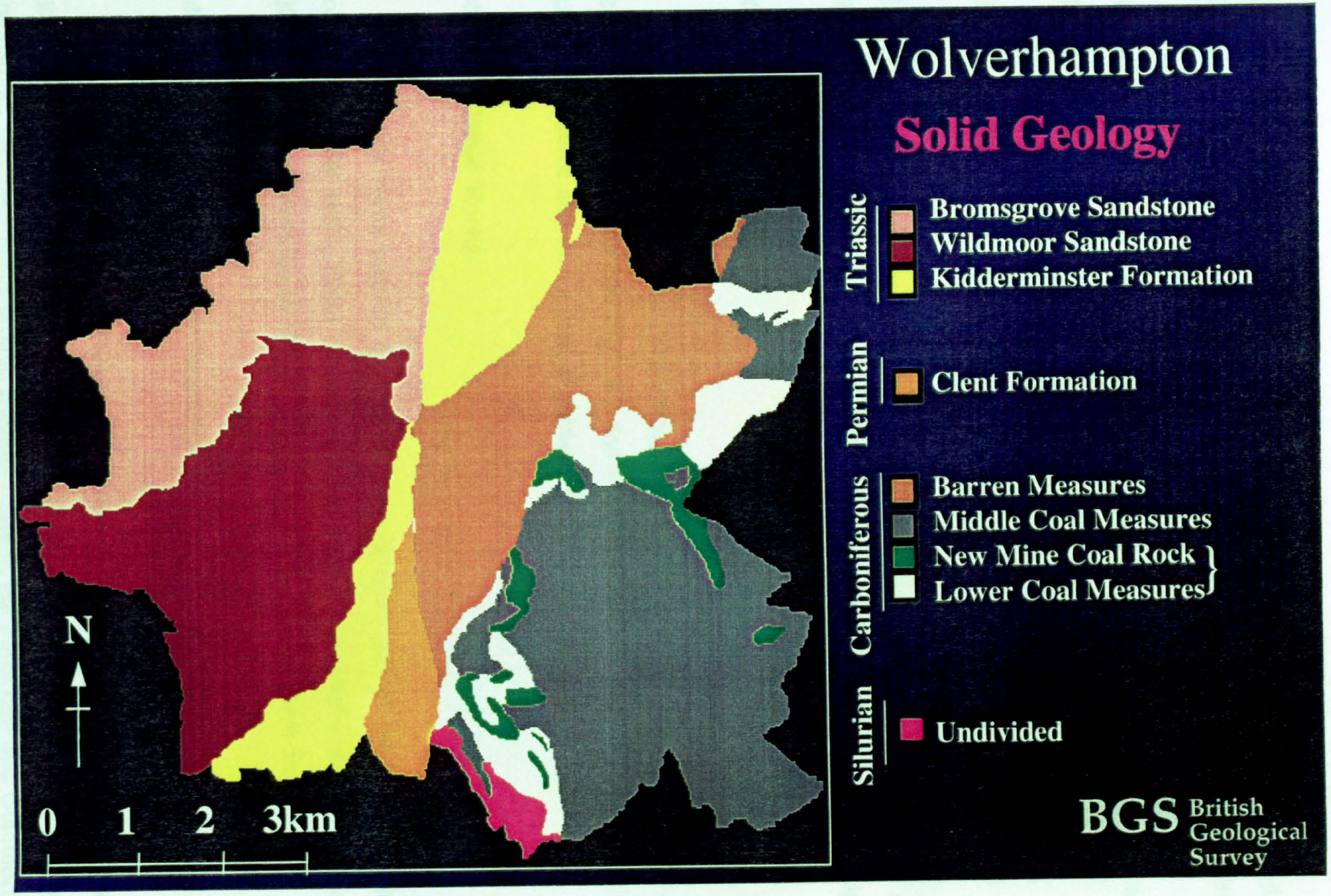

Wolverhampton
Solid Geology
Triassic
Bromsgrove Sandstone
Wildmoor Sandstone
Kidderminster Formation
Permian
Clent Formation
Carboniferous
Barren Measures
Middle Coal Measures
New Mine Coal Rock
Lower Coal Measures
Silurian
Undivided
BGS British Geological Survey
N
0 1 2 3km

Figure 4.4

4). Much Wenlock Limestone Formation - consisting of 3 sub-groups:

i). Upper Quarried Limestone - Hard shelly limestones containing unbedded fossiliferous deposits, exploited in quarries and underground workings on Hurst Hill (7.3m thick).

ii). Nodular Limestone - Nodular shelly limestone interbedded with thin sections of grey-green calcareous mudstone and siltstone (31m thick).

iii). Lower Quarried Limestone - Same asi(1- 12.8m thick).

5). Coalbrookdale formation - Monotonous greyish green shales with thin, nodular limestone beds preserved in the core of the Silurian fold at Hurst Hill (40m thick).

4.7.3 Clent Formation

Rocks of a presumed Permian age, the Clent Formation, outcrop in southern and central Wolverhampton (see Figs. 4.3 and 4.5). This consists of sandstones with thin beds of red mudstone and thin lenses of pebble breccias at a thickness of 90-110m.

4.7.4 Triassic Rocks

Triassic rocks outcrop over most of the western half of the borough with some outcrops in the east. These consist of three formations decreasing in age from the Kidderminster Formation to Wildmoor Sandstone and Bromsgrove Sandstone.

4.7.4.1 Kidderminster formation

The Kidderminster Formation comprises 80-130m of red-brown medium to coarse grained sandstone interbedded with pebble to cobble size conglomerate and subordinate mudstone. Outcrops occur around Bushbury Hill in the north east and Goldthorn Hill in the south (see Figs. 4.3 and 4.5).

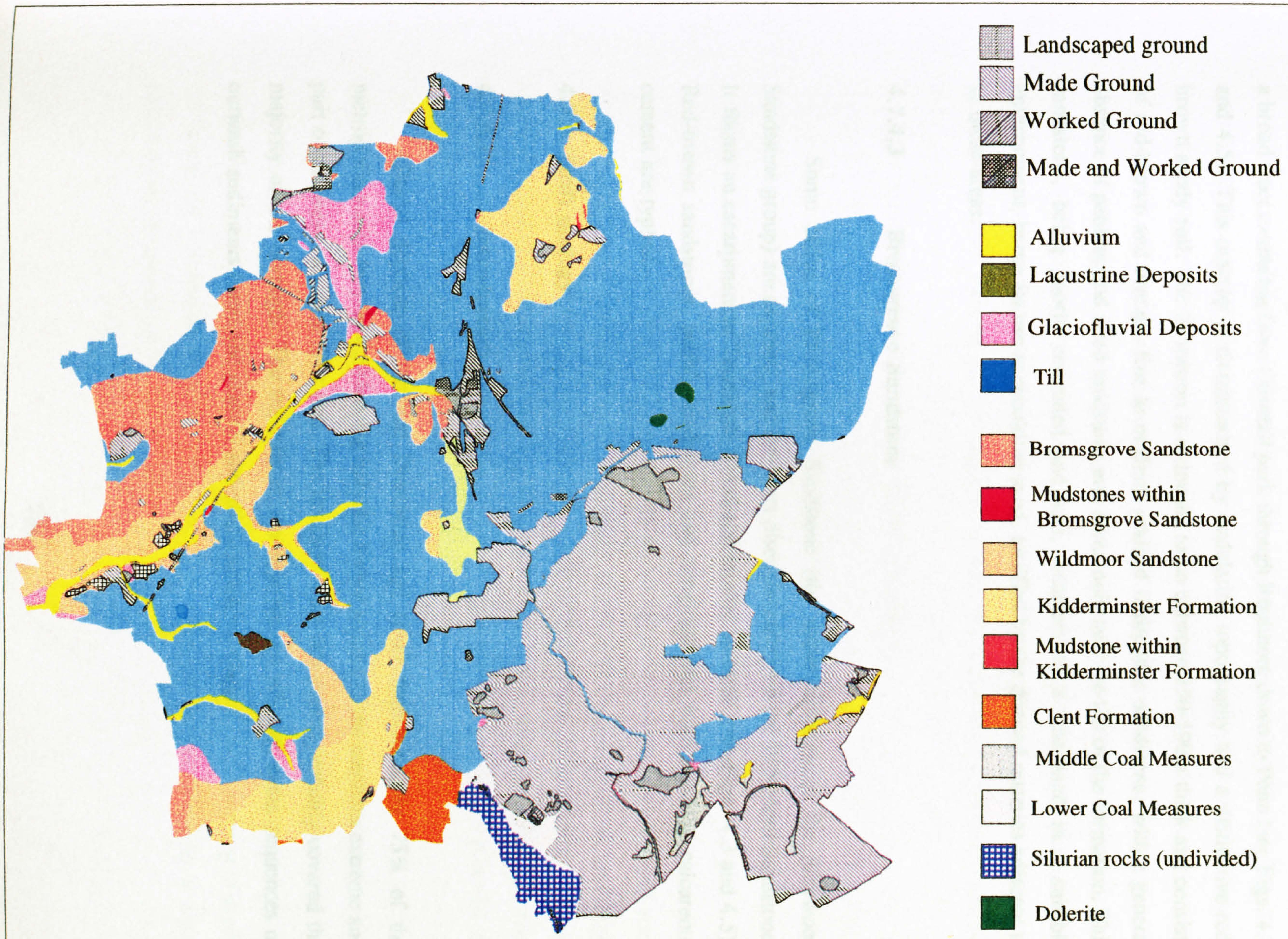


Figure 4.5 The solid and drift geology of Wolverhampton

4.7.4.2 Wildmoor Sandstone

Wildmoor Sandstone outcrops beneath the western suburbs of Wolverhampton in a broad tract extending from Dunstall park through Bradmore down to Penn (see Figs. 4.3 and 4.5). This outcrop is characterised by undulating topography and a distinctive red-brown sandy soil. The formation is estimated to be between 150-190m thick and consists of red-brown and orange, fine to medium grained feldspathic sandstone, with a general absence of pebbles and a red mudstone unit commonly near the top of the formation. This sandstone, being poorly cemented and soft, weathers to a fine sand in a suitable environment, hence its use as moulding sand, testified by the disused quarries adjacent to these areas.

4.7.4.3 Bromsgrove Sandstone

Some 105m of Bromsgrove Sandstone (the upper division of the Sherwood Sandstone group) are exposed, and this rests disconformably on the Wildmoor Sandstone. It forms an escarpment at Tettenhall Wood and around Dunstall (see Figs. 4.3 and 4.5). Red-brown sandstones, pebbly sandstones and conglomerates with a strong calcareous cement are typical.

4.7.5 Drift geology

4.7.5.1 Introduction

Glacial deposits of the late Devensian age cover approximately 75% of the metropolitan area (see fig 4.5) leaving only the higher ground of the southern extreme and part of the western extent drift free. The ice sheet from this period probably covered the majority of the borough. The majority of the deposits are till with some sequences of outwash sediments (sand and gravel) and glaciolacustrine clays.

4.7.5.2 Till

This covers most of the lower ground formed by the less resistant Carboniferous and Triassic formations. The sheet varies in thickness from less than 4m in the north to 12m in central (Springfield) and south-eastern regions (near Bilston - see Figs. 4.3 and 4.5). Lithologically, the till consists of red-brown stiff clay with well rounded to sub-angular pebbles, cobbles and boulders, the latter constituting on average approximately 10% of the bulk of the till. These boulders are a mix of locally derived material, Triassic and Carboniferous sandstones and siltstones, and clasts derived from further afield, mainly Welsh greywackes and igneous rocks. Borehole evidence suggests that the till matrix is very homogenous with the majority defined as silty clay sands with a low permeability.

4.7.5.3 Glacio-fluvial Deposits (sand and gravel)

These deposits are frequently found associated with the till, and in general consist of red-brown to medium grained sands, pebbly sands and gravels which have two categories in Wolverhampton, only one of which is exposed.

This exposure is a meltwater channel following the a course from Stafford road gasworks, through Dunstall park and south-west to the Tettenhall escarpment (see Figs. 4.3 and 4.5). Exposures of sand and gravel, sandy till and pebbly drift infilling channels above the present river are reported in places. A related course extends northwards from Dunstall park to Pendeford with borehole results showing sand and gravel to depths of 17m just south of Oxley Moor (see Figs. 4.3 and 4.5).

4.7.5.4 Supraglacial deposits

Pods and lenses of sand and gravel forming a surface capping to till are also found within Wolverhampton. A BGS borehole at Bantock house located on an outcrop of sandy till found an interleaved sequence of sands and silty clays before entering a more consolidated till unit below.

4.7.5.5 Alluvium

All the streams in the borough are flanked by a narrow alluvial floodplain deposit, consisting of mainly silt and clay overlaying coarser sand and gravel and reaching 5m thickness in places (see Fig. 4.5).

4.7.6 Made Ground

Figure 4.5 shows the extent of made ground in Wolverhampton. Made ground is a fill material which can vary greatly in its nature from inert substances such as sand, gravel and bricks, to domestic refuse and industrial waste (Bell, 1987). The majority of the made ground occupies the eastern part of the city in line with the industrial activity of this area. Spoil from former mineral workings covers much of this area and this consists mainly of fill material with a thickness varying from 4-10m, at times reaching 20m (see figure 4.5). Originally at the turn of the century the material was dumped rather haphazardly in waste mounds at the pitheads and it was not until the onset of urbanisation that the material was levelled. In areas with a long industrial history, spoil is often mixed with other deposits and wastes such as foundry sand, building rubble and variable quantities of metal, timber, glass, plastic and other by-products of industrial activity.

4.7.7 Productive coal measures

The productive coal measures vary in thickness with the thickest in the north-east of the Borough (320m) and a reduction to less than 200m below Central Wolverhampton and 100m below Penn. The Coal Measures comprise a sequence of grey mudstone, sandstone, seatearth and coal, with some coal beds of ironstone. Coal only makes up a very small part of the seam's total thickness, less than 20 % at the very most.

4.7.8 Opencast workings

Very few modern opencast workings have taken place with most of the many seams of coal and ironstone being worked near their outcrops in the early history of mining. The

New cross farm site (not shown) was worked in 1944 and now adjoins a modern development at Bowmans Harbour (not shown). A few very minor private excavations have also occurred.

4.8 Summary

Richmond and Wolverhampton are very contrasting urban environments, providing interesting examples in which to investigate and compare the anthropogenic and geological influences on multi-element concentrations in soils. Richmond, a suburb of London, is unique in so much that a large percentage of the land is given over to open space in the form of the Royal Parks and Kew Gardens and a number of sports grounds and golf courses. This London borough has an expanse of waterfront which has, in keeping with the borough in general, remained free of industrial activity. Richmond is underlain, for the most part, by river terrace gravels laid down in Quaternary times, although deposits of alluvium flank the river in certain locations and London Clay outcrops occur particularly around Richmond Park (see Figs.4.2 and Supp. Fig. 6d).

In contrast, Wolverhampton in the west Midlands is a city with a long history of metal processing industry, particularly the iron industry and later the steel industry. A distinct geographical pattern is apparent with industrial activities primarily in the east of the city (see Plate 8.1). Open space is limited in Wolverhampton, with only a few small parks, some of which have been developed in recent times over former industrial land. A great deal of surface material is made ground or imported topsoil, as a result of the land reclamation that has taken place in the last 100 years as a consequence of industrial decline. The vast majority of Wolverhampton is covered by glacial deposits which consist of a widespread till sheet with subordinate sands, gravels and laminated clays.

CHAPTER FIVE SAMPLING AND ANALYTICAL PROCEDURE

5.1 Sampling

5.1.1 Introduction

A common requirement when surveying soil properties is to obtain a representative value of the property for a specified area of land (Jackson *et al.,* 1987). Perfect representivity in sampling presumes that the analysis of a sample or duplicate samples shows the same results as the object from which is taken, which in the case of this project is a soil. In reality however, the aim is to have the same chemical characteristics for the sample as for the object, or at least be unsubstantially different from it (Barcelona, 1988). This same paper also quoted the following minimum requirements suggested by the American Chemical Society Committee On Environmental Improvement for an acceptable sampling programme.

1. A proper statistical design that takes into account the goals of the study and its certainties and uncertainties.

2. Instructions for sample collection, labelling, preservation and transportation.

3. Training of those involved in the sampling techniques and necessary procedures.

The three guidelines presented above illustrate the importance of an effective pathway from the sample collection to laboratory procedure. Care needs to taken to prevent contact of the sample with either a contaminated sampling device or storage vessel, or any aspect that results in systematic errors which will be unaccounted for in a laboratory oriented quality control scheme using blanks, standards and replicates (Barcelona, 1988).

Once the population which is to be sampled has been defined a method for sampling it then has to be selected. One technique is to select typical or average locations if familiar with the soil or area, so called purposive sampling, and this is useful where the soil is likely to be very variable and only one or two samples can be taken due to limitations in resources. However, it relies on personal judgement and as a result is likely to be biased, as will sampling from convenient spots which by avoiding inconvenient spots is not reaching the target population. Moreover, convenient spots are very often atypical in terms of geochemistry particularly when close to gates and access areas (Webster, 1977).

5.2 Sampling techniques

5.2.1 Introduction

The various merits of a number of sampling techniques have been reviewed in several papers and texts (Webster, 1977; Jackson *et al.*, 1987; Fergusson, 1992 and 1993; DOE, 1994) and although the papers by Fergusson relate to contaminated sites the critique still applies to an urban soil sampling programme.

5.2.2 Random sampling

One way to be sure of avoiding bias is to sample randomly, that is give all sites equal chance of being selected (Webster, 1977). Generally this involves the generation of random numbers or the use of random numbers tables to give x and y coordinates. This very often leads to the clustering of points and hence areas of sparse sampling.

5.2.3 Stratified random sampling

This involves the division of the sampling area into regular cells from which a designated number of samples are randomly placed. These cells are also known as a stratum for sampling and hence the name of the technique. Despite the fact that fairly large areas can remain unsampled, in relation to regular sampling (see section 5.2.4), the technique involves a major improvement in the precision due to the decrease in the size of the overall sampling area into smaller units. Sampling error is then calculated from variation within the strata and soil is likely to vary less in a smaller area, so less samples are necessary to achieve a given standard error compared to random sampling (Webster, 1977). Jackson *et al.* (1987) reported a marked improvement in sampling precision with a change from random sampling to stratified random sampling of semirural land (RSD for Pb improved from 36% to 21% and 15% to 11% for Cu). Fergusson (1992) makes these four recommendations for adopting a sampling technique:

1). It should be stratified.

2). Each stratum should carry only one sampling point.

3). It should be systematic.

4). It should be unaligned.

Random stratified sampling fulfills only 3 of these criteria and Fergusson (1992) finds that this sampling technique is more efficient (has an increased probability) than random sampling for detecting a number of different distributions of contamination.

5.2.4 Regular or systematic sampling

This defines a completely even coverage of the sample area, with sample points at regular intervals. Such a distribution makes the locating of sample points much easier than with the two previous sampling techniques. This technique also ensures a complete cover of the sampling area with an insurance of no gaps or clustering of sample points. It fulfills 3 of the 4 criteria outlined in section 5.2.3 (1, 2 and 3). It is arguably one of the most widely used techniques in environmental sampling, and·is particularly recommended in guidelines for sampling contaminated soil (ICRCL, 1987; DOE, 1988).

5.2.5 Unaligned systematic sampling or herringbone sampling

This sampling technique is a combination of systematic sampling with randomisation (Webster, 1977). It involves the use of stratum and the initial sample point is randomly selected within the first cell. For the next cell the horizontal coordinate remains the same with a random selection for the vertical coordinate. This technique fulfills all four of the criteria outlined in section 5.2.3 and Fergusson (1992 and 1993) reports it as being more effective than the previous three sampling patterns when attempting to detect contamination in a number of different shaped sampling sites. The same paper also suggests that the application of this sampling technique is not really very straightforward in the field and puts forward a herringbone design which also satisfies the four criteria outlined in section 5.2.3 and is easier to implement.

5.3 Sampling in Richmond and Wolverhampton

5.3.1 Introduction

This study aims to carry out a thorough examination of soils in the urban environment and the sampling scheme which was adopted ensured both an even and extensive coverage of the sampling area. Section 5.2 in general illustrated the advantages and disadvantages of a number of sampling techniques and it was felt that both random sampling and stratified random sampling had the potential to leave fairly large tracts of land unsampled. A regular sampling scheme was implemented because it is easy to set up and has been shown to give a good estimation of the mean concentration of Pb in a study involving several of the sampling protocols discussed in section 5.2. (Ramsey *et al.*, 1995). A regular pattern also allows an examination of the influence of factors such as land use on soils in an urban environment. In the national reconnaissance survey (Culbard *et al.*, 1983; Thornton *et al.*, 1985; Culbard *et al.*, 1988 and Thornton, 1989) 100 houses and gardens were sampled also on a grid basis (see section 3.5.3). The current study goes beyond this and investigates agricultural and industrial areas and areas of open space rather than being site selective and concentrating on garden soils.

In this study four samples were taken per km^2 with the sample site selection by means of dividing the km^2 sections of 1:10 000 maps into four equal sections and designating the centre of each of these four smaller units as a sample location. This compares to a sampling density of 1 per 5km x 5km cell for the soil survey of England and Wales (McGrath and Loveland, 1992) and 40 samples per km^2 for the Berlin study (Birke and Rauche, 1994). At each sample site 2 types of sample were taken using a 2.5 cm diameter steel screw auger:

1). A topsoil sample (0-15cm) which was a composite of 9 subsamples from a $4m^2$ grid.

2). A subsurface sample (30-45cm) which was a composite of 3 subsamples from a diagonal of the $4m^2$ grid.

A third type of sample was restricted to back gardens, and this was a composite of 25 subsamples from the top 5cm of exposed soil in the flower beds. This particular sample is a replica of the soil sample taken in the national reconnaissance survey (see section 3.5.3) allowing a direct comparison between 2 surveys separated by approximately 10 years.

All precautions were taken in the field to ensure cross contamination was kept to a minimum. The auger was cleaned between samples using kimwipes blue wipers and the auger was washed regularly with distilled water. All samples were stored in clearly labelled and securely fastened kraft bags.

Sampling in Richmond was undertaken between January and April 1992, whilst Wolverhampton was sampled during June 1993. The sampling technique was the same for the two urban areas, with the only notable exceptions being that Richmond was sampled by one person whilst in Wolverhampton several workers were deployed to carry out the sampling by the British Geological Survey. In Wolverhampton Dutch augers were used rather than screw augers.

5.3.2 Duplicate sampling

Duplicate samples were taken at every 10 sampling locations, at each depth outlined in section 5.3.1. In total over 200 locations were sampled in Richmond and over 300 in Wolverhampton, based on the sampling density outlined in section 5.3.1. It was therefore appropriate to take duplicates at enough sites to permit a good estimate of sampling variance, and therefore duplicate numbers of 20 and 30 for Richmond and Wolverhampton respectively were seen as sufficient for this exercise. In areas of open space it was decided that the duplicate sample would be taken 10m to the east of the original sample point, and in residential areas the sample would be taken, where possible, in the adjacent garden. The distance of 10m from the original sample for duplicates represents the distance with which a sample point can be accurately sited when sampling at this scale. In both Wolverhampton and Richmond it was necessary to keep sampling time to a minimum as a large number of samples were being taken. For this reason most duplicate samples were taken in areas of open space which do not present the added problem of requiring permission for access that residential areas do. As a consequence the measure of sampling error in both urban locations was really restricted to areas of open spaces which introduces bias into the sampling technique, in terms of estimating precision. Chaney *et al.* (1984), see section 3.5.5, reported how Pb topsoils concentrations varied considerably with different locations in the same garden, illustrating that random error in sampling may be very high in residential areas. Urban gardens are exposed to a number of sources of elements (see section 3.4 in general and Tables 3.1 and 3.2), and these can vary greatly with adjacent property as a consequence of the individuals use of the back garden. Therefore, basing estimates of sampling error on samples from areas of open space alone is potentially erroneous and the question of sampling error in residential areas and how this compares to areas of open space needs to be addressed (see section 10.3).

5.3.3 Urban sampling

A number of problems exist when sampling in urban areas which are unique and associated with the built-up environment. Adhering to a pre-planned sampling scheme is often very difficult due to a reliance on the general public for access to private property and the lack of suitable sites in heavily developed areas close to the city centre. A number of uncertainties are also attached to soils in urban environments, and these are often with regard to the history of land-use at a particular site (such as industrial or unscrupulous activity such as fly-tipping) or the actual origin of the topsoil which has been sampled. These factors again emphasise the importance of measuring sampling quality.

In the field an attempt was always made to sample as close to the planned sampling location as possible, something which was much easier in areas of open space (a resolution of ± 10m, hence the siting of duplicate samples - see section 5.3.2). Residential locations were somewhat more difficult and an ideal sampling location was often rendered impossible to sample as a result of the building being unoccupied or access refused. In these circumstances the next best location was selected (i.e. the nearest to the sample point) until a successful sample could be taken.

5.4 Sample preparation and analytical procedures

5.4.1 Sample preparation

Soil samples were air dried at 60°c until water loss stopped, something determined by weighing selected samples over the course of a number of days until no further loss of weight was apparent. Soils were then gently disaggregated using an agate pestle and mortar to prevent contamination and passed through a 2mm mesh nylon sieve. As with procedures in the field, all precautions were taken to ensure cross contamination was kept to a minimum, with a thorough cleaning of the comminution laboratory prior to disaggregation and a change of the filters on the extraction fans. The extraction fans were kept on during the course of disaggregation and the laboratory was cleaned again at the end of each days work. The nylon mesh and pestle and mortar were all brushed extensively between samples and silver sand was used at regular intervals to maintain an uncontaminated pestle and mortar. A minimum number of samples were kept in the laboratory during sieving and disaggregation and these were sealed at all times prior to their preparation.

Sieved soils were then split using a stainless steel riffle, with half the soil put aside for `total' soil analysis and the other half put aside for other types of analysis such as pH and organic carbon determination. The soil which was used for `total' analysis is then ground using an agate swing mill, a Siebtechnic model tema mill, to less than 180 μm. A subsample of approximately 50g (although this varies with the size of the tema pot) was ground for two minutes, a time period found adequate to permit a number of selected soils to pass totally through a 180 μm nylon mesh. These samples were then sealed in labelled plastic bags ready for weighing.

When only a very small fraction of the soil is used for analysis care has to be taken to ensure that a truly representative subsample is taken. In situations when less than 2g is required for analysis, a much larger subsample needs to be finely ground and then subsampled again. This explains the procedure outlined in this section, with the homogenising of a large soil sample to facilitate chemical representation by a much smaller subsample.

5.4.2 Analytical procedures

5.4.2.1 Introduction

All specific descriptions of glassware used are detailed in Appendix 1 along with specific details about the analytical techniques, and it only remains to stress that all test tubes went through a standard cleaning procedure prior to use. This was a three step procedure which involved cleaning the glassware with a nylon brush, removing any permanent marker labels with acetone and placing these in detergent (Decon) overnight. These were then thoroughly rinsed in water and soaked overnight in 2% nitric acid, rinsed three times in DIW and placed in the drying cupboard. Samples for `total' analysis, pH analysis and organic carbon determination were all weighed on a Sartorius three figure top pan balance.

5.4.2.2 Determination of pH

For this study soil pH is determined using a 2.5:1 ratio of deionised water to sample weight. This involved using 10ml of deionised water and 4g of soil sample (< 2mm fraction). The sample was weighed into 15ml disposable polystyrene tubes, 10ml of deionised water was added and the tubes shaken for 1 hour in a box shaker. The pH meter (Orion Research 701A) was calibrated using freshly prepared buffer solutions of pH 4, 7 and 9. The pH of individual samples was obtained by inserting the glass electrode and swirling the suspension until a constant reading was obtained. The electrode was rinsed in deionised water and blotted dry after each sample, and the calibration was checked at regular intervals.

5.4.2.3 Determination of organic matter content

Loss-on-ignition was employed as a technique to determine the organic matter content of soils. This technique is very simple and useful for large number of samples. The technique, however, has been found to overestimate the organic matter content due to loss of bound water and hydroxyl groups from clay minerals and CO_2 from carbonates (Hesse, 1971). An appropriate temperature for soil ignition is therefore necessary to negate this, and research by Ball (1964) and Allen *et al.* (1974) suggests that 450°C is suitable for this.

A 5g sample of air dried soil (< 2mm) was weighed into a prewashed crucible and placed in a drying oven at 105g for 24 hours. The samples were then cooled to room temperature in a desiccator and reweighed to determine the moisture content. Samples were then ignited at 450°C in a furnace for 24 hours, cooled in an oven at 105°C and then cooled to room temperature in a desiccator and reweighed. The percentage loss-on-ignition is calculated using the following equation:

$$\text{LOI\%} = \frac{\text{(mass of oven dried soil) - (mass of ignited soil)}}{\text{(mass of oven dried soil)}}$$

5.4.2.4 Determination of soil texture

Two techniques are generally used to determine the percentage of sand, silt and clay in soils. These are the pipette method and the Bouyoucos hydrometer method (Bouyoucos, 1927), both depending on Stoke's law which governs the settling velocities of particles in liquid (Smith and Atkinson, 1975). The hydrometer technique is used in this study, because it is easy to implement and more rapid than the pipette method. The details of the technique are listed in Appendix 1. To summarise, 60ml of H_2O_2 (30 volume) are carefully added to 50g of air-dried soil to remove organic matter. The 800ml beaker is then gently warmed until all frothing has ceased, with excessive frothing prevented by adding a few drops of capryl or amyl alcohol. On cooling, 10ml of Calgon are added to disperse the mineral particles, and the suspension washed into the cup of a mechanical stirrer and agitated for 15 minutes.

The suspension is then washed into a 1000ml measuring cylinder and diluted with deionised water. The temperature of the suspension is taken and the cylinder shaken for one minute. A hydrometer is gently inserted, and readings are taken after 40 seconds (for the percentage of silt and clay) and 2 hours (for the percentage of clay). The supernatant is then discarded and the processes of filling, stirring, settling out and decanting are repeated until the supernatant was clear. The sand residues are then dried and weighed and individual size fractions are obtained by correcting for the presence of organic matter and using the equation:

$$\text{corrected \%} = \text{determined \%} \times \frac{100}{100 - \text{\% LOI}}$$

The soils are then defined by a textural class as assigned by the ISSS triangular diagram (USDA, 1975).

5.4.2.5 Sample digestion

Samples were to be analysed using an ICP-AES so it was necessary to adopt a digestion technique suitable for this instrumentation. Soils are not easily dissolved and multielement analysis by ICP-AES requires the greatest possible proportion of the sample be brought into solution for analysis (Thompson and Walsh, 1988). Ure (1990) defines a dissolution involving hydrofluoric acid alone and in combination with a number of mineral acids as a *total* analysis, whilst those that involve mineral acids are described as *pseudo-total* analysis.

The soil matrix contains a great deal of silica or silicates and these can be attacked by an aqueous solution of hydrofluoric acid, although this provides storage problems. More common is the combination of hydrofluoric acid and an oxidising acid such as HNO_3 and

$HClO_4$, and this technique carried out in an open vessel is perhaps the most widespread at this time (Thompson and Walsh, 1988). Dilution factors of between 40 and 100 are common permitting a suite of approximately 30 elements to be determined at crustal abundances. A number of drawbacks accompany this technique, such as the incomplete attack of several important oxide minerals such as cassiterite and the volatilization of elements such as boron. The enhancing of the technique by the use of sealed bombs (pressure vessels) has been reviewed elsewhere (Thompson and Walsh, 1988 and Ure, 1990), although the technique is not appropriate for environmental geochemical mapping because it is expensive and inconvenient for a large batch process.

The technique that was applied for analysing soils in this project was digestion with HNO_3 and $HCLO_4$ followed by leaching with HCl (the exact details of the digestion technique are presented in Appendix 1). Although this digestion technique is less `total' than the hydrofluoric acid based attacks, the silica or silicates are not dissolved completely, the digestion is vigorous enough to dissolve the metals not bound in the silicate lattice, a situation which applies to the trace metals in particular (Ure, 1990). Metals are generally sorbed on to clay minerals or other readily decomposed phases (Thompson and Walsh, 1988). In essence the attacks provides an `environmental total', or concentrations of elements that are present in the soil and which may be available to plants. Care is needed to be exercised because of the potentially explosive reaction between $HClO_4$ and organic matter. This is mitigated by adding HNO_3 to the soil first and only using $HClO_4$ in the final oxidation stage. After evaporation of the nitric acid, the perchloric acid and soil solution is completely evaporated, the residue is redissolved in hydrochloric acid bringing it into solution, and after further heating made up to volume with DIW.

5.5 Analytical quality control

5.5.1 Introduction

Before any deductions can be made about environmental data, the quality of the data needs to be assessed in terms of its validity. This can be done in a number of ways which are incorporated within the QUTE (quality test) scheme which is carried out in conjunction with analytical `runs' on the ICP-AES. The QUTE scheme involves the use of synthetic solutions, duplicated samples, reference materials, and reagent blanks. This system allows the investigation of both run time errors of the instrumentation and also those that result from errors in sampling and analytical techniques.

5.5.2 Reagent blanks

Reagent blanks are solutions of 5M hydrochloric acid (2ml) made up to 10ml using deionised water after the initial attack of nitric/perchloric acids has boiled down to dryness. No sample was added to these prior to digestion, so the analysis of reagent blanks measures possible contamination in the analytical system, such as aerial deposition and vessel or reagent impurities which cause translational bias. The mean values for the 25 elements are calculated for the reagent blanks and then a students t-test is performed to see if any of the values are significantly different from zero. Any significant difference is accounted for in the final QUTE report for a batch of samples. Reagent blanks make up 5% of the total test solutions and are distributed randomly throughout the analytical run.

5.5.3 Reference materials

The measurement of reference materials is a necessary means of determining analytical bias. The reference materials used throughout these analytical runs took the form of two house reference materials (HRM1 and HRM2) and two external certified reference materials, the Community Bureau of Reference (BCR 142 and BCR 143 -see section 5.6.2). The use of reference materials which have a known composition are very important for highlighting any inherent errors in the departmental instrumentation. Both the internal and certified reference materials should be similar in composition and mineralogy to the samples that are to be analyzed, and as far as possible particle size distributions should also be similar. The Certified Reference Materials were only run on the first and final batches because they are more expensive and are certified only for Pb, Zn, Cu, Ni and Cd. Reference materials are particularly useful for both examining accuracy within batches and between batches, because the QUTE report calculates an average value for each of the 25 elements from HRM's analyzed over a number of years from each batch, and the percent bias from this mean is reported. As with reagent blanks, reference materials make up 5% of the total test samples and are analyzed at random positions in the batch.

5.5.4 Duplicate samples

The analytical precision is evaluated by analyzing in duplicate 10% of the test samples, which ideally are selected at random and should therefore represent the full range of analyte concentrations and matrices to be found in a particular batch. However, this study was structured to include the taking of field samples (10% in total) so these were automatically used as analytical duplicates for statistical reasons. Again these are inserted into the analytical run at random and treated as separate test portions until the final QUTE report where the two sets of results are brought together and the mean is calculated along with the percent difference for each element. The principle that is employed for duplicates is that after the soil has been homogenised during the preparation stage of drying, sieving, disaggregation and tema milling, the reduction in hetrogenity improves analytical precision. The analytical duplicates are run at random positions in the batch, and it is deemed preferential to avoid running the two subsample solutions too close together as this gives an over-optimistic estimation of precision.

5.5.5 Synthetic solutions

Synthetic solutions are used to calibrate the ICP-AES both before a batch is analyzed and throughout the analytical run. These solutions have a known composition and, unlike reagent blanks and reference materials, are not analysed at random positions but periodically (a full normalisation every 30 minutes and blank normalisation every 15 minutes). This enables the calibration to be monitored and to effect recalibration or to initiate corrective measures in the event of instrument malfunction (Ramsey *et al.*, 1987). In the same paper it was reported that previous work had completely underestimated how bias and precision deteriorate over the course of an analytical run which can take up to several hours. The extent of the contribution of instrumental drift can be partially reduced by frequent recalibration. Two types of synthetic solution are used in analytical work with contrasting analyte concentrations. One is termed an instrumental blank with all analyte concentrations at zero to estimate the statistics of the background emissions, whilst the other has all analytes at high concentrations. This contrast is used to investigate the sensitivity of the instrument, and a calibration deviation of more than 10% means that analysis is temporarily halted to allow recalibration.

5.6 Bias and precision

Bias refers to how close a single concentration estimate is to the true value, and any difference may be due to either random or systematic error. For an unknown sample a true concentration value can never be estimated with 100% confidence, although a consensus of the estimate can be made by a variety of analytical methods to produce a reference material. This is known as the certified, recommended or accepted value (Thompson, 1983). The systematic error of an analytical method is called the bias, and this can be estimated with the use of reference materials as illustrated in section 5.5.3.

Analytical precision is a measure of the random error of an analytical method, and this relates to the reproducibility of a result. Unlike systematic error, random error is different every time but usually follows a normal distribution (Thompson and Howarth, 1980), and can be estimated using the standard deviation. Random error arises from sub-sampling of the original sample and analytical procedure. These can be compared within the context of the QUTE report using the 10% precision charts for both analytical and sampling duplicates (Thompson and Howarth, 1976). The basic principle involves plotting the mean value of the analytical pairs on the X-axis and the absolute difference between the pairs on the Y-axis. The graphs have percentile lines drawn for 10% precision at the 50th, 90th and 99th percentile. Generally results tend to fall either side of the median, although mainly below the 90th and 99th percentile. Random error associated with sampling and analytical procedures can also be estimated using robust ANOVA (analysis of variance) as outlined in section 5.7.1.

5.6.1 ICP-AES accuracy and precision

The precision of the ICP-AES as an analytical technique has often been quoted as

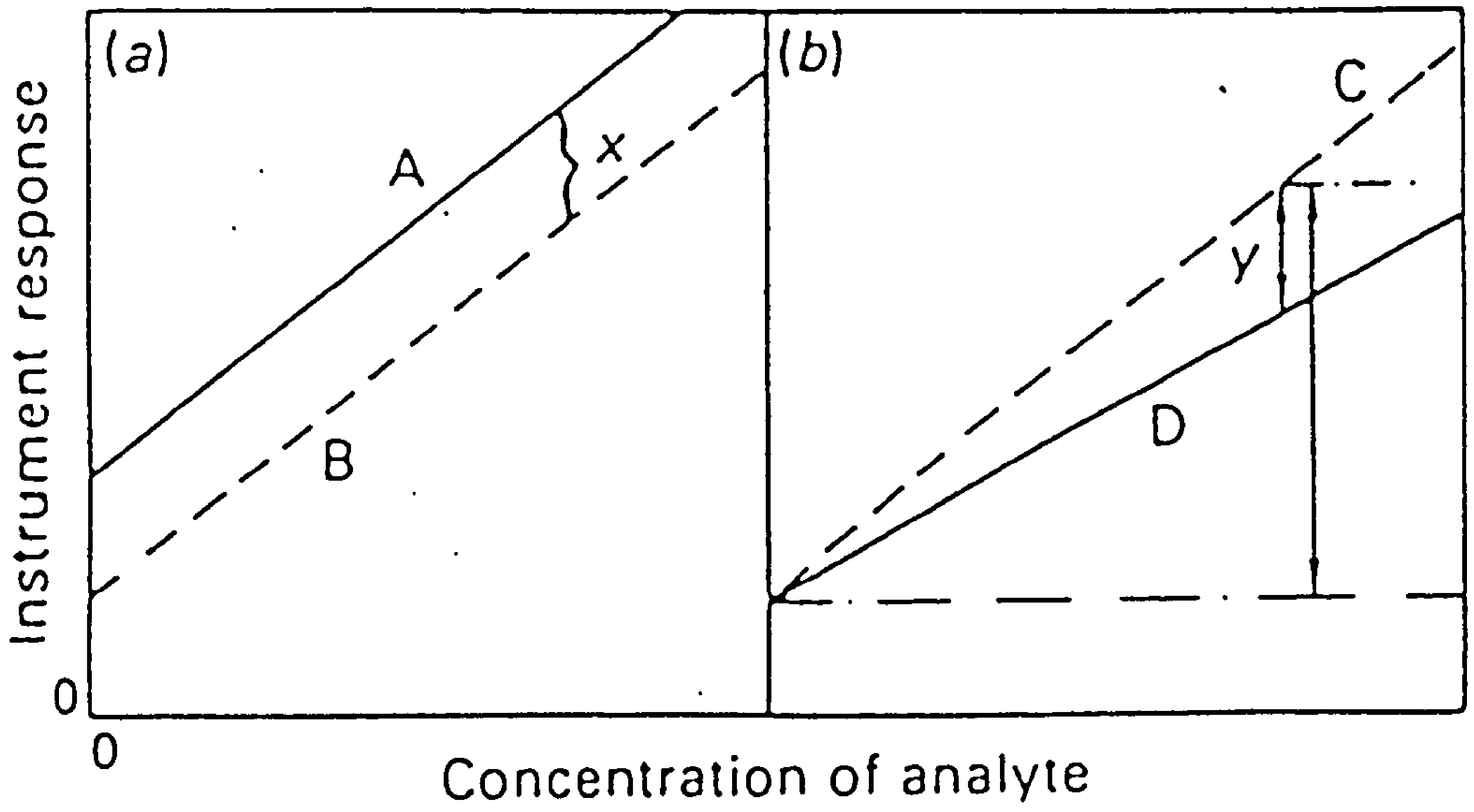
±1% (Boumans, 1978; Walsh and Howie, 1980; Coles, 1989). However, it is now known that analytical precision is not constant but varies as a function of analyte concentration with reports for precision of metals at a level of 5% (Church, 1981). The same paper reported that as detection limit was approached for a particular element, precision tends to increase significantly (that is decrease in terms of quality). The ICP-AES is prone to interference of two kinds which are the causes of analytical bias, fundamentally different and mathematically very distinct in how they effect the calibration line (see Figs. 5.1a and 5.1b). These interferences are:

1). Spectral

2). Matrix

Spectral interference is translational in nature (see Fig. 5.1a), and although there are a variety of ways in which this is produced, they all result from the spectrum of an interfering element adding to the analyte (Coles, 1989)- see Fig. 5.1a. A classic example is found with Mn and Ag who have emission lines at very similar wavelengths (328.08 nm and 328.07 nm respectively), so making separation very difficult and inducing translational bias. Background enhancement is another possible form of translational interference with the background enhancement of La by Ca being an example. Translational bias manifests itself as a constant error to the concentration of the analyte (see Fig. 5.1a). This process has obviously more serious implications for the interpretation of elements that are present at low levels, because an addition of 5 μg/g to a Cu reading which may only actually be 8 μg/g in reality, for example, will produce a greater relative error than an addition of 5 μg/g to a Cu concentration which is actually 1000 μg/g.

Matrix effects are rotational in nature, and the first physical cause of rotation is derived from the concentration of major component elements such as Ca or Fe or acids such as sulphuric or phosphoric acid. This affects the bulk or surface properties of the solution, i.e. density, viscosity, and surface tension, which in turn affect the efficiency of nebulisation. The second physical cause of rotational effects are spectroscopic, whereby the presence of major components influence the excitation conditions and consequently the



(a). Translational interference with B - no interferent; A - interferent present producing a constant bias x.

(b). Rotational interference with C - no interferent; D - interferent present producing a relative change in sensitivity y.

Fig. 5.1 Schematic calibration graphs illustrating the effects of translational (a) and rotational (b) interferences signal output. Maessen et al (1982) found that matrix effects were strongest for Ca in an experiment that included K, Na, and Mg. With rotational bias the effects are much more significant for analytes at high concentrations (see Fig. 5.1b) because the nature of rotational interference is such that a particular level of interferant causes the analyte to be enhanced by a constant factor. Typical values are from -5 to -20 % and from +5 to +20 %.

5.6.2 Estimation of analytical bias for this study

Section 5.6 briefly introduced the concept of accuracy and the importance of this in analytical procedure. The use of `house' reference materials are not strictly suitable for assessment of absolute analytical bias because they are developed internally and any errors inherent in the analytical procedure may still be occurring, irrespective of promising results in terms of between batch bias. In this study HRMs are used to monitor bias across batches. The Community Bureau of Reference (BCR) produce a number of certified reference materials, and in the course of the laboratory work undertaken in this research two were used.

BCR 142 - A light sandy soil taken from a rural, non-residential area devoid of any industrial activity.

BCR 143 - A sewage sludge amended soil taken from the fields of the experimental agriculture research station in Germany.

Both the sample preparation and the analysis of the soils were undertaken throughout a number of institutions in the European Community, and analytical techniques involved a number of different digestions and instrumentation, the latter which included AAS, XRF, ICP, and MS. Statistical analysis of all the data produced a series of accepted values for each of the 5 elements listed in Tables 5.1 to 5.4. Generally the analytical runs on the ICP-AES produced values which were less than the accepted values, but less than 10% in all cases. The overall range of bias for both BCR's throughout all the analyses was from approximately < -10 to +6%. These are probably the result of small matrix effects within the ICP caused by the major elements in the sample. This is a satisfactory standard of accuracy for the interpretation of the geochemistry.

Table 5.1 Estimation of bias in analysis of Richmond soils using BCR-142

Metal	No.	BCR accepted value	Determined mean value	Bias %
Pb	n=4	37.8 µg/g	34.55 µg/g	-8.58 %
Zn	n=4	92.4 µg/g	90.97 µg/g	-1.55 %
Cu	n=4	27.5 µg/g	26.12 µg/g	-5.03 %
Ni	n=4	29.2 µg/g	26.74 µg/g	-8.43 %
Cd	n=4	0.25 µg/g	0.239 µg/g	-4.16 %

Table 5.2 Estimation of bias in analysis of Richmond soils using BCR-143

Metal	No.	BCR accepted value	Determined mean value	Bias %
Pb	n=4	1333 µg/g	1300 µg/g	-2.44 %
Zn	n=4	1272 µg/g	1237 µg/g	-2.73 %
Cu	n=4	236 µg/g	225 µg/g	-4.70 %
Ni	n=4	99.5 µg/g	91.85 µg/g	-7.68 %
Cd	n=4	31.1 µg/g	28.10 µg/g	-9.65 %

Table 5.3 Estimation of bias in analysis of Wolverhampton soils using BCR-142

Metal	No.	BCR accepted value	Determined mean value	Bias %
Pb	n=4	37.8 μg/g	40.14 μg/g	+6.18 %
Zn	n=4	92.4 μg/g	87.57 μg/g	-5.23 %
Cu	n=4	27.5 μg/g	25.41 μg/g	-7.61 %
Ni	n=4	29.2 μg/g	27.52 μg/g	-5.77 %
Cd	n=4	0.25 μg/g	0.27 μg/g	+6.58 %

Table 5.4 Estimation of bias in analysis of Wolverhampton soils using BCR-143

Metal	No.	BCR accepted value	Determined mean value	Bias %
Pb	n=4	1333 μg/g	1390 μg/g	+4.26 %
Zn	n=4	1272 μg/g	1301 μg/g	+2.27 %
Cu	n=4	236 μg/g	244 μg/g	+3.18 %
Ni	n=4	99.5 μg/g	90.95 μg/g	-8.59 %
Cd	n=4	31.1 μg/g	28.66 μg/g	-7.83 %

5.6.3 Within and between batch bias of Richmond samples

House reference materials (HRMs) are used as a means of determining within and between batch bias as a standard procedure of analytical work. Tables 5.5 and 5.6 show the mean concentrations and standard deviations for elements in HRM-1 and HRM-2. The last column in both tables presents the results from the analysis of variance which compares the reference materials within the same analytical batch to those from other analytical batches, to see if there is any significant difference between the two. This is expressed by means of the f-ratio and the probability, the former being the ratio between the sum of squares of the between batch and the sum of squares of the within batch. The lower the ratio the less likely the house reference materials are to differ for each element between subsequent analytical batches. The probability, set at the 95% confidence level states that any value of less than 0.05 shows a significant difference between variance within the batch to that shown between analytical batches. Tables 5.5 and 5.6, for HRM-1 and HRM-2 respectively show that no element has a high enough f-ratio or a low enough probability to imply a significant difference between results for reference materials run in the same batch and those run in other batches. A consistent level of precision was therefore maintained both within and between batches in the analysis of soils from Richmond. Reference materials are not very good for estimating precision, being too fine grained and homogenous, and therefore duplicate samples are employed to give a realistic estimate of precision (see section 5.5.4).

Table 5.5 Comparison of bias of HRM 1 between and within batches for Richmond samples. High probability values (> 0.05) indicate insignificant differences

Element	Grand mean / s.d.	F-ratio/Probability	
Li	2.832 ± 0.09 μg/g	1.24	0.336
Na	34.51 ± 9.22 μg/g	1.04	0.407
K	679.5 ± 18.10 μg/g	1.18	0.355
Be	0.239 ± 0.01 μg/g	1.83	0.191
Mg	411.3 ± 6.81 μg/g	2.58	0.098
Ca	511.8 ± 9.82 μg/g	2.64	0.093
Sr	7.296 ± 0.76 μg/g	0.08	0.969
Ba	20.58 ± 1.69 μg/g	0.14	0.931
Al	4637 ± 118 μg/g	2.48	0.107
La	7.958 ± 0.74 μg/g	1.10	0.384
Ti	359.6 ± 31.30 μg/g	0.68	0.579
V	14.16 ± 0.31 μg/g	1.20	0.348
Cr	14.77 ± 3.58 μg/g	0.81	0.510
Mn	133.3 ± 16.67 μg/g	1.05	0.403
Fe	9009 ± 200 μg/g	1.18	0.355
Co	2.118 ± 0.12 μg/g	0.94	0.450
Ni	5.131 ± 0.33 μg/g	0.16	0.919
Cu	3.108 ± 0.55 μg/g	3.35	0.052
Zn	24.21 ± 0.47 μg/g	1.48	0.266
Cd	0.0746 ± 0.10 μg/g	0.48	0.699
Pb	12.88 ± 1.26 μg/g	0.93	0.454
P	419.00 ± 3.73 μg/g	2.36	0.119

Table 5.6 Comparison of bias of HRM 2 between and within batches for Richmond samples. High probability values (> 0.05) indicate insignificant differences

Element	Grand mean / s.d.	F-ratio / Probability	
Li	141.5 ± 1.50 µg/g	1.73	0.225
Na	829.9 ± 9.63 µg/g	2.28	0.142
K	8184 ± 290 µg/g	0.24	0.867
Be	2.659 ± 0.01 µg/g	0.89	0.496
Mg	13465 ± 470 µg/g	0.20	0.891
Ca	5932 ± 275 µg/g	0.25	0.861
Sr	1324 ± 42.2 µg/g	0.33	0.806
Ba	321.8 ± 4.48 µg/g	0.37	0.775
Al	36034 ± 922 µg/g	1.35	0.314
La	21.76 ± 0.849 µg/g	2.96	0.084
Ti	710.8 ± 26.17 µg/g	2.02	0.175
V	57.60 ± 0.429 µg/g	2.20	1.510
Cr	429.6 ± 4.50 µg/g	1.27	0.324
Mn	1472 ± 62.8 µg/g	0.64	0.609
Fe	46173 ± 1042 µg/g	0.61	0.622
Co	49.17 ± 1.25 µg/g	1.75	0.221
Ni	295.5 ± 7.14	1.68	0.223
Cu	584.4 ± 16.91 µg/g	0.20	0.891
Zn	403.6 ± 8.09 µg/g	1.84	0.204
Cd	2.459 ± 0.16 µg/g	3.06	0.078
Pb	505 ± 18.54 µg/g	0.84	0.505
P	635.9 ± 11.24 µg/g	0.78	0.534

5.6.4 Within and between batch bias of Wolverhampton samples

The same procedure as outlined in section 5.6.3 was implemented for the analysis of soils in the Wolverhampton project. The results from the analysis of variance show that only one element, for HRM 1, has a significant difference in concentration between batches (see tables 5.7 and 5.8). This is Na and is the result of 1 sample. In general the precision was maintained both within batch and between batches and although one element proved to be significantly different between batches this does not alter the confidence in the analytical results.

Table 5.7 Comparison of bias of HRM 1 between and within batches for Wolverhampton samples. High probability values (> 0.05) indicate insignificant differences

Element	Grand mean / s.d.	F-ratio / Probability	
Li	2.955 ± 0.15 μg/g	1.19	0.372
Na	**26.95 ± 4.67 μg/g**	**6.02**	**0.010**
K	681.90 ± 40 μg/g	1.45	0.288
Be	0.267 ± 0.02 μg/g	1.34	0.322
Mg	410.30 ± 20.49 μg/g	1.46	0.286
Ca	505.9 ± 47 μg/g	0.90	0.498
Sr	7.248 ± 0.83 μg/g	0.92	0.491
Ba	19.60 ± 1.00 μg/g	1.19	0.372
Al	4468 ± 128 μg/g	3.19	0.062
La	7.512 ± 0.58 μg/g	2.96	0.075
Ti	320.6 ± 35 μg/g	0.89	0.505
V	14.09 ± 0.51 μg/g	1.64	0.240
Cr	13.13 ± 4.12	0.47	0.758
Mn	127.5 ± 14.10 μg/g	2.29	0.131
Fe	8760 ± 210 μg/g	1.32	0.328
Co	2.114 ± 0.06 μg/g	0.62	0.659
Ni	4.938 ± 0.28 μg/g	0.09	0.983
Cu	2.831 ± 0.33 μg/g	0.20	0.934
Zn	23.26 ± 3.99 μg/g	0.31	0.866
Cd	0.0557 ± 0.08 μg/g	0.53	0.719
Pb	13.06 ± 1.4 μg/g	0.39	0.810
P	435 ± 24.64 μg/g	1.06	0.423

Elements and values shown in bold are those which have a significant difference in results for reference materials within and between analytical batches ($P < 0.05$)

Table 5.8 Comparison of bias of HRM 2 between and within batches in Wolverhampton. High probability values (> 0.05) indicate insignificant differences

Element	Grand mean / s.d.	F-ratio / Probability	
Li	146.4 ± 5.06 μg/g	2.32	0.120
Na	695.9 ± 25 μg/g	1.36	0.315
K	7749 ± 869 μg/g	0.35	0.841
Be	2.54 ± 0.02 μg/g	1.57	0.257
Mg	13066 ± 354 μg/g	1.06	0.426
Ca	5741 ± 153 μg/g	2.44	0.116
Sr	1310 ± 29.5 μg/g	1.42	0.298
Ba	318.1 ± 6.44 μg/g	3.02	0.071
Al	34623 ± 910 μg/g	0.84	0.529
La	21.60 ± 0.86 μg/g	3.16	0.064
Ti	668.3 ± 19.10 μg/g	0.95	0.473
V	56.73 ± 0.88 μg/g	3.21	0.061
Cr	424.3 ± 8.61 μg/g	0.59	0.678
Mn	1442 ± 66.6 μg/g	1.71	0.224
Fe	44568 ± 771 μg/g	3.15	0.064
Co	47.67 ± 5.07 μg/g	2.79	0.086
Ni	250.7 ± 1.07 μg/g	2.83	0.083
Cu	573.9 ± 19.46 μg/g	0.75	0.582
Zn	368.7 ± 10 μg/g	1.23	0.359
Cd	2.675 ± 0.11 μg/g	3.46	0.051
Pb	485.2 ± 11.87 μg/g	1.23	0.357
P	668.3 ± 18.37 μg/g	1.15	0.389

5.7 Sampling and analytical quality control scheme

5.7.1 Introduction

A sampling and analytical quality control scheme (SAX) is an integrated approach to the measurement of random errors in sampling and analysis. The urban geochemical work undertaken in the context of this research incorporated the taking of field duplicates at every tenth site (see section 5.3.2) and both of these samples were analysed twice to give a hierarchical scheme.

In the past classical ANOVA (analysis of variance) has been applied to estimate sampling and analytical errors (e.g. Garrett, 1969). There have been problems in so much that the principle of ANOVA is based on a number of assumptions which are not always true for this data. These include the notion that random errors are normally distributed and that variances are homoscedastic, or not a function of concentration. In reality data from Richmond and Wolverhampton are generally positively skewed, particularly the anthropogenically introduced elements. Standard deviation of analysis also increases with concentration (Ramsey, 1993a). With classical estimates of the variance a sum of squares based on differences between individual samples from the overall mean are used, and such a sum can be dominated by a small proportion of discrepant values because of the squared terms which over emphasises the importance of `unusual' observations (Thompson and Maguire, 1993). For these reasons an alternative approach has been sought.

Robust ANOVA has become increasingly popular in the investigation of environmental samples (Analytical Methods Committee, 1989a and 1989b; Ramsey *et al.*, 1992; Ramsey, 1993a and 1993b; Thompson and Maguire, 1993). Robust ANOVA differs from classical ANOVA by accommodating outlying values rather than rejecting them (Analytical Methods Committee, 1989a and Ramsey, 1993a). Estimates of the mean and standard deviation are made by an iterative process whereby any data that exceed a certain distance from the mean are assigned a new value equal to that distance. The distance is a product of a constant (c) and the standard deviation, c being selected to suit the expected proportion of outliers and generally being 1.5s. Classical methods are used to obtain estimates of the mean and standard deviation and values which then fall outside the confines of x ± cs are adjusted accordingly to equal x ± cs or x ± cs. This then leads to the calculation of a modified mean and standard deviation, with iteration continuing until the new values of mean and standard deviation converge and are known as the robust estimates (Ramsey *et al.*, 1992).

5.7.2 Application of robust ANOVA to urban geochemistry.

Robust ANOVA was applied to estimate sampling and analytical error (the precision) in the urban data and compare this to the geochemical variance. The advantage of variance as a measure of random error is that variances unlike standard deviations are additive (Ramsey *et al.,* 1993a). Sampling and analytical variance are often collectively known as the technical variance, and it has been suggested that this should not exceed more than 20% of the total variance with analytical variance contributing no greater than 4% of the total variance (Ramsey *et al.,* 1993b). A consensus of opinion believes that it is necessary for geochemical variance to account for at least 80% of the total variance to allow a confident interpretation of the spatial distribution of the geochemistry (Ramsey *et al.,* 1993b).

5.7.3 Robust ANOVA results for Richmond.

The results for the SAX scheme in the Richmond project are shown in Tables 5.9 and 5.10. A few elements for topsoil samples (see Table 5.9) are borderline in terms of the criteria outlined in section 5.7.2 and these are Li, Ca and La with the geochemical variance generally being only less than 5% below the recommended 80%, so this will not be expected to seriously affect the interpretation of the results. The exception to this is Al as the geochemical variance falls well below the recommended 80%, with a result of approximately 68%. The Al result is probably as a result of the low concentration range for this element in Richmond soils (see Plate 6.13).

Table 5.10 shows the results of applying robust ANOVA to Richmond subsurface soils. This time it is only one element, Cr, which falls outside the recommended threshold for the specific variances and for most elements the geochemical variance accounts for more than 90% of the overall variance in the data. This dominance of the `true' geochemical variance can probably be explained by the sample type which was taken at a depth of 30-45cm and is therefore less likely to be affected by anthropogenic activity, particularly in view of the fact that these samples were taken in areas of open space. The underlying geochemical material is more homogenous, whilst the topsoil which is strongly influenced by anthropogenic activity is more heterogenous. For Cr, the limiting factor is the analytical procedure (see Table 5.10) which accounts for nearly 18% of the variance, well in excess of the recommended 4%.

Table 5.9 Assessment of the relative importance of sampling, and analytical precision compared with true geochemical variability for Richmond topsoil samples (0-15cm)

Element	Geochemical %	Sampling %	Analytical %
Li	75.08	24.54	0.38
Na	82.23	16.14	1.63
K	81.39	18.48	0.13
Be	90.40	8.42	1.18
Mg	85.04	14.74	1.22
Ca	**77.60**	**22.38**	0.02
Sr	91.45	8.29	0.26
Ba	90.98	8.69	0.32
Al	**67.88**	**32.05**	0.07
La	**74.65**	**24.18**	1.17
Ti	89.86	9.13	1.01
V	93.37	5.76	0.87
Cr	82.04	14.15	3.81
Mn	95.45	4.06	0.49
Fe	93.60	6.33	0.07
Co	91.74	7.86	0.40
Ni	87.79	11.53	0.68
Cu	83.67	16.01	0.32
Zn	81.33	18.56	0.11
Cd	84.62	14.86	0.52
Pb	91.91	7.89	0.20
P	92.16	7.79	0.05

Values in bold indicate the elements and the measurements which fall below the criteria suggested for accurate interpretation of results

Table 5.10 Assessment of the relative importance of sampling, and analytical precision compared with true geochemical variability for Richmond subsurface soils (30-45cm)

Element	Geochemical %	Sampling %	Analytical %
Li	93.03	6.54	0.43
Na	97.69	1.58	0.73
K	93.94	5.39	0.67
Be	91.17	1.92	0.91
Mg	95.98	2.92	1.10
Ca	93.96	6.01	0.03
Sr	95.72	3.81	0.45
Ba	99.04	0.74	0.22
Al	96.38	3.47	0.15
La	86.59	9.71	3.70
Ti	86.35	12.94	0.71
V	93.56	3.72	2.72
Cr	**64.10**	18.38	**17.52**
Mn	97.13	2.56	0.22
Fe	99.03	0.87	0.10
Co	89.04	9.88	1.80
Ni	97.13	1.92	0.95
Cu	96.35	3.19	0.46
Zn	92.24	4.50	0.26
Cd	91.67	7.43	0.90
Pb	96.66	3.16	0.18
P	98.38	1.55	0.06

Values in bold indicate the elements and the measurements which fall below the criteria suggested for accurate interpretation of results

5.7.4 Robust ANOVA results for Wolverhampton soils

Tables 5.11 and 5.12 present the results from analysis of variance for Wolverhampton soils and, in common with Richmond topsoils Ca is very close to the threshold of 80% for geochemical variance, although not significantly enough to hinder interpretation. More problematic are the results for La, Ti and Cr. All of these elements are affected by both sampling and analytical error and it is also the case that these elements do not have a very large concentration range in Wolverhampton soils, something which greatly increases the proportion of the sampling error. Ramsey (1993a) discusses the concept of appropriate precision and how a small variation in `true' analyte concentration requires far greater analytical precision than a case in which the `true' analyte concentration varies over a much larger range.

As with Richmond subsurface soils, the robust ANOVA results for Wolverhampton subsurface soils show geochemical variance to be the dominant feature with this accounting for approximately 81-98% of the total variance. Only Ti falls slightly outside the recommended parameters and only a slight improvement of analytical and sampling error is necessary to give the appropriate ratio of geochemical: sampling: analytical variances.

Table 5.11 Assessment of the relative importance of sampling, and analytical precision compared with true geochemical variability for Wolverhampton topsoils (0-15cm).

Elements	Geochemical %	Sampling %	Analytical %
Li	83.34	15.79	0.87
Na	**79.76**	18.48	1.76
K	89.83	8.26	1.91
Be	82.96	16.74	0.30
Mg	89.82	9.91	0.27
Ca	**79.01**	**20.91**	0.08
Sr	81.72	18.06	0.22
Ba	85.27	14.27	0.46
Al	84.36	15.13	0.51
La	**68.08**	**22.65**	**9.27**
Ti	**69.52**	**22.77**	**7.71**
V	85.54	14.09	0.37
Cr	**47.09**	**39.23**	**13.68**
Mn	87.54	5.93	6.53
Fe	82.34	17.31	0.35
Co	86.98	12.82	0.20
Ni	83.40	16.25	0.35
Cu	87.43	12.44	0.13
Zn	84.41	15.47	0.12
Cd	81.12	15.34	3.54
Pb	85.04	14.84	0.12
P	86.75	12.58	0.67

Values in bold indicate the elements and the measurements which fall below the criteria suggested for accurate interpretation of results

Table 5.12 Assessment of the relative importance of sampling, and analytical precision compared with true geochemical variability for Wolverhampton subsurface soils (30-45cm)

Elements	Geochemical %	Sampling %	Analytical %
Li	88.06	11.33	0.61
Na	91.42	7.84	0.74
K	92.40	6.86	0.74
Be	90.88	8.89	0.23
Mg	83.42	16.27	0.31
Ca	97.65	2.28	0.07
Sr	95.49	4.45	0.06
Ba	93.63	5.99	0.38
Al	92.34	6.26	1.40
La	87.39	10.31	2.30
Ti	**77.02**	18.73	**4.25**
V	95.98	3.76	0.26
Cr	89.63	7.40	2.97
Mn	86.86	11.08	2.06
Fe	88.97	10.83	0.20
Co	89.35	10.55	0.10
Ni	95.95	3.90	0.15
Cu	91.03	8.85	0.12
Zn	90.51	9.39	0.10
Cd	91.51	5.62	2.88
Pb	85.84	14.00	0.16
P	80.82	18.80	0.38

Values in bold indicate the elements and the measurements which fall below the criteria suggested for accurate interpretation of results

5.8 Summary

This chapter reviewed the sampling techniques that have been used in a number of soil surveys to determine various properties. It has been shown that regular or systematic sampling, as employed in this study, is one of the most widely used and recommended techniques because it is easy to implement and able to provide even coverage of an area of interest. It has been demonstrated that the sampling bias for this technique does not differ significantly from other sampling protocols (Thompson and Ramsey, 1995). The suitability of the sampling and analytical techniques was also reviewed using a balanced scheme of field and analytical duplicates, along with reference materials. Sampling and analytical precision were shown to be, in general, satisfactory to permit a confident interpretation of most elements. The use of internal reference materials and Certified Reference Materials has indicated that between batch bias was maintained at an acceptable level throughout this study and that the analytical accuracy was good, respectively.

Despite the assurances provided by the analytical data quality, the acid digestion used throughout this study is not a total attack and is more suitable for metals of interest such as Pb, Zn, Cd, Cu, Ni and Co. The problem lies with comparing results for other elements such as Al, Na, and which have low recovery rates from a nitric/perchloric digestion and therefore comparisons with other studies employing reagents which give a better estimation of `total' concentrations. However, within the context of this study it is perfectly valid to refer to any patterns which arise with these elements regarding land-use or geology.

The application of robust ANOVA has shown that for most elements a confident spatial interpretation [illegible] is possible in soils from Richmond and Wolverhampton. This is vital due to the mapping of these elements (see sections 6.2 and 8.3). In topsoils from Richmond, the spatial distribution of Al, in particular, needs to be interpreted with caution as the sampling variance greatly exceeds the recommended 20% (32% - see Table 5.9). For Wolverhampton topsoils, the spatial distribution of La, Ti and Cr needs to be interpreted with caution due to the high sampling and analytical variance (see Table 5.11).

CHAPTER SIX CONCENTRATIONS OF ELEMENTS IN RICHMOND SOILS

6.1 Introduction

The results discussed in this chapter are from the urban geochemical survey carried out in Richmond (see section 5.3 for sampling details). The data have been used to produce a series of maps for individual elements (see section 6.2 for the presentation and description of these maps). The geochemical classification is based on percentiles, the highest percentile class depicted with dark red and the lowest percentile class represented by dark blue, allowing spatial presentation of variations in concentration for all elements studied. The maps are accompanied by transparent overlays (supplementary Figs. 6a-6d), showing the sample points (Supp. Fig 6a) the geology (Supp. Fig. 6b), the locations of industry past and present (Supp. Fig. 6c), and the major urban centres and areas of open space in the borough (Supp. Fig. 6d). The results of statistical analysis are presented with a basic description of the data and soil properties as defined by land-use. One of the main aims of this study is to determine the degree and extent of multi-element contamination in the borough with consideration of natural variations in the geochemical signature of the different geological units, and to show how this is related to land-use.

6.2 Mapping of elements in topsoils from Richmond

6.2.1 Introduction

The geochemical maps of 21 elements in topsoils from Richmond are presented in this section. The maps were generated using facilities at the British Geological Survey in Keyworth and the GIS methods involved gridding with an Interactive Surface Model Package. The road systems and geological units are shown on the maps, with overlays (Supp. Figs 1a-1d) to aid interpretation. The metals Pb, Zn, Cu, Cd and Ni are discussed first of all, because these have, perhaps, received the most attention in previous urban studies due to their widespread use and environmental importance (see Table 3.1). The distribution of the other 16 elements are then discussed in detail (see sections 6.2.7-6.2.22).

6.2.2 Concentrations of lead in Richmond topsoils (0-15cm)

The distribution of Pb in Richmond topsoils is shown in Plate 6.1. The concentration range for this metal is high with a 97th percentile concentration approximately fifteen times higher than the 25th percentile (1094 μg/g and 75 μg/g, respectively). The lowest concentrations of Pb, those which represent uncontaminated areas, are located in three areas; Richmond Park, Hampton Court/Bushy Park and Kew Gardens (see Plate 6.1 and Supp. Fig 6d). The 25th percentile ranges from ≤ 75 μg/g. Surface soils in Richmond Park, over 2km from major roads, have concentrations of Pb of < 30 μg/g. These overlay drift deposits of high level terraces (see Plate 6.1 and Supp. Fig. 6a). The influence of urbanisation is illustrated around the margins of these large parkland areas where soil Pb concentrations increase close to the areas of housing. Figure 6.1 tests this relationship with a plot of Pb concentrations against sample sites from transect 1, using locations from Richmond Park and the adjacent urbanised area (see Plate 6.1 and Supp. Fig. 6c). Within Richmond Park, the sample nearest the urban area shows an increase in Pb concentration from the 25th percentile range to the 50th percentile range (an increase from ≤ 75 μg/g to 76-185 μg/g). Therefore concentrations of Pb in the 50th percentile range observed at the edges of Richmond Park, are a true reflection of the soil geochemistry and are not an artefact of the gridding system (see Plate 6.1).

It is clearly shown that roads, road junctions and roundabouts in particular, are closely associated with high Pb concentrations (see Plate 6.1). The association is greatest in urban areas, although areas of open space close to roads are also affected. It has previously been reported that vehicular emissions are greater in areas where traffic stops and accelerates (Kenworth *et al.*, 1983; Lyons *et al.*, 1990). These sites occur mainly in the north of the borough, near Richmond town centre and in the area west of east Sheen (see Supp. Fig. 6d). Lead concentrations which exceed the 97th percentile (> 1094 μg/g) are observed near St. Margarets and Twickenham and further west along the same road close to the roundabout. Some areas with the highest Pb concentrations (> 97th percentile; > 1094 μg/g) are not associated with road junctions. These include the residential areas of Kew, south-west of Twickenham and the large Pb anomaly, east of Bushy Park in the Teddington area (see Plate 6.1 and Supp. Fig. 6d). A sewage works and an engineering

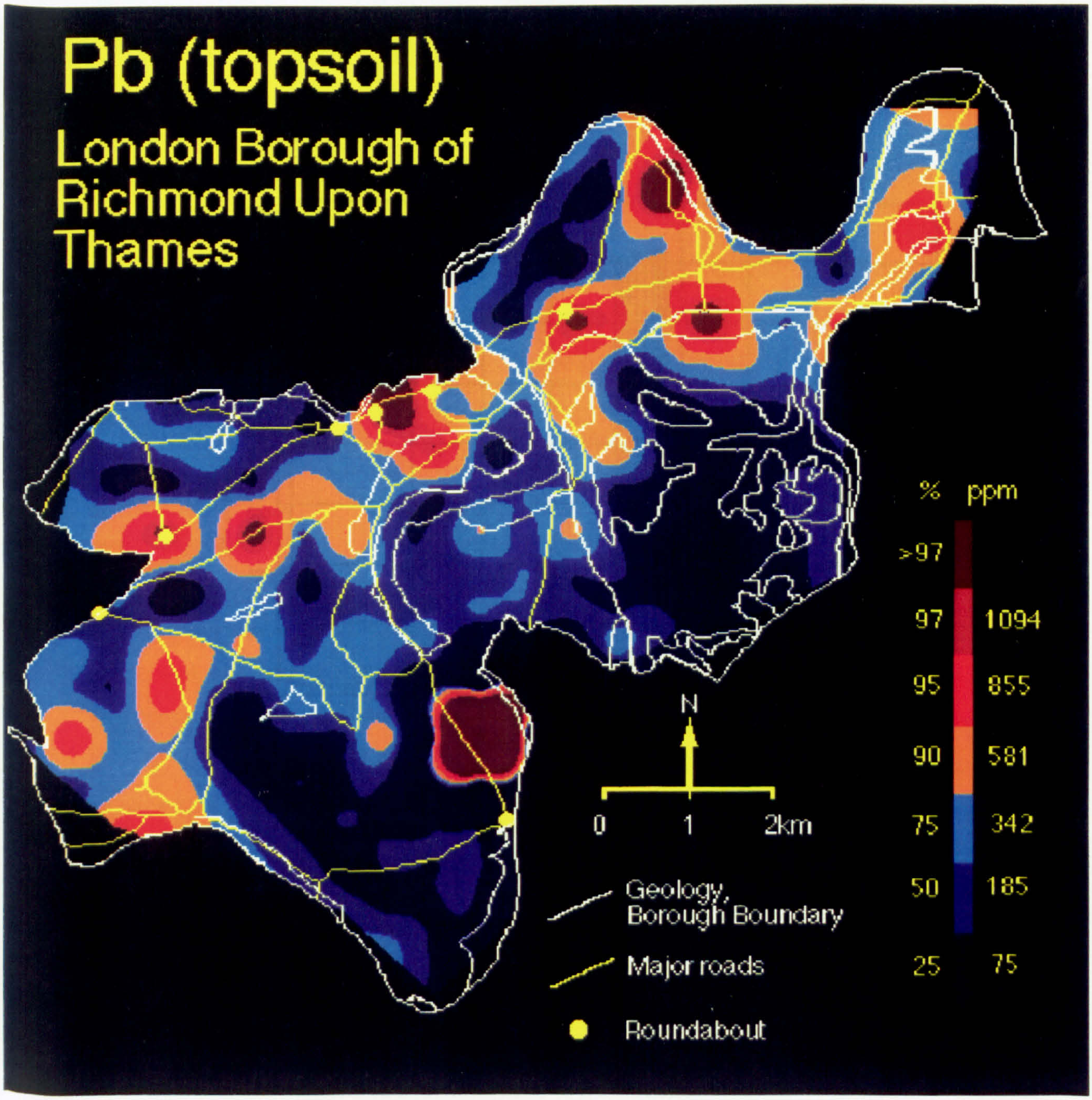

Pb (topsoil)
London Borough of Richmond Upon Thames
% ppm
>97
97 1094
95 855
90 581
75 342
50 185
25 75
N
0 1 2km
Geology, Borough Boundary
Major roads
Roundabout

Plate 6.1

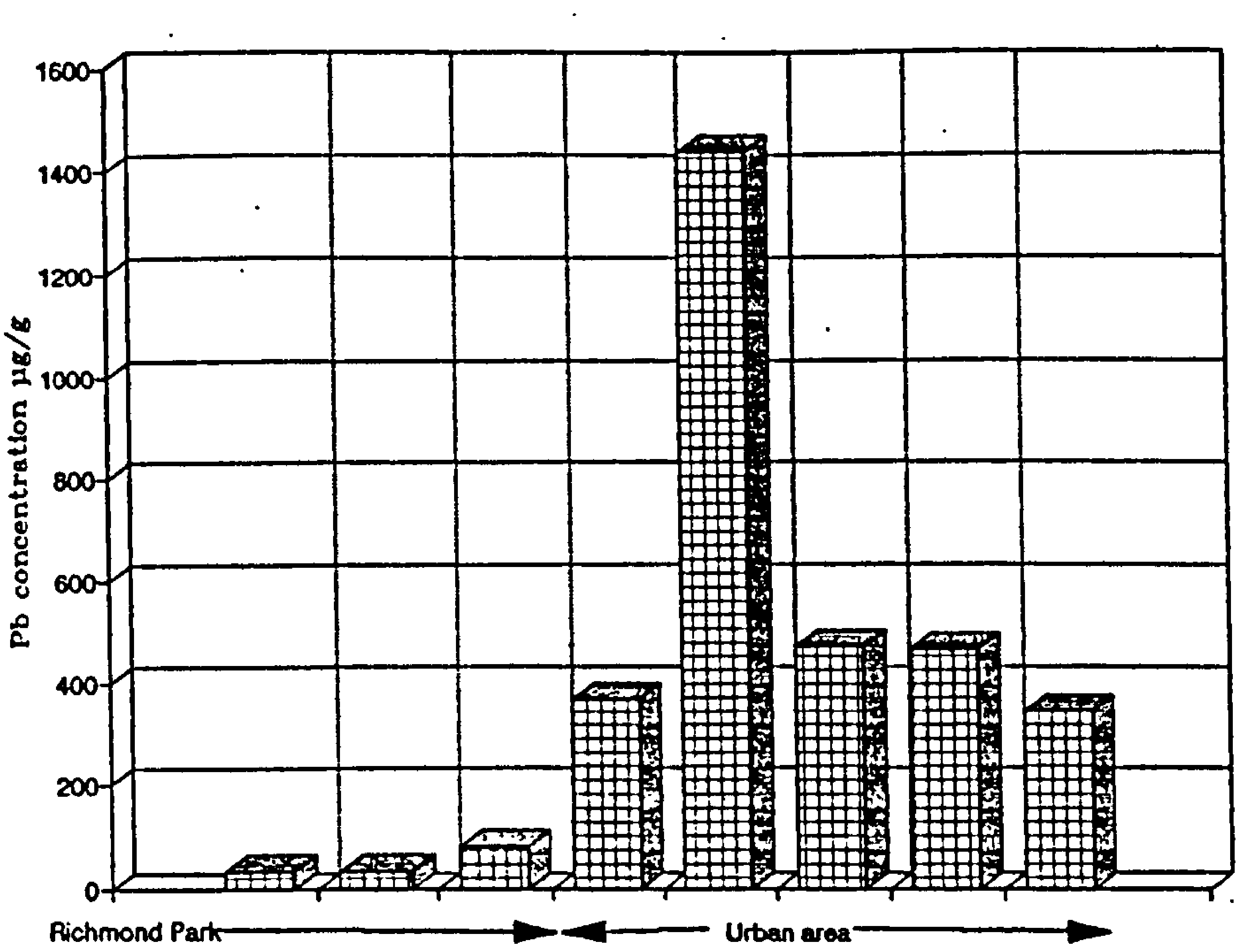


Fig. 6.1 Lead concentrations in topsoils (0-15cm) from Richmond taken across a transect from Richmond Park to Kew (see Supp. Fig. 6a)

works were located in this area close to the Thames until the early part of this century (see Plate 6.1 and Supp. Fig. 6c), whilst a gasworks is currently in operation. These may account for the high concentrations of Pb here. Sludge from the works may have been applied to the soils, and the high metal content of sewage sludge is well documented (Alloway, 1990b). Emissions from engineering works are another potential source of metals. No samples were taken on the site of the gasworks.

In general, Pb concentrations in the 90th-97th percentile range (a total concentration range of 343-1094 μg/g), occur in urban garden soils close to major roads. This pattern extends almost continually from the east to the west of the borough, particularly in the north-east and north west of Richmond. In addition to emissions from traffic, sources of Pb in urban gardens include; the flaking of lead-rich paint, and the disposal of fossil fuel residues (Thornton, 1990; see Tables 3.1 and 3.5 and Appendix 3). The urbanised area in Ham is an exception with concentrations of Pb falling within the 50th percentile range (76-185 μg/g). This may be as a consequence of the housing here being the most recent in the borough (< 50 years old). The influence of house-age on the Pb content of garden soils is discussed in 7.3.2.

Lead concentrations in the 95th percentile range, (582-855 μg/g) are observed in south-west of the borough in Hampton. This is a residential area, but Supp. Fig. 6c illustrates that high concentrations of Pb occur near the sites previously occupied by a sewage works and a water works. Pb concentrations in the 95th percentile range also occur close to the waterworks in the extreme south-west of the borough (see Plate 6.1 and Supp. Fig. 6c).

6.2.3 Concentrations of Zinc in Richmond topsoils (0-15cm)

In general, the distribution of Zn shown in Plate 6.2 is very similar to that of Pb. Zinc concentrations are generally lower than those of Pb as can be seen from a comparison of the percentiles (see Plates 6.1 and 6.2 respectively). The biggest difference is for the > 97th percentiles, which are > 593 μg/g for Zn compared to > 1094 μg/g for Pb. The concentration range of Zn is high with a 97th percentile concentration approximately 10

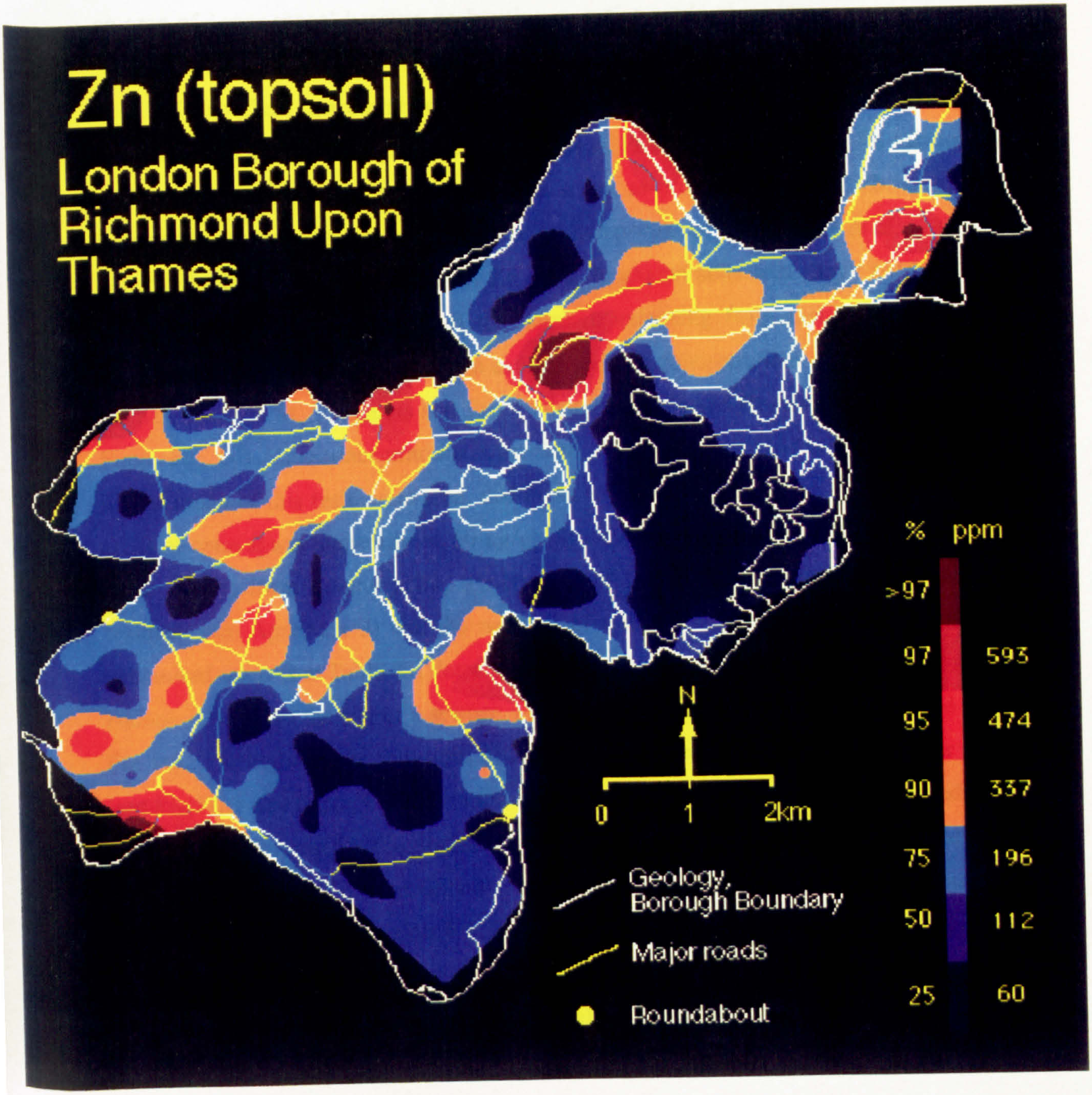

Zn (topsoil)
London Borough of Richmond Upon Thames
% ppm
>97
97 593
95 474
90 337
75 196
50 112
25 60
N
0 1 2km
Geology, Borough Boundary
Major roads
Roundabout

Plate 6.2

times higher than the 25th percentile (593 μg/g and 60 μg/g, respectively). The 25th percentile range for Zn ($\leq$ 60 μg/g), as for Pb ($\leq$ 75 μg/g), is observed in three areas of open space: most of Richmond Park and small parts of Bushy Park and Kew Gardens (see Supp. Fig. 6d). Although Kew Gardens is intensively cultivated, it is referred to as an area of `open space' because no housing or major roads occur there.

The highest concentrations of Zn which exceed the 97th percentile ($>$ 593 μg/g) correspond well with the highest concentrations of Pb. However, for Zn, the relationship with roundabouts and major road junctions is not as pronounced as for Pb. Lead is an important constituent of petrol, whilst Zn is a component of tyres (Ward *et al.*, 1977). In general the highest concentrations of Zn occur in garden soils near major roads. This is seen, particularly, in the north of the borough extending from east to west. A large anomaly occurs near Richmond town centre, with Zn concentrations $>$ 593 μg/g also in Barnes, between St. Margarets and Twickenham, Whitton and Hampton (see Plate 6.2 and Supp. Fig. 6d). Zinc concentrations in the 90th percentile range (197-337 μg/g) also occur across much of this residential area, and these values are significantly higher than for the areas of open space (generally $<$ 60 μg/g). Sources of Zn in urban gardens are similar to those of Pb; from flaking paint, the burning of fossil fuel, the disposal of fossil fuel residues (see Appendix 3) and the wearing of tyres. Zinc is also used in a number of galvanised ware (see Table 3.1 for a summary of the uses of Zn). The residential area in Hampton was also the site of a sewage works and a water works (see Plate 6.2 and Supp. Fig 1c). The highest concentrations of Zn ($>$ 593 μg/g) also occur near the water works (see Plate 6.2 and Supp. Fig. 6c) in the extreme south-west of the borough. Past industrial land-use may account for Zn concentrations in the 90th-97th percentile range in Teddington (351-593 μg/g) with Zn commonly associated with iron works, used as a coating on many iron based products (see section 4.6.3). Supplementary Fig. 6c shows the proximity of an engineering works and a sewage works to this anomaly, which may also account for the high concentrations of Zn here. The Zn anomaly is not as large, spatially, as that observed for Pb.

6.2.4 Concentrations of Cu in Richmond topsoils (0-15cm)

The distribution of Cu in topsoils from Richmond is shown in Plate 6.3. The concentration range for Cu in topsoils is not as large as for Pb. The 97th percentile concentration is approximately ten times higher than the 25th percentile concentration (162 μg/g and 17 μg/g, respectively). The lowest concentrations, ≤ 17 μg/g (in the 25th percentile range), are generally located in the areas of open space, particularly Richmond Park, but also the interiors of Hampton Court/Bushy Park and Kew Gardens (see Plate 6.3 and Supp. Fig. 6d). In Bushy Park, Cu concentrations are in the 50th percentile range in places, (18-31 μg/g). As with Pb and Zn, the highest concentrations of Cu are observed in urbanised locations. Copper concentrations which exceed the 97th percentile (> 162 μg/g) are observed near Richmond town centre, in Barnes, between St. Margarets and Twickenham, east of Bushy Park and in Hampton. The area east of Bushy Park is near the site of an old sewage works (see Plate 6.3 and Supp. Fig. 6c) and metals are widely reported to be present in elevated concentrations in sewage sludge (Alloway, 1990c).

In the urbanised area extending both east and west of the town centre, in general, Cu concentrations are in the 90th to the 97th percentile range (a total range of 55-162 μg/g). In contrast to Pb and Zn, high concentrations of Cu are not widespread in the urban areas of Hampton which suggests a specific source such as flaking paint for Pb and Zn in these areas. In the extreme south-west of the borough Cu concentrations exceed the 97th percentile (> 162 μg/g), near the water works (see Plate 6.3 and Supp. Fig. 6c). Past industrial activity may account for Cu concentrations which exceed the 97th percentile (> 162 μg/g) in the Teddington area. This area is close to sites of past industrial activity (see Plate 6.3 and Supp. Figs. 6c and 6d). Other potential sources of Cu include the burning of fossil fuel and the disposal of residues from this process (see Table 3.1 for a summary of the uses of Cu).

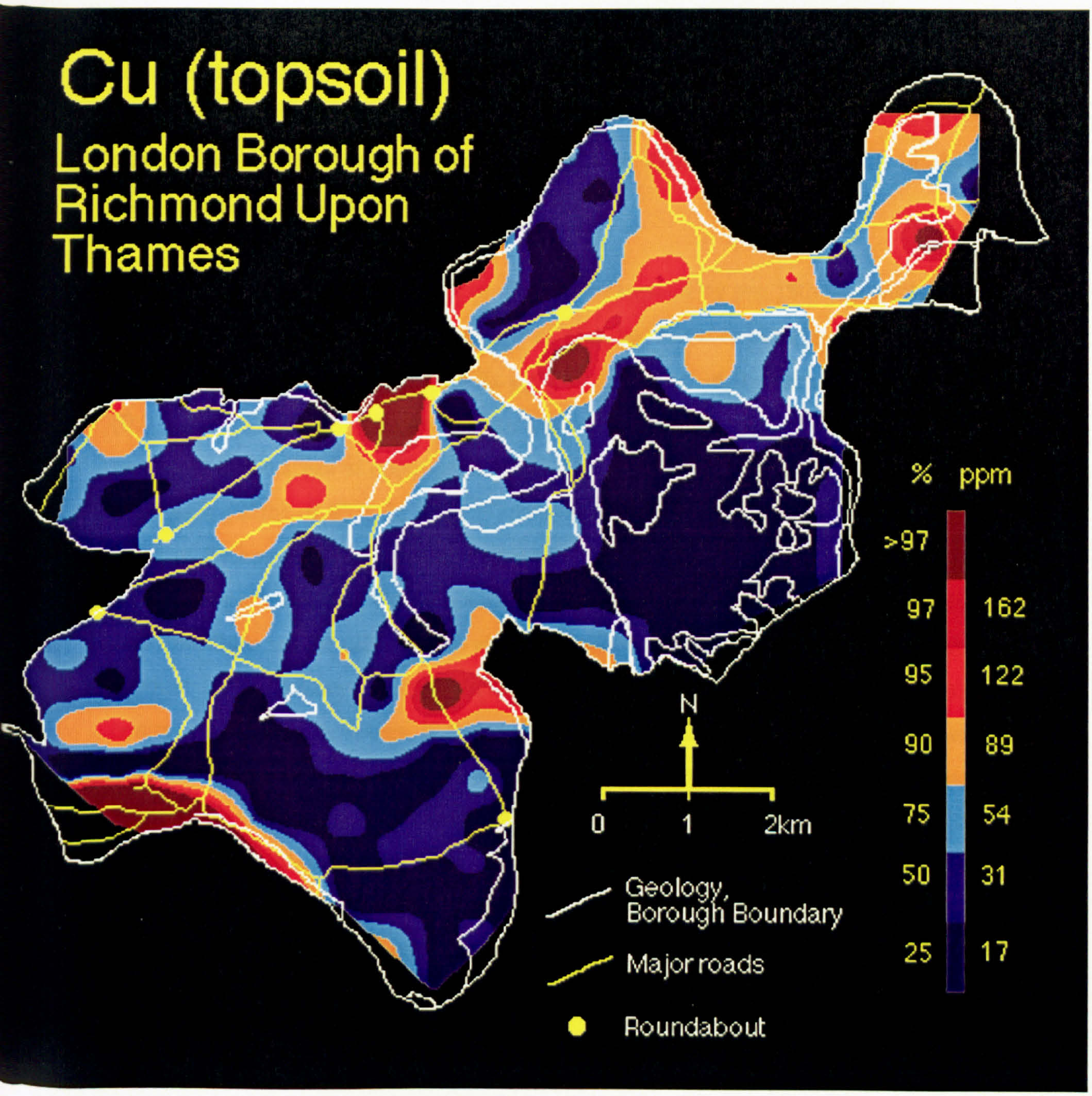

Cu (topsoil)
London Borough of Richmond Upon Thames
% ppm
>97
97 162
95 122
90 89
75 54
50 31
25 17
N
0
1
2km
Geology, Borough Boundary
Major roads
Roundabout

Plate 6.3

6.2.5 Concentrations of cadmium in Richmond topsoils (0-15cm)

Many of the soil samples from Richmond have concentrations of Cd below the analytical detection limit of 0.2 μg/g for the ICP-AES, and the gridding technique used requires these samples to be ascribed a value. This value was set at 0.1 μg/g; half the detection limit. Although this approach generates geochemical maps in which 75% of the samples are below instrument detection limit, it allows an investigation of the spatial distribution of Cd in Richmond.

The lowest concentrations of Cd are represented by the 75th percentile range (see Plate 6.4), illustrating the large number of samples below or close to detection limit. The 75th percentile concentration of 0.24 μg/g is very close to the instrument detection limit (0.2 μg/g). The lowest percentile class occurs throughout most of Richmond, and is not restricted to the areas of open space. The higher percentiles of Cd which range from 0.53-0.92 μg/g (95th), 0.93-1.35 μg/g (97th) and > 1.35 μg/g (> 97th), occur in the urban areas of Richmond. These are located where peaks of Pb, Zn and Cu are found, although the higher percentiles of Cd do not extend across as large areas as the corresponding high concentrations for the other metals already discussed. Garden samples close to major roads account for the highest concentrations of Cd (> 1.35 μg/g). These occur near the town centre, further east in Barnes, between St. Margarets and Twickenham, in Petersham, near Whitton and Fulwell Park and in Hampton near the water works (see Plate 6.4 and Supp. Figs. 1c and 1d). Cadmium concentrations in the 97th percentile range (0.93-1.35 μg/g) occur in the residential areas west of Petersham and in Hampton close to the water works (see Plate 6.4 and Supp. Figs. 1c and 1d). A small Cd anomaly, in the 95th percentile range (0.53-0.92 μg/g), is observed close to the Thames in Teddington near the site of an old engineering works (see Plate 6.4 and Supp. Figs. 1c and 1d).

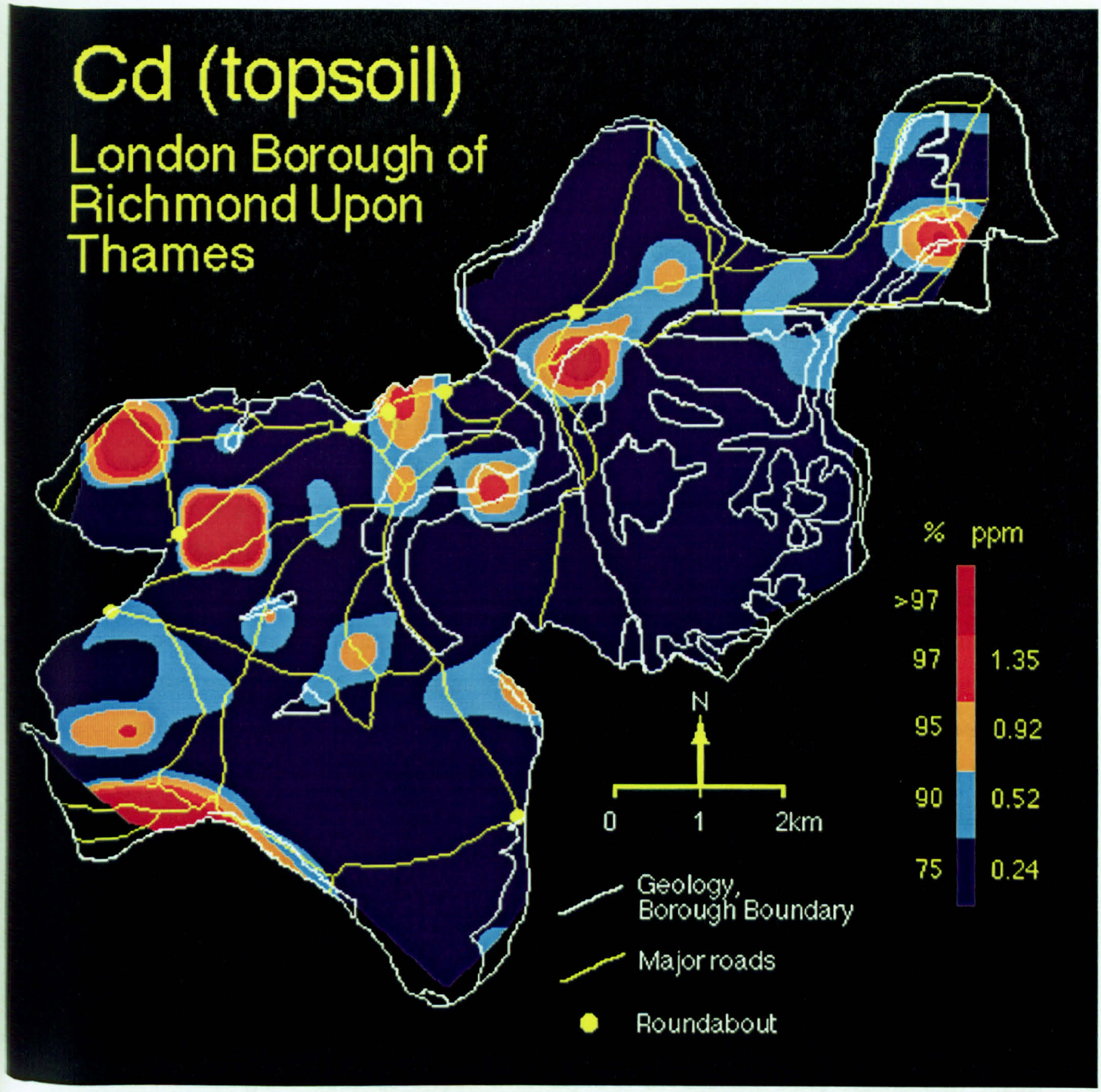

Cd (topsoil)
London Borough of Richmond Upon Thames
% ppm
>97
97
1.35
95
0.92
90
0.52
75
0.24
N
0
1
2km
Geology, Borough Boundary
Major roads
Roundabout

Plate 6.4

6.2.6 Concentrations of nickel in Richmond topsoils (0-15cm)

The distribution of Ni in Richmond topsoils is shown in Plate 6.5. The lowest percentile class is in the range ≤ 16.4 μg/g, and this is very similar to that of Cu which is in the range ≤ 17 μg/g. Nickel concentrations do not vary to the same extent as Pb, Zn and Cu with a 25th percentile less than 3 times the magnitude of the 25th percentile (16.4 μg/g and 40.1 μg/g, respectively). Large areas of Richmond Park and Bushy Park have Ni concentrations in the lowest percentile range (see Plate 6.5 and Supp. Fig 1d). In Hampton Court, however, Ni concentrations are generally in the 50th percentile range (16.5-21.1 μg/g) with a small area close to the Thames where Ni concentrations are in the 97th percentile range (36.3-40 μg/g). In Kew Gardens concentrations of Ni are generally higher than the 25th percentile range, with concentrations generally in the 75th percentile range (21.2-26.7 μg/g). A pattern of Ni enhancement is observed in urban areas of the borough. In the area near Richmond town centre, through to Mortlake and Barnes (see Plate 6.5 and Supp. Fig. 6d), Ni concentrations are in the 90th-95th percentile range (26.8-36.2 μg/g). This pattern is also observed between Twickenham and Petersham (see Plate 6.5 and Supp. Fig 6a). Nickel concentrations in the 90th and 97th percentile ranges (total range 26.8-40.1 μg/g) are also observed in Whitton in the west, and Hampton in the south (see Plate 6.5 and Supp. Fig. 6d). Concentrations of Ni exceeding the 97th percentile (> 40.1 μg/g) are observed in Barnes, Kew, between St. Margarets and Twickenham, and in Hampton and Teddington (see Plate 6.5 and Supp. Fig 6d). Several studies discussed in 3.4.6 reported an increase in Ni concentrations in roadside soils (Lagerwerff and Specht, 1970 and Ward, 1990a).

Urbanisation may not be the only factor influencing Ni concentrations in topsoils. Supplementary Fig. 6c shows that high concentrations of Ni occur close to the course of the Thames. This is observed in Barnes, Kew, Kew Gardens, Petersham, Strawberry Hill and Teddington. Soils developed over deposits of alluvium have significantly higher concentrations of Ni than soils overlying river terraces and London Clay (all $P < 0.001$). Nickel concentrations in the 90th-97th percentile range (26.8-40.1 μg/g), observed in Hampton, occur close to where a sewage works was located until 1945. Nickel concentrations which exceed the 97th percentile, (> 40.1 μg/g), are observed further south

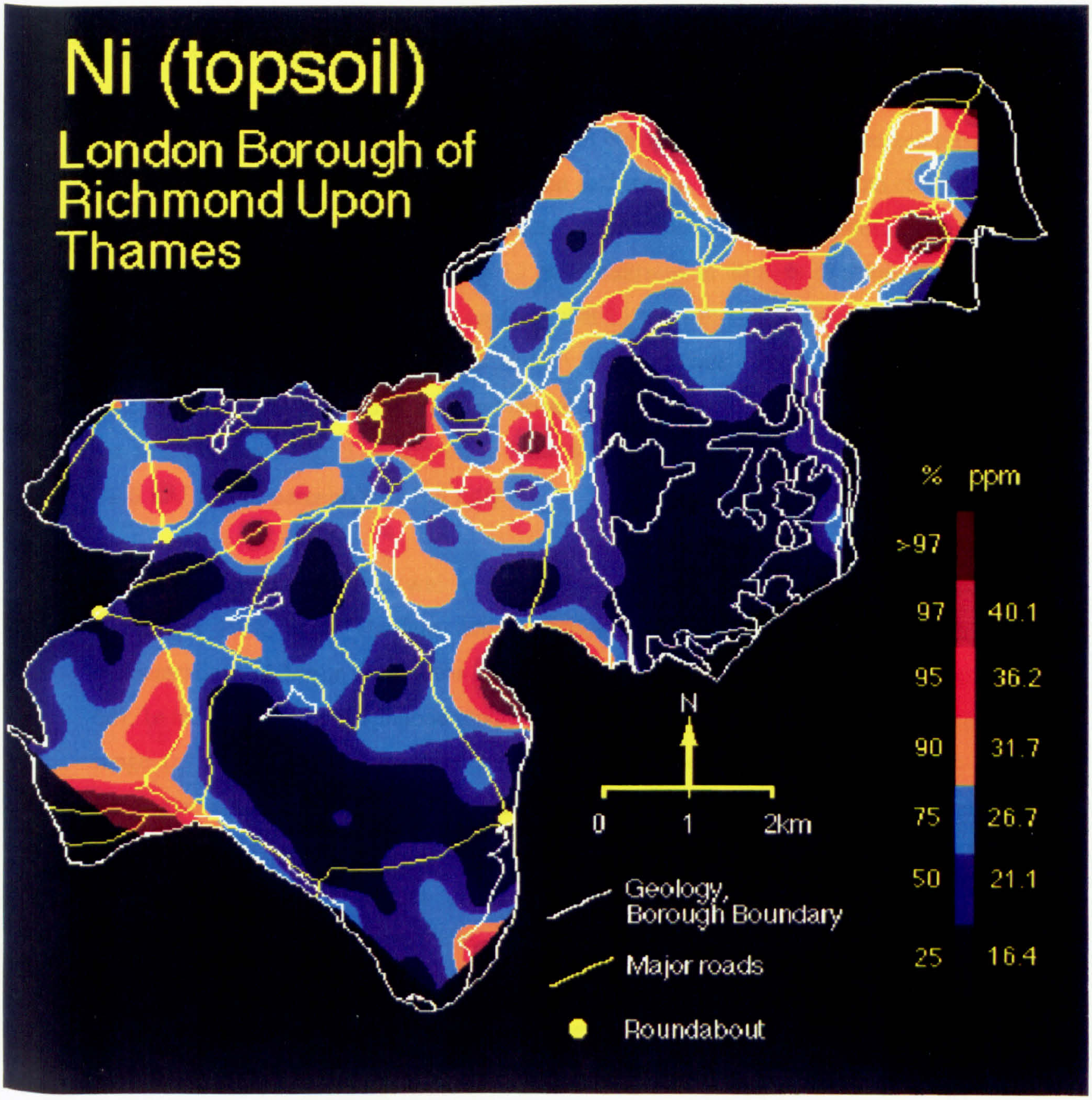

Ni (topsoil)
London Borough of Richmond Upon Thames
% ppm
>97
97 40.1
95 36.2
90 31.7
75 26.7
50 21.1
25 16.4
N
0 1 2km
Geology, Borough Boundary
Major roads
Roundabout

Plate 6.5

near the waterworks close to the Thames (see Plate 6.5 and Supp. Figs 6c and 6d). The Ni anomaly, > 40.1 μg/g, which occurs near the Thames in Teddington could also be as a result of an engineering works that was located here until the early part of this century (see Plate 6.5 and Supp. Figs. 6c and 6d).

6.2.7 Concentrations of lithium in Richmond topsoils (0-15cm)

Lithium is widely distributed throughout the earths crust, and is released relatively easily from primary minerals in oxidising and acid media. Incorporation into clay minerals occurs with some fixation by organic matter. Conditions of soil formation are generally the most important factor controlling Li concentrations in topsoils (Kabata-Pendias and Pendias, 1984). The same authors reported that Li concentrations were at a minimum in soils with a light sandy texture, particularly those derived from glacial drift. A large number of soils in Richmond have developed over glacial drift. The concentration range for this element is small, as shown in Plate 6.6, with a 97th percentile concentration of 21.6 and a 25th percentile of 8.3 μg/g).

Concentrations of Li which exceed the 97th percentile (> 21.6 μg/g) occur in Richmond Park, Kew Gardens and Hampton Court and these coincide with high concentrations of Mg in these areas of open space (see Plates 6.6 and 6.9 and Supp. Fig. 6d). In the area close to Richmond town centre, Li concentrations are in the 25th percentile range (≤ 8.3 μg/g). Lithium concentrations which exceed the 97th percentile (> 21.6 μg/g) are observed in Barnes, Petersham, between Twickenham and St. Margarets and Whitton (see Plate 6.6 and Supp. Fig. 6d). Some relatively high concentrations of Li are observed close to the Thames in Kew, Kew Gardens, Petersham, Strawberry Hill, Teddington and Hampton (see Plate 6.6 and Supp. Fig. 6d). Lithium concentrations are generally in the 90th-97th percentile range in these areas (13.8-21.6 μg/g). However, soils overlying deposits of alluvium do not have significantly higher concentrations of Li than soils overlying river terraces and London Clay (all $P > 0.05$). In general, the distribution of Li is similar to that of Mg, Ca and Sr (see Plates 6.9, 6.10 and 6.11, respectively). Davey and Wheeler (1980) report the strong association of exchangeable Li with Ca and Mg.

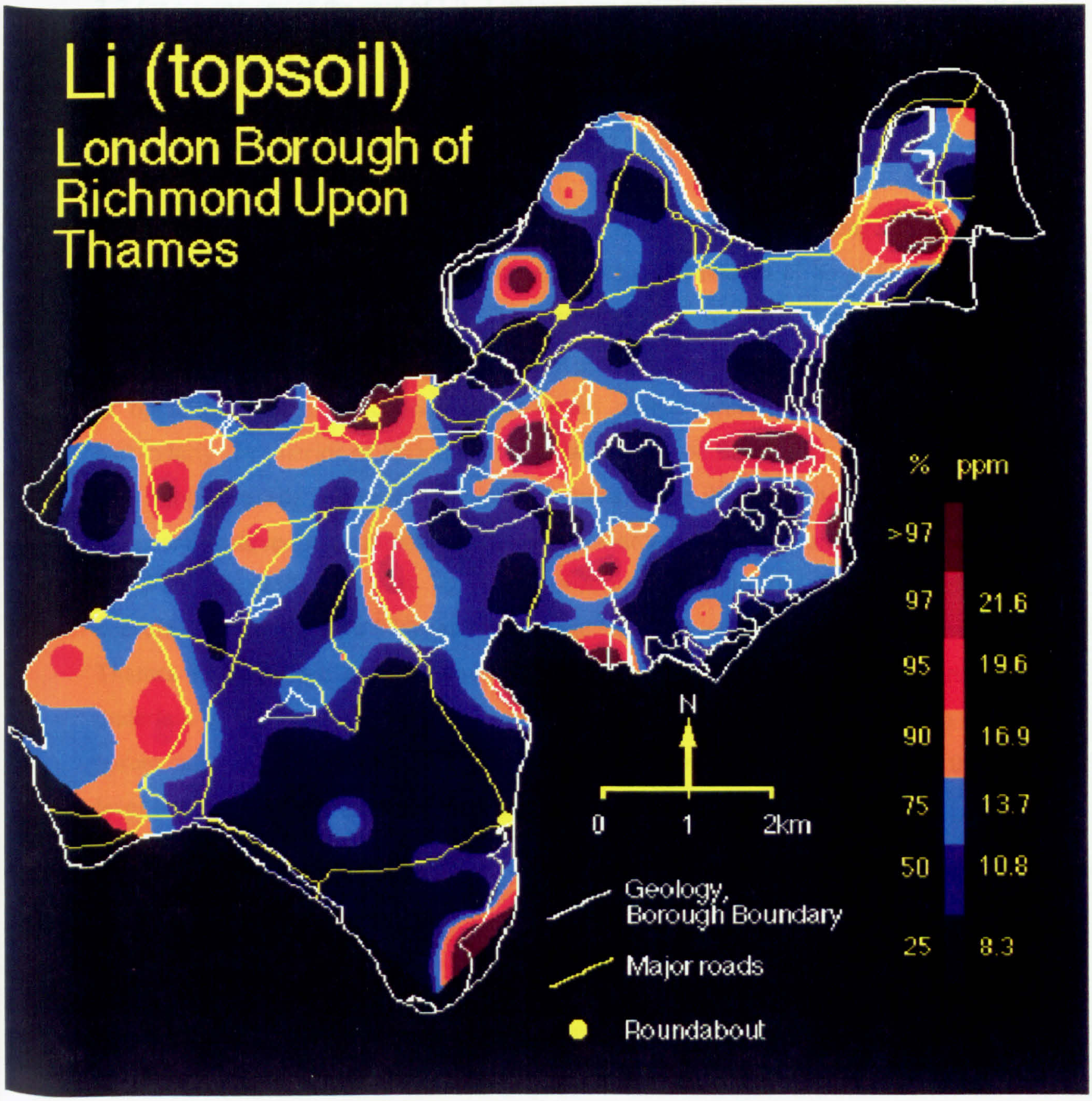

Li (topsoil)
London Borough of Richmond Upon Thames
% ppm
>97
97 21.6
95 19.6
90 16.9
75 13.7
50 10.8
25 8.3
N
0 1 2km
Geology, Borough Boundary
Major roads
Roundabout

Plate 6.6

This pattern close to the Thames in Teddington is also located near to a site of past industrial activity (see Plate 6.6 and Supp. Fig. 6c). In Hampton, relatively high concentrations of Li occur in the residential area, an area which used to have an engineering works and a sewage works (see Plate 6.6 and Supp. Figs. 6c and 6d; see Table 3.2 for a summary of the uses of Li). Lithium concentrations are generally in the 90th-95th percentile range in these areas (13.8-19.6 μg/g).

6.2.8 Concentrations of sodium in Richmond topsoils (0-15cm)

Sodium is naturally abundant and has a large concentration range in Richmond topsoils, as seen in Plate 6.7. The 25th percentile concentration of 83 μg/g compares to 604 μg/g for the 97th percentile. The distribution of Na in Richmond seems to be influenced by both anthropogenic activity and geological/pedogenic processes. Large areas of open space have Na concentrations in the lowest percentile range (≤ 83 μg/g), particularly the interior of Richmond Park, large areas of Bushy Park and Kew Gardens (see Supp. Fig 1d). However, Na concentrations in the 90th percentile range (222-321 μg/g) are observed in Hampton Court. In Kew Gardens Na concentrations which exceed the 97th percentile (> 604 μg/g) are observed close to the Thames, whilst Na concentrations in the 90th-97th percentile range (222-604 μg/g) are also observed near the Thames in Petersham and Teddington (see Supp. Fig. 6d). Most of these areas are underlain by alluvium (see Plate 6.7 and Supp. Fig. 6b) and soils which develop on this parent material have significantly higher concentrations of Na than soils overlying the high level terraces, the youngest river terraces and London Clay (all $P < 0.001$).

In Teddington Na concentrations in the 90th-97th percentile range (222-604 μg/g) occur near to where an engineering and sewage works were located (see Plate 6.7 and Supp. Figs. 6c and 6d). Although Na concentrations in the 25th percentile range occur near Richmond town centre, much of the urban area further east in Mortlake and Barnes have concentrations of Na which are generally in the 90th percentile range (222-321 μg/g - see Plate 6.7 and Supp. Fig. 6d), but higher in places. In St. Margarets and Twickenham, Na concentrations which exceed the 97th percentile (> 604 μg/g) and which are in the 97th percentile range (463-604 μg/g) are observed, with Na concentrations > 604 μg/g

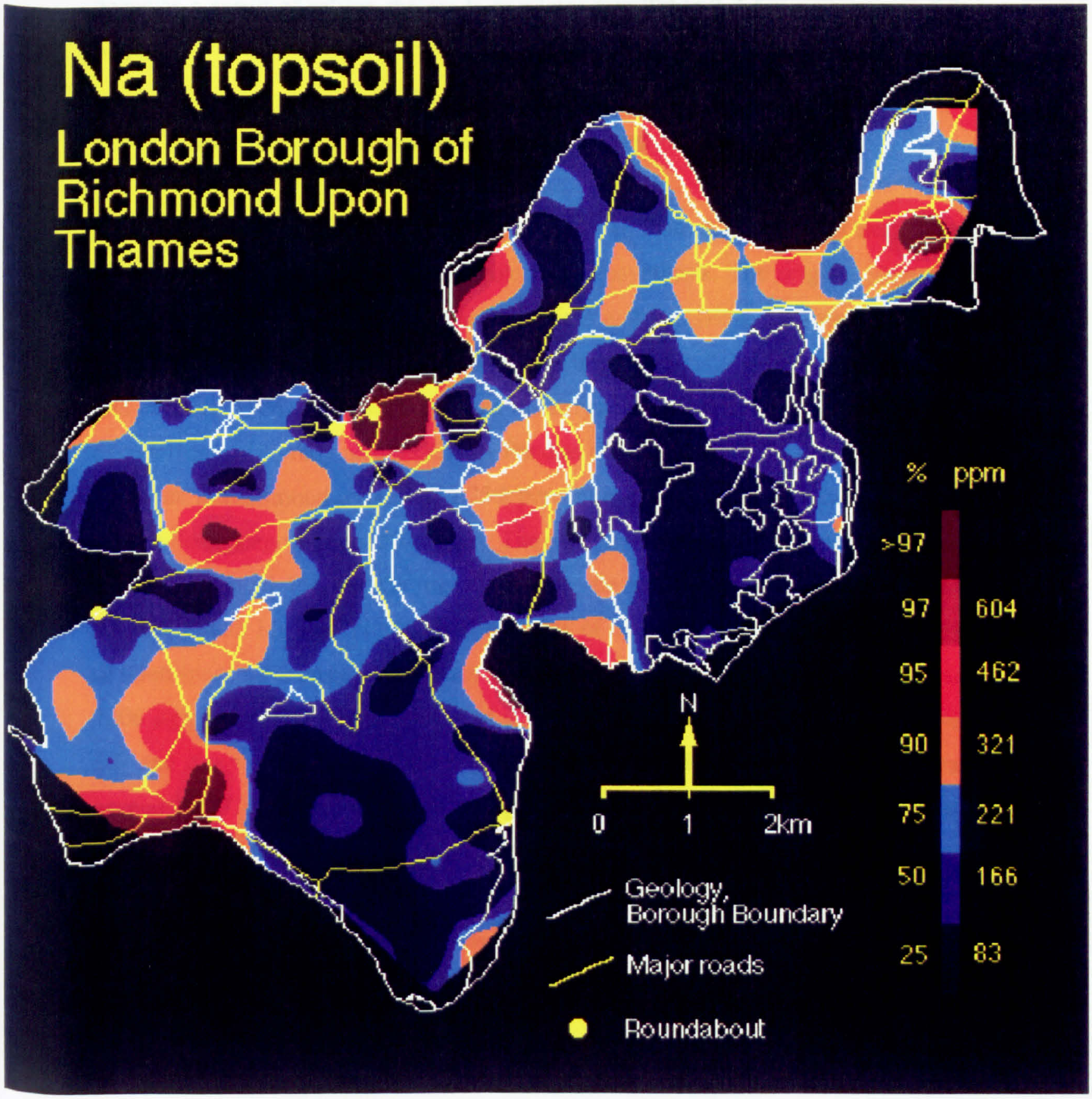

Na (topsoil)
London Borough of Richmond Upon Thames
% ppm
>97
97 604
95 462
90 321
75 221
50 166
25 83
N
0 1 2km
Geology, Borough Boundary
Major roads
Roundabout

Plate 6.7

close to the Thames near the contemporary water works (see Plate 6.7 and Supp. Fig. 6d). In the residential area of Hampton, Na concentrations in the 76th-90th percentile range (222-321 μg/g) occur near areas of past industrial activity (see Plate 6.7 and Supp. Figs. 6c and 6d). High concentrations of Na in the urbanised environment of Richmond may occur as a result of salting the roads in winter (see Table 3.2 for a summary of the uses of Na).

6.2.9 Concentrations of potassium in Richmond topsoils (0-15cm)

Potassium is naturally abundant in soils (see Plate 6.8), being an essential element for plants and playing an important role in photosynthesis. The original sources of K in the soil are the primary minerals such as micas and potassium feldspars. These minerals release the K on weathering, which with time becomes available to plants (Kabata-Pendias and Pendias, 1984). Potassium is found in fairly high concentrations in most mineral soils, except those of a sandy nature (Kabata-Pendias and Pendias, 1984). Potassium is naturally abundant in Richmond soils, with a 25th percentile concentration of 2206 μg/g, and a 97th percentile concentration of 5039 μg/g. The distribution of K in Richmond is similar to that of Al (see Plate 6.13), and the use of multi-variate statistics shows an association of K and Al, along with Mg and Ti in soils from areas of open space (see Appendix 3). The areas of open space have large areas where K concentrations are in the 25th percentile range ($\leq$ 2206 μg/g), especially in the centre of Richmond Park and most of Bushy Park (see Plate 6.8 and Supp. Fig. 6d). In the southern extreme of Hampton Court K concentrations exceed the 97th percentile ($>$ 5039 μg/g), and these soils overlie alluvium (see Supp. Figs. 6b and 6d). Relatively high concentrations of K are observed in a number of locations near the Thames, in Kew, Kew Gardens, Petersham and Strawberry Hill (see Plate 6.8 and Supp. Fig. 6d). However, soils overlying alluvium do not have significantly higher concentrations of K than soils overlying river terraces and London Clay (all $P > 0.05$).

In Petersham and Kew, K concentrations are in the 90th percentile range (3340-3995 μg/g), whilst in Kew Gardens, Strawberry Hill and Hampton Court K concentrations exceed the 97th percentile (5039 μg/g). Potassium concentrations in the 90th percentile

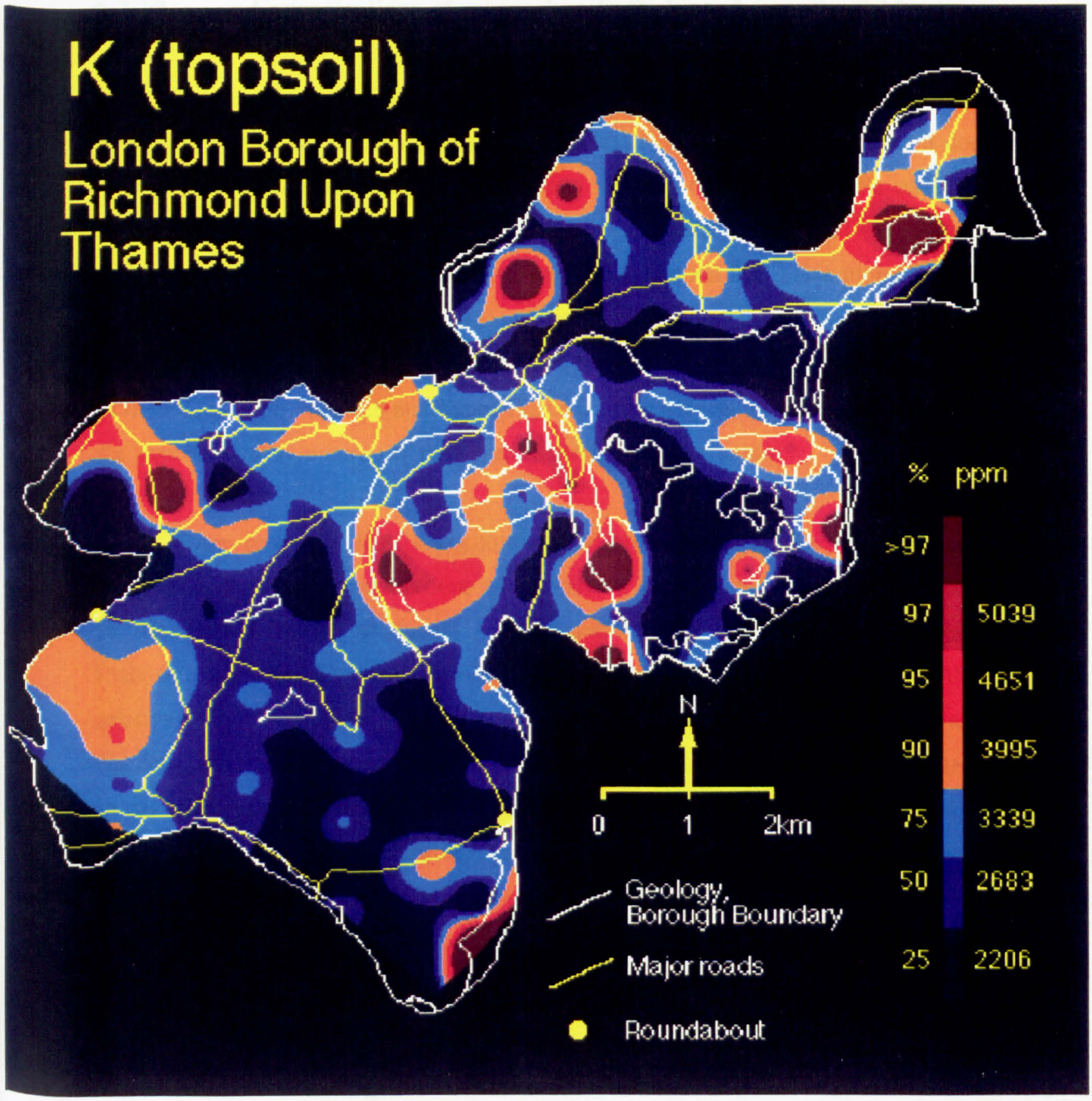

K (topsoil)
London Borough of Richmond Upon Thames
% ppm
>97
97 5039
95 4651
90 3995
75 3339
50 2683
25 2206
N
0 1 2km
Geology, Borough Boundary
Major roads
Roundabout

Plate 6.8

range (3340-3995 μg/g) are observed in Hampton, a residential area and site of past industrial activity (see Plate 6.8 and Supp. Figs. 6c and 6d). Fertilisers may be a source of K to garden soils (see Table 3.2).

6.2.10 Concentrations of magnesium in Richmond topsoils (0-15cm)

The distribution of Mg shown in Plate 6.9 is not strongly linked to land-use. Mg is naturally abundant in soils (Kabata-Pendias and Pendias, 1984). Magnesium does not have a large concentration range in Richmond topsoils; the 97th percentile concentration is less than 3 times greater than the 25th percentile concentration (1314 μg/g and 3364 μg/g, respectively). Although quite large parts of Richmond Park, Hampton Court, Bushy Park and Kew Gardens have concentrations of Mg in the 25th percentile range, concentrations of Mg which exceed the 97th percentile (> 3364 μg/g) are also observed in these areas (see Plate 6.9 and Supp. Fig. 6d). This may result from natural variation of the geochemical signatures of the parent materials in these areas.

Some relatively high concentrations of Mg are seen in the urbanised areas of Richmond, with Mg concentrations which exceed the 97th percentile (> 3364 μg/g) in Barnes, Petersham, St. Margarets, Whitton and between Strawberry hill and Ham (see Plate 6.9 and Supp. Fig. 6d; see Table 3.2 for a summary of the uses of Mg). Although relatively high concentrations of Mg are observed close to the Thames in Kew, Kew Gardens, Petersham, Strawberry hill and the southern part of Hampton Court, generally in the 90th percentile range and higher (> 1946 μg/g), soils overlying alluvium do not have significantly higher concentrations of Mg than soils overlying river terraces and London Clay (all $P > 0.05$). Multi-variate statistics show a grouping of Mg element with K, Al and Ti in soils from areas of open space (see Appendix 3), which suggests a strong influence from geological and pedogenic processes.

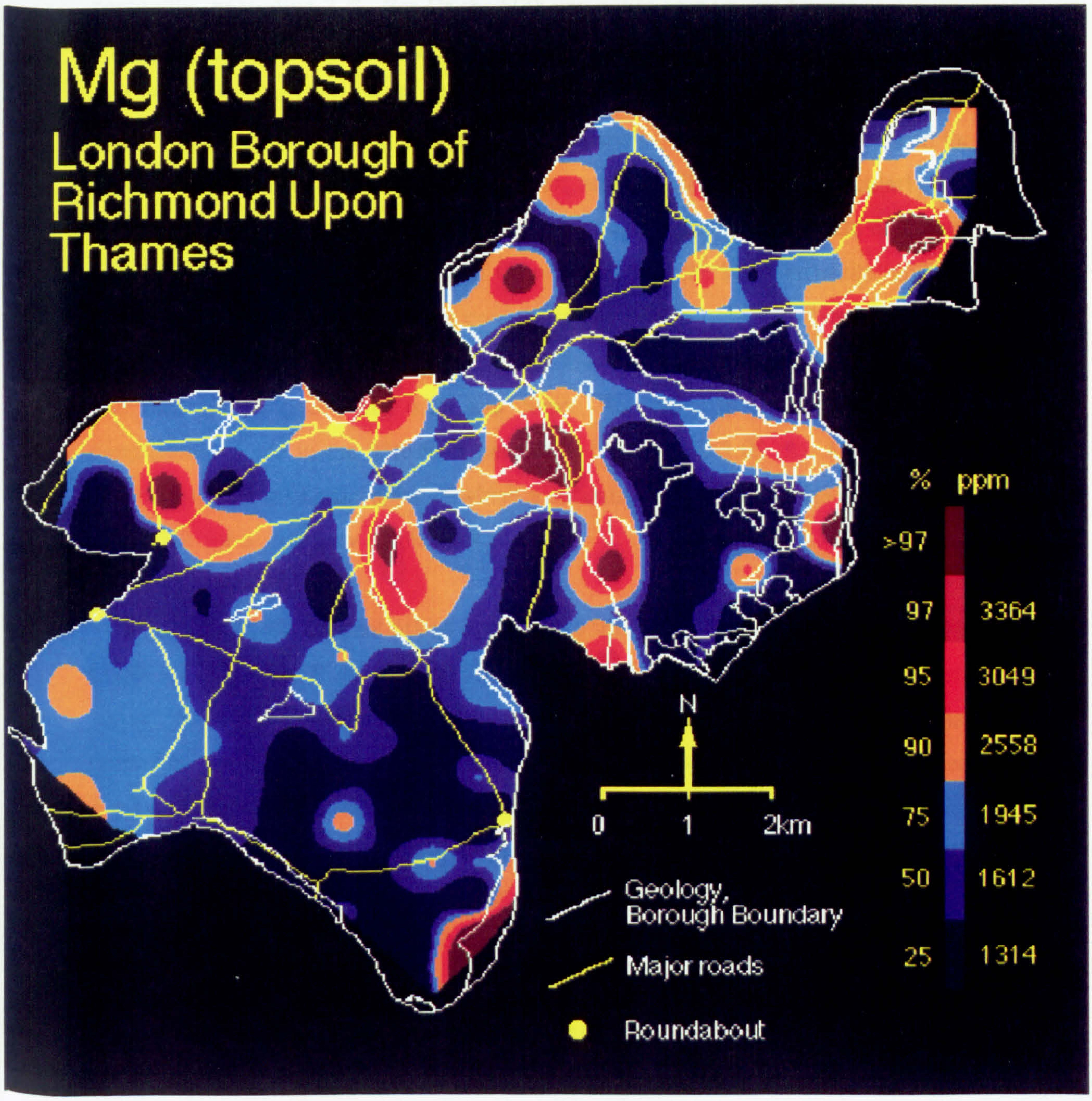

Mg (topsoil)
London Borough of Richmond Upon Thames
% ppm
>97
97 3364
95 3049
90 2558
75 1945
50 1612
25 1314
N
0 1 2km
Geology, Borough Boundary
Major roads
Roundabout

Plate 6.9

6.2.11 Concentrations of calcium in Richmond topsoils (0-15cm)

The distribution of Ca in Richmond topsoils is shown in Plate 6.10. Calcium is naturally abundant in soils, as illustrated by a 50th percentile of 4152 μg/g, and a 97th percentile, exceeding 2 %. For Ca the 50th percentile range is the lowest percentile class, compared to the 25th percentile range for most other elements. Table 5.9 shows that the sampling error for Ca exceeds 20 % (22.38 %) which means that a spatial interpretation needs to be undertaken with caution. Plate 6.8 shows that Ca concentrations in the 50th percentile range occur in topsoils in urban areas of Richmond, particularly north of Richmond Park and much of the west of the borough in general (see Plate 6.10 and Supp. Fig. 6d). However, concentrations of Ca which exceed the 50th percentile range are also observed in urban areas, with Ca concentrations generally in the 75th percentile range (4153-7513 μg/g) observed near Richmond town centre, and extending east to Mortlake and East Sheen (see Plate 6.10 and Supp. Fig. 6d). In Barnes, most of the Ca concentrations are in the 95th-97th percentile range (1.30-2.05 %). Calcium is used in several building materials, some of which was common in samples from urban gardens (see Table 3.2 for a summary of the uses of Ca).

In Kew, Ca concentrations are in the 95th percentile range close to the Thames, (1.30-1.77 % - see Plate 6.10 and Supp. Fig. 6d). Deposits of alluvium may strongly influence the high concentrations of Ca which occur close to the Thames in Petersham and extending south to Strawberry Hill, and in the southern part of Hampton Court (see Plate 6.10 and Supp. Figs. 6c and 6d). Soils overlying alluvium have significantly higher concentrations of Ca than soils overlying London Clay and the river terraces (all $P > 0.001$). Calcium concentrations are generally in the 95th-97th percentile range in these areas (1.30-2.05 %). These locations are also urbanised, making it difficult to attribute the high concentrations of Ca to anthropogenic or geological/pedogenic processes. The large Ca anomaly in Bushy Park (see Plate 6.10 and Supp. Fig. 6c) is probably a result of anthropogenic additions of Ca. This anomaly overlies the youngest river terraces (see Plate 6.10 and Supp. Fig. 6b) which do not have uniformly high concentrations of Ca, and which are not reported to be high in calcareous materials such as shells (BGS, 1981).

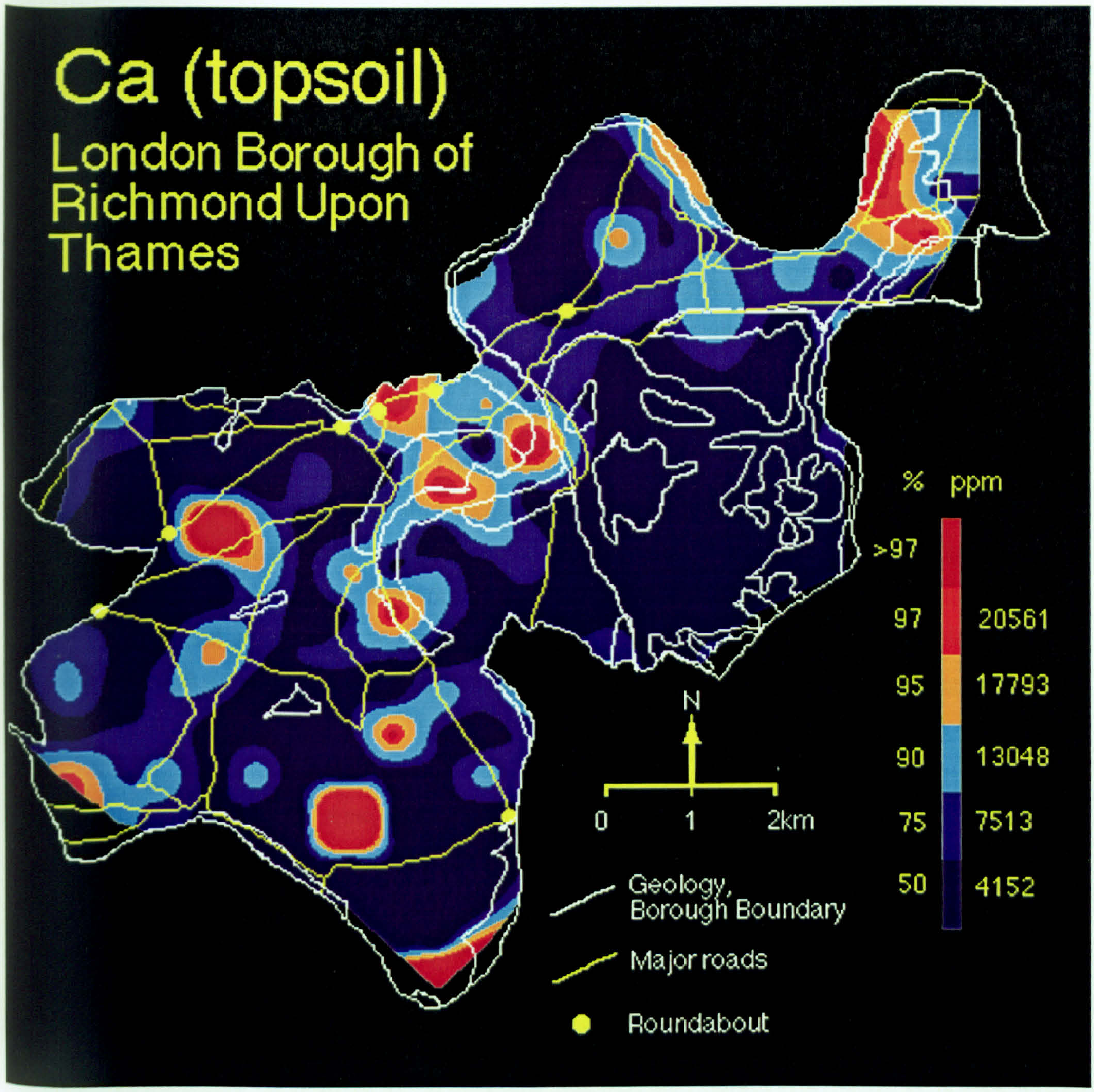

Ca (topsoil)
London Borough of Richmond Upon Thames
% ppm
>97
97 20561
95 17793
90 13048
75 7513
50 4152
N
0 1 2km
Geology, Borough Boundary
Major roads
Roundabout

Plate 6.10

6.2.12 Concentrations of strontium in Richmond topsoils (0-15cm)

Strontium is geochemically very similar to Ca and hence often associated with Ca, and to a lesser extent Mg, in soils. The ratio of Sr to Ca is also relatively stable in the biosphere and can be used to identify any increase in Sr concentrations (Kabata-Pendias and Pendias, 1984). The distribution of Sr is shown in Plate 6.11. Strontium concentrations do not vary greatly, with a 97th percentile concentration approximately 4 times the magnitude of the 97th percentile concentration (19.4 μg/g and 80.2 μg/g, respectively). The distribution of Sr resembles that of Ca in several respects (multi-variate statistics show this association, see Appendix 3). The areas of open space have, in general, Sr concentrations in the lowest percentile range (≤ 19.4 μg/g). The specific anomalies of Sr observed in Bushy Park (overlying the youngest river terraces) and the southern section of Hampton Court (close to deposits of alluvium) are also observed for Ca (see Plates 6.10 and 6.11 and Supp. Fig. 6d). The highest concentrations of Sr are, as with Ca, observed in urbanised areas. Strontium concentrations which exceed the 97th percentile (> 80.2 μg/g) occur in Kew, Barnes, between St. Margarets and Twickenham and in Hampton (see Plate 6.11 and Supp. Fig. 6d). Strontium concentrations are relatively high in the residential areas of St. Margarets through to Fulwell Park (in the 90th percentile range; 43.5-58.5 μg/g), and particularly in Hampton (generally in the 95th percentile range; 58.6-71.3 μg/g).

As with Ca some of the high concentrations of Sr could be as a result of alluvial deposits from the Thames which have significantly higher concentrations of metallic elements such as Sr than soils overlying river terraces and London Clay (all $P < 0.001$). This is observed close to the river, often in residential areas, in north Barnes, Kew, Petersham, Strawberry Hill and Hampton Court (Sr concentrations are generally > 43.5 μg/g - see Plate 6.11 and Supp. Fig. 6d). The high concentrations of Sr close to the Thames in Teddington overly deposits of alluvium, and occur close to where an engineering works and sewage works were located (see Plate 6.11 and Supp. Figs. 6c and 6d - see Table 3.2 for a summary of the uses of Sr).

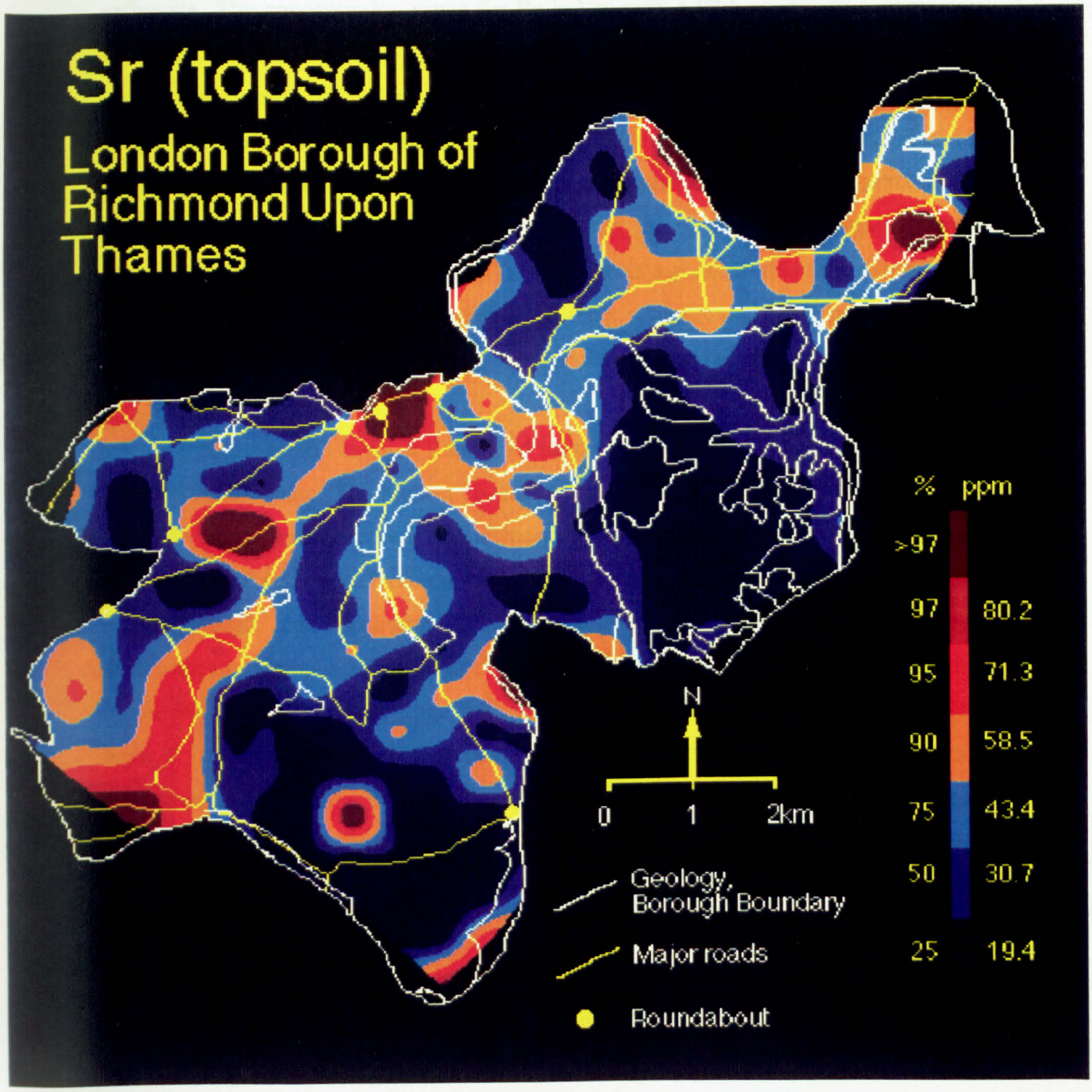

Sr (topsoil)
London Borough of Richmond Upon Thames
% ppm
>97
97 80.2
95 71.3
90 58.5
75 43.4
50 30.7
25 19.4
N
0 1 2km
Geology, Borough Boundary
Major roads
Roundabout

Plate 6.11

6.2.13 Concentrations of barium in Richmond topsoils (0-15cm)

The distribution of Ba in Richmond topsoils is shown in Plate 6.12. The distribution is very similar to that of Pb, and Zn in particular, suggesting a strong anthropogenic influence. The concentration range for Ba is low with a 97th percentile approximately 5 times the magnitude of the 25th percentile (390 μg/g and 82 μg/g, respectively). The lowest concentrations of Ba are generally observed in the three areas of open space; Richmond Park, Hampton Court/Bushy Park and Kew Gardens (see Plate 6.12 and Supp. Fig. 6d). The concentration of Ba in these areas is generally in the 25th percentile range (≤ 82 μg/g), although in parts of Kew Gardens in particular, Ba concentrations are in the 50th percentile range (83-135 μg/g). This may be as a result of alluvium deposits close to the Thames, and soils overlying these deposits have significantly higher concentrations of Ba than soils overlying London Clay and certain river terrace deposits (all $P < 0.001$).

The urbanised areas of Richmond have higher concentrations of Ba relative to the 25th percentile class. The highest concentrations of Ba, which exceed the 97th percentile (> 390 μg/g), are observed in Richmond town centre and further east in Kew, near Mortlake, in Barnes and Teddington (see Plate 6.12 and Supp. Fig. 6d). In the north-west of the borough, high concentrations are observed in the residential areas of St. Margarets, Twickenham, almost continually through to Hampton. Barium concentrations are generally in the 90th-95th percentile range in these areas (208-346 μg/g). Unlike Pb, Ba does not have a traffic source, therefore the higher concentrations of Ba in garden soils are attributed to the burning of fossil fuels (ICPS, 1990b), the disposal of fossil fuel residues, and the flaking of paint in which Ba is a filler and a pigment (ICPS, 1990b-see Table 3.2). Multi-variate statistics show the association of Ba with Cr, Zn and Pb, which the literature suggests is a paint or fossil fuel signature (see Tables 3.1 and 3.2 and Appendix 3). In Hampton and Teddington relatively high concentrations of Ba, in the 90th-95th percentile range in Hampton (208-346 μg/g) and exceeding the 97th percentile in Teddington (> 390 μg/g), occur near sites of past industrial activity. In Hampton relatively high Ba concentrations occur near the sites of an old sewage works and water works, and a contemporary water works close to the Thames (see Plate 6.12 and Supp. Figs. 6c and 6d). In Teddington a Ba anomaly, exceeding the 97th (> 390 μg/g) occurs near an area

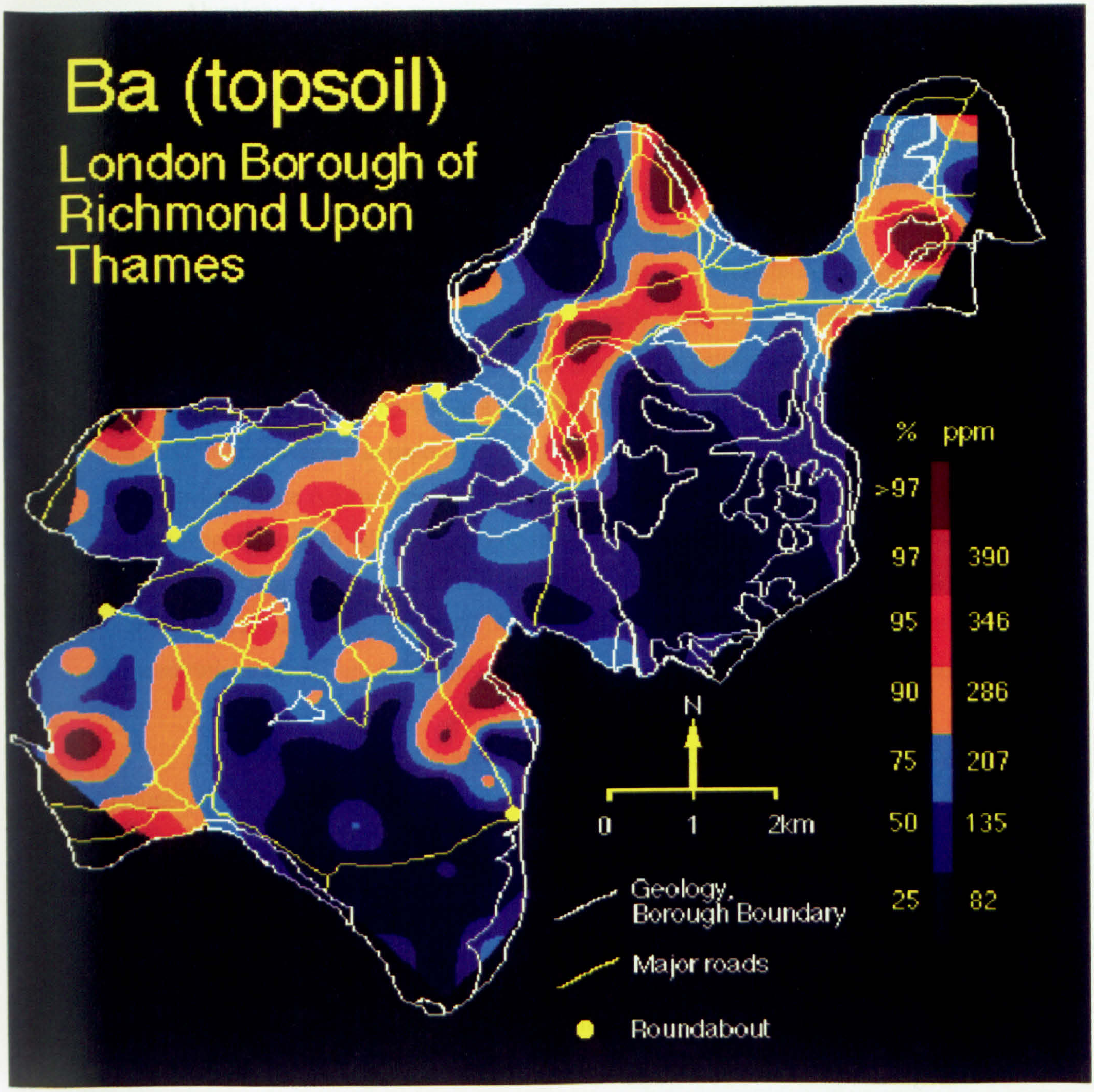

Ba (topsoil)
London Borough of Richmond Upon Thames
% ppm
>97
97 390
95 346
90 286
75 207
50 135
25 82
N
0 1 2km
Geology, Borough Boundary
Major roads
Roundabout

Plate 6.12

of past industrial activity (see Plate 6.12 and Supp. Fig. 6.c).

6.2.14 Concentrations of aluminium in Richmond topsoils (0-15cm)

Aluminium is a main constituent of the earths crust, and the vast majority of Al in soils comes from the weathering of the parent material. On weathering, a series of Al hydroxides are formed from the primary rock minerals and these become the structural components of clay minerals, and contribute greatly to a number of soil properties (Kabata-Pendias and Pendias, 1984). As for Ca, sampling error, 32 % in this case, exceeds the value recommended to allow a confident spatial interpretation (> 16 % - Ramsey *et al.*, 1993). This is a result of the low concentration of Al in Richmond topsoil. Plate 6.13 shows the distribution of Al in Richmond topsoils. The concentration range for Al is similar to that of Fe shown in Plate 6.19. The 25th percentile concentration for Al is approximately 1.22%, compared to a 99th percentile of 3.22 %. The 25th percentile range (≤ 1.22 %) is observed in parts of Bushy Park, Hampton Court, Richmond Park and Kew Gardens (see Plate 6.13 and Supp. Fig. 6d). However, the same areas of open space also have concentrations of Al which exceed the 99th percentile (> 3.22 %) in places. These Al concentrations which exceed the 99th percentile occur over a variety of parent material (see Plate 6.13 and Supp. Fig. 6b). None of these geological units have consistently high concentrations of Al, which suggests natural variation of the geochemical signature.

As with Ca, Sr, Mn, Co and Fe, high concentrations of Al are observed near the Thames in Kew, Kew Gardens, Petersham and Strawberry Hill (see Plate 6.13 and Supp. Fig. 6d). Aluminium concentrations in these areas are either generally in the 90th-97th percentile range or exceed the 99th percentile (ranging from 1.86-2.71 % and > 3.22 % respectively). However, soils overlying alluvium do not have significantly higher concentrations of Al than soils overlying river terraces and London Clay (all $P > 0.05$). Concentrations of Al in the 90th percentile range (1.86-2.2 %) occur close to the Thames in Teddington and in Hampton, sites of past/present industrial activity (see Plate 6.13 and Supp. Figs. 6c and 6d - see Table 3.2 for a summary of the uses of Al).

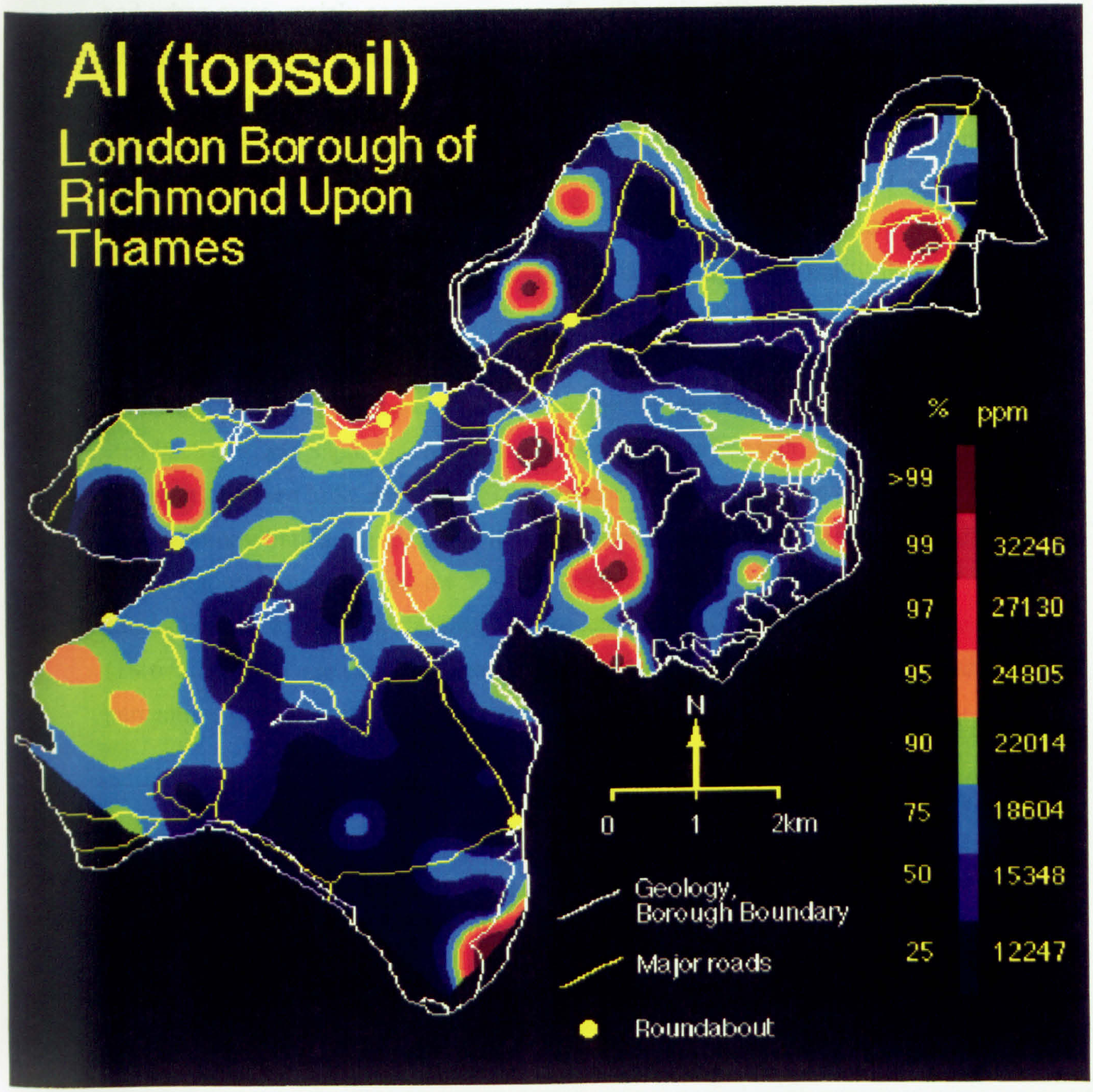

Al (topsoil)
London Borough of Richmond Upon Thames
%
ppm
>99
99
32246
97
27130
95
24805
90
22014
75
18604
50
15348
25
12247
N
0
1
2km
Geology, Borough Boundary
Major roads
Roundabout

Plate 6.13

6.2.15 Concentrations of lanthanum in Richmond topsoils (0-15cm)

Lanthanum is one of the rare earth elements, and Kabata-Pendias and Pendias (1984) report that elevated concentrations of La have been found in the air of industrial and urban areas, mainly as a consequence of coal burning. The sampling error for La in Richmond topsoils is high (> 24 % - see Table 5.9), due to the low concentration range for La. Any spatial interpretation therefore needs to be cautious. Plate 6.14 shows the distribution of La in topsoils from Richmond. The concentration range of this element is small. The 25th percentile concentration of 14.2 μg/g, compares with 21.7 μg/g for the 97th percentile. The lowest concentrations of La (≤ 14.2 μg/g) are observed mainly in areas of open space, particularly the interior of Richmond Park, Bushy Park and Kew Gardens (see Plate 6.14 and Supp. Fig. 6d). The highest concentrations of La are not always observed in residential areas. In the north-east of the borough, near Richmond town centre and Mortlake, La concentrations are in the 75th percentile range (16.5-18.5 μg/g - see Plate 6.14 and Supp. Fig. 6d). In the north-west of the borough, higher concentrations of La are observed in St. Margarets, Twickenham, Whitton and Hampton. In much of this area La concentrations are generally in the 90th percentile range (18.6-20 μg/g), although concentrations which exceed the 97th percentile, (> 21.7 μg/g), are observed in St. Margarets and Whitton. In Hampton, La concentrations in the 90th-97th percentile range (18.6-21.7 μg/g) are observed near a site of past industrial activity which has high percentiles for a suite of elements (see Plate 6.14 and Supp. Figs. 6c and 6d).

Relatively high concentrations of La are observed close to the Thames in Kew, Kew Gardens, Barnes, Petersham, Strawberry Hill and Hampton Court (see Plate 6.14 and Supp. Fig. 6d). Lanthanum concentrations are generally in the 90th-95th percentile range (18.6-20.8 μg/g) in these areas, although La concentrations which exceed the 97th percentile (> 21.7 μg/g) occur in Petersham and Hampton Court. In Teddington, La concentrations in the 90th-97th percentile are observed near a site of past industrial activity (see Plate 6.14 and Supp. Figs. 6c and 6d -see Table 3.2 for a summary of the uses of La). The distribution of La observed in Richmond suggests that both geological/pedogenic processes and anthropogenic activities are important influences.

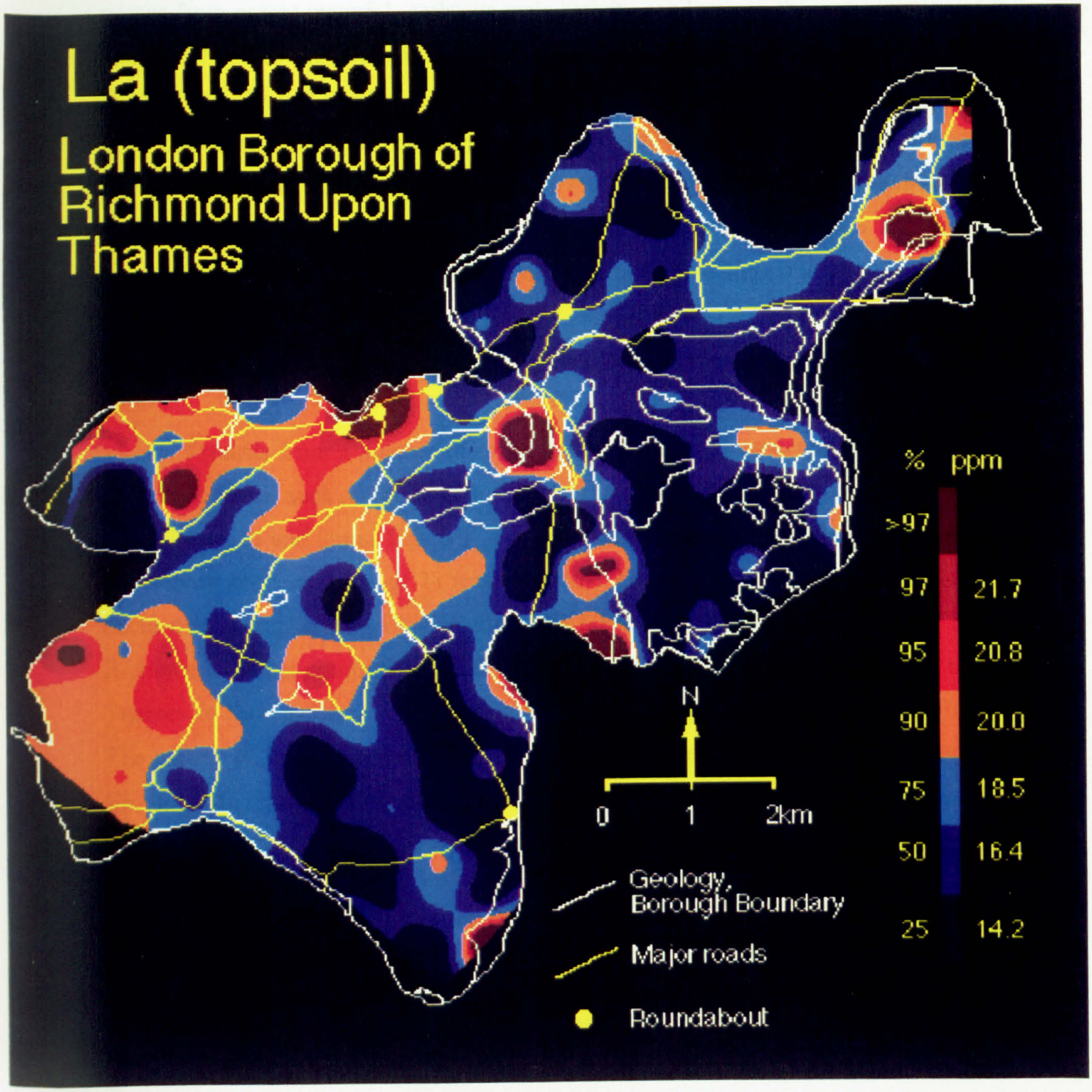

La (topsoil)
London Borough of Richmond Upon Thames
%
ppm
>97
97
21.7
95
20.8
90
20.0
75
18.5
50
16.4
25
14.2
N
0
1
2km
Geology, Borough Boundary
Major roads
Roundabout

Plate 6.14

6.2.16 Concentrations of titanium in Richmond topsoils (0-15cm)

Titanium is a common constituent of soils, and occurs in resistant minerals which remain unaltered in temperate environments. Although most of the Ti content of soils comes from parent material, anthropogenic activity can increase the concentration of this element. Sources include emissions from industries using Ti alloys and from Ti paints (Kabata-Pendias and Pendias, 1984 - see Table 3.2 for a summary of the uses of Ti). Plate 6.15 shows the distribution of Ti in Richmond topsoils. Titanium is naturally abundant in Richmond topsoils with the lowest percentile (50th) having a concentration range of $\leq$ 701 μg/g. The concentration range of Ti in Richmond topsoils is low, with a 97th percentile less than 2 times the magnitude of the 50th percentile (908 μg/g and 701 μg/g). Most of the soils in Bushy Park, Hampton Court and parts of Kew Gardens have Ti concentrations in the 50th percentile range ($\leq$ 701 μg/g - see Plate 6.15 and Supp. Fig. 6d).

Topsoils from a number of residential areas have Ti concentrations in the lowest percentile range, such as Teddington, St. Margarets, Richmond town centre and Mortlake (see Plate 6.15 and Supp. Fig. 6d). Topsoils from various parts of Richmond Park have the highest concentrations of Ti (exceeding the 97th percentile; $>$ 908 μg/g) and these occur over a number of geological units (see Supp. Fig. 6b). A number of other areas in Richmond have concentrations of Ti which exceed the 97th percentile, such as near the Thames in Kew gardens, in Petersham and in Ham (see Plate 6.15 and Supp. Fig. 6d). The pattern of Ti enhancement close to the Thames is not as distinct as that observed for Ca, Sr, Mn, Co and Fe. Soils overlying alluvium do not have significantly higher concentrations of Ti than soils overlying river terraces and London Clay (all $P > 0.05$).

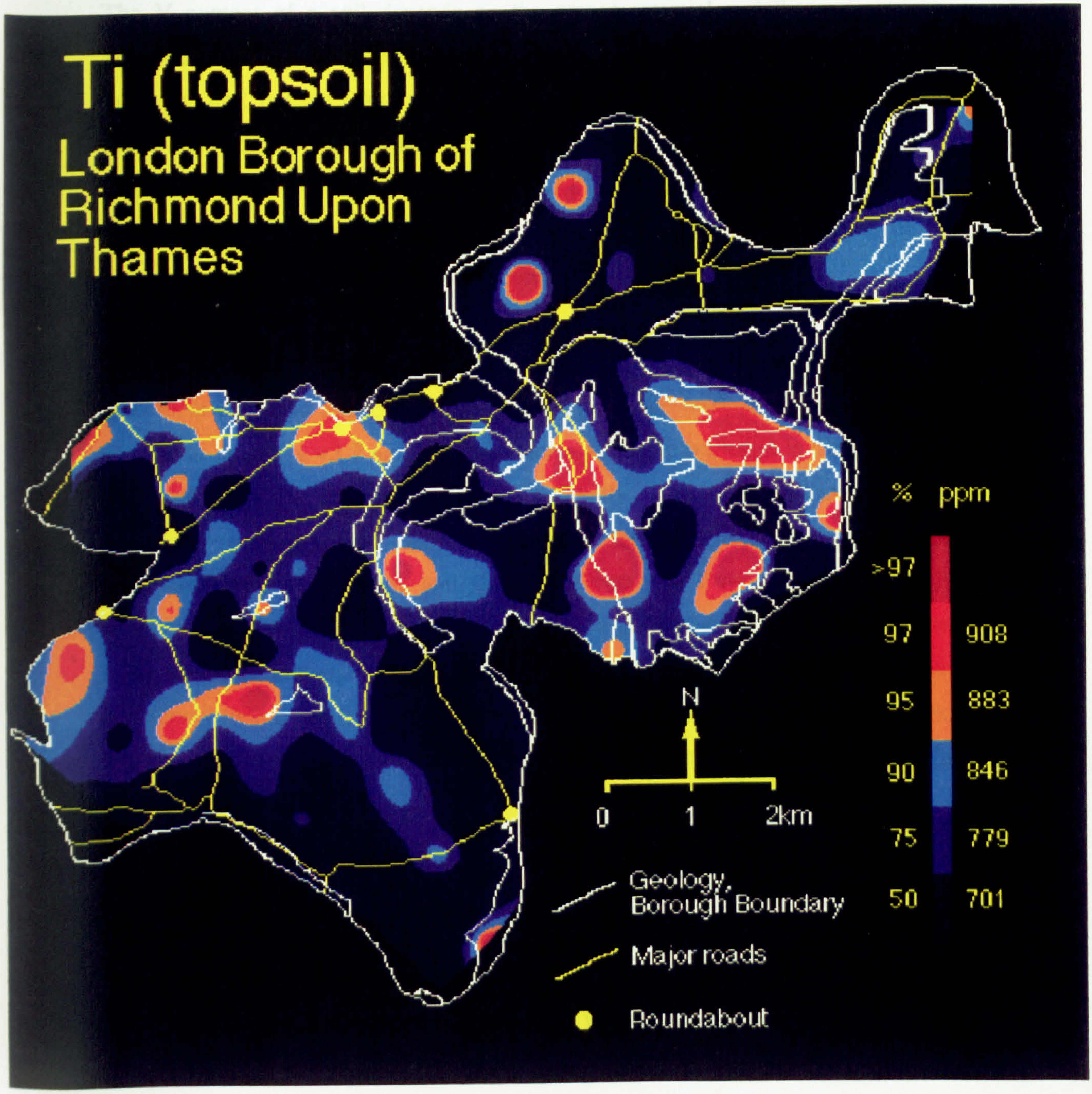

Ti (topsoil)
London Borough of Richmond Upon Thames
N
0
1
2km
Geology, Borough Boundary
Major roads
Roundabout
% ppm
>97
97 908
95 883
90 846
75 779
50 701

Plate 6.15

6.2.17 Concentrations of vanadium in Richmond topsoils (0-15cm)

The crustal abundance of V is similar to that of Ni, Cu, Zn and Pb, although V is much more dispersed than these metals, generally resulting in lower concentrations in soils. The V content of a soil depends on the parent material and the pedogenic processes associated with its development (Jones et *al.*, 1990). Vanadium has a wide and varied industrial use, but the major sources of V enrichment in soil are from the combustion of fossil fuels and the wastes from such processes (*Jones et al.*, 1990). Plate 6.16 shows the distribution of V in Richmond topsoils, and in general the overall concentration range of V in topsoils from Richmond is low. The 25th percentile concentration of 42.7 μg/g compares with 69 μg/g for the 97th percentile.

The areas with the lowest concentrations of V are Richmond Park and Bushy Park (see Plate 6.16 and Supp. Fig. 6d). Vanadium concentrations are generally in the 25th percentile range ($\leq$ 42.7 μg/g) in these locations. Locations close to the Thames (see Plate 6.16 and Supp. Fig. 6d) generally have relatively high concentrations of V compared to the 25th percentile range. This is observed in Barnes, Kew, Kew Gardens, Petersham, Strawberry Hill, Teddington and Hampton Court (see Plate 6.16 and Supp. Fig. 6d). Vanadium concentrations which exceed the 97th percentile ($>$ 69 μg/g), are observed in these locations, although concentrations in the 90th-95th percentile range (54.7-65.9 μg/g) are also observed. Soils overlying alluvium have significantly higher concentrations of V than soils overlying the high level terraces, 1 and 3-river terraces and London Clay (all $P < 0.001$).

In Teddington, the relatively high concentrations of V ($>$ 69 μg/g) near the Thames occur in an area of past industrial activity (see Plate 6.16 and Supp. Figs. 6c and 6d). Relatively high concentrations of V also occur in residential areas near Richmond town centre, Mortlake and Hampton where V concentrations are generally in the 90th percentile range (54.7-62.2 μg/g). In the urban areas of Barnes, St. Margarets and Whitton

V concentrations exceed the 97th percentile ($>$ 69 μg/g - see Plate 6.16 and Supp. Fig. 6d and Table 3.2 for a summary of the uses of V). Multi-variate statistics suggest that natural geochemical processes, in addition to anthropogenic activities, are very important

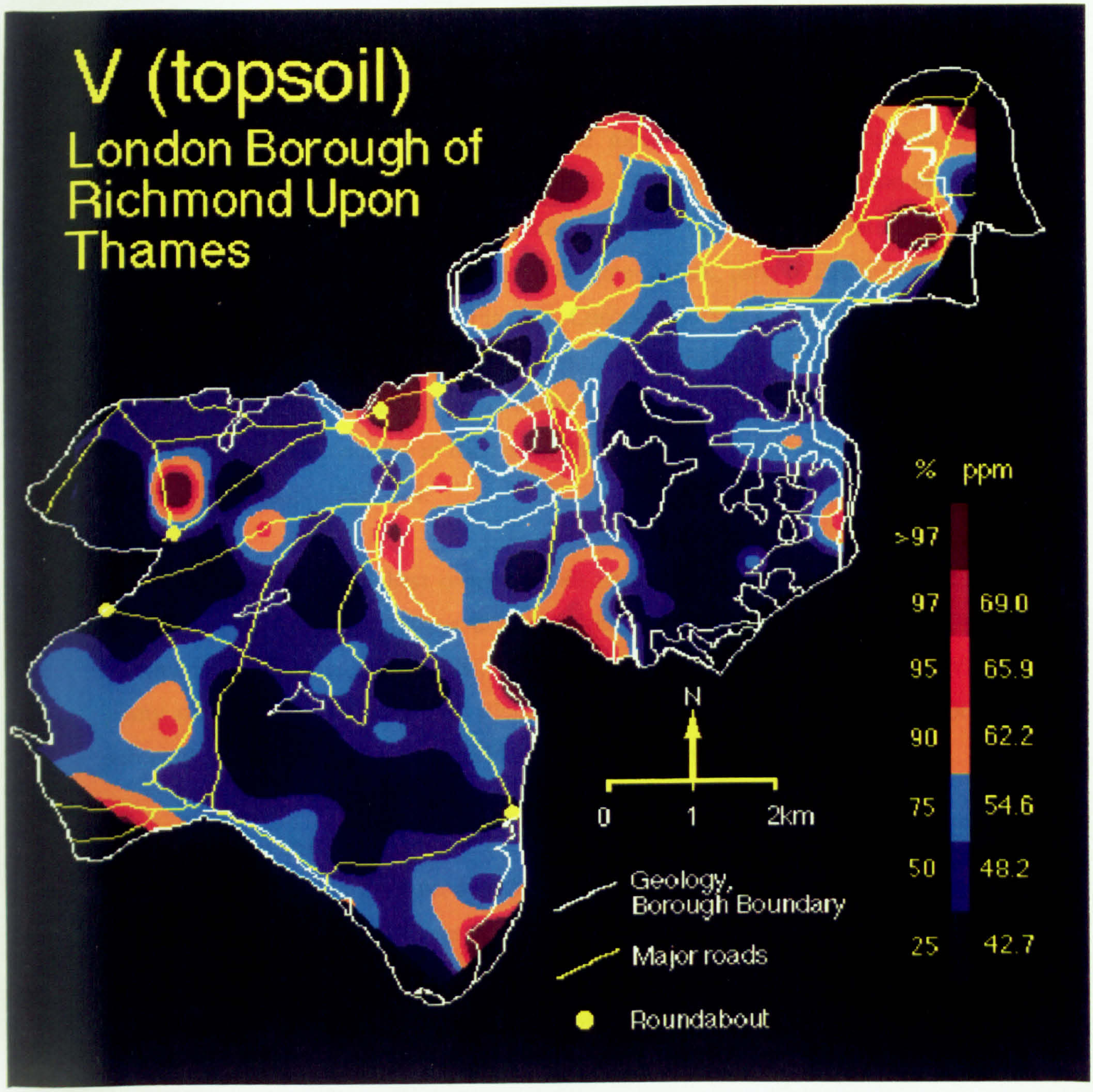

V (topsoil)
London Borough of Richmond Upon Thames
% ppm
>97
97 69.0
95 65.9
90 62.2
75 54.6
50 48.2
25 42.7
N
0 1 2km
Geology, Borough Boundary
Major roads
Roundabout

Plate 6.16

factors influencing the distribution of V. The association of V with Mn and Fe, suggests the co-precipitation of Mn and V with hydrous Fe oxides (Sposito, 1983 - see Appendix 3), and an association with Cr and Mn, geochemically similar elements which, may co-precipitate with clay minerals (Sposito, 1983 - see Appendix 3).

6.2.18 Concentrations of chromium in Richmond topsoils (0-15cm)

The distribution of Cr in Richmond topsoils is shown in Plate 6.17. The concentration range for this metal is low with a 25th percentile concentration of 31 μg/g, compared to 50 μg/g for the 97th percentile (see Plate 6.17). The lowest concentrations of Cr are mainly observed in the middle of Richmond Park, parts of Bushy Park and Kew Gardens (see Plate 6.17 and Supp. Fig. 6d). Concentrations of Cr in these areas are in the 25th percentile range (≤ 31 μg/g). However, concentrations of Cr exceeding the 97th percentile are observed in Bushy Park, with Cr concentrations in the 90th percentile range (40.1-44 μg/g) also observed in Richmond Park, Hampton Court and Kew Gardens (see Plate 6.17 and Supp. Fig. 6d).

In general, the highest concentrations of Cr are in the residential areas of the borough, with Cr concentrations exceeding the 97th percentile (> 50 μg/g) east of Richmond town centre, between St. Margarets and Twickenham, Kew and in Whitton. Many of the residential areas of Richmond have Cr concentrations in the 90th-97th percentile range (40.1-50 μg/g- see Plate 6.17 and Supp. Fig. 6d).

Areas close to the Thames in Kew, Petersham, Teddington and Hampton also have concentrations of Cr which exceed the lowest percentile. In Teddington and Hampton, Cr concentrations exceed the 97th percentile (> 50 μg/g) and are in the 97th percentile range (47.1-50 μg/g), respectively. These are near sites of past industrial activity (see Plate 6.17 and Supp. Figs. 6c and 6d). The pattern of high concentration in soils close to the Thames is not as distinctive as for elements such as Ca and Sr. Soils overlying alluvium do not have significantly higher concentrations of Cr than soils overlying the river terraces and London Clay in Richmond.

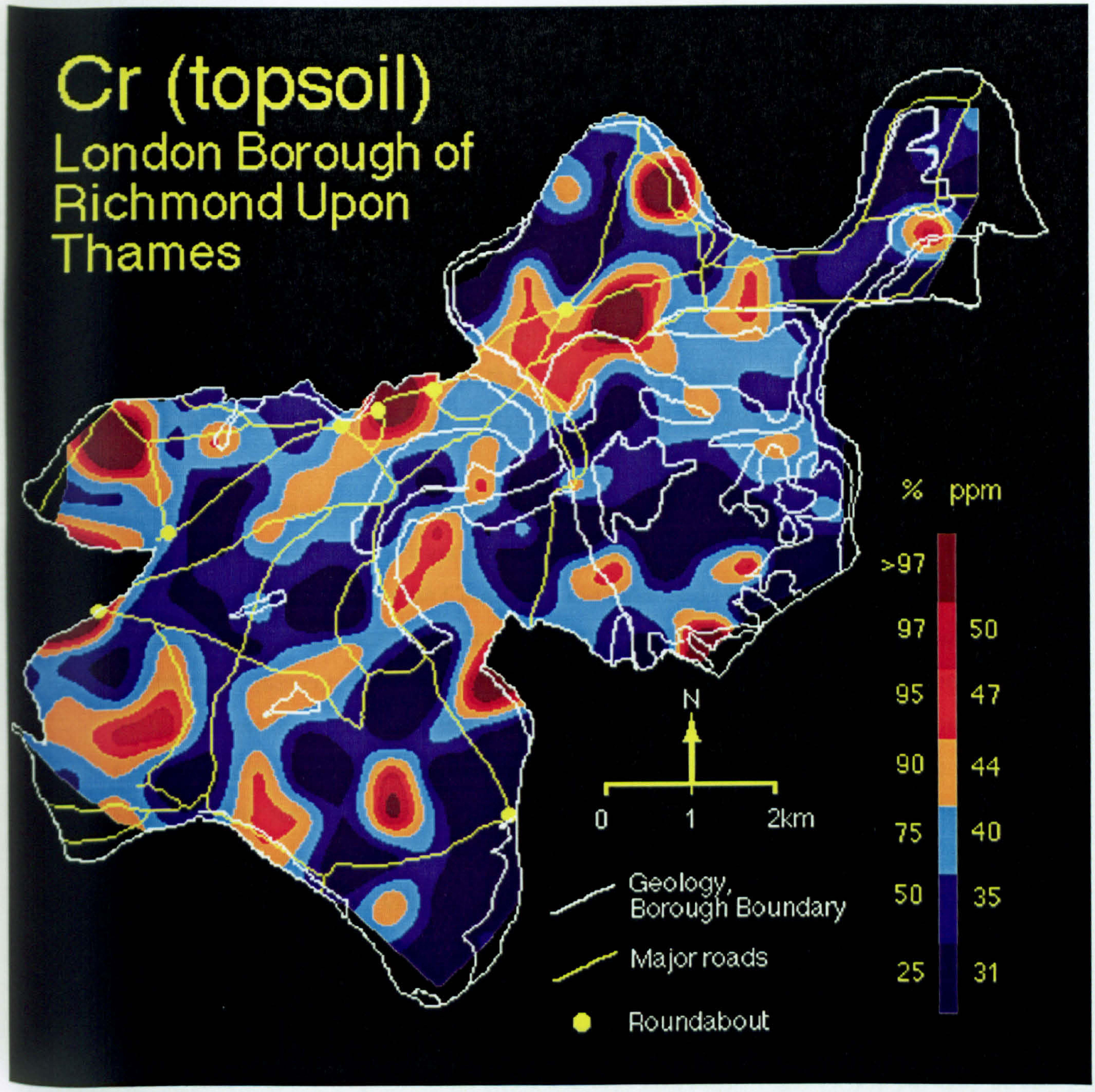

Cr (topsoil)
London Borough of Richmond Upon Thames
N
0
1
2km
Geology, Borough Boundary
Major roads
Roundabout
%
ppm
>97
97
50
95
47
90
44
75
40
50
35
25
31

Plate 6.17

6.2.19 Concentrations of manganese in Richmond topsoils (0-15cm)

Manganese is one of the most abundant trace metals in the lithosphere, with Mn^{2+} being the most frequent oxidation state in rock forming silicate minerals, and the cation Mn^{2+} known to replace the sites of other divalent cations such as Fe^{2+} and Mg^{2+} in silicates and oxides. Soils derive most of their Mn from the parent material (the parent materials for Richmond are shown in Supp. Fig. 6b), and the complex chemical behaviour of this element dictates the form of Mn in the soil (Smith, 1990). Plate 6.18 shows the distribution of Mn in Richmond topsoils. Manganese is naturally abundant in these soils, although the concentration range in Richmond is much lower than that associated with many types of parent material (Levinson, 1980 - see Table 2.3). The analytical technique may be an important influence on this. The 97th percentile concentration is less than 3 times the magnitude of the 25th percentile (613 $\mu g/g$ and 225 $\mu g/g$, respectively).

Concentrations of Mn in the lowest percentile range ($\leq$ 225 $\mu g/g$) are observed over much of Richmond Park and smaller parts of Kew Gardens and Bushy Park (see Plate 6.18 Supp. Fig. 6d). Hampton Court and most parts of Kew Gardens, however, have Mn concentrations greater than the lowest percentile range. Some urban enhancement of Mn is observed, particularly in St. Margarets, Petersham, Ham and parts of Hampton (see Plate 6.18 and Supp. Fig. 6d). In these areas Mn concentrations exceed the 97th percentile ($>$ 613 $\mu g/g$). The major anthropogenic addition of Mn to soils is in the form of macronutrient fertilisers (Smith, 1990 - see Table 3.2 for a summary of the uses of Mn). However, this pattern of urban enhancement is not observed in all residential areas, as much of Hampton, and Whitton in particular, have Mn concentrations in the $\leq$ 50th percentile range ($\leq$ 305 $\mu g/g$). Some of these urbanised areas, Petersham, Ham and Hampton, are located close to the Thames, and the high concentrations of Mn, which are generally in the 90th-95th percentile range ($>$ 391-550 $\mu g/g$), in these areas and in Kew, Kew Gardens and Hampton Court (see Plate 6.18 and Supp. Figs. 6c and 6d) may be as a result deposits of alluvium from the Thames. Soils overlying alluvium have significantly higher concentrations of Mn than soils overlying the high level terraces and London Clay (both $P < 0.001$). Some of these sites occur in areas of past/present industrial activity already discussed (see Plate 6.18 and Supp. Fig. 6c). Multi-variate statistics suggest the

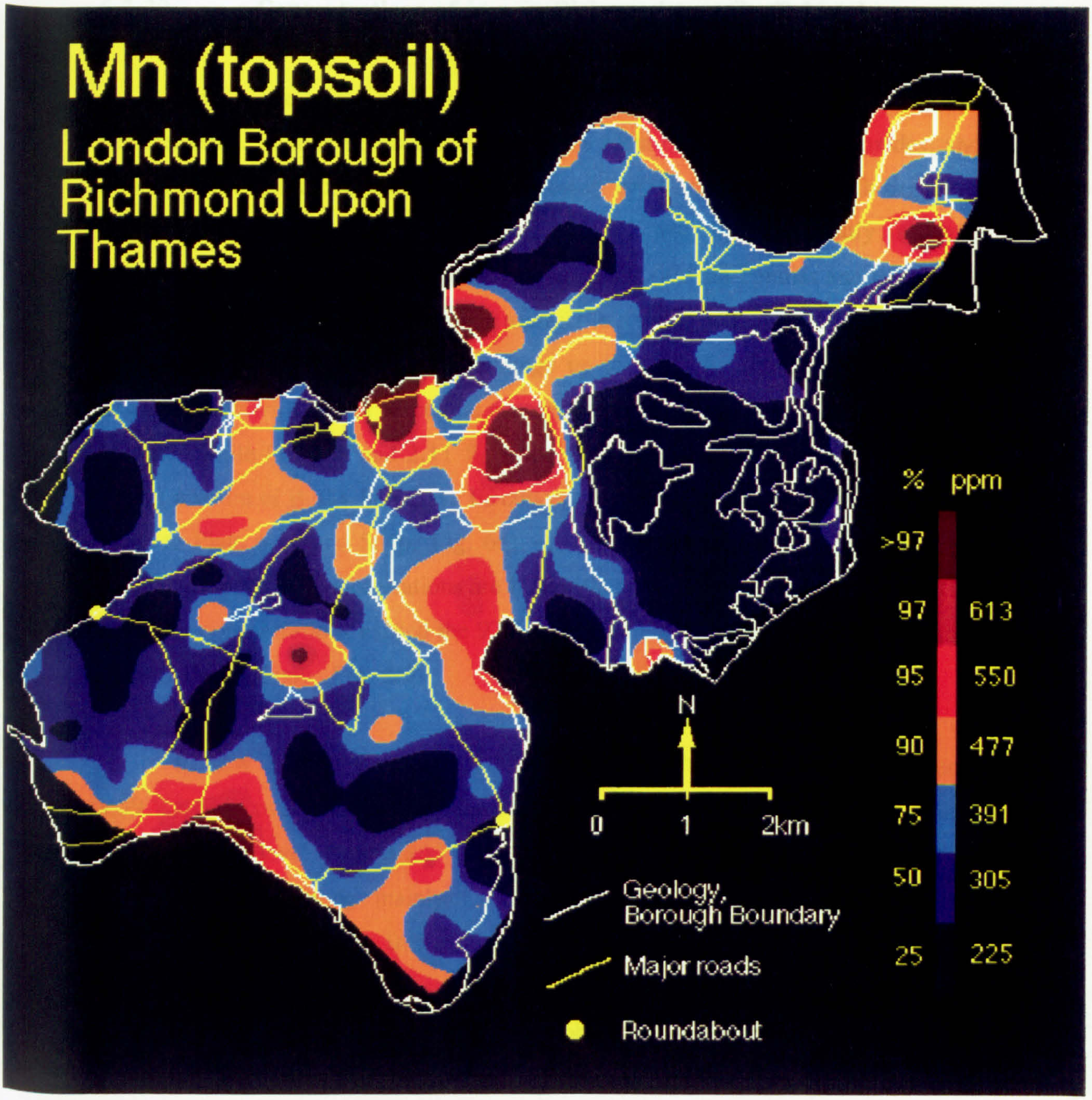

Mn (topsoil)
London Borough of Richmond Upon Thames
N
0
1
2km
% ppm
>97
97 613
95 550
90 477
75 391
50 305
25 225
Geology, Borough Boundary
Major roads
Roundabout

Plate 6.18

strong influence of natural geochemical processes in the distribution of Mn in soils from Richmond, through co-precipitation with hydrous Fe oxides and clay minerals (Sposito, 1983 - see Appendix 3).

6.2.20 Concentrations of iron in Richmond topsoils (0-15cm)

Iron is one of the major constituents of the lithosphere, and has a very complex geochemistry. In soils Fe occurs mainly in the form of oxides and hydroxides, and both mineral and organic compounds of Fe are easily transformed in soils with organic matter and microorganisms strongly influencing this. As with Mn, Fe greatly influences the behaviour of both trace elements and macro-elements (Kabata-Pendias and Pendias, 1984). The distribution of Fe in Richmond topsoils is shown in Plate 6.19. Iron is naturally abundant with the lowest percentile range up to 2.11 %. The concentration range is, however, low with a 97th percentile concentration less than 2 times the magnitude of the 25th percentile (3.58 % and 2.11 %, respectively). The majority of Richmond Park and a large amount of Bushy Park have Fe concentrations in the 25th percentile range ($\leq$ 2.11 % - see Plate 6.19 and Supp. Fig. 6d). At the margins of Bushy Park and in much of Hampton Court, Fe concentrations are higher than the 25th percentile range. In Hampton Court Fe concentrations exceed the 97th percentile ($>$ 3.58 %) close to the Thames (see Plate 6.19 and Supp. Fig. 6c).

In Kew Gardens Fe concentrations near the Thames exceed the 97th percentile ($>$ 3.59 %). Soils overlying alluvium have significantly higher concentrations of Fe than soils overlying high level terraces and London Clay (both $P < 0.001$). Topsoils in Richmond Park, mainly overlying mainly London Clay and high level terraces, have lower concentrations of Fe than Bushy Park and Kew Gardens, overlying the younger river terraces and alluvium (see Plate 6.19 and Supp. Figs. 6b and 6d). The pattern of Fe enrichment, relative to the 25th percentile, observed in Petersham, Strawberry Hill and Teddington also follows the path of the river (see Plate 6.19 and Supp. Fig. 6d). However, in Teddington high concentrations of Fe ($>$ 3.16 % in general) coincide with the engineering works and sewage works which were located here. Relatively high Fe concentrations ($>$ 2.84 %) are observed in Hampton near to where the sewage and water

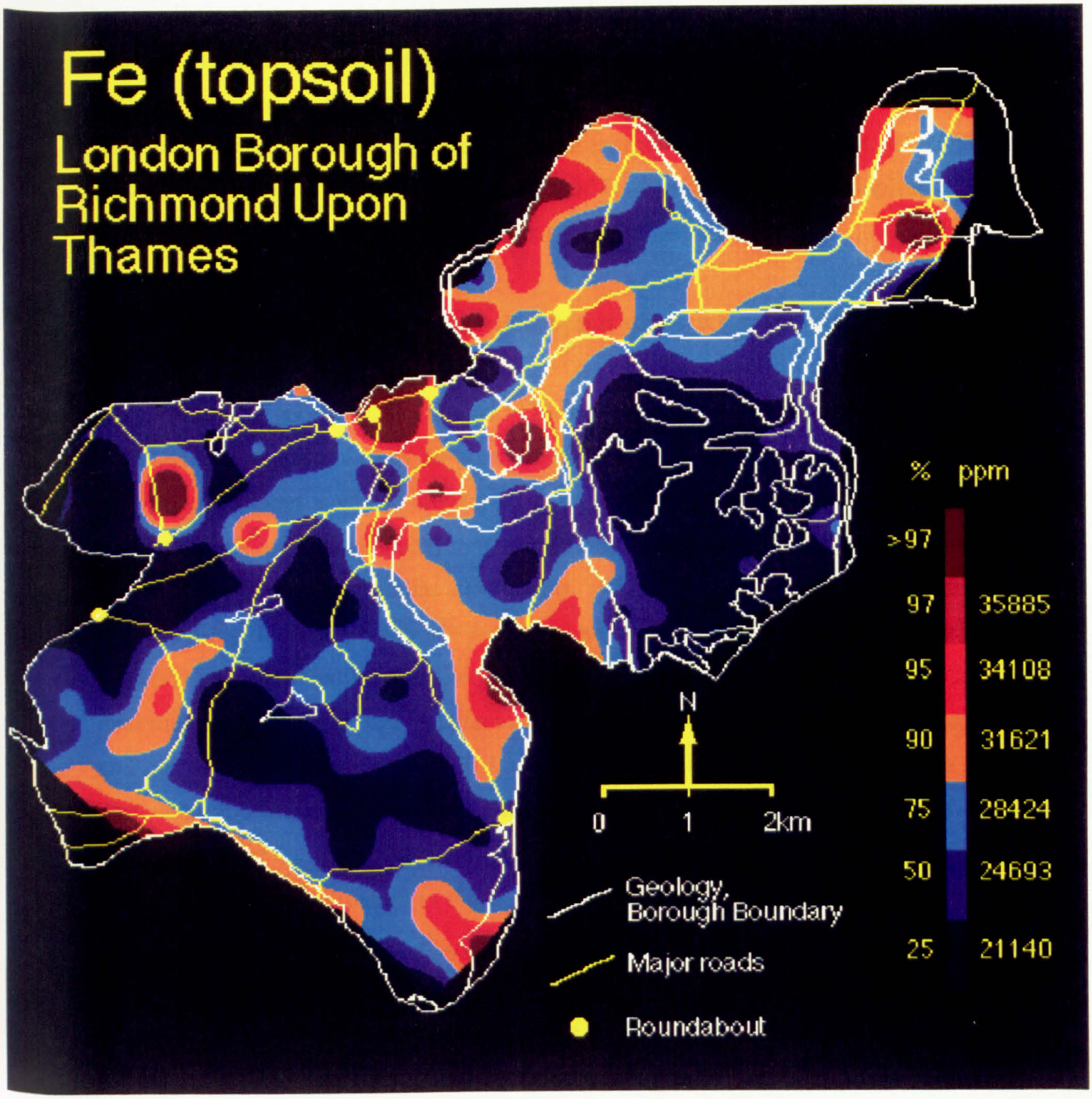

Fe (topsoil)
London Borough of Richmond Upon Thames
% ppm
>97
97 35885
95 34108
90 31621
75 28424
50 24693
25 21140
N
0 1 2km
Geology, Borough Boundary
Major roads
Roundabout

Plate 6.19

works were located and close to a contemporary water works (> 3.58 % - see Plate 6.19 and Supp. Fig. 6c). Natural geochemical processes such as co-precipitation are important influences on the distribution of Fe in Richmond (Sposito, 1983 - see Appendix 3).

Several residential areas have soils enriched in Fe, such as close to Richmond town centre, Mortlake and in Barnes. In Richmond town centre and Mortlake the Fe concentrations are in the 90th percentile range (2.84-3.16 % - see Plate 6.19 and Supp. Fig. 6d), whilst in Barnes Fe concentrations exceed the 97th percentile. A number of studies have reported elevated concentrations of Fe in urban street dust (Hoplee, 1984 and Farmer, 1986 - see Table 3.2 for a summary of the uses of Fe).

6.2.21 Concentrations of cobalt concentrations in Richmond topsoils (0-15cm)

Cobalt is geochemically similar to Fe and Mn, and its distribution in the soil profile seems to be strongly linked by co-precipitation to the Mn oxide phase formation (Sposito, 1983). Iron oxides are also known to have a have a high affinity for the selective adsorption of Co, and a similarity between the concentrations of Fe and Co in soil horizons has been shown (Kabata-Pendias and Pendias, 1984). However, in some soils enriched in Mn, the association of Co and Mn dominates any other factors governing Co distribution in soils (Kabata-Pendias and Pendias, 1984). Anthropogenic sources of Co are; macronutrient fertilisers, the manufacture of steels and the manufacture of blue pigments and glass (Smith, 1990). Plate 6.20 shows the distribution of Co in Richmond topsoils. The concentration range of Co in Richmond topsoils is low with a 25th percentile concentration of 6 μg/g compared to 14 μg/g for the 97th percentile. The lowest percentile range ($\leq$ 6 μg/g) is observed in much of Richmond Park and a large area of Bushy Park (see Plate 6.20 and Supp. Fig. 6d). In Kew Gardens, close to the Thames, Co concentrations are in the 90th-95th percentile range (9.1-12 μg/g). This could be as a result of past flooding from the Thames, addition of fertilisers (see Table 3.2 for a summary of the uses of Co) or a reflection of the geochemical signature for the deposits in this area.

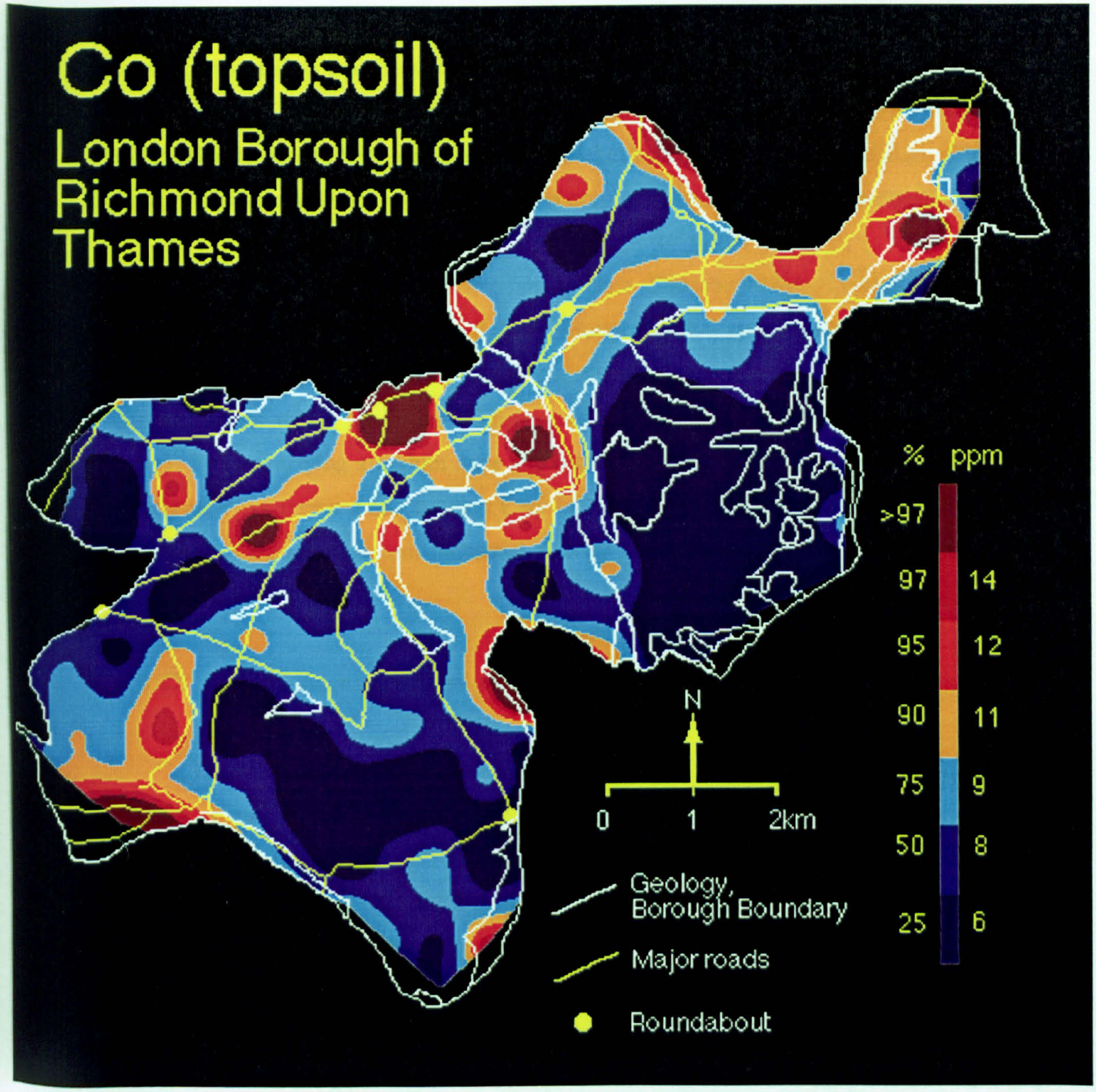

Co (topsoil)
London Borough of Richmond Upon Thames
%
ppm
>97
97
14
95
12
90
11
75
9
50
8
25
6
N
0
1
2km
Geology, Borough Boundary
Major roads
Roundabout

Plate 6.20

Some urban parts of Richmond have higher concentrations of Co, relative to the lowest percentile range. This is observed near Richmond town centre extending east through the residential area to Mortlake and Barnes (see Plate 6.20 and Supp. Fig. 6d). In most of this area, Co concentrations are in the 90th percentile range (9.1-11 μg/g), whilst parts of Kew and Barnes have Co concentrations which exceed the 97th percentile (> 14 μg/g). Cobalt concentrations which exceed the 97th percentile are also observed in the residential areas of St. Margarets and Twickenham (see Plate 6.20 and Supp. Fig. 6d). Smith and Carson (1981) reported elevated concentrations of Co in urban roadside dusts.

The residential areas near Petersham, Ham, Strawberry Hill, Teddington and Kew are close to the Thames (see Plate 6.20 and Supp. Fig. 6d) so anthropogenic activity, past flooding or the geochemical signature for the alluvium deposits may account for Co concentrations which are in the 90th percentile range and higher in these areas (> 9.1 μg/g). Soils overlying alluvium have significantly higher concentrations of Co than soils overlying river terraces and London Clay (all $P < 0.001$). Teddington and Hampton are also sites of past and present industrial activity (see Plates 6.20 and Supp. Figs. 6c and 6d).

6.2.22 Concentrations of phosphor us in Richmond topsoils (0-15cm)

Phosphorous has a distribution in Richmond which is very similar to that of Pb, Zn and Cu. Plate 6.21 shows that P concentrations are higher in urban areas than areas of open space, suggesting a strong anthropogenic input of this element. Phosphorous is naturally abundant in Richmond topsoils, although the concentration range is low. The 97th percentile concentration is approximately 3 times the magnitude of the 25th percentile concentration (2205 μg/g and 711 μg/g, respectively). Many of the topsoils in Richmond Park have P concentrations in the 25th percentile range (≤ 711 μg/g). In Hampton Court P concentrations are generally in the 50th percentile range (712-953 μg/g). Bushy Park and Kew Gardens have large areas isolated from urban development where P concentrations are in the 25th percentile range (≤ 711 μg/g - see Plate 6.20 and Supp. Fig. 6d).

Some urban areas also have concentrations of P which are in the 25th percentile

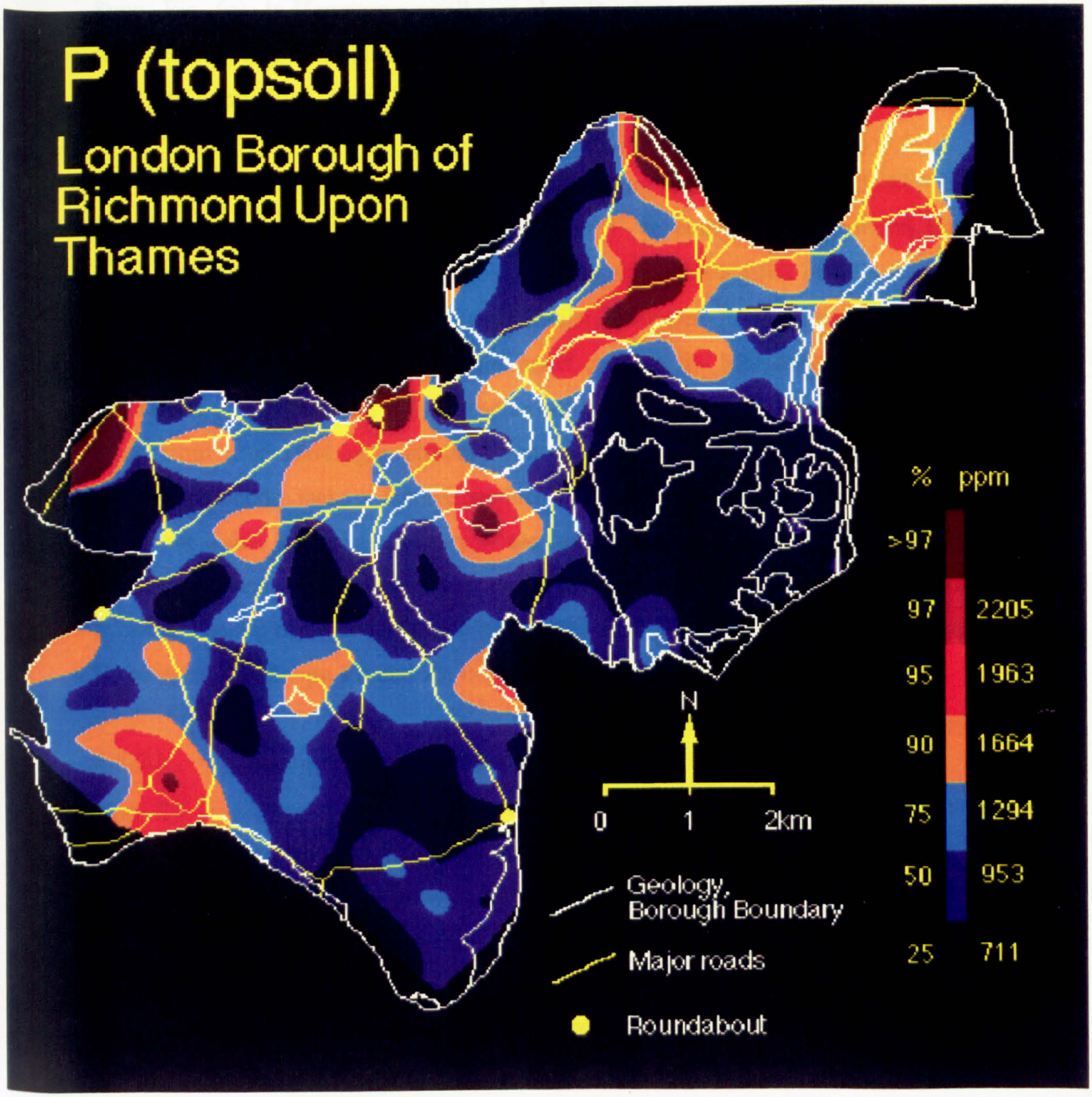

P (topsoil)
London Borough of Richmond Upon Thames
%
ppm
>97
97
2205
95
1963
90
1664
75
1294
50
953
25
711
N
0
1
2km
Geology, Borough Boundary
Major roads
Roundabout

Plate 6.21

range, and in the 50th percentile range (712-953 μg/g). These are observed in Ham, Strawberry Hill and in parts of Teddington and Hampton (see Plate 6.20 and Supp. Fig. 6d). In Teddington, P concentrations in the 90th percentile range (1295-1664 μg/g) are observed near the Thames, close to the site of past industrial activity (see Plate 6.20 and Supp. Fig. 6c). In Hampton a small area close to where a water works and sewage works were located, P concentrations are in the 90th percentile range (1295-1664 μg/g, see Plate 6.20 and Supp. Figs. 6c and 6d).

In the urban areas near Richmond town centre and extending east to Mortlake and Barnes, and north to Kew, concentrations of P generally range from the 90th-97th percentile (1295-2205 μg/g), exceeding the 97th percentile in parts of Kew and Mortlake (see Plate 6.21 and Supp. Fig. 6d). A similar pattern of P enrichment, relative to the lowest percentile range, occurs in the areas close to St. Margarets, Twickenham and Petersham (see Supp. Fig. 6d). Phosphorous concentrations in these locations generally range from 1295-1664 μg/g, although concentrations > 2205 μg/g occur. Phosphorus is an important component of fertilisers which are applied to gardens and allotments in urban areas (see Table 3.2 for a summary of the uses of P). High concentrations of P in urban gardens, relative to the baseline percentile, may also result from natural biogeochemical cycling. The use of multi-variate statistics also shows a strong anthropogenic signature for P, being grouped with Pb and Zn in garden samples (see Appendix 3).

6.2.23 Summary and Discussion

Anthropogenic and geological/pedogenic processes exert a strong influence on the geochemistry of soils in Richmond. The metals, Pb, Zn, Cu and Ba in addition to P are greatly influenced by land-use. The highest concentrations of the metals are generally observed in residential areas near major roads and roundabouts. This is particularly true for Pb, an important component of leaded petrol, but also observed for Zn and Cu. These metals have several sources in urban gardens which vary from household to household. The flaking of paint (see Appendix 3), particularly from older housing, is a source of Pb, Zn and Ba in urban gardens, whilst the burning of fossil fuels and the disposal of residues is a source of many elements (see Tables 3.1 and 3.2). Fertilisers may be applied to private gardens and these, depending on their composition, will increase the concentrations of a number of elements including P and K.

For most elements, Ni, Ba, Ca, Sr, Li, Mn, Co, Fe, Na, La and V, both anthropogenic activity and geological/pedogenic processes seem to strongly influence the distribution in topsoils from Richmond. The specific sources of a number of these elements is uncertain, but the burning and disposal of fossil fuel residues, the application of fertilisers, the flaking of paint, the burial of building material and vehicle emissions are likely to result in high concentrations of a number of these elements in garden soils. A geochemical fingerprint does seem to exist in Richmond, particularly for soils which overlie deposits of alluvium, London Clay and high level terraces. The deposits of London Clay and high level terraces occur mainly in Richmond Park and these tend to have significantly lower concentrations of a suite of elements, particularly in relation to soils which have developed over deposits of alluvium. The location of London Clay and high level terraces in Richmond Park is probably an important factor, but it is tentatively suggested that this trend is also strongly influenced by the underlying geology and the natural geochemical input. The geochemical maps also suggest that for a number of elements natural variation of the geochemical signature, for a particular parent material, is probably an important factor influencing the distribution of elements in topsoils.

6.3 The influence of land-use on concentrations of elements in Richmond soils

6.3.1 Classification of sites in Richmond

The results of the mapping process presented in section 6.2 illustrated the strong influence of land-use on the concentration of a number of elements in Richmond topsoils. To see if this influence is statistically significant the sample sites were classified as either or `openspace' or garden soil. The term garden soil sample refers to samples taken in the back gardens of residential sites. Sample sites defined as `openspace' comprise the parks, Kew Gardens, sports grounds, small recreational grounds and cemeteries. Kew Gardens is a botanical research centre and is defined as `openspace' because the site has no major roads or housing. This provides a basis on which to compare results. Although, cemeteries and sports grounds are affected by development, at the majority of these sites the sample was taken in an isolated location several hundred metres from any major development. Where areas of open space are close to roads it was unnecessary to create a new category for these. Such a simple classification was aided by very limited amount of derelict, industrial or farmland in Richmond.

Data for environmentally important metals in Richmond topsoils and subsurface soils are summarised, in relation to land-use, in Tables 6.1 and 6.2, respectively. Data for other elements are summarised in Tables 6.3 and 6.4. The geometric mean is presented along with the arithmetic mean because the majority of the data do not have a normal distribution. A normal Gaussian distribution is generated by a log transformation of the data. Geometric means therefore provide more robust definitions of central tendency than arithmetic means. The standard deviation is also presented along with the concentration range for each element.

6.3.2 Lead - topsoils (0-15cm)

A geometric mean of 271 μg/g Pb for garden soils compares to 93 μg/g for samples from areas of open spaces (see Table 6.1). This mean concentration for garden soils is nearly 3 times greater than that for areas of open space, a difference which is statistically significant ($P < 0.001$). This was also illustrated in Plate 6.1. The large difference between the geometric and arithmetic means (see Table 6.1) is a result of the log normal distribution. The standard deviations for both garden soils and areas of open space are high, illustrating the extent to which the concentration varies within the same land-use category. The concentration range of Pb for garden soils is greater than that of areas of open space, the latter having a lower background concentration of Pb, 26 μg/g compared to 34 μg/g for garden soils, and a lower peak concentration (see Table 6.1). The one high Pb concentration of 1210 μg/g relates to an area of open space close to a major roundabout. Both arithmetic and geometric means for Pb from areas of open space and urban gardens are significantly higher than corresponding values reported in the Soil Geochemical Atlas of England and Wales (McGrath and Loveland, 1992). An arithmetic mean of 74 μg/g and a geometric mean of 45.6 μg/g, are reported for topsoils in England

and Wales (McGrath and Loveland, 1992), see Table 6.5, compared to 362 μg/g and 271 μg/g, respectively, for urban gardens and 138 μg/g and 93 μg/g, respectively, for areas of open space in Richmond. Both Webb *et al.* (1978) and McGrath and Loveland (1992) reported high concentrations of Pb in stream sediments and soils, respectively, around London.

Davies (1983) estimated that uncontaminated soils are unlikely to contain more than 110 μg/g Pb, and on average, soils in areas of open spaces in Richmond have a lower Pb concentration (a geometric mean of 93 μg/g is reported in Table 6.1). The geometric mean of 271 μg/g for urban gardens is over 2 times greater than this value quoted for uncontaminated soils. The concentrations of Pb for both land-uses are considerably higher than those reported for agricultural soils in England and Wales (Archer and Hodgson, 1987) and Scotland (Reaves and Berrow, 1984). Geometric means of 39.8 μg/g and 14 μg/g are reported, respectively for these studies, reflecting a greater number of Pb sources in an urban area such as Richmond. The geometric mean for urban garden soils is similar to the mean concentration reported for Liverpool allotments of 275 μg/g (Warren *et al.*, 1971), although higher than the mean concentration reported by Davies *et al.* (1979) for the zone 10-30km from the centre of London of 142 μg/g. However, Richmond is only just > 10km from the centre of London and this is reflected in the similarity with the mean concentration for the 4-10km zone of 242 μg/g (Davies *et al.* 1979). The geometric mean for garden soils in Richmond is also similar to the arithmetic mean reported for Pb from 87 urban and rural gardens in England and Wales of 233 μg/g (Davies, 1978). Moir (1992) quotes a geometric mean of 358 μg/g for garden and allotment soil from Richmond, and this higher value may be as a result of samples taken closer to major roads or due to an association with older housing. Another possible explanation for the lower Pb concentration in this later study may be the reduction in the Pb content of petrol that has occurred since 1986 (see section 3.4.6.1). However, with the exception of the 2 London boroughs (Hammersmith and Fulham and Richmond), the geometric mean for garden soils quoted in this study is higher for the other cities/towns in the study by Moir (1992). In west Dublin, most soils had a concentration range of only 70-150 μg/g, much lower than that reported for soils from Richmond (see Table 6.1). Thornton and Jones (1984) reported Pb concentrations in excess of 2000 μg/g for allotment soils from London, higher than the peak concentration for Pb in this study (1840, μg/g).

A number of urban studies based in the U.S.A report a higher concentration of Pb in garden soils than that reported for Richmond. These include arithmetic mean concentrations of Pb of 800 μg/g for Boston (Spittler and Fried, 1979); 460 μg/g for Washington (Preer, 1984); 460 μg/g for Mount Pleasant (Francek *et al.*, 1992) and 840 μg/g and 860 μg/g for New Orleans and Minneapolis, respectively (Mielke, 1993). The higher concentrations of Pb for garden soils from the U.S.A. may be an artefact of differences in sampling depth; most of the American studies involved sampling 0-2.5/5cm of soil (compared to 0-15cm in this study). Another explanation may be the higher number of wooden houses in America compared with Britain, and hence a greater surface area painted (Mielke *et al.*, 1984 and Preer *et al.*, 1984). However, such studies may also have been based in areas close to the city centre, with older housing and a higher traffic density resulting in higher concentrations of Pb. This trend was observed in the National Reconnaissance Survey for the inner city areas of London (Culbard *et al.*, 1983), and a later study in New Orleans by Mielke (1994) which divided the city into inner-city, mid-city and suburban. The mean concentration of 840 μg/g quoted by Mielke (1993), relates to the inner-city area, whilst the other areas have mean concentrations of 110 μg/g and 50 μg/g respectively.

Comparable studies in other parts of Europe include a similar mean value of 221 μg/g for allotments from the industrialised area of Upper Silesia (Gzyl, 1990) and a much higher concentration of 621 μg/g for the centre of Madrid (Sanchez-Camazano *et al.*, 1994). A median concentration of 13 μg/g is reported for soils in Warsaw (PIG, 1992), considerably lower than any measurement of central tendency for soils in Richmond (see Table 6.1). Lux (1991) reports a mean Pb concentration of 168 μg/g for the industrial city of Hamburg.

A study based in Cuenca, Ecuador reports a similar Pb mean to this study of 293 μg/g (Hewitt and Candy, 1990), whilst similar Pb means are also reported for Hong Kong (Tam *et al.*, 1987) and Seoul, South Korea (Chon *et al.*, 1995 - a mean and geometric mean of 268 and 219 μg/g, respectively).

6.3.3 Lead - subsurface soils (30-45cm)

Table 6.2 shows that Pb concentrations are higher in subsurface soils than the other trace metals determined, a trend which was also observed for topsoils. A geometric mean of 208 μg/g for garden soils is nearly 4 times higher than the geometric mean reported for soils from areas of open space (54 μg/g). This difference is statistically significant ($P < 0.001$). The geometric mean for subsurface garden soils of 208 μg/g is not significantly different to that reported for topsoils of 271 μg/g ($P > 0.05$). In areas of open spaces the geometric mean for subsurface soils of 54 μg/g compares with a geometric mean of 93 μg/g for topsoils. Lead concentrations are on average higher at 30-45cm in garden soils than in topsoils from areas of open space. This reflects the disturbance of the soil profile in gardens; in areas of open space, the soil profile, in general, has remained undisturbed. The ratio of Pb in topsoils to subsurface soils in areas of open space is therefore higher than for garden soils, despite lower concentrations of Pb in topsoils. Soils with a sandy texture are common in Richmond (see section 6.4) and this may also aid the movement of metals down the soil profile.

The geometric means for both land-use categories shown in Table 6.2 are lower than the arithmetic means, reflecting the log-normal distribution of these data. The standard deviations all also both higher than the respective arithmetic means. This is explained by the large concentration ranges for Pb for both land-use categories in Table 6.2. These concentration ranges are higher than those reported in topsoils for corresponding land-use categories (see Table 6.1), which suggests that some soils in areas of open space are affected by anthropogenic activity with the profile disrupted. For both land-use categories, the geometric mean concentration of Pb in subsurface soils is higher than that reported for topsoils in England and Wales; 46 μg/g (see Table 6.5 - McGrath and Loveland, 1992). This suggests that subsurface soils in Richmond in general, probably have some anthropogenic additions of Pb.

6.3.4 Zinc - topsoils (0-15cm)

Although Zn is usually present at higher concentrations than Pb in uncontaminated soils (see Tables 2.3 - 2.5), anthropogenic activity has resulted in significantly higher concentrations of Pb in Richmond (compare percentiles for Plate 6.1 and 6.2). A geometric mean of 179 μg/g Zn was found for garden topsoils in Richmond compared to 66 μg/g for areas of open space (see Table 6.1). As with Pb, the geometric mean for garden soils is nearly three times that of the geometric mean for areas of open space ($P < 0.001$). The arithmetic means and geometric means differ greatly, due to the log-normal distribution of the data (see Table 6.1). The standard deviations for both garden soils and soils from areas of open space, are similar to the arithmetic mean, illustrating the high variability of the data. This is also reflected in the large concentration range, particularly for garden soils (37-1810 μg/g). This is greater than that observed for areas of open space (concentrations at both ends of the range are higher for soils sampled in urban gardens). The peak concentration of Zn for gardens soils is also nearly three times greater than the peak concentration reported for soils in areas of open space (1810 μg/g compared to 657 μg/g). The arithmetic and geometric means reported for Zn in the topsoils of England and Wales of 97.1 μg/g and 79 μg/g, respectively (McGrath and Loveland, 1992 - see Table 6.5), are similar to those reported for areas of open space in Richmond, but significantly lower than those reported for urban garden soils (see Table 6.1). However, as with Pb, large scale geochemical surveys such as those by Webb *et al.* (1978) for stream sediments in Britain and McGrath and Loveland (1992) for topsoils in England and Wales, report high concentrations of Zn close to London. Archer and Hodgson (1987) report a similar geometric mean for agricultural soils in England and Wales to that of McGrath and Loveland (1992) of 78.1 μg/g.

Warren *et al.* (1971) report a mean Zn concentration of 185 μg/g for allotment soils in Liverpool, which is similar to the geometric mean of 179 μg/g for garden soils in this study. Thornton and Jones (1984) reported Zn concentrations of > 1500 μg/g for 2 allotments in London, whilst Moir (1992) reported a higher geometric mean for Zn in Richmond than the present study, (271 μg/g compared to 179 μg/g), a trend also observed for Pb. The overall geometric mean for 10 towns and cities in Britain of 218 μg/g (Moir,

1992) is closer to that reported for garden soils in this study (see Table 6.1). Higher average Zn concentrations reported in the studies by Thornton and Jones (1984) and Moir (1992) probably occur due to greater proximity to major roads and an association with older property.

Several studies based in the U.S.A. report a lower mean Zn concentration than this study, a trend not observed for Pb. Median concentrations of 98 μg/g and 92 μg/g are reported, respectively for soils in Washington (Preer *et al.,* 1984) and Baltimore (Mielke *et al.,* 1984). Ritter and Rinefierd (1983) report a mean concentration of 107 μg/g for soils from Dayton, Ohio. Polemio *et al.* (1982) report a mean Zn concentration of 91 μg/g for industrial parts of Bari, Italy whilst Lux (1991) reports a mean Zn concentration of 381 for the industrial city of Hamburg, the only of these studies to report a mean concentration greater than that for garden soils in Richmond (see Table 6.1). A very low median Zn concentration of 34 μg/g is reported for soils from Warsaw (PIG, 1992). The higher concentrations of Zn in urban soils of Britain in general, relative to U.S.A and other parts of Europe may be due to a longer history of fossil fuel combustion in British cities. Open fires were common in Britain until the early 1950's (Davies, 1993).

In Cuenca, Ecuador (Hewitt and Candy, 1990) a high mean Zn concentration of 509 μg/g is reported for soils in the city, whilst Tam *et al.* (1987) report a mean Zn concentration of 281 μg/g for Hong Kong. A recent study of soils in Seoul, South Korea reports a Zn geometric mean concentration of 231 μg/g for soils (Chon *et al.,* 1995). Seoul has a number of metalliferous works. These are all higher than the corresponding measurements for Zn in Richmond garden soils (see Table 6.1), probably as a result of the greater industrial activity in these cities.

6.3.5 Zinc - subsurface soils (30-45cm)

Zinc concentrations in subsurface soils from Richmond are shown in Table 6.2. The geometric mean for subsurface garden soils is almost 3 times higher than that reported for areas of open space (141 μg/g compared with 53 μg/g). This difference is statistically significant ($P < 0.01$). For both land-use categories, the Zn concentrations are higher in topsoil samples than subsurface samples, reflecting greater Zn enrichment in the top 15cm, although the difference is not statistically significant ($P > 0.05$). At depths of 30-45cm the geometric mean Zn in garden soils is greater than the corresponding measurement for the topsoils of England and Wales (79 μg/g - McGrath and Loveland, 1992), suggesting disturbance of the soil profile and the possibility of Zn movement down the soil profile.

For soils from areas of open space the geometric mean shown in Table 6.2 is less than that reported for topsoils from England and Wales (53 μg/g and 79 μg/g respectively), which suggests minor anthropogenic influence at 30-45cm in areas of open space. For both land-use categories, but urban gardens in particular, the arithmetic mean for Zn is lower than the geometric mean reflecting the log-normal distribution of the Zn data. Standard deviations are higher than the arithmetic means, a result of the high concentration ranges (36-1128 μg/g for urban gardens and 6-1020 μg/g for areas of open space).

6.3.6 Copper - topsoils (0-15cm)

Copper concentrations in Richmond topsoils are generally lower than those of Pb and Zn (see Table 6.1 and Plates 6.1-6.3), a trend also observed in large-scale geochemical surveys such as those by Webb *et al.* (1978) and McGrath and Loveland (1992). Garden soils have on average 2.5 times higher concentrations of Cu than soils from areas of open space, a geometric mean of 48 μg/g for garden soils compared to 19 μg/g for areas of open space ($P < 0.01$). The geometric and arithmetic means vary as expected with a log-normal distribution, particularly for garden soils which also have a standard deviation which greatly exceeds the arithmetic mean (see Table 6.1).

The range of Cu concentrations for garden soils is also very large, ranging from 13 μg/g, a value similar to that which studies quote as a background concentration, (Baker, 1990; Levinson, 1980 and Vinogradov, 1959), up to a concentration nearly 100 times greater than this of 1130 μg/g (see Table 6.1). In topsoils from areas of open space the geometric and arithmetic means are very similar, reflecting the normal distribution of Cu (see Table 6.1). The concentration range for Cu in areas of open space is much smaller than that reported for garden soils, with a much smaller standard deviation (see Table 6.1).

The arithmetic and geometric means reported for topsoils in England and Wales, of 23.1 μg/g and 18 μg/g respectively (McGrath and Loveland, 1992 - see Table 6.5), are very similar to those reported for topsoils from areas of open space in Richmond (see Table 6.1). The corresponding measurements for garden soils are nearly 3 times higher (see Tables 6.1 and 6.5). However, large scale geochemical surveys such as those by Webb *et al.* (1978) and McGrath and Loveland (1992) (based on stream sediments and soils, respectively) reported high concentrations of Cu around London. Archer and Hodgson (1987) report a mean Cu concentration of 18.4 μg/g for agricultural soils in England and Wales, similar to the geometric mean for Cu in soils from areas of open spaces in Richmond (see Table 6.1).

Warren *et al.* (1971) report a mean Cu concentration of 62 μg/g for allotment soils from Liverpool, higher than the geometric mean of 48 μg/g for garden soils from Richmond. Moir (1992) reports a geometric mean of 71.1 μg/g for garden and allotment soils from Richmond, which may reflect a decrease in heavy metal contamination with time or greater exposure to urban contamination in the earlier study. Smaller cities/towns such as Brighton and Shrewsbury have similar geometric means of Cu to that reported for garden soils in this study (Moir, 1992). Thornton and Jones (1984) reported a mean Cu concentration of 127 μg/g for an garden/allotment in London close to a railway, mean concentrations comparable to that observed for garden soils in this study are reported for Stoke and Scunthorpe (46 μg/g and 33 μg/g for Stoke and 32 μg/g and 31 μg/g for Scunthorpe - Thornton and Jones, 1984).

In the U.S.A. a number of studies report Cu concentrations lower than the geometric mean for garden soils in Richmond, and these include median concentrations of 29 μg/g and 17.2 μg/g for Washington (Preer *et al.*, 1984) and Baltimore (Mielke *et al.*, 1984) respectively. Ritter and Rinefierd (1983) report a mean Cu concentration of 20 μg/g for urban garden soils in Dayton, Ohio.

Polemio *et al.* (1982) report a mean Cu concentration of 95 μg/g for industrialised parts of Bari, southern Italy, higher than both mean concentrations for garden soils in Richmond (48 and 69 μg/g). Lux (1991) also reports a significantly higher mean Cu concentration of 81 μg/g for the industrial city of Hamburg. A very low median Cu concentration is reported for soils In Warsaw of 6 μg/g. Hewitt and Candy (1990) report a similar mean Cu concentration for Cuenca, Ecuador to that reported for garden soils in Richmond of 70 μg/g, whilst a higher mean concentration of 142 μg/g was reported for Hong Kong (Tam *et al.* 1987 - see Table 6.1). Chon *et al.* (1995) report a geometric mean of 64 μg/g for soils in Seoul, South Korea, higher than that reported for garden soils in Richmond. Copper concentrations in garden soils from Richmond are generally lower in comparison with larger and more industrial cities such as Bari and Seoul.

6.3.7 Copper - subsurface soils (30-45cm)

The geometric mean for Cu in subsurface garden soils of 41 μg/g is approximately 3 times higher than that reported for subsurface soils in areas of open space of 14 μg/g ($P < 0.01$). The geometric means of Cu in topsoils are numerically higher than those reported for corresponding subsurface soils (48 μg/g and 41 μg/g, respectively for garden soils and 19 μg/g and 14 μg/g, respectively for areas of open space), although these are not significantly higher ($P > 0.05$). The average concentrations of Cu in subsurface garden soils are higher than those reported for topsoils in England and Wales (McGrath and Loveland, 1992), with arithmetic and geometric means of 23.1 μg/g and 18 μg/g for topsoils in England and Wales (McGrath and Loveland, 1992) compared to 78 μg/g and 41 μg/g, respectively for subsurface garden soils in Richmond. The corresponding values for Cu in subsurface soils from areas of open space are 21 μg/g and 14 μg/g respectively. This suggests some anthropogenic additions of Cu to subsurface garden soils, probably aided by the disturbance of the soil profile in gardens.

The Cu data in general are log-normally distributed, as illustrated by the differences between the arithmetic and geometric means for the respective land-uses, particularly subsurface garden soils. The standard deviation and concentration range are higher for Cu in subsurface soils (201 μg/g and 9-1420 μg/g, respectively for garden soils and 32 μg/g and 2-246 μg/g, respectively for areas of open space), than those reported for topsoils (see Table 6.1). The geometric mean for Cu in subsurface garden soils from Richmond is higher than those reported for the topsoils of England and Wales (geometric means of 41 μg/g and 18 μg/g, respectively).

6.3.8 Cadmium - topsoils (0-15cm)

The statistical analysis of the Cd data is influenced by the fact that nearly 60 % of garden soils have Cd concentrations below the analytical detection limit (0.2μg/g), whilst for soils from areas of open space this percentage is nearly 80%. Analytical quality for Cd is very good (see Tables 5.1, 5.2, 5.5, 5.6, 5.9 and 5.10), and therefore the results presented in Table 6.1 are a true reflection of Cd concentrations in Richmond soils. For both garden soils and soils from areas of open space the geometric means and the arithmetic means are < 0.2 μg/g. Cadmium is however more abundant in garden soils, as reflected in the lower percentage of soils below the detection limit of 0.2 μg/g for Cd. The standard deviation is also higher for garden soils and the range shows a maximum value of almost 10 times greater than the corresponding value for soils from areas of open space. The arithmetic and geometric means for both the land-use categories in Richmond, < 0.2 μg/g, are significantly lower than the corresponding results for topsoils in England and Wales of 0.8 μg/g and 0.64 μg/g (McGrath and Loveland, 1992 - see Table 6.5). Archer and Hodgson (1987) report a similar geometric mean to McGrath and Loveland (1992) for Cd in agricultural soils from England and Wales of 0.6 μg/g.

A number of urban studies report higher concentrations of Cd than those observed in soils from Richmond. Warren *et al.* (1971) report a Cd mean of 0.8 μg/g for allotment soils in Liverpool, whilst Thornton and Jones report Cd concentrations of > 2 μg/g for garden/allotment sites in London. This paper also reports Cd concentrations of > 0.2 μg/g for several urban locations in Britain. Moir (1992) reports a geometric mean for Cd of 0.41 μg/g for garden/allotments soils from Richmond, with several urban locations having mean Cd concentrations close to the detection limit (Guildford, Leeds, Shrewsbury and York).

In the U.S.A., median Cd concentrations of 0.56 μg/g and 0.70 μg/g are reported for Baltimore (Mielke *et al.*, 1984) and Washington (Preer *et al.*, 1984), respectively. Ritter and Rinefield (1983) report a mean Cd concentration of 1.65 μg/g for Dayton, Ohio, considerably higher than the other north American studies. These concentrations are all higher than the geometric means for soils in Richmond. Mean Cd concentrations of 0.5 μg/g and 0.53 μg/g are reported for an Industrial part of Bari, Italy (Polemio *et al.*, 1982) and Salamanca, Spain (Sanchez-Camazano *et al.*, 1994), respectively. Mean Cd concentrations of 1.2 μg/g and 8.3 μg/g are reported for the industrial city of Hamburg (Lux, 1991) and the industrial area of Upper Silesia (Gzyl, 1990), respectively. A median concentration of < 0.3 μg/g is reported for soils in Warsaw, similar to mean values reported for Richmond (see Table 6.1).

A mean Cd concentration of 0.36 μg/g was reported for soils 5.5 km from the city of Cuenca, Ecuador (Hewitt and Candy, 1990), whilst Tam *et al.* (1987) report a mean Cd concentration of 1.2 μg/g for soils in Hong Kong. Chon *et al.* (1995) report a geometric mean of 3 μg/g for soils from the industrial city of Seoul, south Korea. All of these urban studies report higher concentrations than those reported in this study.

6.3.9 Cadmium - subsurface soils (30-45cm)

A higher percentage of subsurface soils than topsoils have Cd concentrations lower than the ICP-AES analytical detection limit of 0.2 μg/g, see Table 6.2. A lower percentage of these are from urban gardens than areas of open space (approximately 74 % and 94 %, respectively), something which may reflect higher anthropogenic inputs of Cd to urban garden soils. The concentration ranges are also lower for corresponding topsoils, which may reflect some accumulation of Cd in the top 15cm, relative to 30-45cm (see Tables 6.1 and 6.2).

6.3.10 Nickel - topsoils (0-15cm)

The Ni data for both land-uses have a distribution which is closer to Gaussian than that observed for Pb, Zn and Cu, with similar geometric and arithmetic means, and a standard deviation of approximately half the arithmetic mean. The concentration ranges are also much less than that seen for Pb, Zn and Cu, with a peak concentration 11 times greater than the lowest concentration of 10 μg/g for garden soils (see Table 6.1). Although

Ni enhancement in urban gardens is low, the arithmetic mean concentration is significantly higher than that observed for topsoils in areas of open space, see Table 6.1 ($P < 0.01$). The concentration range for soils from areas of open space is less than that for garden soils, with a lower minimum concentration (3 μg/g compared to 10 μg/g), and a lower peak concentration (74 μg/g compared to 110 μg/g). In general, the mean values for Ni from both land-uses, are close to the baseline concentrations for these areas.

The arithmetic and geometric means for topsoils in England and Wales (McGrath and Loveland, 1992) are 24.5 μg/g and 19.6 μg/g, respectively, see Table 6.5, which are similar to those from areas of open space, and lower than those reported for garden soils (see Table 6.1). Archer and Hodgson (1987) report a geometric mean of 22.6 μg/g for agricultural soils in England and Wales, whilst Berrow and Reaves (1984) report a geometric mean of 27 μg/g for Scottish soils.

Warren *et al.* (1971) report a mean concentration of 27 μg/g for allotment/garden soils in Liverpool, whilst Thornton and Jones (1984) report Ni concentrations of 32 μg/g and 26 μg/g for garden/allotments in London. These are generally similar to the geometric mean for garden soils in Richmond (24 μg/g). Moir (1992) reports a geometric mean of 25.6 μg/g for allotment/gardens in Richmond, similar to the geometric mean reported for garden soils in this study (see Table 6.1).

In the U.S.A. a mean concentration of 2.8 μg/g is reported for Baltimore (Mielke *et al.*, 1984), much lower than the reported mean for this study, and something which may relate to differences in the extraction and analytical techniques. In Bari, southern Italy, a mean Ni concentration of 51.5 μg/g is reported for the industrial part of the city. Lux (1991) reports a mean Ni concentration of 31 μg/g for Hamburg an industrial city in Germany, whilst a median concentration of 4 μg/g is reported for soils in Warsaw (PIG, 1992).

6.3.11 Nickel - subsurface soils (30-45cm)

The arithmetic mean concentration for Ni in subsurface garden soils of 25 μg/g, is significantly higher than that for areas of open space (18 μg/g - $P < 0.01$). This is probably the result of small anthropogenic additions of Ni to subsurface soils in urban gardens, a trend also observed for topsoils (see Table 6.1). Sources of Ni are summarised in Table 3.1. The mean concentrations reported in subsurface soils, see Table 6.2, for both land-uses, are not significantly different to those for topsoils for corresponding land-uses, $P > 0.05$ (see Table 6.1). For Ni data in general, the arithmetic mean and geometric means are very similar, reflecting the normal distribution of the data. The concentration range for Ni is also very similar for both depths for areas of open space (see Tables 6.1 and 6.2). The arithmetic mean for Ni in subsurface garden soils is similar to that reported for topsoils in England and Wales (McGrath and Loveland, 1992); 25 μg/g and 24.5 μg/g respectively.

Table 6.1. Concentrations of selected metals (μg/g) in topsoils (0-15cm) in the London Borough of Richmond-upon-Thames

	Garden Soil (n=106)				Open space (n=108)			
	GM	AM	SD	Range		GM	AM	SD
Range								
Pb	271	362	330	34-1840	93	138	169	26-1210
Zn	179	240	240	37-1810	66	84	80	11-657
Cu	48	69	119	13-1130	19	24	22	4-164
Cd*	<0.2	<0.2	1.88	<0.2-11.1	<0.2	<0.2	0.28	<0.2-1.2
Ni	24	26	12	10-110	17	19	10	3-74

* For Cd:

64 of 106 samples were below detection limit (0.2 μg/g) for garden soil samples.
94 of 108 samples were below detection limit (0.2 μg/g) for open space samples.

GM Geometric mean

AM Arithmetic mean

SD Standard Deviation

Table 6.2. Concentrations of selected metals ($\mu g/g$) in subsurface soils (30-45cm) in the London Borough of Richmond-upon-Thames

	Garden soil (n=106)				Open space (n=108)			
	GM	AM	SD	Range	GM	AM	SD	Range
Pb	208	336	565	28-1940	54	108	178	8-1420
Zn	141	214	331	36-1128	53	73	113	6-1020
Cu	41	78	201	9-1420	14	21	32	2-246
Cd*	<0.2	<0.2	1.1	<0.2-3.6	<0.2	<0.2	0.4	<0.2-1.4
Ni	23	25	15	9-78	16	18	11	2-74

* For Cd:

79 of 107 samples were below detection limit (0.2 $\mu g/g$) for garden soil samples.
102 of 108 samples were below detection limit (0.2 $\mu g/g$) for open space samples.

GM	Geometric mean
AM	Arithmetic mean
SD	Standard Deviation

6.3.12 Lithium - Topsoils (0-15cm)

The arithmetic mean values for Li concentrations in topsoils from urban gardens and areas of open space are not significantly different (14 $\mu g/g$ and 11 $\mu g/g$, respectively - $P > 0.05$). This suggests that, in general, anthropogenic additions of this element to topsoils in Richmond are minimal. The arithmetic and geometric means are similar for both land-use categories, reflecting the normal distribution of the data (see Table 6.3). The standard deviation and concentration range for Li are, however, higher for garden topsoils than for topsoils from areas of open space (22 $\mu g/g$ and 4-229 $\mu g/g$, respectively for garden soils and 7 $\mu g/g$ and 3-43 $\mu g/g$, respectively for areas of open space). The high standard deviation and concentration range for garden soils are a result of a single high Li concentration. If this is removed from the data set the standard deviation and concentration range are similar for garden soils and areas of open space. No data for Li are reported in the Soil Geochemical Atlas of England and Wales (McGrath and Loveland, 1992). No Li data exist for other urban areas to make comparisons with.

6.3.13 Lithium - subsurface soils (30-45cm)

The statistics reported for Li in subsurface soils are similar for both land-uses (see Table 6.4). The arithmetic mean concentration for Li in subsurface soils does not vary with land-use (13 μg/g and 12 μg/g - $P > 0.05$). This reflects insignificant anthropogenic additions of Li to soils in Richmond in general, a trend also observed for topsoils. The geometric means and arithmetic means are similar within individual land-use categories, reflecting the normal distribution of the Li data in general (12 μg/g and 13 μg/g, respectively for garden soils and 10 μg/g and 12 μg/g, respectively, for areas of open space). The concentration ranges and standard deviations are small for both land use categories, although the concentration range of Li is higher in areas of open space than in garden soils, the data set being influenced by one high concentration in Richmond Park (see Table 6.4). Li concentrations in subsurface soils are not significantly different to those reported for topsoils in corresponding land-use categories (arithmetic means of 14 μg/g and 13 μg/g for topsoils and subsurface soils, respectively, for garden soils and 11 μg/g and 12 μg/g for topsoils and subsurface soils, respectively, for areas of open space - $P > 0.05$ for both categories).

6.3.14 Sodium - topsoils (0-15cm)

The arithmetic mean of 259 μg/g for Na in garden topsoils is significantly higher than the 155 μg/g for Na in topsoils from areas of open space ($P < 0.01$). This suggests that there are some anthropogenic additions of Na to garden soils, a trend shown in Plate 6.7. The geometric and arithmetic means within individual land-use categories are similar, reflecting the normal distribution of the data (see Table 6.3). The concentration range of Na in garden topsoils is larger than that for areas of open space in Richmond as is the corresponding standard deviation (see Table 6.3). This is influenced by one very high concentration of Na in garden soils (3440 μg/g) and the removal of this produces a similar standard deviation and concentration range for both land-use categories. However, the removal of this high Na concentration does not alter the statistically significant difference for Na in topsoils from areas of open spaces and garden soils. This can probably be explained by the practice of salting roads in the winter, the season when sampling was undertaken.

The arithmetic and geometric mean concentrations for topsoils in England and Wales are 332 μg/g and 262 μg/g, respectively, (McGrath and Loveland, 1992 - see Table 6.6), and these are higher than corresponding measurements for both land-uses in Richmond, particularly those for areas of open space in Richmond (see Table 6.3).

Moir (1992) reports a Na geometric mean concentration of 290 μg/g for garden/allotment soils from Richmond, which compares to a geometric mean of 207 μg/g for garden soils in this study. The higher concentration in the earlier study may reflect differences in the age of property between the two studies, differences regarding the distance of sampling sites from major roads or natural variation of the geochemical signature. The geometric mean observed for Richmond in this study is lower than for any of the other cities/towns studied by Moir (1992), with an overall geometric mean of 376 μg/g reported for ten towns and cities. It is unclear why the geometric mean for Richmond observed in this study should be so much lower than for other parts of England. Parent material may account for this.

6.3.15 Sodium - subsurface soils (30-45cm)

The geometric mean of 206 μg/g reported for subsurface garden soils is significantly higher than the corresponding measurement for subsurface soils from areas of open space of 127 μg/g ($P < 0.01$). This reflects anthropogenic additions of Na to garden soils in general, at depths of 0-15cm and 30-45cm. Urban soils are subject to disturbance and the sandy nature of soils in general in Richmond (see section 6.4) may result in leaching of soil material down the profile. Sodium is highly soluble (Kabata-Pendias and Pendias, 1984). The geometric means for Na in subsurface soils are not significantly different to those reported for topsoils from corresponding land-uses ($P > 0.05$ - see Tables 6.3 and 6.4) illustrating that concentrations of Na do not decrease significantly with depth from the top 15cm to 30-45cm. The arithmetic and geometric means are different within individual land-use categories (see Tables 6.4), reflecting the log-normal distribution of the data.

6.3.16 Potassium - topsoils (0-15cm)

The arithmetic mean concentration of K in topsoils from urban gardens of 2957 μg/g is not significantly different to the arithmetic mean for K in topsoils from areas of open space of 2784 μg/g ($P > 0.05$). This probably suggests insignificant anthropogenic additions of K to topsoils in Richmond, with geological/pedogenic processes exerting the strongest influence on the distribution of K. The geometric and arithmetic means are similar within individual land-use categories (see Table 6.3), reflecting the normal distribution of the data. The concentration range and standard deviation for K in topsoils from areas of open spaces are larger than those reported for urban garden soils (861 μg/g and 1470-7060 μg/g, respectively for garden soils and 1475 μg/g and 928-10100 μg/g, respectively for areas of open space). The arithmetic and geometric means for topsoils in England and Wales (McGrath and Loveland, 1992) are 4921 μg/g and 4074 μg/g, respectively which are significantly higher than corresponding measurements for either land-use in Richmond (see Table 6.3).

Moir (1992) report a geometric mean of 2881 μg/g for garden/allotment soils from Richmond, very similar to the 2844 μg/g reported in this study. Moir (1992) observed that the mean concentration for Richmond was lower than corresponding measurement for the other towns/cities in the study. This is probably a result of the sandy nature of the soils in Richmond (see section 6.4).

6.3.17 Potassium - subsurface soils (30-45cm)

The arithmetic mean for K in subsurface garden soils of 2980 μg/g is not significantly different to that reported for areas of open space of 2800 μg/g ($P > 0.05$). This is consistent with the trend reported for K in topsoils, and probably reflects insignificant anthropogenic additions of K to soils in Richmond. The arithmetic means for both topsoil categories are not significantly different to those reported for corresponding subsurface soils ($P > 0.05$), although the concentration range is higher for garden topsoils (see Tables 6.3 and 6.4). Potassium concentrations do not decrease significantly from the top 15cm to 30-45cm in soils from Richmond. The arithmetic and geometric means are similar within respective land-uses reflecting the normal distribution of the K data in general (see Table 6.4). The concentration range is higher for K in soils from areas of open space (see Table 6.4), although this is due to one very high K concentration in Richmond Park, 13200 μg/g, and the removal of this sample produces a similar concentration range for both land-use categories.

6.3.18 Magnesium - topsoils (0-15cm)

The arithmetic mean for garden soils of 1766 μg/g is not statistically different to the mean for areas of open space of 1725 μg/g ($P > 0.05$). This suggests insignificant additions of Mg to soils in Richmond. Within individual land-use categories, the geometric and arithmetic mean are very similar (1692 μg/g and 1766 μg/g, respectively for garden soils and 1511 μg/g and 1725 μg/g, respectively for soils in areas of open space), reflecting the normal distribution of the data. The concentration range and standard deviation are higher for soils in areas of open space (see Table 6.3) due to a single data point. Removal of this results in similar concentration ranges for the two land-use categories.

McGrath and Loveland (1992) report arithmetic and geometric mean concentrations for Mg of 3736 μg/g and 2735 μg/g, respectively for topsoils in England and Wales, higher than the corresponding values in this study. This relates to variations in Mg concentrations in relation to parent material across England and Wales and possibly due to differences in the extraction techniques used in the two studies (see section 7.1.1). Moir (1992) reports corresponding values of 1731 μg/g and 1797 μg/g for Richmond, similar to the values reported for garden soils in this study. Moir (1992) reported that the geometric mean for Richmond was significantly lower ($P < 0.01$) than the overall mean for ten cities/towns in England. This may reflect the high sand and gravel content of soils in Richmond (see section 6.4).

6.3.19 Magnesium - subsurface soils (30-45cm)

The arithmetic mean concentration of 1815 μg/g for subsurface garden soils is not significantly different to the 1771 μg/g reported for soils of the same depth in areas of open space ($P > 0.05$). This is consistent with the trend observed for topsoils and illustrates that anthropogenic additions of Mg to soils in Richmond are probably minimal. The arithmetic means for the respective topsoil categories are not significantly different to subsurface soils for the corresponding land-use (1766 and 1815 μg/g respectively, for garden soils and 1725 and 1771 μg/g respectively, for areas of open space, both $P > 0.05$). Magnesium concentrations do not decrease in general from 0-15cm to 30-45cm. The arithmetic and geometric means are similar within individual land-use categories, reflecting the normal distribution of the data (see Table 6.4). The concentration range and standard deviation are greater for soils from areas of open space in Richmond, although this is a result of one very high Mg concentration in a sample from Richmond park. The concentration range for garden topsoils is higher than that reported for subsurface garden soils (see Table 6.3 and 6.4), which may result from some anthropogenic additions of Mg in places, or natural variation of the geochemical signature for a particular parent material.

6.3.20 Beryllium - topsoils (0-15cm)

The arithmetic mean concentration of Be in topsoils from urban gardens of 1.29 μg/g, is significantly higher than that reported for topsoils from areas of open space (0.85 μg/g - $P < 0.01$). This suggests that minor anthropogenic additions of Be occur to garden soils, most probably through the disposal of fossil fuel residues (see Table 3.2). For individual land-use categories the geometric and arithmetic mean are very similar, reflecting the normal distribution of the data (see Table 6.3). The concentration ranges and standard deviations are also of a similar magnitude (0.5-7 μg/g and 0.76 μg/g, respectively for garden soils compared with 0.2-5 μg/g and 0.54 μg/g, respectively for areas of open space). In general Be concentrations are low in Richmond soils.

No data for Be are included in the Soil Geochemical Atlas England and Wales (McGrath and Loveland, 1992). Kabata-Pendias and Pendias (1984) report a mean Be concentration of 0.54 μg/g for soils in Great Britain, lower than for both land-use categories in this study, whilst Asami and Kubota (1995) report mean Be concentrations for several countries similar to those reported for garden soils in Richmond. These include 1.17 μg/g for Japan, 1.56 μg/g for the former USSR, 0.99 μg/g for New Zealand and 1.43 μg/g for Thailand.

6.3.21 Beryllium - subsurface soils (30-45cm)

The arithmetic mean concentration of Be for subsurface garden soils of 1.23 μg/g is significantly higher than that reported for areas of open space of 0.85 μg/g ($P < 0.01$). This is consistent with the trend observed for topsoils, and suggests minor anthropogenic additions of Be to garden soils in Richmond. The arithmetic mean for Be in garden topsoils is not significantly different to that reported for subsurface soils (1.29 and 1.23, respectively -$P > 0.05$). This is also observed for soil profiles in areas of open space (0.85 μg/g and 0.85 μg/g, respectively - $P > 0.05$), which illustrates that the concentration of Be does not decrease significantly from 0-15cm to 30-45cm. The arithmetic and geometric means are similar within individual land-use categories (see Table 6.4), reflecting the normal distribution of the data. The concentration range and standard deviation are higher for garden soils, 0.6-6 μg/g and 0.76 μg/g, respectively compared with 0.2-5 μg/g and 0.55 μg/g, respectively for areas of open space. The highest concentration range is observed for garden topsoils (0.5-7 μg/g).

6.3.22 Calcium - topsoils (0-15cm)

The geometric mean of 5539 μg/g for Ca in topsoils from urban gardens is significantly higher than the 1759 μg/g reported for Ca in topsoils from areas of open space, see Table 6.3 ($P < 0.001$). This suggests high anthropogenic additions of Ca to gardens soils, with possible sources being the burial of building material such as gypsum, plaster and concrete, and the use of fertilisers (see Table 3.2). This confirms the trend observed in Plate 6.10 which showed high concentrations of Ca associated with areas of housing in Richmond. The geometric means, particularly for Ca in topsoils from areas of open space, are significantly lower than the arithmetic means within individual land-use categories, due to the log-normal distribution of the data (see Table 6.3). The standard deviation and concentration range are higher for Ca in topsoils from areas of open space (see Table 6.3) and this is a result of one very high concentration in Bushy Park, which is likely to be a result of anthropogenic activity (see section 6.2.11). The removal of this value from the data set greatly decreases the standard deviation and concentration range of Ca in topsoils from areas of open space.

The arithmetic mean of Ca in the topsoils of England and Wales is 13853 μg/g (McGrath and Loveland, 1992) much higher than for soils from Richmond. This is because the arithmetic mean for soils from England and Wales is skewed by data from calcareous soils. There are no calcareous soils in Richmond (see section 4.5). The geometric mean for soils from England and Wales is 3776 μg/g and this compares to 5539 μg/g for garden soils in Richmond, suggesting significant additions of Ca to garden soils in Richmond.

Moir (1992) reports a geometric mean of 8428 μg/g for garden/allotment soils in Richmond, a value significantly higher than the corresponding measurement for this study, and possibly reflects greater use of fertilisers and lime in allotments in particular. The geometric means for the other towns/cities in the study by Moir (1992) are also higher than the corresponding measurement in this study.

6.3.23 Calcium - subsurface soils (30-45cm)

The geometric mean for Ca in subsurface garden soils of 5553 μg/g is significantly higher than that reported for areas of open space of 1691 μg/g ($P < 0.01$). This trend was also observed for topsoils and confirms significant anthropogenic additions of Ca to garden soils. The geometric mean for Ca in garden topsoils, 5539 μg/g, is not significantly different to that reported for subsurface soils, 5553 μg/g ($P > 0.05$). This is also observed for areas of open space; 1759 μg/g compared with 1691 μg/g, respectively ($P > 0.05$), suggesting that Ca concentrations do not decrease significantly from 0-15cm to 30-45cm of the soil profile. The arithmetic and geometric means within individual land-use categories are different reflecting the log-normal distribution of the Ca data (see Table 6.4). The concentration range and standard deviation for Ca are greater in samples from areas of open space (see Table 6.4).

6.3.24 Strontium - topsoils (0-15cm)

The arithmetic mean of 44 μg/g for Sr in garden topsoils is significantly higher than the 25 μg/g reported for areas of open space ($P < 0.01$). This suggests some anthropogenic input of Sr in urban gardens, possibly, through the burial of building material such as gypsum, and the disposal of fossil fuel residues. The geometric and arithmetic means are similar within individual land-use categories (see Table 6.3), as a result of the normal distribution of the data. The standard deviation and concentration range are higher for Sr in topsoils from urban gardens, 25 μg/g and 13-182 μg/g, respectively for garden soils and 19 μg/g and 7-126 μg/g, respectively for areas of open space. This is probably due to greater additions of Sr to urban soils than soils in areas of open space.

The arithmetic and geometric means for topsoils in England and Wales are 45.3 μg/g and 30 μg/g, respectively (McGrath and Loveland, 1992), which are higher than those observed for areas of open space. The geometric mean for garden soils in Richmond is higher than the corresponding concentration for soils in England and Wales (McGrath and Loveland, 1992 - see Tables 6.3 and 6.6).

Moir (1992) reports a geometric mean Sr concentration of 50.5 μg/g for garden/allotment soils in Richmond, higher than the geometric mean observed in this study (39 μg/g). Calcium and Sr are highly correlated due to geochemical similarities (McGrath and Loveland, 1992), and the higher concentrations of Ca observed in the study by Moir (1992) through anthropogenic additions of Ca may be responsible for the observed higher concentrations of Sr. Strontium will undergo isomorphous substitution into many of the same minerals as Ca. As with Ca, all the towns/cities studied by Moir (1992) have higher geometric means of Sr than observed in this study, with an overall geometric mean of 58.8 μg/g.

6.3.25 Strontium - subsurface soils (30-45cm)

The arithmetic mean for Sr in subsurface garden soils of 46 μg/g is significantly higher than that reported for areas of open space of 26 μg/g ($P < 0.01$). This trend was also observed for topsoils, and reflects minor anthropogenic additions of Sr to garden soils in general. The geometric means for Sr in topsoils are not statistically different to those reported for subsurface soils (39 μg/g and 39 μg/g, respectively for garden soils and 21 μg/g and 21 μg/g, respectively for soils from areas of open space - both $P > 0.05$). This illustrates that Sr concentrations do not decrease significantly from 0-15cm to 30-45cm. The arithmetic and geometric means are similar within individual land-use categories, reflecting the normal distribution of the Sr data (see Table 6.4). The concentration range and standard deviation are higher for garden soils, 13-136 μg/g and 34 μg/g, respectively, compared with 5-107 μg/g an 22 μg/g, respectively for areas of open space. The concentration ranges for Sr in subsurface soils in general are lower than those reported for topsoils (see Tables 6.3 and 6.4).

6.3.26 Barium - topsoils (0-15cm)

The geometric mean for Ba in topsoils from urban gardens of 188 μg/g is significantly higher than the 85 μg/g reported for Ba in topsoils from areas of open space, see Table 6.3 ($P < 0.001$). This suggests significant anthropogenic additions of Ba to garden soils possibly through the flaking of paint in which Ba is used as a filler (see Table 3.2), and the burning of fossil fuel and the disposal of coal-ash (see Table 3.2). This confirms the trend observed in Plate 6.13. The standard deviation and concentration range for garden topsoil data are also greater than those observed in topsoils from areas of open space (115 μg/g and 40-608μg/g, respectively for garden soils, compared to 69 μg/g and 26-458 μg/g, respectively for areas of open space).

The geometric and arithmetic means for Ba in the topsoils of England and Wales are 114.5 μg/g and 141 μg/g, respectively (McGrath and Loveland, 1992 - see Table 6.6). These compare with 188 μg/g and 215 μg/g, respectively for garden soils, suggesting significant additions of Ba to garden soils in Richmond. Soils from areas of open space have corresponding values of 85 μg/g and 100 μg/g, respectively.

Moir (1992) reports a geometric mean of 232 μg/g for garden/allotment soils in Richmond, higher than the corresponding measurement in this study (188 μg/g). With the exception of Brighton (GM of 148 μg/g) all the other towns/cities in the study by Moir (1992) have higher geometric mean values, reflecting greater anthropogenic additions of Ba to these allotment/garden soils, or possibly naturally higher concentrations as a result of parent material.

6.3.27 Barium - subsurface soils (30-45cm)

The geometric mean for Ba in subsurface garden soils of 159 μg/g is significantly higher than that reported for areas of open space of 81 μg/g ($P < 0.001$). This trend is also observed in topsoils, and reflects greater anthropogenic additions of Ba to garden soils. There is no significant difference between the geometric means for the different soil sample depths within individual land-use categories; 188 μg/g and 159 μg/g, respectively for garden soils and 85 μg/g and 81 μg/g, respectively for areas of open space (both $P > 0.05$). Barium concentrations do not decrease significantly from 0-15cm to 30-45cm. The arithmetic and geometric means differ within individual land-use categories reflecting the log-normal distribution of the data (see Table 6.4). The concentration ranges and standard deviations are similar for both land-use categories (see Table 6.4) with the concentration range for subsurface garden soils, in particular, similar to that reported for the corresponding topsoils (see Tables 6.3 and 6.4).

6.3.28 Aluminium - topsoils (0-15cm)

The arithmetic mean for Al in topsoils from urban gardens of 1.67 % is significantly higher than that reported for Al in topsoils from areas of open space of 1.54 μg/g, see Table 6.4 ($P < 0.05$). This suggests some anthropogenic additions of Al to urban gardens in Richmond, most probably through the use of fertilisers. This confirms the trend observed in Plate 6.14. The geometric and arithmetic means of Al within individual land-use categories are similar, reflecting the overall normal distribution of the data (see Table 6.3). The standard deviation and concentration range are higher for Al in topsoils from areas of open space than for Al in topsoils from urban gardens (0.72 % and 0.54-4.26 %, respectively for areas of open space compared with 0.48 and 0.6-3.91 %, respectively for garden soils). It seems that a combination of anthropogenic and geological/pedogenic processes strongly influence the concentrations of Al in topsoils from Richmond.

The mean concentrations observed for topsoils from Richmond in general are significantly lower than those reported for topsoils in England and Wales which have geometric and arithmetic means of 2.38% and 2.79% respectively (McGrath and Loveland, 1992 - see Table 6.6). Lower concentrations of Al in soils from Richmond in comparison with topsoils in England and Wales in general, are probably the result of parent material, with Richmond soils generally having a low clay content (on average, approximately 5% - see section 6.4).

Moir (1992) reports a geometric mean of 1.44 % for garden/allotment soils in Richmond, very similar to the 1.61 % observed in this study. In the study by Moir (1992) the concentration for Richmond was significantly lower than the overall mean for ten towns/cities in a study of England, and confirms the importance of geological/pedogenic influences on the distribution of Al.

6.3.29 Aluminium - subsurface soils (30-45cm)

The arithmetic mean for Al in subsurface garden soils of 1.70 % is significantly higher than that reported for areas of open space of 1.58 % ($P < 0.05$). This trend was also observed for topsoils and probably reflects minor additions of Al to garden soils. The arithmetic means for topsoils are not statistically different to those reported for subsurface soils; 1.67 % and 1.70 %, respectively, for garden soils and 1.58 % and 1.54 %, respectively for areas of open space (both $P > 0.05$). Aluminium concentrations do not decrease significantly from 0-15cm to 30-45cm. The arithmetic and geometric means do not differ greatly within individual land-use categories (see Table 6.4), reflecting the normal distribution of the data. The concentration range and standard deviation are higher for areas of open space (see Table 6.4), a trend also observed for topsoils. This may be the result of minor anthropogenic additions of Al in areas of open space or natural variation of the geochemical signature.

6.3.30 Lanthanum - topsoils (0-15cm)

The arithmetic mean for La in topsoils from urban gardens in Richmond of 18 μg/g is not significantly different to that from areas of open space of 15 μg/g ($P > 0.05$). This suggests insignificant anthropogenic inputs of La to garden soils in Richmond, as seen in Plate 6.15. The arithmetic and geometric means are similar for both land-use categories, reflecting the normal distribution of the La data (see Table 6.3). The standard deviation and concentration range for La in topsoils are higher for soils from areas of open space in Richmond; 3 μg/g and 15-20 μg/g, respectively for garden soils compared with 4 μg/g and 8-30 μg/g, respectively for areas of open space (see Table 6.3). No data are reported for La in the Soil Geochemical Atlas of England and Wales (McGrath and Loveland, 1992).

Moir (1992) reports a geometric mean of 16.8 μg/g for garden/allotments soils from Richmond, very similar to the corresponding measurement in this study (17 μg/g). In the study by Moir (1992) the geometric mean for Richmond, with the exception of Guildford, was significantly lower than for the other towns/cities studied, and is probably a reflection of the importance of sand and gravel as a parent material in Richmond (see section 6.4), having naturally low concentrations of La.

6.3.31 Lanthanum - subsurface soils (30-45cm)

The arithmetic mean for La in subsurface garden soils of 18 μg/g is not significantly different to that reported for areas of open space of 16 μg/g ($P > 0.05$). The arithmetic means for topsoils are not statistically different to those reported for corresponding subsurface soils, 18 μg/g and 18 μg/g, respectively for garden soils and 15 μg/g and 16 μg/g, respectively for areas of open space, (both $P > 0.05$). Lanthanum concentrations do not decrease significantly from 0-15cm to 30-45cm. The arithmetic and geometric means do not differ greatly within individual land-use categories, reflecting the normal distribution of the data in general (see Table 6.4). The concentration range for areas of open space is slightly higher than that reported for garden soils (5-31 μg/g and 10-25 μg/g, respectively), with low standard deviations for both. These are similar to those reported for topsoils (see Table 6.3). In general, the concentration of La does not vary greatly in Richmond soils with regard to land-use or sample depth.

6.3.32 Titanium - topsoils (0-15cm)

The arithmetic mean concentration for Ti in garden topsoils of 686 μg/g is not significantly different to that reported for Ti in topsoils from areas of open space of 712 μg/g ($P > 0.05$). This was also observed in Plate 6.16. The arithmetic and geometric means are similar for both land-use categories, reflecting the normal distribution of the data. The standard deviation and concentration range are slightly higher for Ti in topsoils from areas of open space (131 μg/g and 356-942 μg/g, respectively for garden soils and 161 μg/g and 365-1200 μg/g, respectively for areas of open space). This is influenced by a single high concentration of Ti in Hampton Court, and if this is removed from the data set the standard deviations and concentration ranges for both land-uses are very similar. No data are reported for Ti in the Soil Geochemical Atlas of England and Wales (McGrath and Loveland, 1992).

Moir (1992) reports a geometric mean of 616 μg/g for garden/allotment soils in Richmond, a very similar value to that observed in this study (673 μg/g). As with this study, parent material was considered to be the most important factor influencing the concentration of Ti in urban soils.

6.3.33 Titanium - subsurface soils (30-45cm)

The arithmetic mean for Ti in subsurface garden soils of 704 μg/g is not significantly different to that reported for areas of open space of 723 μg/g ($P > 0.05$). This was also observed for topsoils. The arithmetic means for Ti in topsoils are also not statistically different to those reported for corresponding subsurface soils; 686 μg/g and 704 μg/g, respectively for garden soils and 712 μg/g and 723 μg/,g respectively for areas of open space (both $P > 0.05$). Titanium concentrations do not decrease significantly from 0-15cm to 30-45cm. The arithmetic and geometric means do not differ greatly within individual land-use categories reflecting the normal distribution of the data, see Table 6.4. The standard deviation and concentration range are higher for soils from areas of open space; 407-1170 μg/g and 166 μg/g, respectively compared with 335-985 μg/g and 137 μg/g, respectively for areas of open space. This trend was also observed for topsoils.

6.3.34 Vanadium - topsoils (0-15cm)

The arithmetic mean for V in topsoils from urban gardens of 51 μg/g is significantly higher than that reported for V in topsoils from areas of open space of 47 μg/g ($P < 0.01$). This suggests small anthropogenic additions of V to garden soils, the most likely source being the disposal of fossil fuel residues in gardens (see Table 3.2). This confirms the trend observed in Plate 6.17. The arithmetic and geometric means are very similar for the individual land-use categories (see Table 6.3), reflecting the overall normal distribution of V data in Richmond topsoils. The standard deviations and concentration ranges for V in topsoils from Richmond are also very similar, reflecting very minor anthropogenic sources of V in general (10 μg/g and 29-91 μg/g, respectively for garden soils and 13 μg/g and 21-88 μg/g, respectively, for areas of open space). No data are reported for V in the Soil Geochemical Atlas of England and Wales (McGrath and Loveland, 1992).

Moir (1992) reports a geometric mean V concentration of 50 μg/g V for gardens/allotments soils in Richmond, very similar to the corresponding value observed in this study (51 μg/g). Moir (1992) observed that the concentration for Richmond is similar to the other towns/cities studied, the overall geometric mean being 48.6 μg/g. The burning of fossil fuel and the deposition of the residues from this, probably represent the greatest input of V to urban soils (Jones *et al.*, 1990).

6.3.35 Vanadium - subsurface soils (30-45cm)

The arithmetic mean for V in subsurface garden soils of 50 μg/g is significantly higher than that reported for areas of open space of 46 μg/g ($P < 0.01$). This was also observed for topsoils. The arithmetic means for V in topsoils do not differ statistically to those reported for subsurface soils from corresponding land-uses; 51 μg/g and 50 μg/g, respectively for garden soils and 47 μg/g and 46 μg/g, respectively for areas of open space (both $P > 0.05$). The arithmetic and geometric means do not differ greatly within individual land-use categories (see Table 6.4), reflecting the normal distribution of the data. The concentration range for V is low in general, with a higher standard deviation and concentration range observed for areas of open space (10 μg/g and 35-80 μg/g, respectively for garden soils compared with 14 μg/g and 17-101 μg/g, respectively for areas of open space). These are similar to those reported for topsoils (see Table 6.3).

6.3.36 Chromium - topsoils (0-15cm)

The arithmetic mean for Cr in topsoils from urban gardens of 38 μg/g is significantly higher than that reported for topsoils from areas of open space of 35 μg/g ($P < 0.01$). Small anthropogenic additions of Cr occur close to major roads (Ward *et al.*, 1977 and Ward, 1990a) and through the use of fertilisers and the disposal of fossil fuel residues (see Table 3.2). The arithmetic and geometric means are very similar within individual land-use categories (see Table 6.3), reflecting the normal distribution of the Cr data for topsoils in general. The standard deviations reported in Table 6.3 are low (9 and 8 μg/g) as a result of the low Cr concentration range in topsoils from Richmond. The concentration range is larger for Cr in urban garden topsoils, 23-83 μg/g compared with 17-60 μg/g for areas of open space, probably reflecting greater anthropogenic additions of Cr in urban gardens.

The arithmetic and geometric means for Cr in the topsoils of England and Wales (McGrath and Loveland, 1992) are reported as 41.2 μg/g and 34.2 μg/g, respectively (see Table 6.6). These are similar to those observed for Cr in topsoils from urban gardens in Richmond, and higher than those observed for areas of open space (see Tables 6.3 and 6.6). Archer and Hodgson (1987) report a geometric mean of 42.4 μg/g for agricultural soils from England and Wales, whilst Berrow and Reaves report a geometric mean of 62 μg/g for soils in Scotland. The higher geometric mean for soils in Scotland may result from differences in parent material.

Lux (1991) reports a Cr mean concentration of 52 μg/g in soils from the industrial city Hamburg, Germany. Moir (1992) reports a Cr geometric mean concentration of 32.6 μg/g for garden/allotment soils in Richmond, similar to the corresponding value for this study (38 μg/g). Moir (1992) reported that the mean Cr concentration for Richmond was significantly higher than the overall mean for towns/cities in England (25.7 μg/g). However, in comparison to the large-scale soil surveys such as those by Archer and Hodgson (1987), McGrath and Loveland (1992) and a study by Lux (1991) in Hamburg, the present study suggests that anthropogenic additions to garden soils in Richmond are very minor.

6.3.37 Chromium - subsurface soils (30-45cm)

The arithmetic mean for Cr in subsurface garden soils of 37 μg/g is significantly higher than that reported for areas of open space of 35 μg/g ($P < 0.01$). This trend was also observed for topsoils and probably reflects minor anthropogenic additions of Cr to garden soils in general. The arithmetic means reported for topsoils are not significantly different to those reported for corresponding subsurface soils; 38 μg/g and 37 μg/g, respectively for urban gardens and 35 μg/g and 35 μg/g, respectively for areas of open space (both $P > 0.05$). Chromium concentrations do not decrease significantly from 0-15cm to 30-45cm. The arithmetic and geometric means within individual land-use categories are very similar (see Table 6.4), a result of the normal distribution of the data. The concentration ranges for Cr are generally low and similar for both land-use categories; 23-65 μg/g for garden soils compared with 13-73 μg/g for areas of open space. The standard deviations are also very low, 9 μg/g and 8 μg/g, respectively. The concentration range for garden topsoils is slightly higher than that reported for the corresponding subsurface soils (see Tables 6.3 and 6.4).

6.3.38 Manganese - topsoils (0-15cm)

The geometric mean for Mn in topsoils from urban gardens of 325 μg/g is significantly higher than that reported for areas of open space of 219 μg/g ($P < 0.01$). This probably reflects small anthropogenic additions of Mn to garden soils in Richmond. The arithmetic and geometric means within individual land-use categories are different (see Table 6.3) as a result of the log-normal distribution of the data. The standard deviation and concentration range for Mn are greater in topsoils from areas of open space (180 μg/g and 20-1310 μg/g, respectively for areas of open space, compared with 126 μg/g and 102-985 μg/g, respectively for garden soils). This may be a result of natural variation of the geochemical signature, or an anthropogenic source and both geological/pedogenic and anthropogenic processes are likely to strongly influence the distribution of Mn in topsoils from Richmond, a trend observed in Plate 6.19.

The arithmetic and geometric means of Mn reported for topsoils in England and Wales (McGrath and Loveland, 1992) of 760.9 μg/g and 485 μg/g, respectively, are significantly higher than those observed for topsoils from Richmond. This may be due to high concentrations of Mn associated with clay rich soils in certain areas of Britain (McGrath and Loveland, 1992), or the application of fertilisers to agricultural land (Smith, 1990).

Warren *et al.* (1971) reported a mean of 240 μg/g for allotments in Liverpool, a lower concentration than that for garden soils in Richmond, whilst Polemio *et al.* (1983) report a mean Mn concentration of 329 μg/g for the industrial part of Bari, southern Italy, similar to the geometric mean for garden soils in Richmond (325 μg/g). Moir (1992) reports a geometric mean of 327 μg/g for garden/allotment soils from Richmond (325 for this study) and this is significantly lower than the overall geometric mean for 10 towns/cities in the same study (485 μg/g). This is probably a result of sand dominating soil texture in Richmond (see section 6.4).

6.3.39 Manganese - subsurface soil (30-45cm)

As for topsoils, the geometric mean of Mn in subsurface garden soils of 333 μg/g is significantly higher than that reported for areas of open space of 255 μg/g ($P < 0.01$). The geometric means within the individual land-use categories, for different sample depths are not significantly different; 325 μg/g and 333 μg/g, respectively for garden soils and 219 μg/g and 255 μg/g respectively, for areas of open space (both $P > 0.05$). Manganese concentrations do not decrease significantly from 0-15cm to 30-45cm. The arithmetic and geometric means differ within individual land-use categories (see Table 6.4), a result of the log-normal distribution of the data. The concentration range for Mn is far greater in areas of open space, 35-1820 μg/g compared with 115-913 μg/g for garden soils, although this is influenced by one very high concentration (1820 μg/g). The concentration ranges in subsurface soils are similar to those reported for the corresponding topsoils, particularly for garden soils (see Tables 6.3 and 6.4).

6.3.40 Iron - topsoils (0-15cm)

The arithmetic mean concentration of Fe in topsoils from urban gardens of 2.63 % is significantly higher than that reported for Fe in topsoils from areas of open space, of 2.32% ($P < 0.01$). Elevated concentrations of Fe have been reported in soils close to roads (Harrison *et al.* 1985 and Tam *et al.*, 1987) and the burning of fossil fuels and the disposal of residues may be another source of Fe in urban gardens (see Table 3.2). The arithmetic and geometric means are similar within individual land-use categories (see Table 6.3), as a result of the normal distribution of the Fe data. The concentration range for Fe in topsoils from urban gardens is greater than that reported for areas of open space; 1.36-6.24 % for garden soils compared with 0.28-4.85 % for areas of open space. Higher concentrations of Fe in urban gardens confirm the trend observed in Plate 6.20. The arithmetic and geometric mean concentrations of Fe in the topsoils of England and Wales are reported as 2.78 % and 2.34 % respectively (see Table 6.6), and these are similar to those observed for topsoils from urban gardens in Richmond (see Table 6.3).

Thornton and Jones (1984) report Fe concentrations of 3.1 % and 2.3 % for garden/allotment soils in London, whilst Moir (1992) reports a geometric mean of 2.72 % for Fe in Richmond garden/allotment soils. These compare with a geometric mean of 2.58 % for garden soils in this study. As with this study, the two earlier studies referenced here suggest some anthropogenic additions of Fe to London garden soils. Differences in the underlying geology, along with anthropogenic activities, are also probably responsible for distribution of Fe shown in Plate 6.20. A very low median concentration of 0.46 % is reported for soils in Warsaw (PIG, 1992).

6.3.41 Iron - subsurface soils (30-45cm)

The arithmetic mean for Fe in subsurface garden soils of 2.68 % is significantly higher than that for areas of open space of 2.42 % ($P < 0.01$). This trend was also observed for topsoils. The arithmetic means for the different soil depths within the same land-use categories are not significantly different; 2.63 % and 2.68 %, respectively for garden soils and 2.32 % and 2.42 %, respectively for areas of open space (both $P > 0.05$). Iron concentrations do not decrease significantly from 0-15cm to 30-45cm. The arithmetic and geometric means within individual land-use categories are similar (see Table 6.4) a result of the normal distribution of the data. The concentration range of Fe in garden soils is greater than that reported for areas of open space; 1.46-5.59 % for garden soils compared with 0.47-4.85 % for areas of open space, with similar standard deviations. The concentration ranges for subsurface soils are similar to those reported for topsoils (see Tables 6.3 and 6.4).

6.3.42 Cobalt - topsoils (0-15cm)

The arithmetic mean of Co in topsoils from urban gardens of 9 μg/g is significantly higher than that reported for Co in topsoils from areas of open space of 7 μg/g ($P < 0.01$). This probably reflects small anthropogenic additions to garden soils through the use of fertilisers and the disposal of fossil fuel residues (Smith *et al.*, 1990). This confirms the pattern of Co distribution shown in Plate 6.21. The geometric and arithmetic means are similar within individual land-use categories, reflecting the overall normal distribution of the Co data (see Table 6.3). The standard deviations reported in Table 6.3 are low (both 3 μg/g), a function of the low concentration range of Co in Richmond topsoils. The concentration ranges are very similar for both land-use categories (4-34 μg/g for garden soils and 2-23 μg/g for areas of open space).

The arithmetic and geometric mean concentrations for topsoils in England and Wales (McGrath and Loveland, 1992) are reported as 10.6 μg/g and 8.1 μg/g, respectively (see Table 6.6). These are similar to those reported for urban garden samples from Richmond, see Table 6.3. Archer and Hodgson (1987) report a geometric mean of 7.9 μg/g for agricultural soils in England and Wales, similar to that reported by McGrath and Loveland (1992).

Warren *et al.* (1971) report a mean Co concentration of 8 μg/g for allotments in Liverpool, whilst a median Co concentration of 6 μg/g is reported for soils in Warsaw (PIG, 1992). Moir (1992) reports a Co geometric mean of 10.5 μg/g for garden/allotment soils from Richmond which compares to 9 μg/g for this study. The overall mean for 10 towns and cities in the study by Moir (1992) was 11 μg/g. Moir (1992) suggests that Co concentrations in urban soils are strongly influenced by the use of fertilisers and parent material.

6.3.43 Cobalt - subsurface soils (30-45cm)

The arithmetic mean for Co in subsurface garden soils of 9 μg/g is significantly higher than that observed for areas of open space of 8 μg/g ($P < 0.05$). This trend was also observed for topsoils. The arithmetic means for Co within the individual land-use categories at depths of 0-15cm and 30-45cm are not significantly different; 10 μg/g and 9 μg/g respectively, for garden soils and 8 μg/g and 7 μg/g respectively, for areas of open space (both $P > 0.05$). The arithmetic and geometric means are similar within individual land-use categories (see Table 6.4) as a result of the normal distribution of the data. The concentration range for garden soils is higher than that reported for areas of open space; 4-25 μg/g for garden soils compared with 1-22 μg/g for areas of open space. In general, Co concentrations do not vary greatly across Richmond.

6.3.44 Phosphorus - topsoils (0-15cm)

The geometric mean of P in urban garden topsoils of 1257 μg/g is almost 2 times greater than the geometric mean reported for areas of open space of 693 μg/g - see Table

6.3 ($P < 0.01$). This is considered to be the result of large anthropogenic additions of P through fertiliser use and possibly, through biogeochemical cycling from decaying vegetation. This confirms the P distribution observed in Plate 6.22. The arithmetic and geometric means differ greatly within individual land-use categories (see Table 6.3) as a result of the log-normal distribution of the P data in general. The standard deviation and concentration range are much higher for P in urban garden topsoils (1340 μg/g and 362-10105 μg/g, respectively for garden soils compared with 366 μg/g and 200-2300 μg/g, respectively for areas of open space).

The arithmetic and geometric mean concentrations for topsoils in England and Wales are reported as 848 μg/g and 752 μg/g (McGrath and Loveland, 1992 - see Table 6.6) lower than both land-use categories in Richmond, particularly urban gardens (see Table 6.3).

Moir (1992) reports a geometric mean of 1800 μg/g for allotment/garden soils in Richmond, a value higher than the geometric mean reported for garden soils in this study of 1257 μg/g. The present study did not involve the sampling of allotments which may have greater additions of phosphatic fertilisers. The overall geometric mean for ten towns/cities in England (Moir, 1992) was 1614 μg/g, higher than for this study. Despite this, the present study clearly indicates the importance of anthropogenic additions of P, through greater use of fertilisers and manures in domestic gardens, and possibly greater biogeochemical cycling compared to areas of open space.

6.3.45 Phosphor us - subsurface soils (30-45cm)

The geometric mean for P in subsurface garden soils of 1019 μg/g is significantly higher than that reported for areas of open space of 532 μg/g ($P < 0.01$). This trend was also observed for topsoils and probably reflects significant anthropogenic additions of P to garden soils. The geometric means for topsoils and subsurface soils within individual land-use categories are also significantly different; 1257 μg/g compared with 1019 μg/g, respectively, for garden soils and 693 μg/g and 532 μg/g, respectively for areas of open space (both $P < 0.05$). Phosphorus concentrations are significantly higher in topsoils than in subsurface soils. The arithmetic and geometric means are different within individual land-use categories (see Table 6.4) as a result of the log-normal distribution of the data. The concentration range for P in subsurface garden soils is higher than that reported for areas of open space (249-3810 μg/g compared with 82-1730 μg/g for areas of open space) with a higher standard deviation for garden soils (see Table 6.4). The concentration range for P is highest in garden topsoils, 362-10105 μg/g.

Table 6.3. Concentrations of elements (μg/g) in topsoils (0-15cm) in the London Borough of Richmond-upon-Thames

	Garden soil (n=106)				Open space (n=108)			
	GM	AM	SD	Range	GM	AM	SD	Range
Li	12	14	22	4-229	10	11	7	3-43
Na	207	259	343	59-3440	134	155	108	43-870
K	2844	2957	861	1470-7060	2498	2784	1475	928-10100
Mg	1692	1766	552	750-4450	1511	1725	1044	450-7630
Be	1.18	1.29	0.76	0.5-7	0.75	0.85	0.54	0.2-5
Ca	5539	7381	6297	263-43500	1759	4624	10215	138-75400
Sr	39	44	25	13-182	21	25	19	7-126
Ba	188	215	115	40-608	85	100	69	26-458
Al*	1.61	1.67	0.48	0.6-3.91	1.41	1.54	0.72	0.54-4.26
La	17	18	3	15-20	15	15	4	8-30
Ti	673	686	131	356-942	693	712	161	365-1200
V	50	51	10	29-91	46	47	13	21-88
Cr	38	38	9	23-83	34	35	8	17-60
Mn	325	355	126	102-985	219	276	180	20-1310
Fe*	2.58	2.63	0.59	1.36-6.24	2.18	2.32	0.76	0.28-4.85
Co	9	10	3	4-34	6	7	3	2-23
P	1257	1488	1340	362-10105	693	775	366	200-2300

* Results presented as percentages rather than μg/g

GM	Geometric mean
AM	Arithmetic mean
SD	Standard Deviation

Table 6.4. Concentrations of elements (μg/g) in subsurface soils (30-45cm) in the London Borough of Richmond-upon-Thames

	Garden soil (n=106)				Open space (n=107)			
	GM	AM	SD	Range	GM	AM	SD	Range
Li	12	13	5	3-27	10	12	7	3-52
Na	206	261	326	60-1488	127	154	132	45-1210
K	2876	2980	818	1460-3510	2470	2800	1728	764-13200
Mg	1730	1815	593	852-350	1498	1771	1350	368-10600
Be	1.12	1.23	0.76	0.6-6	0.74	0.85	0.55	0.2-5
Ca	5553	8114	7889	208-49000	1691	5439	9595	71-78400
Sr	39	46	34	13-136	21	26	22	5-107
Ba	159	175	83	50-613	81	99	86	18-676
Al*	1.63	1.70	0.52	0.7-3.29	1.42	1.58	0.82	0.48-5.85
La	17	18	3	10-25	15	16	4	5-31
Ti	690	704	137	335-985	704	723	166	407-1170
V	49	50	10	35-80	44	46	14	17-101
Cr	36	37	9	23-65	34	35	8	13-73
Mn	333	364	169	115-913	255	323	243	35-1820
Fe*	2.61	2.68	0.72	1.46-5.59	2.27	2.42	0.86	0.47-4.85
Co	9	9	4	4-25	7	8	4	1-22
P	1019	1155	632	249-3810	532	625	344	82-1730

* Results presented as percentages rather than μg/g

GM	Geometric mean
AM	Arithmetic mean
SD	Standard Deviation

Table 6.5 Concentrations of metals (μg/g) in topsoils (0-15cm) from England and Wales (McGrath and Loveland, 1992)

	topsoil (n=5692)			
	GM	AM	SD	Range
Pb	45.6	74		3-16338
Zn	79	97.1		5-3648
Cu	18	23.1		1.2-1508
Cd	0.64	0.8		<0.2-40.9
Ni	19.6	24.5		0.8-440

GM Geometric mean

AM Arithmetic mean

SD Standard Deviation

Table 6.6 Concentrations of elements (μg/g) in topsoils (0-15cm) from England and Wales (McGrath and Loveland, 1992)

	topsoil (n=5692)			
	GM	AM	SD	Range
Na	262	332		31-25152
K	4074	4921		60-20444
Mg	2735	3736		41-62690
Ca	3776	13853		50-339630
Sr	30	45.3		3-1445
Ba	114.5	141		11-2973
Al	23823	27917		491-79355
Cr	34.2	41.2		0.2-838
Mn	485	760.9		3-42603
Fe	23496	27852		395-264405
Co	8.1	10.6		0.2-322
P	752	848		41-6273

GM Geometric mean

AM Arithmetic mean

SD Standard Deviation

6.4 The influence of land-use on soil properties

Tables 6.7-6.12 summarise the results of loss-on-ignition, pH and particle size analysis for Richmond soils. The soils in Richmond are dominated by the sand fraction and are mainly defined as sands or loamy sands. Sand generally accounts for approximately 80% of the total size fraction, both for topsoils and subsurface soils, irrespective of land-use. Sand, silt and clay do not vary significantly with parent material ($P > 0.05$), although the percentage of sand is significantly higher in subsurface soils than topsoils ($P < 0.05$) for all parent materials with the exception of London clay (see Tables 6.11 and 6.12). Loss-on-ignition does not vary significantly with land-use or parent material (both $P > 0.05$). Mean percentages of 7.5 and 7.8 are reported for areas of open space and urban gardens, respectively. Soil pH, however, does vary significantly with regard to land-use. A mean pH of 6.5 for garden topsoils is significantly higher than a mean pH of 5.5 for topsoils in areas of open space ($P < 0.001$). This trend is also observed for subsurface soils, with a mean pH of 6.6 for garden soils compared to a mean pH of 5.5 for areas of open space ($P < 0.001$). Soil pH is not observed to vary significantly for different sample depths within the same profile ($P > 0.05$). Significantly higher pH values for garden soils, compared with soils from areas of open space, may result from additions of lime and fertilisers and the prevalence of building materials in garden soil (a source of Ca - see Table 3.2).

Table 6.7. Summary of soil properties in topsoils (0-15cm) from areas of open space in the London Borough of Richmond-upon-Thames

	open space			
	N	AM	SD	Range
pH	50	5.5	1.1	3.7-7.2
LOI%	30	7.5	2.2	4.6-12.8
Sand%	12	80	7.9	75-89
Silt%	12	10	3.2	2-13.2
Clay%	12	7	1.2	3-8.2

N	Sample number
AM	Arithmetic mean
SD	Standard deviation

Table 6.8. Summary of soil properties in topsoils (0-15cm) from urban gardens in the London Borough of Richmond-upon-Thames

	Urban gardens			
	N	AM	SD	Range
pH	50	6.5	0.8	4.2-7.8
LOI%	30	7.8	2.7	4.0-14.3
Sand%	12	81	5.4	74-91
Silt%	12	9	2.2	4.2-11.6
Clay%	12	6	0.8	3.2-6.0

N	Sample number
AM	Arithmetic mean
SD	Standard deviation

Table 6.9 Summary of soil properties in subsurface soils (30-45cm) from areas of open space in the London Borough of Richmond-upon-Thames

	Open space			
	N	AM	SD	Range
pH	50	5.5	1.1	3.9-7.5
LOI%	30	7.5	2.2	4.6-12.8
Sand%	12	84	7.9	72-89
Silt%	12	8	3.2	2-13.2
Clay%	12	5	1.2	3-8.2

N Sample number

AM Arithmetic mean

SD Standard deviation

Table 6.10 Summary of soil properties in subsurface soils (30-45cm) from urban gardens in the London Borough of Richmond-upon-Thames

	Urban gardens			
	N	AM	SD	Range
pH	50	6.6	0.9	4.6-7.8
LOI%	30	7.8	2.7	4.0-14.3
Sand%	12	83	8.4	70-96
Silt%	12	8	3.2	2-12
Clay%	12	6	1.2	2-7

N Sample number

AM Arithmetic mean

SD Standard deviation

Table 6.11 Summary of particle size analysis in topsoils (0-15cm) developed over different parent materials in the London Borough of Richmond-upon-Thames

	mean %			
	N	sand	silt	clay
London clay	3	79	9	7
High level terraces	3	80	10	7
4-river terraces	3	81	10	6
3-river terraces	3	78	14	6
1-river terraces	3	81	9	7
River brickearths	3	83	8	6
alluvium	3	80	10	7

N Sample number

Table 6.12 Summary of particle size analysis in subsurface soils (30-45cm) developed over different parent materials in the London Borough of Richmond-upon-Thames

	mean %			
	N	sand	silt	clay
London clay	3	80	10	6
High level terraces	3	83	8	6
4-river terraces	3	83	8	6
3-river terraces	3	83	9	5
1-river terraces	3	89	5	4
River brickearths	3	85	7	5
alluvium	3	86	6	5

N Sample number

6.5 Overall Summary

In this chapter geochemical maps for 21 elements are presented. These showed the distribution of these elements in topsoils (0-15cm) in Richmond. A number of elements, particularly the metals, were shown to have a distribution strongly linked to the location of housing and road networks in the borough. High concentrations of a number of elements are observed close to the Thames, and the application of students t-tests shows that soils developed over alluvium have significantly higher concentrations of Ca, Sr, Co, Ni, and Cu than soils overlying river terraces and London Clay.

A study of the data as defined by land-use showed that a number of elements were present at significantly higher concentrations in garden soils than in areas of open space. These include Pb, Zn, Cu, Ni, Cr, Be, Sr, Ba, V, Co, Na, Ca, Al, Mn, Fe and P. It is believed that this is probably the result of anthropogenic additions of these elements to soils through vehicle emissions, wearing of vehicle-parts, flaking paint, the burning of fossil fuels and the disposal of fossil fuel residues, the application of various fertilisers, the burial of building materials and the salting of roads in winter. The use of multi-variate statistics (PCA) has shown an association of Ba, Cr, Pb and Zn in garden soils, which is characteristic of a paint or fossil fuel source (see Tables 3.1 and 3.2, and Appendix 3). In general, concentrations of most elements are shown not to differ significantly ($P < 0.05$) with sample depth, despite the generally higher geometric means for a number of elements in topsoils (see Table 6.1-6.4). This may be a result of the general disturbance of soils profiles in urban areas or leaching of elements down the soil profile, the high sand content of soils in Richmond (see Tables 6.7-6.12) may aid this process.

Comparison of the data with those reported by Moir (1992) for garden and allotment soils in Richmond, shows that those elements which have a distribution strongly influenced by anthropogenic activities, Pb, Zn, Cu, Cd, Na, Ca, Sr, Ba and P, are present at higher concentrations in the earlier study. This may be due to the reduction of Pb in petrol which has occurred in recent times (see section 3.4.6.1), greater applications of fertilisers to allotment soils (no allotments were sampled in this study), and perhaps, sampling of soils associated with older property and with greater proximity to specific anthropogenic sources in the study by Moir (1992). Elements such as Ni, K, Mg, Be, Al, Ti, V, Mn, Fe and Co are present at similar concentrations in both studies. This is probably because these elements are not so strongly influenced by anthropogenic activity.

Comparison of data with other urban studies is difficult, as so many factors influence the concentrations of metals in soils. Sampling sites which are close to major roads or major urban centres and which are associated with older property results in higher concentrations of a number of elements, and very often average concentrations are reported for towns without consideration of these factors. Studies such as those by Davies et al., (1979) in London and Mielke (1994) in New Orleans split the city into different zones (inner-city, mid-city and suburban). These studies show a decrease in the average Pb concentration with increasing distance from the city. Most studies based in the United states generally report higher concentrations of Pb and lower concentrations of Zn and Cu than the present study in Richmond. This may relate to intrinsic differences in the sample areas, such as those just discussed, or a larger number of wooden houses in America, hence a greater surface area painted, resulting in higher concentrations of Pb in garden soils from the United States. Open fires were important in Britain until the 1950's (Davies, 1993). Fossil fuels are an important source of Zn and Cu (see Table 3.4).

CHAPTER SEVEN INVESTIGATION OF THE INFLUENCE OF GEOLOGY AND ANTHROPOGENIC ACTIVITY ON THE SOIL GEOCHEMISTRY OF RICHMOND

7.1 Normalisation of the data set to concentrations reported in the Soil Geochemical Atlas of England and Wales (McGrath and Loveland, 1992)

7.1.1 Introduction

The data were normalised to geochemical data for soils of England and Wales (McGrath and Loveland, 1992) to facilitate inter-comparison of datasets in relation to relevant common standard values. The data from the Soil Geochemical Atlas of England and Wales were selected because:

1). The data set produced for soils from England and Wales (McGrath and Loveland, 1992), are based on 5629 samples analysed for 17 elements, and is the most comprehensive available.

2). The topsoil sample depth selected is 0-15cm, as in this project. Subsurface samples (30-45cm) from Richmond and Wolverhampton are also normalised to topsoils from England and Wales (McGrath and Loveland, 1992).

3). A partial extraction technique was used involving an aqua regia digestion, which the authors report to be comparable to results from a nitric/perchloric digestion; analysis was carried out on an ICP-OES, the same instrumentation as used in this project.

4). The sampling programme did not include urban areas, allowing a comparison of element concentrations from an urban environment with average concentrations for the non-urban environment.

Sample numbers are very different for both projects, with approximately 200 and 300 topsoils taken in the Richmond and Wolverhampton projects respectively, compared to 5692 samples taken by McGrath and Loveland (1992). The sampling density also varied quite considerably between the two studies, with 4 samples per km² taken in these urban studies and sampling based on a 5x5 km cell for the study in England and Wales. The study carried out over England and Wales included soils which have developed over a wide variety of geological units which in turn give rise to an extensive range of concentrations for a number of elements. However, making comparisons to a study based on England and Wales is a more suitable technique than making comparisons to average concentrations for world soils which include a much wider range of climatic zones and parent materials, and which are often based on a range of different extraction procedures.

7.2 Graphical representation of a suite of elements from soils in Richmond normalised to soils from England and Wales (McGrath and Loveland 1992) in relation to land-use and geological units

7.2.1 Introduction

The graphs presented in this section present data for a suite of 16 elements which are common to this study and to a comprehensive study of soils in England and Wales (McGrath and Loveland 1992). The elements which have been analysed in this study which were not analysed in the study by McGrath and Loveland (1992) are discussed in chapter 6. Figure 7.1a shows the normalisation of elements from areas of open space overlying London Clay to concentrations in soils from England and Wales (McGrath and Loveland 1992). Median concentrations have been used to normalise the results from Richmond because McGrath and Loveland (1992) report that, in general, their data are positively skewed, and therefore median values provide a robust method of representing central tendency. The primary y-axis represents this normalisation ratio on a log scale. Such a technique means that the distance above and below the line which runs across the graph (set at 0 on the log scale and 1 on the arithmetic scale) is equal, illustrating which elements are present at higher or lower concentrations in soils from Richmond, relative to soils in England and Wales (McGrath and Loveland 1992). The log ratio on the y-axis can be compared to the secondary y-axis which is an arithmetic or real ratio. Subsurface samples (30-45cm) from Richmond are also normalised to soils from England and Wales (McGrath and Loveland 1992). Normalising subsurface data to topsoil data facilitates a comparison between the different sample depths for the soils from this study. The geological units are described in chronological order, starting with the oldest outcrop, London Clay (aged at approximately 50 million years old), and moving through the drift deposits to the most recent deposits of river brickearth and alluvium (aged at 1800-3200 years old).

7.2.2 London Clay - topsoils (0-15cm) in areas of open space

Figure 7.1a shows the normalisation of topsoil data from areas of open space overlying outcrops of London clay. Twenty three soil samples were taken in this category (see Table 7.1). Most of these sites are located in Richmond Park (see Supp. Figs 1b and 1d). Figure 7.1a shows that with the exception of Pb, all elements have ratios of < 1 in topsoils from Richmond in relation to median values reported from soils in England and Wales (McGrath and Loveland, 1992). The low concentrations of elements such as Al, K and Mg, which have very similar ratios, and Ca and Mn may be a function of the sandy nature of most of the soils developed on this parent material (see Table 6.11). The description of geological beds underlying Richmond (see section 4.5) illustrated that the near surface section of this deposit contains fine grained sand (BGS, 1981), something confirmed by the results of a particle size analysis, showing an average sand content of nearly 80% (see Table 6.11). Clay-rich soils frequently have high concentrations of Al, K and Mg which are derived from the layer silicates (McGrath and Loveland, 1992). The elements Cr, Fe and Cu have ratios of just below 1 (similar to concentrations reported for soils in England and Wales (McGrath and Loveland, 1992). Chromium in particular is very close to the median concentration reported for England and Wales of 39.3 μg/g. The concentration range of Cr in Richmond soils is low, see Tables 6.3-6.4; This is due to both land-use and geology. A Cr ratio just below 1 is generally observed in Richmond soils. It may be inferred that the anthropogenic use of Cr in Richmond is minimal.

Iron is naturally abundant in most soils, although the texture of the soil is an important factor influencing this. Soils with a sandy texture generally have lower concentrations of Fe than fine textured soils and are dominated by quartz, although Fe is present in other primary minerals such as micas (McGrath and Loveland, 1992). The ratio of > 1 for Pb in soils overlying London Clay in Richmond Park (Pb was normalised to

40 μg/g) probably results from anthropogenic additions of Pb which extend to areas of open space. This is a consequence of the widespread use of Pb in the urban environment as an additive to petrol and the other uses detailed in Table 3.1. Zinc, Cu, Ni have ratios < 1, which reflects the fact that soils developed over the outcrops of London Clay have naturally low concentrations of these metals, with only small inputs from anthropogenic sources.

7.2.3 London Clay - subsurface soils (30-45cm) in areas of open space

The pattern for subsurface soils is very similar to that of topsoils (see Fig 7.1b). The low concentrations of the metallic elements i.e. Ca, Sr, Ba, Mn, Fe, Co, Ni, Zn and Pb, probably result from the sandy nature of these soils (a mean sand content of 80% - see Table 6.12). The biggest difference is observed for Pb which has a ratio of 1.3 in topsoils, and a ratio of 0.58 in subsurface soils (see Table 7.1). In areas of open space such as Richmond Park, soil profiles remain undisturbed and subsurface soils are, in general, unexposed to anthropogenic additions of metals. Lead, in particular, shows greater accumulation in the top 15cm relative to 30-45cm.

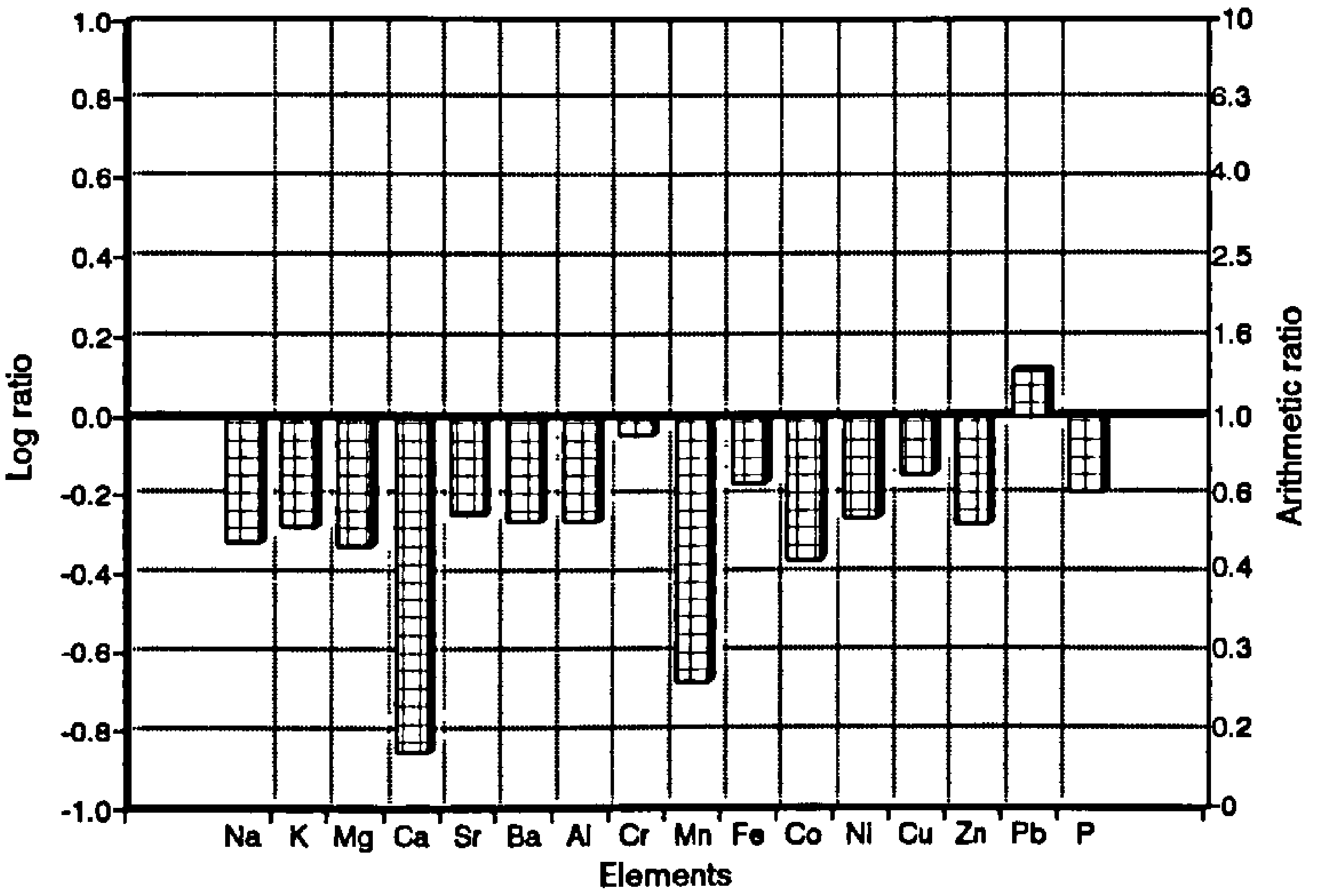


Fig. 7.1a Median concentrations of selected elements in topsoils (0-15cm) from areas of open space overlying London Clay in Richmond, normalised to median concentrations for soils in England and Wales (McGrath and Loveland, 1992) and expressed on a log-scale

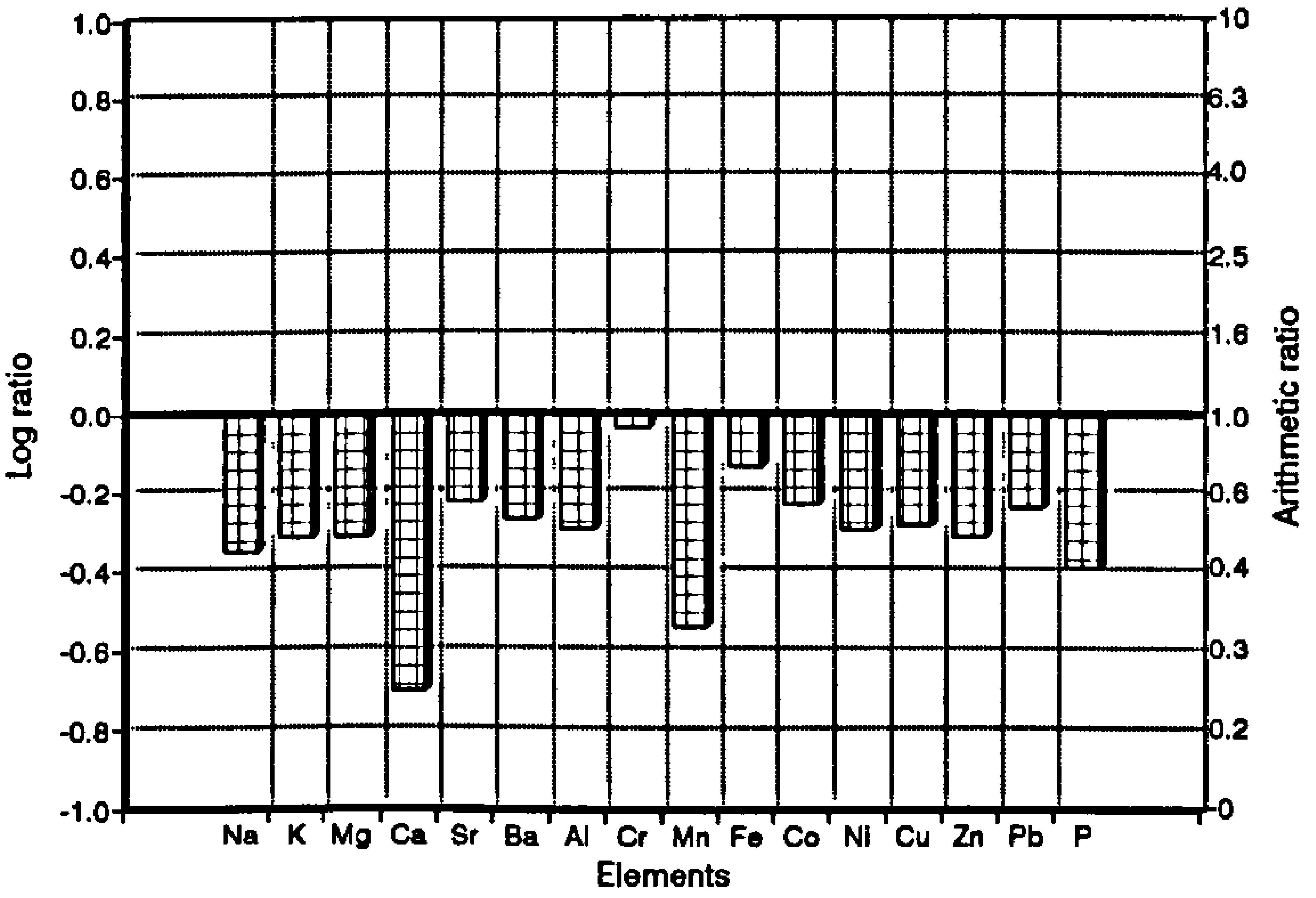


Fig. 7.1b Median concentrations of selected elements in subsurface soils (30-45cm) from areas of open space overlying London Clay in Richmond, normalised to median concentrations for soils in England and Wales (McGrath and Loveland, 1992) and expressed on a log-scale

7.2.4 London Clay - topsoils (0-15cm) in urban gardens

Five samples were taken from gardens overlying London Clay, compared with twenty three samples from areas of open space. Interpretation of the data therefore, has to be made with caution. Figures 7.2a shows the normalisation of elements in garden topsoils to concentrations in soils across England and Wales (McGrath and Loveland, 1992). The contrast with soils from areas of open space overlying the same parent material is very distinct (see Fig. 7.1a), and the enhancement of several elements in urban areas is confirmed.

For Na and Mg, the difference is quite substantial, despite ratios of < 1 for both garden soils and soils from areas of open space. These may reflect minor anthropogenic additions through the use of fertilisers in gardens and the salting of roads in winter (see Table 3.2) or natural variation of the geochemical signature. The soil texture does not vary significantly with land-use for these soils ($P > 0.05$ - see Tables 6.7-6.10). For Ca, Sr and Ba, the ratio to soils in England and Wales (McGrath and Loveland, 1992) is > 1 for each element. These represent significant increases compared with soils overlying London Clay in areas of open space, with Ca and Sr having very similar ratios (see Table 7.1). These elements are geochemically very similar. Barium concentrations are over twice the median value reported in the Soil Geochemical Atlas of England and Wales (McGrath and Loveland, 1992). Barium has several sources in the urban environment, particularly from the burning of coal and the use of Ba as a filler in paint (see Table 3.2). Calcium, and possibly Sr, are likely to be present in a building material such as gypsum, plaster, tiles, bricks and concrete which were often observed in garden soils in Richmond.

The Al ratio is very similar to that observed for topsoils from areas of open space, whilst Cr, Mn, Fe and Co all show a slight enhancement in garden soils (see Tables 7.1). Several studies report increased concentrations of these elements in urban roadside soils, relative to soils in a rural environment (Smith and Carson, 1981; Albasel and Cottenie, 1984; Hoplee, 1984; Farmer, 1986 and Ward 1990a). Of these elements, only Cr has a ratio of > 1. The metals Cu, Zn and Pb, have the highest ratios (see Fig. 7.2a and Table 7.1), both in relation to areas of open space and soils from England and Wales (McGrath and Loveland, 1992). The extensive sources of metals in urban areas, are discussed in chapter 3. This trend is shown in Fig. 7.2a with Pb almost 12 times greater than the median value for England and Wales (McGrath and Loveland, 1992). This may be influenced by the age of the houses and their proximity to major roads. Phosphorus also has a ratio > 1; this element has a number of sources in the urban environment, such as the application of fertilisers to gardens (see Table 3.2) and from biogeochemical cycling of vegetation in gardens (e.g. compost heaps).

7.2.5 London Clay - subsurface soils (30-45cm) from urban gardens

Subsurface garden soils overlying London Clay show a trend similar to that of topsoils, particularly for Pb and Zn which have the highest ratios (see Figs 7.2a and 7.2b). However, the ratios are generally lower in subsurface soils than in topsoils. Although topsoil enhancement is to be expected because of accumulation of metals in the top 5cm of the soil profile from anthropogenic sources (Adriano, 1986), the disturbance of garden soils over the years has resulted in elevated concentrations of metals in subsurface soil. The sandy nature of the soils may have also have facilitated the movement of metals down the profile (see Table 6.11). The ratios for Na, K, Mg, Al and Fe, elements possibly less affected by anthropogenic activity than Pb, Zn and Cu, are very similar to those observed in topsoils and probably represent a consistent part of the geochemical signature. Although Ca, Sr and Ba are all significantly enhanced in topsoil, only Sr has a ratio > 1 in subsurface samples. Chromium and Mn have significantly lower concentrations at depth, suggesting some anthropogenic accumulation in the top 15cm or variation of the geochemical signature.

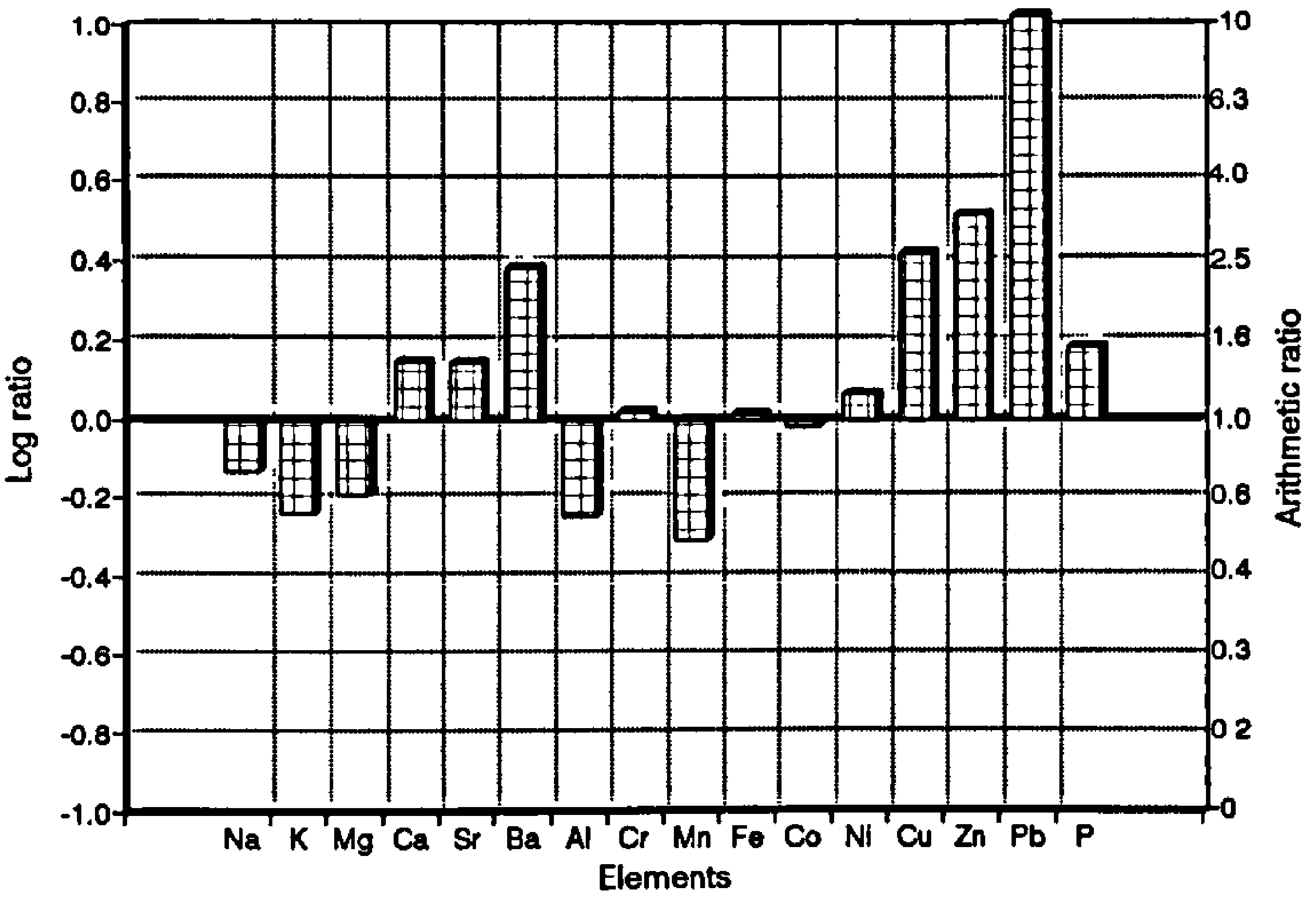


Fig. 7.2a Median concentrations of selected elements in topsoils (0-15cm) from urban gardens overlying London Clay in Richmond, normalised to median concentrations for soils in England and Wales (McGrath and Loveland, 1992) and expressed on a log-scale

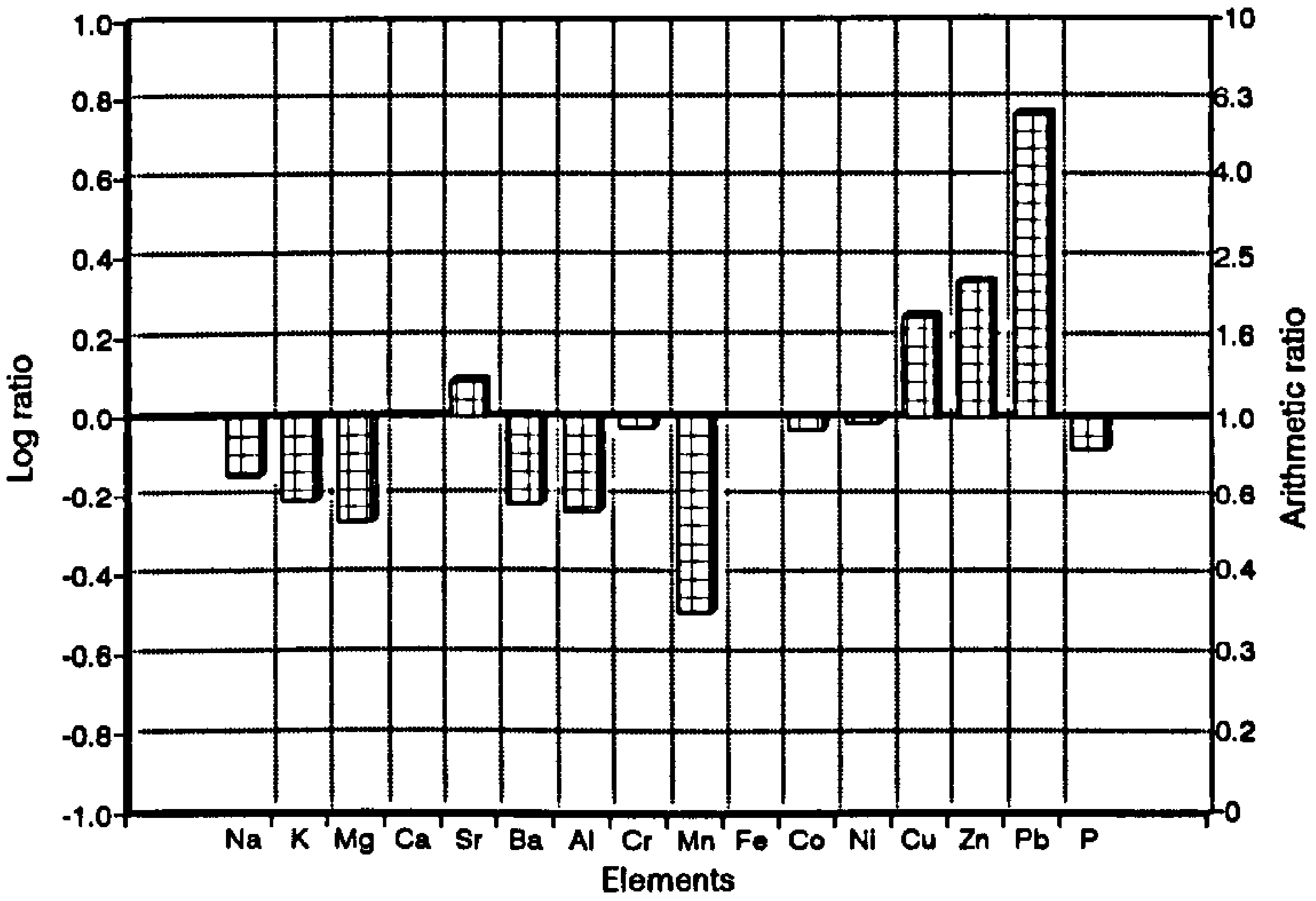


Fig. 7.2b Median concentrations of selected elements in subsurface soils (30-45cm) from urban gardens overlying London Clay in Richmond, normalised to median concentrations for soils in England and Wales (McGrath and Loveland, 1992) and expressed on a log-scale

Table 7.1 Ratios of elements in soils overlying London Clay, as designated by land-use, after normalisation to median concentrations for soils in England and Wales (McGrath and Loveland, 1992)

	topsoils		subsurface soils	
	n=23	n=5	n=23	n=5
	OS	UG	OS	UG
Na	0.48	0.74	0.45	0.71
K	0.52	0.57	0.49	0.61
Mg	0.47	0.64	0.49	0.54
Ca	0.14	1.41	0.20	1.00
Sr	0.56	1.40	0.60	1.22
Ba	0.54	2.41	0.54	0.60
Al	0.54	0.56	0.51	0.57
Cr	0.90	1.04	0.92	0.93
Mn	0.21	0.49	0.29	0.32
Fe	0.68	1.03	0.74	1.00
Co	0.43	0.96	0.59	0.92
Ni	0.55	1.15	0.51	0.96
Cu	0.71	2.62	0.52	1.78
Zn	0.53	3.28	0.49	2.17
Pb	1.30	11.8	0.58	5.80
P	0.64	1.52	0.41	0.83

OS Soils from areas of open space UG Soils from urban gardens

7.2.6 High level terraces - topsoils (0-15cm) in areas of open space

Six samples overlying this parent material were taken in Richmond, all located in Richmond Park. These sites are located at distance from roads and residential areas. This is reflected in the trend for topsoils shown in Fig 7.3a. The ratios of the elements, also listed in Table 7.2, are the lowest for any of the parent materials. The elements K, Mg, Al, Mn and Fe have lower ratios in these soils than for the other parent materials. This probably reflects the natural geochemical signature for these soils. Soil texture, however, does not differ significantly ($P > 0.05$) for the different parent materials in Richmond. Soils are dominated by the sand size fraction (see Tables 6.11 and 6.12). Most elements are present in these soils at concentrations less than half that reported as median concentrations for soils of England and Wales (McGrath and Loveland, 1992). Lead, which has a ratio of > 1 in topsoils from areas of open spaces overlying all the other parent materials in Richmond, has a ratio of < 1 in topsoils overlying high level terraces. This reflects the naturally low concentrations of Pb in these soils and the isolation of these sample sites from anthropogenic activity. The reported median concentration of Pb for soils in England and Wales is 40 μg/g, so these concentrations of Pb, which range from 26-45 μg/g, represent the lowest concentrations of Pb in Richmond as a whole.

7.2.7 High level terraces - subsurface soils (30-45cm) in areas of open space

The trend observed in topsoils is also seen in subsurfaces soils (see Fig. 7.3b). Sodium, Mg, Ca, Sr, Ba, Al, Mn, Ni and Zn have similar ratios in topsoils and subsurface soils, which probably results from a consistent geochemical signature. The soil texture is very similar to that for topsoils (see Tables 6.11 and 6.12), although the sand content is significantly higher in subsurface soils than topsoils ($P < 0.05$). Copper and Pb show a decrease in ratio from topsoils to subsurface soils, which may reflect minor anthropogenic additions to topsoils or natural biogeochemical cycling.

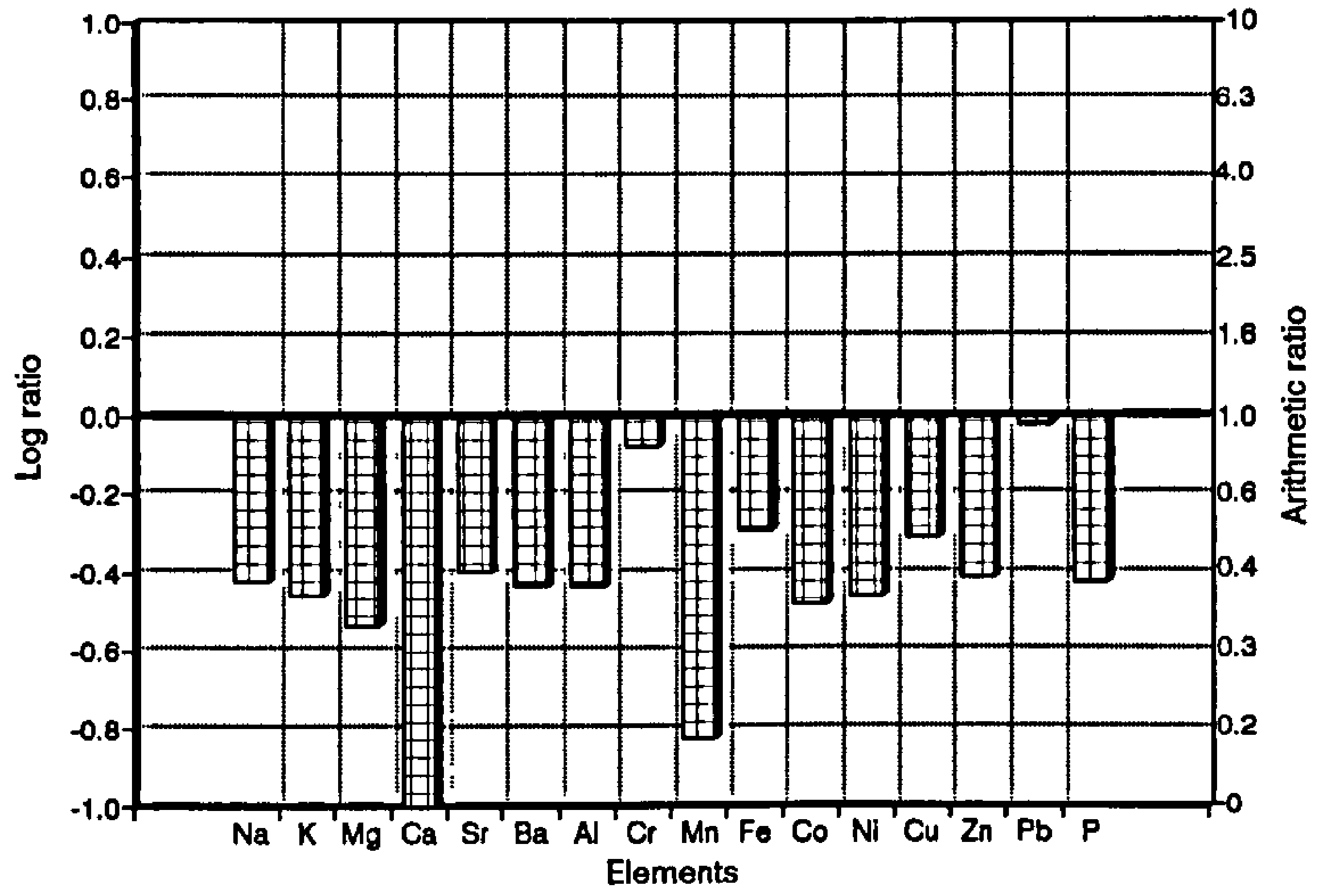


Fig. 7.3a Median concentrations of selected elements in topsoils (0-15cm) from areas of open space overlying high level terraces in Richmond, normalised to median concentrations for soils in England and Wales (McGrath and Loveland, 1992) and expressed on a log-scale

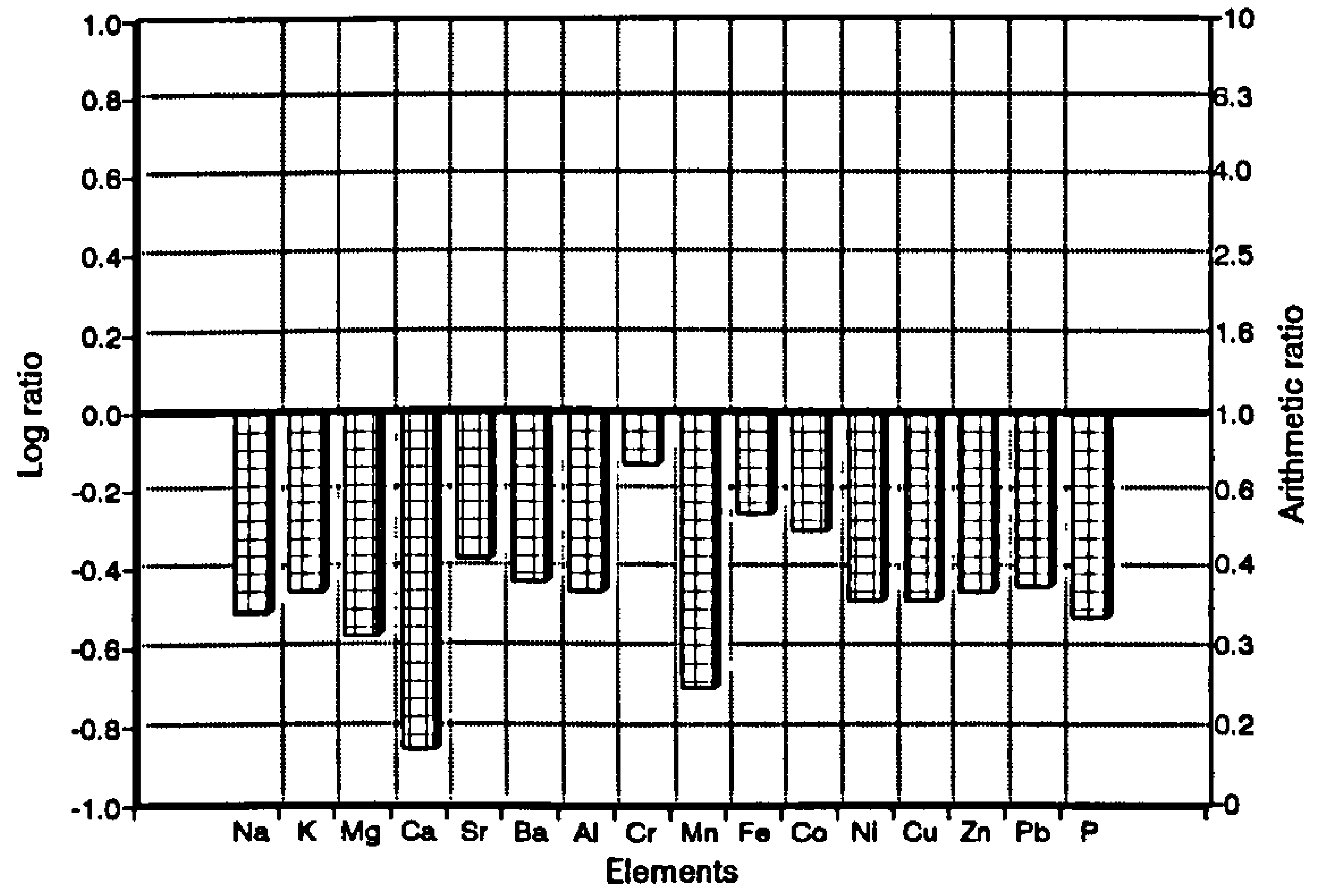


Fig. 7.3b Median concentrations of selected elements in subsurface soils (30-45cm) from areas of open space overlying high level terraces in Richmond, normalised to median concentrations for soils in England and Wales (McGrath and Loveland, 1992) and expressed on a log-scale

Table 7.2 Ratios of elements in soils overlying high level terraces, as designated by land-use, after normalisation to median concentrations for soils in England and Wales (McGrath and Loveland, 1992)

	topsoils	subsurface soils
	n=6	n=6
	OS	OS
Na	0.38	0.31
K	0.35	0.35
Mg	0.29	0.27
Ca	0.10	0.14
Sr	0.40	0.42
Ba	0.37	0.37
Al	0.37	0.35
Cr	0.84	0.74
Mn	0.15	0.20
Fe	0.51	0.55
Co	0.33	0.50
Ni	0.35	0.33
Cu	0.49	0.33
Zn	0.39	0.35
Pb	0.95	0.36
P	0.38	0.30

OS Soils in areas of open space

7.2.8 4-River terraces - topsoils (0-15cm) in areas of open space

These samples are located in Richmond Park, and these terraces are older and higher than the river terraces prefixed with a lower number (i.e 1- and 3-river terraces). Four samples were taken of soils which developed over this parent material. Samples overlying this parent material are closer to urban development than soil overlying the high level terraces (see supp. Figs. 6b and 6d). Figure 7.4a shows the normalisation ratios for topsoils developed over 4-river terraces. In general, ratios for the elements are similar to those reported for topsoils in areas of open space overlying the younger river terraces and London Clay in particular. This is the case for Na, K, Mg, Al and Cr in particular (ratios all < 1) and may reflect similarities in the geochemical signature for these parent materials. This may be a result of the consistent soil texture in Richmond, irrespective of parent material or land-use (see Tables 6.7-6.12). The ratios of Ca, Sr, Ba, Mn, Fe, Co, Ni, Cu, Zn and P are generally lower than those reported for most parent materials, although higher than for soils overlying high level terraces and very similar to those for soils overlying London Clay (see Tables 7.1-7.3). This may reflect the fact that the majority of soils developed over London Clay and 4-river terraces occur in Richmond Park. These sites are closer to the housing and major roads in the borough than the high level terraces at the centre of Richmond Park. Lead has a ratio of 2 in topsoils overlying 4-river terraces compared to 0.95 for high level terraces.

7.2.9 4-River terraces - subsurface soils (30-45cm) in areas of open space

In subsurface soils, see Fig. 7.4b, a number of elements show a slight decrease in normalisation ratio, the exceptions being Cr, Mn, Fe, Co, Ni and Zn. This may reflect natural variation of the geochemical signature, accumulation of these elements in topsoils through biogeochemical cycling, or accumulation from anthropogenic sources. For Cu and Pb, normalisation ratios are much lower than those for topsoils, which suggests the accumulation of these elements in topsoils, probably due to anthropogenic processes (see Table 7.3).

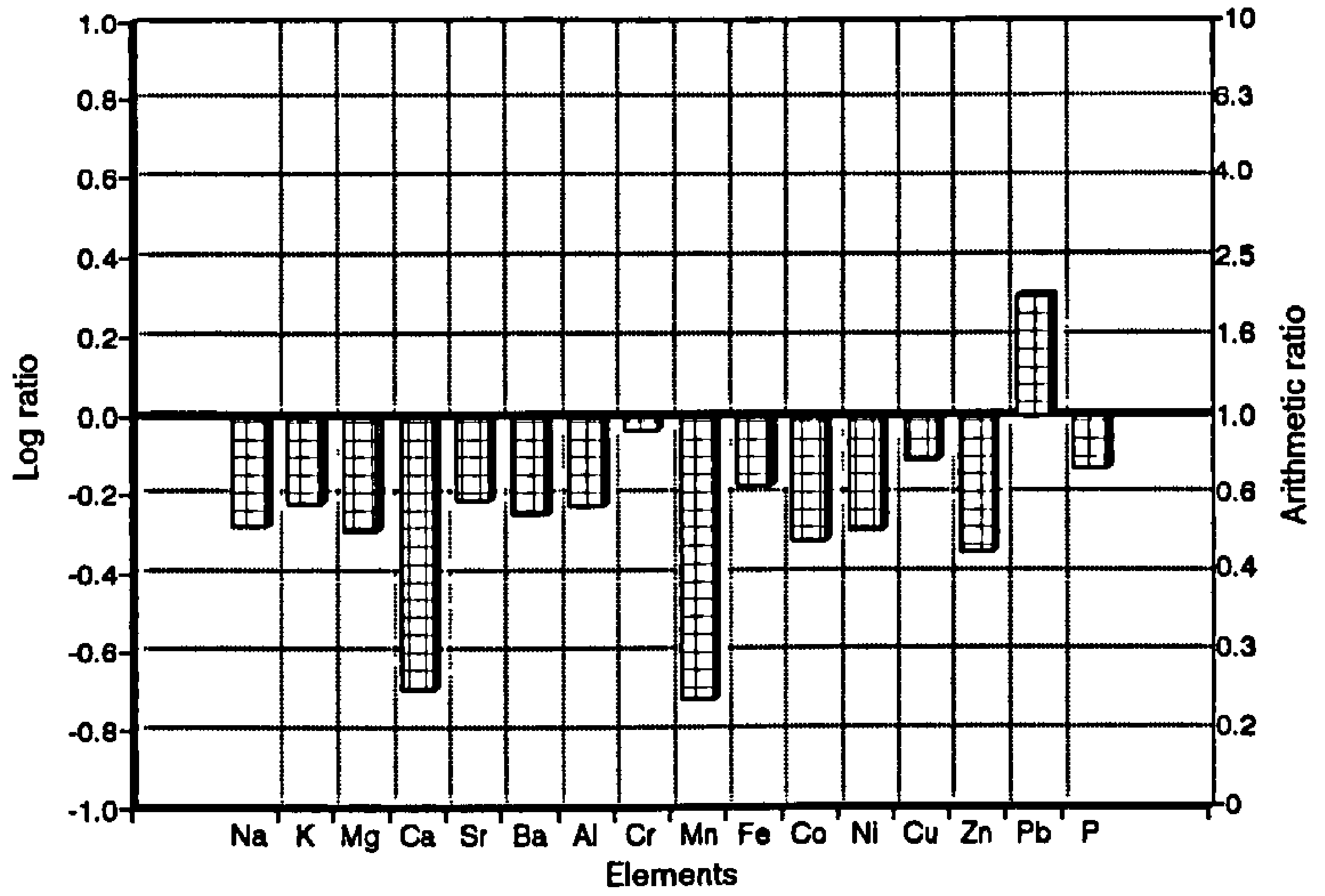


Fig. 7.4a Median concentrations of selected elements in topsoils (0-15cm) from areas of open space overlying 4-river terraces in Richmond, normalised to median concentrations for soils in England and Wales (McGrath and Loveland, 1992) and expressed on a log-scale

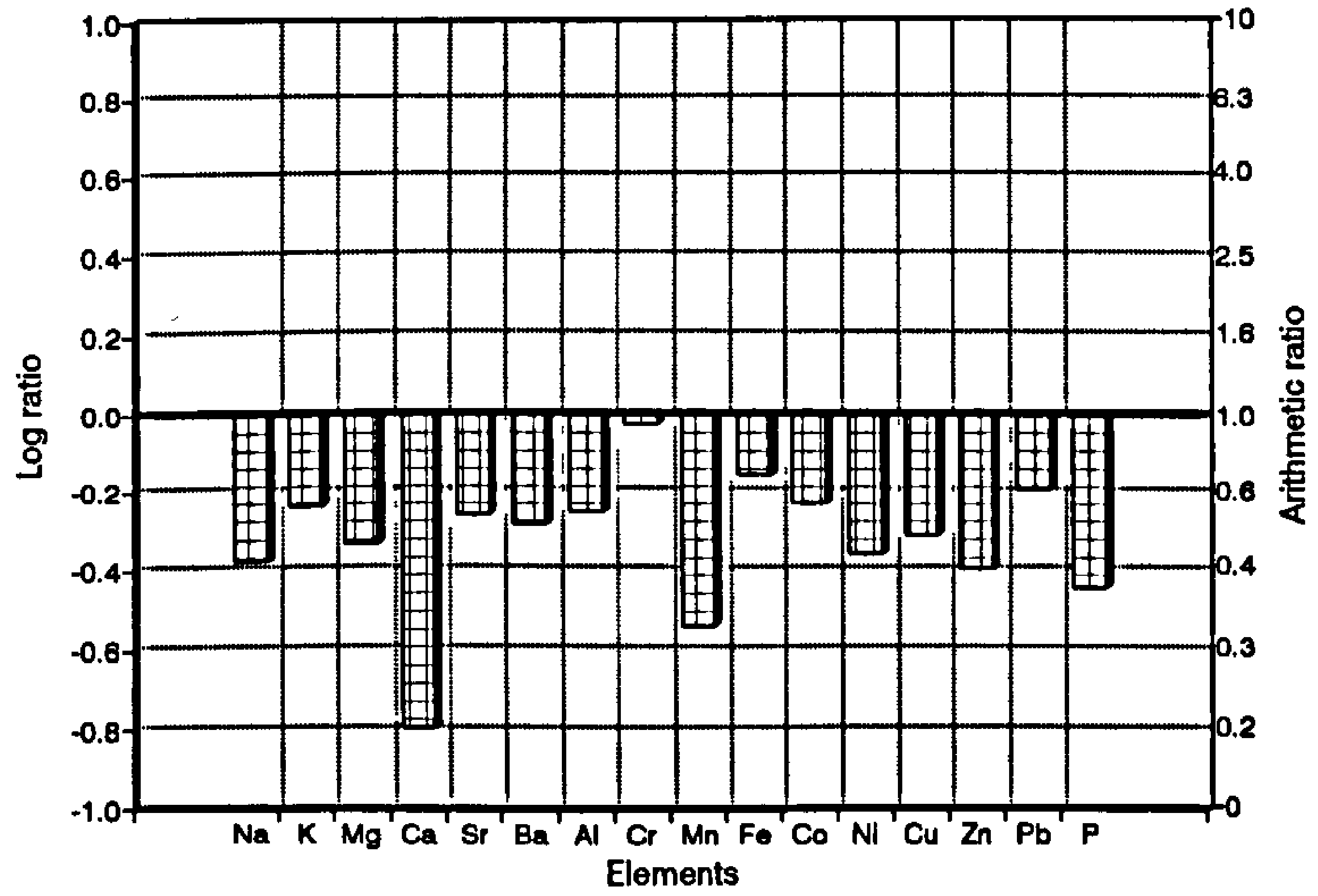


Fig. 7.4b Median concentrations of selected elements in subsurface soils (30-45cm) from areas of open space overlying 4-river terraces in Richmond, normalised to median concentrations for soils in England and Wales (McGrath and Loveland, 1992) and expressed on a log-scale

Table 7.3. Ratios of elements in soils overlying 4-river terraces, as designated by land-use, after normalisation to median concentrations for soils in England and Wales (McGrath and Loveland 1992)

	topsoils	subsurface soils
	n=4	n=4
	OS	OS
Na	0.52	0.42
K	0.60	0.58
Mg	0.51	0.47
Ca	0.20	0.16
Sr	0.61	0.55
Ba	0.56	0.52
Al	0.59	0.56
Cr	0.92	0.94
Mn	0.19	0.29
Fe	0.66	0.70
Co	0.48	0.59
Ni	0.51	0.44
Cu	0.77	0.49
Zn	0.45	0.40
Pb	2.00	0.64
P	0.73	0.36

OS Soils in areas of open space

7.2.10 3-River terraces - topsoils in areas of open space

Figure 7.5a shows the normalisation ratios of soils overlying 3-river terraces in areas of open space. These river terraces are higher and older than the 1-river terraces (see section 4.5, in general, for a full description of the geology). The number of soil samples taken overlaying these river terraces is lower than for the younger and lower river terraces (12 compared with 55). The pattern observed for topsoils in Fig. 7.5a is very similar to that for other topsoils from areas of open space, particularly those overlying 1-river terraces, shown in Fig. 7.7a. The elements associated with clays, K, Mg, Al and Mn, have ratios of approximately 0.5 - half the median concentrations reported for soils in England and Wales (McGrath and Loveland, 1992), and similar to that observed for the younger river terraces and London Clay. This may reflect the similarities observed in soil texture for these parent materials (see Table 6.11). Calcium, Sr and Ba also have normalisation ratios of < 1, although these are higher than for topsoils from areas of open space overlying London Clay and 1-river terraces.

Iron, Co and Ni have very similar ratios, approximately 0.7, which are lower than those reported for soils overlying the younger river terraces. Chromium has a ratio of approximately 1, which is similar to that reported for soils in both urban gardens and areas of open space, underlain by any of the parent materials. Lead, Cu and P have normalisation ratios of > 1, with Pb nearly 3 times the reported median concentration for soils in England and Wales (McGrath and Loveland, 1992). These are similar to ratios observed for the younger river terraces, although higher than ratios observed for London Clay in areas of open space. The Zn ratio is just below 1.

7.2.11 3-River terraces - subsurface soils (30-45cm) in areas of open space

The normalisation ratios for subsurface soils overlying 3-river terraces areas in open space are shown in Figs. 7.5b. Sodium, Mg, Sr, Al, Cr, Mn, Fe and Co have ratios which are very similar to those for topsoils, see Fig. 7.5a, probably reflecting a consistent geochemical signature for these elements. Sodium, K, Mg, Ca, Ba and Al have higher concentrations than in subsurface soils overlying 1-river terraces and London Clay, a trend also observed for topsoils, and this probably represents differences in the geochemical signatures for these parent materials (see Tables 7.1, 7.4 and 7.5). Calcium, Ni, Cu, Zn, Pb and P have lower ratios in subsurface soils than topsoils which probably results from greater accumulation of these elements in the top 15cm of the profile, rather than variation of the geochemical signature. This is despite Ca, Ni and Zn ratios of < 1 in topsoils. Only Pb has a ratio greater than 1 in subsurface soils. This reflects the undisturbed nature of soils in areas of open space.

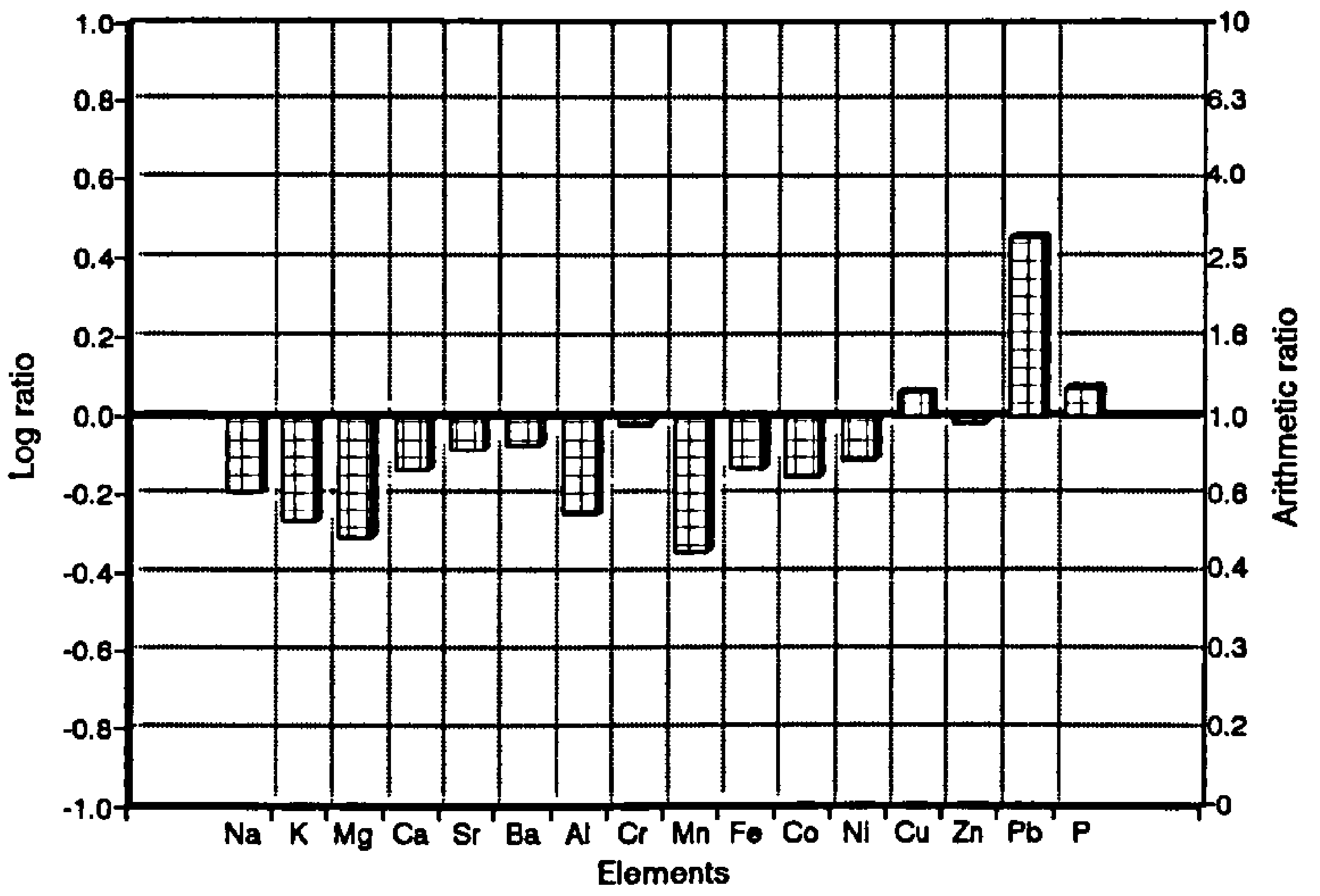


Fig. 7.5a Median concentrations of selected elements in topsoils (0-15cm) from areas of open space overlying 3-river terraces in Richmond, normalised to median concentrations for soils in England and Wales (McGrath and Loveland, 1992) and expressed on a log-scale

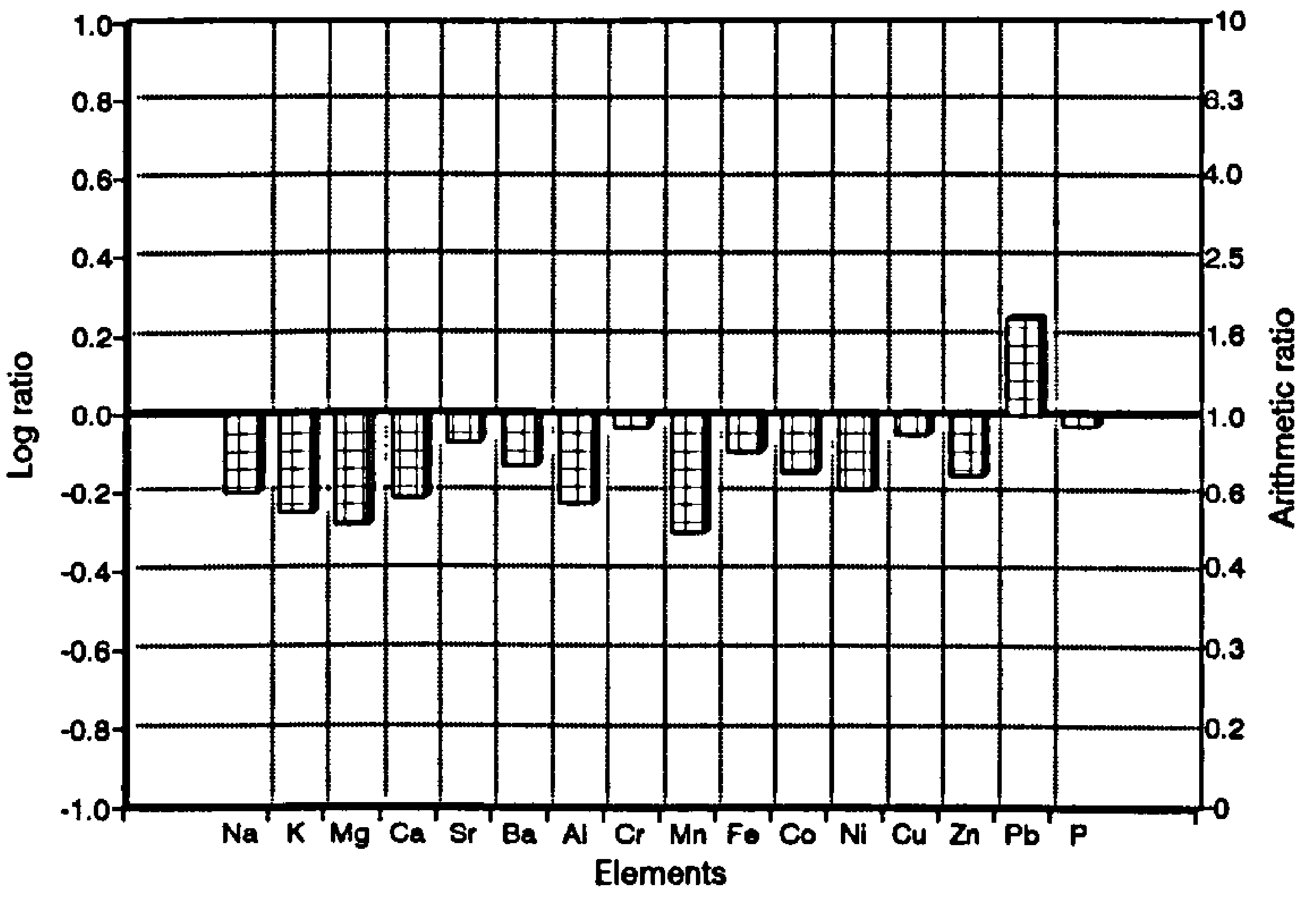


Fig. 7.5b Median concentrations of selected elements in subsurface soils (30-45cm) from areas of open space overlying 3-river terraces in Richmond, normalised to median concentrations for soils in England and Wales (McGrath and Loveland, 1992) and expressed on a log-scale

7.2.12 3-River terraces - topsoils (0-15cm) in urban garden soils

Topsoils from gardens overlying 3-river terraces and normalised to soils from England and Wales (McGrath and Loveland 1992) are shown in Fig. 7.6a. The sample number is 34. The trend observed for garden topsoils is similar to that observed for garden soils overlying the younger and lower river terraces and London clay. The elements which have a normalisation ratio > 1 are those with strong anthropogenic sources in the urban environment. These elements are Ca, Sr, Ba, Cu, Zn, Pb and P (see Fig. 7.6a and Table 7.4). Although these elements have ratios > 1 in garden soils overlying London Clay and 1-river terraces, Tables 7.1-7.4 show that the ratios for garden soils overlying 3-river terraces are generally lower than for garden soils overlying the younger river terraces and London Clay. This is probably a result of differences in house age in Richmond and proximity to major roads.

Calcium and Sr are geochemically very similar. It is postulated that these elements are found in building material such as gypsum, plaster and concrete and in ceramics, (commonly found in garden soils) and in fertilisers (see Table 3.2). Barium was used as both a filler and a pigment in paints (see Table 3.2). Zinc and Cu have ratios of approximately 2, whilst Pb has a ratio close to 6, reflecting the abundance of Pb in the urban environment. Phosphorus also has a ratio of > 1, although lower than that of Pb, Zn and Cu. Particle size analysis indicated a high sand content for these soils (an average of 78% - see Table 6.11), and this may result in low ratios of elements such as K, Mg, Al and Mn. However, garden topsoils overlying 3-river terraces generally have higher ratios of these elements than soils overlying London clay in particular, 1-river terraces, and soils from areas of open space overlying the same parent material, despite similar soil textures (see Tables 6.11 and 7.4). Anthropogenic activity may be responsible for this trend, or differences in the geochemical signatures for the individual parent materials. Iron, Co and Ni have ratios close to 1 which are higher than soils of the same parent material from areas of open space. Chromium has a ratio of just below 1, similar to that found in all types of soil in Richmond.

7.2.13 3-River terraces - subsurface soils (30-45cm) in urban garden soils

In subsurface soils a very similar pattern exists to that observed for topsoils, see Figs. 7.6a and 7.6b. The same elements, Ca, Sr, Ba, Cu, Zn, Pb and P, have normalisation ratios > 1. Comparison of Figs. 7.6a and 7.6b and Table 7.4 shows that with the exception of Cu, the ratios are lower for these elements in subsurface soils. The ratios of the elements in subsurface soils from urbanised areas are higher than for subsurface soils from areas of open space (see Table 7.4). Sodium, K, Mg, Al, Cr and Mn have similar ratios in topsoils and subsurface soils, which probably results from a consistent geochemical signature. The soil texture does not vary greatly with depth, see Tables 6.11 and 6.12, despite a significantly higher sand content in subsurface soils ($P < 0.05$). Iron, Co, and Ni have lower ratios in subsurface soils, suggesting that either anthropogenic activity, natural biogeochemical cycling, or variation of the geochemical signature has increased the concentration of these metals in topsoils.

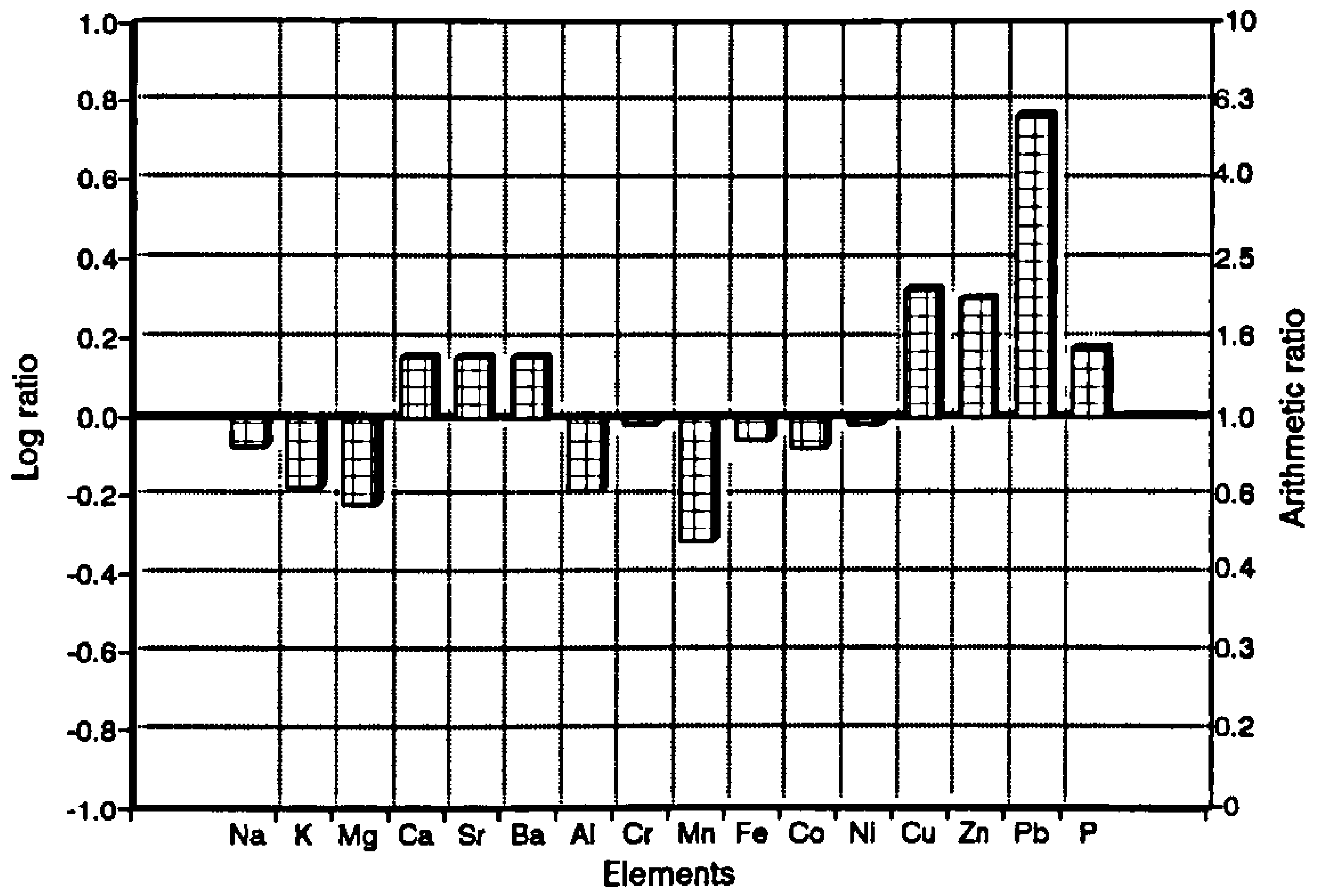


Fig. 7.6a Median concentrations of selected elements in topsoils (0-15cm) from urban gardens overlying 3-river terraces in Richmond, normalised to median concentrations for soils in England and Wales (McGrath and Loveland, 1992) and expressed on a log-scale

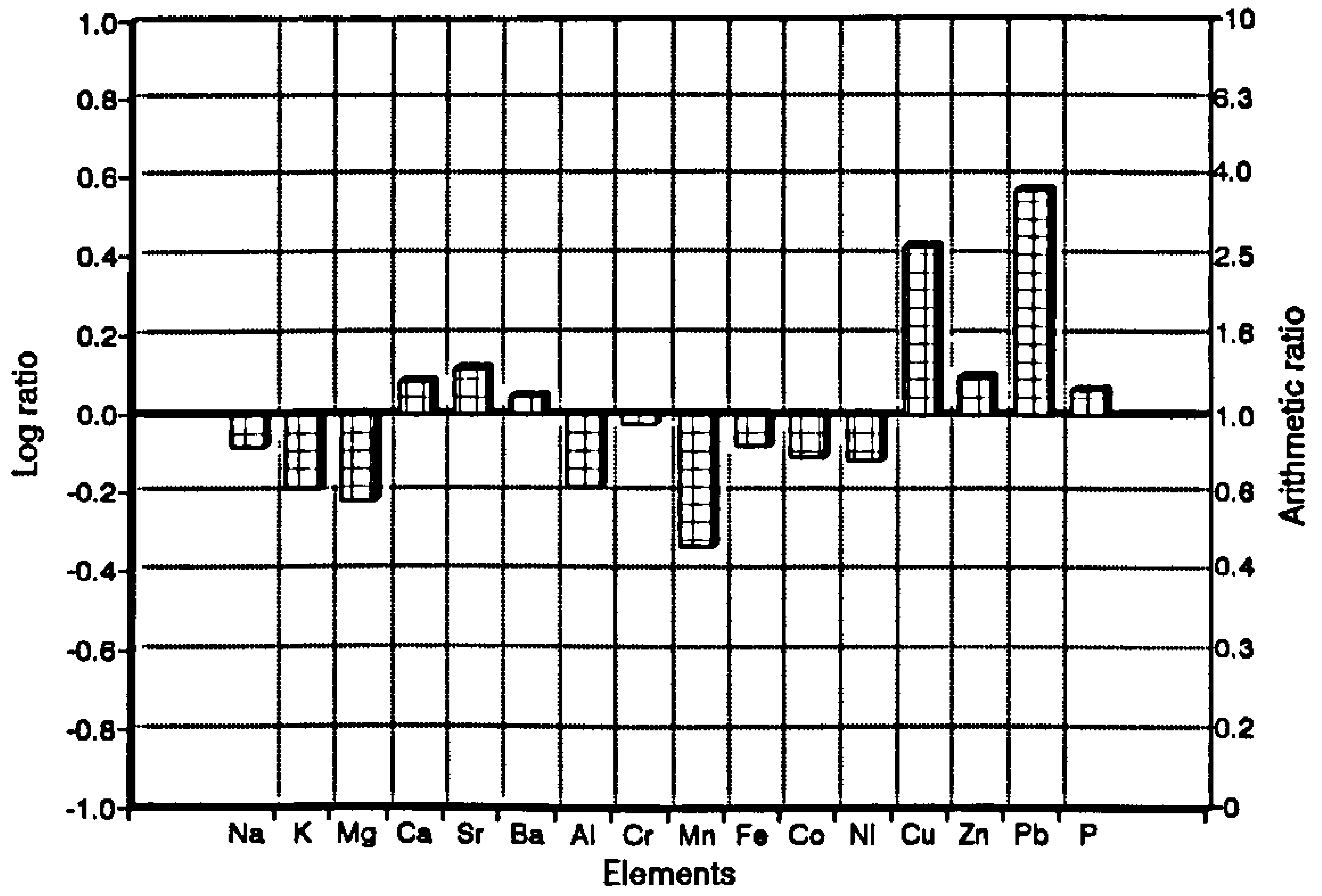


Fig. 7.6b Median concentrations of selected elements in subsurface soils (30-45cm) from urban gardens overlying 3-river terraces in Richmond, normalised to median concentrations for soils in England and Wales (McGrath and Loveland, 1992) and expressed on a log-scale

Table 7.4. Ratios of elements in soils overlying 3-river terraces, designated by land-use, after normalisation to median concentrations for soils in England and Wales (McGrath and Loveland, 1992)

	topsoils		subsurface soils	
	n=12	n=34	n=12	n=34
	OS	UG	OS	UG
Na	0.64	0.85	0.63	0.82
K	0.54	0.66	0.56	0.64
Mg	0.49	0.60	0.52	0.60
Ca	0.73	1.42	0.61	1.20
Sr	0.82	1.42	0.85	1.29
Ba	0.85	1.42	0.74	1.10
Al	0.56	0.65	0.59	0.65
Cr	0.95	0.96	0.92	0.94
Mn	0.45	0.48	0.50	0.46
Fe	0.74	0.88	0.80	0.83
Co	0.70	0.84	0.71	0.78
Ni	0.77	0.96	0.64	0.76
Cu	1.14	2.10	0.89	2.65
Zn	0.96	1.99	0.70	1.24
Pb	2.85	5.83	1.75	3.70
P	1.17	1.50	0.93	1.14

OS Soils in areas of open space UG Soils from urban gardens

7.2.14 1-River terraces - topsoils (0-15cm) in areas of open space

Figure 7.7a shows the normalisation of topsoils from areas of open space overlying the youngest and lowest river terraces to soils in England and Wales. Approximately half of the soil samples from Richmond overlie this parent material. Topsoils in this category generally have lower concentrations of most elements relative to median values for England and Wales (McGrath and Loveland, 1992). Elements associated with clay rich soils, Al, K and Mg, have ratios of < 1, possibly reflecting the sandy nature of these soils (see Table 6.11). The ratios for these three elements are very similar to those observed for soils overlying London Clay. This is consistent with results from the particle size analysis which shows that soils in Richmond, in general, have a low clay content (see Tables 6.7-6.12).

However, the Fe content of soils developed over 1-River terraces is much higher than that of topsoils developed from London Clay, being very close to the median concentration reported for the soils of England and Wales (McGrath and Loveland, 1992). This may be a characteristic of the geochemical signature for this parent material (see Table 7.5).

The ratios of Ni and Co, and to a lesser extent Ca, Sr, Ba and Mn, are higher than those observed for topsoils in areas of open space overlying London Clay. Chromium, as with topsoils and subsurface soils derived from London Clay, has a ratio of just below 1. The geochemical signatures for these parent materials may differ, despite similarities in soil texture (see Table 6.11), or anthropogenic additions may also differ. Copper, Zn and P have normalisation ratios of > 1 in topsoils derived from 1-river terraces in areas of open space, but Pb has a ratio of > 2. This illustrates the widespread use of Pb in the urban environment, and the fact that small particles of Pb which are emitted in exhaust fumes can be carried several kilometres (Wheeler and Rolfe, 1979). For topsoils in areas of open space overlying London Clay the Pb ratio was also > 1.

7.2.15 1-River terraces - subsurface soils (30-45cm) in areas of open space

For subsurface soils, see Fig. 7.7b, only Pb has a ratio of > 1, although this ratio is lower than that observed for topsoils. Metals tend to accumulate in the top 5cm of soil (Adriano, 1986). The other elements for which normalisation ratios > 1 are observed in topsoils, (Cu, Zn and P) have ratios of < 1 in subsurface soils. As with Pb, this is a reflection of the enhancement of these elements in topsoils as a result of anthropogenic activity. Most elements have similar concentrations in topsoils and subsurface soils. These are Na, K, Mg, Sr, Ba, Al, Cr, Mn, Fe, Co, and Ni. This suggests that most elements in these soils are unaffected by anthropogenic activity with a consistent geochemical signature (despite a significantly higher sand content at depth, $P < 0.05$ - see Tables 6.11 and 6.12). In general these soils remain undisturbed being located in Bushy Park and Hampton Court.

7.2.16 1-River terraces - topsoils (0-15cm) in urban gardens

Figure 7.8a shows the normalisation of elements in garden soils overlying 1-river terraces. Half of the elements shown in Fig 7.8a have normalisation ratios > 1, and this is in contrast to topsoils overlying 1-river terraces in areas of open space. The elements which have ratios < 1, Na, K, Mg, Al, and Mn, are probably less important in anthropogenic processes than those which have ratios > 1. Despite this, the ratios of these elements are generally higher than in topsoils overlying the same parent material in areas of open space (see Table 7.5). This may result from of minor anthropogenic additions or variation of the geochemical signature. However, the low ratios of K, Mg, Al and Mn for both land-uses may be the result of the high sand content of these soils (see Tables 6.7 and 6.12). Calcium, Sr and Ba have normalisation ratios of > 1 in garden soils, and these ratios are higher than those observed in areas of open space. A similar trend was also observed in garden soils overlying London Clay. Probable anthropogenic sources of Ca, Sr and Ba have been discussed extensively in this study, and are summarised in Table 3.2. Iron, Co and Ni have very similar ratios (see Fig. 7.8a); all approximately 1. These elements are geochemically very similar and the pattern in fig 7.8a suggests a similar source. The ratios of these 3 elements are higher than those found in areas of open space over the same parent material, particularly Ni and Co. This probably reflects anthropogenic additions of these to soils, and several studies have reported the enhancement of these elements in the urban environment (Lagerwerff and Specht, 1970 and Smith and Carson, 1981, respectively). Garden Soils in Richmond have metal ratios in the order: Pb > Cu > Zn > Ni. The Pb ratio is nearly 7 times greater than the median concentration for England and wales (McGrath and Loveland, 1992). Copper and Zn are widely reported to be enhanced in the urban environment, particularly in roadside soils (Ward et al., 1977 and Warren and Birch, 1987). These metals have higher ratios than in soils in areas of open space overlying the same parent material (see Table 7.5). Phosphorus also has a ratio of > 1, which may be as a result of the use of fertilisers or biogeochemical cycling from garden vegetation. Chromium has a ratio of < 1, similar to that found in areas of open space.

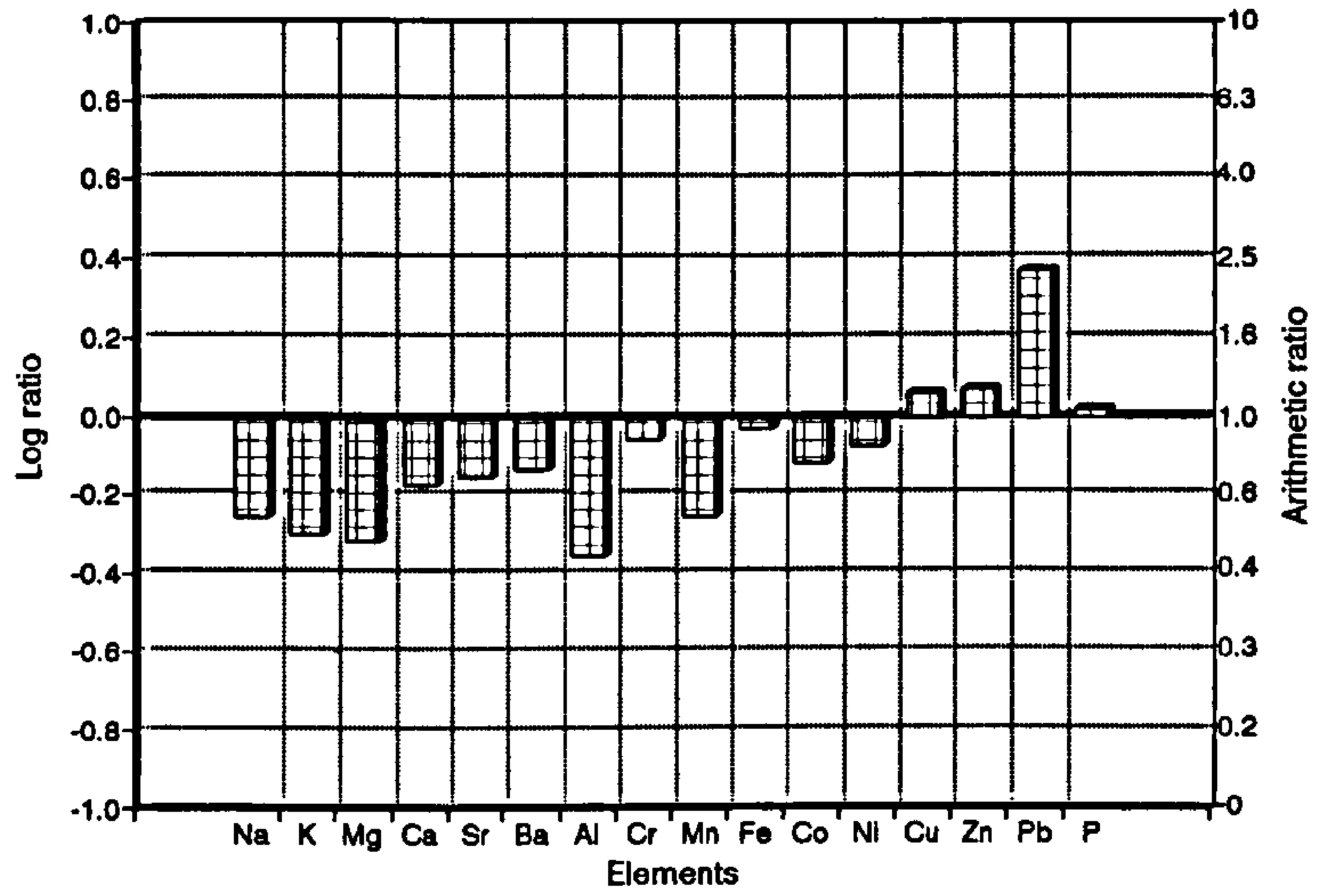


Fig. 7.7a Median concentrations of selected elements in topsoils (0-15cm) from areas of open space overlying 1-river terraces in Richmond, normalised to median concentrations for soils in England and Wales (McGrath and Loveland, 1992) and expressed on a log-scale

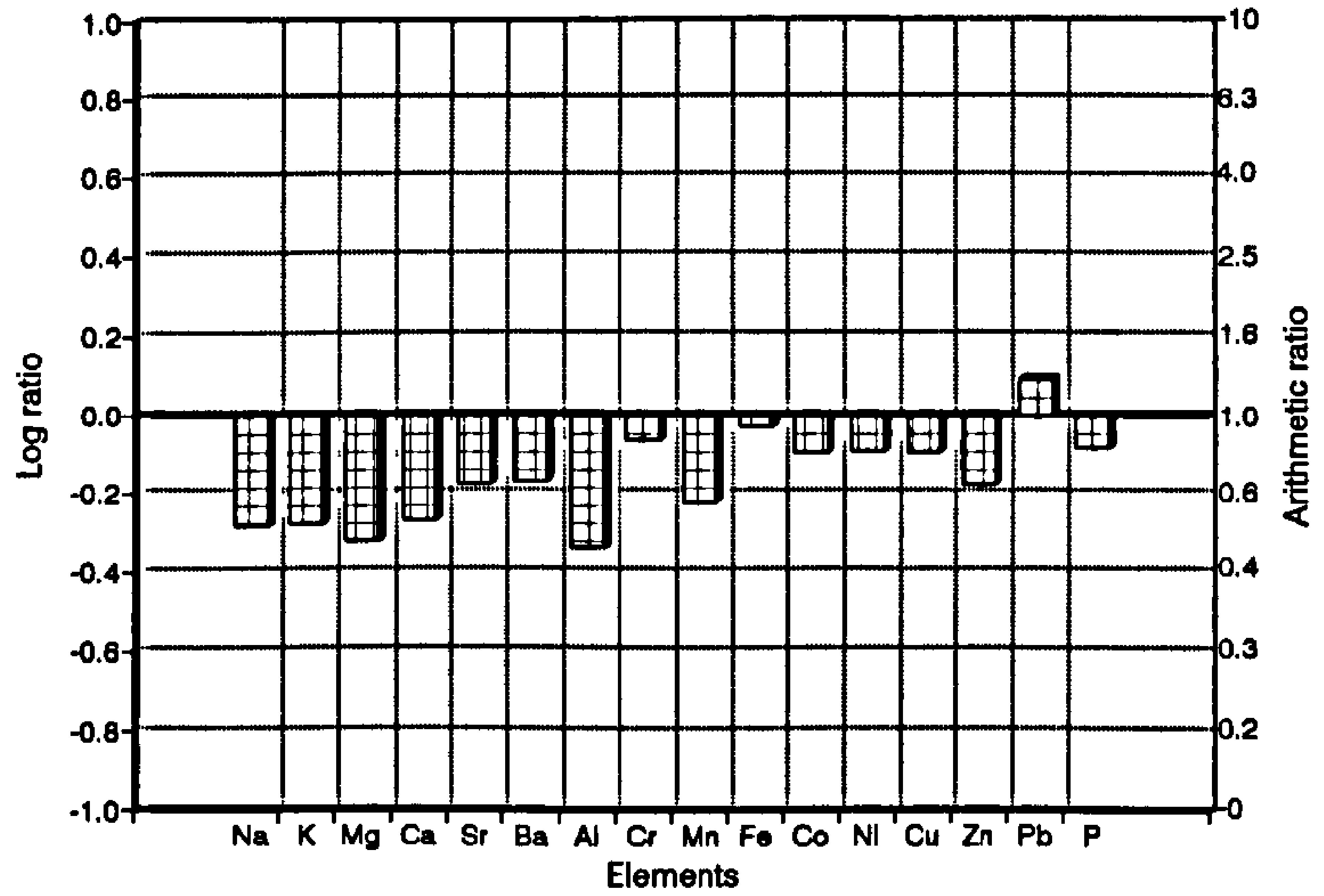


Fig. 7.7b Median concentrations of selected elements in subsurface soils (30-45cm) from areas of open space overlying 1-river terraces in Richmond, normalised to median concentrations for soils in England and Wales (McGrath and Loveland, 1992) and expressed on a log-scale

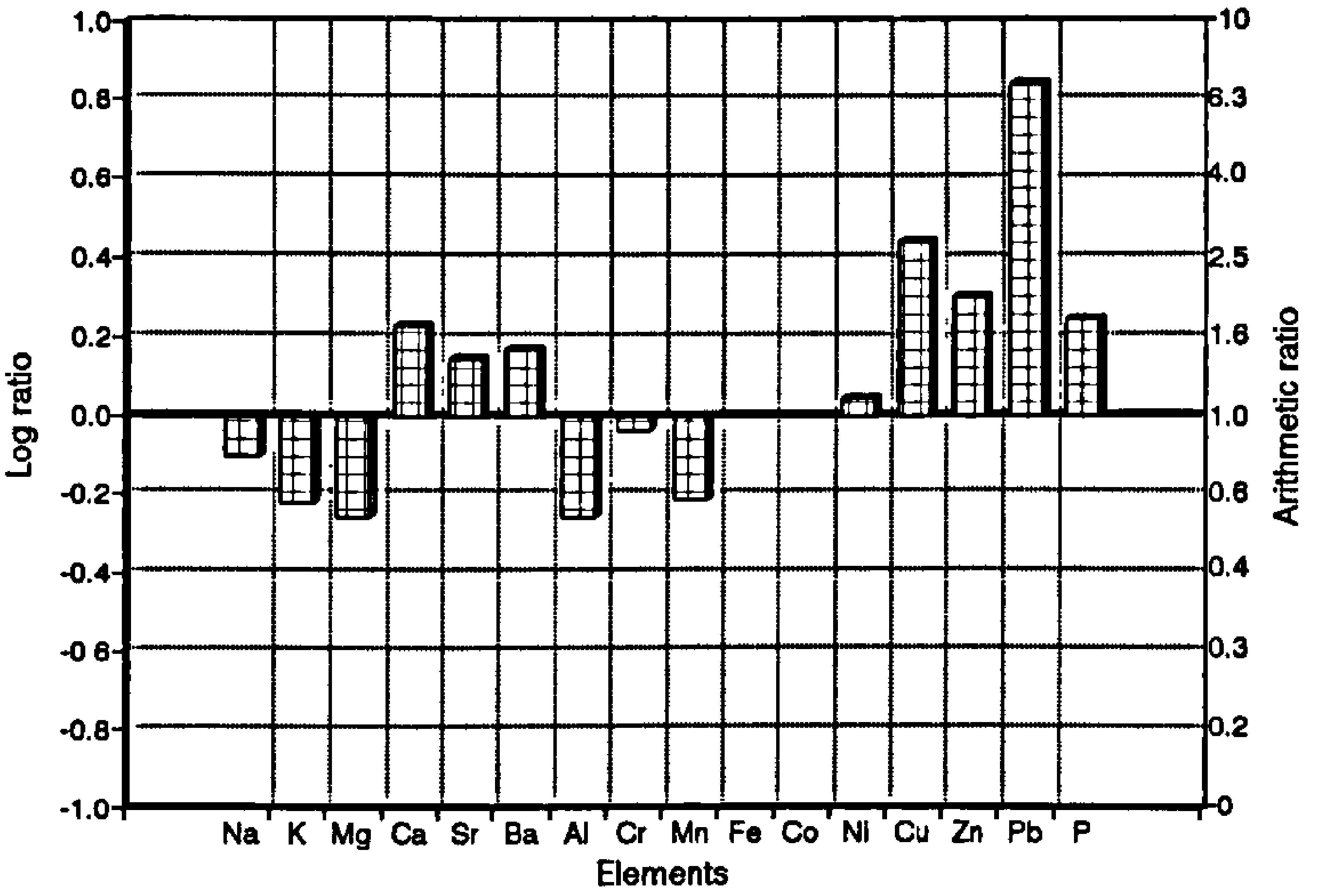


Fig. 7.8a Median concentrations of selected elements in topsoils (0-15cm) from urban garden overlying 1-river terraces in Richmond, normalised to median concentrations for soils in England and Wales (McGrath and Loveland, 1992) and expressed on a log-scale

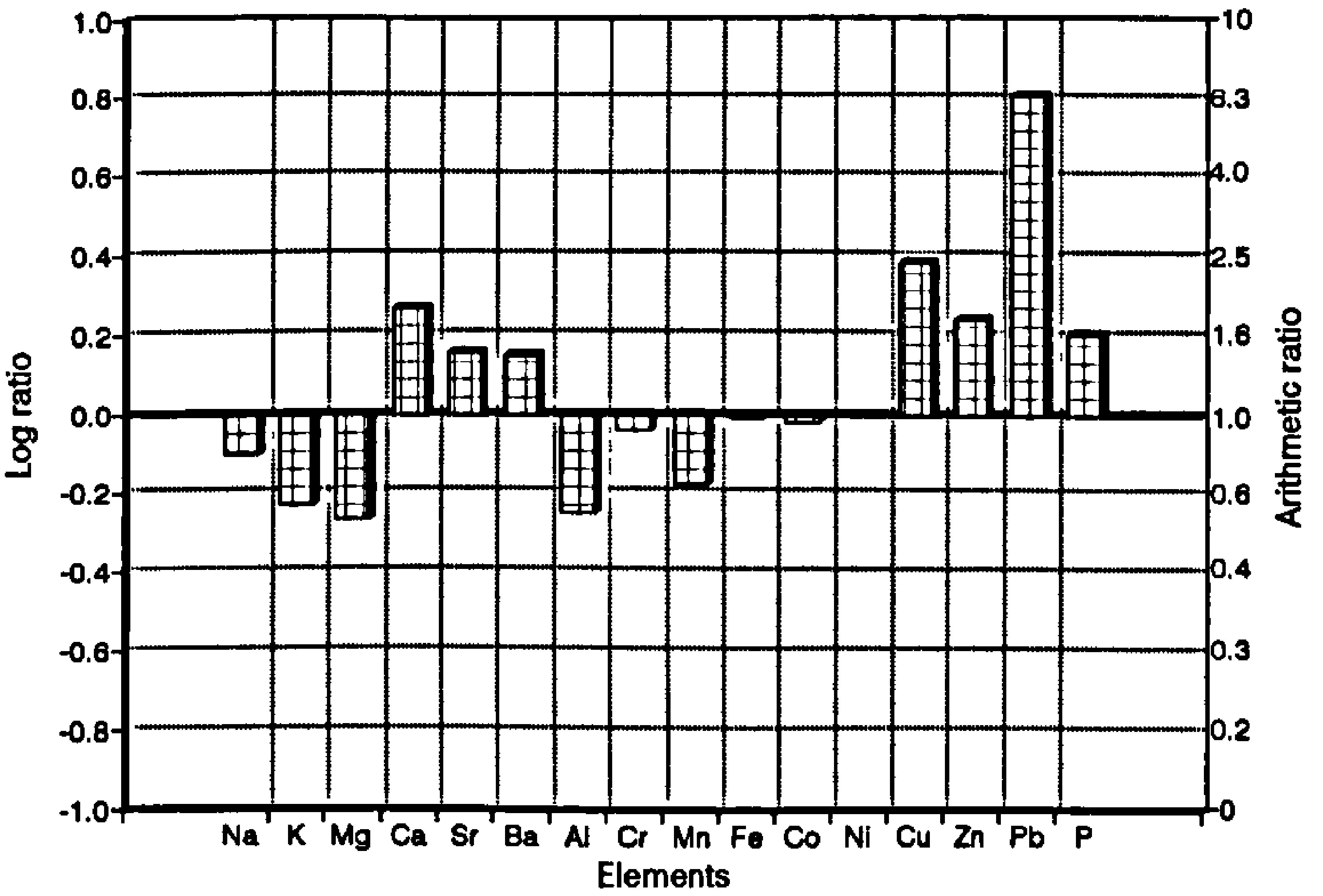


Fig. 7.8b Median concentrations of selected elements in subsurface soils (30-45cm) from urban gardens overlying 1-river terraces in Richmond, normalised to median concentrations for soils in England and Wales (McGrath and Loveland, 1992) and expressed on a log-scale

7.2.17 1-River terraces - subsurface soils (30-45cm) in urban gardens

Subsurface soils, see Fig. 7.8b, have a very similar pattern to that of topsoils. Sodium, K, Mg, Al, Cr, and Mn have ratios < 1 which are very similar to those reported for topsoils, probably reflecting a consistent part of the geochemical signature (see Table 7.5). Calcium, Sr and Ba have normalisation ratios of > 1 and these ratios are equal to or greater than the ratios for topsoils, possibly as a result of the burial of building material (see Table 3.2). Copper, Zn, Pb and P have ratios very similar to those found in topsoils, although slightly lower, reflecting greater accumulation in the top 15cm. Garden soils are subjected to a great deal of disturbance during building activity. This relationship is not so apparent in soils from areas of open space, where profiles remain intact and elements with anthropogenic sources are generally present at higher concentrations in topsoils. The ratios of Fe, Co and Ni are slightly lower in subsurface soils than in topsoils, but close to 1. Higher concentrations of elements at depth could also be as a result of movement down the soil profile, and the sandy nature of the soil would aid this (see Table 6.12).

Table 7.5 Ratios of elements in soils overlying 1-river terraces, designated by land-use, after normalisation to median concentrations for soils in England and Wales (McGrath and Loveland, 1992)

	topsoils		subsurface soils	
	n=55	n=50	n=55	n=50
	OS	UG	OS	UG
Na	0.55	0.79	0.52	0.79
K	0.50	0.60	0.53	0.59
Mg	0.48	0.55	0.48	0.54
Ca	0.67	1.70	0.54	1.85
Sr	0.70	1.40	0.67	1.43
Ba	0.73	1.48	0.68	1.41
Al	0.44	0.55	0.46	0.56
Cr	0.88	0.92	0.86	0.91
Mn	0.55	0.61	0.60	0.66
Fe	0.94	1.00	0.93	0.98
Co	0.76	1.00	0.80	0.96
Ni	0.85	1.10	0.81	1.00
Cu	1.14	2.77	0.80	2.41
Zn	1.17	2.00	0.67	1.73
Pb	1.04	6.95	1.24	6.41
P	1.01	1.76	0.82	1.59

OS Soils in areas of open space UG Soils from urban gardens

7.2.18 River brickearths - topsoils (0-15cm) from areas of open space

Three soil samples were taken from areas of open space overlying river brickearths; thus interpretation of the data must be made with great caution. The trend observed for topsoils in Fig 7.9a is similar to that observed for soils from areas of open space overlying alluvium. The normalisation ratios for Na, K, Mg and Al, although < 1, are higher than observed for soils overlying river terraces and London Clay. This is probably due to the geochemical signature for this parent material, although a particle size analysis shows these soils do not differ significantly in their sand, silt and clay content ($P > 0.05$ - see Table 6.11), from soils overlying other parent materials. Iron, Co and Ni have ratios close to 1, which is typical for soils from areas of open space. The Pb, Cu and P ratios are all > 1, indicating either naturally higher concentrations of these elements and/or anthropogenic additions of these metals to topsoils. Many of these sites are located close to the Thames near St. Margarets and Twickenham, areas where high concentrations of most elements are observed. In the past, periodic flooding from the Thames may have been an important source of elements to these soils.

7.2.19 River brickearths - subsurface soils (30-45cm) from areas of open space

In subsurface soils, the ratios for many elements are higher than those observed for soils overlying river terraces and London Clay, see Fig. 7.9b and Tables 7.1-7.6. However the trend observed is typically that of an undisturbed soil profile. Most elements have a lower ratio in subsurface soils relative to those for topsoils; these are Na, Ca, Sr, Cr, Ni, Cu, Zn, Pb and P. This is likely to be as a result of anthropogenic activity and the accumulation of these elements in the top 15cm and/or a variation of the geochemical signature. Elements such as K, Mg, Al and Mn have similar ratios in topsoils and subsurface soils, which may be the result of a consistent geochemical signature for these particular elements. Lead and P are the only elements which have ratios of > 1 in subsurface soils.

7.2.20 River brickearths - topsoils (0-15cm) from urban gardens

Six samples were taken from garden soils overlying river brickearths. Figure 7.10a shows the normalisation ratios for the garden soils. The ratios for elements in topsoils are very similar to those observed for garden soils from Richmond in general. Calcium, Sr, Ba, Ni, Cu, Zn, Pb and P have ratios > 1, with the heavy metals in the order: Pb > Cu > Zn. This reflects the widespread anthropogenic use of these metals, Pb in particular. Calcium, Sr and Ba have ratios > 1 for all garden soils, and this is most likely a result of their being constituents of materials used for construction (see Table 3.2). Iron, Co and Cr have ratios of approximately 1.

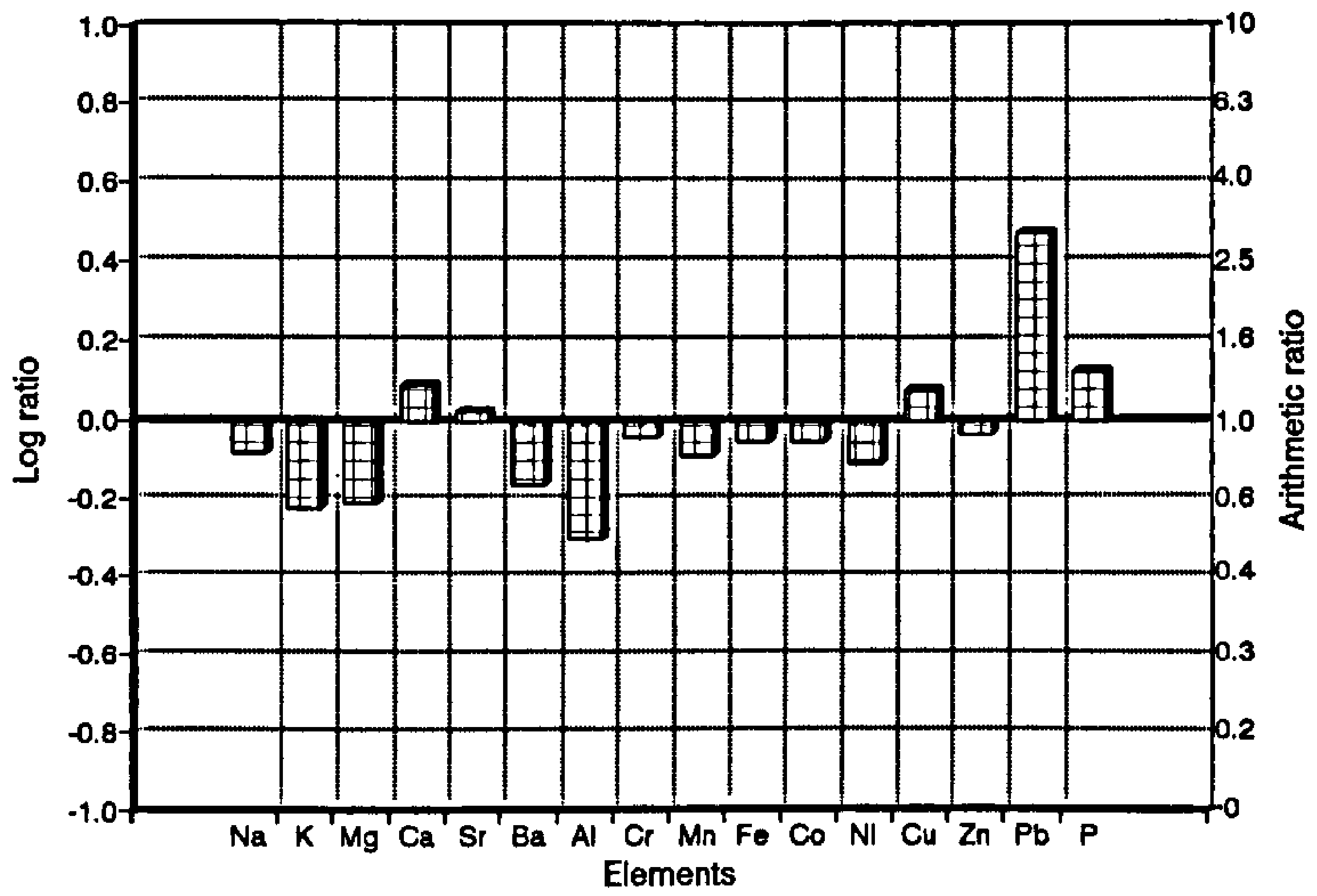


Fig. 7.9a Median concentrations of selected elements in topsoils (0-15cm) from areas of open space overlying river brickearths in Richmond, normalised to median concentrations for soils in England and Wales (McGrath and Loveland, 1992) and expressed on a log-scale

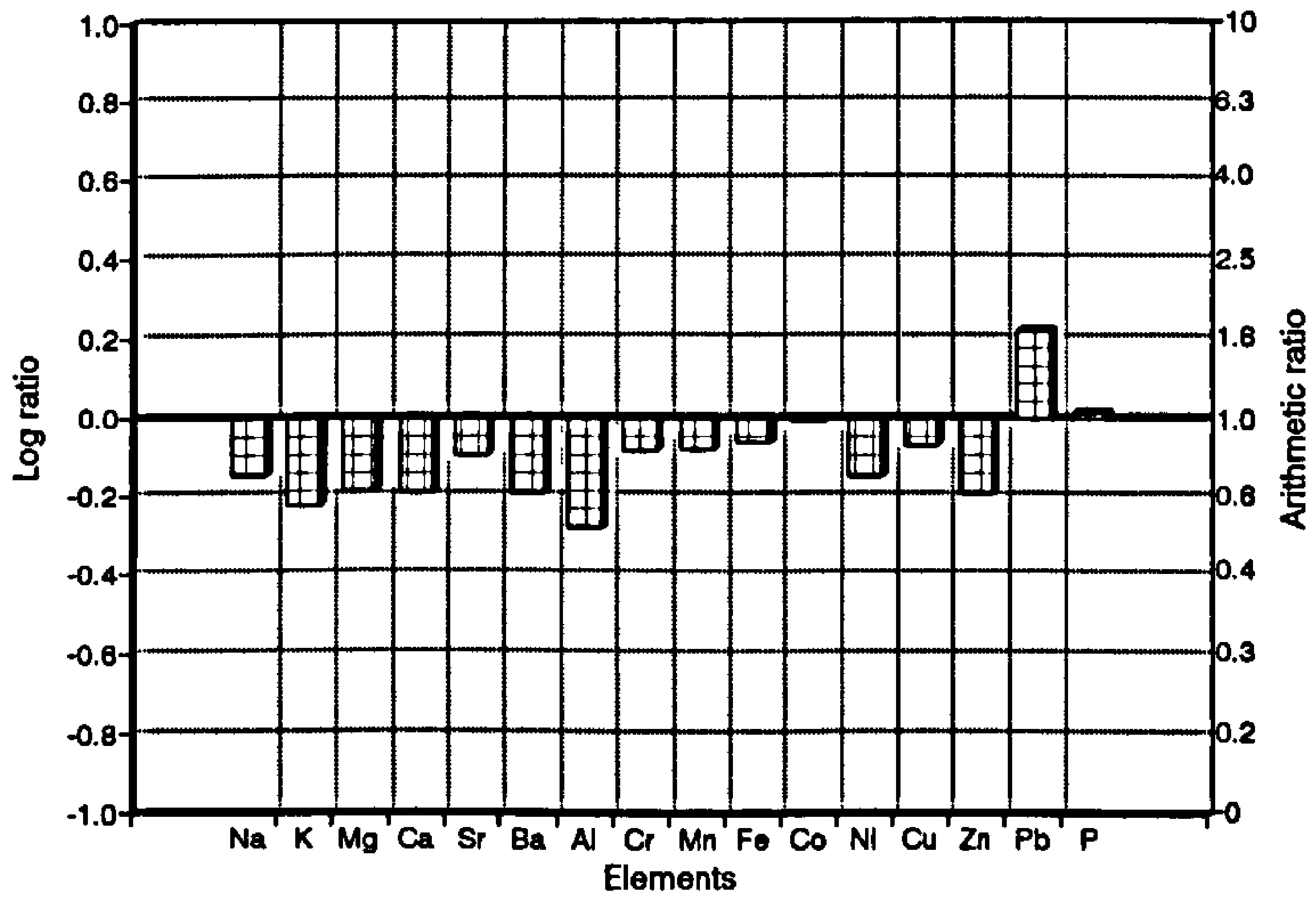


Fig. 7.9b Median concentrations of selected elements in subsurface soils (30-45cm) from areas of open space overlying river brickearths in Richmond, normalised to median concentrations for soils in England and Wales (McGrath and Loveland, 1992) and expressed on a log-scale

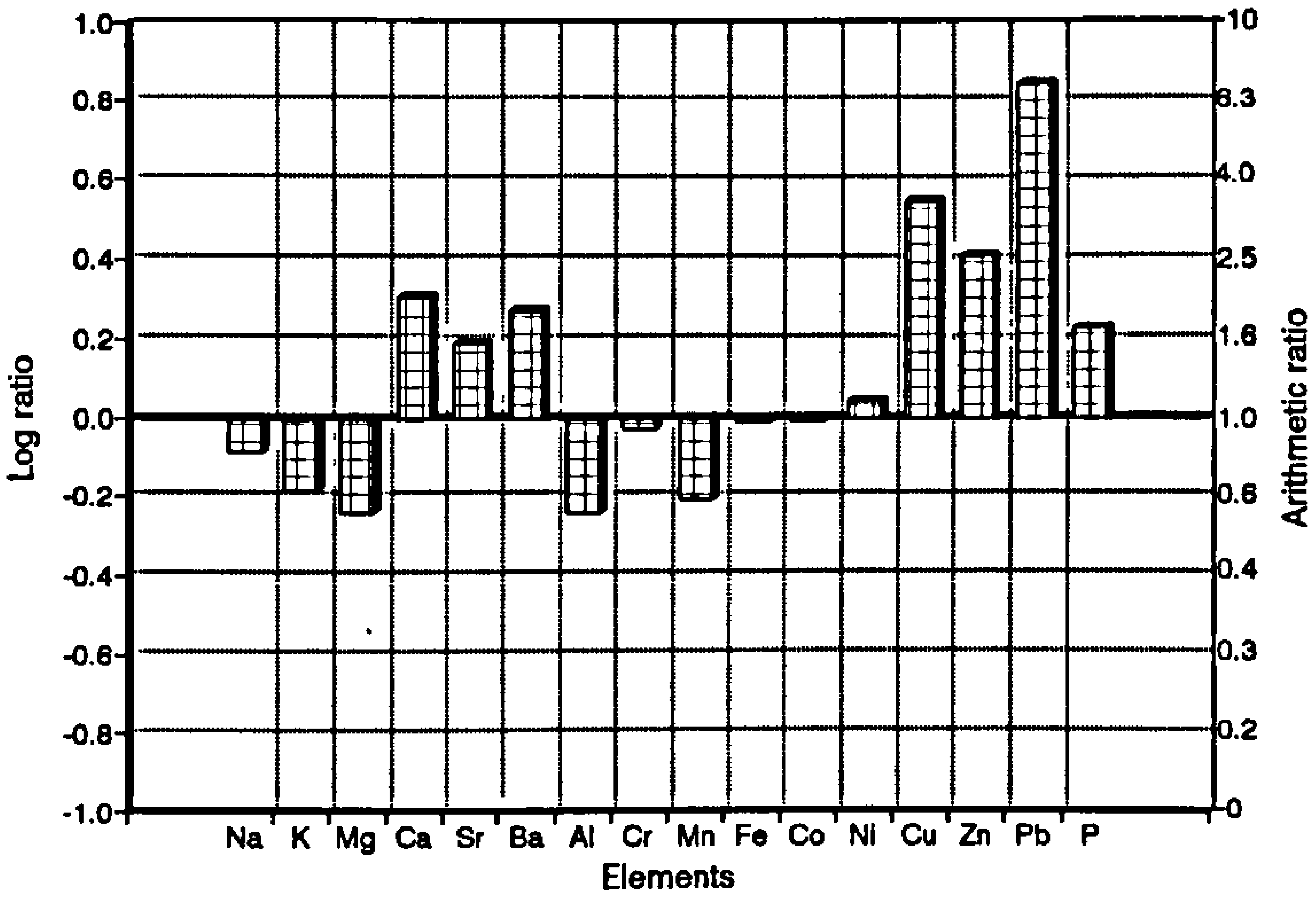


Fig. 7.10a Median concentrations of selected elements in topsoils (0-15cm) from urban gardens overlying river brickearths in Richmond, normalised to median concentrations for soils in England and Wales (McGrath and Loveland, 1992) and expressed on a log-scale

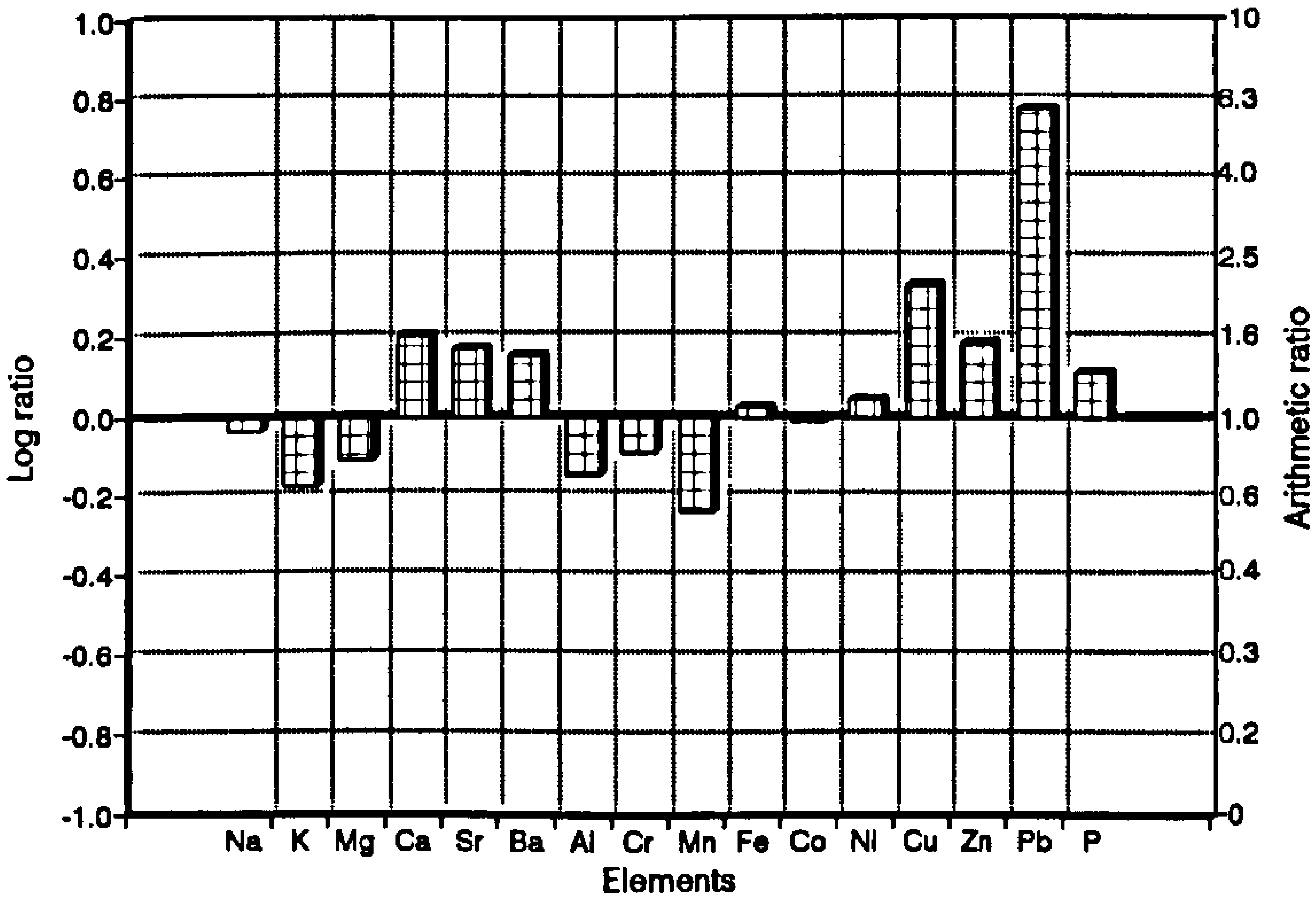


Fig. 7.10b Median concentrations of selected elements in subsurface soils (30-45cm) from urban gardens overlying river brickearths in Richmond, normalised to median concentrations for soils in England and Wales (McGrath and Loveland, 1992) and expressed on a log-scale

7.2.21 River brickearths - subsurface soils (30-45cm) from urban gardens

The elements which were observed to have ratios > 1 in topsoils also have ratios > 1 in subsurface soils, see Figs. 7.10a and 7.10b. However, Ca, Sr, Ba, Cr, Co, Cu, Pb, Zn and P all have lower ratios in subsurface soils (see Table 7.6), as do Co and Cr in this case. This confirms that although disturbance of the soil has occurred, the greatest accumulation of these elements occurs in the top 15cm. These soils have higher ratios of Mg, Al and Fe than topsoils, which probably reflects variation of the geochemical signature. A comparison of results for particle size analysis shows a similar texture for both sample depths, although subsurface soils have a significantly higher sand content (see Tables 6.11 and 6.12).

Table 7.6 Ratios of elements in soils overlying river brickearths, designated by land-use, after normalisation to median concentrations for soils in England and Wales (McGrath and Loveland, 1992)

	topsoils		subsurface soils	
	n=3	n=6	n=3	n=6
	OS	UG	OS	UG
Na	0.82	0.82	0.71	0.92
K	0.60	0.65	0.60	0.67
Mg	0.62	0.57	0.65	0.78
Ca	1.23	2.02	0.64	1.59
Sr	1.05	1.55	0.80	1.48
Ba	0.69	1.87	0.64	1.42
Al	0.50	0.57	0.52	0.71
Cr	0.90	0.94	0.82	0.81
Mn	0.81	0.62	0.83	0.57
Fe	0.88	0.97	0.86	1.05
Co	0.88	0.98	0.98	0.97
Ni	0.77	1.10	0.71	1.10
Cu	1.19	3.52	0.85	2.14
Zn	0.92	2.57	0.64	1.53
Pb	2.98	6.79	1.65	6.00
P	1.32	1.69	1.03	1.29

OS Soils in areas of open space UG Soils from urban gardens

7.2.22 Alluvium - topsoils (0-15cm) in areas of open space

Most of the soils in Richmond overly river terraces of varying age. As a consequence the sample numbers for other types of parent materials are generally low. This is the case with soils in Richmond overlying alluvium (n=8, see Table 7.7). Alluvium deposits are the most recent in Richmond, and have been aged at between 1800-3200 years (BGS, 1981). Figure 7.11a shows a pattern which is normally associated with garden soils in Richmond with ratios > 1; these are Sr, Ba, Ca, Fe, Co, Ni, Cu, Pb, Zn, and P. This was not observed for soils overlying London Clay or river terraces in areas of open space. Although Na, K, Mg, and Al have ratios of < 1, these ratios are higher than those observed for the same elements in areas of open space overlying river terraces and London Clay (see Tables 7.1-7.5 and 7.7). This is not explained by differences in soil texture as the sand, silt and clay content does not vary significantly in Richmond for land-use or parent material ($P > 0.05$ - see Table 6.11). Soils overlying alluvium have significantly higher concentrations of Be, Ca, Sr, Co, Ni and Cu than soils overlying London Clay and the different river terraces (all $P < 0.001$).

Calcium, Sr and Ba all have ratios > 1, with the ratio for Ca 2.5 times the reported median concentration for soils in England and Wales (McGrath and Loveland, 1992). This pattern is generally only observed in garden soils. Ratios of Fe, Co and Ni are > 1, and higher than ratios associated with other parent materials in Richmond (see Table 7.1-7.7). Copper, Zn, Pb and P have ratios greater than 1 and comparable with ratios observed in garden soils (see Table 7.7).

There are several possible explanations why soils overlying deposits of alluvium in areas of open space have higher concentrations of a suite of elements compared with soils overlying other parent materials in areas of open space. Deposits of alluvium flank the Thames in several location (see Figure 4.2), and some of these sites are close to a contemporary water works and areas of past industrial activity (see Supp. Figs. 6b and 6c). Emissions from these industries may have increased concentrations of elements in these soils. In addition, flooding from the Thames in the past may have been a source of several elements. In contrast, the natural geochemical signature for these soils may produce higher concentrations of a suite of elements compared with soils developed on river terraces and London Clay. A detailed examination of the mineralogy of the soils in Richmond would be necessary to test this; percentages of sand, silt and clay, soil pH and organic matter content do not vary significantly for soils, irrespective of parent material.

7.2.23 Alluvium - subsurface soils (30-45cm) in areas of open space

For subsurface soils overlying alluvium in areas of open space, see Fig. 7.11b, the pattern is very different to that observed for most soils in Richmond, irrespective of land-use or parent material. Sodium, Sr, Ba, Cr and Ni in particular have higher ratios at 30-45cm compared with 0-15cm, which may have resulted from disturbance of the soil profile or natural variation of the geochemical signature. Potassium, Mg, Fe, Mn, and Co also have higher ratios than topsoil samples. Soil texture does not differ greatly with depth, although the sand content is significantly higher in subsurface soils ($P < 0.05$ - see Tables 6.11 and 6.12). Copper, Zn and Pb have lower ratios in subsurface soils, suggesting greater accumulation of these metals in topsoils relative to 30-45cm.

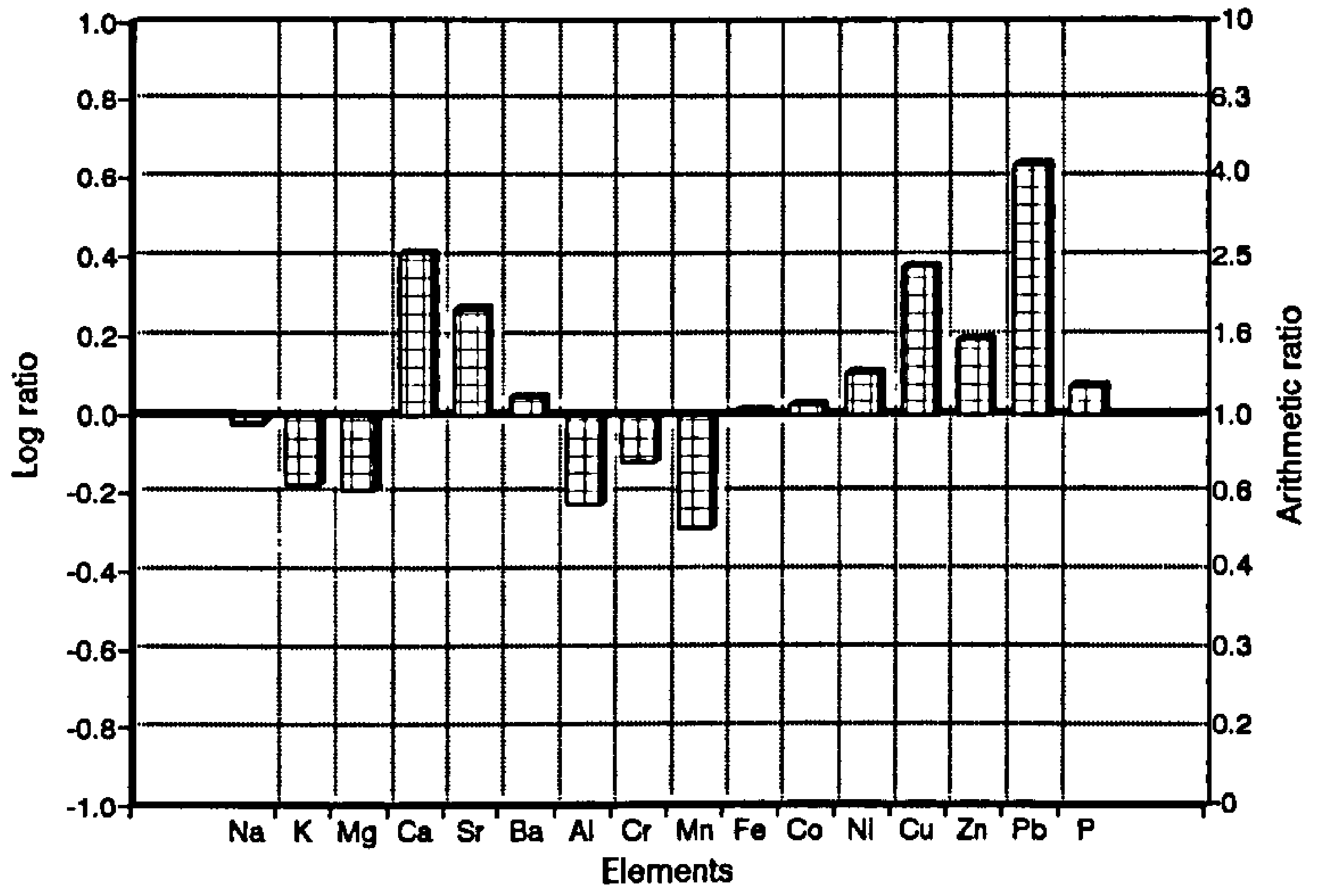


Fig. 7.11a Median concentrations of selected elements in topsoils (0-15cm) from areas of open space overlying alluvium in Richmond, normalised to median concentrations for soils in England and Wales (McGrath and Loveland, 1992) and expressed on a log-scale

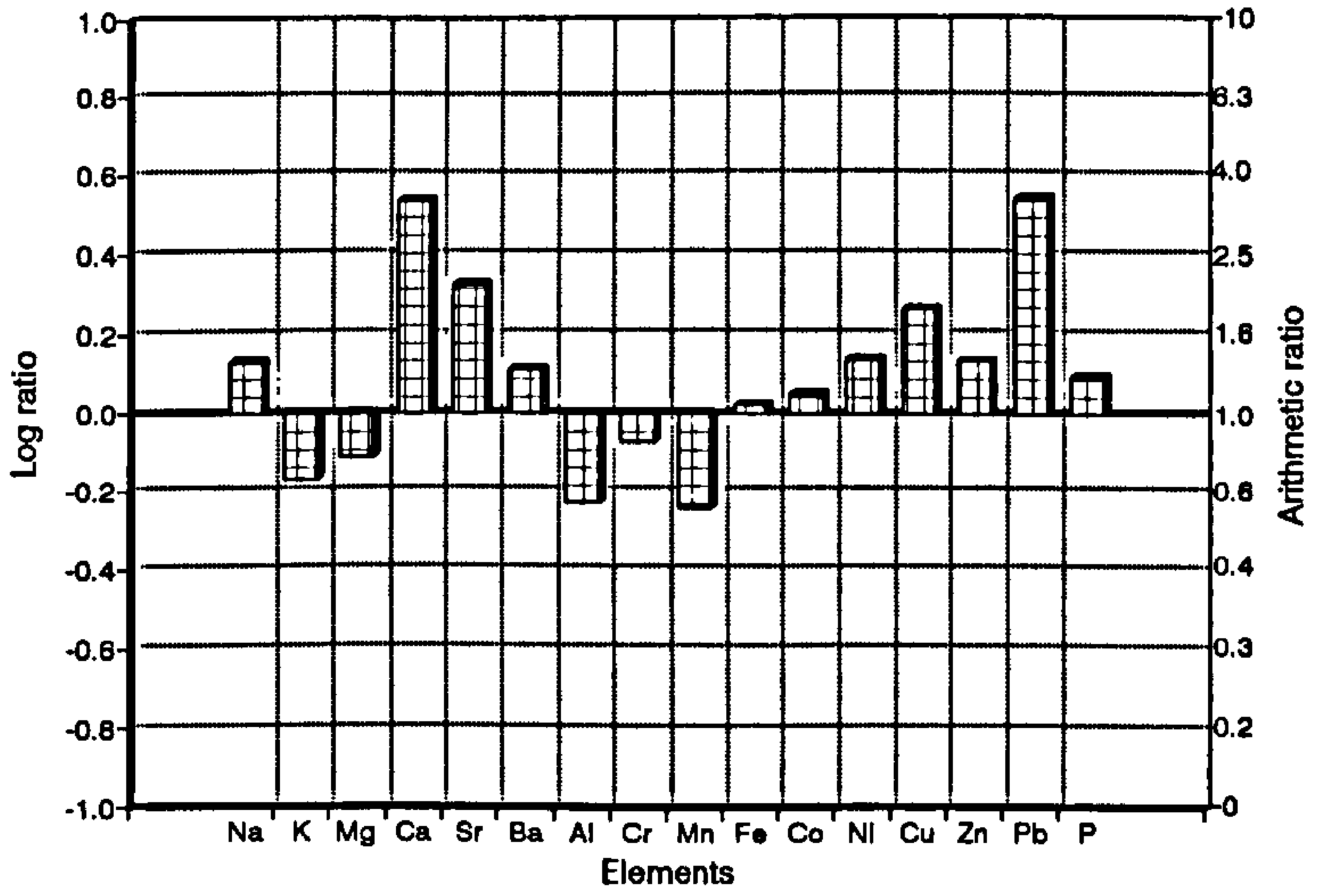


Fig. 7.11b Median concentrations of selected elements in subsurface soils (30-45cm) from areas of open space overlying alluvium in Richmond, normalised to median concentrations for soils in England and Wales (McGrath and Loveland, 1992) and expressed on a log-scale

7.2.24 Alluvium - topsoils (0-15cm) from urban garden soils

Figure 7.12a shows the normalisation ratios for garden soils overlying alluvium. The trend is very similar to that observed for garden soils from Richmond in general. Calcium, Sr, Ba, Ni, Cu, Zn, Pb and P have ratios > 1, Pb and Cu the highest of these (4.85 and 3.33, respectively - see Table 7.7), which is a typical trend for garden topsoils. Iron, Co and Cr have ratios of approximately 1, similar to other garden soils. Sodium, K, Mg, Al, and Mn have ratios of < 1, which may reflect the sandy nature of the soil (see Table 6.11). The ratios for K, Al and Mn are higher than those reported for the same parent material in areas of open space (see Table 7.7) which may reflect variation of the geochemical signature for alluvium. The ratios of these elements remain generally higher than in soils overlying London Clay and river terraces. The normalisation ratios for Pb and Zn are slightly lower than for garden soils overlying other parent materials, which may reflect the age of the houses in these areas and their distance from major roads. However, Cu has a higher ratio for garden soils overlying alluvium, than for any other parent material. Phosphorus has a normalisation ratio similar to that for garden soils overlying other parent materials (see Tables 7.1-7.7).

7.2.25 Alluvium - subsurface soils (30-45cm) from urban gardens

For subsurface soils, see Fig. 7.12b, the overall pattern is similar to that observed for other subsurface garden soils in Richmond. In contrast, however, several elements have higher ratios at 30-45cm than at 0-15cm in these soils. This is observed for Ca, Sr, Ba, Fe, Ni, Zn and Pb. Disturbance of the soil profile by anthropogenic activity may have caused this, as could migration of elements down the soil profile or variation of the geochemical signature. In subsurface soils the normalisation ratios of Mg and Al, although < 1, are slightly higher than in topsoils which probably results from variation of the geochemical signature. Elements such as Na, K and Cr have similar ratios in subsurface soils and topsoils, whilst Cu and P have lower ratios at depth 30-45cm. In general, these soils have higher ratios for a number of elements compared with other parent materials for soils at depths of 30-45cm. This trend was also observed for topsoils.

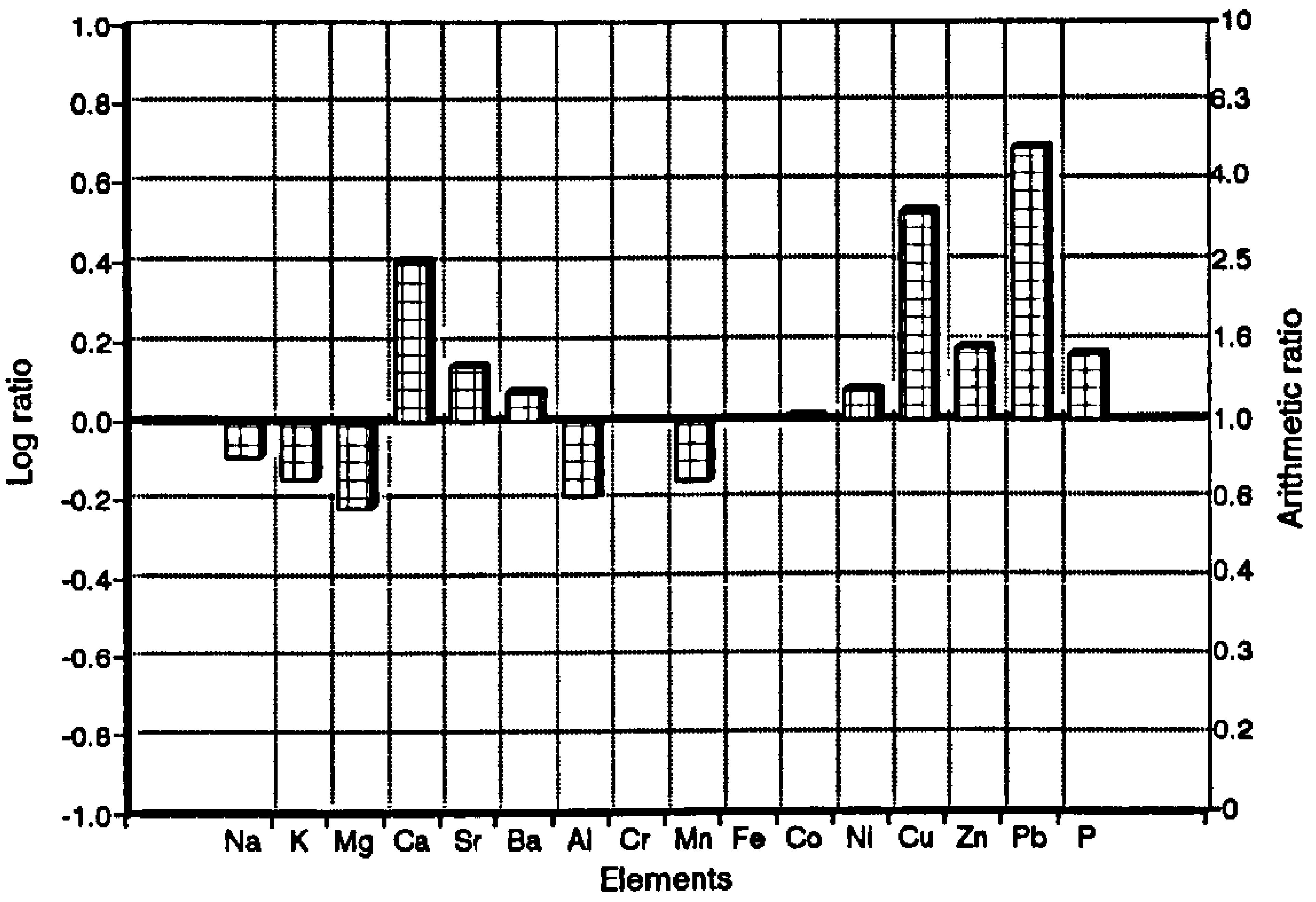


Fig. 7.12a Median concentrations of selected elements in topsoils (0-15cm) from urban gardens overlying alluvium in Richmond, normalised to median concentrations for soils in England and Wales (McGrath and Loveland, 1992) and expressed on a log-scale

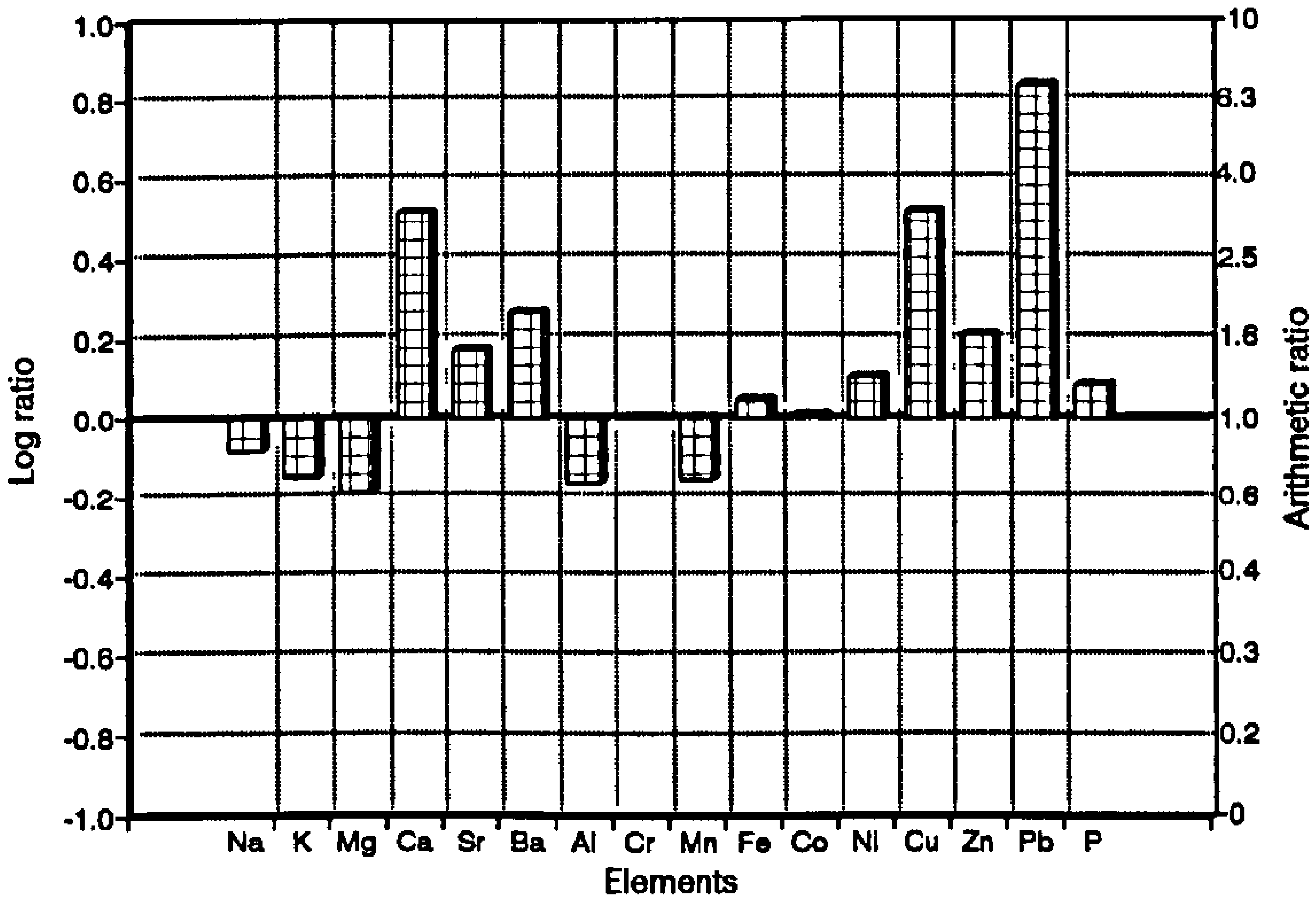


Fig. 7.12b Median concentrations of selected elements in subsurface soils (30-45cm) from urban gardens overlying alluvium in Richmond, normalised to median concentrations for soils in England and Wales (McGrath and Loveland, 1992) and expressed on a log-scale

Table 7.7 Ratios of elements in soils overlying alluvium, designated by land-use, after normalisation to median concentrations for soils in England and Wales (McGrath and Loveland, 1992)

	topsoils		subsurface soils	
	n=8	n=7	n=8	n=7
	OS	UG	OS	UG
Na	0.95	0.81	1.35	0.83
K	0.66	0.71	0.68	0.71
Mg	0.64	0.60	0.77	0.65
Ca	2.56	2.52	3.45	3.29
Sr	1.86	1.38	2.11	1.49
Ba	1.10	1.17	1.28	1.83
Al	0.59	0.64	0.59	0.69
Cr	0.76	1.00	0.85	1.00
Mn	0.51	0.70	0.57	0.70
Fe	1.02	1.00	1.05	1.11
Co	1.05	1.02	1.12	1.02
Ni	1.27	1.18	1.38	1.26
Cu	2.37	3.33	1.83	3.30
Zn	1.54	1.52	1.36	1.62
Pb	4.30	4.85	3.50	6.90
P	1.48	1.46	1.24	1.21

OS Soils in areas of open space UG Soils from urban gardens

7.2.26 Discussion and summary

Soils in Richmond generally have a high content of sand (see Tables 6.7-6.12) which seems to be reflected in low concentrations of K, Mg, Al and Mn, irrespective of parent material (see Tables 7.1 - 7.7). Soils overlying deposits of London Clay have a high sand content, consistent with the description of the geology (BGS, 1981). Deposits of alluvium and river brickearths have higher concentrations of a number of elements, including those elements associated with clays such as K, Mg, Al and Mn. However, this is not due to differences linked to soil texture, as particle size analysis of the soils in Richmond shows that the sand, silt and clay content does not vary significantly with parent material ($P > 0.05$ - see Tables 6.11 and 6.12). Calcium, Sr, Br, Fe, Co, Ni, Cu, Zn, Pb and P have ratios of > 1 in topsoils overlying alluvium in areas of open space; this is not observed in other areas of the same land-use overlying different parent materials. High concentrations of a number of elements are observed in deposits close to the Thames (see section 6.2) and this may be due to the influence of periodic flooding or past industrial activity in these areas. An examination of soil mineralogy in Richmond, in relation to parent material, is necessary to test the hypothesis that higher concentrations of a suite of elements in soils overlying alluvium and river brickearths are a feature of the natural geochemical signatures.

Land-use has an important influence on the soil geochemistry in Richmond. With the exception of soils from areas of open space overlying alluvium, several elements have ratios of > 1 in garden soils only. This is observed for Ca, Br, Sr, and Ni, and for Zn and P in most cases. The widespread use of Pb in the urban environment results in ratios of > 1 in soils from areas of open space and garden soils, irrespective of parent material. The exception to this is the small number of samples overlying the high river terraces in the centre of Richmond Park. Naturally low concentrations of Pb, associated with the parent material, coupled with their distance from major roads, results in Pb concentrations of < 40 μg/g. Soils overlying the high level terraces have the lowest ratios of every element, with the exception of Cr, which results from naturally low concentrations and minimal anthropogenic additions.

Calcium, Br and Sr are present at significantly higher concentrations in garden soils compared with soils from areas of open space. In areas of open space, only soils developed over alluvium have ratios of all these elements which exceed 1. In general, it is considered that anthropogenic additions of these elements are responsible for the higher concentrations observed in garden soils. These elements are geochemically very similar and the most likely sources in soils are the burial of building materials such as gypsum, plaster, bricks and concrete, ceramics which are rich in Ca, and fertilisers and lime. A large number of houses were bombed during the second world war; this may be a source of building material in garden soils. Barium is also a component of paint and present in fossil fuel residues (see Table 3.2).

Zinc, Cu and Ni are generally observed in higher concentrations in urban soils than in areas of open space. These have several sources in the urban environment, including the disposal of fossil fuel residues and the flaking of paint. Several studies report elevated concentrations of these elements in roadside soils (Lagerwerff and Specht, 1970; Ward *et al.*, 1977; Warren and Birch, 1987; Muskett and Jones, 1990 and Ward, 1990a). Phosphorus is another element which is present in significantly higher concentrations in garden soils compared with soils from areas of open space and soils from England and Wales in general(McGrath and Loveland, 1992). The application of fertilisers in urban gardens coupled with the disposal of fossil fuel residues would account for this pattern.

7.3 The influence of house age on metal concentrations in soils

7.3.1 Introduction

A number of studies have reported the influence of house age on the Pb content of house-dusts and garden soils (Davies *et al.,* 1987; Davies and Thornton, 1987). These studies concluded that the older the housing the higher the concentration of Pb in associated soils and dusts. This was reported to be as a result of the flaking of paint from older property, which has higher concentrations of Pb than those permitted in contemporary paints, and a greater length of exposure time to various other sources of pollution (Thornton, 1990). One of the aims of this research is to investigate factors which may influence the multi-element trends in urban soils. For the purpose of this study, houses in Richmond have been separated into 3 age categories:

1. < 50 years old - (n= 33)

2. 50-100 years old - (n= 41)

3. > 100 years old - (n= 8)

7.3.2 Discussion

The geometric and arithmetic means for 22 elements in garden topsoils (0-15cm) are summarised in Table 7.8. In general most elements show a numerical increase in concentration with increasing house age, although this may not be statistically significant. This confirms the trends observed in chapter 6, where these elements were not found at significantly higher concentrations in urban gardens than in areas of open space. Students t-tests are used to investigate the importance of house-age.

The data can be split into 4 groups:

1. Those elements which do not show any increase in concentration across the age categories - K, Al, La and Ti.

2. Those elements which although showing an increase in concentration, the increase is not statistically significant - Li, Na, Mg, Cr, Mn, and Cd ($P > 0.05$).

3. Those elements which show a statistically significant increase in concentration from soils associated with property that is < 50 years old to soils associated with property that is aged 50-100 years old (Be, Ca, Sr, Co, Ni, Cu, Zn and P).

4. Those elements which show a statistically significant increase in concentration in soils across the 3 age categories (from < 50 years old to < 50-100 years old and also to > 100 years old). This is observed for Ba, V, Fe and Pb.

Using geometric means as a measure, Li concentrations increase in garden soils by 2.4 μg/g from the youngest to oldest category, whilst for the same time period Na increases by 76 μg/g, Mg by 203 μg/g, Cr by 7.3 μg/g, Mn by 86 μg/g and Cd by approximately 0.4 μg/g (see Table 7.8). These may reflect small anthropogenic additions of these elements through the use of fertilisers, and the burning and subsequent disposal of fossil fuel or natural variation of the geochemical signature.

When comparing garden soils associated with houses which are < 50 years old with those associated with houses which range from 50-100 years in age, a number of elements show a statistically significant increase in concentration. The geometric mean for Be increases from 1.0 μg/g to 1.28 μg/g ($P < 0.05$), Ca from 4050 μg/g to 6673 μg/g ($P < 0.05$), Sr from 32 μg/g to 44 μg/g ($P < 0.01$), Ba from 143 μg/g to 228 μg/g ($P < 0.01$), V from 47.5 μg/g to 51 μg/g ($P < 0.05$), Fe from 2.39 % to 2.67 % ($P < 0.05$), Co from 8.2 μg/g to 9.6 μg/g ($P < 0.05$), Ni from 21 μg/g to 25.6 μg/g ($P < 0.05$), Cu from 32 μg/g to 61 μg/g ($P < 0.05$), Zn from 122 μg/g to 232 μg/g ($P < 0.01$), Pb from 163 μg/g to 387 μg/g ($P < 0.01$) and P from 958 μg/g to 1401 μg/g ($P < 0.01$) - see Table 7.8.

When comparing the geochemistry of garden soils associated with property of between 50-100 years in age with those associated with property of > 100 years in age, only four elements show significantly higher concentrations in soil associated with the older property. These are Pb, Ba, V and Fe. The geometric mean for Pb increases from 387 μg/g to 753 μg/g ($P < 0.01$), for Ba from 228 μg/g to 351 μg/g ($P < 0.01$), V from 51 μg/g to 60 μg/g ($P < 0.05$) and Fe from 2.67 % to 3.06 % ($P < 0.05$ - see Table 7.18). Lead and Ba were important components in paint, and houses > 100 years in age would have commonly been decorated in such paint. This has been reported to increase the Pb content of soil and dust (Schwar and Alexander, 1988) and is consistent with the findings here. Iron, V and Zn are likely to be present in higher concentrations as a result of a longer history of fossil fuel burning with the older properties. Iron and V are similar geochemically, due to comparable ionic radii (Jones et al., 1990).

A number of other elements show a numerical increase in concentration in gardens associated with gardens of > 100 years compared with those of 50-100 years old, although the difference is not statistically significant (all $P < 0.05$). These are Li, Na, K, Be, Mg, Ca, Sr, Al, La, Ti, Cr, Mn, Co, Ni, Cu, Zn, Cd, and P (see Table 7.18). These probably reflect small anthropogenic additions and/or natural variation of the geochemical signature. The smaller number of elements which show a statistically significant increase in concentration across these two age categories may be the result of houses in 2 separate age groups only differing in age by a few years (i.e. houses of age 90-99 years and houses just over 100 years old). Moreover, some changes in anthropogenic practices have occurred in very recent history, with open fires still common until the 1950's in this country and the reduction of Pb in paint a fairly recent development. The last decade has also seen a significant decrease in the permissible Pb content of petrol for EC countries (see section 3.4.6.1). As a result houses of between 50-100 years and > 100 years in age would have been exposed to many of the same sources. These may account for insignificant statistical differences for a number of elements between the two age categories.

Table 7.8 Geometric and arithmetic mean concentrations of elements in garden soils in relation to house-age

Age	< 50 years		50-100 years		> 100 years	
n	33		41		8	
	GM	AM	GM	AM	GM	AM
Li	11.2	11.9	12.2	17	13.6	14
Na	180	203	223	295	256	289
K	2827	2952	2799	2880	2898	2971
Be	1.0	1.04	1.28	1.42	1.68	1.79
Mg	1634	1702	1692	1747	1837	1875
Ca	4050	5391	6673	8198	6686	7626
Sr	32	34.8	44	48	48	52.3
Ba	**143**	**151**	**228**	**251**	**351**	**358**
Al	1.63	1.70	1.57	1.61	1.70	1.74
La	17.3	17.6	17.2	17.4	18.3	18.4
Ti	690	701	660	669	668	688
V	**47.5**	**48**	**51**	**52**	**60**	**60**
Cr	36	37	39	40	43.3	44
Mn	300	322	336	354	386	393
Fe	**2.38**	**2.41**	**2.67**	**2.73**	**3.06**	**3.08**
Co	8.2	8.45	9.6	10	11.5	11.9
Ni	21	21.4	25.6	27.3	31.5	32.5
Cu	32	40.3	61	74	83	95
Zn	122	137	232	281	377	522
Cd	<0.2	<0.2	0.2	0.4	0.5	0.6
Pb	**163**	**174**	**387**	**470**	**753**	**817**
P	958	1009	1401	1555	1608	1669

Elements and data shown in bold are those which show a significant increase in concentration across each of the age categories.

GM Geometric mean

AM Arithmetic mean

Table 7.9 A summary of the statistical significance of soil data in relation to age of property

Age	< 50 years	50-100 years	> 100 years
n	33	41	8
Li		X	X
Na		X	X
K		X	X
Be		***	X
Mg		X	X
Ca		*	X
Sr		**	X
Ba		***	***
Al		X	X
La		X	X
Ti		X	X
V		**	**
Cr		X	X
Mn		X	X
Fe		**	**
Co		**	X
Ni		**	X
Cu		***	X
Zn		***	X
Cd		X	X
Pb		***	***
P		***	X

X	No statistically significant relationship
*	Statistically significant increase ($P < 0.05$)
**	Statistically significant increase ($P < 0.01$)
***	Statistically significant increase ($P < 0.001$)

Elements shown in bold are those which show a significant increase in concentration across each of the age categories.

7.4 Comparisons with results from the National Reconnaissance Survey

7.4.1 Introduction

A third type of soil sample was taken in urban gardens (see section 5.3.1) to facilitate a comparison with the results from the National Reconnaissance Survey of metals in urban dusts and soils (see section 3.5.3). Results were published for Pb, Zn, Cd and Cu in soils from exposed garden beds (0-5cm) in 50 towns/cities in England and Wales (Culbard *et al.*, 1983; Thornton *et al.*, 1985; Culbard *et al.*, 1988 and Thornton, 1989). The data presented in Table 7.10 summarise the data for selected metals from this study.

7.4.2 Discussion

As with data for topsoils and subsurface soil (0-15cm and 30-45cm, respectively), these data generally have a log-normal distribution (see Table 7.10). Nickel is the exception to this with very similar geometric and arithmetic mean concentrations, a trend also observed for garden soils of depth 0-15cm and 30-45cm. The standard deviations for Pb, Zn, Cu and Cd are all high in relation to the arithmetic means reflecting the high concentration range for trace metals, particularly Pb and Zn. The geometric mean concentrations reported for Pb, Zn, Cu, and Cd (351 μg/g, 262 μg/g, 25 μg/g and 0.3 μg/g) are significantly higher than those reported for gardens soils of 0-15cm and 30-45cm within this study (see Tables 6.1 and 6.2), reflecting the tendency for metals to accumulate in the top 5cm of a soil (Adriano, 1986).

In general, the geometric mean concentrations reported for Pb, Zn and Cd in garden soils in this study are lower than those reported for Richmond in the National Reconnaissance Survey (see Tables 3.18 and 7.10). This may be as a result of weighing towards sampling soil from older properties in the National Reconnaissance Survey a factor which studies by Davies *et al.* (1987) and Davies and Thornton (1987), as well as this present study, have shown results in higher concentrations of Pb. Another explanation for the generally lower concentrations of metals in this study may be due to a reduction in the Pb content of petrol that occurred after the National Reconnaissance Survey in the early

1980's. The geometric mean for Cu is the same as that reported in the National Reconnaissance Survey (57 μg/g).

Comparison of Table 7.11 with that of Table 6.3 shows that Ca, Sr, Ba and P are significantly higher in soils from exposed garden beds (0-5cm) than in garden soils of depth 0-15cm. These elements are believed to have strong anthropogenic sources, and their accumulation in the top 5cm of the soil relative to the top 15cm may be a feature of this. The other elements are not present at significantly higher concentrations in the top 5cm than in the top 15cm.

Table 7.10 Concentrations of metals (μg/g) in garden soils (0-5cm) in the London Borough of Richmond-upon-Thames as reported in the National Reconnaissance Survey and the present study

	Garden soil (n=106)				Garden soil (n=100)			
	This study				NRS			
	GM	AM	SD	Range	GM	AM	SD	Range
Pb	351	442	356	78-2630	516			80-2240
Zn	262	311	196	60-1080	310			84-5620
Cu	57	77	100	17-861	57			16-752
Cd*	0.3	0.7	1.4	<0.2-11.5	1.2			<1-6.0

GM Geometric mean

AM Arithmetic mean

SD Standard Deviation

Table 7.11 Concentrations of selected elements ($\mu g/g$) in garden soils (0-5cm) from the London Borough of Richmond-upon-Thames

	topsoil (n=106)			
	GM	AM	SD	Range
Li	11.6	12.1	3.8	5-26.1
Na	222	241	110	80-727
K	3022	3102	685	1700-4730
Mg	1799	1886	674	862-6300
Ca	8354	10074	7765	1300-62600
Sr	48	53	29	16-260
Ba	225	243	97	82-483
Al	15284	15734	3721	7400-25600
La	17	17.2	2.8	8.2-27
Ti	633	643	115	364-944
V	50	50.4	10	28.5-113
Cr	38	40	20	19.2-197
Mn	344	359	114	174-876
Fe	25659	26007	4320	13500-40500
Co	9	9.3	2.4	4.8-21
Ni	25	26	8.9	13-70
P	1562	1646	539	641-3660

GM	Geometric mean
AM	Arithmetic mean
SD	Standard Deviation

7.5 Overall Summary

In this chapter a comparison of the data set, as defined by land-use, geology and sample depth, has been made with an overall data set for soils in England and Wales (McGrath and Loveland, 1992). This normalisation technique has shown several trends:

1. Normalisation ratios of > 1 for Ca, Sr, Ba, Ni, Cu, Zn, Pb and P in most garden topsoils (0-15cm), irrespective of geology.

2. Normalisation ratios of > 1 for Ca, Sr, Ba, Cu, Zn, Pb and in most subsurface garden

soils (30-45cm), irrespective of geology.

3. Normalisation ratios of > 1 for Pb for topsoils, although also for Cu, Zn and P depending on geology, in areas of open space which are underlain by most river terraces or London Clay.

4. Normalisation ratios of > 1 for Ca, Sr, Ba, Ni, Cu, Zn, Pb and P for topsoils from areas of open space overlying deposits of alluvium.

The normalisation technique has shown that garden soils in Richmond have, in general, higher concentrations of a suite of elements than both soils in areas of open space in Richmond and soils in England and Wales as a whole. A study of the literature and the use of multi-variate statistics (see Appendix 3) suggests that several anthropogenic sources are responsible for this. The technique also showed that soils in areas of open space overlaying deposits of alluvium, and to a lesser extent river brickearths, have higher concentrations of a number of elements than soils overlying the other parent materials in Richmond.

Students t-tests were used to investigate whether soils overlying deposits of alluvium (in areas of open space) have significantly higher concentrations of certain elements than soils overlying London Clay and river terraces. Beryllium, Ca, Sr, Co, Ni and Cu, in particular, were shown to be present at significantly higher concentrations (generally, $P < 0.001$) in soils overlying alluvium.

House-age is shown to be an important factor influencing the concentration of a suite of elements in garden soils. The relationship is strongest for Pb, Ba, V and Fe which are present at significantly higher concentrations in each house-age category. That is, concentrations of these elements are significantly higher in soils associated with property of between 50-100 years old than in soils associated with houses of < 50 years old. In turn, these elements are present at significantly higher concentrations in garden soils associated with property > 100 years old than in garden soils of houses of between 50-100 years old. Beryllium, Ca, Sr, Co, Ni, Cu, Zn and P are all present at significantly higher concentrations in garden soils of houses of between 50-100 years old than in garden soils of houses of < 50 years old.

CHAPTER EIGHT CONCENTRATIONS OF ELEMENTS IN WOLVERHAMPTON SOILS AND COMPARISON WITH RICHMOND AND OTHER URBAN STUDIES

8.1 Introduction

The results discussed in this chapter are from the urban geochemical survey carried out in Wolverhampton in the summer of 1994 (see section 5.3.1 for sampling details). The data have been used to produce a series of maps for individual elements (see section 8.3 for the presentation of these maps). As with the geochemical maps for Richmond, the geochemical classification is based on percentiles, with the red and blue colours used to depict the highest and lowest classes, respectively. The sample points are shown on the map along with a depiction of the road system in the Metropolitan borough. A transparent overlay (Supplementary Figure 8) shows the locations of the major urban centres in the city. As for Richmond, the influence of land-use on the soil geochemistry is assessed.

8.2 Land-classification of Wolverhampton

The land-use in Wolverhampton was classified by staff at the British Geological Survey as an aid to the interpretation of the geochemical data, and this is shown in Plate 8.1. The result is a very detailed map which shows that modern Wolverhampton is primarily a residential city, with industry comprising the second most important land-use in the city and concentrated mainly in the east. Very little of the city comprises areas of public open space which is often redeveloped industrial land. A number of large sports grounds are also present, particularly golf courses and race courses. In general, the major differences between Richmond and Wolverhampton, in terms of land-use, are that the areas of open space in Wolverhampton are much smaller and occupy less of the land-area (approximately 5 %), and Wolverhampton is more industrialised.

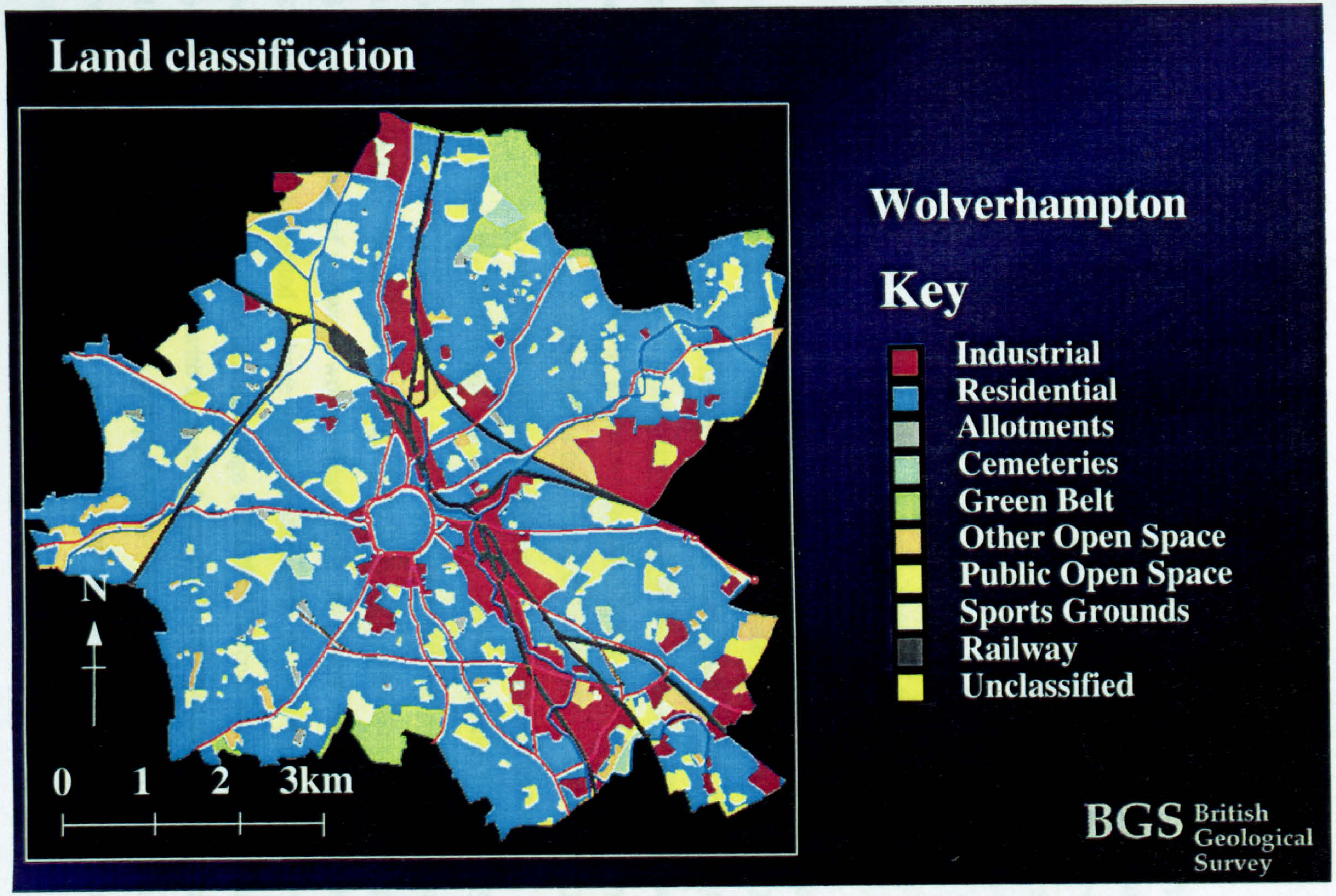

Land classification
Wolverhampton
Key
Industrial
Residential
Allotments
Cemeteries
Green Belt
Other Open Space
Public Open Space
Sports Grounds
Railway
Unclassified
N
0 1 2 3km
BGS British Geological Survey

Plate 8.1

8.3 Mapping of elements in topsoils from Wolverhampton

8.3.1 Introduction

The geochemical maps for 21 elements in topsoils (0-15cm) for Wolverhampton are presented in this section, along with maps for Pb, Zn, Cu and Cd in subsurface soils (30-45cm). The maps were generated using facilities at the British Geological Survey (by gridding with a triangular algorithm on a G-MAP) in Keyworth. Sample points are shown on the geochemical maps for Wolverhampton to aid interpretation.

8.3.2 Concentrations of lead in Wolverhampton topsoils (0-15cm)

Plate 8.2 shows the distribution of Pb in topsoils from Wolverhampton. The variation in concentration of Pb in these soils is high with the 99th percentile over 20 times the magnitude of the 5th percentile (see Plate 8.2). The highest concentrations of Pb are generally observed in areas of contemporary industrial activity, (see Plates 8.1 and 8.2) such as Springfield, Heath town, Monmore Green, Bilston and north of the city centre close to the Goodyear engineering works (see Plates 8.1 and 8.2 and Supp. Fig. 8). In the area close to the Goodyear works, Pb concentrations exceed the 99th percentile (> 1116 μg/g) whilst for the other industrial sites Pb concentrations are generally in the 95th-99th percentile range (242-1116 μg/g). To the west of the Goodyear plant, Pb concentrations are also in the 95th-99th percentile range (242-1116 μg/g - see Plate 8.2 and Supp. Fig. 8), close to the site of a sewage works where sludge may have been applied to the soils. Sludge is well documented to have high concentrations of metals (Alloway, 1990c and Jones, 1994). The same concentration range (95th-99th percentile) is also observed south of the city centre, coinciding with an area of industrial activity (see Plates 8.1 and 8.2). The metal processing industry is still present in Wolverhampton, although in a greatly reduced form compared with the last century, and the burning of fossil fuel is probably still extensive in these areas.

Several other sites in Wolverhampton have Pb concentrations in the 95th-99th percentile range (242-1116 μg/g) which are unrelated to industrial activity. These are in

Pb in Wolverhampton topsoils (0-15cm)

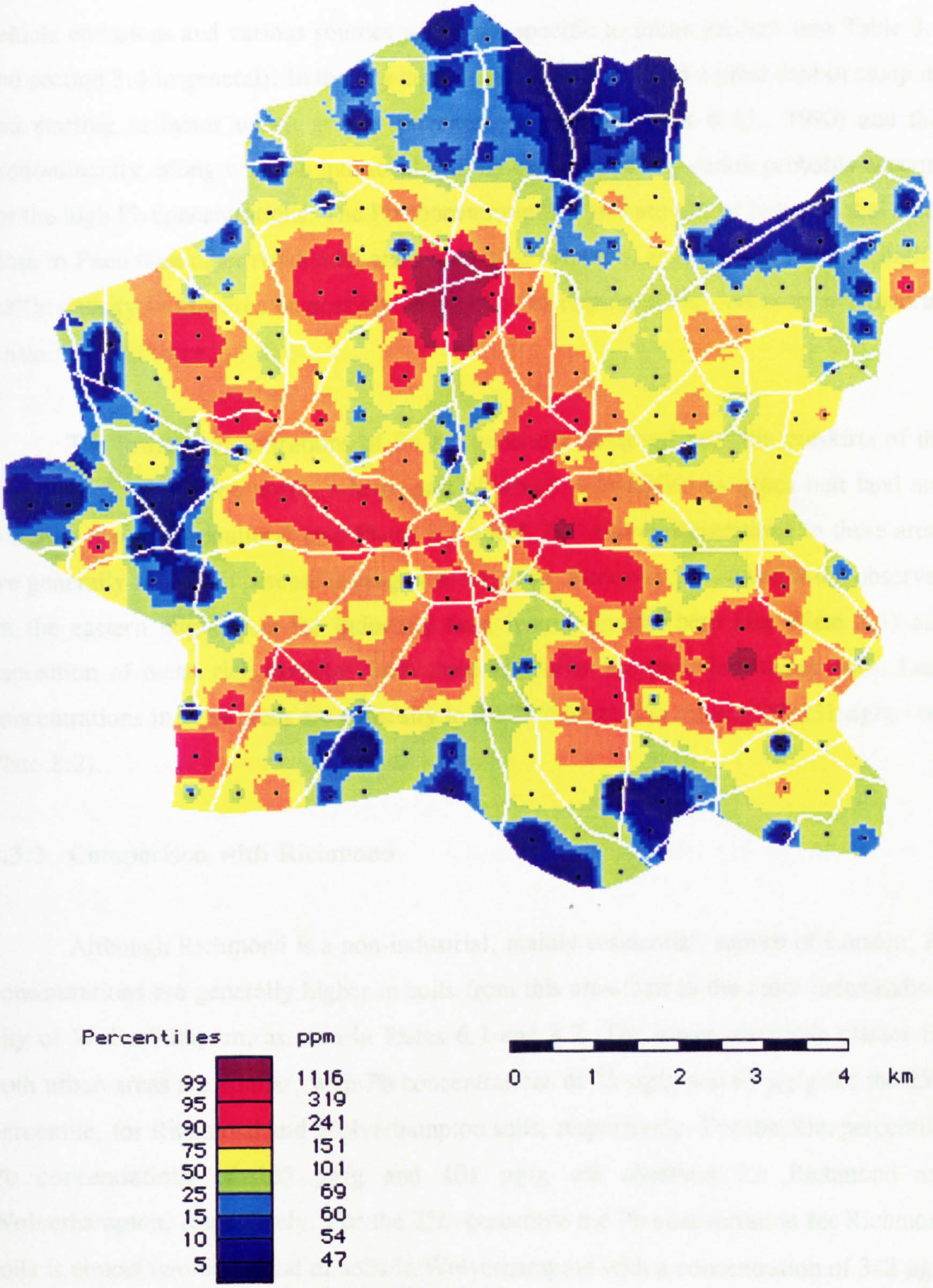


Plate 8.2

the city centre, once an industrially important region, in Merridale and close to Penn (see Plate 8.2 and Supp. Fig. 8). Merridale and Penn are residential areas and high concentrations of Pb may result from inputs found to be important in Richmond, such as vehicle emissions and various sources which are specific to urban gardens (see Table 3.1 and section 3.4 in general). In the city centre, traffic will undergo a great deal of stopping and starting, a factor which greatly increases emissions (Lyons et al., 1990) and this predominantly, along with the industrial activity close to the city centre probably account for the high Pb concentrations. The Pb concentrations which are higher in residential areas close to Penn than other residential areas in Wolverhampton, are probably due to a higher traffic density in this area or possibly an incident of tipping either domestic or industrial waste material there.

The lowest concentrations of Pb are generally observed near the outskirts of the city, particularly in the north, a large part of which is classified as green belt land and which is mainly agricultural (see Plates 8.1 and 8.2). Lead concentrations in these areas are generally in the 5th percentile range (≤ 54 μg/g). However, this trend is not observed on the eastern edge since the industrial base is still present here (see Plate 8.1) and deposition of metal rich particles from these industries are probably higher here. Lead concentrations in these areas are generally in the 75th percentile range (102-151 μg/g - see Plate 8.2).

8.3.3 Comparison with Richmond

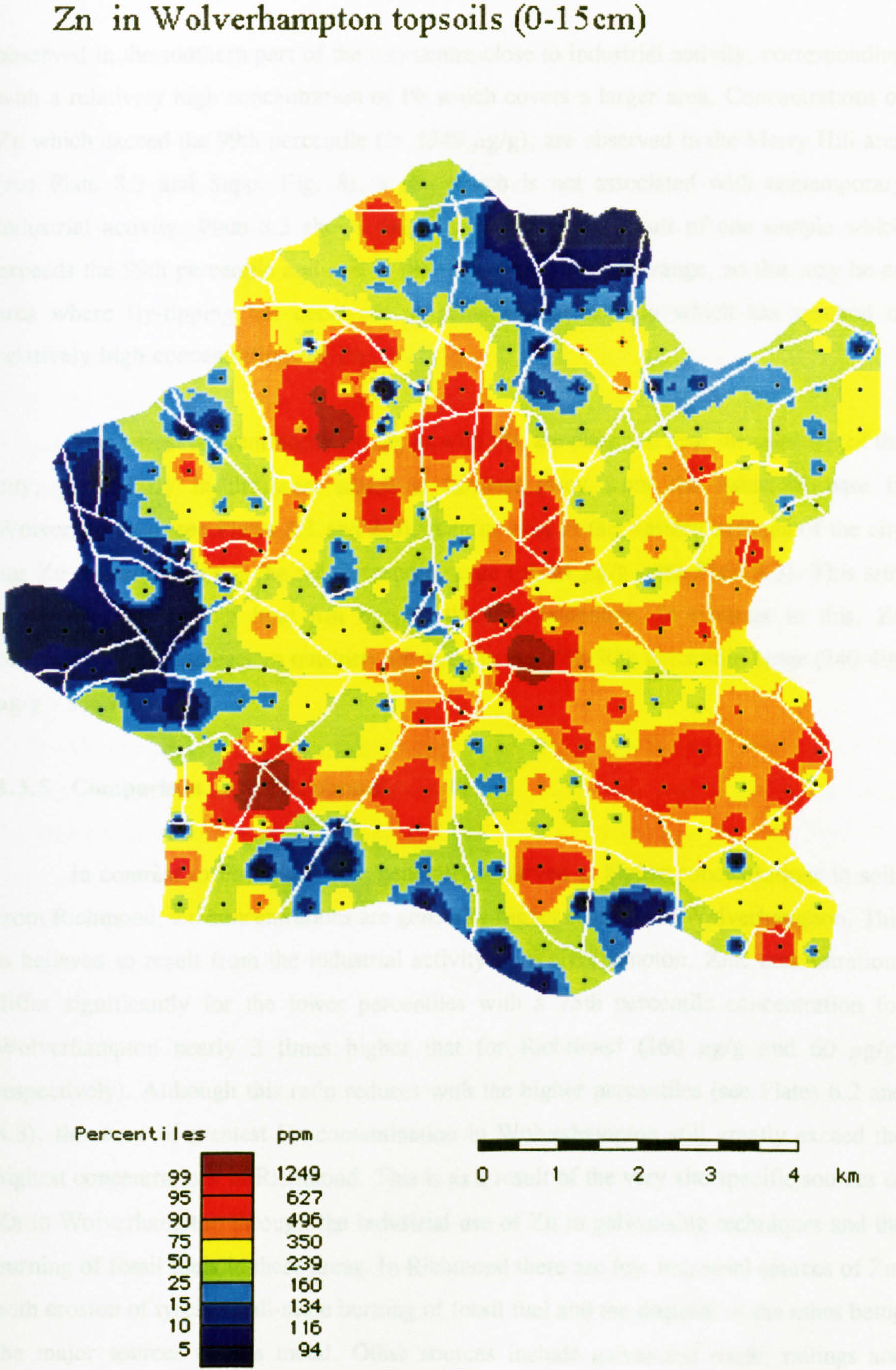
Although Richmond is a non-industrial, mainly residential, suburb of London, Pb concentrations are generally higher in soils from this area than in the more industrialised city of Wolverhampton, as seen in Plates 6.1 and 8.2. The lower percentile classes for both urban areas are similar, with Pb concentrations of 75 μg/g and 69 μg/g for the 25th percentile, for Richmond and Wolverhampton soils, respectively. For the 50th percentile, Pb concentrations of 185 μg/g and 101 μg/g are observed for Richmond and Wolverhampton, respectively. For the 75th percentile the Pb concentration for Richmond soils is almost two times that of soils in Wolverhampton with a concentration of 342 μg/g compared to 151 μg/g for Wolverhampton. This trend is observed for corresponding percentiles > 75th percentile, although the 99th percentile for the Wolverhampton data is a concentration of 1116 μg/g and comparable with the higher concentrations observed in soils from Richmond.

The higher concentrations of Pb in Richmond, in general, despite the extensive history of metal-working industry in Wolverhampton, probably result from the recent redevelopment of Wolverhampton. This has resulted in great disturbance of soils in the city with made ground and imported topsoil a common feature. Discussions with the local councils for the two areas has shown that houses are of comparable age and traffic densities similar, so there has probably been an overall longer period of deposition of metals in Richmond due to the redevelopment of Wolverhampton. The industry in Wolverhampton is probably not an important source of Pb.

8.3.4 Concentrations of zinc in Wolverhampton topsoils (0-15cm)

Plate 8.3 shows the distribution of Zn in topsoils from Wolverhampton. The concentration range for Zn in these soils is large with a 99th percentile concentration approximately 12 times the 5th percentile concentration. In general, a very similar pattern is observed to that for Pb, although a comparison of the percentiles illustrates that Zn concentrations are generally two times higher than those of Pb (see Plates 8.2 and 8.3). This probably results from the industrial importance of Zn to Wolverhampton, both historically and today, with the extensive burning of fossil fuel and the use of Zn in galvanising processes.

The highest concentrations of Zn are generally observed in areas of contemporary industrial activity, particularly east of the city centre in Springfield, Monmore Green, Priestfield and Bilston, near the Goodyear works and the sewage works (see Plates 8.1 and 8.3 and Supp. Fig. 8). Zinc concentrations > 99th percentile (> 1249 μg/g) are observed in these areas, although a 95th-99th percentile range (497-1249 μg/g) is also observed. In contrast to the distribution of Pb, no high percentile is observed for Zn in Merridale (see Plate 8.3 and Supp. Fig. 8), which suggests that the source of Pb at this site is probably non-industrial. Concentrations of Zn in the 95th-99th percentile range (497-1249 μg/g) are



Zn in Wolverhampton topsoils (0-15cm)

Plate 8.3

observed in the southern part of the city centre close to industrial activity, corresponding with a relatively high concentration of Pb which covers a larger area. Concentrations of Zn which exceed the 99th percentile (> 1249 μg/g), are observed in the Merry Hill area (see Plate 8.3 and Supp. Fig. 8), a site which is not associated with contemporary industrial activity. Plate 8.3 shows that this pattern is the result of one sample which exceeds the 99th percentile and one in the 95th-99th percentile range, so this may be an area where fly-tipping has occurred, or some similar activity which has resulted in relatively high concentrations of Zn.

The lowest concentrations of Zn, as with Pb, are observed near the outskirts of the city, particularly in the west which is furthest away from the industrial base in Wolverhampton (see Plates 8.1 and 8.3). A large area in the western extreme of the city has Zn concentrations in the 5th Percentile range (≤ 94 μg/g - see Plate 8.3). This area is adjacent to farming land just outside the city boundary. In contrast to this, Zn concentrations in the eastern outskirts are often in the 75th-90th percentile range (240-496 μg/g - see Plate 8.3).

8.3.5 Comparison with Richmond

In contrast to Pb, which was generally observed at higher concentrations in soils from Richmond, Zn concentrations are generally higher for soils in Wolverhampton. This is believed to result from the industrial activity in Wolverhampton. Zinc concentrations differ significantly for the lower percentiles with a 25th percentile concentration for Wolverhampton nearly 3 times higher that for Richmond (160 μg/g and 60 μg/g, respectively). Although this ratio reduces with the higher percentiles (see Plates 6.2 and 8.3), the areas of greatest Zn contamination in Wolverhampton still greatly exceed the highest concentrations in Richmond. This is as a result of the very site-specific sources of Zn in Wolverhampton through the industrial use of Zn in galvanising techniques and the burning of fossil fuels in these areas. In Richmond there are few industrial sources of Zn, with erosion of tyres, small-scale burning of fossil fuel and the disposal of the ashes being the major sources of this metal. Other sources include galvanised roofs, railings and various hardware goods (see Table 3.1).

8.3.6 Concentrations of copper in Wolverhampton topsoils (0-15cm)

Plate 8.4 shows the distribution of Cu in topsoils from Wolverhampton. Many similarities are observed for the distribution of Cu and the distribution of Pb and Zn. The concentration range of Cu in these soils is large with the 99th percentile approximately 20 times the magnitude of the 5th percentile (see Plate 8.4). In general, however, the areas with relatively high concentrations of Cu, are smaller (in terms of size) than those for Pb and Zn, and mainly occur in areas of contemporary industrial activity (see Plates 8.1 and 8.4). The largest area where Cu concentrations exceed the 99th percentile (> 472 μg/g) is east of the city centre, in the area between Springfield and Monmore Green (see Plate 8.4 and Supp. Fig. 8). Copper concentrations in the 95th-99th percentile range (170-472 μg/g) are also observed east of the town centre in this industrial area (see Plate 8.4 and Supp. Fig. 8). The same concentration range is observed in the industrial area of the south-east near Bilston, further north in the Wednesfield area, close to the Goodyear factory, near the sewage works and in the city centre (see Plates 8.1 and 8.4 and Supp. Fig. 8).

Copper concentrations which are generally in the 95th-99th percentile range (170-472 μg/g) are observed west of the city centre near Tettenhall, west of Merridale and in the area between Bradmore and Merry Hill (see Plate 8.4 and Supp. Fig. 8). These also correspond with relatively high concentrations of Pb and Zn and may be as a result of past industrial activity and/or inputs from established residential sources of metals (see Table 3.1 and section 3.4 in general).

The lowest concentrations of Cu are observed at the outskirts of the city, particularly near the western periphery where Cu concentrations are in the 5th percentile range (≤ 23 μg/g - see Plate 8.4). This relates to a change in the land-use with farming land adjacent to these residential areas, and the distance from industrial land in Wolverhampton. This is in contrast to the east side of the city where Cu concentrations are generally in the 90th percentile range, or higher (> 103 μg/g - see Plate 8.4).

Cu in Wolverhampton topsoils (0-15cm)

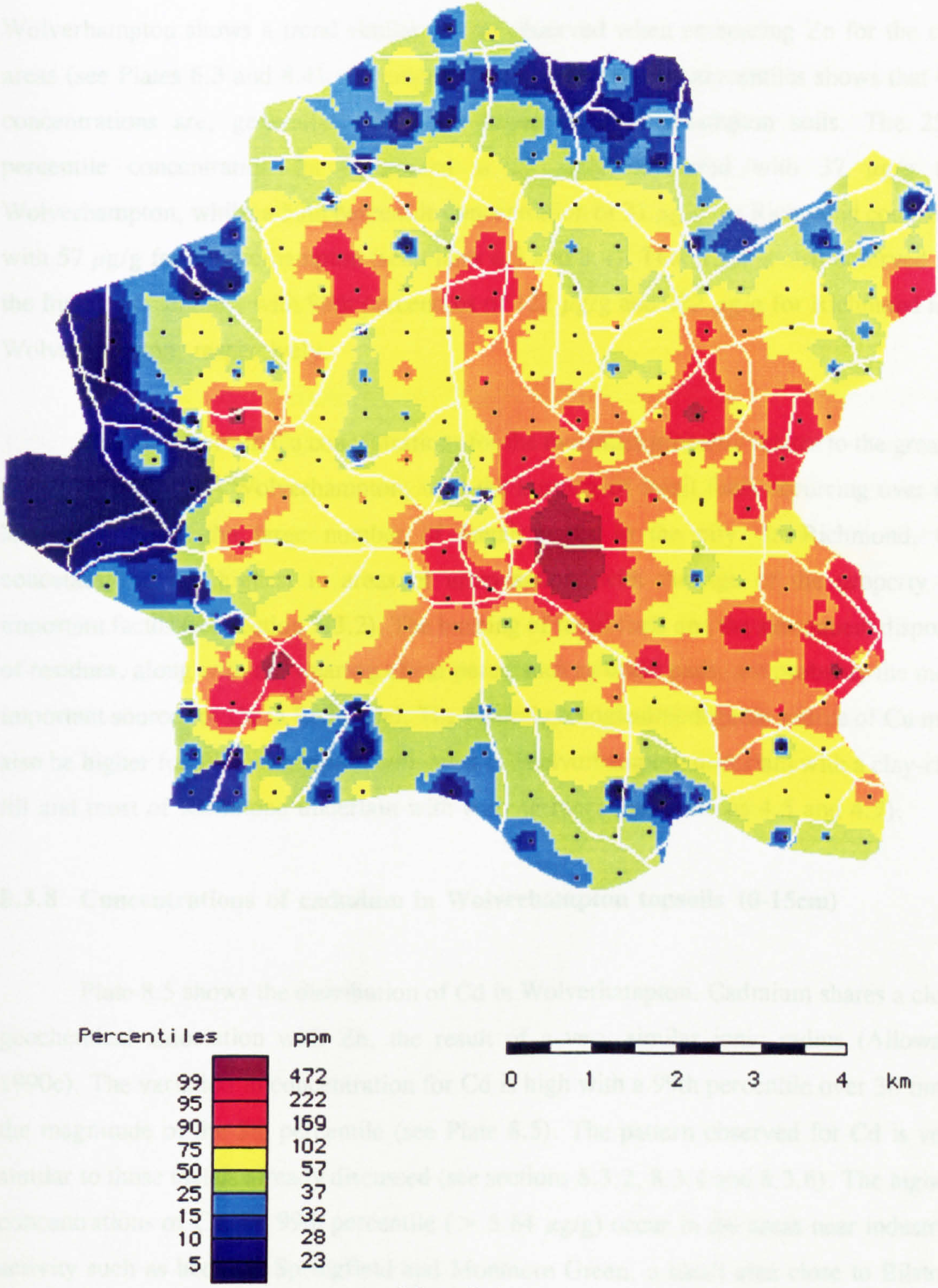


Plate 8.4

8.3.7 Comparison with Richmond

A comparison between Cu concentrations in soils from Richmond and Wolverhampton shows a trend similar to that observed when comparing Zn for the two areas (see Plates 6.3 and 8.4). A comparison of corresponding percentiles shows that Cu concentrations are, generally, two times higher in Wolverhampton soils. The 25th percentile concentration for Richmond is 17 μg/g compared with 37 μg/g for Wolverhampton, whilst a 50th percentile concentration of 31 μg/g for Richmond compares with 57 μg/g for Wolverhampton (see Plates 6.3 and 8.4). This trend is also observed for the higher percentiles, with 95th percentiles of 122 μg/g and 222 μg/g for Richmond and Wolverhampton, respectively.

The difference in Cu concentrations for the two cities probably relates to the greater industrial activity in Wolverhampton, with the burning of fossil fuels occurring over the last century and the large number of metal works in the city. In Richmond, Cu concentrations are highest in areas of urbanisation, with the age of the property an important factor (see section 7.3.2). The burning of fossil fuels and the subsequent disposal of residues, along with the wearing of car parts, such as brake pads, are probably the most important sources of Cu in Richmond. The natural geological/pedogenic source of Cu may also be higher for Wolverhampton with most of Wolverhampton underlain with a clay-rich till and most of Richmond underlain with river terraces (see sections 4.5 and 4.7).

8.3.8 Concentrations of cadmium in Wolverhampton topsoils (0-15cm)

Plate 8.5 shows the distribution of Cd in Wolverhampton. Cadmium shares a close geochemical association with Zn, the result of a very similar ionic radius (Alloway, 1990c). The variation in concentration for Cd is high with a 99th percentile over 30 times the magnitude of the 5th percentile (see Plate 8.5). The pattern observed for Cd is very similar to those metals already discussed (see sections 8.3.2, 8.3.4 and 8.3.6). The highest concentrations of Cd, > 99th percentile (> 5.64 μg/g) occur in the areas near industrial activity such as between Springfield and Monmore Green, a small area close to Bilston, near the sewage works, with the largest anomaly in the residential area between Bradmore and Merry Hill (see Plates 8.1 and 8.5, and Supp. Fig. 8). Cadmium concentrations in the 95th-99th percentile range (1.77-5.64 μg/g) are also observed in other industrial areas of Wolverhampton and the city centre (see Plate 8.5 and Supp. Fig 8).

The lowest concentrations of Cd, in the 5th percentile range (≤ 0.22 μg/g), close to the instrument detection limit (0.2 μg/g), are observed near the outskirts of the city, particularly in the north and west. This corresponds with the distribution of Pb, Zn and Cu in topsoils (see Plates 8.2-8.5).

8.3.9 Comparison with Richmond

Cadmium concentrations are significantly higher in soils from Wolverhampton than Richmond. For Richmond, a large number of samples were found to have Cd concentrations below the instrument detection limit of 0.2 μg/g, the result of naturally low levels in soils and few sources of Cd. In Wolverhampton, naturally higher concentrations of Cd may result from the clay-rich till which underlays most of the city (see Plate 4.5), although the distribution of Cd suggests that the metal working industries are also an important factor. Comparison of corresponding percentiles shows higher concentrations of Cd for Wolverhampton (a 90th percentile of 0.52 μg/g for the Richmond data compares with 1.76 μg/g for Wolverhampton).

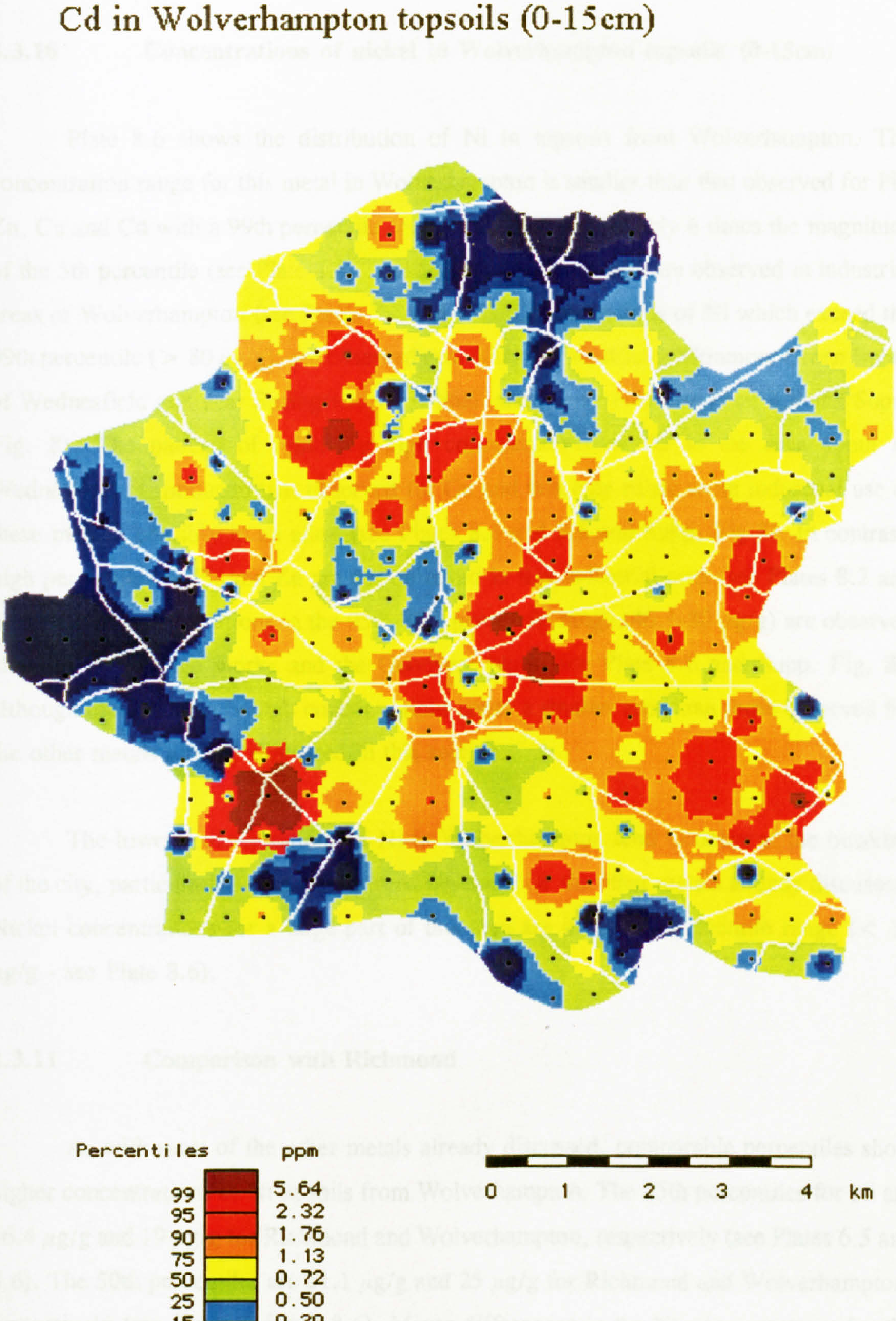

Cd in Wolverhampton topsoils (0-15cm)
Percentiles
ppm
99
95
90
75
50
25
15
10
5
5.64
2.32
1.76
1.13
0.72
0.50
0.39
0.31
0.22
0
1
2
3
4
km

Plate 8.5

8.3.10 Concentrations of nickel in Wolverhampton topsoils (0-15cm)

Plate 8.6 shows the distribution of Ni in topsoils from Wolverhampton. The concentration range for this metal in Wolverhampton is smaller than that observed for Pb, Zn, Cu and Cd with a 99th percentile concentration approximately 6 times the magnitude of the 5th percentile (see Plate 8.6). The highest concentrations are observed in industrial areas of Wolverhampton (see Plates 8.1 and 8.6). Concentrations of Ni which exceed the 99th percentile (> 80 μg/g), are observed near Bilston, Priestfield, Monmore Green, south of Wednesfield and near Springfield, Tettenhall and Merry Hill (see Plate 8.6 and Supp. Fig. 8). The pattern of relatively high concentrations of Ni in the area south of Wednesfield is similar to that observed for Cu and this may relate to an industrial use of these metals, possibly in an alloy (see Plates 8.4 and 8.6 and Supp. Fig 8). In contrast, high percentiles of Pb and Zn are not observed in this industrial area (see Plates 8.2 and 8.3). Nickel concentrations in the 95th-99th percentile range (46.1-80 μg/g) are observed close to the sewage works and the Goodyear plant (see Plate 8.6 and Supp. Fig. 8), although these relatively high concentrations cover a smaller area than those observed for the other metals already discussed in this section.

The lowest concentrations of Ni in Wolverhampton tend to occur at the outskirts of the city, particularly in the west a trend observed for the other metals already discussed. Nickel concentrations for a large part of this area are in the 5th percentile range (< 14 μg/g - see Plate 8.6).

8.3.11 Comparison with Richmond

As with most of the other metals already discussed, comparable percentiles show higher concentrations of Ni in soils from Wolverhampton. The 25th percentiles for Ni are 16.4 μg/g and 19 μg/g for Richmond and Wolverhampton, respectively (see Plates 6.5 and 8.6). The 50th percentiles are 21.1 μg/g and 25 μg/g for Richmond and Wolverhampton, respectively (see Plates 6.5 and 8.6). Minor differences in the Ni concentrations for the two cities may be a result of few sources of Ni in either city. The extensive burning of fossil fuels and the dominance of a clay-rich parent material may account for the higher

Ni in Wolverhampton topsoils (0-15cm)

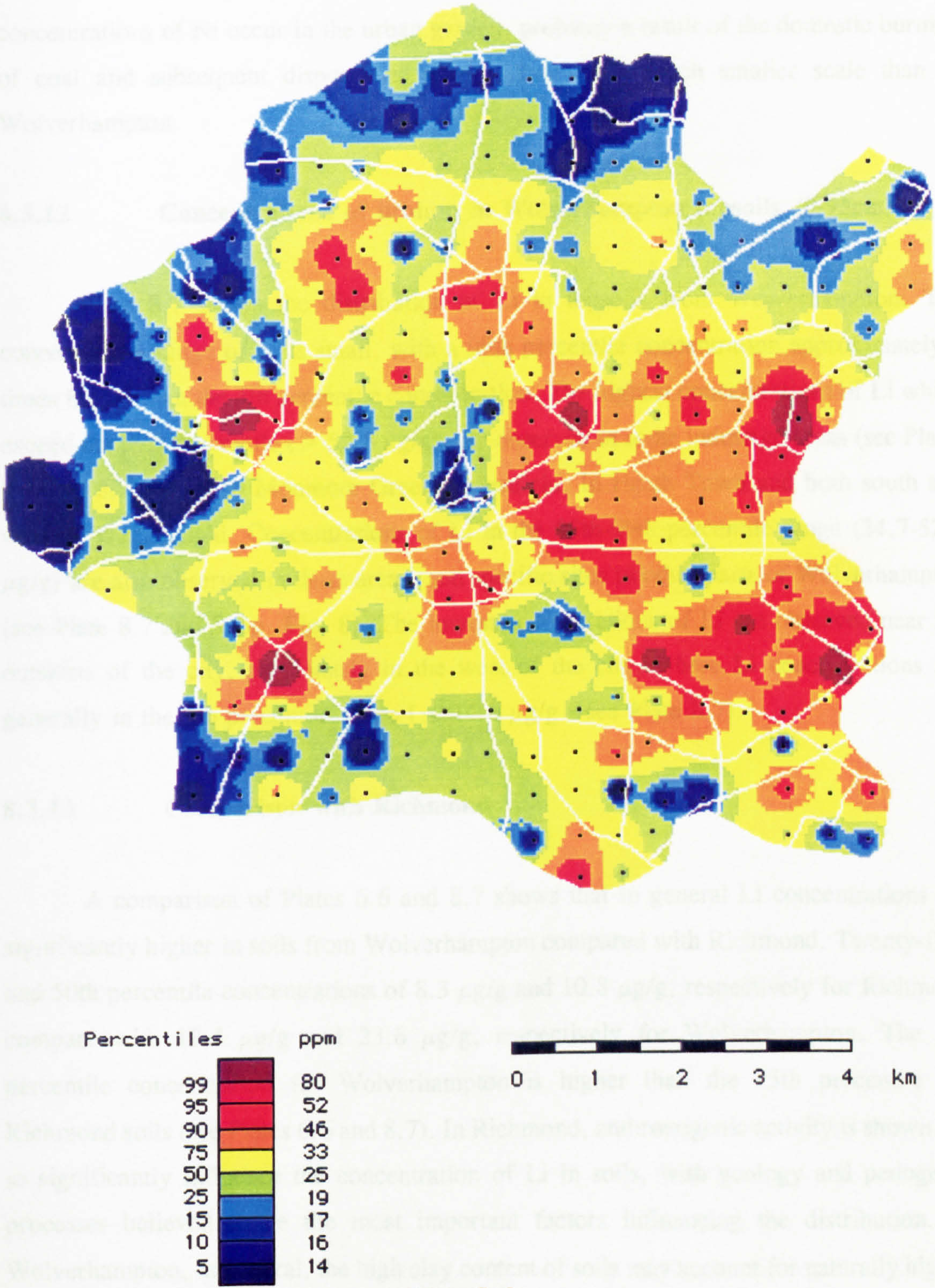


Plate 8.6

concentrations of Ni in Wolverhampton. However, a site specific source of Ni may occur near Wednesfield as a result of the use of nickel, probably with Cu which shows a similar distribution in this area (see Plates 8.4 and 8.6 and Supp. Fig. 8). In Richmond the highest concentrations of Ni occur in the urban garden, probably a result of the domestic burning of coal and subsequent disposal of ashes, albeit on a much smaller scale than in Wolverhampton.

8.3.12 Concentrations of lithium in Wolverhampton topsoils (0-15cm)

Plate 8.7 shows the distribution of Li in topsoils from Wolverhampton. The concentration range of Li is small, with a 99th percentile concentration approximately 4 times higher than the 5th percentile concentration. The highest concentrations of Li which exceed the 99th percentile (> 52.8 μg/g), are observed in some industrial areas (see Plates 8.1 and 8.7), close to Monmore Green, Priestfield, in Heath Town and both south and west of Wednesfield. Concentrations of Li in the 95th-99th percentile range (34.7-52.8 μg/g) are also observed in these areas, and specific sites in other parts of Wolverhampton (see Plate 8.7 and Supp. Fig. 8). The lowest concentrations of Li are observed near the outskirts of the city, particularly in the west of the city, where Li concentrations are generally in the 5th percentile range (≤ 14.8 μg/g - see Plate 8.7).

8.3.13 Comparison with Richmond

A comparison of Plates 6.6 and 8.7 shows that in general Li concentrations are significantly higher in soils from Wolverhampton compared with Richmond. Twenty-fifth and 50th percentile concentrations of 8.3 μg/g and 10.8 μg/g, respectively for Richmond compare with 19.4 μg/g and 23.6 μg/g, respectively for Wolverhampton. The 5th percentile concentration for Wolverhampton is higher than the 75th percentile for Richmond soils (see Plates 6.6 and 8.7). In Richmond, anthropogenic activity is shown not to significantly influence the concentration of Li in soils, with geology and pedogenic processes believed to be the most important factors influencing the distribution. In Wolverhampton, in general, the high clay content of soils may account for naturally higher concentrations of Li, whilst in several of the industrial areas minor anthropogenic

Li in Wolverhampton topsoils (0-15cm)

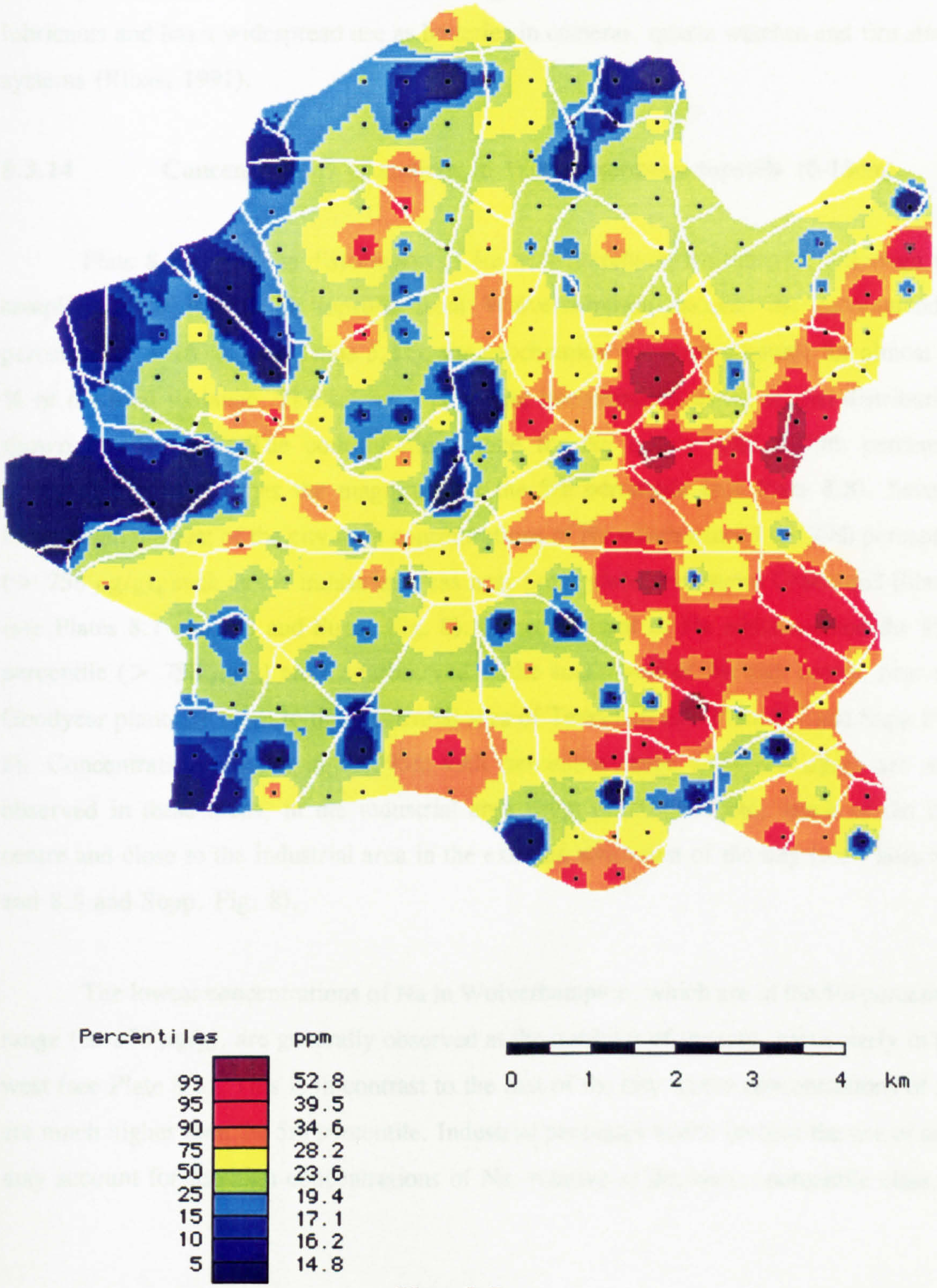


Plate 8.7

additions of Li seem to have occurred (see Plates 8.1 and 8.7 and Supp. Fig.8). Lithium is predominantly used in the nuclear industry, although it is also used in the ceramics industry and as an alloy with Pb in bearings. Lithium is also used as an additive to lubricants and has a widespread use as batteries in cameras, quartz watches and fire alarm systems (Ribas, 1991).

8.3.14 Concentrations of sodium in Wolverhampton topsoils (0-15cm)

Plate 8.8 shows the distribution of Na in Wolverhampton topsoils. Although the sampling error for Na in topsoils from Wolverhampton exceeds the recommended percentage (> 16 % - see Table 5.11), the geochemical variance accounts for almost 80 % of the total variance. This allows a confident interpretation of the spatial distribution shown in Plate 8.8. The concentration range for Na is low with a 99th percentile concentration < 5 times the magnitude of the 5th percentile (see Plate 8.8). Several locations in the east of the city have concentrations of Na which exceed the 99th percentile (> 758 μg/g), such as the industrial areas near Springfield, Monmore Green and Bilston (see Plates 8.1 and 8.8 and Supp. Fig. 8). Concentrations of Na which exceed the 99th percentile (> 758 μg/g) are also observed in the south-west of the city centre, near the Goodyear plant and close to the residential area of Tettenhall (see Plate 8.7 and Supp Fig. 8). Concentrations of Na in the 95th-99th percentile range (477-758 μg/g) are also observed in these areas, in the industrial area south of Wednesfield, much of the city centre and close to the industrial area in the extreme south-east of the city (see Plates 8.1 and 8.8 and Supp. Fig. 8).

The lowest concentrations of Na in Wolverhampton, which are in the 5th percentile range ($\leq$ 176 μg/g), are generally observed at the outskirts of the city, particularly in the west (see Plate 8.8). This is in contrast to the east of the city where concentrations of Na are much higher than the 5th percentile. Industrial processes which involve the use of salts may account for the high concentrations of Na, relative to the lowest percentile class.

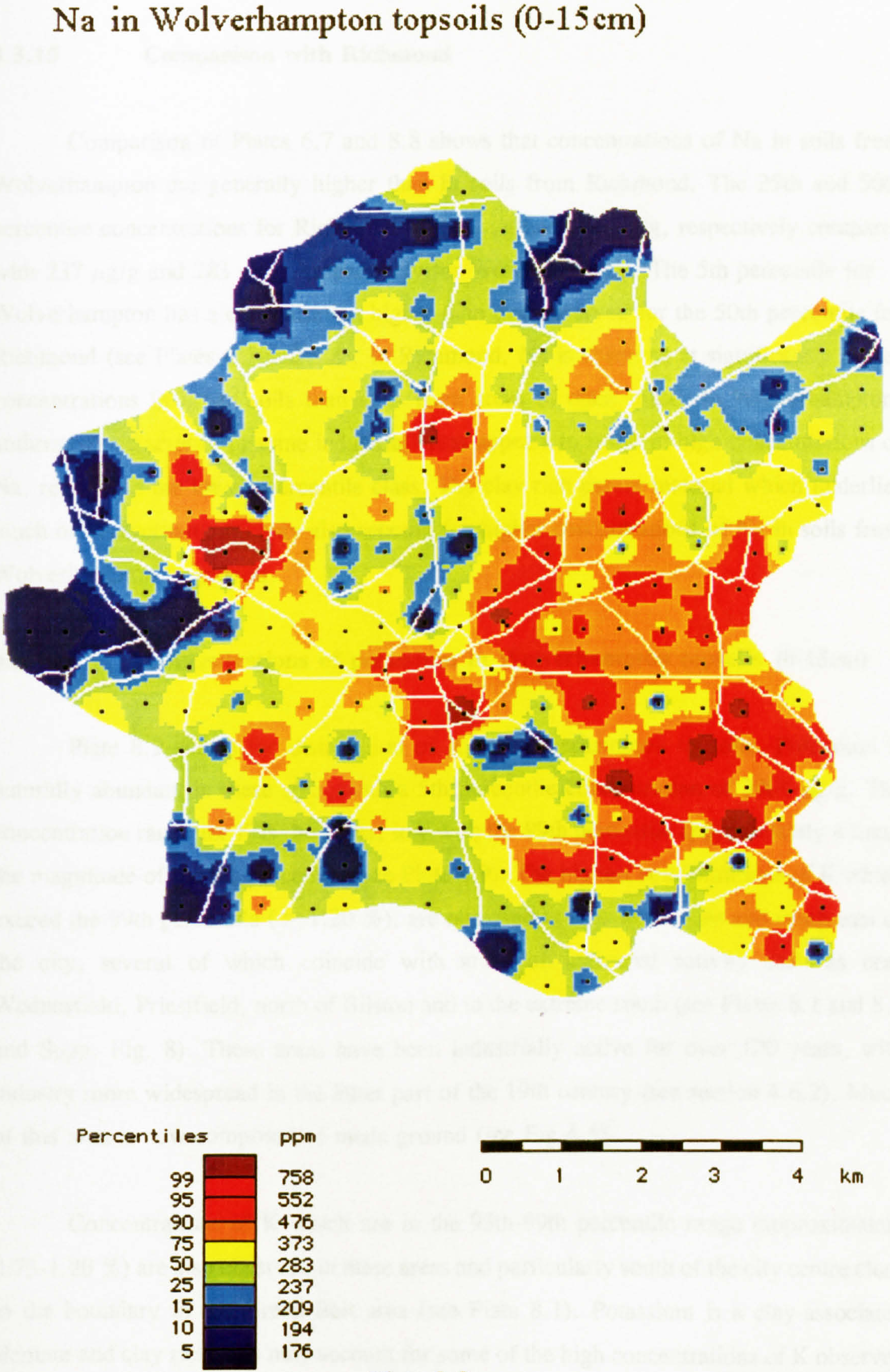

Na in Wolverhampton topsoils (0-15cm)
Percentiles
ppm
99
95
90
75
50
25
15
10
5
758
552
476
373
283
237
209
194
176
0
1
2
3
4
km

Plate 8.8

8.3.15 Comparison with Richmond

Comparison of Plates 6.7 and 8.8 shows that concentrations of Na in soils from Wolverhampton are generally higher than in soils from Richmond. The 25th and 50th percentile concentrations for Richmond of 83 μg/g and 166 μg/g, respectively compare with 237 μg/g and 283 μg/g, respectively for Wolverhampton. The 5th percentile for Wolverhampton has a concentration higher than that observed for the 50th percentile for Richmond (see Plates 6.7 and 8.8). In Richmond, Na is observed at significantly higher concentrations in urban soils than soils from areas of open space. In Wolverhampton, anthropogenic activity in some industrial areas appears to result in high concentrations of Na, relative to the lowest percentile class. The clay rich parent material which underlies much of Wolverhampton may also account for higher concentrations of Na in soils from Wolverhampton in general.

8.3.16 Concentrations of potassium in Wolverhampton topsoils (0-15cm)

Plate 8.9 shows the distribution of K in Wolverhampton topsoils. Potassium is naturally abundant in these soils, with a 5th percentile concentration of 3909 μg/g. The concentration range for K is, however, low with the 99th percentile approximately 4 times the magnitude of the 5th percentile (see Plate 8.9). The highest concentrations of K which exceed the 99th percentile (> 1.20 %), are observed at sites in the east and south-east of the city, several of which coincide with areas of industrial activity such as near Wednesfield, Priestfield, north of Bilston and in the extreme south (see Plates 8.1 and 8.9 and Supp. Fig. 8). These areas have been industrially active for over 100 years, with industry more widespread in the latter part of the 19th century (see section 4.6.2). Much of this area is now composed of made ground (see Fig 4.5).

Concentrations of K which are in the 95th-99th percentile range (approximately 0.73-1.20 %) are also observed in these areas and particularly south of the city centre close to the boundary in the Green Belt area (see Plate 8.1). Potassium is a clay-associated element and clay rich soils may account for some of the high concentrations of K observed in Wolverhampton. The application of K fertilisers may also be a source of K, although

K in Wolverhampton topsoils (0-15cm)

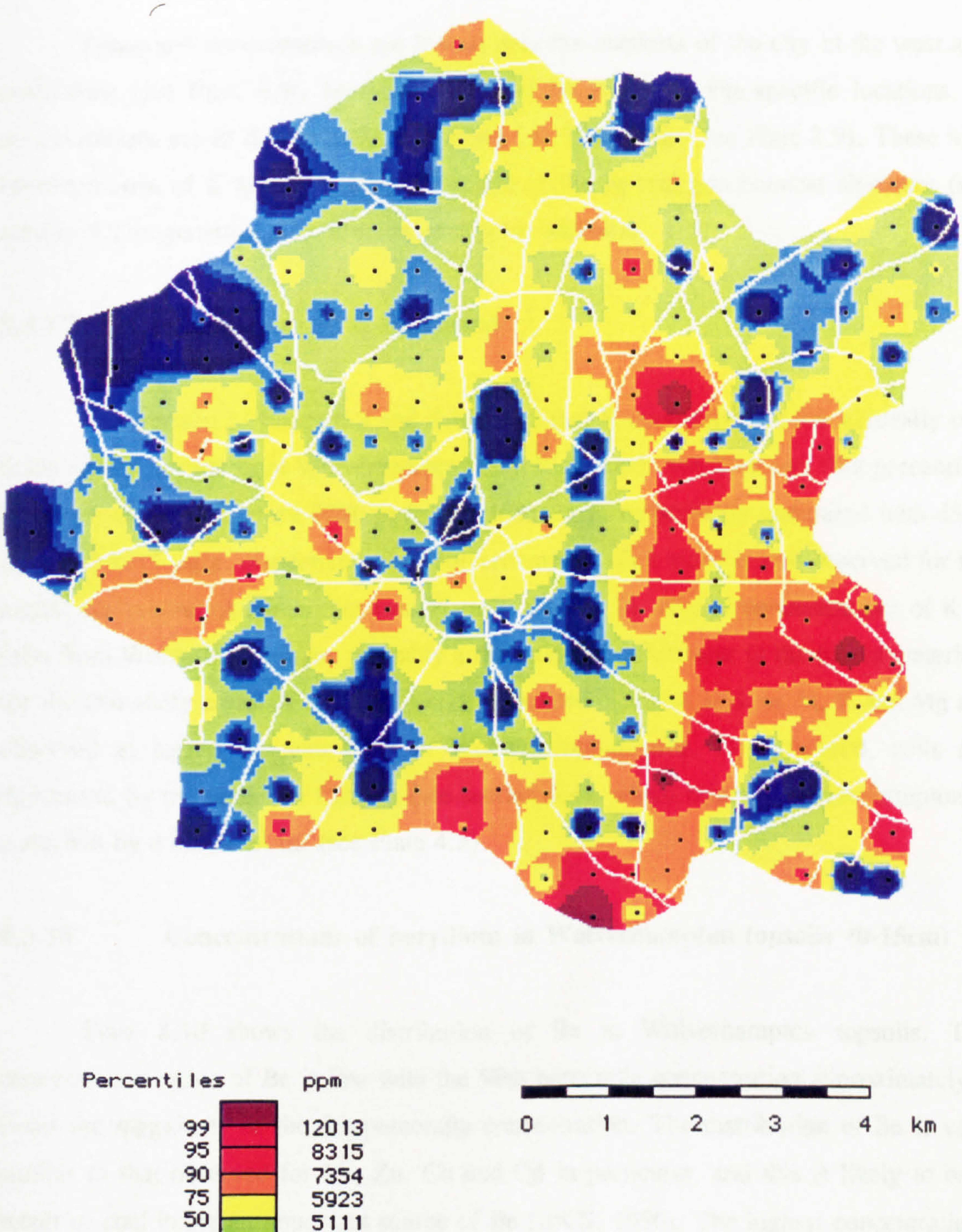


Plate 8.9

the residential areas of the city are often not the sites of the highest concentrations of K (see Plates 8.1 and 8.8).

Potassium concentrations are lowest near the outskirts of the city in the west and north-west (see Plate 8.9). In these areas and several other site-specific locations, K concentrations are in the 5th percentile range (≤ 3909 μg/g - see Plate 8.9). These low concentrations of K are probably a reflection of the natural geochemical signature (see section 9.2 in general), with low anthropogenic additions.

8.3.17 Comparison with Richmond

Comparison of Plates 6.8 and 8.9 shows that K concentrations are generally two times higher in soils from Wolverhampton than Richmond. The 25th and 50th percentiles for the Richmond data are 2206 μg/g and 2683 μg/g, respectively compared with 4510 μg/g and 5111 μg/g, respectively for Wolverhampton. This trend is also observed for the higher corresponding percentiles (see Plates 6.8 and 8.9). Higher concentrations of K in soils from Wolverhampton are probably a reflection of differences in the parent materials for the two study areas. A number of clay associated elements such as Al, K and Mg are observed at higher concentrations in Wolverhampton soils. In Richmond, soils are dominated by the sand size fraction (see section 6.4), whilst much of Wolverhampton is underlain by a clay-rich till (see Plate 4.5).

8.3.18 Concentrations of beryllium in Wolverhampton topsoils (0-15cm)

Plate 8.10 shows the distribution of Be in Wolverhampton topsoils. The concentration range of Be is low with the 99th percentile concentration approximately 4 times the magnitude of the 5th percentile concentration. The distribution of Be is very similar to that observed for Pb, Zn, Cu and Cd in particular, and this is likely to be a result of coal being an important source of Be (IPCS, 1990). The highest concentrations of Be, which exceed the 99th percentile (> 4.04 μg/g), are observed in the industrial parts of the city, close to Monmore Green near Priestfield and between Priestfield and Bilston (see Plate 8.10 and Supp. Fig. 8). The largest area where Be concentrations are at their

Be in Wolverhampton topsoils (0-15cm)

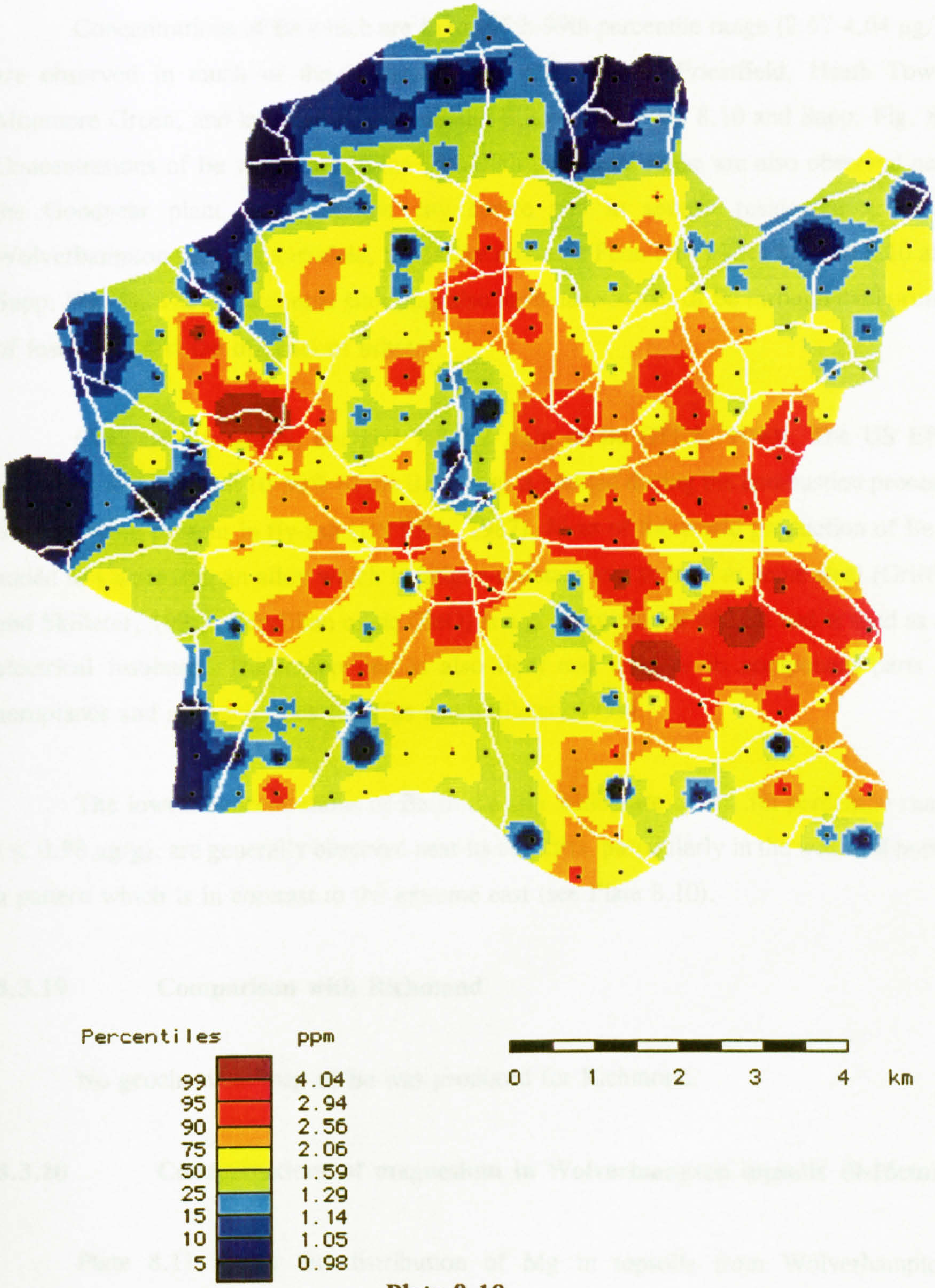


Plate 8.10

highest is observed near the residential area of Tettenhall (see Plates 8.10 and Supp. Fig. 8).

Concentrations of Be which are in the 95th-99th percentile range (2.57-4.04 μg/g) are observed in much of the industrial area near Bilston, Priestfield, Heath Town, Monmore Green, and between Priestfield and Bilston (see Plate 8.10 and Supp. Fig. 8). Concentrations of Be which are in the 95th-99th percentile range are also observed near the Goodyear plant, south of the city centre and in several residential areas of Wolverhampton such as Merridale, Bradmore and near Penn (see Plates 8.1 and 8.10 and Supp. Fig. 8). These residential sites may also have had sources of Be through the burning of fossil fuel and the disposal of ashes.

Coal ash, generally, contains 1.8-2.2 μg/g of Be (IPCS, 1990). The US EPA estimated that between 10-30% of the Be in coal is emitted during the combustion process, the rest being present in fly-ash (US EPA, 1987). Most of the world production of Be is added to Cu making an alloy which is fatigue-resistant and as hard as some steel (Griffits and Skilleter, 1991). Beryllium oxide (BeO) is a good conductor of heat and is used as an electrical insulator. This compound is also light and used as in component parts of aeroplanes and as brake discs (Griffits and Skilleter, 1991).

The lowest concentrations of Be in the city which are in the 5th percentile range ($\leq$ 0.98 μg/g), are generally observed near its outskirts, particularly in the west and north, a pattern which is in contrast to the extreme east (see Plate 8.10).

8.3.19 Comparison with Richmond

No geochemical map of Be was produced for Richmond.

8.3.20 Concentrations of magnesium in Wolverhampton topsoils (0-15cm)

Plate 8.11 shows the distribution of Mg in topsoils from Wolverhampton. Magnesium is naturally abundant in soils, with a 5th percentile concentration of 2348 μg/g.

Mg in Wolverhampton topsoils (0-15cm)

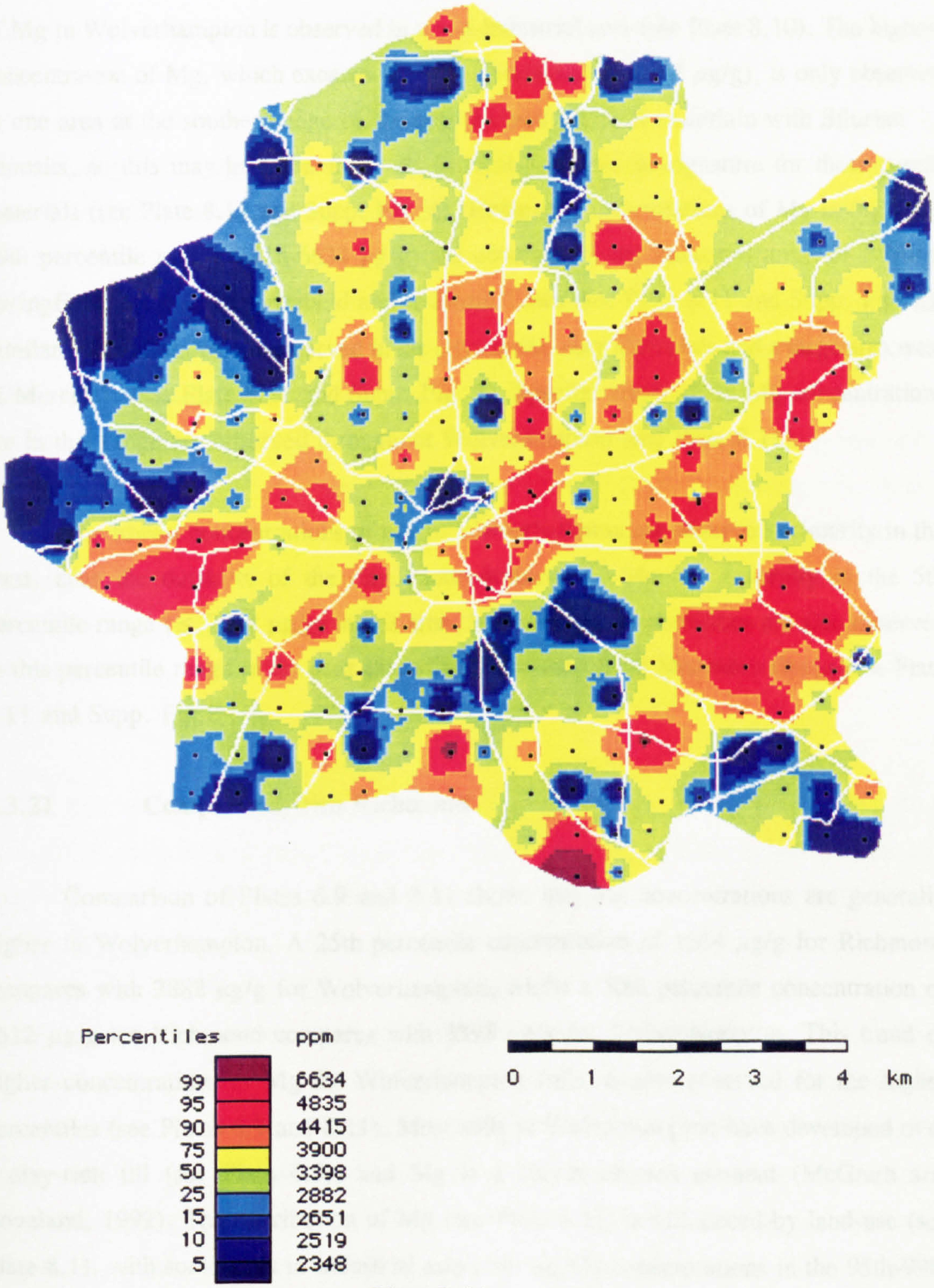


Plate 8.11

The concentration range for this element is low with the 99th percentile concentration < 3 times the magnitude of the 5th percentile (see Plate 8.11). In contrast to the trends observed for a number of the other elements already discussed, the highest concentration of Mg in Wolverhampton is observed in a non-industrial area (see Plate 8.10). The highest concentration of Mg, which exceeds the 99th percentile (> 6634 μg/g), is only observed in one area at the southern edge of the city, an area which is underlain with Silurian deposits, so this may be a feature of the natural geochemical signature for these parent materials (see Plate 8.11 and Supp. Fig. 8). However, concentrations of Mg in the 95th-99th percentile range (4416-6634 μg/g) are observed in the industrial areas of Bilston, Springfield, south of Wednesfield and in Heath Town (see Plate 8.11 and Supp. Fig. 8). Similar concentrations are observed in the city centre, near Merridale and a large area west of Merridale (see Plate 8.11 and Supp. Fig. 8). Specific areas where Mg concentrations are in this range are observed throughout Wolverhampton (see Plate 8.11).

The lowest concentrations of Mg in Wolverhampton are observed primarily in the west, near the outskirts of the city. Concentrations of Mg are generally in the 5th percentile range ($\leq$ 2348 μg/g) in this area. Magnesium concentrations are also observed in this percentile range in the area extending south-west from Monmore Green (see Plate 8.11 and Supp. Fig.8).

8.3.21 Comparison with Richmond

Comparison of Plates 6.9 and 8.11 shows that Mg concentrations are generally higher in Wolverhampton. A 25th percentile concentration of 1314 μg/g for Richmond compares with 2882 μg/g for Wolverhampton, whilst a 50th percentile concentration of 1612 μg/g for Richmond compares with 3398 μg/g for Wolverhampton. This trend of higher concentrations of Mg for Wolverhampton soils, is also observed for the higher percentiles (see Plates 6.9 and 8.11). Most soils in Wolverhampton have developed over a clay-rich till (see Plate 4.5), and Mg is a clay-associated element (McGrath and Loveland, 1992). The distribution of Mg (see Plate 8.11) is influenced by land-use (see Plate 8.1), with some soils in industrial areas having Mg concentrations in the 95th-99th percentile range (4416-6634 μg/g). Over fifty percent of the world production of Mg is used in Al alloys as components in aeroplanes and for containers and cans. Some is also used as an additive to fertilisers and animal feeds (Aikawa, 1991).

8.3.22 Concentrations of calcium in Wolverhampton topsoils (0-15cm)

Plate 8.12 shows the distribution of Ca in topsoils from Wolverhampton. As for Na, although the sampling error for Ca exceeds the recommended value (> 16 % - see Table 5.11), the geochemical variance accounts for nearly 80 % of the total variance. This allows a confident interpretation of the spatial distribution shown in Plate 8.12. Calcium has naturally high concentrations in soils with a 5th percentile concentration of 1997 μg/g. The concentration range of Ca in Wolverhampton soils is large with a 99th percentile concentration approximately 10 times higher than the 5th percentile (see Plate 8.12). The highest concentrations of Ca are observed, predominately, in the industrial area east of the city centre. The distribution follows the pattern of current industrial location more clearly than that observed for Pb, Zn, or Cu (see Plates 8.2-8.4 and 8.12). Limestone is used in the blast-furnaces along with coke and iron-ore during the iron and steel making process. Limestone then combines with impurities, mainly silica to form a slag of calcium silicate (Huebers, 1991). This process may account for the distribution of Ca observed in Plate 8.12.

Relatively high concentrations of Ca are observed in the industrial area from Springfield south-east to Monmore Green and Bilston, with similar concentrations also observed near Heath Town, another area close to industrial activity (see Plates 8.1 and 8.12 and Supp. Fig. 8). In several of these areas Ca concentrations exceed the 99th percentile (> 2.12 %) with most Ca concentrations in the 95th-99th percentile range (1.12-2.12 %) in other parts of this industrial area (see Plate 8.12). Similar concentrations are observed close to the Goodyear works, in the industrial area south of this, and near the sewage works (see Plate 8.12 and Supp. Fig. 8). The city centre and the area close to Merry Hill are two non-industrial areas where Ca concentrations are in the 95th-99th percentile range (1.12-2.12 %). Calcium is contained in several building materials such as plaster, gypsum, concrete and cement which are probably important sources of Ca in the urban garden along with the application of lime and fertilisers (see Table 3.2).

Ca in Wolverhampton topsoils (0-15cm)

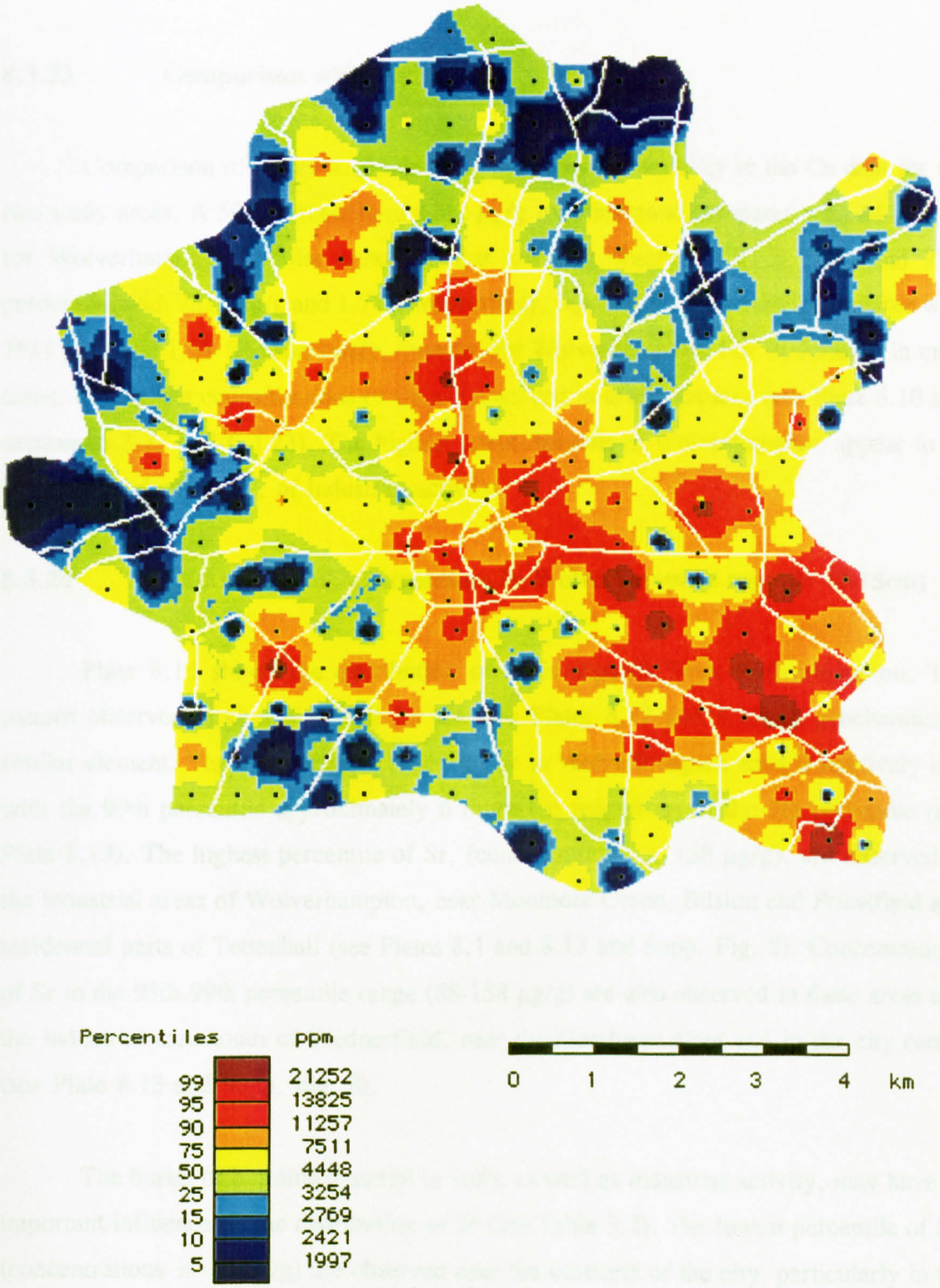


Plate 8.12

The lowest concentrations of Ca are observed near the outskirts of the city, where Ca concentrations are in the 5th percentile range (≤ 1197 μg/g), approximately twenty times less than the highest percentile class.

8.3.23 Comparison with Richmond

Comparison of Plates 6.10 and 8.12 shows some similarity in the Ca data for the two study areas. A 50th percentile of 4152 μg/g for Richmond compares with 4448 μg/g for Wolverhampton. Similar concentrations are also observed for the 75th and 95th percentile, with 7513 μg/g and 1.77% respectively, reported for Richmond, compared with 7511 μg/g and 1.38 % respectively, reported for Wolverhampton. For Richmond, in most cases, the highest concentrations of Ca are observed in urban gardens (see Plate 6.10 and sections 6.3.22 and 6.3.23). The highest concentrations in Wolverhampton appear to be a result, predominantly, of industrial activity.

8.3.24 Concentrations of strontium in Wolverhampton topsoils (0-15cm)

Plate 8.13 shows the distribution of Sr in topsoils from Wolverhampton. The pattern observed is similar to that for Ca (see Plates 8.12 and 8.13), a geochemically similar element. The concentration range for Sr in Wolverhampton soils is relatively low with the 99th percentile approximately 6 times the magnitude of the 5th percentile (see Plate 8.13). The highest percentile of Sr, (concentrations > 158 μg/g), are observed in the industrial areas of Wolverhampton, near Monmore Green, Bilston and Priestfield and residential parts of Tettenhall (see Plates 8.1 and 8.13 and Supp. Fig. 8). Concentrations of Sr in the 95th-99th percentile range (88-158 μg/g) are also observed in these areas and the industrial area south of Wednesfield, near the Goodyear plant and in the city centre (see Plate 8.13 and Supp. Fig. 8).

The burial of building material in soils, as well as industrial activity, may have an important influence on the distribution of Sr (see Table 3.2). The lowest percentile of Sr, (concentrations ≤ 25 μg/g) are observed near the outskirts of the city, particularly in the west and north, away from the industrial base (see Plate 8.13).

Sr in Wolverhampton topsoils (0-15cm)

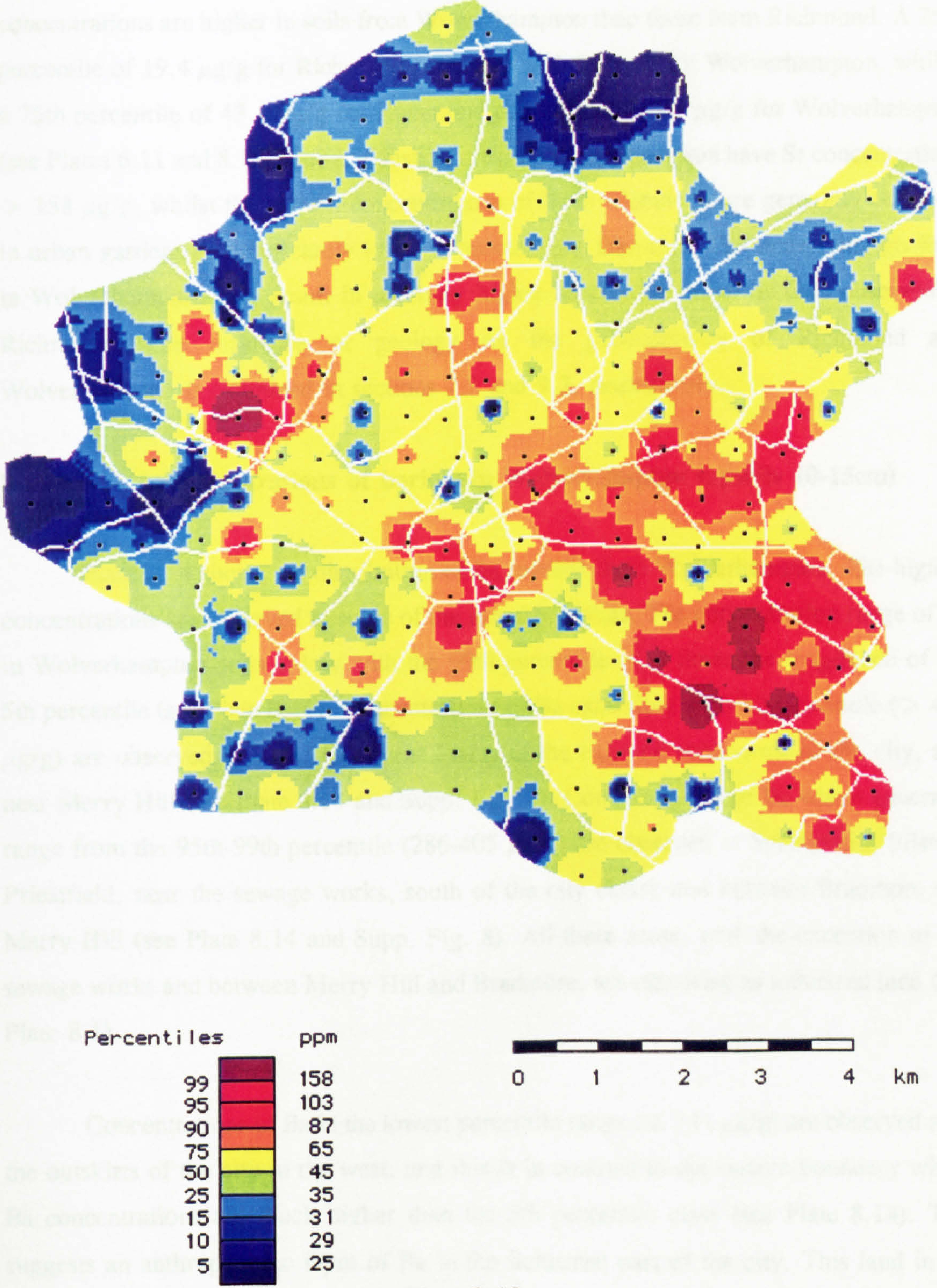


Plate 8.13

8.3.25 Comparisons with Richmond

Comparison of the Sr data for Richmond and Wolverhampton shows that Sr concentrations are higher in soils from Wolverhampton than those from Richmond. A 25th percentile of 19.4 μg/g for Richmond compares with 35 μg/g for Wolverhampton, whilst a 75th percentile of 43.4 μg/g for Richmond compares with 65 μg/g for Wolverhampton (see Plates 6.11 and 8.13). Some industrial areas of Wolverhampton have Sr concentrations > 158 μg/g, whilst the highest concentrations of Sr in Richmond are generally observed in urban gardens at significantly lower concentrations than this. The underlying geology in Wolverhampton may result in naturally higher concentrations of Sr than observed in Richmond. The influence of geology on the geochemistry of Richmond and Wolverhampton is examined in sections 7.2 and 9.2, respectively.

8.3.26 Concentrations of barium in Wolverhampton topsoils (0-15cm)

Plate 8.14 shows the distribution of Ba topsoils from Wolverhampton. The highest concentrations are observed in some of the industrial areas. The concentration range of Ba in Wolverhampton soils is low with the 99th percentile < 4 times the magnitude of the 5th percentile (see Plate 8.14). Concentrations of Ba exceeding the 99th percentile (> 405 μg/g) are observed near the Goodyear Plant, in the extreme south-west of the city, and near Merry Hill (see Plate 8.14 and Supp. Fig. 8). Concentrations of Ba which generally range from the 95th-99th percentile (286-405 μg/g) are observed in Springfield, Bilston, Priestfield, near the sewage works, south of the city centre and between Bradmore and Merry Hill (see Plate 8.14 and Supp. Fig. 8). All these areas, with the exception of the sewage works and between Merry Hill and Bradmore, are classified as industrial land (see Plate 8.1).

Concentrations of Ba in the lowest percentile range (≤ 111 μg/g) are observed near the outskirts of the city in the west, and this is in contrast to the eastern boundary where Ba concentrations are much higher than the 5th percentile class (see Plate 8.14). This suggests an anthropogenic input of Ba in the industrial part of the city. This land in the west is adjacent to farmland just outside the metropolitan boundary. The extensive burning

Ba in Wolverhampton topsoils (0-15cm)

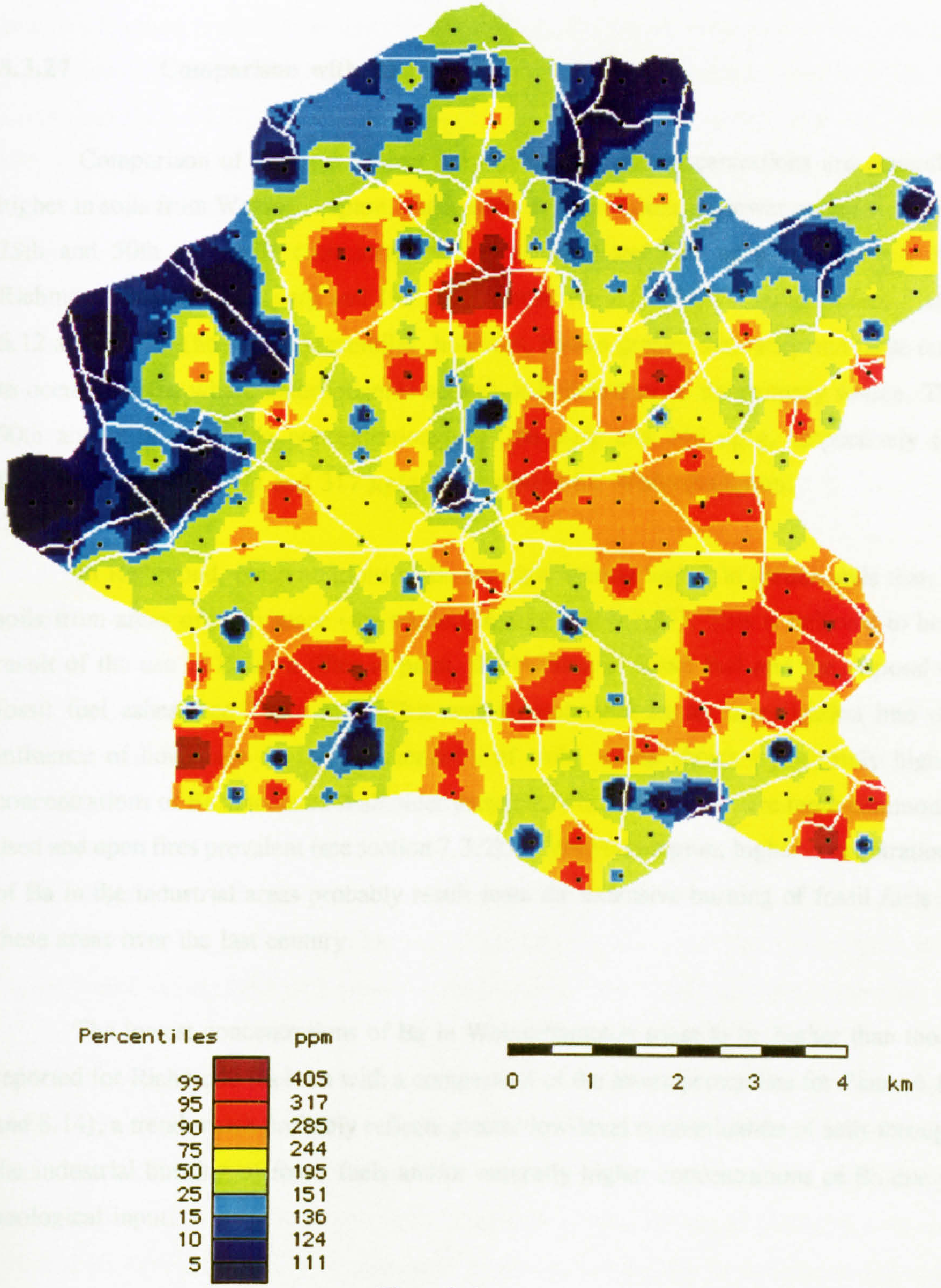


Plate 8.14

of fossil fuels over the last century may account for the distribution of Ba observed in Plate 8.14. Barium concentrations in coal can be as high as 3000 μg/g (Bowen, 1966), whilst the Ba concentration in coal ash ranges from 100-500 μg/g (Miner, 1969).

8.3.27 Comparison with Richmond

Comparison of Plates 6.12 and 8.14 shows that Ba concentrations are generally higher in soils from Wolverhampton, particularly the corresponding lower percentiles. The 25th and 50th percentile concentrations are 82 μg/g and 135 μg/g, respectively for Richmond soils and 151 μg/g and 195 μg/g, respectively for Wolverhampton (see Plates 6.12 and 8.14). The higher percentiles, however, have a greater similarity and these tend to occur in areas where anthropogenic activity is believed to be the primary source. The 90th and 95th percentile concentrations are 286 μg/g and 346 μg/g, respectively for Richmond and 285 μg/g and 317 μg/g, respectively for Wolverhampton.

In Richmond, concentrations of Ba are significantly higher in garden soils than in soils from areas of open space (see sections 6.3.26 and 6.3.27). This is believed to be a result of the use of Ba as a filler in paint, the burning of fossil fuel and the disposal of fossil fuel ashes (see Table 3.2). This was substantiated by an investigation into the influence of house-age on the geochemistry of soils, which shows significantly higher concentrations of Ba associated with older property, when Pb paints were more commonly used and open fires prevalent (see section 7.3.2). In Wolverhampton, higher concentrations of Ba in the industrial areas probably result from the extensive burning of fossil fuels in these areas over the last century.

The lowest concentrations of Ba in Wolverhampton seem to be higher than those reported for Richmond (as seen with a comparison of the lower percentiles for Plates 6.12 and 8.14), a trend which probably reflects greater low-level contamination of soils through the industrial burning of fossil fuels and/or naturally higher concentrations of Ba due to geological input.

8.3.28 Concentrations of aluminium in Wolverhampton topsoils (0-15cm)

Plate 8.15 shows the distribution of Al in topsoils from Wolverhampton. The pattern observed is similar to that for many elements already discussed in this section. Aluminium is naturally abundant in soils with a 5th percentile concentration of approximately 1.69 %. The concentration range for the element is low, however, with a 99th percentile < 3 times the concentration of the 5th percentile (see Plate 8.15). The highest concentrations of Al which exceed the 99th percentile (> 4.80 %) are observed mainly in industrial areas such as north of Bilston, Priestfield, near Monmore Green, Heath Town and Wednesfield (see Plates 8.1 and 8.15, and Supp. Fig. 8). Concentrations of Al in the 95th-99th percentile range (3.55-4.8 %) are also observed in these areas and several sites east of the city centre. The lowest concentrations of Al in Wolverhampton are generally observed at the outskirts of the city, particularly in the west and north-west, where Al concentrations are in the 5th percentile range in places (< 1.69 % - see Plate 8.15).

8.3.29 Comparison with Richmond

A comparison of Plates 6.13 and 8.15 shows that concentrations of Al are generally higher in soils from Wolverhampton than Richmond. Twenty-fifth and 50th percentile concentrations of 1.22 % and 1.53 %, respectively for Richmond soils compare with 2.07 % and 2.41 %, respectively for Wolverhampton. The 5th percentile concentration for Al in Wolverhampton soils is higher than the 50th percentile for Richmond data. In general, the concentration range of Al in the two urban areas is low, with the highest percentile concentration approximately 3 times the magnitude of the lowest reported percentile.

In general, the higher concentrations of Al concentrations in Wolverhampton are probably the result of two processes; naturally higher concentrations from the clay rich parent material, and the industrial activity in the city, which produces site specific high concentrations of Al. The high percentile classes of Al in a number of industrial area may result from the extensive use of this metal in alloys, particularly in containers and cans. The composition of the made ground, which is common in the south-east of the

Al in Wolverhampton topsoils (0-15cm)

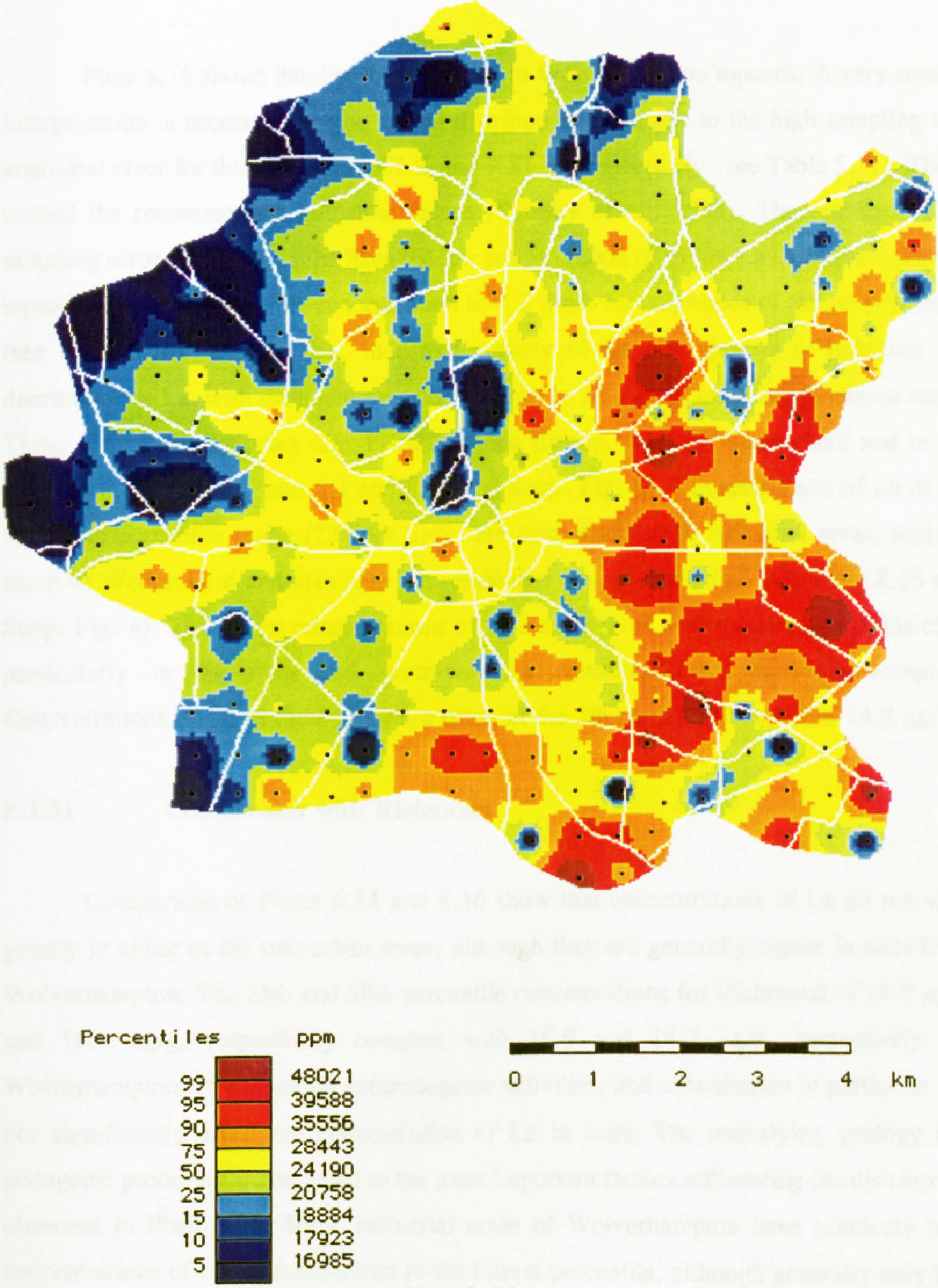


Plate 8.15

city (see Fig 4.5) may also influence concentrations of Al in these areas.

8.3.30 Concentrations of lanthanum in Wolverhampton topsoils (0-15cm)

Plate 8.16 shows the distribution of La in Wolverhampton topsoils. A very careful interpretation is necessary for the spatial distribution of La due to the high sampling and analytical error for this element (2.67 % and 9.27 %, respectively - see Table 5.11). These exceed the recommended guideline values (Ramsey *et al.,* 1993). The relatively high sampling error probably results from the low concentration range for La in Wolverhampton topsoils. The 99th percentile concentration is < 2 times the magnitude of the 5th percentile (see Plate 8.16). Despite this, industrial activity in the city appears to influence the distribution of La, with the highest concentrations (> 28.4 μg/g) observed in industrial areas. These include several sites near Priestfield and Bilston, west of Wednesfield and in the south of the city (see Plates 8.1 and 8.16 and Supp. Fig. 8). Concentrations of La in the 95th-99th percentile range (23-28.4 μg/g) are also observed in industrial areas, such as south of Wednesfield and also near the residential area of Tettenhall (see Plate 8.16 and Supp. Fig. 8). The lowest concentrations of La are observed near the outskirts of the city, particularly in the west and north-west, a common trend in Wolverhampton. Concentrations of La in these areas are often in the 5th percentile range (≤ 14.8 μg/g).

8.3.31 Comparison with Richmond

Comparison of Plates 6.14 and 8.16 show that concentrations of La do not vary greatly in either of the two urban areas, although they are generally higher in soils from Wolverhampton. The 25th and 50th percentile concentrations for Richmond of 14.2 μg/g and 16.4 μg/g, respectively compare with 16.9 and 18.7 μg/g, respectively for Wolverhampton. In Richmond anthropogenic activities, and urbanisation in particular, do not significantly affect the concentration of La in soils. The underlying geology and pedogenic processes are believed to the most important factors influencing the distribution observed in Plate 6.14. Some industrial areas of Wolverhampton have relatively high concentrations of La, in comparison to the lowest percentile, although generally only two times greater in magnitude. Specific industrial processes and/or the abundance of made

La in Wolverhampton topsoils (0-15cm)

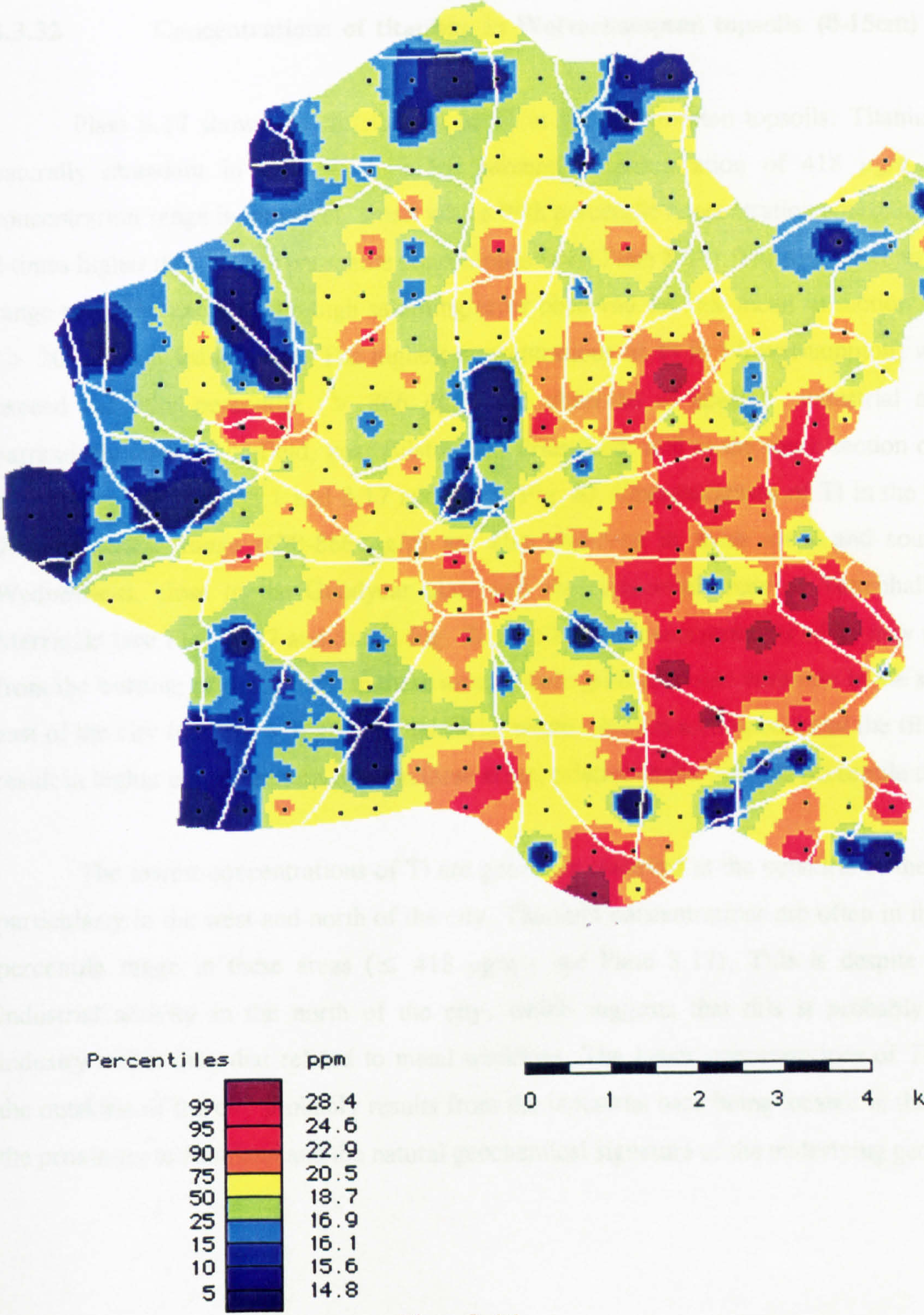


Plate 8.16

ground may account for this. Lanthanum is sometimes used to improve the mechanical properties of steels, giving increased resistance to erosion (Goering et al., 1991).

8.3.32 Concentrations of titanium in Wolverhampton topsoils (0-15cm)

Plate 8.17 shows the distribution of Ti in Wolverhampton topsoils. Titanium is naturally abundant in soils, with a 5th percentile concentration of 418 μg/g. The concentration range is, however, small with a 99th percentile concentration approximately 2 times higher than the 5th percentile concentration (see Plate 8.17). The low concentration range probably explains the high sampling error observed for this metal in section 5.7.4 (> 20 % - see Table 5.11). The highest concentrations of Ti in Wolverhampton, which exceed the 99th percentile (> 866 μg/g) are observed in several industrial areas, particularly near Springfield, near Bilston and Priestfield, and in the south section of the city centre (see Plates 8.1 and 8.17 and Supp. Fig. 8). Concentrations of Ti in the 95th-99th percentile range (670-866 μg/g) are also observed in these areas and south of Wednesfield, close to the Goodyear plant and the residential areas of Tettenhall and Merridale (see Plate 8.17 and Supp. Fig. 8). The highest concentrations of Ti may result from the burning of fossil fuels in these areas. Made ground is also common in the south-east of the city (see Fig 4.5) and the industrial waste which is a component of the fill may result in higher concentrations of Ti in these areas, relative to the baseline percentile range.

The lowest concentrations of Ti are generally observed at the outskirts of the city, particularly in the west and north of the city. Titanium concentrations are often in the 5th percentile range in these areas (≤ 418 μg/g - see Plate 8.17). This is despite some industrial activity in the north of the city, which suggests that this is probably light industry rather than that related to metal workings. The lower concentrations of Ti near the outskirts of the city probably results from the industrial base being located in the east, the proximity to farmland and the natural geochemical signature of the underlying geology.

Ti in Wolverhampton topsoils (0-15cm)

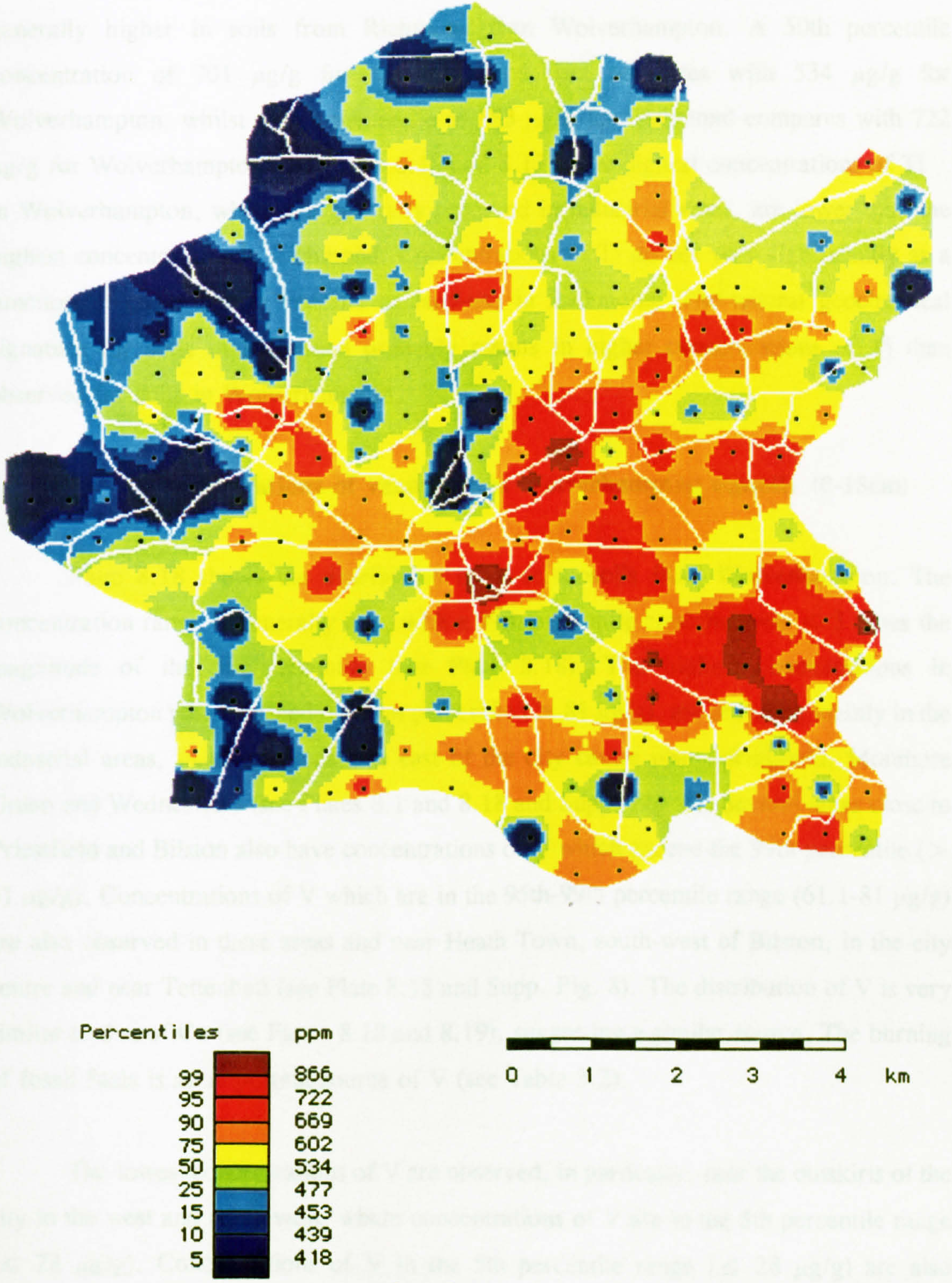


Plate 8.17

8.3.33 Comparison with Richmond

Comparison of Plates 6.15 and 8.17 shows that in general Ti concentrations are generally higher in soils from Richmond than Wolverhampton. A 50th percentile concentration of 701 μg/g for the Richmond data compares with 534 μg/g for Wolverhampton, whilst a 95th percentile of 883 μg/g for Richmond compares with 722 μg/g for Wolverhampton (see Plates 6.15 and 8.17). The highest concentrations of Ti in Wolverhampton, which are generally observed in industrial areas, are lower than the highest concentrations in Richmond. Concentrations of Ti do not vary significantly as a function of either parent material or land-use in Richmond. The natural geochemical signature for soils in Richmond probably results in higher concentrations of Ti than observed for soils in Wolverhampton.

8.3.34 Concentrations of vanadium in Wolverhampton topsoils (0-15cm)

Plate 8.18 shows the distribution of V in topsoils from Wolverhampton. The concentration range is generally low, with a 99th percentile concentration $<$ 3 times the magnitude of the 5th percentile (see Plate 8.18). The highest concentrations in Wolverhampton which exceed the 99th percentile ($>$ 81 μg/g), are observed mainly in the industrial areas, in several locations east of the city centre near Springfield, Monmore Green and Wednesfield (see Plates 8.1 and 8.18 and Supp. Fig. 8). Several areas close to Priestfield and Bilston also have concentrations of V which exceed the 99th percentile ($>$ 81 μg/g). Concentrations of V which are in the 95th-99th percentile range (61.1-81 μg/g) are also observed in these areas and near Heath Town, south-west of Bilston, in the city centre and near Tettenhall (see Plate 8.18 and Supp. Fig. 8). The distribution of V is very similar to that of Co (see Plates 8.18 and 8.19), suggesting a similar source. The burning of fossil fuels is an important source of V (see Table 3.2).

The lowest concentrations of V are observed, in particular, near the outskirts of the city in the west and north-west, where concentrations of V are in the 5th percentile range ($\leq$ 28 μg/g). Concentrations of V in the 5th percentile range ($\leq$ 28 μg/g) are also observed at specific locations in the city, particularly north of the city centre.

V in Wolverhampton topsoils (0-15cm)

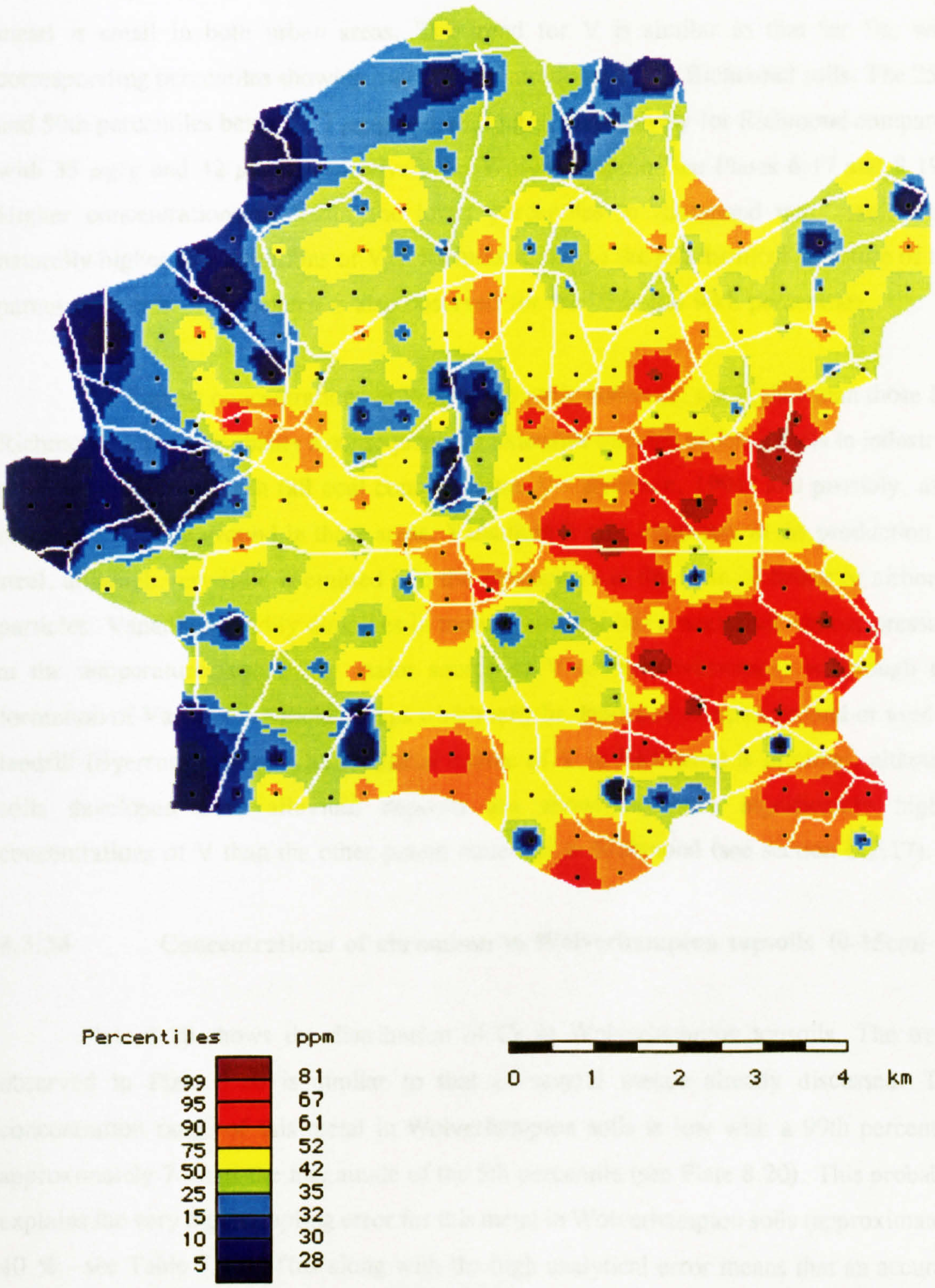


Plate 8.18

8.3.35 Comparison with Richmond

Comparison of Plates 6.17 and 8.19 shows that the concentration range of this metal is small in both urban areas. The trend for V is similar to that for Fe, with corresponding percentiles showing higher concentrations of V in Richmond soils. The 25th and 50th percentiles being 42.7 μg/g and 48.2 μg/g, respectively for Richmond compared with 35 μg/g and 42 μg/g, respectively for Wolverhampton (see Plates 6.17 and 8.19). Higher concentrations of V for the lower percentiles in Richmond may result from naturally higher concentrations of V in Richmond, due to the geochemical signature of the parent materials. This pattern is also observed for the 75th and 90th percentiles.

The highest concentrations in Wolverhampton, however, are higher than those for Richmond, and are probably a consequence of extensive burning of fossil fuels in industrial areas of Wolverhampton (all coal contains some V - Byerrum, 1991) and possibly, as a result of the made ground in these areas. Vanadium is also important in the production of steel, although very little is emitted into the atmosphere in the form of fumes or airborne particles. Vanadium readily dissolves in molten iron and has a negligible vapour pressure at the temperatures used. The major source of V to the environment is through the formation of Vanadium-enriched slags which may be deposited on open ground or used as landfill (Byerrum, 1991). The industrial source of V in Richmond is minimal, although soils developed over alluvium deposits are shown to have significantly higher concentrations of V than the other parent materials in Richmond (see section 6.2.17).

8.3.36 Concentrations of chromium in Wolverhampton topsoils (0-15cm)

Plate 8.20 shows the distribution of Cr in Wolverhampton topsoils. The trend observed in Plate 8.20 is similar to that of several metals already discussed. The concentration range of this metal in Wolverhampton soils is low with a 99th percentile approximately 7 times the magnitude of the 5th percentile (see Plate 8.20). This probably explains the very high sampling error for this metal in Wolverhampton soils (approximately 40 % - see Table 5.11). This along with the high analytical error means that an accurate interpretation of the spatial distribution of Cr is very difficult. The highest concentrations

Cr in Wolverhampton topsoils (0-15cm)

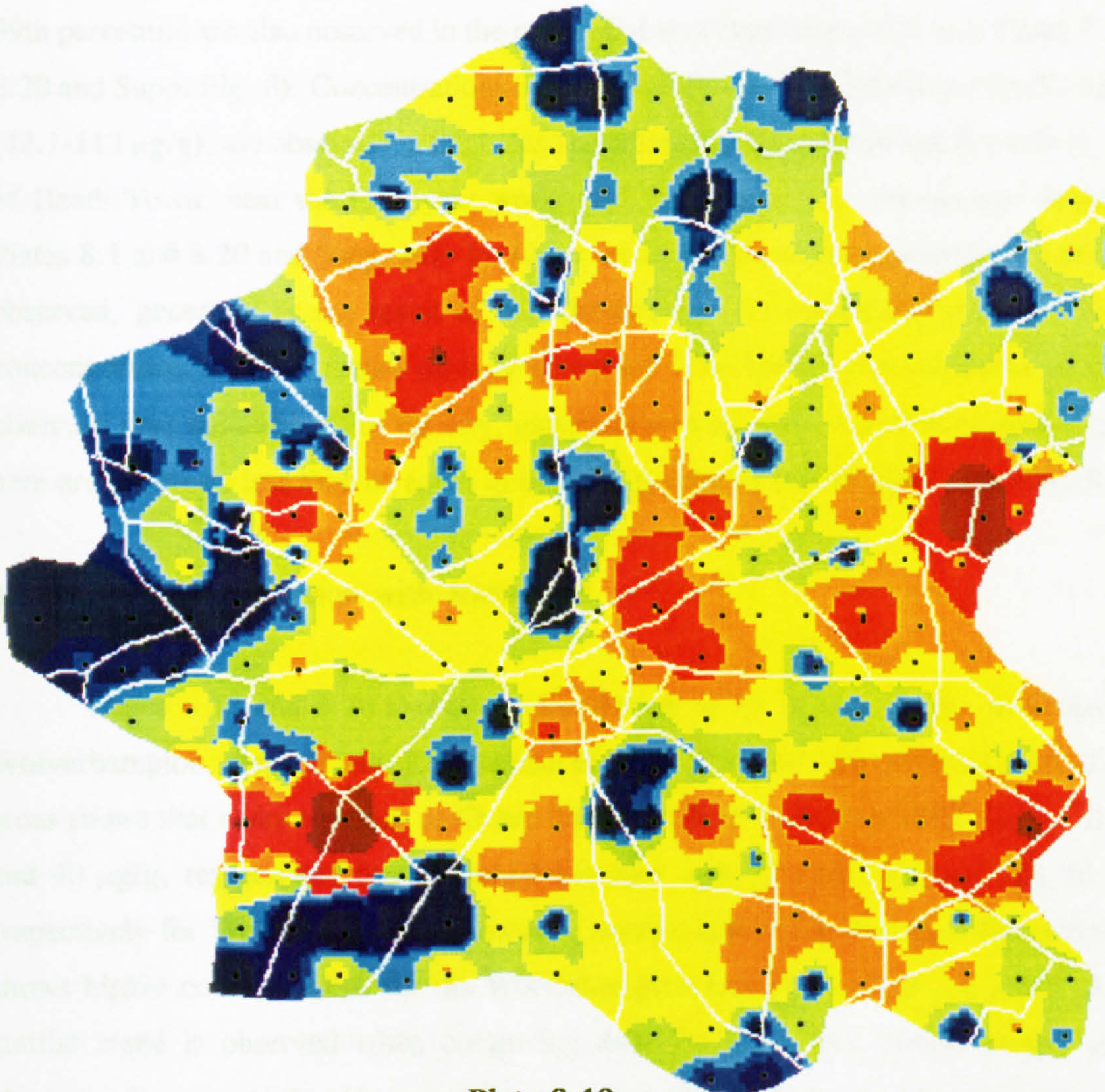


Plate 8.19

Plate 8.19

of Cr, which exceed the 99th percentile (> 113 μg/g) are observed in the industrial areas south of Wednesfield (although this is the result of one high concentration), and near Bilston (see Plates 8.1 and 8.20 and Supp. Fig. 8). Concentrations of Cr exceeding the 99th percentile are also observed in the residential area near Merry Hill (see Plates 8.1 and 8.20 and Supp. Fig. 8). Concentrations of Cr, generally in the 95th-99th percentile range (42.1-113 μg/g), are observed in the industrial areas near Springfield and Priestfield, south of Heath Town, near the Goodyear works and in the area near the sewage works (see Plates 8.1 and 8.20 and Supp. Fig. 8). Other areas where similar concentrations of Cr are observed, generally as the result of one sample, tend to coincide with relatively high concentrations of other metals already discussed. The lowest concentrations of Cr are observed near the outskirts of the city, particularly in the west. Chromium concentrations here are generally less than or equal to the 10th percentile (≤ 18 μg/g - see Plate 8.20).

8.3.37 Comparison with Richmond

Plates 6.18 and 8.20 shows the distribution of Cr in topsoils for Richmond and Wolverhampton, respectively. Comparison of 25th, 50th and 75th percentiles for the two areas shows that concentrations of Cr are higher for soils in Richmond (31 μg/g, 35 μg/g and 40 μg/g, respectively for Richmond compare with 21 μg/g, 24 μg/g and 30 μg/g, respectively for Wolverhampton). However, comparison of the 95th and 99th percentiles shows higher concentrations for the Wolverhampton (see Plates 6.18 and 8.20). A very similar trend is observed when comparing data for V and Fe, geochemically similar elements. It suggests that Cr concentrations are naturally higher in soils from Richmond compared with soils from Wolverhampton. The highest concentrations of Cr are observed mainly in industrial areas of Wolverhampton and these are higher than the highest concentrations of Cr in soils from Richmond. Richmond has an insignificant history of industrial activity compared with Wolverhampton (see sections 4.2.2 and 4.6). Chromium concentrations are significantly higher in soils from industrial areas of Wolverhampton than for soils from other land-uses in the city.

8.3.38 Concentrations of manganese in Wolverhampton topsoils (0-15cm)

Plate 8.21 shows the distribution of in Mn in topsoils from Wolverhampton. In general, the highest concentrations of Mn are observed in areas of industry, which probably results from the industrial use of Mn and/or the composition of made ground. The concentration range of Mn is low, with the 99th percentile approximately 6 times the magnitude of the 5th percentile (see Plate 8.21). The highest concentrations of Mn which exceed the 99th percentile (> 1593 μg/g), are observed close to Monmore Green, south of Heath Town, in Bilston, and in the industrial area south-east of this (see Plates 8.1 and 8.21 and Supp. Fig. 8). Manganese concentrations which exceed the 99th percentile (> 1593 μg/g) are also observed in the area north-east of Wednesfield, not coinciding with anomalies for any of the other elements already discussed (see Plates 8.2-8.20 and Supp. Fig. 8). Concentrations of Mn, generally in the 95th-99th percentile range (875-1593 μg/g), are also observed close to these areas, particularly between Monmore Green and Bilston, but also in the extreme south-east of the city centre close to an area of industrial activity (see Plates 8.1 and 8.21 and Supp. Fig. 8).

Since 1839 Mn has been used in the production of steel (Mena, 1980). Ninety percent of Mn is processed into ferro-manganese in the blast furnace and is used for alloying, as manganese is necessary for binding oxygen and sulphur during steel production (Schiele, 1991). This probably explains the distribution of Mn in Plate 8.21; the iron and steel industry has a long history in the city (see section 4.6.2).

The lowest concentrations of Mn which are in the 5th percentile range (≤ 274 μg/g), are most common in the northern extreme of the city, some in areas of industrial activity (see Plates 8.1 and 8.21). Some low concentrations of Mn do occur close to the edge of the city in the west, although not to the same extent as observed for a number of elements in Wolverhampton (see Plates 8.2-8.21). This may reflect the natural geochemical signature for the parent materials in these areas and the distance from industrial activity.

Mn in Wolverhampton topsoils (0-15cm)

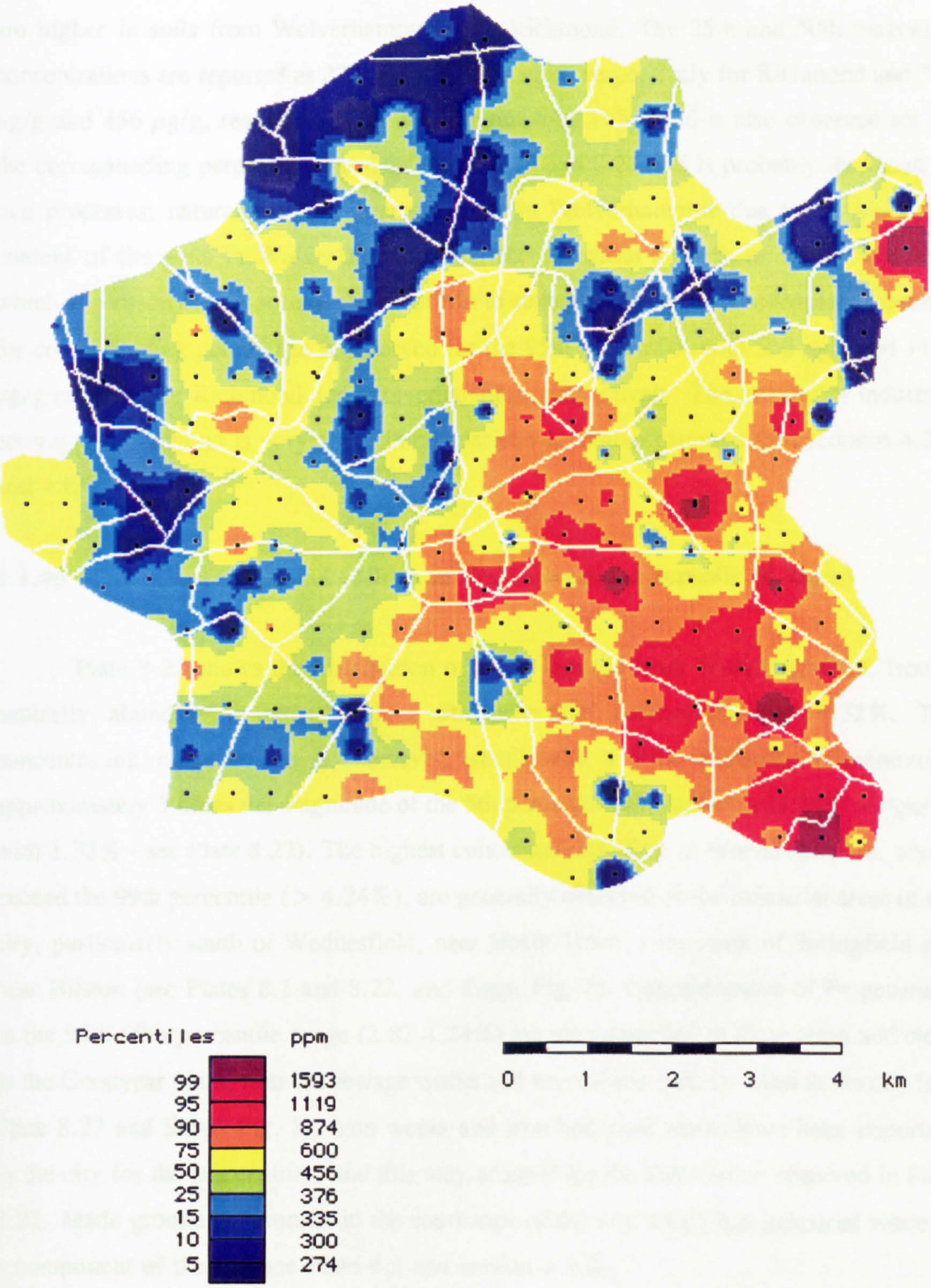


Plate 8.20

8.3.39 Comparison with Richmond

Comparison of Plates 6.19 and 8.21 shows that in general, concentrations of Mn are higher in soils from Wolverhampton than Richmond. The 25th and 50th percentile concentrations are reported as 225 μg/g and 305 μg/g, respectively for Richmond and 376 μg/g and 456 μg/g, respectively for Wolverhampton. This trend is also observed for all the corresponding percentiles listed in Plates 6.19 and 8.21 and is probably the result of two processes; naturally higher concentrations in Wolverhampton due to the high clay content of the soils in Wolverhampton, and the industrial activity in Wolverhampton, which is probably an important source of Mn to soils in these areas. The largest difference for corresponding percentiles is observed for the 95th percentile, with 550 μg/g and 1119 μg/g reported for Richmond and Wolverhampton, respectively. The amount of industrial activity in Richmond is very small in comparison to Wolverhampton (see sections 4.2.2 and 4.6).

8.3.40 Concentrations of Iron in Wolverhampton topsoils (0-15cm)

Plate 8.22 shows the distribution of Fe in topsoils from Wolverhampton. Iron is naturally abundant in soils, with a 5th percentile concentration of 1.32%. The concentration range of Fe is, however, small with a 99th percentile concentration approximately 3 times the magnitude of the 5th percentile concentration (4.24% compared with 1.32% - see Plate 8.22). The highest concentrations of Fe in Wolverhampton, which exceed the 99th percentile (> 4.24%), are generally observed in the industrial areas of the city, particularly south of Wednesfield, near Heath Town, sites south of Springfield and near Bilston (see Plates 8.1 and 8.22, and Supp. Fig. 8). Concentrations of Fe generally in the 95th-99th percentile range (2.82-4.24%) are also observed in these areas and close to the Goodyear plant, near the sewage works and several site specific areas in the city (see Plate 8.22 and Supp. Fig. 8). Iron works and iron and steel works have been important in the city for the last century, and this may account for the distribution observed in Plate 8.22. Made ground is common in the south-east of the city which has industrial waste as a component of the fill (see Plate 4.5 and section 4.7.6).

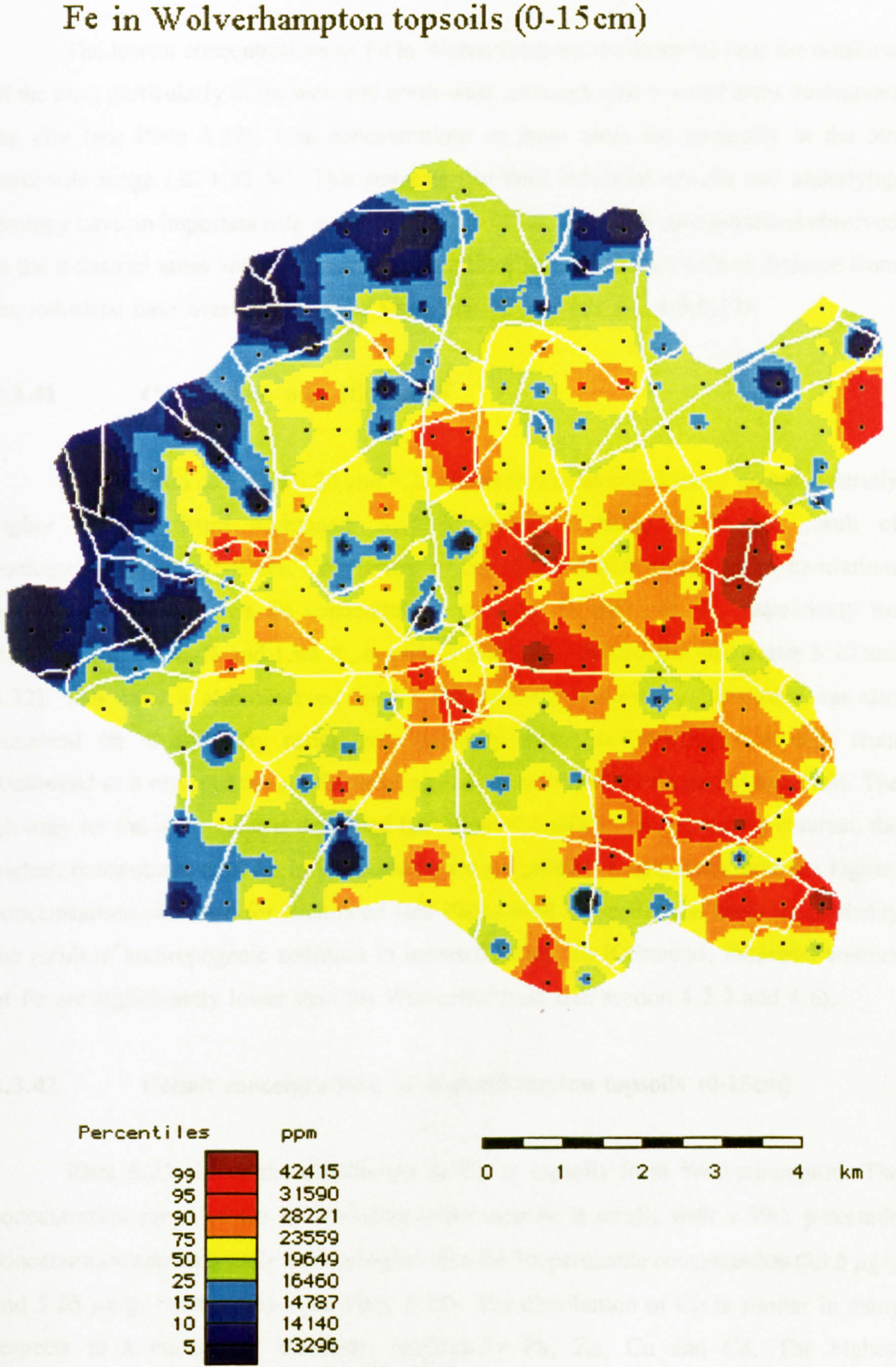

Fe in Wolverhampton topsoils (0-15cm)
Percentiles
ppm
99 42415
95 31590
90 28221
75 23559
50 19649
25 16460
15 14787
10 14140
5 13296
0
1
2
3
4
km

Plate 8.21

The lowest concentrations of Fe in Wolverhampton are observed near the outskirts of the city, particularly in the west and north-west, although also in small areas throughout the city (see Plate 8.22). Iron concentrations in these areas are generally in the 5th percentile range (≤ 1.32 %). This suggests that both industrial activity and underlying geology have an important role in the distribution of Fe, with high concentrations observed in the industrial areas and the lowest concentrations associated with soils at distance from the industrial base overlying Triassic Sandstone (see section 9.2.4-9.2.17).

8.3.41 Comparison with Richmond

Comparison of Plates 6.20 and 8.22 shows that concentrations of Fe are generally higher in soils from Richmond, a trend which is likely to be the result of geology/pedogenic processes. Comparison of the 25th and 50th percentile concentrations for the two areas shows Fe concentrations of 2.11 % and 2.46 %, respectively for Richmond and 1.64 % and 1.96 %, respectively for Wolverhampton (see Plates 6.20 and 8.22). This trend is also observed for the 75th and 90th percentiles. This trend was also observed for V and may result from naturally higher concentrations in soils from Richmond as a result of the geochemical signatures for the different parent materials. The geology for the study areas is described in sections 4.5 and 4.7 in general. In contrast, the highest concentrations of Fe in Wolverhampton are greater in magnitude than the highest concentrations observed for Richmond (see Plates 6.20 and 8.22) and these are probably the result of anthropogenic additions in industrial areas. In Richmond, industrial sources of Fe are significantly lower than for Wolverhampton (see section 4.2.2 and 4.6).

8.3.42 Cobalt concentrations in Wolverhampton topsoils (0-15cm)

Plate 8.23 shows the distribution of Co in topsoils from Wolverhampton. The concentration range of Co in Wolverhampton topsoils is small, with a 99th percentile concentration approximately 4 times higher than the 5th percentile concentration (23.5 μg/g and 5.65 μg/g, respectively - see Plate 8.23). The distribution of Co is similar in many respects to a number of elements, particularly Pb, Zn, Cu and Cd. The highest concentrations of Co, which exceed the 99th percentile (> 23.5 μg/g), are observed

Co in Wolverhampton topsoils (0-15cm)

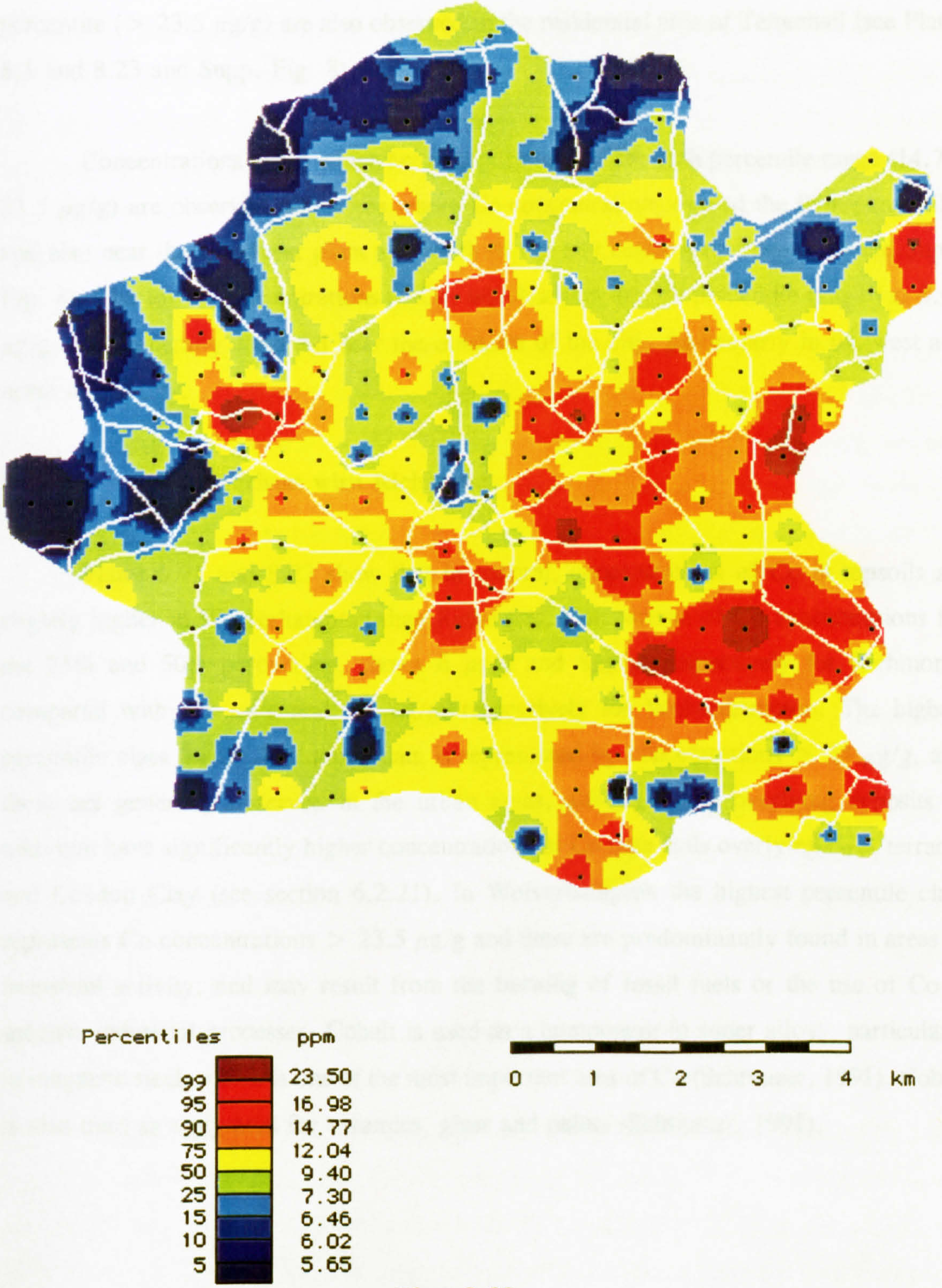


Plate 8.22

between Springfield and Monmore Green, near Priestfield and Bilston, and south of Wednesfield (see Plate 8.23 and Supp. Fig. 8). Several of these areas coincide with, or are near industrial activity (see Plate 8.1). Concentrations of Co which exceed the 99th percentile (> 23.5 μg/g) are also observed in the residential area of Tettenhall (see Plates 8.1 and 8.23 and Supp. Fig. 8).

Concentrations of Co which are generally in the 95th-99th percentile range (14.78-23.5 μg/g) are observed near areas where Co concentrations exceed the 99th percentile, and also near the Goodyear plant and south of the city centre (see Plate 8.23 and Supp. Fig. 8). The lowest concentrations of Co, which are in the 5th percentile range (≤ 5.65 μg/g), are generally observed near the outskirts of the city, particularly in the west and north of the city.

8.3.43 Comparison with Richmond

Plates 6.21 and 8.23 show that in general, concentrations of Co in topsoils are slightly higher in Wolverhampton than Richmond. Comparison of Co concentrations for the 25th and 50th percentiles, shows 6 μg/g and 8μg/g, respectively for Richmond, compared with 7.3 μg/g and 9.4 μg/g, respectively for Wolverhampton. The highest percentile class for the Richmond data is represented by concentrations > 14 μg/g, and these are generally observed in the urban areas, although soils overlying deposits of alluvium have significantly higher concentrations of Co than soils overlying river terraces and London Clay (see section 6.2.21). In Wolverhampton the highest percentile class represents Co concentrations > 23.5 μg/g and these are predominantly found in areas of industrial activity, and may result from the burning of fossil fuels or the use of Co in specific industrial processes. Cobalt is used as a component in super alloys, particularly in magnetic steels which is one of the most important uses of Co (Schrauzer, 1991). Cobalt is also used as a pigment for ceramics, glass and paints (Schrauzer, 1991).

8.3.44 Concentrations of phosphorus in Wolverhampton topsoils (0-15cm)

Plate 8.24 shows the distribution of P in Wolverhampton topsoils. The distribution is similar to that observed for Pb, Zn, Cu and Cd in Wolverhampton (see Plates 8.2-8.5 and 8.24). Phosphorus is naturally abundant in soils with a 5th percentile concentration of 587 μg/g, although the concentration range in the city is low; the 99th percentile concentration is approximately 4 times the magnitude of the 5th percentile (see Plate 8.24). The highest concentrations of P which exceed the 99th percentile (> 2141 μg/g), are observed mainly in the industrial areas, particularly the areas near Priestfield and Bilston and near the sewage works (see Plates 8.1 and 8.24 and Supp. Fig. 8). Concentrations which exceed the 99th percentile (> 2141 μg/g) are also observed in the residential areas between Bradmore and Merry Hill and near Merridale (see Plates 8.1 and 8.24 and Supp. Fig. 8). Concentrations of P in the 95th-99th percentile range (1327-2151 μg/g) are also observed in these areas, and near Tettenhall and several other residential areas in the city (see Plates 8.1 and 8.24, and Supp. Fig. 8). There are probably several sources of P in the urban garden, through the addition of fertilisers, the accumulation of rotting vegetation on compost heaps and the burial of bones.

The largest area where P concentrations are at their lowest is observed near the outskirts of the city in the west (see Plate 8.24). Phosphorus concentrations are in the 5th percentile range (≤ 587 μg/g) for much of this area. The absence of industrial activity in this area, the distance from the industrial base, and the natural geochemical signature probably explain the relatively low concentrations of P in this area (see section 9.2 in general).

8.3.45 Comparison with Richmond

Comparison of Plates 6.22 and 8.24 shows that concentrations of P are generally higher in soils from Richmond. This is seen when comparing corresponding percentile concentrations, with 25th and 50th percentiles of 711 μg/g and 953 μg/g, respectively for Richmond and 725 μg/g and 851 μg/g, respectively for Wolverhampton (see Plates 6.22 and 8.24). A trend of higher concentrations for Richmond data is also observed for the

P in Wolverhampton topsoils (0-15cm)

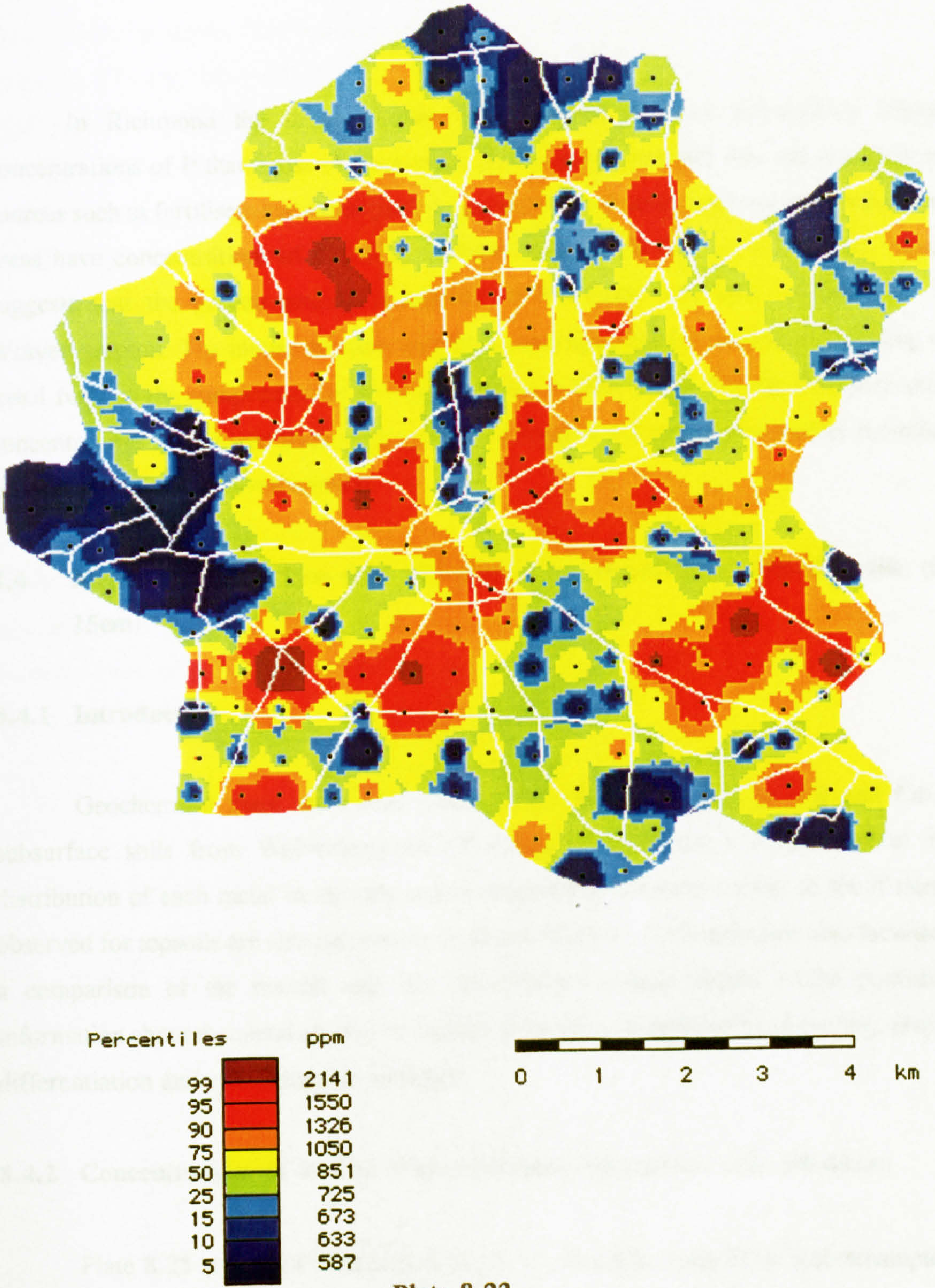


Plate 8.23

75th, 90th and 95th percentiles (see Plates 6.22 and 8.24). The highest percentile in Richmond is also higher than the highest percentile in Wolverhampton, despite the industrial activity in this city and the influence this appears to have on the distribution of P.

In Richmond the urban garden was observed to have significantly higher concentrations of P than areas of open space. It was postulated that this was the result of sources such as fertilisers and decomposing vegetation. In Wolverhampton some residential areas have concentrations of P similar to those observed in the industrial areas, which suggests that the garden sources recognised in Richmond may also be important in Wolverhampton. The industrial areas may have other sources of P through the burning of fossil fuels or the composition of the made ground in these areas. Similar 25th percentile concentrations for the two areas suggests that the input of P from natural sources is similar for Richmond and Wolverhampton.

8.4 Metals in Subsurface soils (30-45cm) and comparison with Topsoils (0-15cm)

8.4.1 Introduction

Geochemical maps were also produced for the metals Pb, Zn, Cu and Cd in subsurface soils from Wolverhampton (30-45cm). This allows a comparison of the distribution of each metal in topsoils and corresponding subsurface soils, to see if trends observed for topsoils are also apparent at depths of 30-45cm. This technique also facilitates a comparison of the overall data for the different sample depths whilst providing information about the metal content of the parent material, biogeochemical cycling, profile differentiation and anthropogenic additions.

8.4.2 Concentrations of lead in Wolverhampton Subsurface soils (30-45cm)

Plate 8.25 shows the distribution of Pb in subsurface soils from Wolverhampton. In general, the trend observed is very similar to that for Pb in topsoils (see Plate 8.2), with concentrations exceeding the 99th percentile, (> 555 μg/g), mainly observed in areas of industrial activity (see Plates 8.1 and 8.25). This is probably attributable to the made ground in these regions which extends to depths of several metres and is likely to comprise much industrial waste. The lowest concentrations of Pb which are in the 5th percentile range (≤ 27 μg/g) are observed near the outskirts of the city, particularly in the north and north-east. Comparison of corresponding percentiles shows that Pb concentrations are generally higher in topsoils than subsurface samples. The 25th and 50th percentile concentrations for the topsoil data are 69 μg/g and 101 μg/g, respectively and 49 μg/g and 74 μg/g, respectively for subsurface soils. This trend is also observed for all the higher percentiles and reflects the greater accumulation of Pb in the top 15cm of the profile from anthropogenic activity and biogeochemical cycling, compared to depths of 30-45cm.

The major differences in the distribution of Pb for topsoils and subsurface soils are observed near the Goodyear plant, the sewage works and in the residential area close to Bradmore. In these areas Pb is observed at lower percentiles than in topsoils. This is a result of much greater accumulation of Pb in the top 15cm in these areas. The Pb concentrations in these regions are, however, significantly higher than the lowest concentrations of Pb observed at the outskirts of the city (≤ 36 μg/g compared with 117-190 μg/g).

Pb in Wolverhampton subsurface soils (30-45cm)

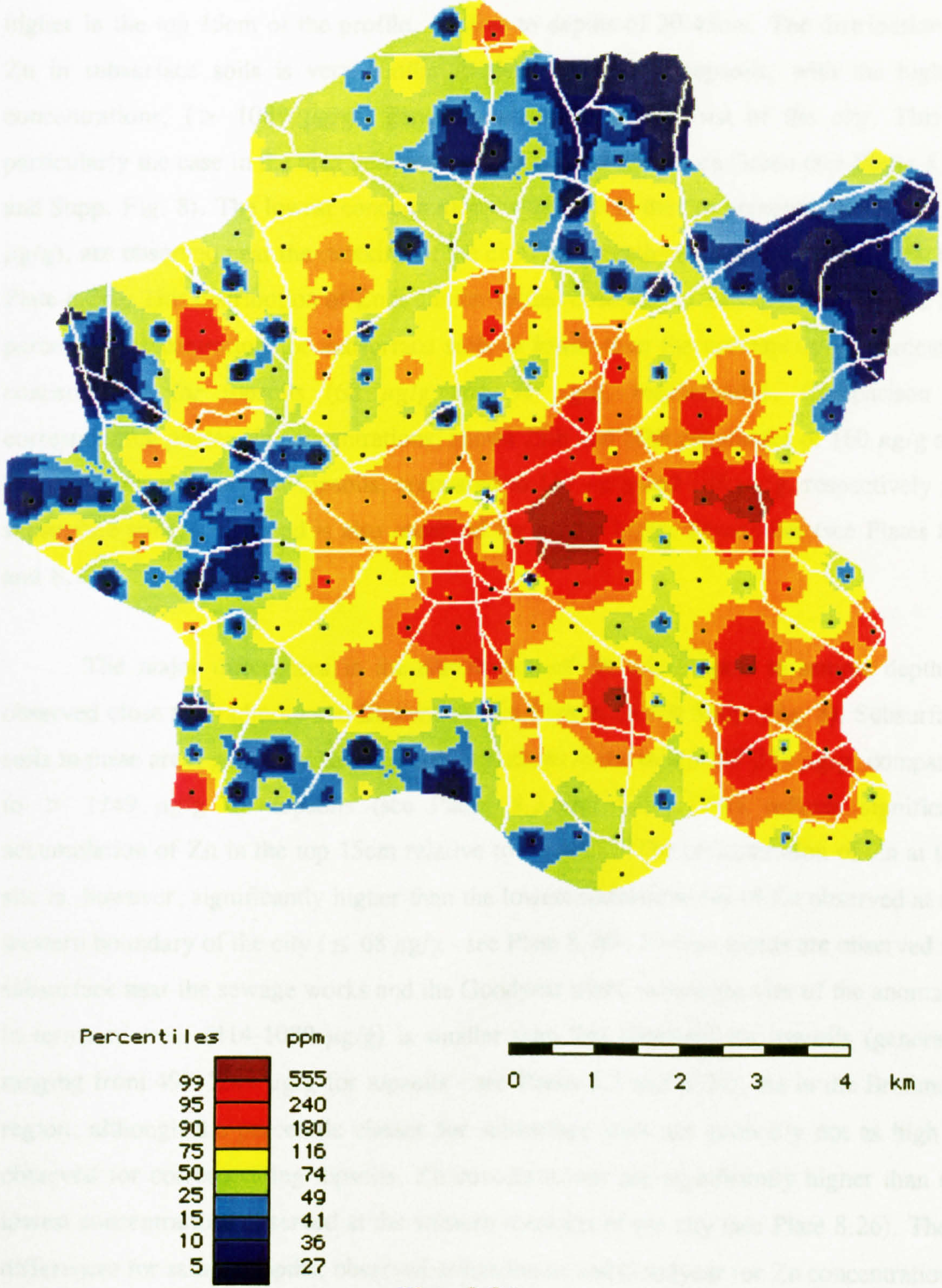


Plate 8.24

8.4.3 Concentrations of zinc in Wolverhampton Subsurface soils (30-45cm)

Comparison of Plates 8.3 and 8.26 shows that Zn concentrations are generally higher in the top 15cm of the profile, relative to depths of 30-45cm. The distribution of Zn in subsurface soils is very similar to that observed in topsoils, with the highest concentrations, (> 1089 μg/g), generally observed in the east of the city. This is particularly the case in the area between Springfield and Monmore Green (see Plates 8.26 and Supp. Fig. 8). The lowest concentrations which are in the 5th percentile range (≤ 68 μg/g), are observed near the outskirts of the city in the north-east and west of the city (see Plate 8.26). This distribution of Zn is similar to that observed in topsoils, although the 5th percentile concentration for subsurface soils is lower than the corresponding percentile concentration for topsoils (68 μg/g and 94 μg/g, respectively). Comparison of corresponding percentile concentrations, shows 25th and 50th percentiles of 160 μg/g and 239 μg/g, respectively for topsoils, compared to 117 μg/g and 186 μg/g, respectively for subsurface soils. This trend is also observed for all the higher percentiles (see Plates 8.3 and 8.26).

The major differences in the distribution of Zn with regard to sample depth is observed close to Bradmore and Blakenhall (see Plate 8.26 and Supp. Fig. 8). Subsurface soils in these areas generally have Zn concentrations in the range 187-273 μg/g, compared to > 1249 μg/g for topsoils (see Plates 8.3 and 8.26). This reflects significant accumulation of Zn in the top 15cm relative to 30-45cm. The concentration of Zn at this site is, however, significantly higher than the lowest concentrations of Zn observed at the western boundary of the city (≤ 68 μg/g - see Plate 8.26). Similar trends are observed for subsurface near the sewage works and the Goodyear plant, where the size of the anomaly, in terms of area, (414-1089 μg/g) is smaller than that observed for topsoils (generally ranging from 497-1249 μg/g for topsoils - see Plates 8.3 and 8.26). As in the Bradmore region, although the percentile classes for subsurface soils are generally not as high as observed for corresponding topsoils, Zn concentrations are significantly higher than the lowest concentrations observed at the western outskirts of the city (see Plate 8.26). These differences for sample depths, observed at Bradmore and Goodyear for Zn concentrations, are also observed for Pb and probably reflect superficial contamination. This is in contrast

Zn in Wolverhampton subsurface soils (30-45cm)

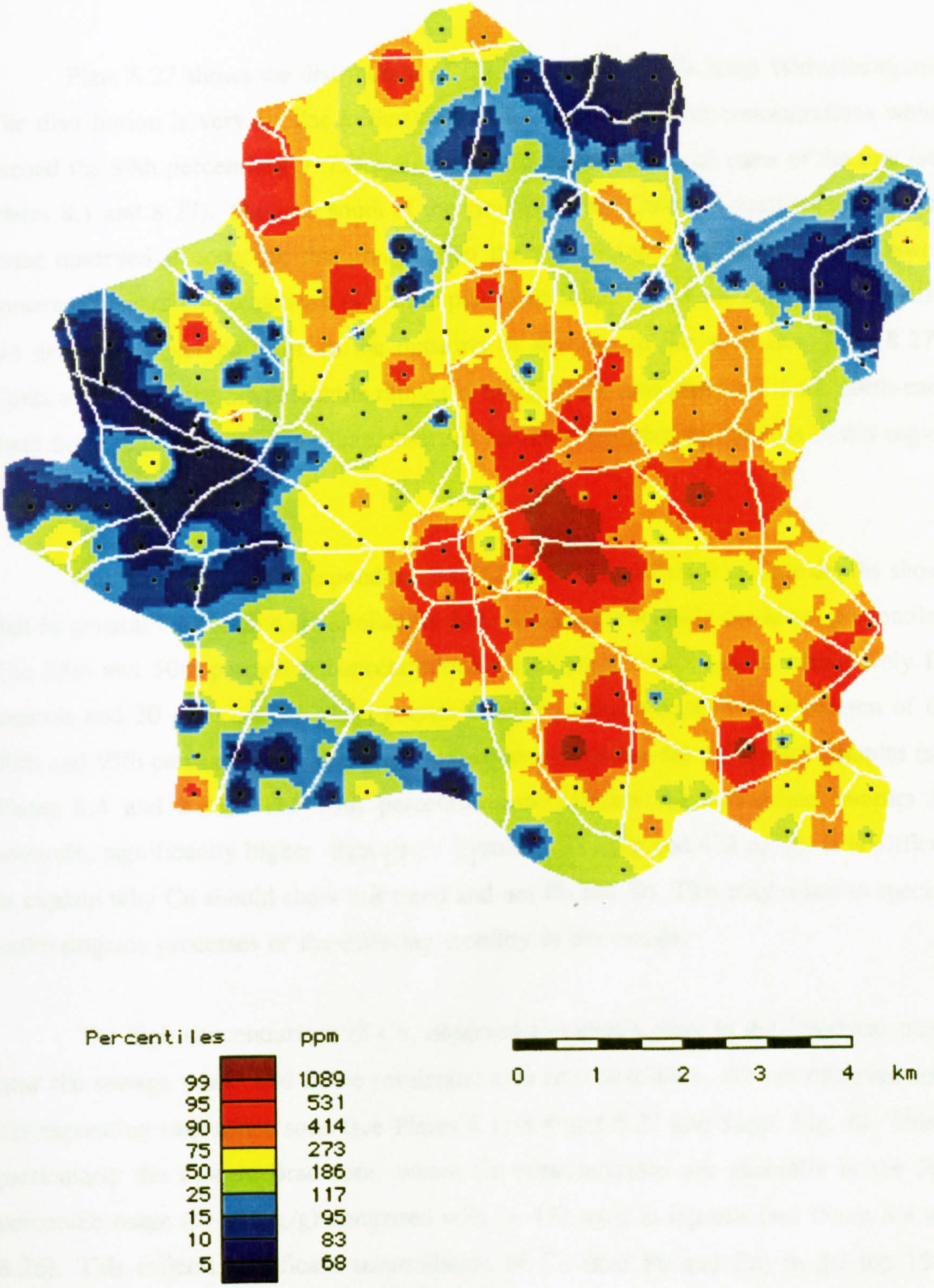


Plate 8.25

to the industrial base where metal concentrations are similar at 0-15cm and 30-45cm.

8.4.4 Concentrations of copper in Wolverhampton Subsurface soils (30-45cm)

Plate 8.27 shows the distribution of Cu in subsurface soils from Wolverhampton. The distribution is very similar to that observed for topsoils, with concentrations which exceed the 99th percentile (> 754 μg/g) generally in the industrial parts of the city (see Plates 8.1 and 8.27). The area south of the city centre has Cu concentrations higher than those observed in topsoils; this area is also the site of industrial activity. The lowest concentrations of Cu, which are in the 5th percentile range (≤ 19 μg/g), as with topsoils, are generally observed close to the outskirts of the city in the west (see Plate 8.27). Concentrations in the 5th percentile range (≤ 68 μg/g) are also observed in the north-east, these being significantly lower than observed for the corresponding topsoils in this region (see Plates 8.4 and 8.27).

A comparison of corresponding percentiles for the different sample depths shows that in general the Cu data are similar for both depths, particularly the lower percentiles. The 25th and 50th percentile concentrations are 37 μg/g and 57 μg/g, respectively for topsoils and 30 μg/g and 51 μg/g, respectively for subsurface soils. Comparison of the 90th and 95th percentiles show slightly higher concentrations for subsurface samples (see Plates 8.4 and 8.27). The 99th percentile concentration for subsurface samples is, however, significantly higher than for topsoils (754 μg/g and 472 μg/g). It is difficult to explain why Cu should show this trend and not Pb and Zn. This may relate to specific anthropogenic processes or the differing mobility of the metals.

The high concentrations of Cu, observed in topsoils close to the Goodyear plant, near the sewage works and in the residential area near Bradmore, are not observed for corresponding subsurface soils (see Plates 8.1, 8.4 and 8.27 and Supp. Fig. 8). This is particularly the case in Bradmore, where Cu concentrations are generally in the 50th percentile range (31-51 μg/g) compared with > 472 μg/g in topsoils (see Plates 8.4 and 8.26). This reflects significant accumulation of Cu (and Pb and Zn) in the top 15cm relative to depths of 30-45cm and is probably the result of a fly-tipping or dumping

Cu in Wolverhampton subsurface soils (30-45cm)

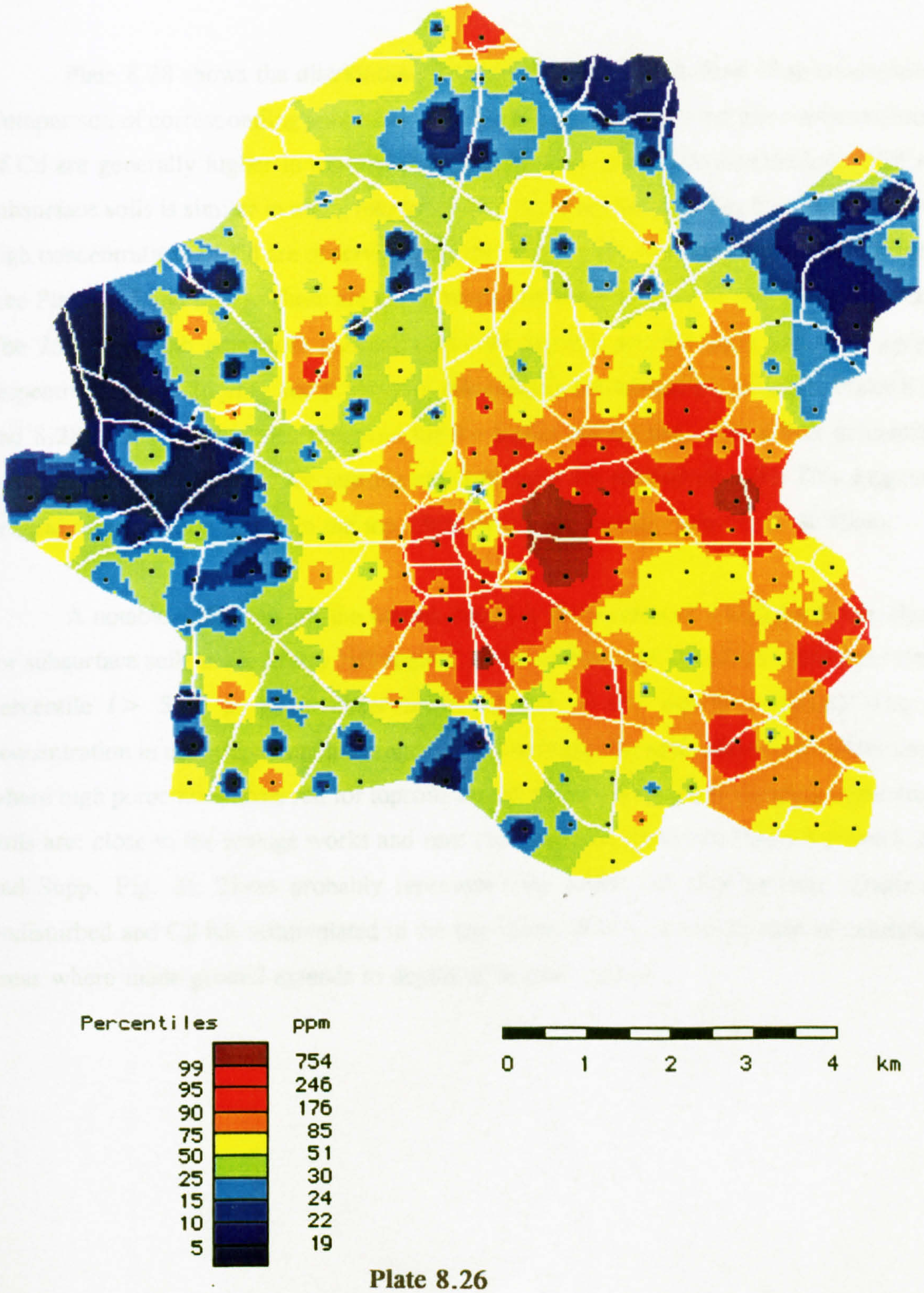


Plate 8.26

incident in this area.

8.4.5 Concentrations of cadmium in Wolverhampton Subsurface soils (30-45cm)

Plate 8.28 shows the distribution of Cd in subsurface soils from Wolverhampton. Comparison of corresponding percentiles for Plates 8.5 and 8.28 shows that concentrations of Cd are generally higher in topsoils than in subsurface soils. The distribution of Cd in subsurface soils is similar in many respects to that observed for topsoils. Most areas where high concentrations of Cd are observed coincide with similar percentiles for Cd in topsoils (see Plates 8.5 and 8.27). These are the industrial locations of the east and the city centre. The 25th and 50th percentile concentrations for topsoils are 0.5 μg/g and 0.72 μg/g, respectively and 0.26 μg/g and 0.53 μg/g, respectively for subsurface soils (see Plates 8.5 and 8.28). This trend is also observed for the higher percentiles, with a 99th percentile concentration of 5.64 μg/g for topsoils and 3.60 μg/g for subsurface soils. This suggests general accumulation of Cd in the top 15cm of the soil profile, relative to 30-45cm.

A notable difference for the sample depths is the absence of a high percentile class for subsurface soils in the Merry Hill region. A concentration of Cd which exceedsthe 99th percentile (> 5.64 μg/g) is observed in topsoils in this region compared with a concentration in the 90th percentile range (0.92-1.45 μg/g) for subsurface soils. Other sites where high percentiles observed for topsoils are not observed for corresponding subsurface soils are: close to the sewage works and near the Goodyear plant (see Plates 8.5 and 8.28 and Supp. Fig. 8). These probably represent sites where soil profiles have remained undisturbed and Cd has accumulated in the top 15cm. This is not be the case in industrial areas where made ground extends to depths of several metres.

Cd in Wolverhampton subsurface soils (30-45cm)

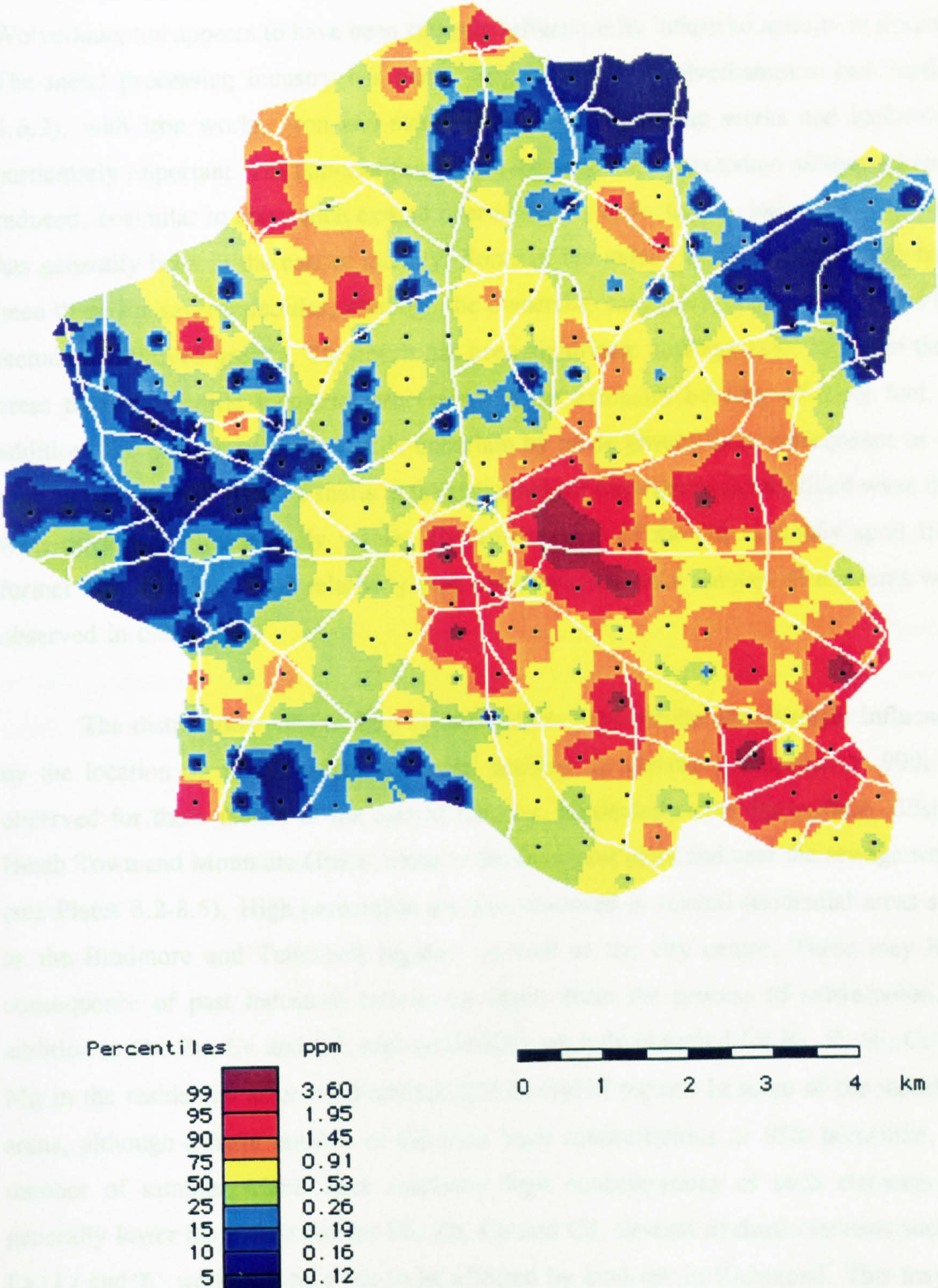


Plate 8.27

8.5 Discussion and Summary

The distribution of a number of elements in topsoils and subsurface soils from Wolverhampton appears to have been strongly influenced by industrial activity in the city. The metal processing industry has had a long history in Wolverhampton (see section 4.6.2), with iron works, iron and steel production, galvanising works and locksmiths particularly important. The pattern of industrial location that exists today, although greatly reduced, is similar to that which existed over a century ago - that is, industrial settlement has generally been in the east of the city. Some of the industries that remain today have been there for several decades, although the ownership may have changed hands and the techniques evolved greatly. The result has been significant anthropogenic inputs in these areas through specific industrial processes and the extensive burning of fossil fuel. In addition, the area in the south east is underlain by made ground as a consequence of the number of disused coal mine shafts in the region which were subsequently filled when they were no longer economically viable. The composition of the fill is mainly spoil from former coal workings, and relatively high concentrations of a number of elements were observed in this region.

The distributions of Pb, Zn, Cu and Cd are very similar and strongly influenced by the location of contemporary industrial activity. In general percentiles > 90th are observed for these metals in the east of the city, particularly near Springfield, Bilston, Heath Town and Monmore Green, close to the Goodyear plant and near the sewage works (see Plates 8.2-8.5). High percentiles are also observed in several residential areas such as the Bradmore and Tettenhall regions, as well as the city centre. These may be a consequence of past industrial activity or inputs from the process of urbanisation. In addition to Pb, Zn, Cu and Cd, high percentiles are only observed for Ba, P, Ni, Cr and Mg in the residential areas of Bradmore and Merryhill region. In some of the industrial areas, although a large number of elements have concentrations ≥ 95th percentile, the number of samples which have relatively high concentrations of such elements are generally lower than observed for Pb, Zn, Cu and Cd. Several of these elements such as La, Li and Ti were observed not to be affected by land-use in Richmond. This may be because Richmond has so little industrial activity. In section 8.6, the data for

Wolverhampton are examined in more detail to see if the spatial observations made in section 8.3 are statistically significant.

The comparison of geochemical maps for topsoils (0-15cm) and subsurface soils (30-45cm) shows that for Pb, Zn, Cu and Cd the distribution is similar at both depths. In general, metal accumulation is greatest in the top 15cm. The highest concentrations at a depth of 30-45cm for these metals are also generally observed close to the city centre. In most of these areas concentrations ≥ 95th percentile are observed, a trend also observed for topsoils. A comparison also reveals that in some areas the very high concentrations of metals are restricted to the top 15cm. This is true for the residential areas between Bradmore and Merry Hill, and to a lesser extent for the areas close to the sewage works and the Goodyear plant. Despite this trend, the corresponding subsurface soils in these areas often have concentrations of these metals higher than the baseline percentile. Large differences in concentrations at 0-15cm compared with 30-45cm at these non-industrial sites suggests different processes to those operating in industrial areas. In the industrial areas the greater vertical extent of the contamination may be a result of the long-term inputs in these areas, and possibly the burial of waste material, an important component of made ground in these areas. In the residential areas and the regions near the sewage works and the Goodyear Plant, the input has resulted in relatively high concentrations in the top 15cm of the soil profile. In the sewage works this would be consistent with an application of sewage sludge to these soils. Relatively high concentrations of a number of elements were also observed close to sewage works in Richmond (see section 6.2 in general). The soils from residential areas of Wolverhampton are likely to been considerably less disturbed than soils in the industrial parts of the city. As a consequence, relatively high concentrations of a number of elements are observed in the top 15cm of the profile. It is unclear why these residential areas of Wolverhampton have concentrations of metals higher than other residential parts of Wolverhampton. This may relate to past land-use, or incidents of dumping domestic or industrial waste.

Comparison of the geochemical maps for Richmond and Wolverhampton shows that most elements are present at higher concentrations in soils from Wolverhampton than in soils from Richmond. This probably results from a combination of anthropogenic activity and geological and pedogenic processes. The exceptions to this are Pb, Ti, V, Cr, Fe and P which generally have higher concentrations in soils from Richmond. Vanadium, Cr, Fe, Ti are likely to be present at higher concentrations in Richmond soils as a result of the underlying geology; However, some industrial areas of Wolverhampton have higher concentrations of V, Cr, and Fe than the highest concentrations of these metals in Richmond. The trend for Pb may relate to the strong urban sources of this element in Richmond and the lack of redevelopment of Richmond. Phosphorus was another element strongly influenced by anthropogenic activity in Richmond and it may be that the sources of P through the addition of fertilisers and the presence of rotting vegetation in the gardens, are greater in Richmond. The importance of parent material also needs to be considered for all elements studied.

In Wolverhampton sources of Zn, Cu and Cd are greater than in Richmond through the large number of metalliferous works, both historically and today, in the city. Other elements which are significantly higher in Wolverhampton soils are Mg, Al and K. These are clay-associated elements (McGrath and Loveland, 1992) and the differences in the general geochemical signatures for the two study areas probably account for this trend. The highest concentrations of most elements in Wolverhampton soils are generally observed in industrial areas, particularly where made ground is common. Made ground is rich in waste material from mining and industrial activity and appears to be a source of multi-element contamination.

8.6 The influence of land-use on concentrations of elements in Wolverhampton soils

8.6.1 Introduction.

Plate 8.1 showed that the agricultural land, classified as green belt land, was located near the edges of the city, particularly in the north. Table 8.1 summarises the results for selected metals from soils in these regions. The data for the trace metals listed in Table 8.1 are separated from the other elements because they are considered to be environmentally important.

8.6.2 Selected metals in topsoils (0-15cm) from agricultural areas

The data in Table 8.1 are, generally, normally distributed with similar geometric and arithmetic means (51 μg/g and 58 μg/g, respectively for Pb, 125 μg/g and 130 μg/g, respectively for Zn, 32 and 33 μg/g, respectively for Cu, 0.46 and 0.42 μg/g for Cd and 19 μg/g and 21 μg/g, respectively for Ni). The standard deviations are also all lower than the arithmetic means, reflecting the generally low concentration ranges for these metals in agricultural soils (see Table 8.1).

The suite of metals listed in Table 8.1 are present at significantly lower concentrations in topsoils from agricultural areas than in topsoils from industrial areas ($P < 0.001$ for Cu and Cd and $P < 0.01$ for Pb, Zn and Ni). This is probably due to the location of the agricultural areas at the outskirts of the city. Zinc and Pb are also present at significantly higher concentrations in topsoils from urban gardens than in topsoils from agricultural areas (all $P < 0.01$). Urban gardens are generally closer to the industrial base than agricultural areas, and probably have additional sources of metals through the flaking of paint, disposal of fossil fuel ashes and higher traffic densities.

8.6.3 Selected metals in subsurface soils (30-45cm) from agricultural areas

The data for trace metals in subsurface soils are in general, log-normally distributed, illustrated by the differences in the geometric and arithmetic means (33 μg/g and 45 μg/g, respectively for Pb, 85 μg/g and 102 μg/g, respectively for Zn, 30 μg/g and 47 μg/g, respectively for Cu, <0.2 μg/g and 0.3 μg/g, respectively for Cd and 18 μg/g and 21 μg/g, respectively for Ni). The standard deviations for Pb, Zn, Cu and Cd are all higher than the corresponding arithmetic means, reflecting the higher concentration range of these metals in subsurface soils compared with topsoils (see Table 8.1). This may be the result of one sample with high concentrations of these metals.

The data for topsoils and subsurface soils were logged and compared using a students t-test. The results showed that concentrations of Zn and Cd were significantly higher in topsoils than subsurface soils (both $P < 0.05$). This is not observed for Pb, Cu and Ni ($P > 0.05$). This suggests significant additions of Zn and Cd to topsoils, probably as a consequence of the industrial activity in the city with transport of emissions to agricultural land at the outskirts of the city. Some anthropogenic additions may also have occurred through applications of fertilisers and sewage sludge. Similar concentrations at both depths in these soils may also result from the disturbance of the soils through ploughing which would redistribute the topsoil lower down the profile.

The suite of metals listed in Table 8.1 are present at significantly lower concentrations in subsurface soils from agricultural areas than in subsurface soils from industrial areas ($P < 0.001$, except for Ni, $P < 0.01$). This probably results from the industrial waste material component of made ground (see section 4.7.6). Lead, Zn and Cd are also present at significantly lower concentrations in subsurface agricultural soils than in subsurface soils from urban gardens (all $P < 0.001$). This may be due to greater proximity of urban gardens to the industrial base, or sources of metals specific to urban gardens (see Table 3.1 and section 3.4 in general).

Table 8.1 Concentrations of selected metals (μg/g) in Agricultural soils from Wolverhampton

	topsoil (0-15cm) n=15				Subsurface soils (30-45cm) n=15			
	GM	AM	SD	Range	GM	AM	SD	Range
Pb	51	58	30	23-129	33	45	51	18-214
Zn	125	130	37	81-200	85	102	87	49-384
Cu	32	33	10	20-60	30	47	73	15-294
Cd*	0.46	0.42	0.2	<0.2-0.7	<0.2	0.3	0.6	<0.2-2.4
Ni	19	21	12	11-60	18	21	15	8-59

* For Cd:

2 of 15 samples were below the detection limit (0.2 μg/g) for topsoil samples.
10 of 15 samples were below the detection limit (0.2 μg/g) for subsurface soil samples.

GM	Geometric mean
AM	Arithmetic mean
SD	Standard Deviation

8.6.4 Other Elements in topsoils (0-15cm) from agricultural areas

Table 8.2 summarises the results for 17 elements in agricultural soils from Wolverhampton. A comparison of geometric and arithmetic means shows that, in general, these are similar for most elements, a reflection of the normal distribution of the data. The exceptions to this are for K and Mg (5777 μg/g and 6530 μg/g, respectively for K and 3431 μg/g and 4191 μg/g, respectively for Mg - see Table 8.2). For most elements the standard deviation is considerably lower than the arithmetic mean, something which is reflected in the low concentration range for these elements listed in Table 8.2. The exceptions to this are K and Mg which have high standard deviations relative to the arithmetic means and large concentration ranges (see Table 8.2). In general, the low concentration range results from few anthropogenic sources of these elements in these areas, and reflects the natural concentration ranges associated with the parent materials and pedogenic processes.

Concentrations of Mg, Ca, Cr and Fe are significantly lower in agricultural topsoils than in topsoils from industrial areas ($P < 0.001$ for Mg and Ca, and $P < 0.01$ for Cr and Fe). Chromium, Ca and Fe are used in the iron and steel industry (see Table 3.2). Higher concentrations of Mg in industrial areas, relative to agricultural areas, may be due to the use of Mg in Al alloys or differences in the geochemical signature for the two areas. Sodium and Ba concentrations are significantly lower in agricultural soils than in topsoils from urban gardens ($P < 0.05$ for Na and $P < 0.01$ for Ba). This may result from the greater proximity of urban gardens in general to industrial activity, or sources specific to residential areas. Barium is associated with a paint source, whilst Na may possibly be linked to the salting of roads in winter (see Table 3.2).

8.6.5 Other Elements in subsurface soils (30-45cm) from agricultural areas

The trends observed for subsurface soils are very similar to those for topsoils, with most elements having data which are normally distributed. This is seen when comparing arithmetic and geometric means for individual elements. The exceptions to this are K, Mg and Ca which have arithmetic means significantly higher than their geometric means. These three elements also have large standard deviations and large concentration ranges. In general most elements at 30-45cm have low concentration ranges, which is probably a result of low anthropogenic additions of these elements and a reflection of the natural geological input. Potassium and Mg, in particular, are clay-associated and seventy percent of Wolverhampton is underlain by a till which is clay-rich, which may explain the large concentration ranges of these elements.

A comparison of elements in topsoils and subsurface soils shows that, with the exception of P, concentrations do not vary significantly at the different depths ($P > 0.05$). These elements probably have few anthropogenic sources in agricultural soils and concentrations that do not vary significantly from 0-15cm to 30-45cm. Geological inputs and pedogenic processes are likely to be the most important factors influencing the concentration of most elements listed in Table 8.2. For P, significantly higher concentrations are observed at 0-15cm compared with 30-45cm ($P < 0.05$). A geometric mean of 766 $\mu g/g$ in topsoils compares with 516 $\mu g/g$ for subsurface soils (see Table 8.2), and the difference may be the result of applications of P fertilisers to these soils or a reflection of the natural geochemical signature.

Concentrations of Na, Be, Ca, Sr, V, Cr, Fe, Co and P are significantly lower in subsurface soils from agricultural areas than in subsurface soils in industrial areas ($P < 0.001$ for Ca, and $P < 0.01$ for Na, Be, Sr, V, Cr, Fe, Co and P). High concentrations of a number of elements at depths of 30-45cm is a feature of the industrial areas in Wolverhampton, probably due to the prevalence of made ground in this region. Beryllium, Ca, Sr, Fe and P are also observed at significantly lower concentrations in subsurface soils from agricultural areas, than in subsurface soils form urban gardens ($P < 0.001$ for Ca, $P < 0.01$ for Be, Sr, Fe and P). This may be due to gardens being closer to industrial areas in general, or sources specific to urban gardens, such as the burial of building materials, the use of fertilisers and the disposal of ashes from open fires. Natural differences in the geochemical signatures for these areas may also account for higher concentrations of these elements in subsurface soils, compared with agricultural areas.

Table 8.2 Concentrations of elements (μg/g) in Agricultural soils from Wolverhampton

	topsoil (n=15)				subsurface soils (n=15)			
	GM	AM	SD	Range	GM	AM	SD	Range
Li	23	24	7.2	11.6-37.5	22	24	8.8	9-37.7
Na	237	243	55	157-367	234	246	75	136-361
K	5777	6530	4594	3330-22000	6209	7026	4475	3340-21300
Be	1.3	1.3	0.47	0.8-2.66	1.1	1.2	0.5	0.6-2.7
Mg	3431	4191	3171	1830-14800	3723	4404	3168	1580-14400
Ca	3235	3540	1304	814-5500	2451	3077	2557	656-10600
Sr	33	34	10	18-54	31	33.5	14	17-70
Ba	150	162	70	87-322	152	170	83	70-322
Al•	2.47	2.63	1.10	1.44-5.98	2.53	2.77	1.23	1.26-5.81
La	19	20	5.8	14.6-38	19	19	6	14-38
Ti	513	519	72	334-631	524	532	94	381-682
V	45	47	14	26-75	39	41	14	23-72
Cr	24	25	6.2	12-38	20	21	7	11-40
Mn	439	457	125	236-611	382	413	165	200-738
Fe•	1.78	1.84	0.6	1.37-3.79	1.85	1.93	0.65	1.23-3.75
Co	7.7	8	3.2	4.1-17	7	8	4	3.3-17
P	766	815	335	424-1820	516	567	281	283-1160

• Results for Al and Fe are reported as % rather than μg/g.

GM	Geometric mean
AM	Arithmetic mean
SD	Standard Deviation

8.6.6 Selected metals in topsoils (0-15cm) from areas of open space

Table 8.3 summarises the data for selected metals in soils from areas of open space in Wolverhampton. The topsoil data, in general, are log-normally distributed, something which is reflected in the large differences between the arithmetic and geometric mean concentrations (129 μg/g and 97 μg/g, respectively for Pb, 294 μg/g and 208 μg/g, respectively for Zn, 73 μg/g and 55 μg/g, respectively for Cu, 1 μg/g and 0.7 μg/g for Cd and 28 μg/g and 25 μg/g, respectively for Ni - see Table 8.7). The same metals have large standard deviations, a value similar to corresponding arithmetic means, and large concentration ranges.

The suite of metals listed in Table 8.3 are present at significantly lower concentrations in topsoils from areas of open space than in topsoils from industrial areas ($P < 0.001$, for Cu and Cd and $P < 0.01$ for Pb, Zn and Ni). This probably reflects greater deposition of these metals in industrial areas, or greater additions through the formation of waste tips.

8.6.7 Selected metals in Subsurface soils (30-45cm) from areas of open space

The data for metals in subsurface soils from areas of open space are generally, log-normally distributed. This is characterised by the large differences that are observed between arithmetic and geometric means (206 μg/g and 144 μg/g, respectively for Zn, 70 μg/g and 39 μg/g, respectively for Cu and 30 μg/g and 24 μg/g, respectively for Ni - see Table 8.3). Although the measures of central tendency for Pb and Cd are very similar the data do not have a normal distribution, illustrated by the large standard deviations, in relation to the arithmetic means, and large concentration ranges. Similar trends are observed with these parameters for Zn, Cu and Ni. The distribution of the data suggests that anthropogenic activity may be important in influencing the distribution of these metals in soils from areas of open space.

A comparison of topsoil and subsurface soil data for this land-use shows that, in general, the metals have higher concentrations in topsoils than in subsurface soils, particularly when geometric means are used for comparison (see Table 8.3). If the data is logged and compared using a students t-test, Pb ($P < 0.001$), Zn ($P < 0.05$), Cu ($P < 0.05$), and Cd ($P < 0.01$) are observed to be present at significantly higher concentrations in topsoils compared with subsurface soils. This suggests significant anthropogenic additions of these trace metals to topsoils, probably as a consequence of industrial activity and the burning of fossil fuel in the city. A number of parks and sports grounds in Wolverhampton have been redeveloped from industrial sites, particularly sites which were once actively mined. This may account for the relatively high concentrations of metals observed at 30-45cm (see Table 8.7).

The suite of metals listed in Table 8.3 are present at significantly lower concentrations in subsurface soils from areas of open space than in subsurface soils from industrial areas (all $P < 0.001$). This reflects greater deposition of these metals in industrial areas and perhaps, more significantly, the prevalence of made ground in industrial areas which contains by-products of industrial activities (see section 4.7.6).

Table 8.3 Concentrations of selected metals (μg/g) in soils from areas of open space

	Topsoils (0-15cm) n=57				Subsurface soils (30-45cm) n=57			
	GM	AM	SD	Range	GM	AM	SD	Range
Pb	97	129	121	23-678	97	93	142	14-865
Zn	208	294	398	54-2950	144	206	214	43-1100
Cu	55	73	63	12-387	39	70	139	11-1010
Cd*	0.7	1	1.6	<0.2-10.7	0.7	0.7	0.8	<0.2-4
Ni	25	28	14	9-70	24	30	31	10-212

* For Cd:

2 of 57 samples were below the detection limit (0.2 μg/g) for samples from open spaces.
16 of 57 samples were below the detection limit (0.2 μg/g) for samples from open spaces.

GM	Geometric mean
AM	Arithmetic mean
SD	Standard Deviation

8.6.8 Other elements in topsoils from areas of open space

Table 8.4 summarises the data for the other elements analysed in soils from areas of open space in Wolverhampton. Most elements have a normal distribution with the exceptions being Ca, Cr, and Mn in particular. This is a trend observed for the data for other land-uses and characterised by the differences between the measures of central tendency, and the large standard deviations and concentration ranges (see Table 8.8). Most of the other elements have relatively low concentration ranges, which are probably a result of low anthropogenic additions, with geological and pedogenic processes being the most important factors affecting the concentrations of the elements in these soils.

Magnesium, Ca, Cr, Fe, Mn and Co are present at significantly lower concentrations in topsoils from areas of open space than in topsoils from industrial areas ($P < 0.001$ for Mg, Ca and Fe, $P < 0.01$ for Cr and $P < 0.05$ for Mn and Co). These differences are probably the result of specific industrial processes and the prevalence of made ground containing industrial waste (see section 4.7.6). Sodium, Mg, Ca, Ba and P are observed at significantly lower concentrations in topsoils from areas of open space than in topsoils from urban gardens ($P < 0.01$ for Mg, Ca, Ba and P and $P < 0.05$ for Na) and these probably result from sources which are more important in urban gardens than agricultural areas, such as additions of fertilisers (Mg and P, in particular), the burial of building material (Ca), the use of paints (Ba) and the salting of road (Na). Variation of the geochemical signatures for the parent materials which underlie the city may also be an important factor (see section 9.2 in general).

8.6.9 Other Elements in subsurface soils (30-45cm) from areas of open space

The data for subsurface soils has a number of differences compared with topsoils, particularly with regard to the distribution of the data for individual elements. The data for Na, Ca, Sr, Cr and Mn generally have a log-normal distribution, with standard deviations and concentration ranges generally larger than observed for these elements in topsoils (see Table 8.4).

An overall comparison of the data for the two land-uses, shows that the a number of elements are observed at higher concentrations in subsurface soils, particularly if geometric means are used as a comparison. However, logging the data and making comparisons using a students t-test shows that only P is present at significantly higher concentrations in topsoils, compared with subsurface soils ($P < 0.001$). This may result from minor anthropogenic additions of this element, or variation in the geochemical signature at depths of 0-15cm and 30-45cm.

The concentrations of Na, Be, Ca, Sr, V, Cr and Co are significantly lower in subsurface soils from areas of open space than in subsurface soils from industrial areas ($P < 0.001$ for Ca and V and $P < 0.01$ for Na, Be, Sr, Cr and Co). These metals were also observed at significantly higher concentrations in subsurface soils from industrial areas than in subsurface soils from agricultural areas. This reflects greater additions of metals through specific industrial processes, particularly the industrial waste component of made ground and the burning of fossil fuels in industrial areas. Concentrations of Ca and Sr are also significantly lower in subsurface soils from areas of open space than in subsurface soils from urban gardens (both $P < 0.01$). This trend was also observed for Ca in topsoils and is probably the result of building material mixed with garden soils and additions of fertilisers and lime in urban gardens (see Table 3.2).

Table 8.4 Concentrations of elements ($\mu g/g$) in soils from areas of open space

	topsoil (n=57)				subsurface soils (n=57)			
	GM	AM	SD	Range	GM	AM	SD	Range
Li	23	25	11	9-56	24	26	11	9-54
Na	268	292	126	124-737	286	331	266	103-2000
K	4958	5361	2795	2210-22000	5505	5860	2333	2670-15900
Be	1.56	1.70	0.8	0.7-4.8	1.54	1.8	1.4	0.8-10.4
Mg	3226	3556	1933	1190-14800	3662	3979	1825	1520-11500
Ca	3457	4611	3694	499-18500	2782	4370	4851	365-24400
Sr	42	47	26	17-132	42	49	35	20-176
Ba	179	198	87	74-420	175	193	93	74-530
Al*	2.36	2.52	0.95	1.11-5.98	2.43	2.76	1.04	1.24-6.93
La	19	19	4.7	10-38	19	20	4	18-30
Ti	527	542	123	272-859	535	557	202	310-1780
V	42	44	14	19-77	43	46	19	21-116
Cr	25	29	21	10-128	24	31	49	8 363
Mn	422	521	480	111-3570	473	601	524	80-3350
Fe*	1.88	1.98	0.65	0.91-3.79	2.13	2.35	1.25	1.04-8.51
Co	9	10	5	3-25	10	11	7	4-36
P	886	965	449	394-3170	635	716	369	175-2100

* Results for Al and Fe are reported as % rather than $\mu g/g$.

GM	Geometric mean
AM	Arithmetic mean
SD	Standard Deviation

8.6.10 Selected metals in topsoils (0-15cm) from Urban gardens

Table 8.5 summarises the data for selected metals in urban garden soils from Wolverhampton. The data for topsoils have a distribution which is not Gaussian, something which is reflected in the differences between the arithmetic and geometric means for these metals (233 $\mu g/g$ and 111 $\mu g/g$, respectively for Pb, 335 $\mu g/g$ and 241 $\mu g/g$, respectively for Zn, 88 $\mu g/g$ and 62 $\mu g/g$, respectively for Cu, 1.3 $\mu g/g$ and 0.7 $\mu g/g$, respectively for Cd and 31 $\mu g/g$ and 26 $\mu g/g$, respectively for Ni - see Table 8.5). These metals also have large standard deviations, which with the exception of Ni, exceed the arithmetic mean and large concentration ranges (see Table 8.4). The soils from urban gardens in Richmond were observed to have relatively high concentrations of several metals as a result of various anthropogenic sources (see section 6.3 in general). One sample in particular has a very high concentration of Pb and Zn (14900 μg/g and 6740 μg/g, respectively). This was an urban garden which was derelict and covered in waste material which varied from domestic refuse to scrap metal.

The suite of metals listed in Table 8.5 are significantly lower than concentrations reported for topsoils in industrial areas of the city ($P < 0.001$ for Cu and Cd, $P < 0.01$ for Pb, Zn and Ni). Greater deposition of these metals and the formation of waste tips in industrial areas probably explains this. Concentrations of Zn and Pb are, however, significantly higher in garden topsoils than in topsoils from agricultural areas (both $P < 0.01$). This is probably the result of specific sources in the urban gardens and greater proximity of these sites to industrial processes.

8.6.11 Selected metals in subsurface soils (30-45cm) from urban gardens

As with topsoil data for this land-use, the data for subsurface soils are generally log-normally distributed. This is reflected in the differences between the arithmetic and geometric means for these metals (105 μg/g and 76 μg/g, respectively for Pb, 243 μg/g and 177 μg/g, respectively for Zn, 81 μg/g and 51 μg/g, respectively for Cu, 0.75 μg/g and 0.44 μg/g, respectively for Cd and 30 μg/g and 26 μg/g, respectively for Ni - see Table 8.5). The standard deviations are also high for these elements, relative to the arithmetic mean, although the standard deviations for Cu and Cd are higher concentrations than the arithmetic means.

In comparison with the topsoil data, the measures of central tendency for subsurface soils are lower with concentration ranges and standard deviations also higher for topsoils (see Table 8.5). Concentrations of Pb, Zn, Cu and Cd are all significantly higher in topsoils than in subsurface soils ($P < 0.001$ for Pb, Zn and Cd, $P < 0.05$ for Cu). There is no significant difference in Ni concentrations for the two sample depths. These results suggest significant anthropogenic additions of Pb, Zn, Cu and Cd to urban garden topsoils, a trend also observed in Richmond. In Richmond, however, metal concentrations do not vary significantly with depth.

The suite of metals listed in Table 8.5 are significantly lower than present in subsurface soils from industrial areas of the city (all $P < 0.001$, except $P < 0.01$ for Ni). Greater disturbance of soils in industrial areas and the prevalence of made ground in the south-east probably explain high concentrations of metals at depths of 30-45cm. However concentrations of Pb, Zn and Cd are significantly higher in subsurface garden soils than in subsurface soils from agricultural areas (all $P < 0.001$). Greater proximity of garden sites to industrial activity, the disturbance of garden soils and sources specific to urban gardens are factors which are probably responsible for the significant differences in metal concentrations between the two land-uses.

Table 8.5 Concentrations of selected metals (µg/g) in urban garden soils

	topsoil (0-15cm) n=176				Subsurface soils (30-45cm) n=176			
	GM	AM	SD	Range	GM	AM	SD	Range
Pb	111	233	1125	16-14900	76	105	101	9-710
Zn	241	335	532	55-6740	177	243	240	10-1510
Cu	62	88	97	10-841	51	81	111	3-779
Cd*	0.7	1.3	4.1	<0.2-55	0.44	0.75	0.9	<0.2-6
Ni	26	31	22	8-178	26	30	16	6-107

* For Cd:

11 of 176 samples were below the detection limit (0.2 µg/g) for garden soil samples.
37 of 176 samples were below the detection limit (0.2 µg/g) for open space samples.

GM Geometric mean

AM Arithmetic mean

SD Standard Deviation

8.6.12 Other Elements in Garden topsoils (0-15cm)

Table 8.6 summarises the data for elements in garden soils. The majority of the topsoil data are normally distributed. These are generally the elements which have arithmetic and geometric mean concentrations which do not differ significantly. The exceptions are Ca, Sr, Cr, Mn, Co and P in particular, elements which also have large standard deviations and large concentration ranges (see Table 8.6). In Richmond Ca, Sr, Co and P were observed at higher concentrations in garden soils compared with soils from areas of open space and it may be that anthropogenic processes influence the distribution of these elements in particular.

Magnesium, Ca, Cr, Mn and Fe have significantly lower concentrations in garden topsoils than topsoils from industrial areas ($P < 0.001$ for Mg, Ca, and Fe, $P < 0.01$ for Cr and $P < 0.05$ for Mn). This probably results from the specific use of these elements in industrial processes (see Table 3.2). Concentrations of Na, Mg, Ca, Ba and P are significantly higher in garden topsoils than in topsoils from areas of open space ($P < 0.01$ for Mg, Ca, Ba and P and $P < 0.05$ for Na), whilst concentrations of Na and Ba are also significantly higher than for soils in agricultural areas ($P < 0.01$ for Ba and $P < 0.05$ for Na). This probably results from important sources of these elements in urbanised areas (Na from the salting of roads and Ba in paint - see Table 3.2).

8.6.13 Other elements in subsurface garden soils (30-45cm)

A similar trend is observed for subsurface soils with the majority of elements having data which are normally distributed. The exceptions being Na, Ca, Sr, and Mn, a trend also observed for topsoils (see Table 8.6). These elements have arithmetic and geometric means which vary significantly (398 μg/g and 343 μg/g, respectively, for Na, 7952 μg/g and 5466 μg/g, respectively, for Ca, 70 μg/g and 58 μg/g, respectively, for Sr and 535 μg/g and 465 μg/g, respectively, for Mn - see Table 8.6), which may reflect natural variation of the geochemical signatures or anthropogenic additions of these metals.

A comparison of the data for the different depths shows many of the elements analysed are present at higher concentrations at depths of 30-45cm relative to 0-15cm. When using geometric means for comparison only Cr, Mn and P have higher concentrations in topsoils (see Table 8.6). This is in contrast to the metals reported in Table 8.5 which were generally present at significantly higher concentrations in topsoils. The use of a students t-test has shown that Li, K, Mg, Sr, Al and La are present at significantly higher concentrations in subsurface soils (all $P < 0.001$ except Li - $P < 0.01$ and Sr - $P < 0.05$). Chromium and P are observed to be present at significantly higher concentrations in topsoils ($P < 0.01$ and < 0.001, respectively). These differences may relate to natural variation of the geochemical signature or greater accumulation of Cr and P in the top 15cm from anthropogenic activity coupled with the disturbance of the profile in urban gardens.

Concentrations of Na, Be, Sr, V, Cr, Fe and Co are present at significantly lower [illegible] in subsurface soils in urban gardens than in subsurface soils from industrial areas (all $P < 0.01$). This probably results from specific industrial processes, widespread disturbance of soils in industrial areas and the prevalence of made ground containing by-products of industrial processes, in industrial areas. However, significantly higher concentrations of Be are observed in subsurface garden soils than in subsurface soils from agricultural areas ($P < 0.01$), whilst significantly higher concentrations of Ca and Sr are observed in subsurface garden soils than in subsurface soils from both agricultural areas and areas of open space (both $P < 0.001$). These differences probably result from the disturbance of garden soils, and sources of Be (through the disposal of ashes from open fires - see Table 3.2) and Ca and Sr (through the burial of building materials - see Table 3.2) which are not so important in agricultural areas and areas of open space.

Table 8.6 Concentrations of elements (μg/g) in soils from urban gardens

	topsoil (n=176)				subsurface soils (n=176)			
	GM	AM	SD	Range	GM	AM	SD	Range
Li	23	25	12	9-118	26	29	15	4-94
Na	310	351	198	74-1340	343	398	257	52-2280
K	5171	5439	2035	2510-17700	6114	6819	3696	2230-21600
Be	1.7	1.9	1.14	0.68-10.5	1.73	1.93	0.92	0.4-5.4
Mg	3327	3471	1010	1470-6350	3696	3998	1753	862-13100
Ca	4826	6855	6864	426-38800	5466	7952	7618	340-48900
Sr	50	59	42	15-275	58	70	50	11-315
Ba	202	223	108	66-685	202	227	122	36-1050
Al*	2.45	2.58	0.96	1.17-8.14	2.83	3.13	1.63	1.09-8.9
La	19	19	4	9.6-35	20	21	5.3	5-36
Ti	557	576	160	282-1430	566	592	226	190-2720
V	43	45	16	19-104	45	49	21	12-131
Cr	25	29	42	7.6-552	22	24	15	6-166
Mn	466	540	398	169-3310	465	535	328	119-2440
Fe*	1.98	2.08	0.75	0.88-6.37	2.07	2.22	0.89	0.61-6.18
Co	9.5	11	5.5	3.3-41	10	11	6	1.7-32
P	899	1030	704	192-7410	694	769	373	164-2040

* Results for Al and Fe are reported as % rather than μg/g.

GM	Geometric mean
AM	Arithmetic mean
SD	Standard Deviation

8.6.14 Selected metals in topsoils (0-15) from Industrial areas

Data for selected metals in topsoils from industrial areas, generally have a log-normal distribution. Arithmetic mean concentrations for Pb, Zn, Cu and Cd are considerably higher than corresponding geometric mean concentrations (233 μg/g and 144 μg/g, respectively for Pb, 598 μg/g and 368 μg/g, respectively for Zn, 311 μg/g and 139 μg/g, respectively for Cu and 2.2 μg/g and 1.25 μg/g, respectively for Cd - see Table 8.7). The standard deviations for these metals are also higher than the reported arithmetic means and consequently the corresponding concentration ranges are large. For Ni, although the arithmetic mean is higher than the geometric mean, the difference is not as great as that observed for the other metals listed in Table 8.7 which may relate to the fewer anthropogenic sources of Ni.

Concentrations of Pb, Zn, Cu, Cd and Ni are significantly higher in soils from industrial areas than all the other land-uses in Wolverhampton (generally $P < 0.01$, but varying on which data comparisons are made with). This illustrates the importance of the industrial areas as sources of metals, and the greater deposition of metals that occur in these regions, relative to other parts of the city.

8.6.15 Selected metals in subsurface soils (30-45cm) from Industrial areas

The data for selected metals in subsurface soils, as for topsoils, are log-normally distributed and are characterised by greatly differing geometric and arithmetic means for Pb, Zn, Cu and Cd (431 μg/g and 193 μg/g, respectively for Pb, 799 μg/g and 447 μg/g, respectively for Zn, 547 μg/g and 189 μg/g, respectively for Cu and 2.3 μg/g and 1.3 μg/g, respectively for Cd - see Table 8.7) a trend also observed for topsoils. The arithmetic and geometric means for Ni, although different do not vary as significantly as those for the other metals listed in Table 8.7. The standard deviations for all the metals listed are higher concentrations than the corresponding arithmetic means (see Table 8.7). The concentration ranges for all the metals are large which reflects the significant anthropogenic sources of Pb, Zn, Cu and Cd in industrial parts of Wolverhampton.

A comparison of metals at different depths shows that all the metals listed in Table 8.7 are present at higher concentrations at depths of 30-45cm compared with 0-15cm. Geometric means at 0-15cm of 144 μg/g Pb, 368 μg/g Zn, 139 μg/g Cu, 1.25 μg/g and 37 μg/g Ni compare with 193 μg/g Pb, 447 μg/g Zn, 189 μg/g Cu, 1.3 μg/g Cd and 42 μg/g Ni at 30-45cm. The use of a students t-test on logged data shows that there is no significant difference in concentrations between the depths despite the higher measurements of central tendency for subsurface soils. Many of the industrial areas in the south-east of Wolverhampton are underlain by made ground which contains the waste of former mineral workings and other by-products of industrial activity, so relatively high concentrations of a number of metals are likely to extend to depths of several metres (see section 4.7.6).

In subsurface soils, concentrations of Pb, Zn, Cu, Cd and Ni are significantly higher in industrial areas than in soils associated with the other land-uses (all $P < 0.001$). This was also observed for topsoils (see section 8.6.14).

Table 8.7 Concentrations of selected metals (μg/g) in soils from Industrial areas

	Topsoils (0-15cm) n=25				Subsurface soils (30-45cm) n=25			
	GM	AM	SD	Range	GM	AM	SD	Range
Pb	144	233	312	28-1400	193	431	795	49-3330
Zn	368	598	717	66-3040	447	799	1394	131-6070
Cu	139	311	562	18-2750	189	547	1076	45-4380
Cd*	1.25	2.2	3	<0.2-12.6	1.3	2.3	3.3	<0.2-14.2
Ni	37	45	31	13-142	42	53	48	20-224

* For Cd:

1 of 25 samples was below the detection limit (0.2 μg/g) for topsoil samples.
1 of 25 samples was below the detection limit (0.2 μg/g) for subsurface soil samples.

GM Geometric mean

AM Arithmetic mean

SD Standard Deviation

8.6.16 Other elements in topsoils (0-15cm) from industrial areas

Table 8.8 summarises the data for the other elements analysed, in soils from industrial areas of Wolverhampton. A number of elements have a log-normal distribution, due to several samples having relatively high concentrations of a number of elements. Elements such as Ca, Sr, Cr and Mn in particular have large differences between geometric and arithmetic means, and large standard deviations and concentration ranges (see Table 8.8).

The geochemical maps for Wolverhampton, see section 8.3, illustrated high concentrations of a suite of elements in the industrial parts of Wolverhampton, relative to the areas at the western edge of the city in particular. In addition to the industrial activity in these areas which is varied and provides a source of several elements, much of the area is underlain with made ground, composed of the waste of several generations of industrial activity and mixed with a material which has a variety of sources.

Topsoils from industrial areas of Wolverhampton have significantly higher concentrations of Mg, Ca, Cr and Fe than all the other land-uses in the city (all $P < 0.001$, except Cr; $P < 0.01$). The metals Ca, Cr and Fe are all used extensively in industrial processes (see Table 3.2) which probably explains the relatively high concentrations observed in industrial areas. Concentrations of Mn are significantly higher in soils from industrial areas than in soils from areas of open space and urban gardens (both $P < 0.001$), whilst concentrations of Co are significantly higher in soils from industrial areas than areas of open space ($P < 0.05$). Manganese is used in the production of steel and the burning of fossil fuel is a source of Co (see Table 3.2).

8.6.17 Other Elements in subsurface soils (30-45cm) from industrial areas

The data for subsurface soils summarised in Table 8.8 show a number of trends which are similar to those observed for topsoils. A number of elements have a log-normal distribution. These are Na, Be, Ca, Sr, Mn and Co in particular, with large differences between the arithmetic and geometric means, large standard deviations and large concentration ranges (see Table 8.8). Large concentration ranges for a number of elements may suggest an anthropogenic source, either as a result of specific industrial activities or the heterogenous composition of made ground.

A comparison of topsoils and subsurface soils for this particular land-use shows that most elements are present at higher concentrations at depths of 30-45cm. A comparison of geometric means shows that only K, Mg, Cr and P have higher concentrations in topsoils. Logging the data and comparing the data for the different depths by means of students t-tests shows that, statistically, the differences are insignificant ($P > 0.05$). This trend was observed for the selected metals in soils listed in Table 8.7, and reflects the fact that anthropogenic additions of a number of elements are important to the top 45cm of soils in industrial parts of Wolverhampton.

At depths of 30-45cm, concentrations of Na, Be, Sr, V, Cr, Co are significantly higher in soils from industrial areas than any other land-use in the city (all $P < 0.01$). In topsoils from industrial areas this relationship was observed for Mg, Ca, Cr and Fe. Many of the industrial areas are underlain with made ground which has industrial waste as a component. This may explain the higher concentrations of these metals at depths of 30-45cm compared with the same depth for other land-uses. Measures of central tendency show that for most land-uses, concentrations of elements generally decrease numerically from 0-15cm to 30-45cm (see Tables 8.1-8.6), whilst for industrial areas concentrations are very often numerically higher, although not significantly higher, at 30-45cm (see Tables 8.7 and 8.8).

Calcium concentrations in subsurface soils from industrial areas are significantly higher than in subsurface soil from agricultural areas and areas of open space ($P < 0.001$). Limestone has an important use in the iron and steel industry (see Table 3.21). Iron concentrations in subsurface soils from industrial areas are significantly higher than in subsurface soils from agricultural areas and urban gardens ($P < 0.01$), a trend which is probably also explained by the importance of the iron and steel industry in the city (see section 4.6.2).

Table 8.8 Concentrations of elements (µg/g) in soils from industrial areas

	topsoil (n=25)				subsurface soils (n=25)			
	GM	AM	SD	Range	GM	AM	SD	Range
Li	26	29	17	11.5-82	29	33	19	18-80
Na	352	406	231	158-1090	479	625	596	200-2430
K	5390	5909	2859	2830-13800	5018	5423	2320	2490-10800
Be	1.92	2.13	1	0.75-4.2	2.58	3.5	4.4	1.14-20
Mg	3553	3844	1574	1860-7620	3527	3938	1953	1750-7670
Ca	7397	10640	9599	864-38700	8710	12588	11563	1130-42200
Sr	68	83	50	23-180	83	102	72	29-312
Ba	205	221	89	85-421	211	228	94	111-467
Al*	2.54	2.78	1.32	1.39-6.34	2.77	2.9	1.0	1.89-5.93
La	20	20	4.3	14-29	22	22	5.3	17-39
Ti	549	566	154	356-1090	612	628	158	432-1080
V	50	56	29	26-143	58	64	32	34-146
Cr	38	56	82	17-431	33	37	19	20-77
Mn	613	739	616	216-3280	572	726	645	225-2860
Fe*	2.63	2.96	1.66	1.37-8.41	2.91	3.24	1.64	1.26-7.55
Co	12	14	7.4	5-32	15	18.5	14.1	6.1-54.1
P	925	1036	594	438-3260	862	932	418	542-1980

* Results for Al and Fe are reported as % rather than µg/g.

GM	Geometric mean
AM	Arithmetic mean
SD	Standard Deviation

8.7 Comparison of Wolverhampton data with other urban studies

8.7.1 Introduction

Establishing trends for multi-element data in Wolverhampton, in relation to land-use (this chapter, in particular) and geology (chapter nine, in particular) is a very important exercise. Comparison of the data from Wolverhampton with data from other urban studies is also necessary to provide a perspective on the concentrations of elements in terms of other cities around the world which may differ in terms of population density, industrial activity and traffic density.

8.7.2 Comparison of Pb concentrations in Wolverhampton soils with other urban studies

A mean Pb concentration of 275 μg/g is reported for allotments in Liverpool (Warren *et al.,* 1971), whilst a mean of 242 μg/g is reported for soils 4-10km from the centre of London (Davies *et al.,* 1979). Thornton and Jones (1984) report a variety of Pb concentrations for their study of garden/allotment soils in 5 cities. Concentrations vary from > 2000 μg/g for London to 64 μg/g for Scunthorpe. Most soils in west Dublin were observed to have Pb concentrations in the range 70-150 μg/g (Fleming and Parle, 1977). These studies generally report significantly higher concentrations of Pb than are observed for any of the land-uses in Wolverhampton (see Tables 8.1, 8.3, 8.5 and 8.7), although city gardens/allotments such as those in Scunthorpe and Stoke-on-Trent have lower reported concentrations of Pb than garden soils in Wolverhampton (geometric mean of 111 μg/g). The geometric means for all the land-uses, with the exception of agricultural areas, all fall within the range reported for Pb in soils of west Dublin. In Wolverhampton, geometric mean concentrations of Pb, as designated by land-use are all considerably lower than those reported for all the summarised categories of the National Reconnaissance Survey (see Tables 3.17-3.21 and Tables 8.1, 8.3, 8.5 and 8.7). This may be due to a number of factors, such as the difference in sample depth, with 0-5cm samples having systematically higher concentrations of Pb than samples of 0-15cm, or the reduction in the Pb content of petrol which has occurred since the National Reconnaissance Survey was undertaken (see section 3.4.6.1). The major re-development of Wolverhampton in recent years is probably also an important factor.

Moir (1992) reported multi-element results for ten towns and cities in England, taking soil samples from the top 15cm of the profiles of gardens/allotments. The results for Pb are all higher in the ten towns and cities studied by Moir (1992), with the exception that the geometric mean Pb concentration reported for soils from industrial areas of Wolverhampton is similar to those reported for Birmingham, Leeds and Guildford, areas which were observed by Moir (1992) to have significantly lower concentrations of Pb than the overall geometric mean for the study. A geometric mean of 271 μg/g reported in this study for garden soils in Richmond is higher than all the geometric means for the different land-uses in Wolverhampton (see Tables 8.1, 8.3, 8.5 and 8.7).

Most of the other studies in Europe and America report considerably higher concentrations of Pb than observed in this study for any of the land-uses in Wolverhampton. In the USA these include the results for Boston (Splitter and Fried, 1979), Washington (Preer *et al.,* 1984), Mont Pleasant (Mielke, 1992) and New Orleans and Minneapolis (Mielke, 1993 - see section 3.5.5). In a later study by Mielke (1994) in New Orleans the city was divided into 3 areas, with mid-city and suburban areas having mean Pb concentrations of 110 μg/g and 50 μg/g, respectively. These values are similar to the geometric mean reported for garden soils and agricultural soils in Wolverhampton, respectively (see Tables 8.1 and 8.5). Higher concentrations of Pb reported in most American studies may relate to sampling only the top few centimeters of soil, the greater prevalence of wooden housing in America (hence greater surface area painted compared with British housing), and perhaps, a concentration of these studies in inner-city areas.

Most of the studies based in other parts of Europe and elsewhere in the world also report higher concentrations of Pb than for Wolverhampton. These include studies in Madrid, Spain (Sanchez-Camazano *et al.,* 1994), Upper Silesia, Poland (Gzyl, 1990), Cuenca, Ecuador (Hewitt and Candy, 1990), Hong Kong (Tam *et al.,* 1987) and South Korea (Chon *et al.,* 1995). Lux (1991) reports a mean Pb concentration of 168 μg/g for the industrial city of Hamburg, Germany which is slightly higher than the geometric mean for Pb in soils from industrial areas of Wolverhampton of 144 μg/g (although a higher arithmetic mean of 233 μg/g is reported for soils from industrial areas of Wolverhampton). A geochemical map has been produced for Warsaw, Poland composed of over 1700 soil samples from Warsaw and the surrounding areas, soils being sampled at a density of 1 per km^2 to depths of 0.2m (PIG, 1992). The study reports a median Pb concentration of 13 μg/g for soils in Warsaw, with a maximum of 401 μg/g. The median Pb concentration for soils in industrial areas of the city is 84 μg/g. These are considerably lower than for corresponding land-uses in Wolverhampton, a trend which may relate to the difference in soil depths between the two studies, or greater anthropogenic additions of Pb to soils in

Wolverhampton.

8.7.3 Comparison of Zn concentrations in soils from Wolverhampton with other urban studies

A mean concentration of 185 μg/g is reported by Warren et al. (1971) for allotment soils in Liverpool, whilst Jones and Thornton (1984) report Zn concentrations which vary greatly for individual cities in England, from > 2000 μg/g for allotments in London to 174 μg/g for Stoke-on-Trent, an industrial city similar to Wolverhampton. The geometric mean concentrations for the different land-uses in Wolverhampton, with the exception of agricultural soils, are all higher than the mean values reported for Liverpool allotments and Stoke-on-Trent. In comparison, the National Reconnaissance Survey of metals and dusts (Culbard *et al.,* 1983; Thornton *et al.,* 1985; Culbard *et al.,* 1988; and Thornton 1989 - see Tables 3.17-3.21), reports higher concentrations of Zn in the urban gardens of London as a whole and the hotspot areas excluding Derbyshire than in urban gardens from Wolverhampton (see Tables 3.20 and 8.5). The geometric mean for residential areas of Britain as a whole is comparable to that for garden soils in Wolverhampton (278 μg/g and 241 μg/g, respectively). This is despite the difference in the sample depths for the two studies (0-15cm in Wolverhampton and 0-5cm for the National Reconnaissance Survey). The geometric mean for the industrial areas of Wolverhampton is significantly higher than the corresponding measurement for residential areas of Britain excluding the hotspots (368 μg/g and 278 μg/g, respectively).

Moir (1992) in a study of ten towns/cities in England reports geometric mean concentrations of Zn lower for each of the study areas than the geometric mean for industrial sites in Wolverhampton, the exception to this being Shrewsbury (a geometric mean of 367 μg/g compared to 368 μg/g for Wolverhampton). A direct comparison of the geometric mean for urban gardens in Wolverhampton shows that the result for this study is comparable to results obtained by Moir (1992) for Birmingham, Brighton, Darlington, Hammersmith and Fulham and Richmond (geometric means ranging from 219-271 μg/g) and higher than results for Guildford, Leeds and York (geometric means ranging from 120-199 μg/g). A geometric mean of 179 μg/g is reported in this study for garden soils in

Richmond, which is lower than for the corresponding land-use in Wolverhampton (241 μg/g), although higher than for soils from agricultural areas in Wolverhampton (125 μg/g).

Most of the studies undertaken in the USA report significantly lower concentrations of Zn than observed for all of the land-uses in Wolverhampton. This was a trend also observed when comparing results from Richmond (see section 6.3.4). Studies by Preer *et al.* (1984), Mielke *et al.* (1984) and Ritter and Rinefierd (1983) in Washington, Baltimore and Ohio, respectively, report median Zn concentrations lower than those observed in agricultural soils in Wolverhampton (see section 3.5.5 and 8.1). This relationship may result due to the longer history of open fires in England (Davies, 1993). A mean Zn concentration of 361 μg/g for soils in the industrial city of Hamburg, Germany (Lux, 1991) is similar to the geometric mean for soils in industrial areas of Wolverhampton of 368 μg/g, although the latter is significantly higher than the mean concentration for the industrial areas of Bari, Italy (91 μg/g - Polemio *et al.*, 1982). A median concentration of 34 μg/g is reported for soils in Warsaw, Poland with a maximum concentration of 1432 μg/g (PIG, 1992). This median concentration is much lower than geometric mean concentrations for any of the land-uses in Wolverhampton (see Tables 8.1, 8.3, 8.5 and 8.7). Zn concentrations of 281 μg/g and 231 μg/g for Hong Kong and Seoul, South Korea respectively (Tam *et al.*, 1987 and Chon *et al.*, 1995) are comparable with the geometric mean for Zn in Wolverhampton garden soils of 241 μg/g.

8.7.4 Comparison of Cu concentrations in soils from Wolverhampton with other urban studies

Warren *et al.* (1971) report a mean Cu concentration of 62 μg/g for allotment soils in Liverpool, whilst Thornton and Jones (1984) report Cu concentrations which vary considerably from London (205 μg/g and 127 μg/g) to Stoke-on-Trent (46 μg/g and 33 μg/g). The mean concentration for Liverpool is the same as that reported for garden soils in Wolverhampton (62 μg/g), whilst allotment soils in Stoke-on-Trent have similar concentrations to those observed for agricultural soils in Wolverhampton (46 and 33 μg/g and 32 μg/g, respectively). The geometric mean for Cu in soils from industrial areas of Wolverhampton is close to one of the Cu concentrations reported for allotment soils in

London (Thornton and Jones, 1984 -139 µg/g and 127 µg/g, respectively).

The National Reconnaissance Survey (Culbard *et al.*, 1983) reports a geometric mean for residential areas of Britain as a whole, except the hotspots, of 56 µg/g which is similar to that reported for garden soils in Wolverhampton (62 µg/g). The geometric mean Cu concentration for soils from industrial areas of Wolverhampton of 139 µg/g is much higher than the summarised results from the National Reconnaissance Survey, even the hotspots excluding Derbyshire (63 µg/g). This is despite the difference in sample depths between the two studies (0-5cm for the National Reconnaissance Survey and 0-15cm for these particular soils in Wolverhampton). This probably relates to the importance of Cu in Wolverhamptons industrial activity. Conversely, the geometric mean for Cu in agricultural soils in Wolverhampton is much lower than those reported for any of the categories of the National Reconnaissance Survey summarised in Tables 3.17-3.21 (see Table 8.1). The Cu concentration for London parks is similar to the corresponding measurements reported for open spaces in Wolverhampton (49 µg/g and 55 µg/g, respectively).

Moir (1992) reports an overall geometric mean of 75.2 µg/g for the study of 10 towns/cities in England. This is higher than the corresponding measurement for Wolverhampton garden soils (62 µg/g). The highest concentrations were observed in London and Birmingham (90.5 µg/g for Hammersmith and Fulham and 103 µg/g for Birmingham - Moir, 1992). A geometric mean of 48 µg/g is reported in this study for garden soils in Richmond, lower than the corresponding value in Wolverhampton (62 µg/g).

In comparison with studies based in the USA, geometric mean concentrations of Cu in soils from all land-uses in Wolverhampton are higher than average concentrations reported for cities in the USA. Median concentrations of 29 µg/g, 17.2 µg/g are reported for Washington and Baltimore, respectively (Preer *et al.*, 1984 and Meilke *et al.*, 1984). Ritter and Rinefierd (1983) report a mean concentration of 20 µg/g for garden soil in Ohio. As for Zn, a longer history of open fires in Britain may account for higher concentrations of Cu in Wolverhampton and Richmond, as well as the long industrial history of Wolverhampton.

In comparison with studies in other parts of the world, mean Cu concentrations of 95.5 μg/g for soils in the industrial areas of Bari, Italy (Polemio *et al.,* 1982), and 81 μg/g for the industrial city of Hamburg, Germany (Lux, 1991) are lower than the geometric mean for soils in industrial parts of Wolverhampton (139 μg/g). A median Cu concentration of 6 μg/g is reported for Warsaw, Poland with a maximum of 560 μg/g. This median concentration for Warsaw is significantly lower than any of the measures of central tendency in Wolverhampton, and the maximum concentration only higher than the corresponding measurement for soils from agricultural areas and areas of open space in Wolverhampton (see Tables 8.1 and 8.3). Hewitt and Candy (1990) report a mean Cu concentration of 70 μg/g for soils in Cuenca, Ecuador, whilst a geometric mean of 64 μg/g is reported for soils from Seoul, South Korea (Chon *et al.,* 1995). These are similar to the concentrations reported for garden soils in Wolverhampton of 62 μg/g. A much higher mean Cu concentration is reported for Hong Kong of 142 μg/g, which is very similar to soils from industrial areas of Wolverhampton (a geometric mean of 139 μg/g).

8.7.5 Comparison of Cd concentrations in soils from Wolverhampton with other urban studies

Warren *et al.* (1971) report a mean Cd concentration of 0.8 μg/g for allotment soils in Liverpool, whilst Thornton and Jones (1984) report a variety of Cd concentration for allotment soils in England, ranging from < 0.1 for Scunthorpe to 2.8 for London. Garden soils in Wolverhampton have a geometric mean of 0.7 μg/g, similar to the mean concentration reported by Warren *et al.* (1971), with 1.25 μg/g for soils in industrial areas of Wolverhampton. The geometric mean Cd concentration for garden soils in Wolverhampton (0.7 μg/g) is similar to that reported for Stoke-on-Trent (0.8 μg/g and 0.6 μg/g - Thornton and Jones 1984). The National Reconnaissance Survey reports concentrations of Cd > 1 μg/g for all categories, even for parks in London which are higher than all the land-use categories in Wolverhampton, with the exception of industrial areas. The geometric mean for industrial areas of 1.25 μg/g is similar to the National Reconnaissance Survey results for the residential areas of London, all residential areas of Britain except the hotspots, and Richmond-upon-Thames (see Tables 8.7, 3.17, 3.20 and 3.18, respectively). The Cd data for the National Reconnaissance Survey may not provide the most reliable comparison, as samples which had Cd concentrations below the detection limit of 1 μg/g were assumed to be equal to this value. This probably resulted in an overestimation of results presented in Tables 3.17-3.21.

Moir (1992) reported geometric means for 10 towns/cities in Britain, with measures varying from < 0.2-1.64 μg/g. The geometric mean for Cd in garden soils from Wolverhampton of 0.7 μg/g is similar to the geometric mean reported for Birmingham, 0.72 μg/g, and slightly higher than towns such as Leeds, Darlington, Hammersmith and Fulham, Richmond and Nottingham (ranging from 0.27-0.5 μg/g). The higher concentrations of Cd in Wolverhampton probably relates to the industrial activity in Wolverhampton and the underlying geology. The geometric mean of 1.25 μg/g for industrial areas is lower than that reported for Brighton of 1.64 μg/g, something which is difficult to explain in view of Brighton's lack of industry. A geometric mean of < 0.2 μg/g is reported in this study for garden soils in Richmond, lower than all of the land-use categories in Wolverhampton (see Tables 8.1, 8.3, 8.5 and 8.7). This is probably the result in differences in the geochemical signatures for the two areas (naturally higher concentrations of Cd in Wolverhampton) and the long history of industrial activity in Wolverhampton.

A number of studies of cities in the USA report similar Cd concentrations to those observed for garden soils in Wolverhampton (0.7 μg/g). These are 0.56 μg/g and 0.7 μg/g for Baltimore and Washington, respectively (Mielke *et al.,* 1984 and Preer *et al.,* 1984). The mean concentration for Ohio of 1.65 μg/g is higher than the geometric mean for industrial areas of Wolverhampton of 1.25 μg/g. A mean Cd concentration of 1.2 μg/g is reported for the soils in the industrial city of Hamburg, Germany (Lux, 1991), which is comparable with the Cd concentration for industrial parts of Wolverhampton. Mean concentrations of 0.5 μg/g and 0.53 μg/g are reported for Bari, Italy and Salamanca, Spain, respectively (Polemio *et al.,* 1982 and Camazano *et al.,* 1994), which are lower than for urban gardens in Wolverhampton (0.7 μg/g). A median concentration of < 0.3 (the detection limit) is reported for soils in Warsaw, Poland with a maximum of 19.1 μg/g (PIG, 1992). A mean concentration of 0.36 μg/g is reported for soils 5.5 km from Cuenca, Ecuador, (Hewitt and Candy, 1990), a concentration lower than that reported for all the land-use categories in Wolverhampton (see Tables 8.1, 8.3, 8.5 and 8.7). A mean Cd concentration of 1.2 is reported for Hong Kong (Tam *et al.,* 1987) which is very similar to the geometric mean concentration for industrial parts of Wolverhampton, whilst a considerably higher geometric mean of 3 μg/g is reported for Seoul, South Korea (Chon *et al.,* 1995).

8.7.6 Comparison of Ni concentrations in soils from Wolverhampton with other urban studies

Warren *et al.* (1971) report a mean Ni concentration of 27 μg/g for allotments in Liverpool, whilst Thornton and Jones (1984) report a variety of Ni concentrations ranging from 18-32 μg/g for garden/allotment soils in England, the highest observed in London and the lowest in Stoke-on-Trent. The geometric mean for urban gardens in Wolverhampton is similar to that observed for Liverpool (26 μg/g), whilst soils in agricultural areas of Wolverhampton have a geometric mean of Ni similar to that observed in gardens/allotments in Stoke-on-Trent (19 μg/g). The geometric mean for Ni in soils from industrial parts of Wolverhampton is higher than that observed by Thornton and Jones (1984) for London (37 μg/g and 32 and 26 μg/g, respectively).

Moir (1992) reports an overall geometric mean for ten towns and cities in England of 26.7 μg/g which is similar to the geometric mean for garden soils in Wolverhampton of 26 μg/g. The geometric mean of 37 μg/g reported for industrial areas of Wolverhampton is higher than the corresponding measurement for any of the study areas reported by Moir (1992). However, using garden soils as a direct comparison, towns/cities such as Birmingham, Shrewsbury and Hammersmith and Fulham have higher concentrations of Ni than observed for Wolverhampton. A geometric mean for Ni of 24 μg/g is reported in this study for garden soils for Richmond similar to garden soils in Wolverhampton (a geometric mean 26 μg/g).

A mean concentration of 51.5 μg/g is reported for soils in industrial parts of Bari, Italy (Polemio *et al.,* 1982), whilst Lux (1991) reports a mean Ni concentration of 31 μg/g for Hamburg, an industrial city in Germany. Soils in industrial parts of Wolverhampton have a geometric mean concentration of 36 μg/g which falls between the results for these two cities, which may relate to the measures of central tendency (an arithmetic mean of 45 μg/g is reported for industrial parts of Wolverhampton which is closer to the mean of 51 μg/g reported for Bari), or the nature of the industrial activities in these areas. A median concentration of 4 μg/g is reported for soils in Warsaw (PIG, 1992) which is comparable with a mean of 2.8 μg/g reported for Baltimore (Mielke *et al.*, 1984). These are considerably lower than any of Ni concentrations for the different land-use categories in Wolverhampton (see Tables 8.1, 8.3, 8.5 and 8.7).

8.7.7 Comparison of Na concentrations in soils from Wolverhampton with other urban studies

The comprehensive study of urban areas by Moir (1992) included results for Na concentrations in soils from the ten towns/cities studied. The geometric mean for urban gardens in Wolverhampton of 310 μg/g is similar to the results reported for Richmond (290 μg/g), although lower than the overall mean for the ten towns/cities in the study of 376 μg/g. The geometric mean concentration for Na in soils from industrial areas of Wolverhampton (352 μg/g) is closer to this value. Lower concentrations of Na in soils from Wolverhampton in general compared with the towns and cities studied by Moir (1992) probably results from differences in parent material. A geometric mean for Na of 207 μg/g is reported in this study for garden soils in Richmond which compares to 290 μg/g for garden soils in Wolverhampton. This is despite sampling in Wolverhampton in the summer (compared to winter in Richmond) and probably results from differences in parent material for the two areas (see sections 4.5 and 4.7). However, high concentrations of Na are observed in some industrial parts of Wolverhampton (see Plate 8.8), suggesting an anthropogenic influence.

8.7.8 Comparison of K concentrations in soils from Wolverhampton with other urban studies

In the study by Moir (1992) an overall geometric mean of 4647 μg/g is reported for K in soils from ten town/cities in England. This is lower than for all the land-use categories in Wolverhampton (see Tables 8.2, 8.4, 8.6 and 8.8), with a geometric mean of 5171 μg/g for garden soils. Towns and cities such as Birmingham, Shrewsbury and Darlington are observed to have higher geometric mean concentrations of K than Wolverhampton (6634 μg/g, 8358 μg/g and 6430 μg/g, respectively - Moir, 1992). The generally higher concentrations of K in soils from Wolverhampton compared with most of the towns/cities studied by Moir (1992) are probably the result of differences in parent material. A geometric mean of 2844 μg/g is reported in this study for garden soils in Richmond which is lower than the corresponding value for Wolverhampton (5171 μg/g). All the land-uses in Wolverhampton have considerably higher concentrations of K than in Richmond (see Tables 8.2, 8.4, 8.6 and 8.8), which is probably due to differences in parent material as concentrations of K do not vary significantly with land-use in either area.

8.7.9 Comparison of Be concentrations in soils from Wolverhampton with other urban studies

Very few urban studies report data for Be. Comparisons are possible with more general studies of countries. Kabata-Pendias and Pendias (1984) report a mean Be concentration of 0.54 μg/g for soils from Great Britain, whilst Asami and Kubota (1995) report mean Be concentrations for a number of counties. These include 1.17 μg/g for Japan, 1.56 μg/g for the former USSR, 0.99 μg/g for New Zealand and 1.43 μg/g for Thailand. The concentrations of Be for all the different land-uses in Wolverhampton are significantly higher than the average value reported by Kabata-Pendias (1989) of 0.56 μg/g for British soils (see Tables 8.2, 8.4, 8.6 and 8.8). The geometric mean for Be in urban garden soils from Wolverhampton (1.7 μg/g) is higher than the average values for all the countries reported by (Asami and Kubota, 1995). This suggests some anthropogenic additions of Be in Wolverhampton, probably through the burning of fossil fuels in industrial parts of the city. A geometric mean of 1.18 μg/g is reported for Be in garden soils in Richmond, and this is lower than for all the land-use categories in Wolverhampton (the lowest, a geometric mean of 1.3 μg/g for agricultural soils). Differences in parent material and the greater industrial activity in Wolverhampton result in higher concentrations of Be in Wolverhampton soils (see sections 4.2.2, 4,5 and 4.7 in general).

8.7.10 Comparison of Mg concentrations in soils from Wolverhampton with other urban studies

Moir (1992) has been one of very few workers to report Mg concentrations in urban soils. The overall geometric mean for ten towns/cities in England is reported as 2984 µg/g, which is lower than the geometric mean for garden soils in Wolverhampton (3327 µg/g). Cities such as Birmingham, Nottingham and Shrewsbury have geometric mean concentrations of Mg higher than for all the land-use categories reported for Wolverhampton (4850 µg/g, 4698 µg/g and 5107 µg/g, respectively, compared to geometric means ranging from 3226-3631 µg/g in Wolverhampton). These differences are likely to be the result of parent material, with a similar trend observed for K in comparison with the towns/cities studied by (Moir, 1992). This may be due to K and Mg being clay-associated elements. A geometric mean of 1692 µg/g is reported in this study for garden soils in Richmond, which compares to 3327 µg/g for garden soils in Wolverhampton, the difference probably the result of parent material, although soils in industrial areas of Wolverhampton have significantly higher concentrations of Mg [illegible] than soils from other parts of Wolverhampton (see section 8.6 in general).

8.7.11 Comparison of Ca concentrations in soils from Wolverhampton with other urban studies

Moir (1992) has been one of very few workers to report data for Ca in urban soils. An overall geometric mean of 10612 µg/g is reported for the study of ten towns/cities in England. One of the towns in the study, Brighton, has a Ca geometric mean of 61263 µg/g, which is the result of these soils overlying chalk. All the study areas in the study by Moir (1992) have higher concentrations of Ca than urban gardens in Wolverhampton (4826 µg/g), although the geometric mean for industrial areas of Wolverhampton (7397 µg/g), is higher than for some of the towns/cities reported (Birmingham, Leeds, and York). The generally higher concentrations in the study by Moir (1992) relate to parent material and, possibly, greater additions of lime and fertilisers to allotment soils. A geometric mean of 5539 µg/g is reported for Ca in garden soils in Richmond, compared with 4826 µg/g for garden soils in Wolverhampton. This is probably a result of both differences in parent material between the two areas and possibly greater anthropogenic additions of Ca in Richmond through building materials, fertilisers and lime. This concentration for garden soils in Richmond is lower than that observed for soils in industrial areas of Wolverhampton (a geometric mean of 7397 μg/g), which probably results from the industrial use of Ca (see Table 3.2).

8.7.12 Comparison of Sr concentrations in soils from Wolverhampton with other urban studies

Moir (1992) has been one of very few workers to report data for Sr in urban soils. The overall geometric mean for the ten towns/cities in this study was 58.8 μg/g, higher than the geometric mean for garden soils in Wolverhampton (50 μg/g). This value for garden soils in Wolverhampton is higher than those reported for Birmingham and Leeds (42.2 μg/g and 45.4 μg/g, respectively). The generally lower concentrations of Sr observed in Wolverhampton follows the pattern observed for Ca, a geochemically similar element. The importance of chalk as a parent material for some of the areas studied by Moir (1992) may account for this. In Wolverhampton, the geometric mean for Sr in soils from industrial areas of 68 μg/g is comparable with results reported by Moir (1992) for Hammersmith and Fulham and Nottingham (61.3 μg/g and 61.4 μg/g, respectively). The present study reports a geometric mean of 39 μg/g for Sr in garden soils from Richmond, which compares to 50 μg/g for garden soils in Wolverhampton. Higher concentrations of Sr in Wolverhampton, compared with Richmond, is in contrast to the relationship observed for Ca. This may be caused by differences in parent material and, perhaps, differences in the anthropogenic sources of Ca and Sr in Wolverhampton (see Table 3.2).

8.7.13 Comparison of Ba concentrations in soils from Wolverhampton with other urban studies

Moir (1992) has been one of very few workers to report data for Ba in urban soils. An overall geometric mean of 258 μg/g is reported for ten towns/cities in England. This is higher than the geometric mean reported for urban gardens in Wolverhampton (202 μg/g). However, this concentration for garden soil in Wolverhampton is higher than that reported for Guildford (148 μg/g) and comparable to Brighton (197 μg/g). The generally lower concentration of Ba in Wolverhampton soils may result from differences in parent material, with lower concentrations of Ba in garden soils from Wolverhampton, compared with the study by Moir (1992), following the trends observed for Ca and Sr. Differences in anthropogenic inputs may also be important as land-use is observed to significantly affect concentrations of Ba in Wolverhampton and Richmond. A geometric mean of 188 μg/g is reported for Ba in garden soils from Richmond, which compares to 202 μg/g for garden soils in Wolverhampton. This follows the trend observed for Sr of higher concentrations in garden soils from Wolverhampton and probably relates to naturally higher concentrations of Sr in Wolverhampton and greater anthropogenic inputs.

8.7.14 Comparison of Al concentrations in soils from Wolverhampton with other urban studies

Moir (1992) has been the only worker to report data for Al in urban soils. An overall geometric mean of 2.39% was reported for ten towns/cities in England which is similar to the geometric mean for garden soils in Wolverhampton of 2.45%. Aluminium concentrations were not observed to vary significantly with regard to land-use in Wolverhampton. The geometric mean concentrations for Al in the 10 towns/cities studied by Moir (1992) varied considerably, with the underlying geology believed to be the most important factor. The lowest concentrations were observed in Richmond, with a geometric mean of 1.44%, comparable with results from this study (a geometric mean of 1.61%) and Guildford, a geometric mean of 1.33%. These are significantly lower than for any of the land-use categories listed for Wolverhampton (see Tables 8.2, 8.4, 8.6 and 8.8). A clay-rich till predominates in Wolverhampton whilst in Richmond most of the borough is underlain by river deposits which are dominated by sand (see section 6.4).

8.7.15 Comparison of La concentrations in soils from Wolverhampton with other urban studies

Moir (1992) has been the only worker to report data for La in urban soils. An overall geometric mean of 21.6 was reported for ten towns/cities in England, which is higher than the geometric mean for garden soils in Wolverhampton of 19 μg/g. This is probably a result of differences in the underlying geology. Lanthanum was not observed to vary significantly as a consequence of land-use in this study, and Moir (1992) reported that Richmond had concentrations of La significantly lower than the overall mean for ten towns and cities in England. This trend is observed for a number of elements which are most influenced by the underlying geology. A geometric mean of 17 μg/g is reported in this study for garden soils in Richmond, which is lower than the corresponding measurement for garden soils in Wolverhampton of 19 μg/g. Differences in concentrations are probably related to parent material.

8.7.16 Comparison of Ti concentrations in soils from Wolverhampton with other urban studies

Moir (1992) has been the only worker to report data for Ti in urban soils. An overall arithmetic mean of 606 μg/g is reported for ten towns/cities in England, which is similar to the arithmetic mean for garden soils in Wolverhampton of 576 μg/g. In the study by Moir (1992), parent material is believed to be the most important factor influencing Ti concentration in soils. This study has also shown that land-use does not significantly influence concentration of Ti in soils from Wolverhampton and Richmond. A geometric mean of 673 μg/g is reported in this study for garden soils from Richmond, which is higher than the corresponding measurement for Wolverhampton (576 μg/g). Higher concentrations of Ti in Richmond soils are probably related to parent material.

8.7.17 Comparison of V concentrations in soils from Wolverhampton with other urban studies

Moir (1992) has been the only worker to report data for V in urban soils. An overall geometric mean of 48.6 μg/g is reported for ten towns/cities in England, which is higher than the geometric mean for garden soils in Wolverhampton (43 μg/g). The overall geometric mean for the study is closer to the geometric mean for V in soils from industrial areas of Wolverhampton (50 μg/g). In Wolverhampton the concentration of V is not observed to vary significantly in soils with regard to land-use (see section 8.6 in general).

The geometric mean for garden soils in Wolverhampton of 43 μg/g is similar to those reported for Birmingham, Guildford and York, which have geometric means of 45.3 μg/g, 42.7 μg/g and 42.8 μg/g, respectively (Moir, 1992). Important sources of V are from the combustion of fossil fuels and the deposition of fossil fuel residues (Jones *et al.,* 1990). Parent material is the primary source of V, and differences in parent material will result in varying concentrations of V; Moir (1992) reported the highest concentration of V in Brighton (84.5 μg/g), an area where a superficial deposit of clay overlies the chalk. A geometric mean of 50 μg/g is reported in this study for garden soils in Richmond, higher than the corresponding measurement for garden soils in Wolverhampton (43 μg/g). The geometric mean for V in soils from industrial areas of Wolverhampton is the same as that for garden soils from Richmond (50 μg/g). Generally, higher concentrations of V in Richmond, compared with Wolverhampton, probably results from differences in the parent material for the study areas (see sections 4.5 and 4.7).

8.7.18 Comparison of Cr concentrations in soils from Wolverhampton with other urban studies

Moir (1992) has been the one of few workers to report data for Cr in urban soils. An overall geometric mean of 25.7 μg/g was reported for ten towns/cities in England, which is very similar to the geometric mean for garden soils in Wolverhampton of 25 μg/g. The industrial areas of Wolverhampton are observed to have significantly higher concentrations of Cr, (a geometric mean of 38 μg/g) and industrial point sources such as foundries, metal works and power plants and the combustion of fossil fuel are well known sources of Cr (Adriano, 1986). The geometric mean for Hammersmith and Fulham of 39.2 μg/g is similar to that observed in the industrial parts of Wolverhampton. This part of London once had foundries, and this coupled with emissions from cars (see section 3.4.6) is a significant source of Cr.

A geometric mean of 38 μg/g is reported in this study for garden soils in Richmond and this compares with a corresponding measurement of 25 μg/g for garden soils in Wolverhampton. Despite the extensive industrial activity in Wolverhampton, the geometric mean for soils in industrial areas is the same as that reported for garden soils in Richmond

(38 μg/g). A higher geometric mean for Cr in garden soils from Richmond, compared with Wolverhampton, probably results from differences in parent material for the study areas (see sections 4.5 and 4.7).

8.7.19 Comparison of Mn concentrations in soils from Wolverhampton with other urban studies

Warren *et al.* (1971) report a mean Mn concentration of 240 μg/g for allotment soils in Liverpool whilst Moir (1992) reports an overall geometric mean for Mn of 485 μg/g for garden allotment soils in ten towns/cities in England. The overall geometric mean reported by Moir (1992) is very similar to the geometric mean for garden soils in Wolverhampton (466 μg/g). Smith (1990) suggested that soils derive most of their Mn from parent material and therefore, when comparing Mn concentrations in the soils of several cities, this factor needs consideration. Moir (1992) reported geometric mean concentrations of 1109 μg/g for soils in Brighton and 684 μg/g for soils in Shrewsbury, both of which are higher concentrations than observed for garden soils in Wolverhampton. This is probably due to differences in parent material. For Brighton, the high pH of the Cretaceous chalk may immobilise the metals in these soils (McGrath and Loveland, 1992). For soils in industrial areas of Wolverhampton, a geometric mean of 613 μg/g was observed, which is significantly higher than the Mn concentration in garden soils. In these regions, specific industrial activities, the composition of the made ground and the natural underlying geology, may account for this pattern.

Polemio *et al.* (1982) report a mean Mn concentration of 329 μg/g for soils in industrial parts of Bari, Italy, which is significantly lower than the geometric mean for soils in industrial parts of Wolverhampton. In the geochemical Atlas for Warsaw (PIG, 1992) a median concentration of 148 μg/g is reported for Mn. A geometric mean of 325 μg/g is reported in this study for Mn in garden soils from Richmond, and this compares to a corresponding measurement of 466 μg/g for garden soils in Wolverhampton. This is probably due to larger anthropogenic additions in Wolverhampton and perhaps, naturally higher concentrations as a result of the natural geochemical signature (see section 9.2 in general).

8.7.20 Comparison of Fe concentrations in soils from Wolverhampton with other urban studies

Thornton and Jones (1984) report Fe concentrations for garden/allotment soils in England which range from 2.3% in London to 11.3% in Scunthorpe. The highest concentrations in Scunthorpe occur near the site of a steelworks. The geometric mean for Fe in garden soils in Wolverhampton is 1.98%, with the highest concentrations of Fe observed in industrial areas, (a geometric mean of 2.63%). Moir (1992) reported an overall geometric mean of 2.54% for garden/allotment soils from ten towns/cities in England, which, when compared with results for Wolverhampton, is similar to the geometric mean for soils in industrial area, but higher than that for other land-uses in Wolverhampton (see Tables 8.2, 8.4, 8.6 and 8.8). The geometric mean for garden soils in Wolverhampton, 1.98%, is lower than the overall geometric mean for garden/allotment soils from ten towns/cities (Moir, 1992). The highest concentrations of Fe were observed in Darlington and Shrewsbury, towns which had iron-works in the last century (Moir, 1992). In Wolverhampton, excluding industrial areas, parent material is probably the most important source of Fe and this may account for the relatively low concentrations when compared with other urban areas in England. The Geochemical Atlas for Warsaw (PIG, 1992) reports a median Fe concentration of 0.46% which is considerably lower than reported for this study and many of the other studies in Britain. This is likely to be a result of differences in underlying geology and differences in the analytical processes used.

A geometric mean of 2.58% is reported in this study for garden soils in Richmond, which compares with a corresponding measurement of 1.98% for garden soils in Wolverhampton. Concentrations of Fe are significantly higher in soils from industrial areas of Wolverhampton than any other land-use in Wolverhampton, although a geometric mean of 2.63% for industrial areas is very similar to that reported for garden soils in Richmond (2.58%). The natural input for Fe, as a reflection of the natural geochemical signature, is probably higher than that for Wolverhampton, something observed when comparing corresponding percentiles for Plates 6.20 and 8.22.

8.7.21 Comparison of Co concentrations in soils from Wolverhampton with other urban studies

Warren *et al.* (1971) report a mean Co concentration of 8 μg/g for allotment soils in Liverpool, whilst Moir (1992) reports an overall geometric mean of 11 μg/g for soils in gardens/allotment from ten towns/cities in England. The geometric mean of 9.5 μg/g for garden soils in Wolverhampton falls between the results for these two studies. The study by Moir reported a variety of mean Co concentrations, with Guildford and York having the lowest Co concentrations (geometric means of 8.11 μg/g and 8.71 μg/g, respectively), and the highest geometric mean concentration observed for Shrewsbury (a geometric mean of 14.7 μg/g). Soils in industrial areas of Wolverhampton are observed to have significantly higher concentrations of Co than soils in agricultural areas and areas of open spaces (see sections 8.6.16 and 8.6.17). The geometric mean for industrial areas of 12 μg/g is higher than the overall geometric mean for Co in soils from 10 towns/cities in England (Moir, 1992)

The high concentrations of Co that were observed by Moir (1992) correspond with high concentrations of Mn. This suggests that parent material is an important source of Co, as suggested by Smith (1990). A median Co concentration of 6 μg/g is reported for soils from Warsaw (PIG, 1992), lower than that observed for any of the land-use categories in Wolverhampton (see Tables 8.2, 8.4, 8.6 and 8.8). This follows the trend observed when comparing corresponding elements for the these two studies. A geometric mean of 9 μg/g is reported in this study for garden soils from Richmond, which compares to a corresponding measurement of 9.5 μg/g for garden soils in Wolverhampton.

8.7.22 Comparison of P concentrations in soils from Wolverhampton with other urban studies

Moir (1992) has been the only worker to report data for P in urban soils. An overall geometric mean of 1614 μg/g was reported for garden/allotment soils from ten towns/cities in England, which is significantly higher than the geometric mean for garden soils in Wolverhampton of 899 μg/g. All of the towns/cities studied by Moir (1992) have much higher concentrations of P than observed for soils in any of the land-uses in Wolverhampton. This is likely to be a result of sampling in allotments, which probably have greater inputs of P through additions of phosphate fertilisers and the use of compost heaps. A geometric mean of 1257 µg/g is reported in this study for garden soils in Richmond, which compares to a corresponding measurement of 899 µg/g for garden soils in Wolverhampton. Garden topsoils have significantly higher concentrations of P than areas of open space in Richmond and Wolverhampton (see sections 6.3.44 and 8.6.12). A combination of the natural geochemical signature and greater anthropogenic additions of P probably result in higher average concentrations of P in soils from Richmond, compared with Wolverhampton.

8.8 Overall Summary

1. Mapping of 21 elements in topsoils and 4 metals in subsurface soils from Wolverhampton has shown that high concentrations of a suite of elements are observed in industrial areas of the city, with high concentrations of several elements in the residential areas of Bradmore and Merry Hill.

2. Comparison of data for Richmond-upon-Thames and Wolverhampton, shows that most elements are present at higher concentrations in soils from Wolverhampton. It is suggested that for metals such as Zn, Cu and Cd this is particularly as a result of emissions from the metalliferous works which have a long history in the city. For elements such as Mg, Al, and K, higher concentrations in soils from Wolverhampton probably result from differences in the natural geochemical signatures for the two areas. Most of Wolverhampton is underlain with a clay-rich glacial-till, whilst Richmond is underlain, predominantly, by river terraces which results in soils which are dominated by the sand-size fraction. Soils in Richmond, in general, appear to have naturally higher concentrations V, Cr and Fe than soils in Wolverhampton. However, in Wolverhampton, soils in some industrial areas have higher concentrations of these metals than any soils in Richmond.

3. Topsoils in industrial areas of Wolverhampton have significantly higher concentrations Pb, Zn, Cu, Cd, Ni, Mg, Ca, Cr and Fe than soils from other land-uses in the city. In

industrial areas most elements are present at numerically higher concentrations in subsurface soils than topsoils. The differences are, however, statistically insignificant (all $P > 0.05$).

4. Topsoils in urban gardens from Wolverhampton have significantly higher concentrations of Zn, Cd, Na and Ba than soils in agricultural areas. This probably results from the general greater proximity of urban gardens to industrial areas and perhaps, sources of these elements which are more important in urban gardens than agricultural areas such as flaking paint and the disposal of ashes from open fires. Urban gardens have significantly higher concentrations of Na, Mg, Ca, Ba and P than soils in areas of open space. This probably also results from sources of these elements which are more important in urban gardens than in areas of open space.

5. Concentrations of Pb in urban gardens from Wolverhampton are generally lower than those reported for other urban studies in Britain and the United States, in particular. A greater number of wooden houses in the United States compared with Britain may explain higher concentrations of Pb in America, with flaking paint believed to be the primary source of Pb in the United States. Concentrations of Zn and Cu in garden soils from Wolverhampton are comparable with those for a number of other studies in Britain and generally higher than those reported for the United States. Higher concentrations of Zn and Cu in soils from Wolverhampton probably result from the industrial activity in the city and the prevalence of open fires in Britain until the 1950's.

CHAPTER NINE INVESTIGATION OF THE INFLUENCE OF GEOLOGY AND ANTHROPOGENIC ACTIVITY ON THE SOIL GEOCHEMISTRY OF WOLVERHAMPTON

9.1 Normalisation of the data set to concentrations reported in the Soil Geochemical Atlas of England and Wales (McGrath and Loveland, 1992)

9.1.1 Introduction

In chapter seven the data set for Richmond were normalised to geochemical data reported for the soils of England and Wales (McGrath and Loveland, 1992). The factors which facilitate such a comparison, and the details of the survey undertaken by McGrath and Loveland are outlined in section 7.1.1. The data set for Wolverhampton are also normalised to the same data set to investigate the importance of land-use and geology.

9.2 Graphical representation of a suite of elements from soils from Wolverhampton normalised to data for soils in England and Wales (McGrath and Loveland, 1992) in relation to land-use and geological units

9.2.1 Introduction

The graphs in this section present data for 17 elements which are common to this study and to a comprehensive study of soils in England and Wales (McGrath and Loveland, 1992). The details of how the normalisation is calculated are presented in section 7.2.1. Land-use is an important factor influencing the concentrations of many elements in soils from Wolverhampton (see section 8.6) and urban soils in general (see chapter 3.4). Anthropogenic activities, however, are not the only influence on the concentration of elements in soils; geology is an important natural source of elements and the geochemical signature of a particular parent material can result in concentrations of elements which are very different to those for another parent material. This is observed by examining Table 2.2, which shows, on average higher concentrations for several elements in shales compared with limestone. In Richmond, soils overlying alluvium have significantly higher concentrations of several elements than soils overlying London Clay and the river terraces (see sections 6.2.23 and 7.2.22). Separating the data set for Wolverhampton by land-use and parent material is an important tool to assess the importance of these two factors as influences on multi-element concentrations in soils. Normalisation with a standard data set such as that for the soils of England and Wales (McGrath and Loveland, 1992) permits a very useful visual comparison and allows the data set for Wolverhampton to be compared to those for soils which have developed under the same climatic conditions, but, in general, away from urbanisation.

Normalisation takes place in categories defined by parent material and land-use. The geological units are discussed in chronological order, starting with the oldest outcrop the Clent Formation, permian in age (between 250-290 million years old) through the drift deposits (approximately 10000 years old), with the man-made deposit, made ground, examined last. The land-uses are discussed in the order, agricultural, open space, urban gardens and industrial.

9.2.2 Clent Formation - topsoils (0-15cm) in agricultural areas

The normalisation ratios for these topsoils are shown in Fig. 9.1a and reported in Table 9.1. These sites are located in the southern outskirts of the city very close to the industrial base. The Clent Formation is of Permian age and are mainly sandstones with thin red mudstone and lenses of pebble breccais (see section 4.7.3). The pattern shown in Fig, 9.1a is very different to that observed for most agricultural soils in Wolverhampton (see Figs. 9.2a, 9.9a and 9.14a), with a suite of elements having ratios which exceed 1. The highest ratios are observed for the metals Cu and Ba (both > 2), with ratios exceeding 1 observed for Pb, Zn, Ni, Na, K, Mg, Sr, Al and Co. Although the ratios of Cu, Zn and Pb are lower than for sites specifically located in industrial areas, the ratios for the other suite of elements are similar to those in industrial areas (see Figs. 9.12a and 9.19a). High ratios for a number of elements is atypical of soils in agricultural areas (see Figs. 9.2a, 9.9a and 9.14a), and the location of the Clent Formation, close to intense industrial activity makes it difficult to separate the natural geochemical signature from anthropogenic inputs. However, Ratios for K, Mg, Ba and Al are higher than those observed for any other land-use or parent material in Wolverhampton, and K, Mg and Al are, perhaps, less important in anthropogenic activities than several other elements normalised in this exercise.

9.2.3 Clent Formation - subsurface soils (30-45cm) in agricultural areas

The normalisation ratios for these soils are shown in Fig. 9.1b and reported in Table 9.1. The pattern shown in Fig. 9.1b is very different to that observed for the corresponding topsoils, with all elements having lower ratios at a depth of 30-45cm than 0-15cm. The biggest ratio reductions are observed for the metals Cu, Pb, Cd and Zn. Of these only Cu has a ratio > 1, and the large ratio decreases represent greater accumulation of these metals in the top 15cm of the profile, probably from industrial emissions. Most of the reduction in ratios are probably the result of greater accumulation of elements in the top 15cm, although natural variation in the geochemical signature may be responsible for some of the differences between Figs. 9.1a and 9.1b.

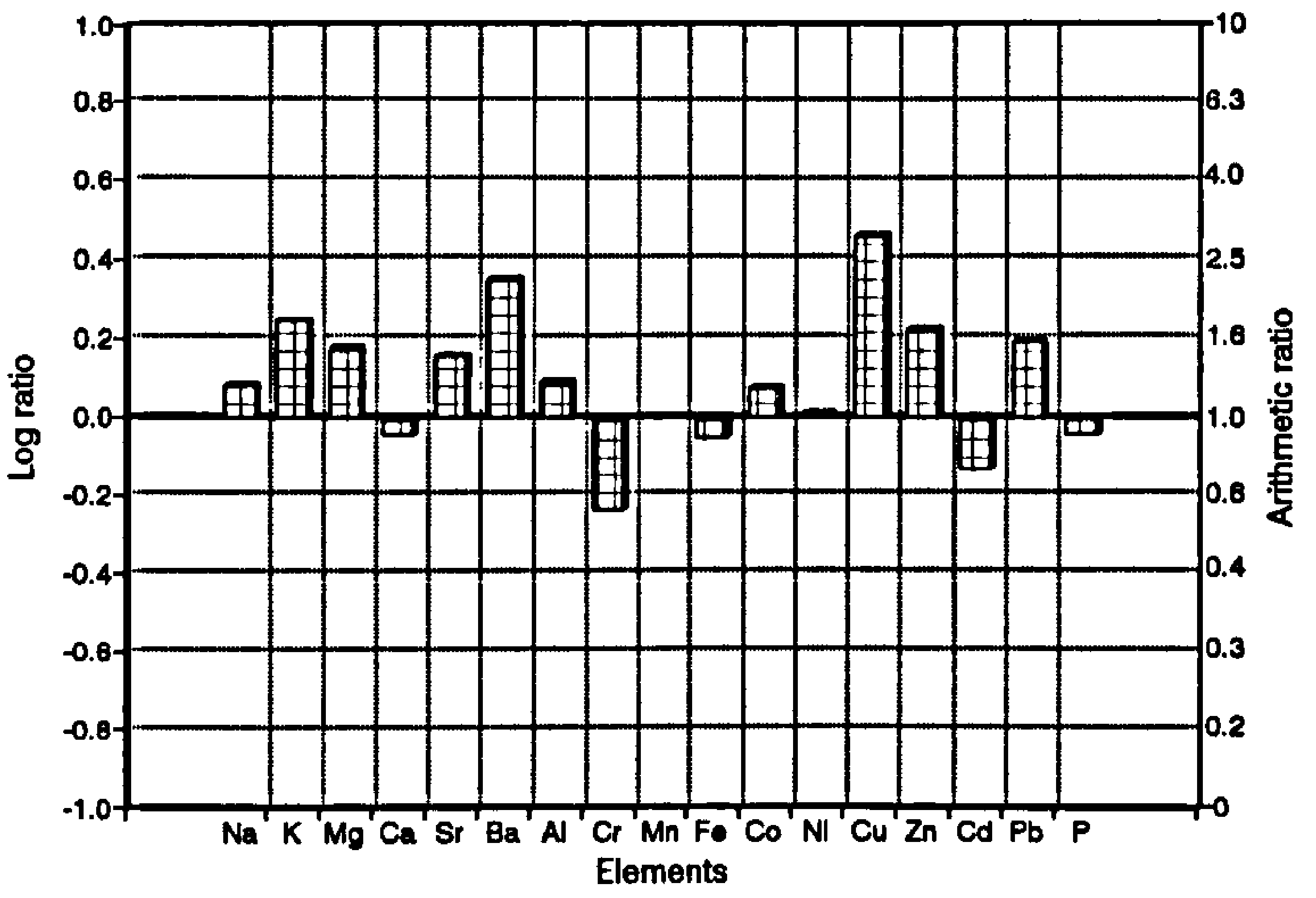


Fig. 9.1a Median concentrations of selected elements in topsoils (0-15cm) in agricultural areas overlying the Clent Formation in Wolverhampton, normalised to median concentrations for soils in England and Wales (McGrath and Loveland, 1992) and expressed on a log-scale

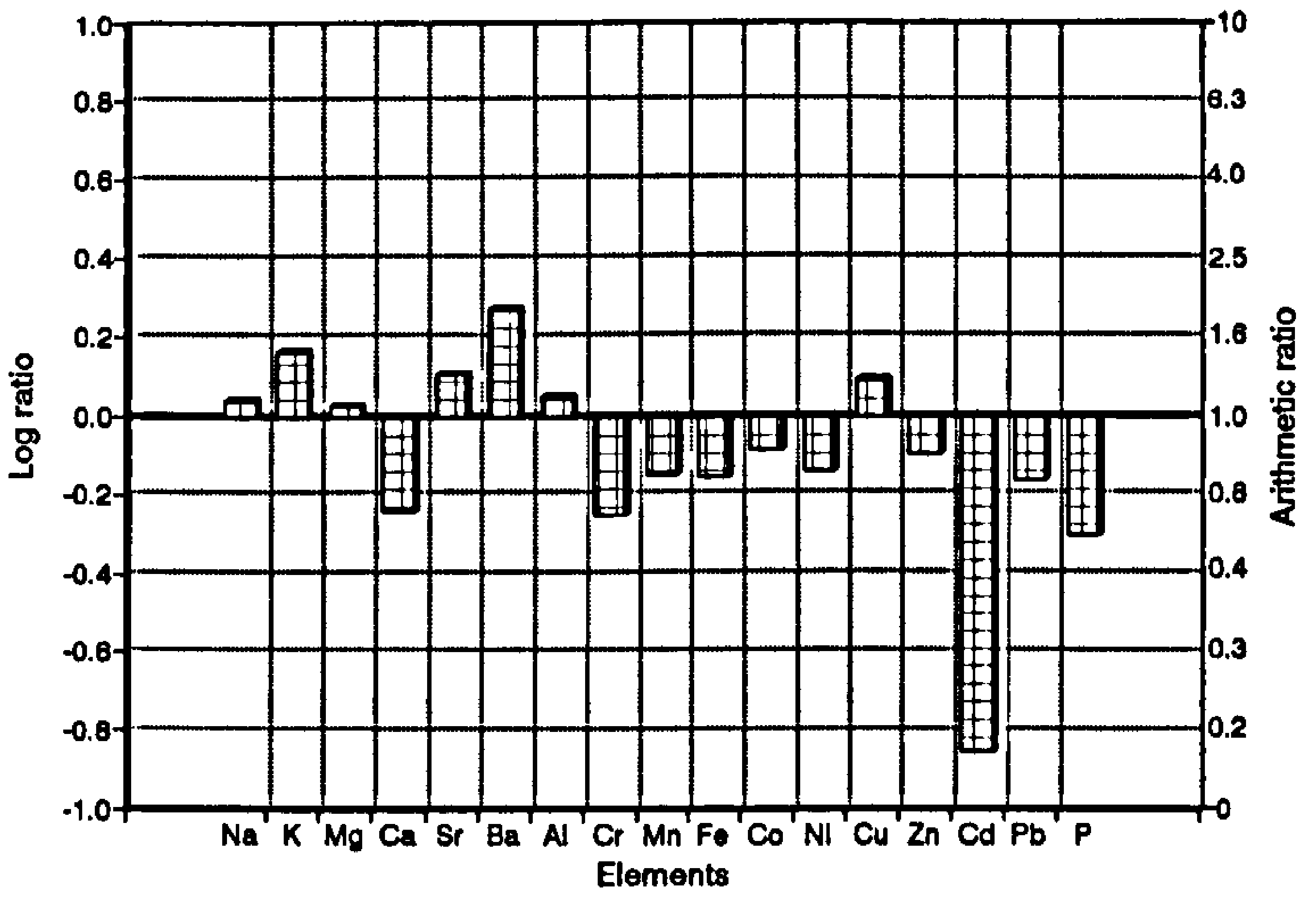


Fig. 9.1b Median concentrations of selected elements in subsurface soils (30-45cm) in agricultural areas overlying the Clent Formation in Wolverhampton, normalised to median concentrations for soils in England and Wales (McGrath and Loveland, 1992) and expressed on a log-scale

Table 9.1 Ratios of elements in soils overlying the Clent Formation, as designated by land-use, after normalisation to median concentrations for soils in England and Wales (McGrath and Loveland (1992) for soils

	topsoils	subsurface soils
	n=4	n=4
	AG	AG
Na	1.20	1.09
K	1.75	1.45
Mg	1.51	1.06
Ca	0.90	0.57
Sr	1.43	1.27
Ba	2.23	1.87
Al	1.23	1.12
Cr	0.58	0.56
Mn	1.00	0.71
Fe	0.89	0.70
Co	1.18	0.82
Ni	1.02	0.72
Cu	2.89	1.24
Zn	1.67	0.80
Cd	0.74	0.14
Pb	1.54	0.69
P	0.90	0.50

AG Soils in agricultural areas

9.2.4 Kidderminster Formation - topsoils (0-15cm) in agricultural areas

The normalisation ratios for these topsoils are shown in Fig. 9.2a and reported in Table 9.2. These sites are generally located in the north, close to the outskirts of the city. As for most of the topsoils in Wolverhampton, the highest ratios are observed for Cu (approximately 2), Zn (> 1), Pb (> 1) and P (> 1). No other element has a ratio which exceeds 1 (see Fig.9.2a). This reflects the land-use, the location of the sites and the natural geological input of these elements. This is the oldest of the Triassic rocks, and is a medium to coarse grained sandstone (see section 4.7.4.1). The ratios of most elements are lower than those for the same land-use overlying glacial-till (see Figs. 9.2a and 9.10a). The exceptions to this are Mn, Cu and P. This is probably explained by differences in soil texture

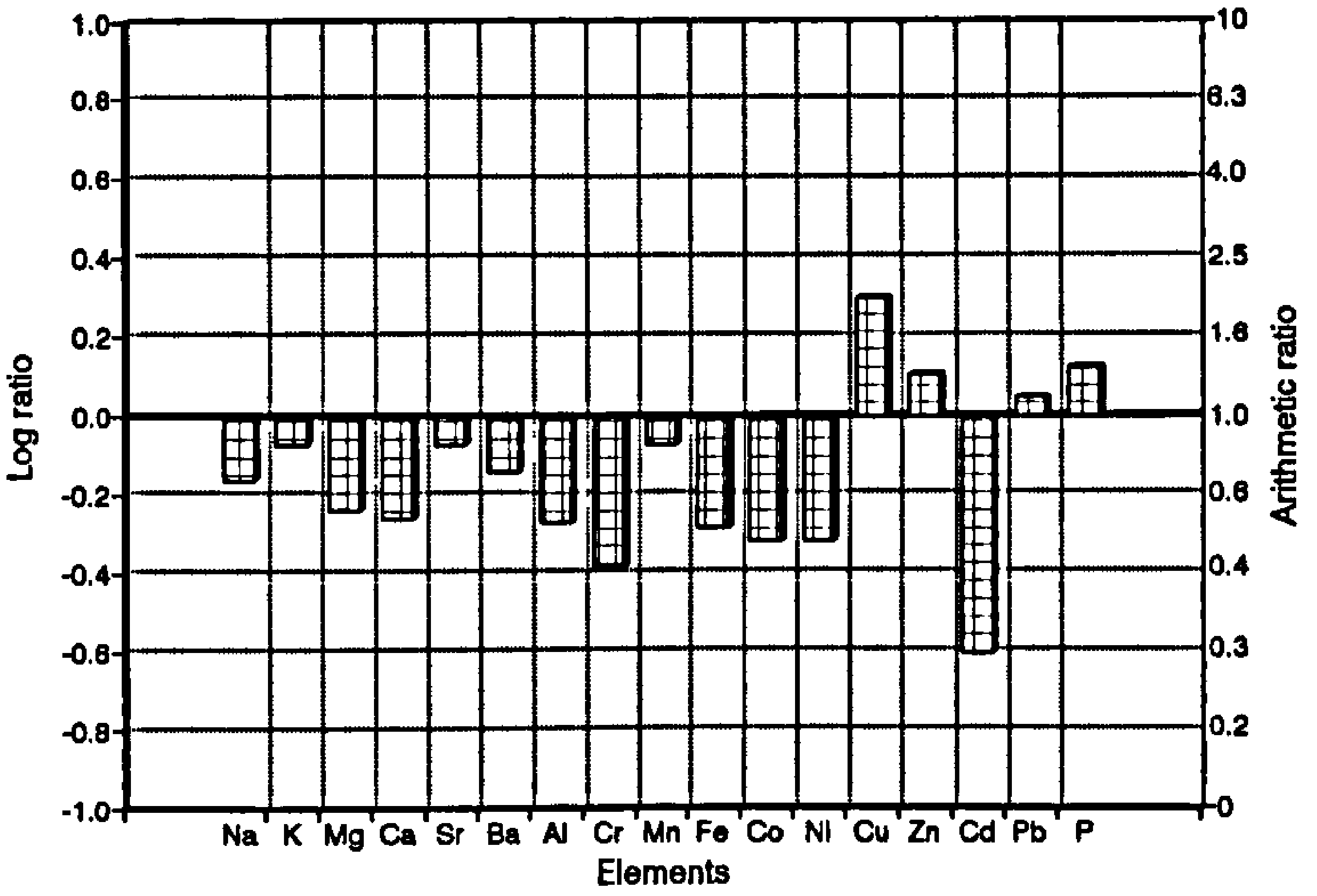


Fig. 9.2a Median concentrations of selected elements in topsoils (0-15cm) in agricultural areas overlying the Kidderminster Formation in Wolverhampton, normalised to median concentrations for soils in England and Wales (McGrath and Loveland, 1992) and expressed on a log-scale

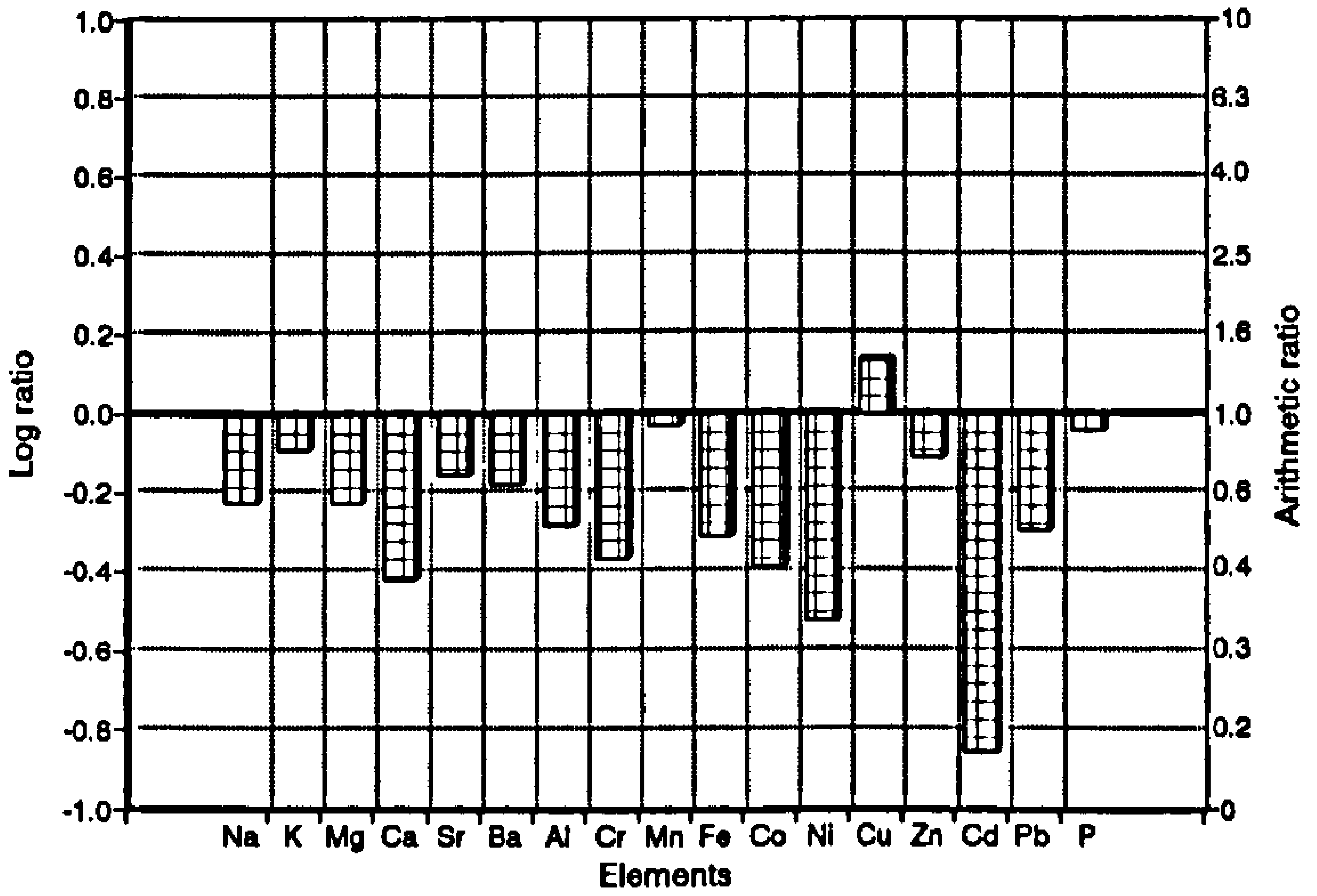


Fig. 9.2b Median concentrations of selected elements in subsurface soils (30-45cm) in agricultural areas overlying the Kidderminster Formation in Wolverhampton, normalised to median concentrations for soils in England and Wales (McGrath and Loveland, 1992) and expressed on a log-scale

associated with these deposits, with clay rich soils developing on the glacial-till and sandy soils developing on the Kidderminster Formation (see sections 4.7.5.2 and 4.7.4.1, respectively).

9.2.5 Kidderminster Formation - subsurface soils (30-45cm) in agricultural areas

The normalisation ratios for these soils are shown in Fig. 9.2b and reported in Table 9.2. In general, most elements have lower ratios in subsurface soils compared with topsoils (see Figs. 9.2a and 9.2b). In subsurface soils, only Cu has a ratio which is > 1 (1.38). Accumulation of the heavy metals in particular, is generally greater in topsoils, relative to 30-45cm. Very similar ratios are observed at depths of 0-15cm and 30-45cm for K, Mg, Cr, Al and Fe which suggests a consistent input from the geological source.

9.2.6 Kidderminster Formation - topsoils (0-15cm) in areas of open space

The normalisation ratios for these topsoils are shown in Fig. 9.3a and reported in Table 9.2. These sites overlie outcrops in the north and south of the city. The contrast with soils overlying the same parent material on agricultural sites is clear (see Figs. 9.2a and 9.3a). The highest ratios are observed for the metals Cu (> 4), Pb (> 3) and Zn (> 3). Ratios of approximately 2 are observed for Ca, Sr and Ba, with ratios of > 1 for Na, K, Mg, Co, Ni and P. The ratios for Cu, Zn and Cd are comparable to those observed for soils in industrial areas or overlying made ground. All ratios are higher in these soils than for agricultural soils overlying the Kidderminster Formation. Taking into account natural variation in the concentration range, the most important factor causing this difference is probably the location of these areas of open space. The sites in the south are close to the industrial base of the city.

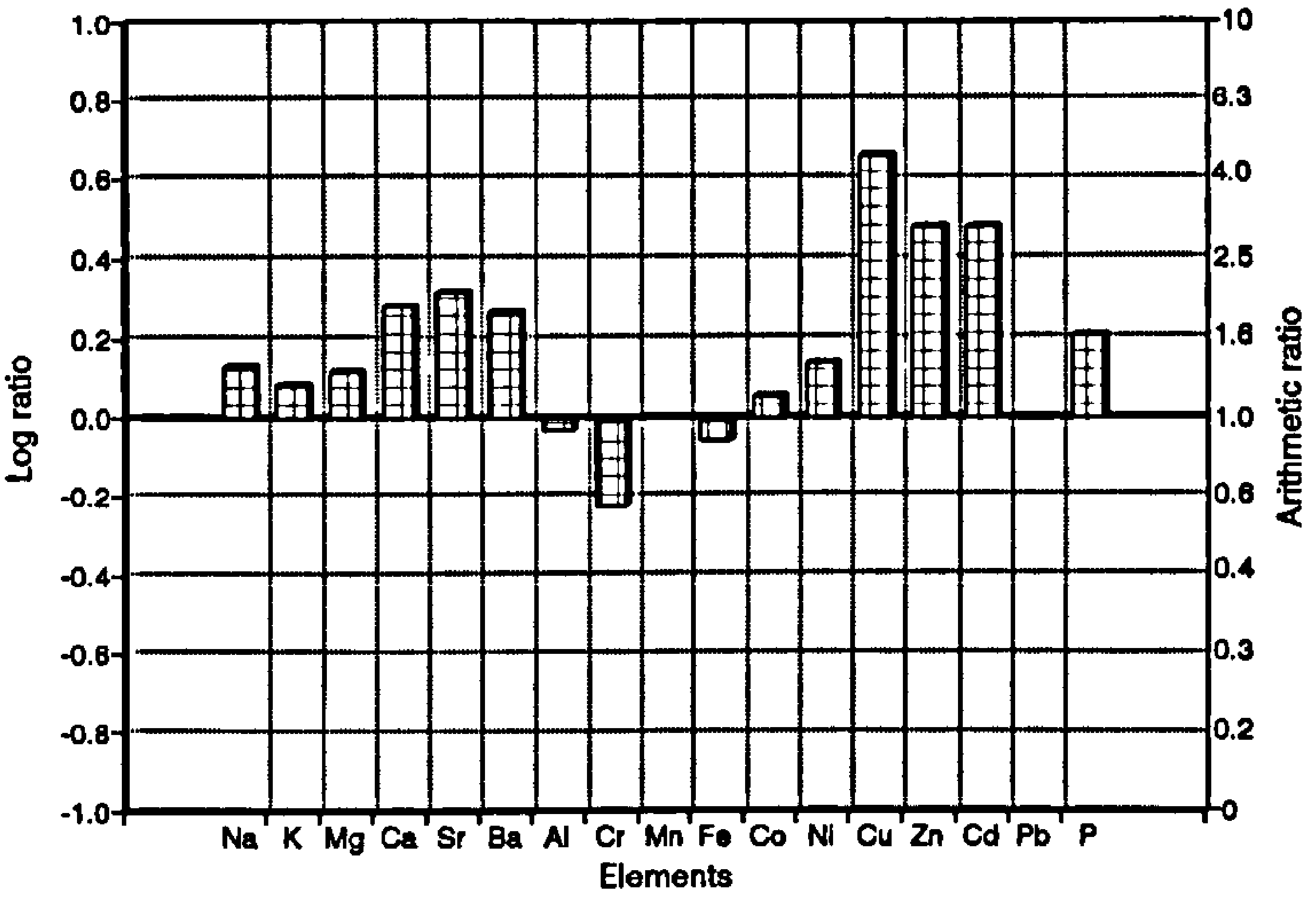


Fig. 9.3a Median concentrations of selected elements in topsoils (0-15cm) from areas of open space overlying the Kidderminster Formation in Wolverhampton, normalised to median concentrations for soils in England and Wales (McGrath and Loveland, 1992) and expressed on a log-scale

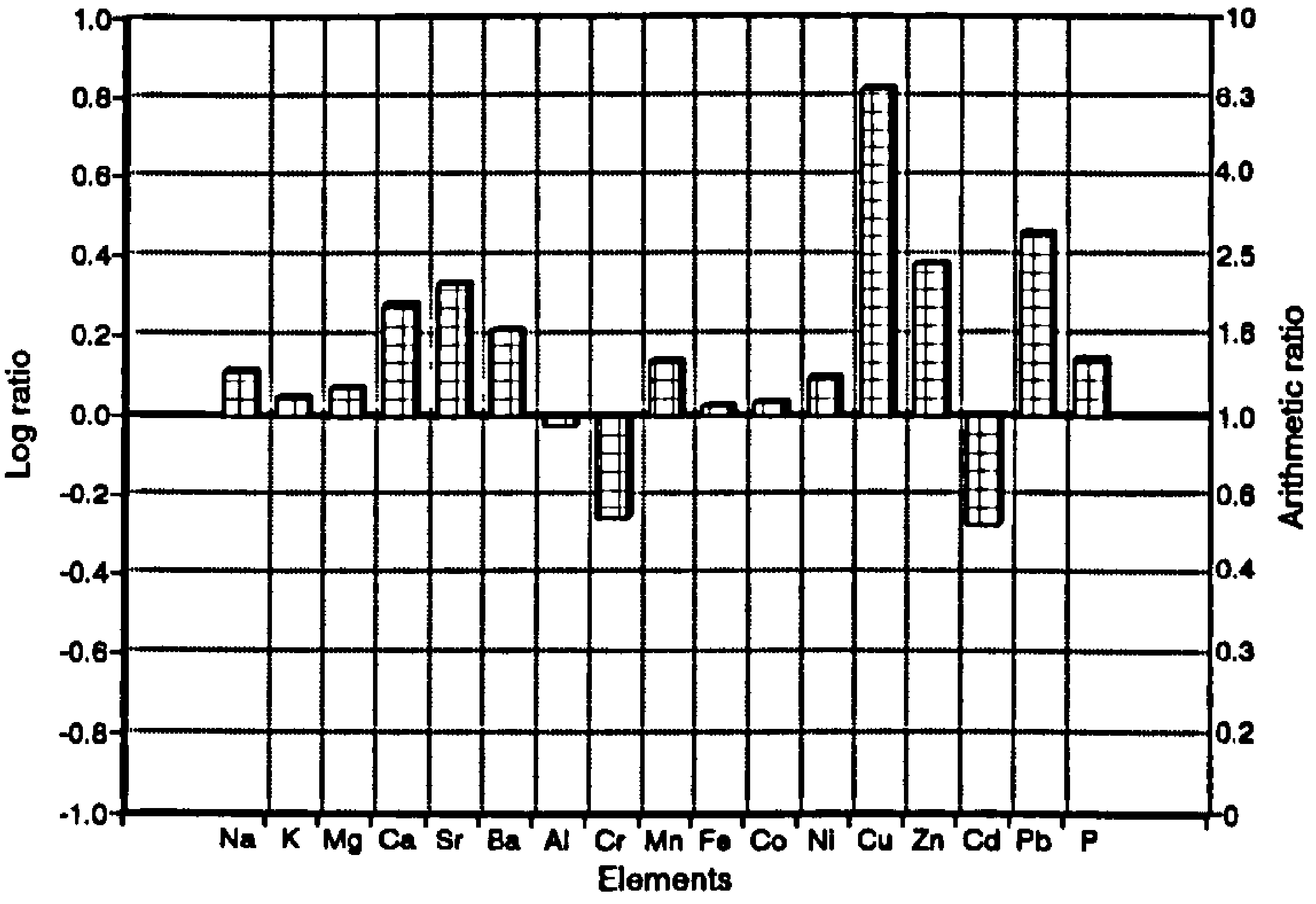


Fig. 9.3b Median concentrations of selected elements in subsurface soils (30-45cm) from areas of open space overlying the Kidderminster Formation in Wolverhampton, normalised to median concentrations for soils in England and Wales (McGrath and Loveland, 1992) and expressed on a log-scale

9.2.7 Kidderminster Formation - subsurface soils (30-45cm) in areas of open space

The normalisation ratios for these soils are shown in Fig. 9.3b and reported in Table 9.2. The overall pattern for these subsurface soils is similar to that observed for topsoils, with the highest ratios observed for Cu, Zn, Pb, Ca, Sr and Ba (see Fig. 9.3b). The ratios for Cu (> 6) and Fe (> 1) are higher than those observed for topsoils. Higher ratios for Mn and Fe in subsurface soils, relative to topsoils and may be due to natural variation in the geochemical signature (see Figs. 9.3a and 9.3b), although both of these metals are influenced by industrial activity in the city (see section 8.6.16). Ratios for Pb, Zn, Cd, Ni, Co and P are lower than those observed in topsoils which is probably due to greater accumulation of these metals in the top 15cm, relative to depths of 30-45cm.

9.2.8 Kidderminster Formation - topsoils (0-15cm) in urban gardens

The normalisation ratios for these topsoils are shown in Fig. 9.4a and reported in Table 9.2. These sites are located in the north and south-west of the city. The general pattern observed in Fig. 9.4a is fairly typical of a garden soil, both in Richmond and Wolverhampton. The highest ratios are observed for the metals Cu (> 2), Zn (2) and Pb (> 1). In Richmond, Pb was generally observed to have the highest ratio in garden soils. In Wolverhampton Cu and Pb are observed to have the highest ratios in garden soils, depending on parent material. The difference is probably explained by the industrial activity in Wolverhampton, and the general absence of industry in Richmond.

Ratios which exceed 1 are also observed for Sr, Ba, and P in Fig. 9.4a, again typical of a garden soil. With the exception of the Ca which has a ratio of 1, the ratios for all the other elements shown in Table 9.2 are < 1. This probably reflects the natural concentration range of these elements, with low anthropogenic inputs. In general, most elements have lower ratios in these soils than from areas of open space, although higher than soils from agricultural areas. In comparison with other garden soils in Wolverhampton, most ratios are lower in these soils than garden soils overlying made ground and glacial-till.

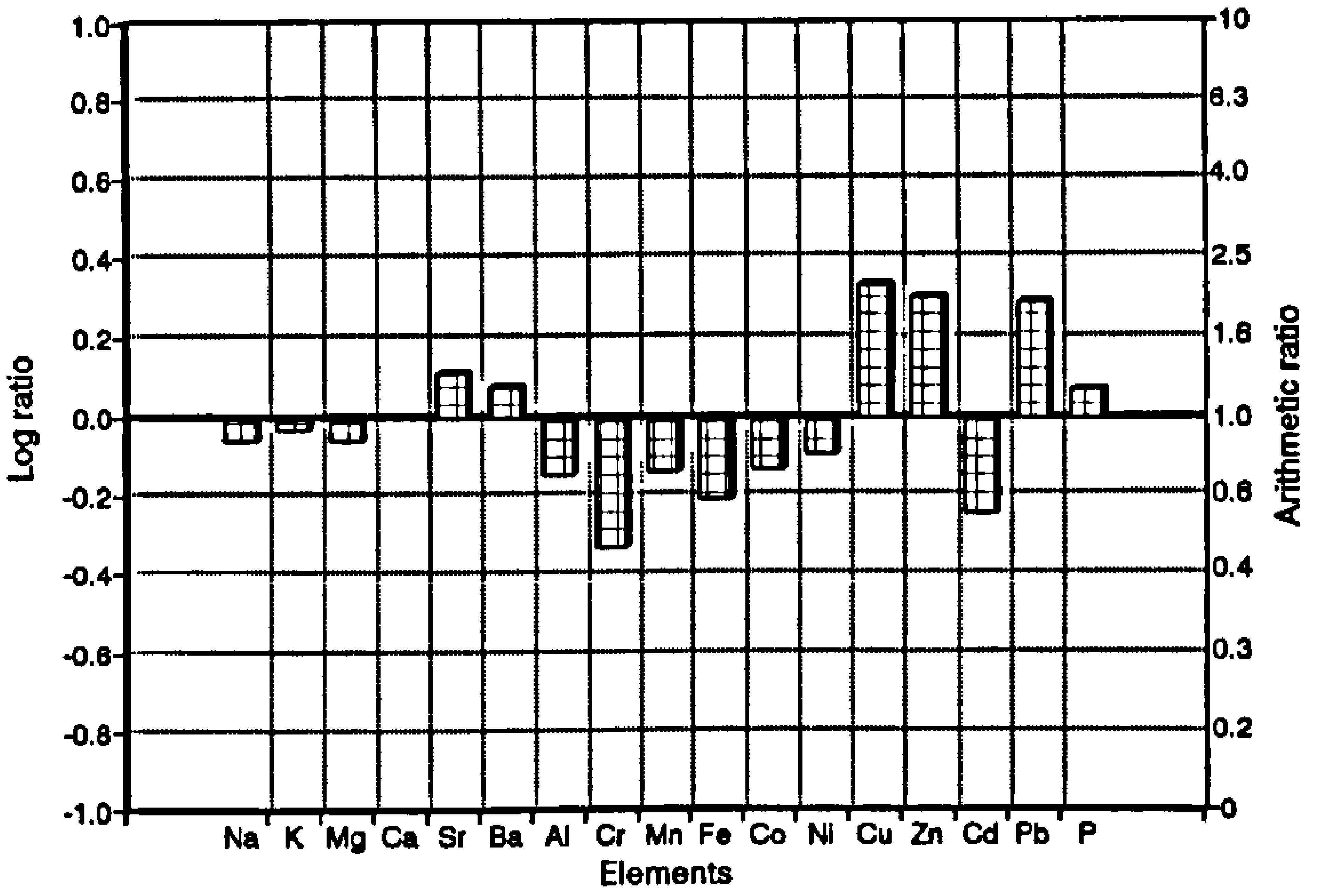


Fig. 9.4a Median concentrations of selected elements in topsoils (0-15cm) from urban gardens overlying the Kidderminster Formation in Wolverhampton, normalised to median concentrations for soils in England and Wales (McGrath and Loveland, 1992) and expressed on a log-scale

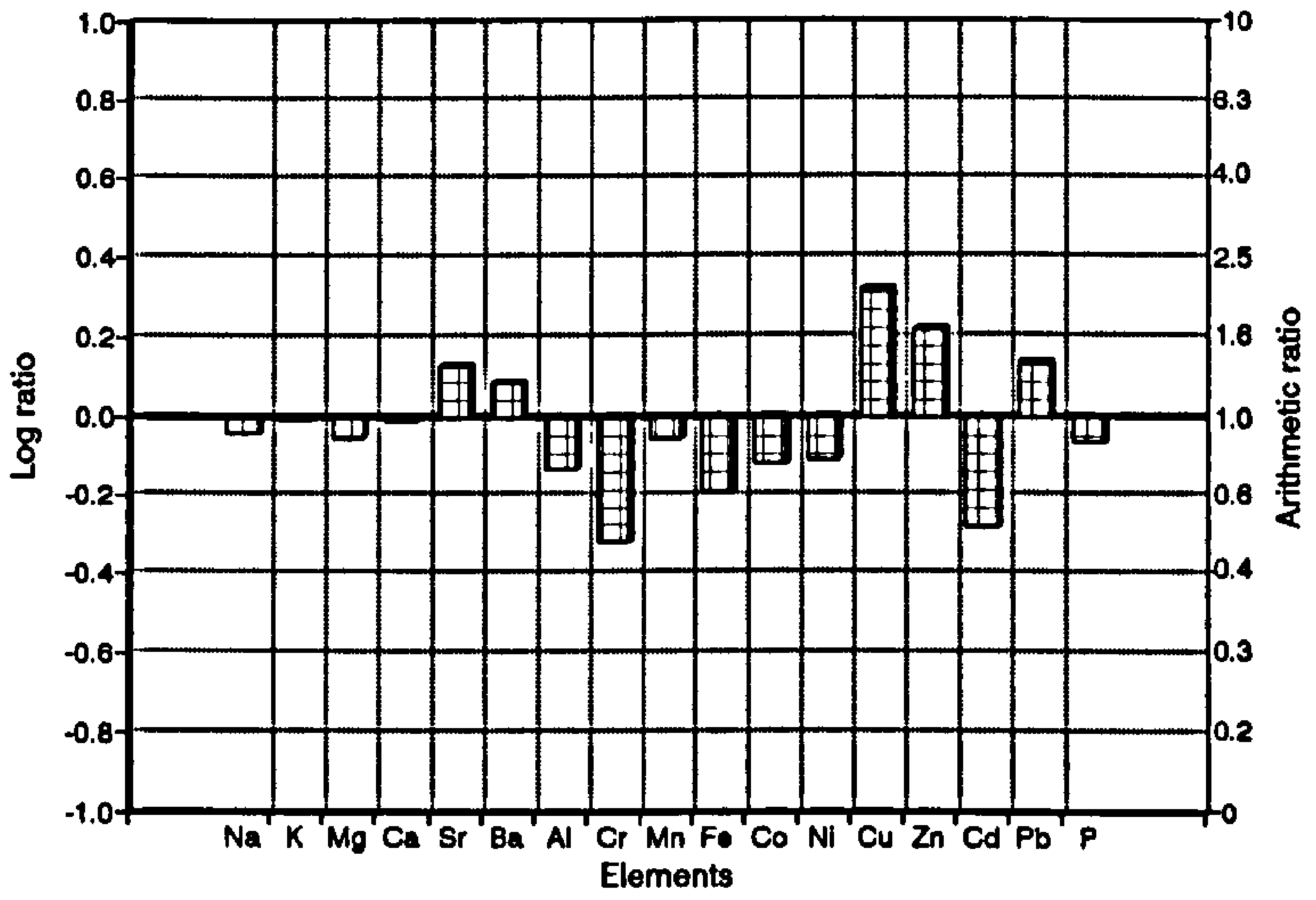


Fig. 9.4b Median concentrations of selected elements in subsurface soils (30-45cm) from urban gardens overlying the Kidderminster Formation in Wolverhampton, normalised to median concentrations for soils in England and Wales (McGrath and Loveland, 1992) and expressed on a log-scale

Table 9.2 Ratios of elements in soils overlying the Kidderminster Formation, as designated by land-use, after normalisation to median concentrations for soils in England and Wales (McGrath and Loveland 1992)

	topsoils			subsurface soils		
	n=2	n=2	n=9	n=2	n=2	n=9
	AG	OS	UG	AG	OS	UG
Na	0.69	1.35	0.87	0.60	1.28	0.91
K	0.85	1.21	0.93	0.81	1.11	0.98
Mg	0.58	1.30	0.87	0.60	1.17	0.88
Ca	0.55	1.90	1.00	0.38	1.89	0.97
Sr	0.85	2.07	1.29	0.70	2.14	1.34
Ba	0.72	1.85	1.19	0.66	1.63	1.22
Al	0.54	0.93	0.71	0.52	0.94	0.74
Cr	0.41	0.60	0.47	0.43	0.55	0.48
Mn	0.85	1.00	0.72	0.93	1.37	0.88
Fe	0.52	0.88	0.62	0.49	1.05	0.64
Co	0.48	1.13	0.73	0.41	1.08	0.76
Ni	0.48	1.38	0.80	0.30	1.24	0.78
Cu	1.99	4.53	2.15	1.38	6.70	2.10
Zn	1.27	3.03	2.00	0.77	2.40	1.65
Cd	0.25	0.99	0.57	0.14	0.53	0.52
Pb	1.11	3.03	1.95	0.51	2.86	1.38
P	1.32	1.60	1.17	0.91	1.39	0.86

AG	Soils in agricultural areas	OS	Soils in areas of open space
UG	Soils from urban gardens		

9.2.9 Kidderminster Formation - subsurface soils (30-45cm) in urban gardens

The normalisation ratios for these soils are shown in Fig. 9.4b and reported in Table 9.2. The pattern shown in Fig. 9.4b is similar to that for topsoils, with the highest ratios for the metals Cu (> 2), Zn (> 1) and Pb (> 1). The ratios of these metals, and those of Cd and P are lower than those for topsoils, suggesting greater accumulation of these in the top 15cm relative to depths of 30-45cm. This is a common trend for garden soils in Wolverhampton and Richmond. Ratios which exceed 1 are also observed for Sr and Ba which are similar to those for topsoils. Most of the other elements have similar ratios to those observed for topsoils (see Figs. 9.4a and 9.4b), which may reflect a consistent geochemical signature.

9.2.10 Wildmoor sandstone - topsoils (0-15cm) in areas of open space

The normalisation ratios for these topsoils are shown in Fig. 9.5a and reported in Table 9.3. These sites are mainly located in the west in the city, away from the industrial base located in the east. This outcrop is characterised by the distinctive red-brown sandy soils which develop over it (see section 4.7.4.2 for details). The pattern shown in Fig. 9.5a has certain characteristics which are common to many soils in Wolverhampton. The highest ratios are observed for the metals Pb (> 2), Cu (1.76) and Zn (1.67), with ratios > 1 also observed for P, Sr and Ca. The ratios for all the other elements shown in Fig. 9.5a are all < 1. The ratios for this parent material are generally lower than those observed for other parent materials associated with this land-use (see Figs. 9.3a, 9.7a, 9.10a, 9.13a, 9.15a and 9.17a). This is probably a result of the location of these sites at the western outskirts of the city, and naturally low concentrations of many elements due to the sandy parent material. The west of Wolverhampton has never been associated with industrial activity, so the areas of open space in this area are not redeveloped from industrial wasteland.

9.2.11 Wildmoor sandstone - subsurface soils (30-45cm) in areas of open space

The normalisation ratios for these soils are shown in Fig. 9.5b and reported in Table 9.3. The overall pattern shown in Fig. 9.5b is very similar to that observed for topsoils. The same elements have ratios which are > 1 at depths of 30-45cm as at depths of 0-15cm (Cu, Zn, Pb, P, Ca and Sr). These ratios are however, lower than those observed for topsoils, which probably results from greater accumulation of these elements in the top 15cm, relative to depths of 30-45cm. Similar ratios are observed for Na, K, Mg, Ba, Al, Cr, Mn, Fe and Co at both sample depths which is probably the result of a consistent geochemical signature and minimal anthropogenic inputs.

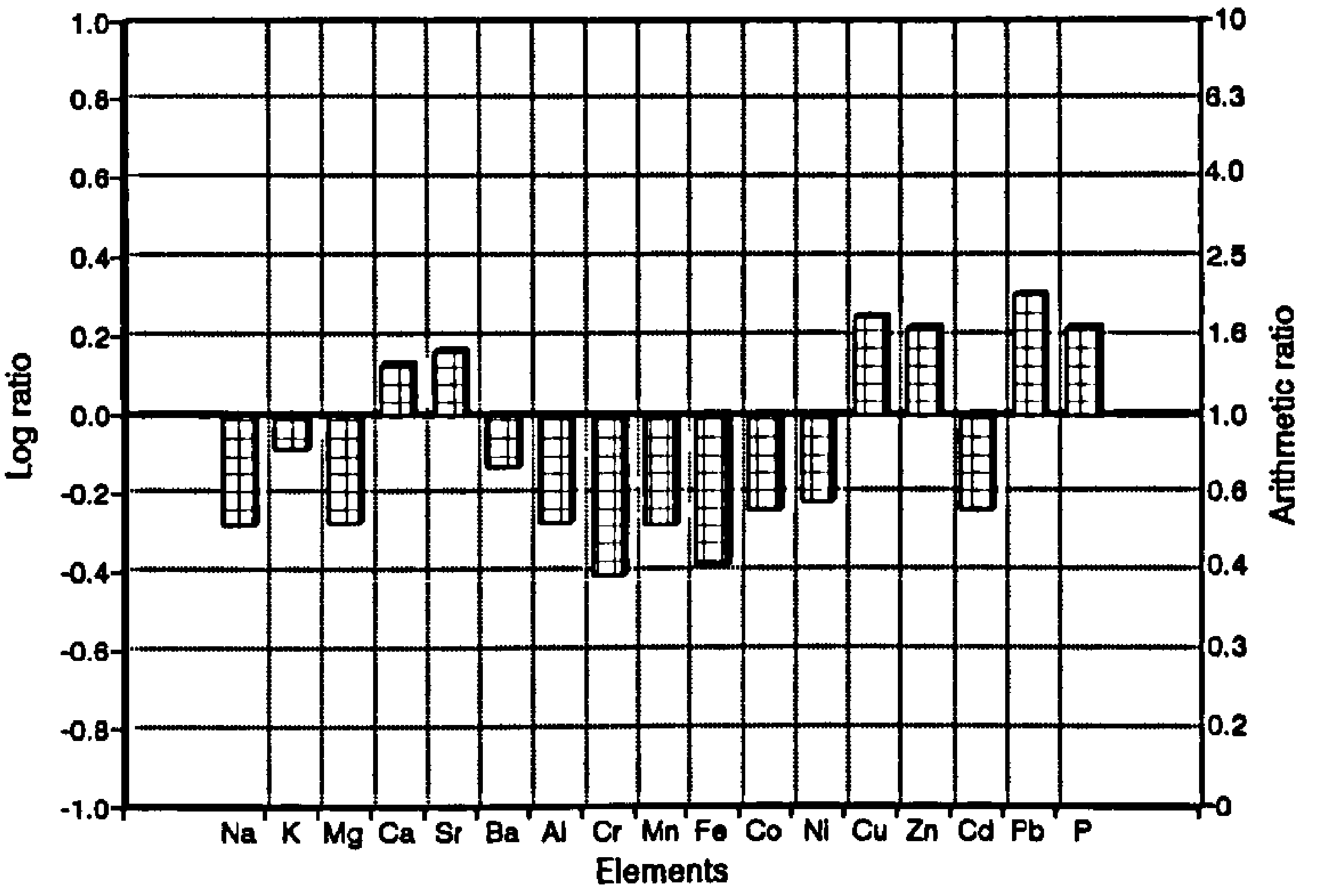


Fig. 9.5a Median concentrations of selected elements in topsoils (0-15cm) from areas of open space overlying Wildmoor sandstone in Wolverhampton, normalised to median concentrations for soils in England and Wales (McGrath and Loveland, 1992) and expressed on a log-scale

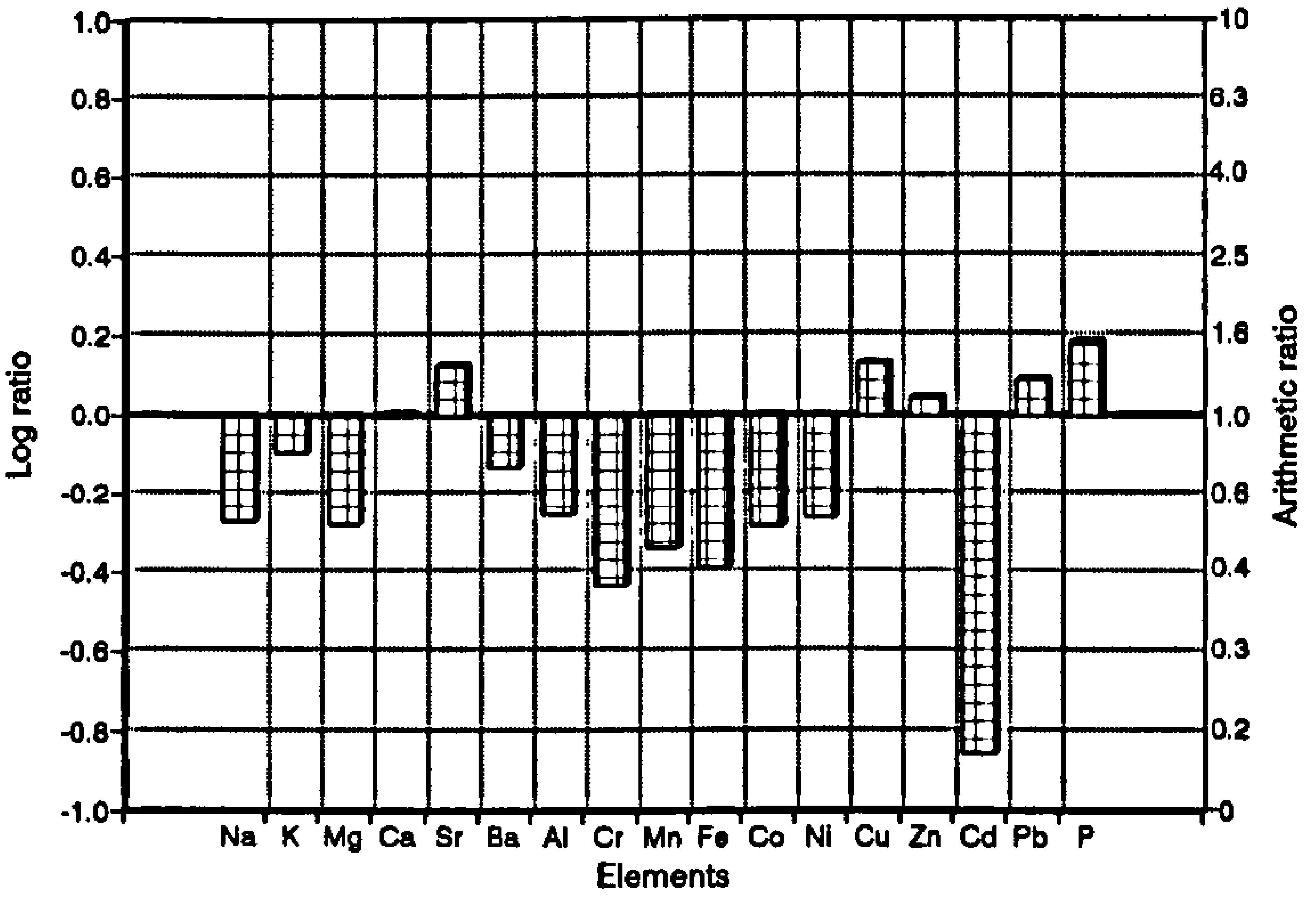


Fig. 9.5b Median concentrations of selected elements in subsurface soils (30-45cm) from areas of open space overlying Wildmoor sandstone in Wolverhampton, normalised to median concentrations for soils in England and Wales (McGrath and Loveland, 1992) and expressed on a log-scale

9.2.12 Wildmoor sandstone - topsoils (0-15cm) in urban gardens

The normalisation ratios for these topsoils are shown in Fig. 9.6a and reported in Table 9.3. These sites are mainly located in the west and south-west of the city, with those in the south-west close to areas of industrial activity. The pattern observed in Fig. 9.6a is, in general, similar to that for most topsoils in the city, with the highest ratios for the metals Pb (> 2), Zn (> 2) and Cu (> 2). Ratios exceeding 1 are also observed for Na, Mg, Ca, Sr, Ba and P. With the exception of Mg, these ratios are commonly observed for garden soils in Wolverhampton and Richmond.

In general, although the overall pattern shown in Fig. 9.6a is similar to that for the same parent material in areas of open space, ratios for garden soils are generally higher (those for Na and Ba are over 2 times higher). This is probably the result of the location of some of these gardens in areas close to past and present industrial activity. However, urban gardens also have specific sources of a suite of elements (see Tables 3.1 and 3.2) which are less important in areas of open space.

9.2.13 Wildmoor sandstone - subsurface soils (30-45cm) in urban gardens

The normalisation ratios for these soils are shown in Fig. 9.6b and reported in Table 9.3. The pattern shown in Fig. 9.6b shows that most elements have lower ratios at depths of 30-45cm than 0-15cm. Copper, Zn, Sr and Ba are the only elements that have ratios which exceed 1, with the highest ratio being Cu (1.39). With the exception of K, Al and Mn which have very similar ratios at both depths, the lower ratios at depths of 30-45cm probably reflect greater accumulation of a suite of elements in the top 15cm, from anthropogenic inputs. The consistent ratios of K, Al and Mn probably best reflect the natural geochemical signature for this parent material.

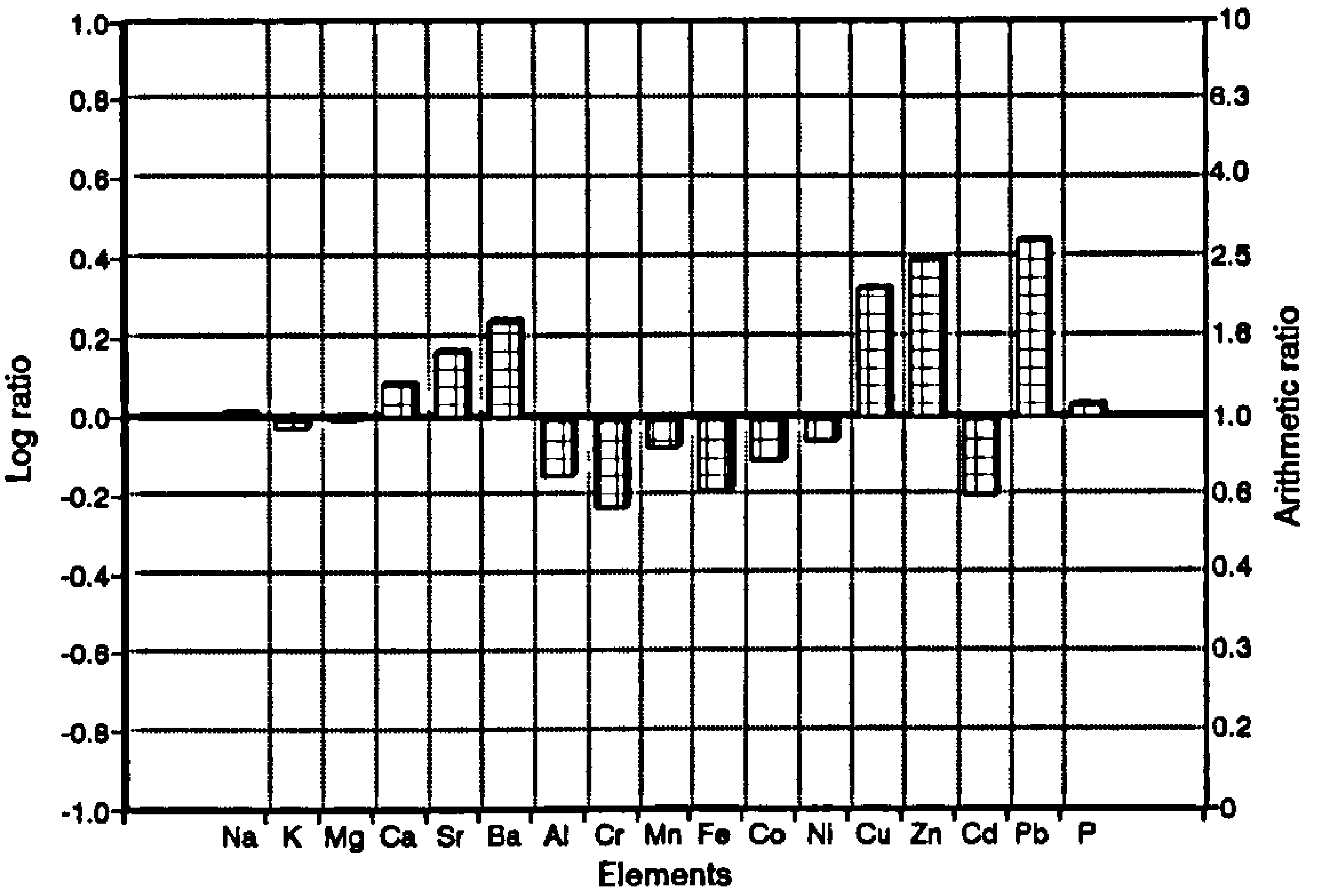


Fig. 9.6a Median concentrations of selected elements in topsoils (0-15cm) from urban gardens overlying Wildmoor sandstone in Wolverhampton, normalised to median concentrations for soils in England and Wales (McGrath and Loveland, 1992) and expressed on a log-scale

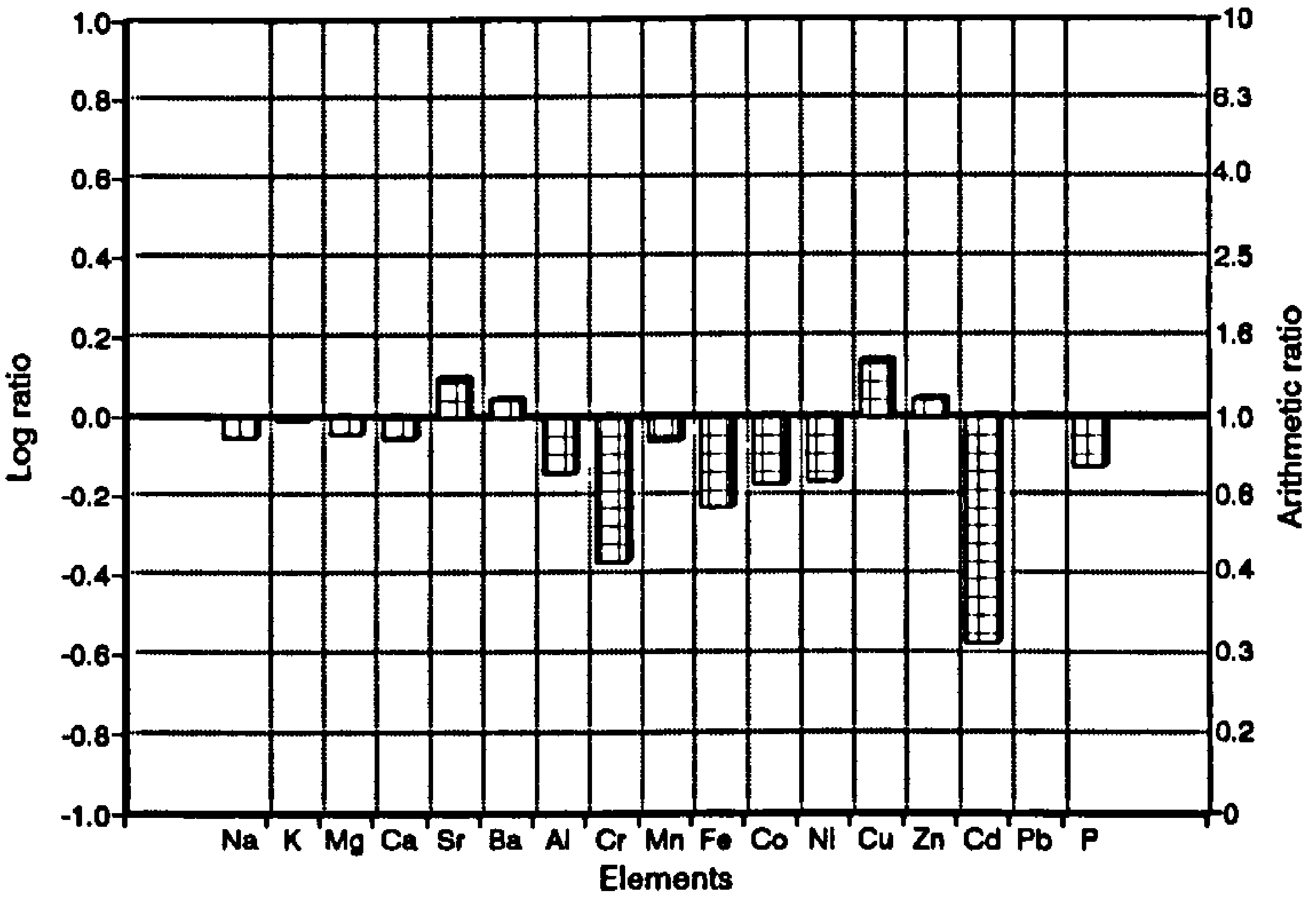


Fig. 9.6b Median concentrations of selected elements in subsurface soils (30-45cm) from urban gardens overlying Wildmoor sandstone in Wolverhampton, normalised to median concentrations for soils in England and Wales (McGrath and Loveland, 1992) and expressed on a log-scale

Table 9.3 Ratios of elements in soils overlying Wildmoor Sandstone, as designated by land-use, after normalisation to median concentrations for soils in England and Wales (McGrath and Loveland, 1992)

	topsoils		subsurface soils	
	n=3	n=9	n=3	n=9
	OS	UG	OS	UG
Na	0.52	1.03	0.54	0.89
K	0.82	0.94	0.80	0.97
Mg	0.53	1.01	0.53	0.90
Ca	1.35	1.21	1.01	0.88
Sr	1.45	1.46	1.33	1.25
Ba	0.74	1.73	0.74	1.10
Al	0.53	0.71	0.56	0.72
Cr	0.39	0.59	0.37	0.43
Mn	0.52	0.84	0.46	0.87
Fe	0.41	0.65	0.41	0.59
Co	0.57	0.78	0.52	0.68
Ni	0.60	0.87	0.55	0.69
Cu	1.77	2.11	1.36	1.39
Zn	1.67	2.47	1.11	1.10
Cd	0.57	0.63	0.14	0.27
Pb	2.02	2.77	1.23	1.00
P	1.67	1.07	1.53	0.75

OS Soils in areas of open space UG Soils from urban gardens

9.2.14 Bromsgrove sandstone - topsoils (0-15cm) in areas of open space

The normalisation ratios for these topsoils are shown in Fig. 9.7a and reported in Table 9.4. These sites are mainly located in the western outskirts of the city. These soils overlie the youngest Triassic rocks which are described as a red-brown sandstone (see section 4.7.4.3). Copper, Zn, Pb and P are the only elements which have ratios > 1 (1.74, 1.43, 2.2 and 1.01, respectively - see Table 9.4). This reflects the location of these site in the western extremes of the city, well away from the industrial base. In comparison with areas of open space overlying glacial-till, made ground, alluvium and the kidderminster formation, the ratios for most elements are lower. This is probably a result of naturally low concentrations of these elements and few anthropogenic additions, as a consequence of the land-use and the distance from the industrial base.

9.2.15 Bromsgrove sandstone - subsurface soils (30-45cm) in areas of open space

The normalisation ratios for these soils are shown in Fig. 9.7b and reported in Table 9.4. The ratios for the metals Cu, Zn, Cd, Pb and P, in particular show a decrease at depths of 30-45cm, compared to the top 15cm. The is probably the result of greater accumulation of these metals in the top 15cm of the profile from anthropogenic activity. The ratios for these metals are all < 1 in subsurface soils. In contrast to topsoils, K, Mg, and Mn have ratios greater than 1 for subsurface soils, and these along with Sr, Ba, Al, Fe and Co have higher ratios at depths of 30-45cm than 0-15cm. This is probably due to natural variation of the geochemical signature.

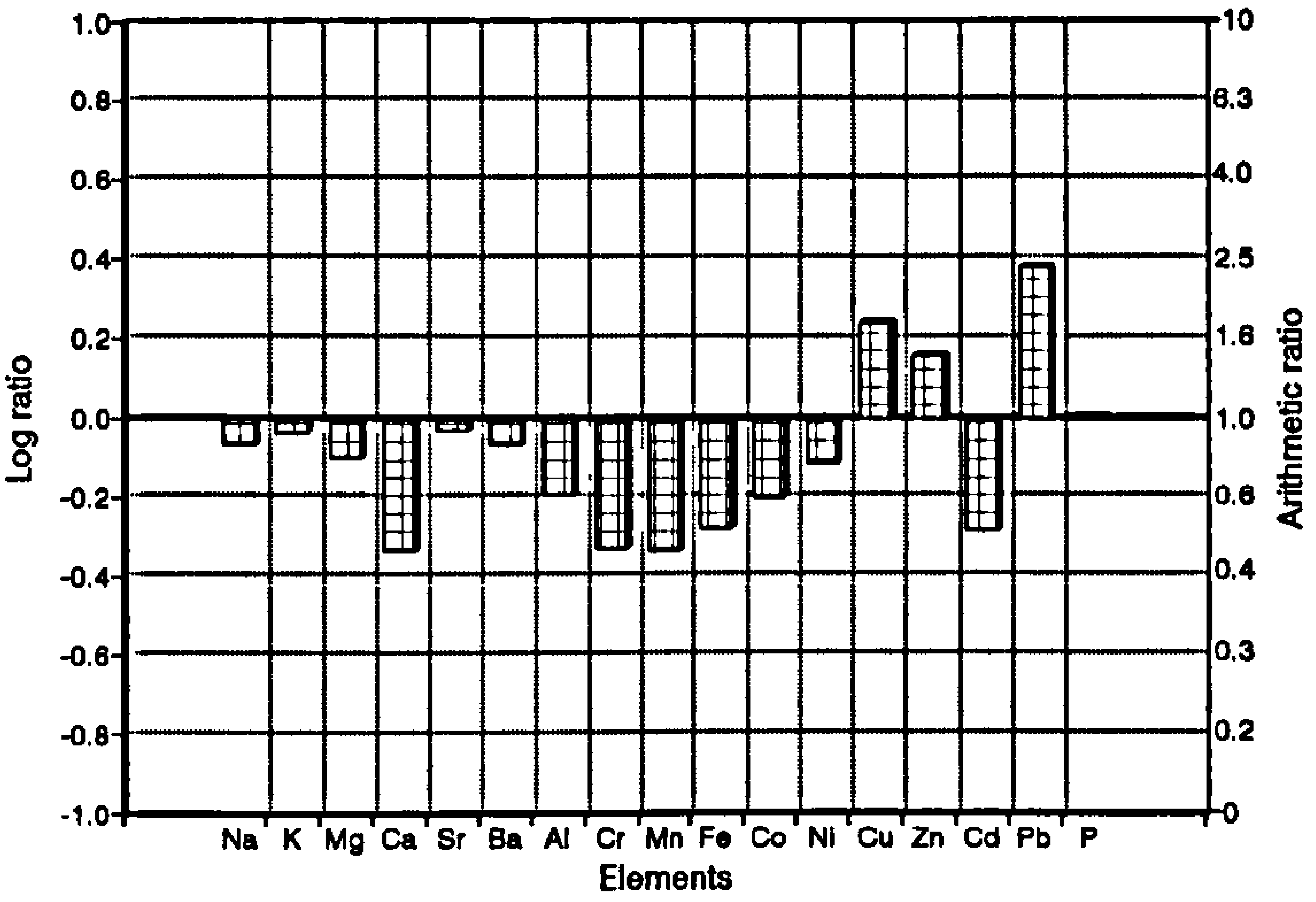


Fig. 9.7a Median concentrations of selected elements in topsoils (0-15cm) from areas of open space overlying Bromsgrove sandstone in Wolverhampton, normalised to median concentrations for soils in England and Wales (McGrath and Loveland, 1992) and expressed on a log-scale

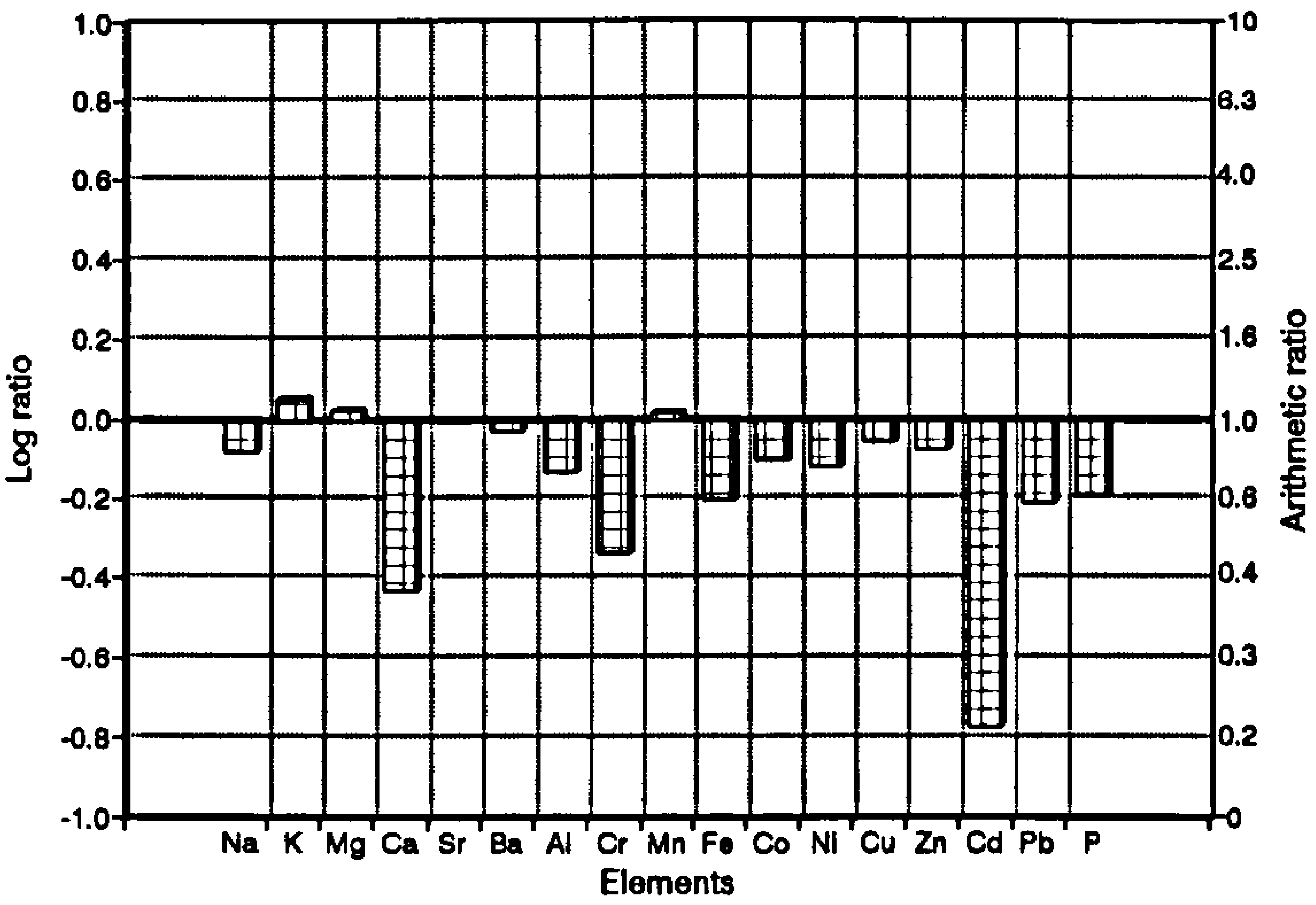


Fig. 9.7b Median concentrations of selected elements in subsurface soils (30-45cm) from areas of open space overlying Bromsgrove sandstone in Wolverhampton, normalised to median concentrations for soils in England and Wales (McGrath and Loveland, 1992) and expressed on a log-scale

9.2.16 Bromsgrove sandstone - topsoils (0-15cm) in urban gardens

The normalisation ratios for these topsoils are shown in Fig. 9.8a and reported in Table 9.4. These sites are generally located in the west, with a few sites in the south-west. The pattern shown in Fig. 9.8a is similar, in certain respects, to that observed for the same parent material in areas of open space. Ratios for Cu, Zn and Pb are all > 1, > 2 in the case of Pb. Ratios for Pb and Cu are comparable with those for areas of open space, probably as a consequence of both land-uses having a similar proximity to the industrial base. Ratios for Sr, Ba and P are also > 1 in these soils, something not observed in areas of open space. This suggests sources which are more important in urban gardens, such as building materials, paint and the application of fertilisers, although some variation of the natural geochemical signature may also be important. Higher ratios of these elements are common for garden soils in Richmond compared with areas of open space (see section 7.2 in general).

Although no other element has a ratio of > 1 in these garden soils, the ratios are generally higher than those observed for topsoils overlying Bromsgrove sandstone in areas of open space (see Figs. 9.7a and 9.8a). This may be a result of natural variation in the geochemical signature or minor anthropogenic additions.

9.2.17 Bromsgrove sandstone - subsurface soils (30-45cm) in urban gardens

The normalisation ratios for these soils are shown in Fig. 9.8b and reported in Table 9.4. The general pattern for subsurface soils is similar to that for topsoils (see Figs. 9.8a and 9.8b). The metals Cu, Zn and Pb and Ca and Sr are the only elements which have ratios that exceed 1. The highest of these is 1.73 for Pb. The ratios for these are lower than those observed in topsoils, probably reflecting greater accumulation in the top 15cm, relative to depths of 30-45cm. In general most elements have higher ratios in topsoils for this category, with similar ratios for K, Al, and Fe. The higher ratios in topsoils for metals such as Sr and Ba are probably due to greater accumulation from anthropogenic activities. Small variations in the ratios of K, Al and Fe are probably due to natural variation of the geochemical signature.

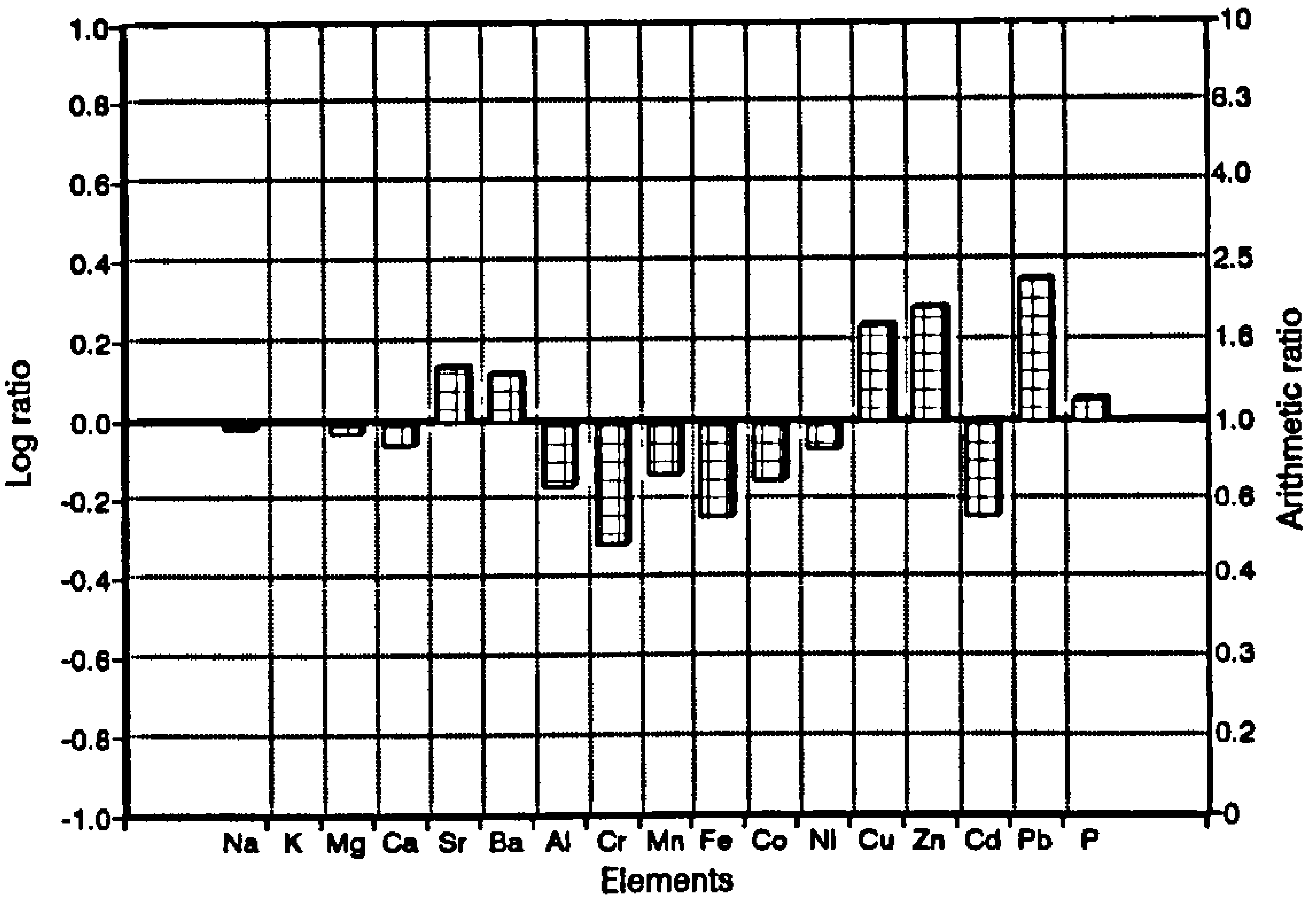


Fig. 9.8a Median concentrations of selected elements in topsoils (0-15cm) from urban gardens overlying Bromsgrove sandstone in Wolverhampton, normalised to median concentrations for soils in England and Wales (McGrath and Loveland, 1992) and expressed on a log-scale

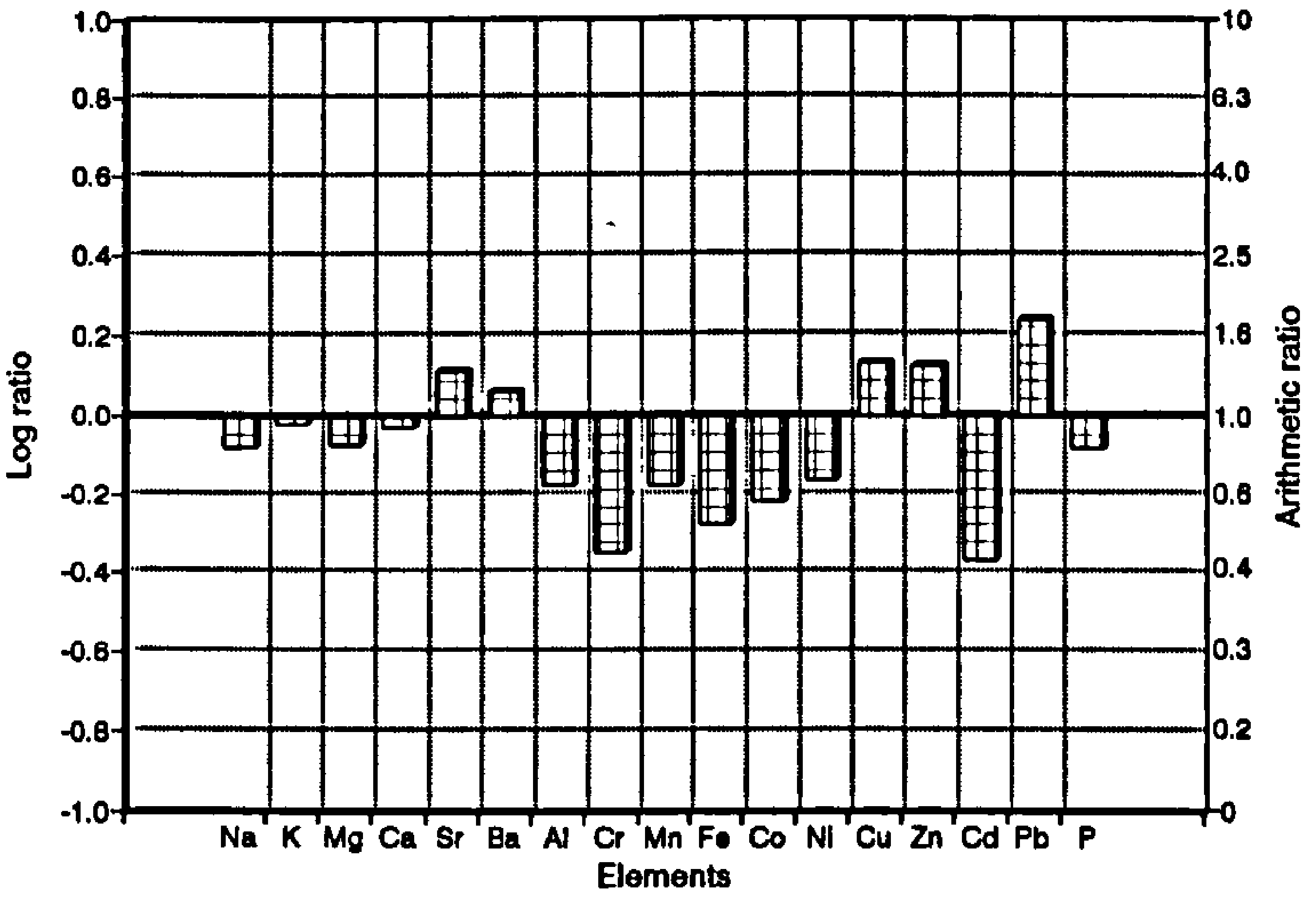


Fig. 9.8b Median concentrations of selected elements in subsurface soils (30-45cm) from urban gardens overlying Bromsgrove sandstone in Wolverhampton, normalised to median concentrations for soils in England and Wales (McGrath and Loveland, 1992) and expressed on a log-scale

Table 9.4 Ratios of elements in soils overlying Bromsgrove Sandstone, as designated by land-use, after normalisation to median concentrations for soils in England and Wales (McGrath and Loveland, 1992)

	topsoils		subsurface soils	
	n=5	n=12	n=5	n=12
	OS	UG	OS	UG
Na	0.86	0.96	0.83	0.83
K	0.92	1.00	1.13	0.95
Mg	0.80	0.93	1.05	0.84
Ca	0.46	0.87	0.37	0.93
Sr	0.93	1.37	0.99	1.29
Ba	0.86	1.31	0.94	1.14
Al	0.64	0.69	0.74	0.67
Cr	0.47	0.49	0.46	0.45
Mn	0.46	0.73	1.04	0.67
Fe	0.53	0.57	0.63	0.53
Co	0.63	0.71	0.79	0.61
Ni	0.77	0.85	0.76	0.69
Cu	1.74	1.74	0.88	1.36
Zn	1.43	1.91	0.84	1.33
Cd	0.52	0.57	0.17	0.43
Pb	2.40	2.26	0.62	1.73
P	1.01	1.13	0.64	0.82

OS Soils in areas of open space UG Soils from urban gardens

9.2.18 Glacial-till - topsoils (0-15cm) in agricultural areas

The normalisation ratios for these topsoils are shown in Fig. 9.9a and reported in Table 9.5. These sites are mainly located in the northern outskirts of the city. This deposit covers most of Wolverhampton, with borehole evidence suggesting the matrix is very homogenous with the majority defined as silty clay sands (see section 4.7.5.2). As for most soils in Wolverhampton, the highest ratios are observed for Zn, Cu (> 2) and Pb which suggests accumulation of these metals from industrial emissions. These ratios are generally lower than for topsoils in other land-use categories, which is probably due to the location of the agricultural sites at the outskirts of the city. Ratios of > 1 are also observed for K, Ca, Sr, Ba, and P. These are also generally lower than for topsoils associated with other land-uses in Wolverhampton. The other elements shown in Fig 9.9a have ratios of < 1, and ratios of < 1 for Al, Cr, Mn, Fe and Co are common to soils overlying glacial-till in Wolverhampton (see Table 9.5).

9.2.19 Glacial-till - subsurface soils (30-45cm) in agricultural areas

The normalisation ratios for these soils are shown in Fig. 9.9b and reported in Table 9.5. The pattern observed for these soils is different to those for the other subsurface soils examined so far in Wolverhampton. Only K, Mg, Sr, Ba and Cu have ratios of > 1, the highest of these being Mg (1.32) and K (1.29). Anthropogenic additions of most elements to soils of this land-use and depth are low. With the exception of K, Mg, Al and Cr the ratios of elements for this category are generally lower than for samples of the same depth overlying glacial-till associated with industrial activity, urban gardens and areas of open space (see Table 9.5). As for other subsurface soils overlying glacial-till, ratios of Na, K, Mg, Al and Fe, in this particular case, are higher at depths of 30-45cm than in topsoils. This is a diagnostic feature of soils overlying glacial-till and probably reflects some natural variation of the geochemical signature.

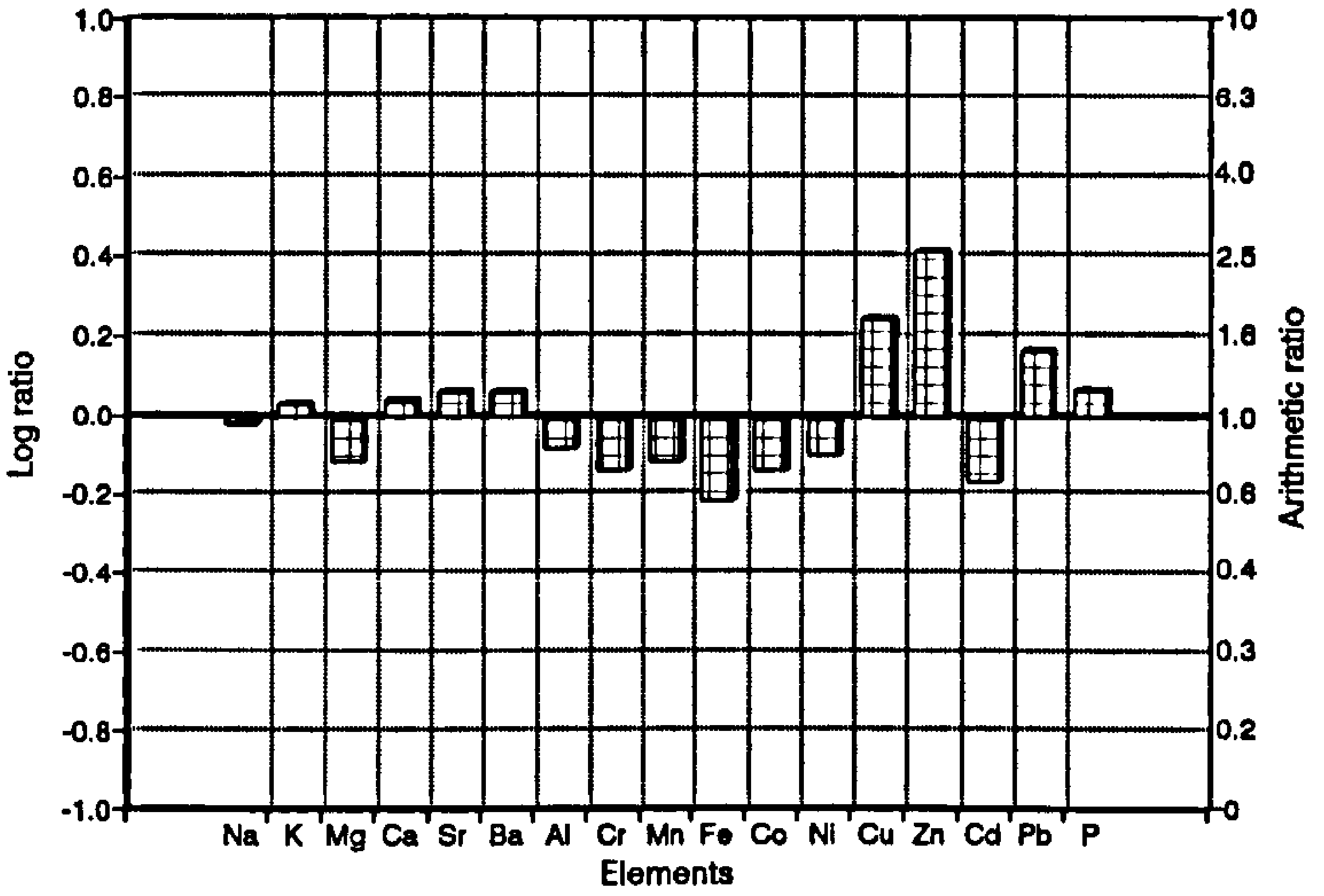


Fig. 9.9a Median concentrations of selected elements in topsoils (0-15cm) from agricultural areas overlying glacial-till in Wolverhampton, normalised to median concentrations for soils in England and Wales (McGrath and Loveland, 1992) and expressed on a log-scale

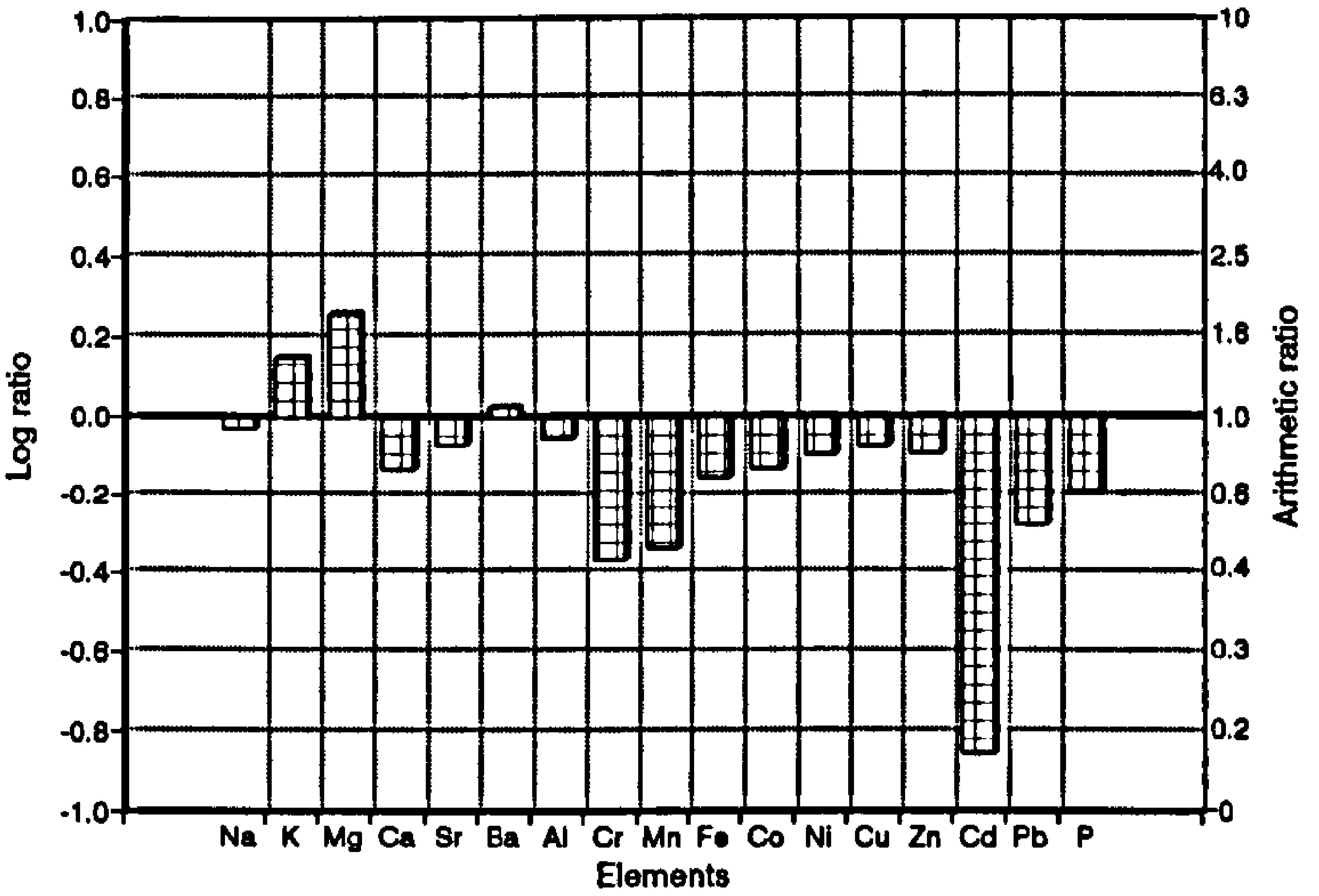


Fig. 9.9b Median concentrations of selected elements in subsurface soils (30-45cm) from agricultural areas overlying glacial-till in Wolverhampton, normalised to median concentrations for soils in England and Wales (McGrath and Loveland, 1992) and expressed on a log-scale

9.2.20 Glacial-till - topsoils (0-15cm) in areas of open space

The normalisation ratios for these topsoils are shown in Fig. 9.10a and reported in Table 9.5. As for urban gardens, these sites are widespread across the glacial-till deposit. The general pattern for the metals Cu, Zn and Pb and Sr and Ba is similar to that observed for many topsoils in Wolverhampton, although these ratios are generally lower than those for garden topsoils overlying glacial-till (see Table 9.5). Areas of open space in Wolverhampton are generally small, with many close to the industrial base. This explains metal ratios of > 1 in these soils. Nickel, Cd, Na, K, Ca and P also have ratios which exceed 1, although again, generally lower than for topsoils in gardens overlying deposits of till. This may relate to additional sources of these in the urban garden (see chapter 6). Magnesium, Al, Cr, Mn and Fe have ratios of < 1, which is common for topsoils overlying glacial-till.

9.2.21 Glacial-till - subsurface soils (30-45cm) in areas of open space

The normalisation ratios for these soils are shown in Fig. 9.10b and reported in Table 9.5. The highest ratios are those of the metals Cu, Zn and Pb (all > 1) and Sr and Ba. This is common to most soils in Wolverhampton. These ratios are lower than those observed for corresponding topsoils, particularly Cu, Zn, and Pb, and lower than the same depth samples for soils in industrial areas and urban gardens. Lower ratios of Ca, Ba, Cr, Ni, Cd and P are also observed in subsurface soils, relative to topsoils, which is probably the result of greater accumulation in the top 15cm of the profile from anthropogenic sources. Ratios of Na, K, Mg, Al and Co are higher in subsurface soils, relative to topsoils. This relationship for Na, K, Mg and Al is common for soils overlying glacial-till.

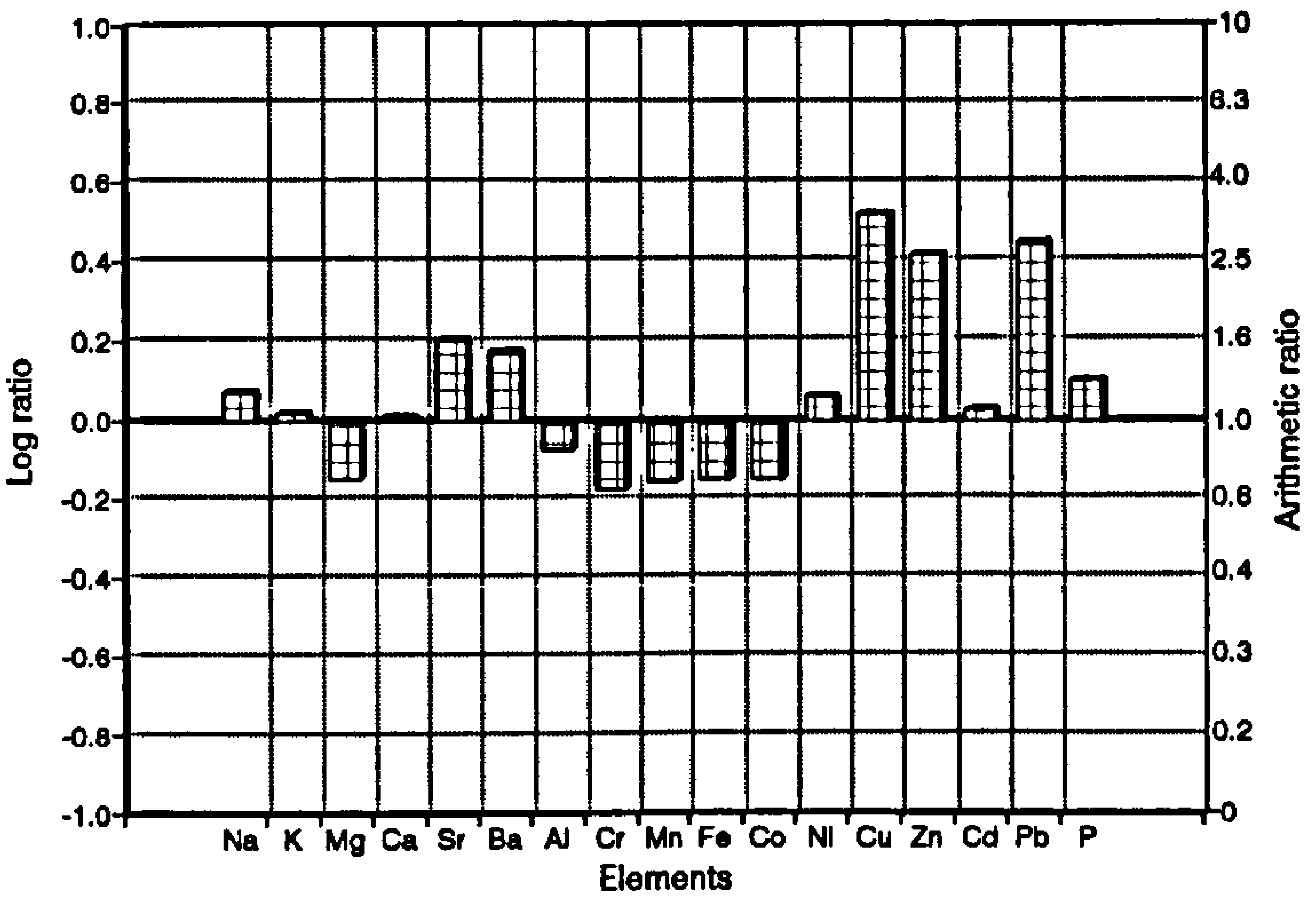


Fig. 9.10a Median concentrations of selected elements in topsoils (0-15cm) from areas of open space overlying glacial-till in Wolverhampton, normalised to median concentrations for soils in England and Wales (McGrath and Loveland, 1992) and expressed on a log-scale

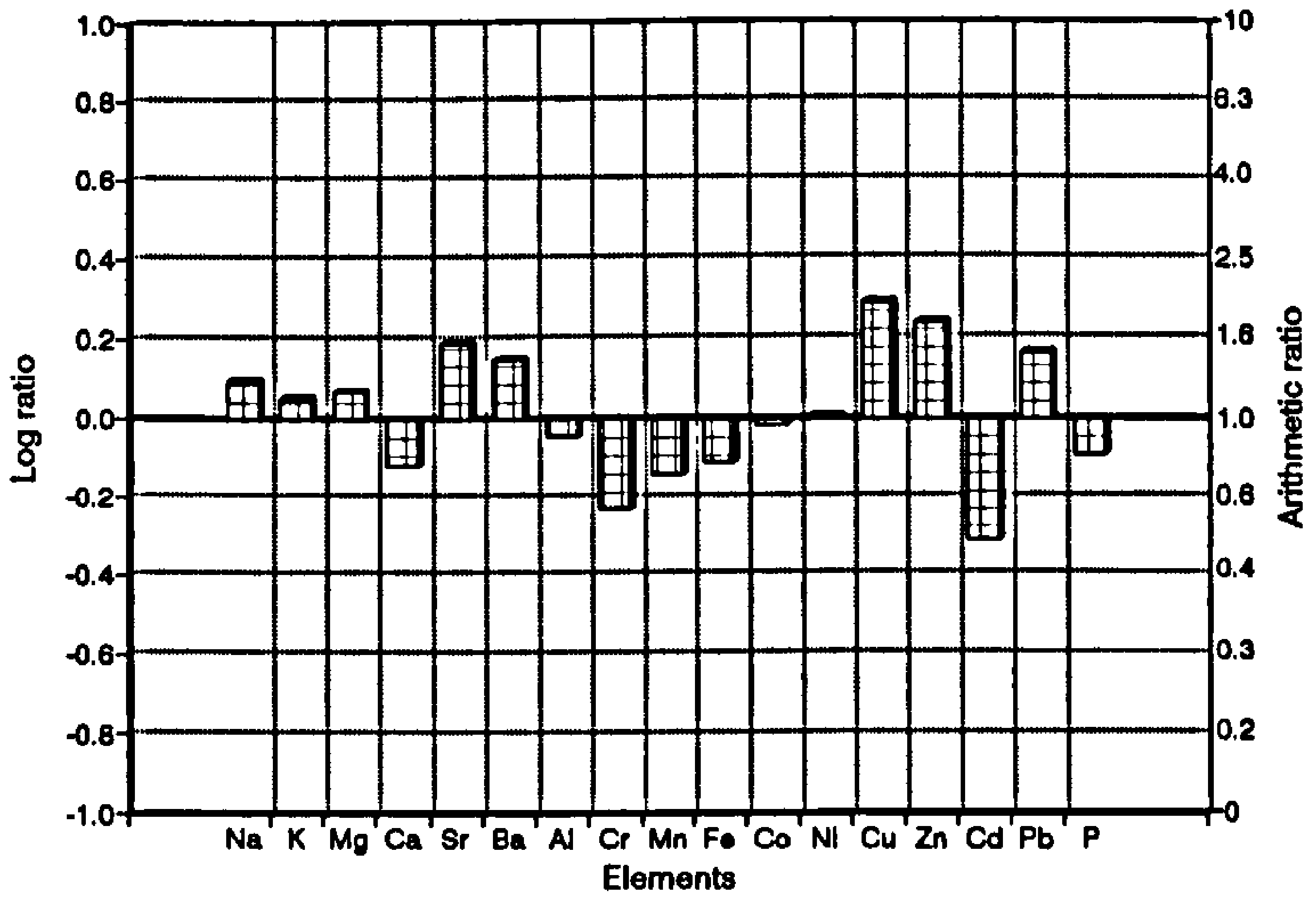


Fig. 9.10b Median concentrations of selected elements in subsurface soils (30-45cm) from areas of open space overlying glacial-till in Wolverhampton, normalised to median concentrations for soils in England and Wales (McGrath and Loveland, 1992) and expressed on a log-scale

9.2.22 Glacial-till - topsoils (0-15cm) in urban gardens

The normalisation ratios for these topsoils are shown in Fig. 9.11a and reported in Table 9.5. This is the largest category in Wolverhampton with samples covering the extent of the glacial-till deposit in the city (see Fig. 4.5). As for most of the categories already examined, the highest ratios are observed for Cu (> 3), Zn (> 3) and Pb (3). The metals Ni and Cd also have ratios > 1, with probable sources the emissions from industrial activities along with the many urban sources of these metals discussed in chapter 6. Ratios > 1 are also observed for Na, K, Ca, Sr, Ba, Ni, Cd and P. The highest ratios for this particular suite are observed for Ca, Sr and Ba (see Fig. 9.11a), and ratios exceeding 1 for these three elements are common in Wolverhampton soils and garden soils in Richmond. Ratios of < 1 are observed for Mg, Al, Cr, Mn and Co.

9.2.23 Glacial-till - subsurface soils (30-45cm) in urban gardens

The normalisation ratios for these soils are shown in Fig. 9.11b and reported in Table 9.5. The overall pattern for subsurface soils is similar to that for topsoils with the highest ratios, in general, for the metals Cu (> 2), Zn (> 2) and Sr (> 1). Calcium, Ba and Pb also have ratios which exceed 1. In particular, the ratios for Ni, Cu, Zn, Cd, Pb and P are lower than those observed for topsoils, suggesting greater accumulation in the top 15cm of the profile. Ratios for Na, K, Mg and Al are higher in subsurface soils than topsoils. This trend is observed for this parent material irrespective of land-use and probably relates to natural variation of the geochemical signature.

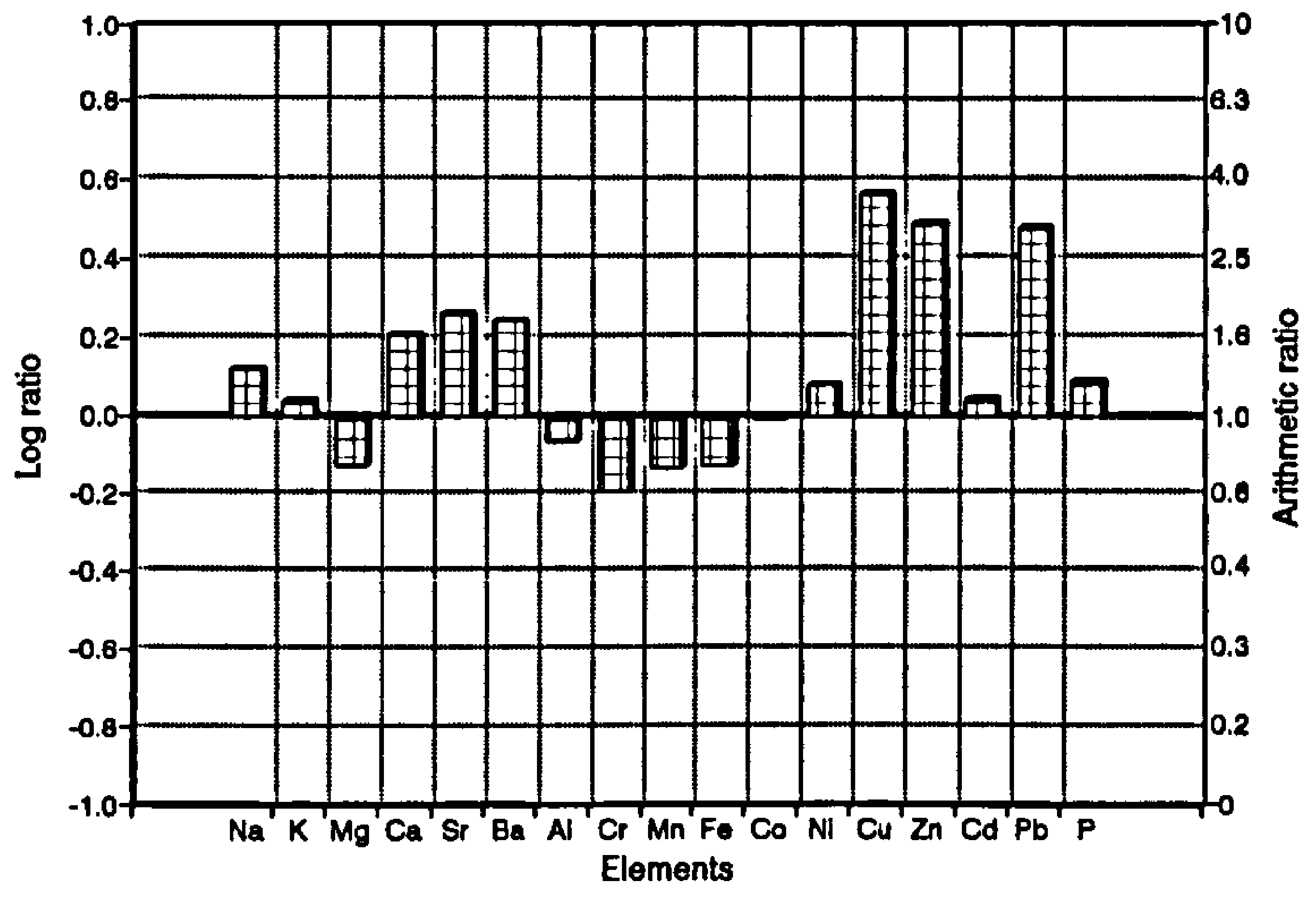


Fig. 9.11a Median concentrations of selected elements in topsoils (0-15cm) from urban gardens overlying glacial-till in Wolverhampton, normalised to median concentrations for soils in England and Wales (McGrath and Loveland, 1992) and expressed on a log-scale

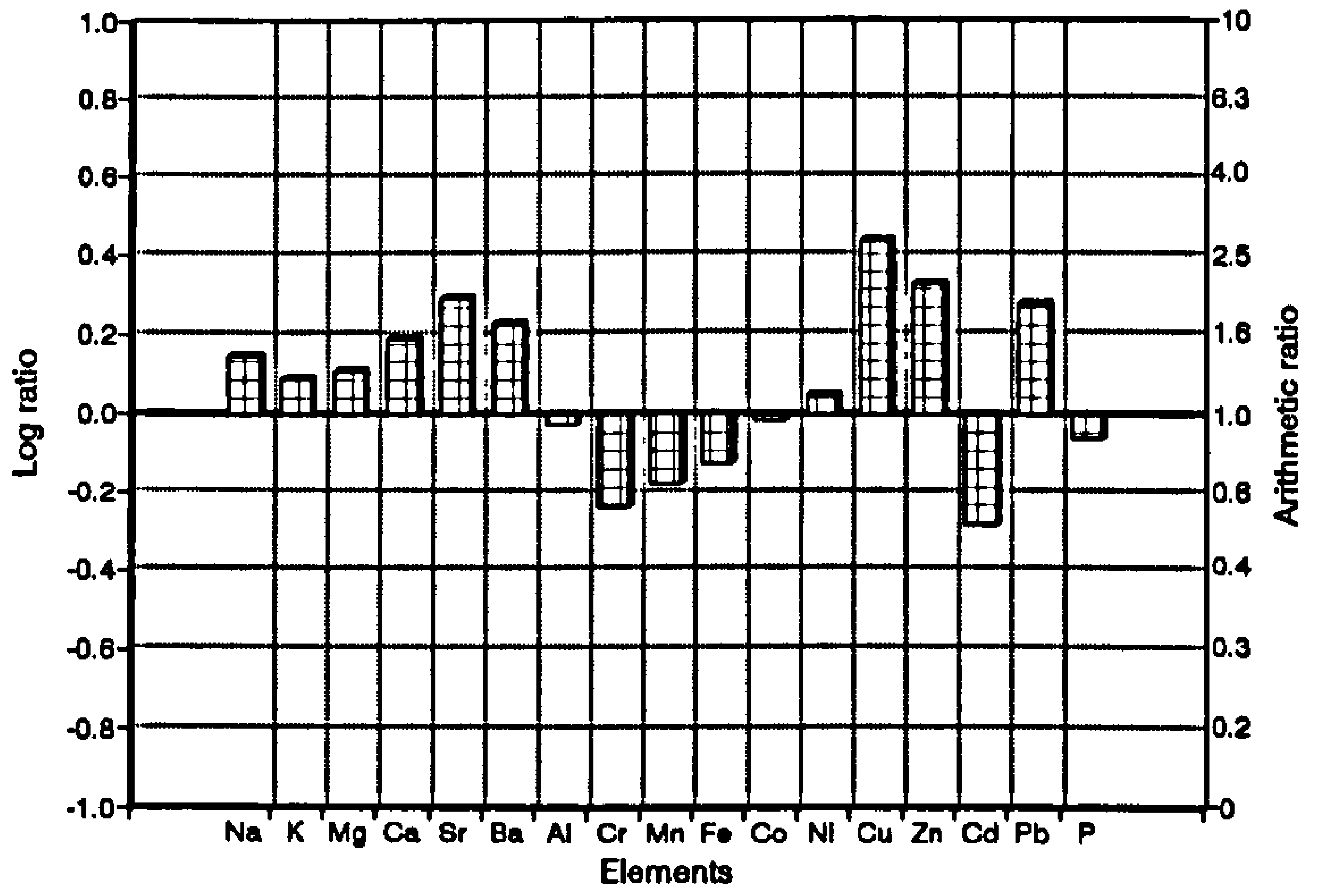


Fig. 9.11b Median concentrations of selected elements in subsurface soils (30-45cm) from urban gardens overlying glacial-till in Wolverhampton, normalised to median concentrations for soils in England and Wales (McGrath and Loveland, 1992) and expressed on a log-scale

9.2.24 Glacial-till - topsoils (0-15cm) in industrial areas

The normalisation ratios for these topsoils are shown in Fig. 9.12a and reported in Table 9.5. Most of the sites in this category are located away from the main body of industry in the south-east. This is one explanation for the generally lower ratios for elements in these soils compared for the same land-use overlying made ground. Another important factor is that made ground contains waste products from industrial activity, which may not be the case for industrial sites overlaying glacial-till.

The highest ratios for these soils are the metals Cu (> 6), Zn (> 3), and Pb (> 3), with ratios of > 2 for Ca, Sr and Ni and ratios of > 1 for Na, K, Ba, Co, Cd and P. These are probably the result of emissions from industrial activity, although the glacial-till deposit is also an important factor influencing the soil geochemistry. Ratios of Mg, Al, Cr, Mn and Fe are all < 1, generally much lower than those observed in industrial areas overlaying made ground. This is probably due to the composition of the fill material.

9.2.25 Glacial-till - subsurface soils (30-45cm) in industrial areas

The normalisation ratios for these soils are shown in Fig. 9.12b and reported in Table 9.5. The pattern is similar to that for topsoils, with the highest ratios for Cu (> 5), Zn (> 3), and Pb (> 2). The ratios for Ni, Cu, Zn, Cd and Pb in subsurface soils are lower than those for topsoils (see Figs 9.12a and 9.12b and Table 9.5). Lower ratios are also observed for Mn, Fe, Co and P in subsurface soils. This suggests greater accumulation of these metals in topsoils relative to subsurface soils, something which is not found in industrial areas overlaying made ground. Differences in the composition of the underlying materials in these areas is probably responsible for this.

High ratios are also observed for Ca (> 3), Sr (> 2) and Ba (> 1), generally higher than those observed for topsoils. Ratios of Na, K, Mg and Al are higher than those for topsoils, particularly Mg which has a ratio of < 1 in topsoils. These differences probably result from natural variation of the geochemical signature, although disturbance of the soil profile has also probably occurred.

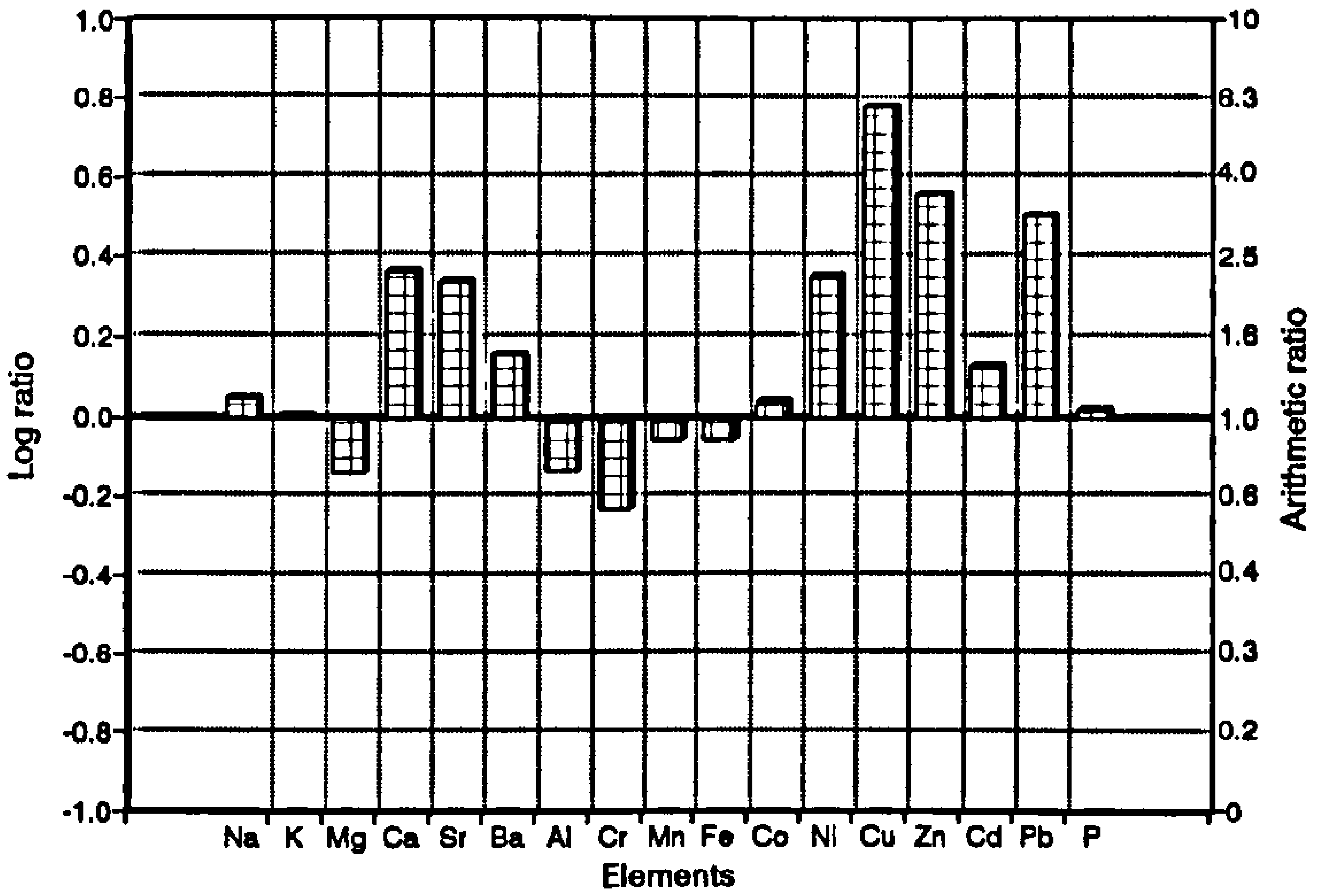


Fig. 9.12a Median concentrations of selected elements in topsoils (0-15cm) from industrial areas overlying glacial-till in Wolverhampton, normalised to median concentrations for soils in England and Wales (McGrath and Loveland, 1992) and expressed on a log-scale

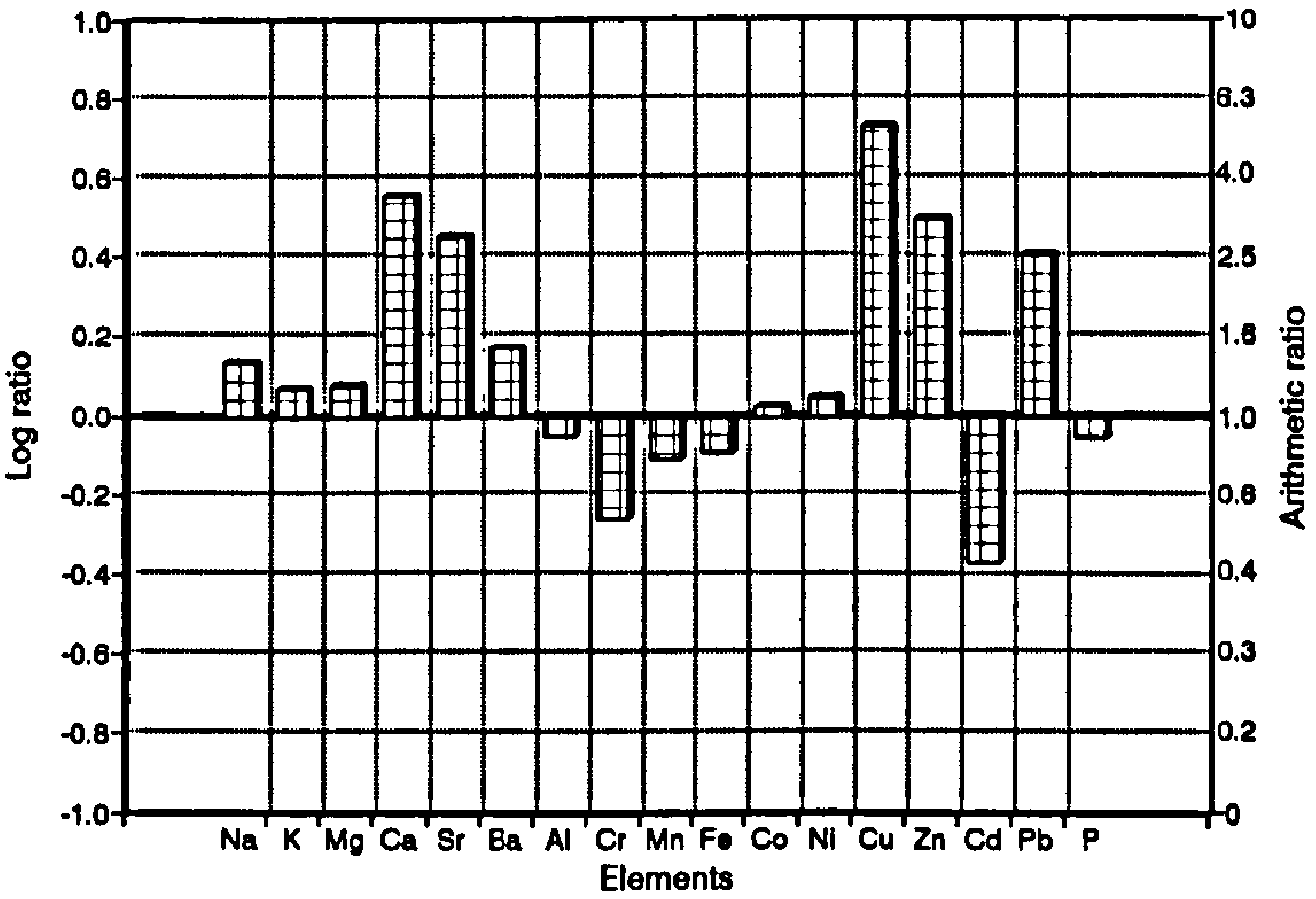


Fig. 9.12b Median concentrations of selected elements in subsurface soils (30-45cm) from industrial areas overlying glacial-till in Wolverhampton, normalised to median concentrations for soils in England and Wales (McGrath and Loveland, 1992) and expressed on a log-scale

Table 9.5 Ratios of elements in soils overlying glacial-till, as designated by land-use, after normalisation to median concentrations for the soils of England and Wales (McGrath and Loveland, 1992)

	topsoils				subsurface soils			
	n=5	n=23	n=78	n=4	n=5	n=23	n=78	n=4
	AG	OS	UG	IN	AG	OS	UG	IN
Na	0.95	1.18	1.32	1.12	0.99	1.25	1.40	1.36
K	1.07	1.04	1.09	1.01	1.29	1.13	1.23	1.17
Mg	0.76	0.71	0.75	0.72	1.32	1.17	1.28	1.19
Ca	1.09	1.03	1.61	2.31	0.58	0.76	1.54	3.61
Sr	1.14	1.59	1.83	2.18	1.08	1.55	1.94	1.94
Ba	1.14	1.50	1.75	1.44	1.10	1.41	1.70	1.48
Al	0.82	0.85	0.86	0.73	0.90	0.90	0.94	0.89
Cr	0.72	0.67	0.64	0.59	0.54	0.59	0.58	0.55
Mn	0.76	0.70	0.74	0.88	0.50	0.72	0.67	0.78
Fe	0.61	0.71	0.75	0.88	0.68	0.77	0.75	0.81
Co	0.72	0.71	0.98	1.09	0.68	0.96	0.96	1.05
Ni	0.79	1.14	1.20	2.23	0.71	1.02	1.12	1.11
Cu	1.75	3.29	3.65	6.03	1.04	1.95	2.74	5.41
Zn	2.59	2.61	3.10	3.63	0.80	1.74	2.12	3.15
Cd	0.68	1.06	1.10	1.34	0.15	0.49	0.52	0.43
Pb	1.45	2.81	3.00	3.22	0.76	1.46	1.89	2.54
P	1.15	1.26	1.23	1.04	0.55	0.81	0.86	0.88

AG Soils in agricultural areas OS Soils in areas of open space

UG Soils from urban gardens IN Soils in industrial areas

9.2.26 Glacio-fluvial deposits - topsoils (0-15cm) in areas of open space

The normalisation ratios for these topsoils are shown in Fig. 9.13a and reported in Table 9.6. These site are located in the north-west, very close to areas of past industrial activity, with deposits generally described as red-brown medium grained sands, pebbly sands and gravels (see section 4.7.5.3). In many respects the pattern shown in Fig. 9.13a is similar to that observed for soils overlying the Clent Formation (see Fig. 9.1a). Although neither of the land-uses is specifically industrial, they are located near industrial areas and this is probably the most important factor influencing the patterns shown in Figs. 9.1a and

9.13a.

The highest ratios are observed for Cu (approximately 5), Zn (> 4), and Pb (> 2), with ratios > 2 also observed for Ca, Ba and Cd. The ratios for these elements are similar to those for soils overlying till in industrial areas. Ratios of < 1 are only observed for Mn, Fe and Co. This is probably the result of few anthropogenic inputs of these metals and naturally low concentrations.

9.2.27 Glacio-fluvial deposits - subsurface soils (30-45cm) in areas of open space

The normalisation ratios for these soils are shown in Fig. 9.13b and reported in Table 9.6. The general pattern for these soils is similar to that for topsoils, although the ratios are generally lower (see Figs. 9.13a and 9.13b). Ratios exceeding 1 are observed for most elements, the highest of these for Cu and Zn (> 2). Copper, Zn and Cd show the largest decrease in ratios from topsoils to subsurface soils, suggesting greater accumulation of these metals in topsoils, probably as a result of industrial emissions. As for topsoils, Mn and Fe have ratios of < 1. Sodium, Mg, Sr, Al, Mn, Fe and Co have higher ratios at depths of 30-45cm. This is probably the result of natural variation in the geochemical signature.

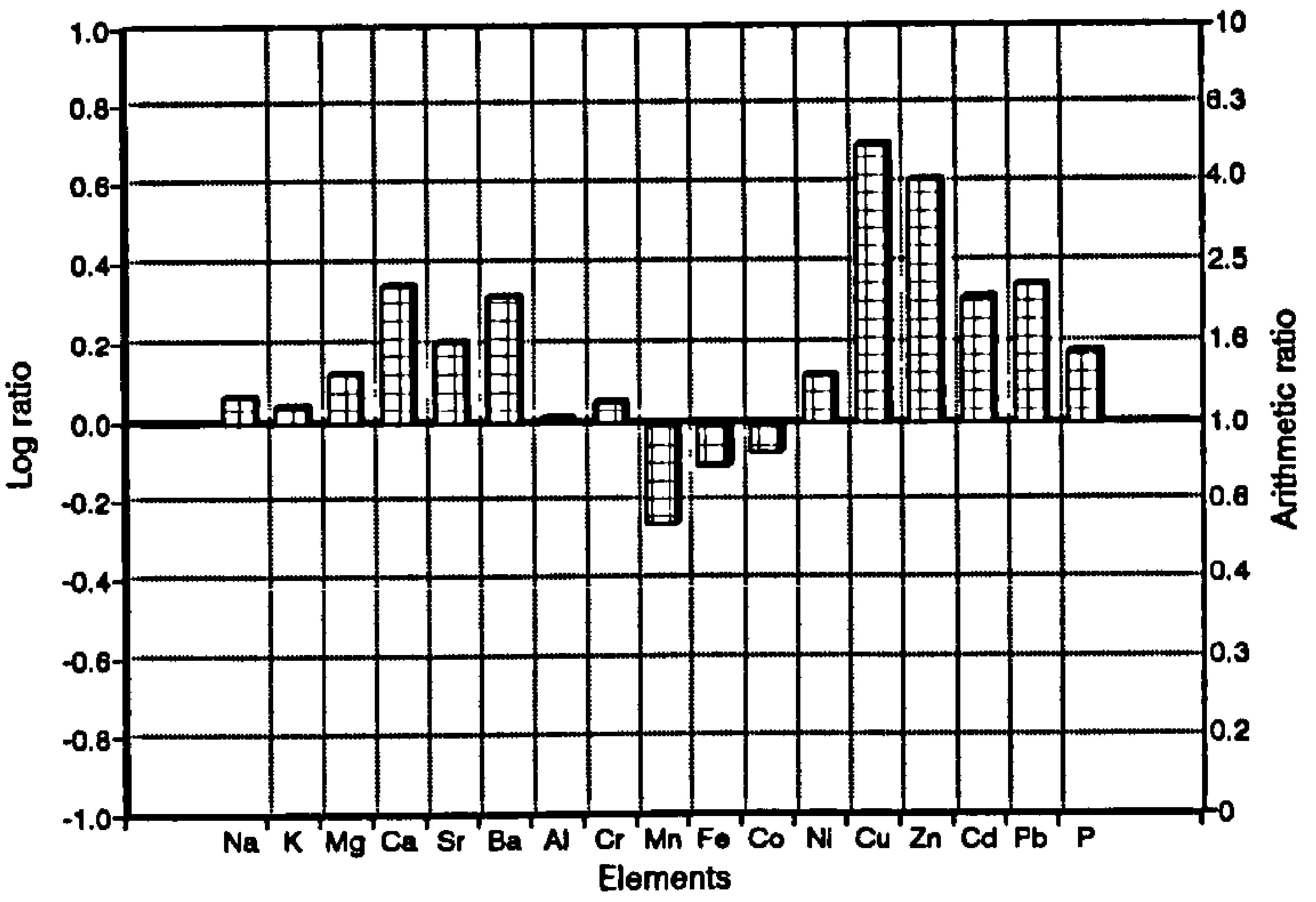


Fig. 9.13a Median concentrations of selected elements in topsoils (0-15cm) from areas of open space overlying glacio-fluvial deposits in Wolverhampton, normalised to median concentrations for soils in England and Wales (McGrath and Loveland, 1992) and expressed on a log-scale

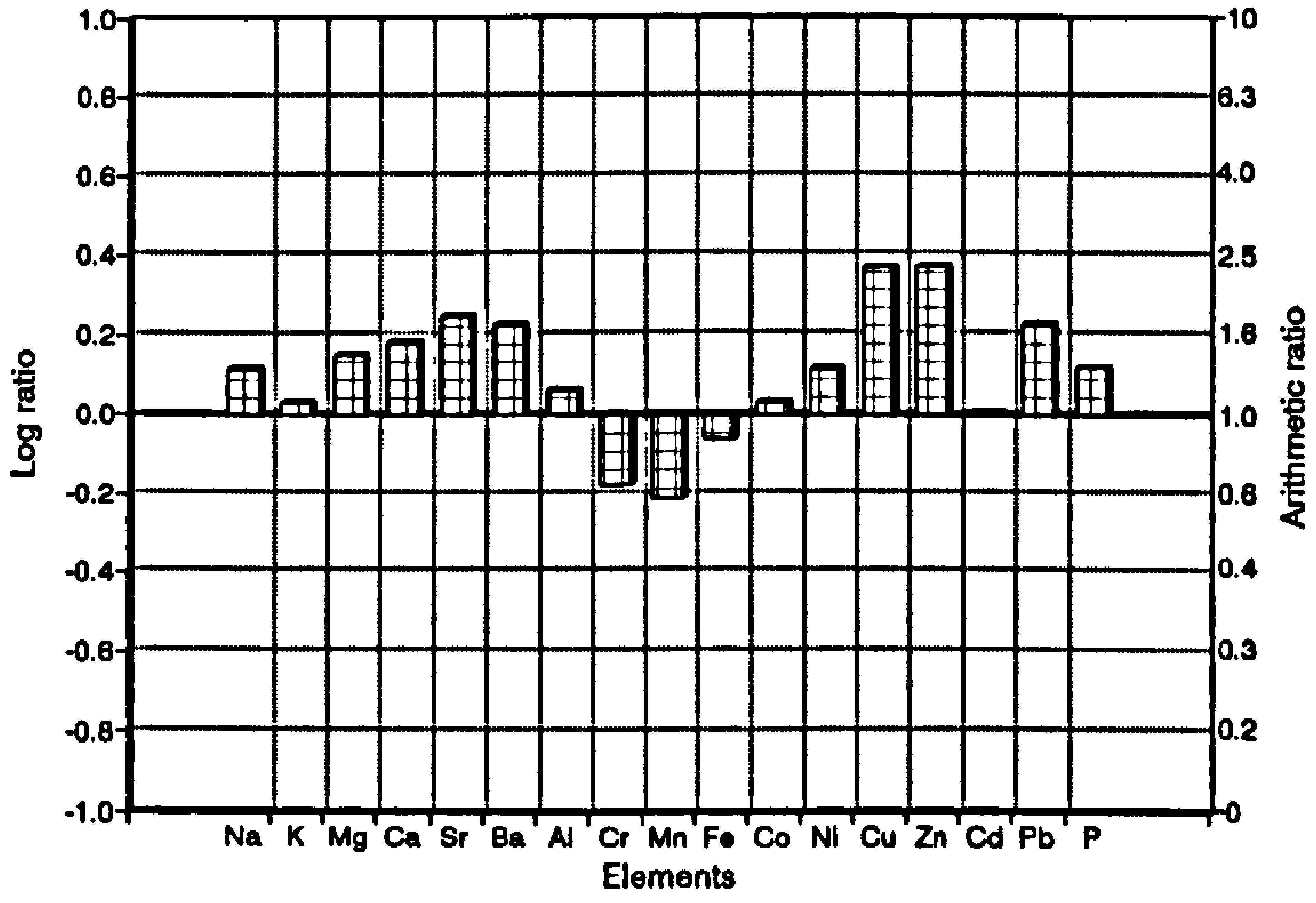


Fig. 9.13b Median concentrations of selected elements in subsurface soils (30-45cm) from areas of open space overlying glacio-fluvial deposits in Wolverhampton, normalised to median concentrations for soils in England and Wales (McGrath and Loveland, 1992) and expressed on a log-scale

Table 9.6 Ratios of elements in soils overlying glacio-fluvial deposits, as designated by land-use, after normalisation to median concentrations for soils in England and Wales (McGrath and Loveland, 1992)

	topsoils	subsurface soils
	n=5	n=5
	OS	OS
Na	1.16	1.29
K	1.10	1.07
Mg	1.32	1.41
Ca	2.21	1.52
Sr	1.59	1.76
Ba	2.07	1.68
Al	1.03	1.14
Cr	1.13	0.67
Mn	0.55	0.62
Fe	0.77	0.86
Co	0.84	1.07
Ni	1.30	1.29
Cu	4.93	2.34
Zn	4.06	2.36
Cd	2.05	1.01
Pb	2.20	1.68
P	1.51	1.30

OS Soils in areas of open space

9.2.28 Alluvium - topsoils (0-15cm) in agricultural areas

The normalisation ratios for these topsoils are shown in Fig. 9.14a and reported in Table 9.7. The deposit mainly consists of silt and clay overlaying coarser sand and gravel (see section 4.7.5.5). These sites are located in the north and north-east of the city, generally away from industrial activity. This is reflected in the pattern observed in Fig. 9.14a with Cu, Zn and Mg the only elements which have ratios which exceed 1, the highest of these being 1.20 for Cu. Low inputs from anthropogenic sources, as a consequence of the land-use and the location of the sites away from industrial activity, is an important factor influencing the pattern shown in Fig. 9.14a. The underlying geology is probably the most important factor influencing the distribution of elements in these soils.

9.2.29 Alluvium - subsurface soils (30-45cm) in agricultural areas

The normalisation ratios for these soils are shown in Fig. 9.14b and reported in Table 9.7. The general pattern shown for subsurface soils is similar to that for topsoils, with most elements having ratios of < 1. The metals Cu, Zn and Pb have lower ratios in subsurface soils, all < 1, than for topsoils. This suggests greater accumulation of these metals from anthropogenic activities in the top 15cm relative to depths of 30-45cm. Phosphorus and Ca also have higher ratios in topsoils than in subsurface soils (see Figs. 9.14a and 9.14b). In contrast, Na, K, Mg, Ba, Al, Fe, Co and Ni have higher ratios in subsurface soils than topsoils, with ratios of > 1 for K, Mg and Ba. Higher ratios of K, Mg, Al and Fe in subsurface soils is common for soils overlying glacial-till, and higher ratios of this suite of elements may reflect natural variation of the geochemical signature for alluvium.

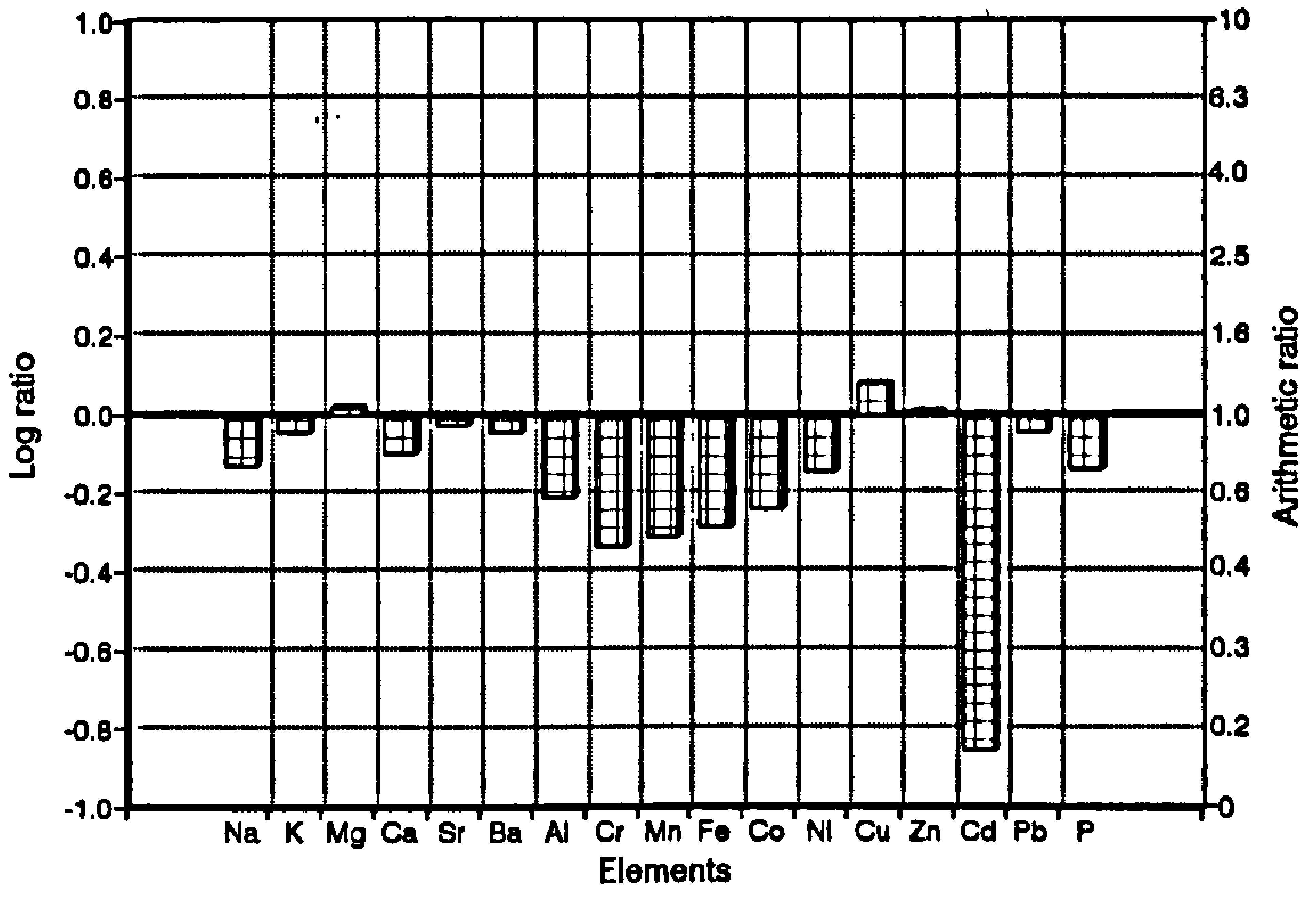


Fig. 9.14a Median concentrations of selected elements in topsoils (0-15cm) from agricultural areas overlying alluvium in Wolverhampton, normalised to median concentrations for soils in England and Wales (McGrath and Loveland, 1992) and expressed on a log-scale

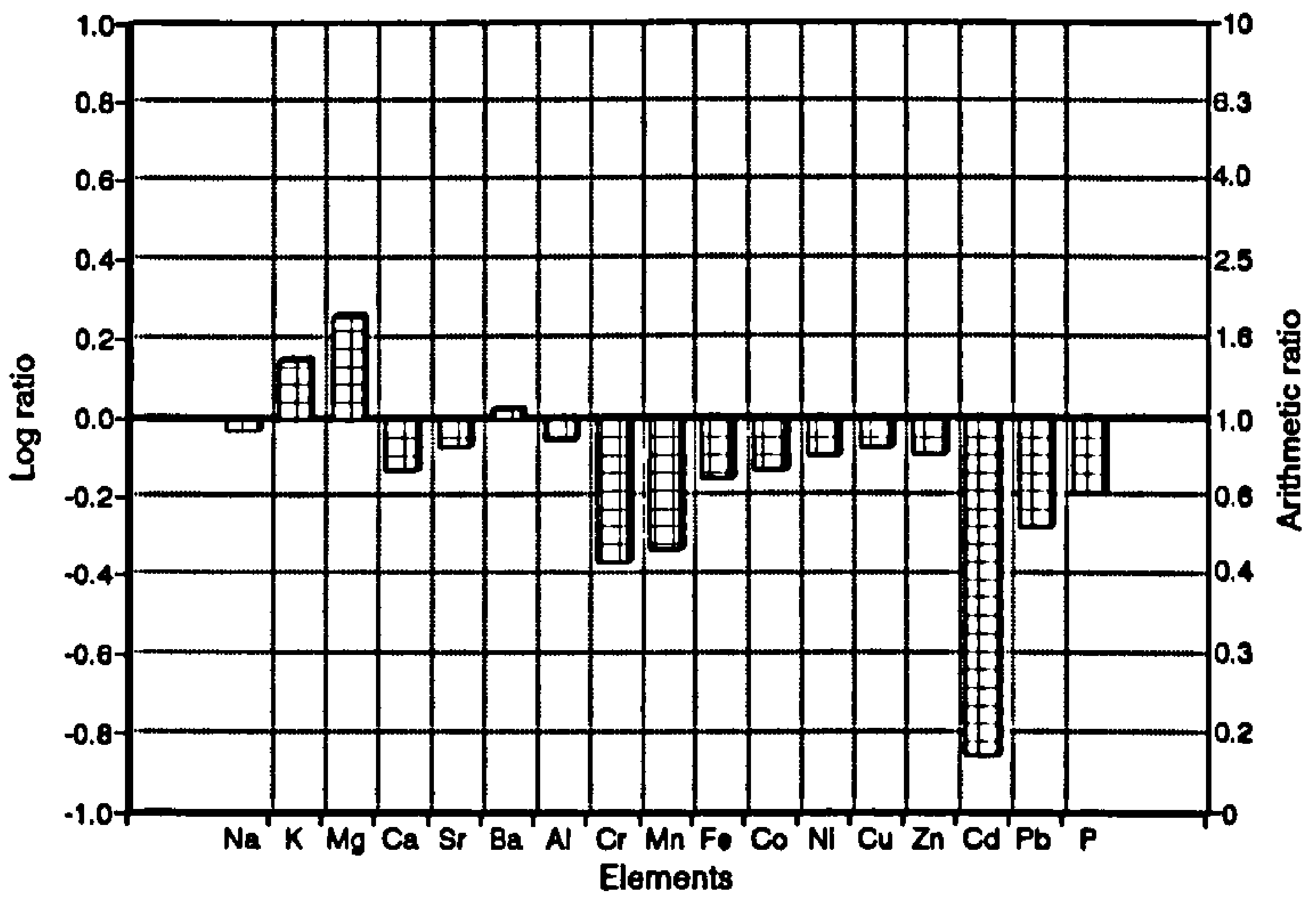


Fig. 9.14b Median concentrations of selected elements in subsurface soils (30-45cm) from agricultural areas overlying alluvium in Wolverhampton, normalised to median concentrations for soils in England and Wales (McGrath and Loveland, 1992) and expressed on a log-scale

9.2.30 Alluvium - topsoils (0-15cm) in areas of open space

The normalisation ratios for these topsoils are shown in Fig. 9.15a and reported in Table 9.7. These sites are located in the south-west of the city, near an area of made ground, suggesting past industrial activity. This is reflected in Fig. 9.15a with high ratios of Cu (> 4), Zn (> 4), Pb (> 3) and Cd (> 1), not dissimilar to those observed in industrial areas (see Figs. 9.12a and 9.19a). Ratios exceeding 1 are also observed for Na, K, Mg, Ca, Sr, Ba, Al, Cr, Ni and P, the highest of these being P (1.98), Ba (1.97) and Sr (1.72). Only Mn, Fe and Co have ratios of < 1. The pattern is very different to that observed for soils overlying alluvium in agricultural areas, with higher ratios for all 17 elements for soils in areas of open space. For certain elements, such as Al, Mn, and Fe, this is probably due to a combination of natural variation of the geochemical signature and greater proximity to industrial activities. However, the location of the sites near areas of past industrial activity is probably a more important factor influencing the differences between the two land-uses.

9.2.31 Alluvium - subsurface soils (30-45cm) in areas of open space

The normalisation ratios for these soils are shown in Fig. 9.15b and reported in Table 9.7. The overall pattern observed in Fig. 9.15b is similar to that observed for topsoils, although ratios are generally lower in subsurface soils (see Figs. 9.15a and 9.15b). The largest ratios for subsurface soils are those for Cu (1.63), Ca (1.43), Zn (1.39), Mg (1.38) and Sr (1.29). Ratios which exceed 1 are also observed for Na, K, Ba, Cr and Pb. The largest differences between ratios for different sample depths are observed for the metals Cu, Zn, Cd, Pb and P. This is probably the result of greater accumulation of these elements from anthropogenic sources in the top 15cm of the profile, relative to depths of 30-45cm. Only Mg has a higher ratio at depths of 30-45cm for these soils, with ratios of Na and Fe remaining consistent with depth (see Figs. 9.15a and 9.15b), probably best representing a consistent feature of the geochemical signature for these soils.

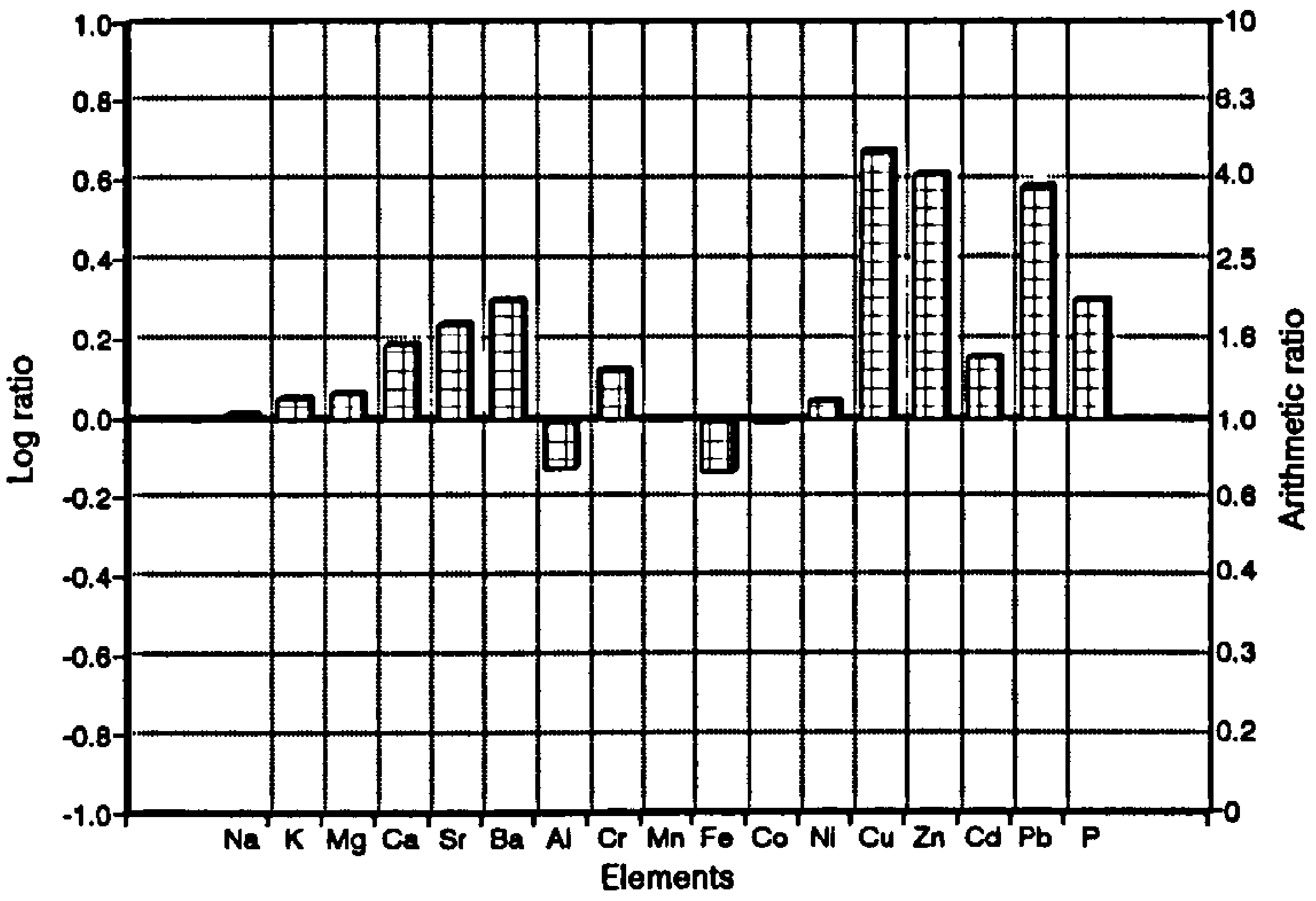


Fig. 9.15a Median concentrations of selected elements in topsoils (0-15cm) from areas of open space overlying alluvium in Wolverhampton, normalised to median concentrations for soils in England and Wales (McGrath and Loveland, 1992) and expressed on a log-scale

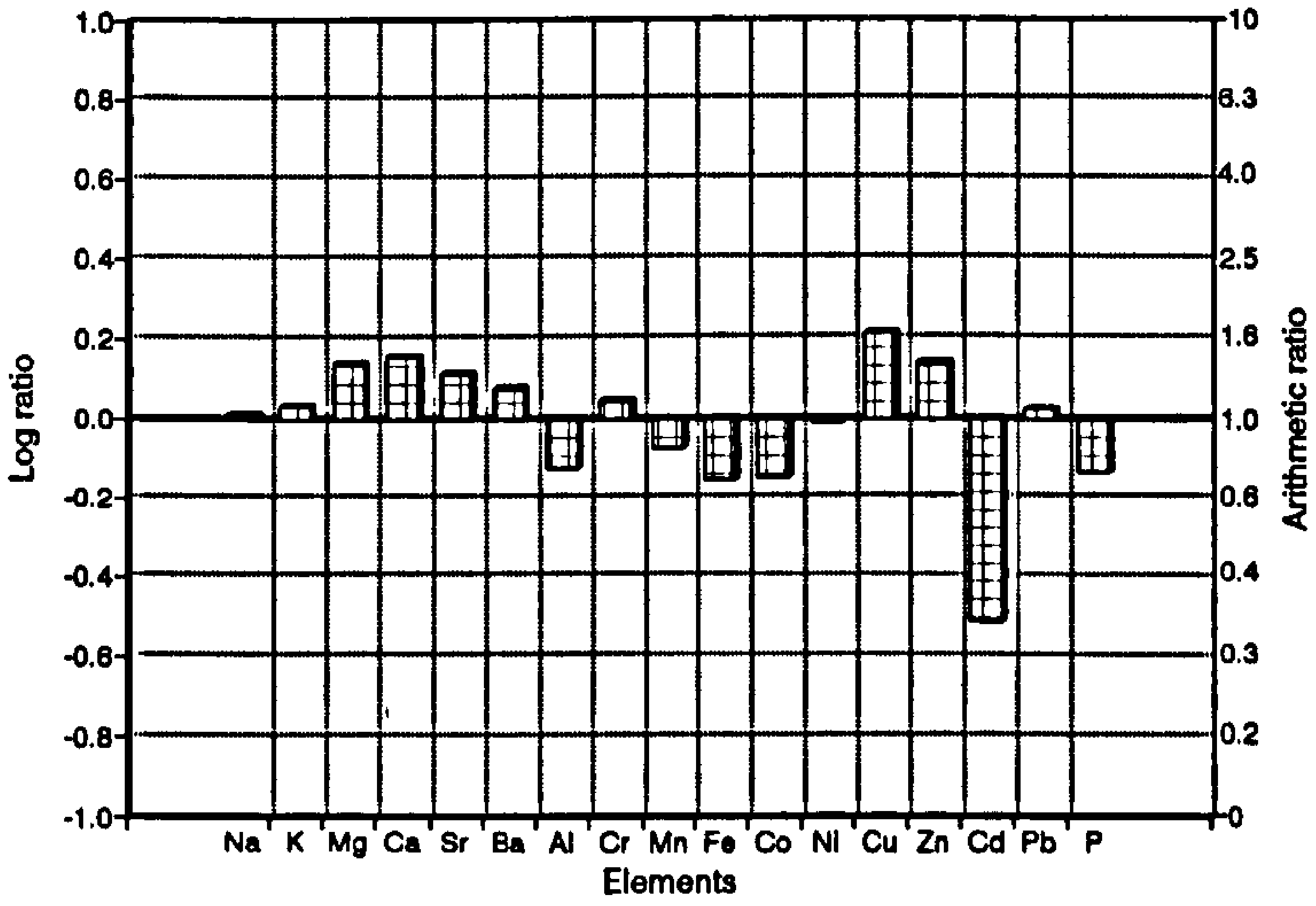


Fig. 9.15b Median concentrations of selected elements in subsurface soils (30-45cm) from areas of open space overlying alluvium in Wolverhampton, normalised to median concentrations for soils in England and Wales (McGrath and Loveland, 1992) and expressed on a log-scale

9.2.32 Alluvium - topsoils (0-15cm) in urban gardens

The normalisation ratios for these topsoils are shown in Fig. 9.16a and reported in Table 9.7. These sites are mainly located in the west of the city, some close to areas of made ground. The general pattern shown in Fig. 9.16a is similar to that for soils overlying the same parent material in areas of open space, with high ratios for Pb (> 7), Cu, (> 3), Zn (> 2) and Sr (> 2). Ratios > 1 are observed for Na, K, Mg, Ca, Ba, Co, Ni, Cd and P. The ratio for Pb is higher than for any parent material and land-use in the city, and the generally high ratios for a number of metals is probably the result of past industrial activity in the area and other sources specific to urban gardens (see Tables 3.1 and 3.2 and sections 6.2 and 6.3 in general). As with areas of open space for this parent material, the ratios for garden soils are systematically higher than those for agricultural areas. This is probably a consequence of past industrial activity rather than a natural variation of the geochemical signature. In comparison with areas of open space, ratios for Na, Ca and Sr are higher in garden soils. This may be a result of greater sources of these elements in residential areas, through the salting of roads and building materials such as concrete, plaster and gypsum.

9.2.33 Alluvium - subsurface soils (30-45cm) in urban gardens

The normalisation ratios for these soils are shown in Fig. 9.16b and reported in Table 9.7. The pattern at this depth is markedly different to that observed for topsoils, with ratios of > 1 for K, Sr, Cu, Zn and Pb, the highest of these being 1.24 for Sr. The pattern for these soils is similar to that observed for subsurface soils overlying alluvium in agricultural areas. All seventeen elements have lower ratios in subsurface soils, which suggests greater accumulation of elements in the top 15cm, particularly the metals Pb, Cu, Zn, Cd, and possibly some natural variation of the geochemical signature for elements which are not so strongly influenced by anthropogenic activities (particularly Al, Mn and Fe).

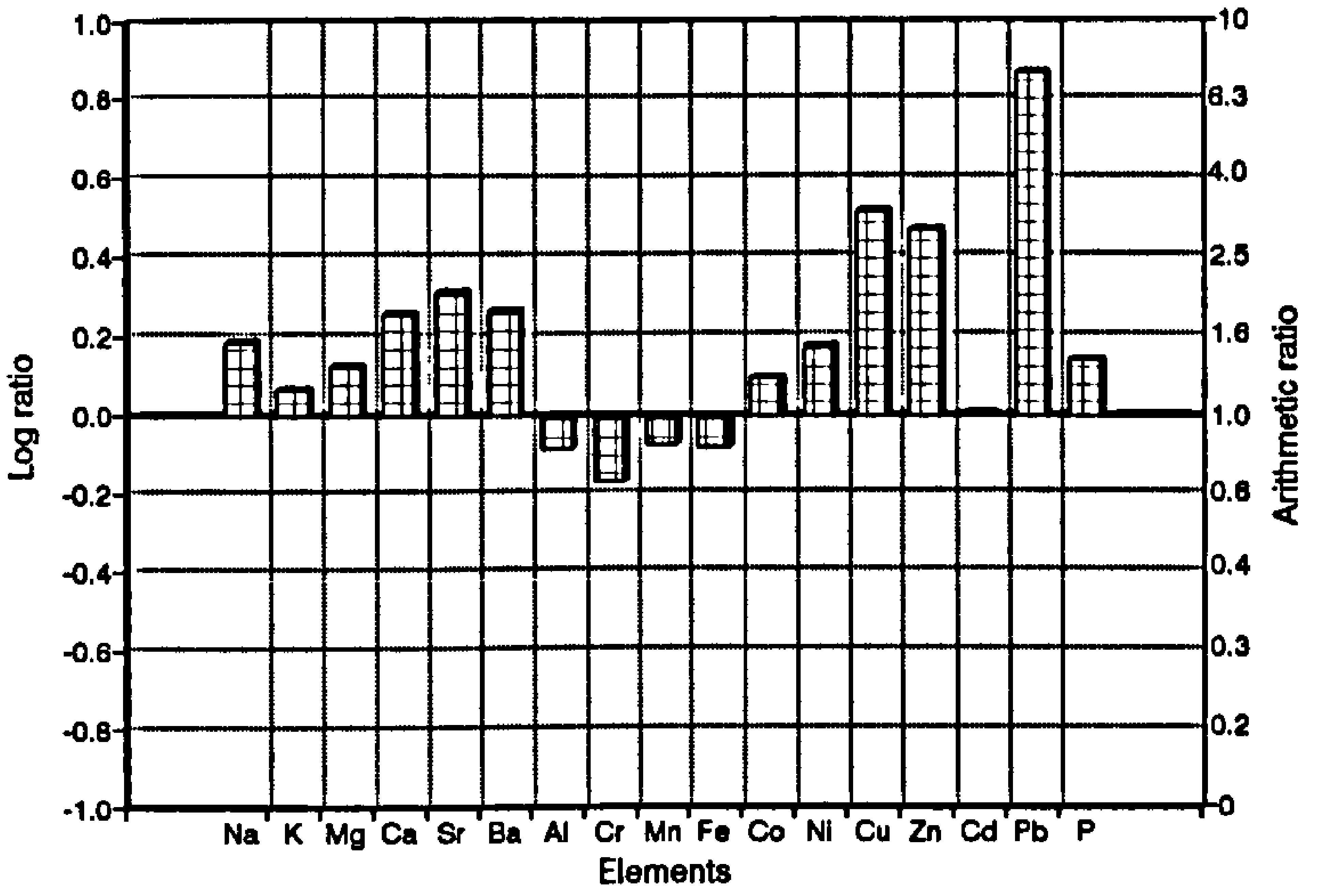


Fig. 9.16a Median concentrations of selected elements in topsoils (0-15cm) from urban gardens overlying alluvium in Wolverhampton, normalised to median concentrations for soils in England and Wales (McGrath and Loveland, 1992) and expressed on a log-scale

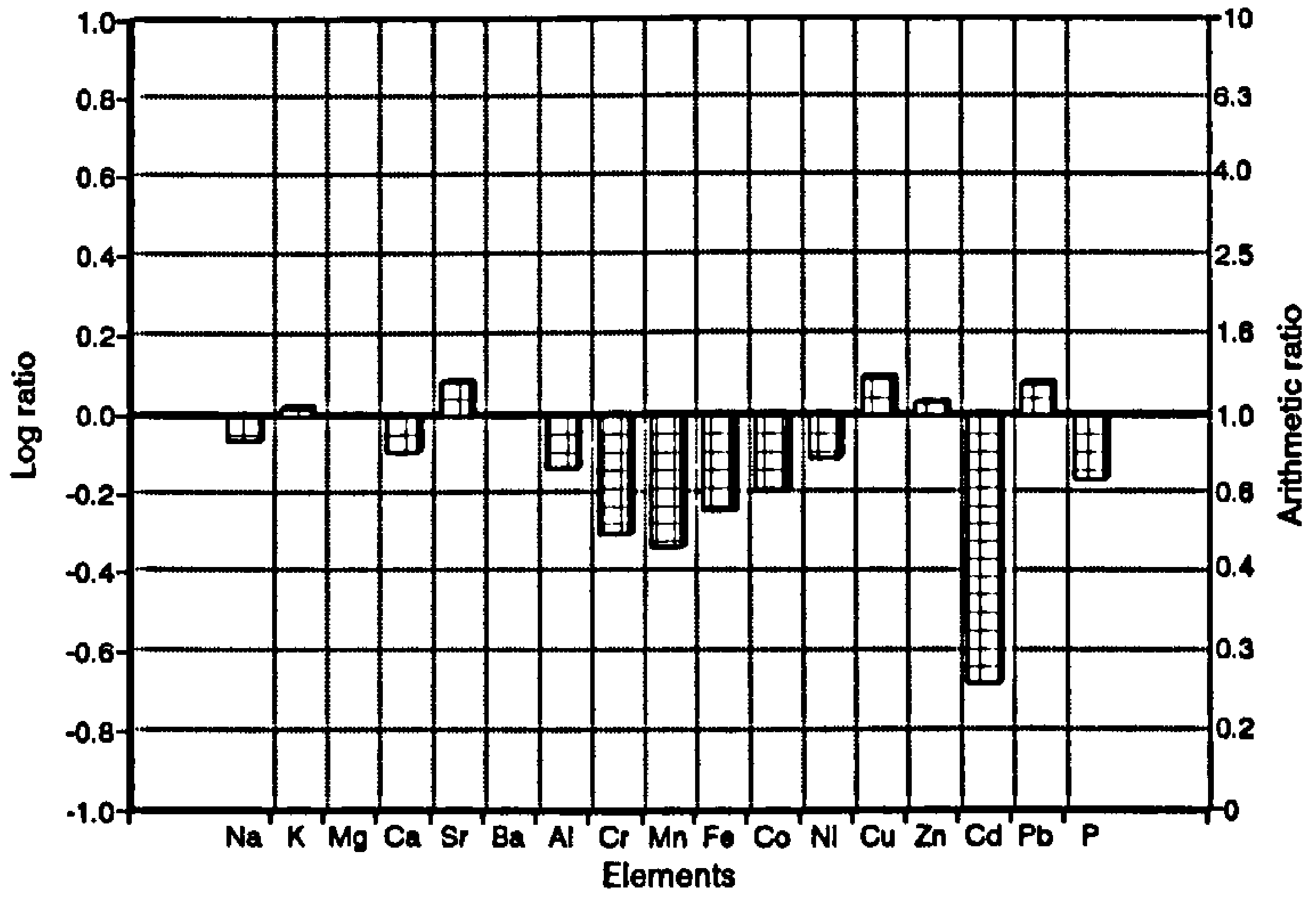


Fig. 9.16b Median concentrations of selected elements in subsurface soils (30-45cm) from urban gardens overlying alluvium in Wolverhampton, normalised to median concentrations for soils in England and Wales (McGrath and Loveland, 1992) and expressed on a log-scale

Table 9.7 Ratios of elements in soils overlying deposits of alluvium, as designated by land-use, after normalisation to median concentrations for soils in England and Wales (McGrath and Loveland, 1992)

	topsoils			subsurface soils		
	n=2	n=4	n=2	n=2	n=4	n=2
	AG	OS	UG	AG	OS	UG
Na	0.75	1.03	1.53	0.93	1.03	0.86
K	0.90	1.13	1.16	1.41	1.08	1.04
Mg	1.04	1.16	1.33	1.80	1.38	1.00
Ca	0.80	1.53	1.80	0.74	1.43	0.81
Sr	0.94	1.72	2.06	0.85	1.29	1.21
Ba	0.90	1.97	1.84	1.05	1.19	0.99
Al	0.62	1.75	0.82	0.88	0.75	0.73
Cr	0.46	1.32	0.68	0.43	1.11	0.50
Mn	0.49	0.99	0.84	0.46	0.84	0.46
Fe	0.52	0.73	0.83	0.70	0.70	0.57
Co	0.58	0.97	1.25	0.74	0.71	0.64
Ni	0.72	1.11	1.50	0.80	0.97	0.78
Cu	1.20	4.68	3.27	0.84	1.63	1.24
Zn	1.02	4.11	2.92	0.81	1.39	1.07
Cd	0.14	1.42	1.01	0.14	0.31	0.21
Pb	0.90	3.82	7.39	0.53	1.05	1.19
P	0.73	1.98	1.39	0.64	0.73	0.69

AG	Soils in agricultural areas	OS	Soils in areas of open space
UG	Soils from urban gardens		

9.2.34 Made ground - topsoils (0-15cm) in areas of open space

Although made ground is not a geological unit, a number of soils in Wolverhampton overlay this material (see Fig. 4.5). This is a result of the large amount of industrial activity in the city, both past and present. Spoil from past mineral workings covers much of the south-east and this is often mixed with a variety of materials, including by-products of industrial activity (see section 4.7.6). The normalisation ratios for these topsoils are shown in Fig. 9.17a and reported in Table 9.8. The pattern shown in Fig 9.17a is similar to that observed for garden topsoils overlying made ground (see Fig.

9.18a). Most of these sites are located in the south-east, so as with urban gardens, are close to contemporary industrial activity. The highest ratios are for the metals Cu (> 4), Zn (approximately 3) and Pb (> 2), similar to those found in urban gardens. Unlike Richmond, areas of open space in Wolverhampton are generally small and redeveloped from areas of past industrial activity. Ratios of Mg, Mn and Fe are also similar to those observed in garden soils, although lower than for topsoils in industrial areas overlying the same parent material (see Figs. 9.17a, 9.18a and 9.19a). The ratios of Na, Ca, Sr, Ba, Co, Ni, Cd and P however, although > 1 in soils from areas of open space are lower than those observed in garden soils (see Figs 9.17a and 9.18a). This may relate to additional sources of these elements in gardens from waste building materials, flaking paint, additions of lime, fertilisers and fossil fuel residues to garden soils and the salting of urban roads.

9.2.35 Made ground - subsurface soils (30-45cm) in areas of open space

The normalisation ratios for these soils are shown in Fig. 9.17b and reported in Table 9.8. The pattern observed is similar to that for topsoils although the ratios are all higher than those observed for topsoils. The highest ratios are the metals Cu (> 6), Pb (> 3) and Zn (> 3). The largest differences in ratio between the 2 sample depths are observed for Sr, Ba, Cu, Ni and Pb, Co, Fe and Na. This is probably a result of the fill composition and reflects the disturbance of these soil profiles.

9.2.36 Made ground - topsoils (0-15cm) in urban gardens

The normalisation ratios for these topsoils are shown in Fig. 9.18a and reported in Table 9.8. A number of similarities exist between soils in industrial areas and garden soils overlying made ground. These garden soils are mainly located close to sites of present industrial activity in the south-east, but also in central areas and the north-west. The highest ratios are observed for Cu (approximately 5), Zn (approximately 4) and Pb (approximately 3 - see Table 9.8), lower than those for industrial areas. This can be explained by greater proximity of industrial sites to emissions. A similar pattern is observed for Na, Mg, Ca, Sr, Ba, Al, Mn, Co, Ni, Cd and P, with ratios that are > 1, although lower than for soils in industrial areas. The ratio for K is higher in garden soils

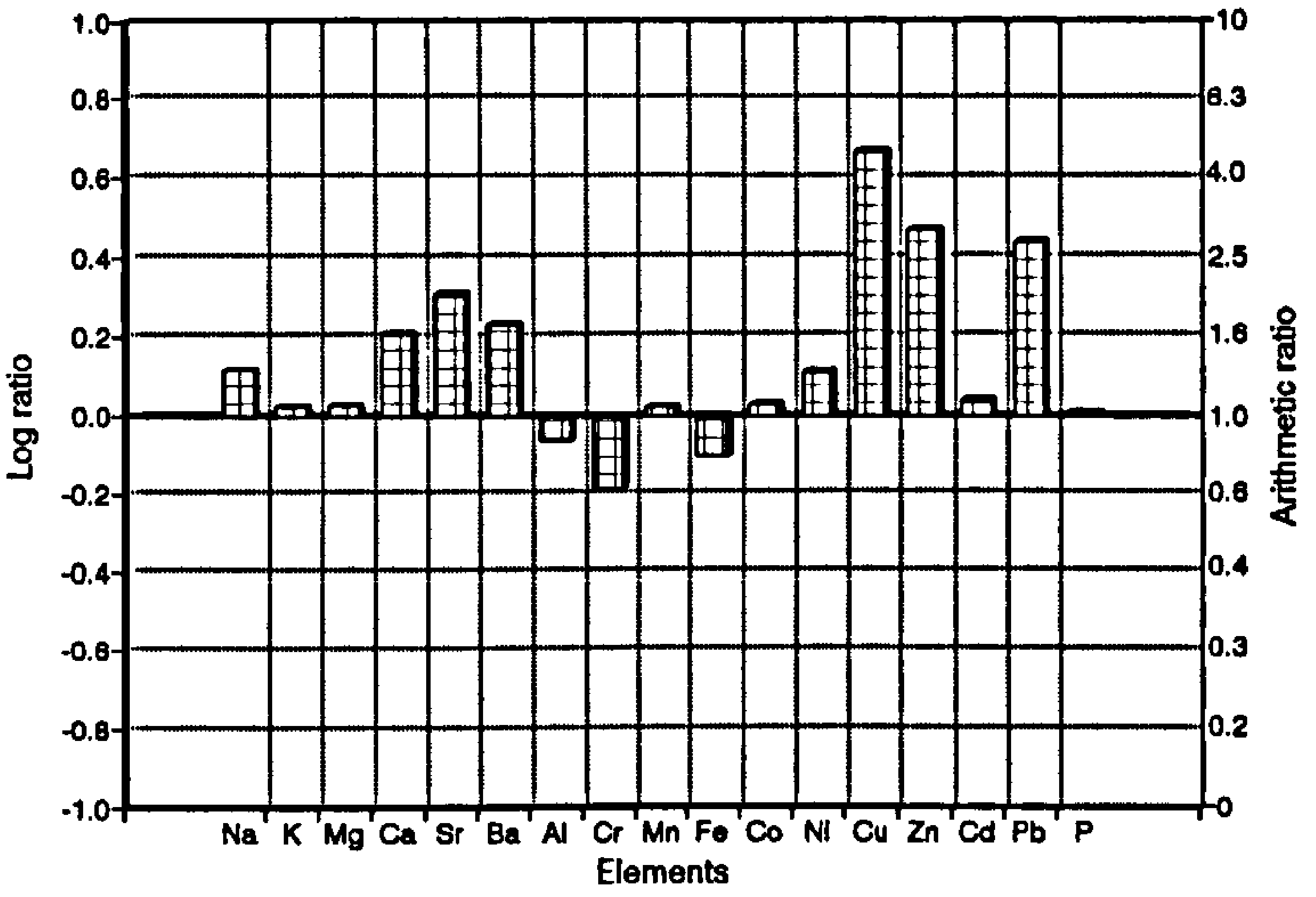


Fig. 9.17a Median concentrations of selected elements in topsoils (0-15cm) from areas of open space overlying made ground in Wolverhampton, normalised to median concentrations for soils in England and Wales (McGrath and Loveland, 1992) and expressed on a log-scale

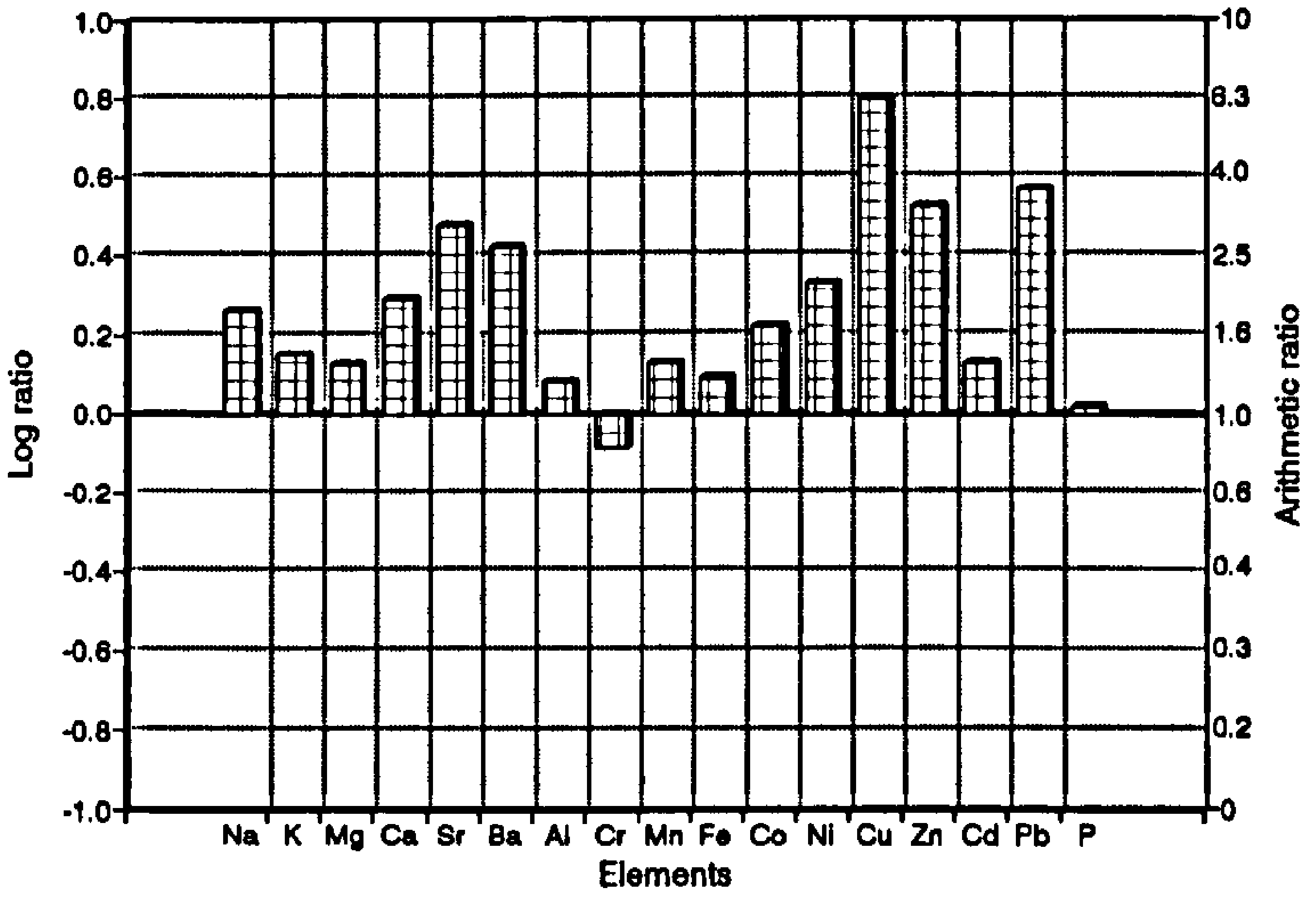


Fig. 9.17b Median concentrations of selected elements in subsurface soils (30-45cm) from areas of open space overlying made ground in Wolverhampton, normalised to median concentrations for soils in England and Wales (McGrath and Loveland, 1992) and expressed on a log-scale

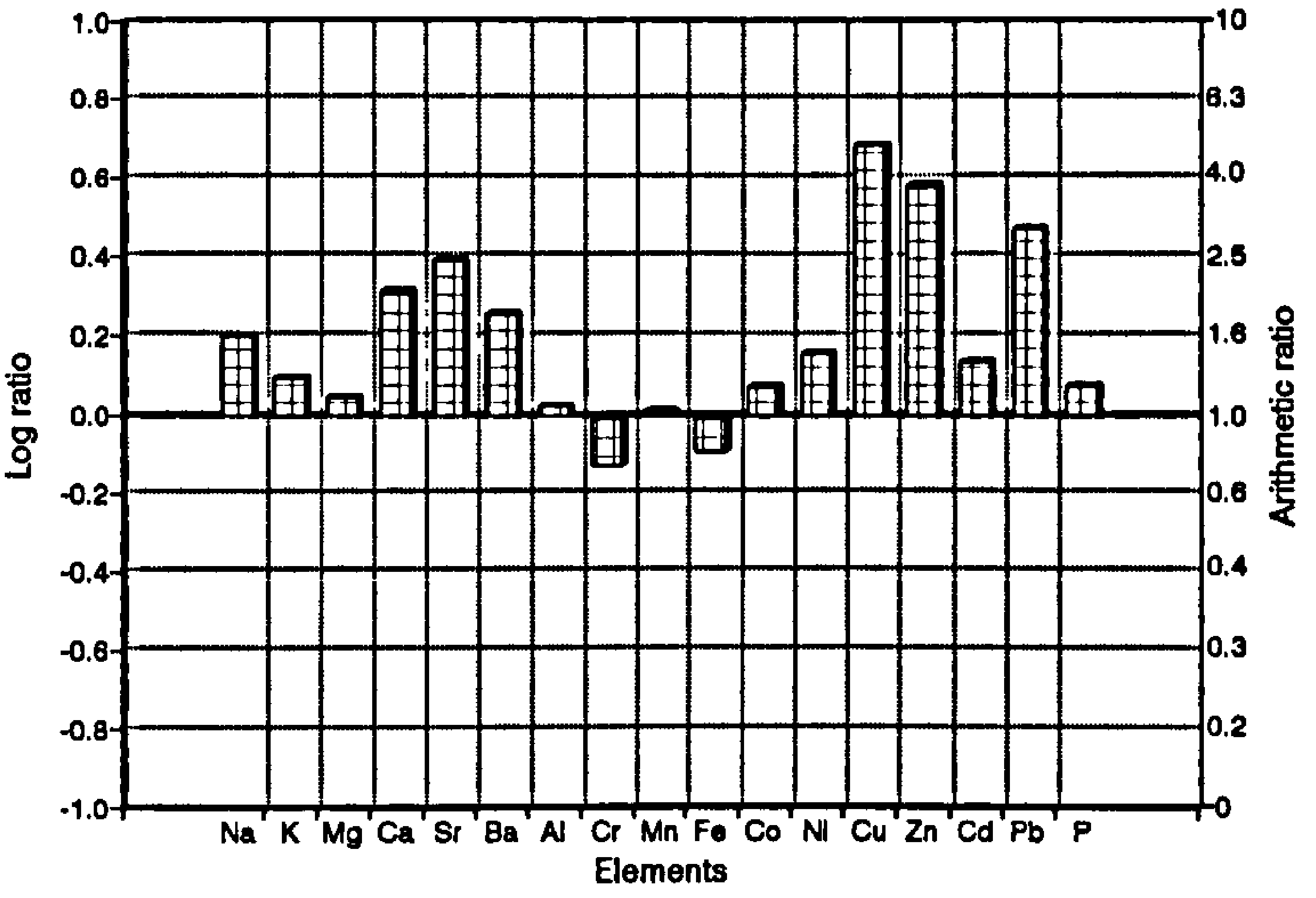


Fig. 9.18a Median concentrations of selected elements in topsoils (0-15cm) from urban gardens overlying made ground in Wolverhampton, normalised to median concentrations for soils in England and Wales (McGrath and Loveland, 1992) and expressed on a log-scale

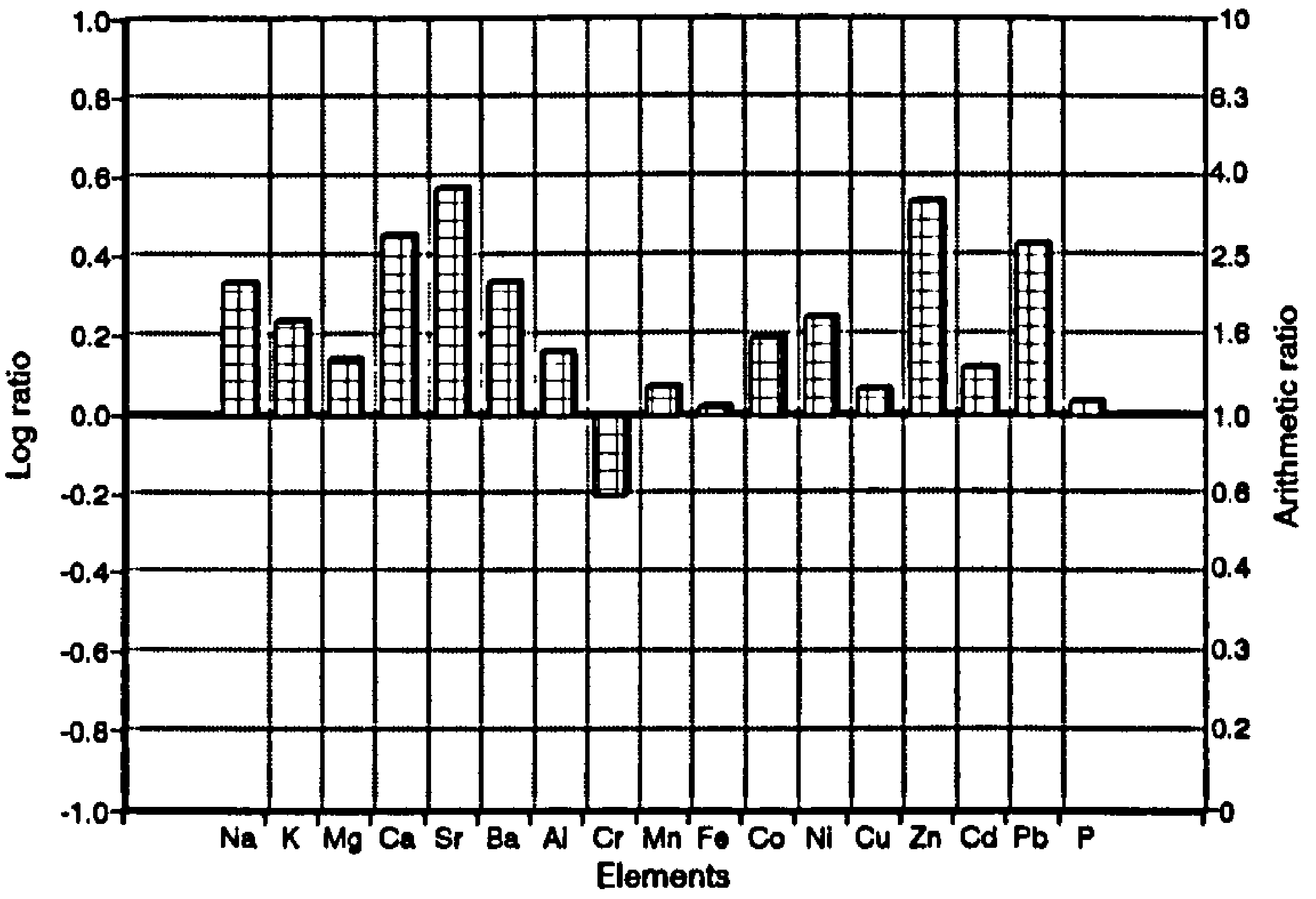


Fig. 9.18b Median concentrations of selected elements in subsurface soils (30-45cm) from urban gardens overlying made ground in Wolverhampton, normalised to median concentrations for soils in England and Wales (McGrath and Loveland, 1992) and expressed on a log-scale

than industrial areas and this could result from greater applications of fertilisers. Imported topsoils are common in urban gardens in Wolverhampton which is probably another factor resulting in lower ratios compared with industrial areas.

9.2.37 Made ground - Subsurface soils (30-45cm) in urban gardens

The normalisation ratios for these soils are shown in Fig. 9.18b and reported in Table 9.7. The overall pattern is similar to topsoils with the highest ratios for the metals Sr, Zn, Ca and Pb. The relationship between topsoils and subsurface soils for urban gardens is however, different to that for soils in industrial areas and areas of open space. In industrial areas, the metals Cu, Zn and Pb are observed to have higher ratios in subsurface soils. In urban gardens ratios for these metals are higher in topsoils, suggesting greater accumulation in the top 15cm, relative to depths of 30-45cm. Ratios for Cd and P are also higher in topsoils than subsurface soils (see Figs. 9.18a and 9.18b). Ratios for Na, K, Mg, Ca, Sr, Ba, Al, Mn, Fe, Co, and Ni all exceed 1, as for topsoils, although ratios are generally higher than in topsoils. This probably relates to the composition of the fill material, although imported topsoils may also be an influence.

9.2.38 Made ground - topsoils (0-15cm) in industrial areas

The normalisation ratios for these topsoils are shown in Fig. 9.19a and reported in Table 9.8. With the exception of K (0.89) all ratios are > 1. The highest ratios are observed for Cu > Zn > Pb > Sr > Ca > Cd (see Fig 9.20a and Table 9.8). The ratios for Cu, Zn and Pb, in particular, are high (approximately 10, 5 and 4 times, respectively, higher than median concentrations for soils of England and Wales). This reflects the importance of metal works in these areas as soils in these areas are subject to inputs through both waste materials and emissions.

Ratios of approximately 2 are observed for Ca, Sr, Ba and Ni (see Fig. 9.19a and Table 9.8). Calcium, Sr and Ba are commonly observed at ratios of > 1 in garden soils in Richmond, and this appeared to be a signature of the land-use with probable sources being lime, building material such as plaster, gypsum and concrete, fossil fuel burning and paint for Ba in particular. The composition of the fill and industrial emissions are probable sources of these elements in Wolverhampton. Sodium, Mg, Al, Cr, Mn, Fe, Co and P also have ratios of > 1 in these soils, and specific uses in industrial processes (particularly Mn and Fe - see Table 3.2), emissions from industrial activities and the composition of the fill material probably result in ratios of > 1 for these elements.

9.2.39 Made ground - Subsurface soils (30-45cm) in industrial areas

The normalisation ratios for these soils are shown in Fig. 9.19b and reported in Table 9.8. With the exception of Cr (0.89) all ratios are > 1. As for topsoils, the highest ratios are for the metals Cu, Zn and Pb (ratios of > 12, 6 and > 5, times higher, respectively, than median concentrations for soils of England and Wales). These ratios are higher than for corresponding topsoils. In section 4.7.6 made ground was stated as varying in thickness from 4-10m, at times reaching 20m. This probably explains the high ratios of elements at depths of 30-45cm. Sodium, Mg, Ca, Sr, Fe, Co and Ni also have higher ratios at 30-45cm than at 0-15cm, with similar ratios for Al, Mn, Cd and P. This is probably a result of the fill composition.

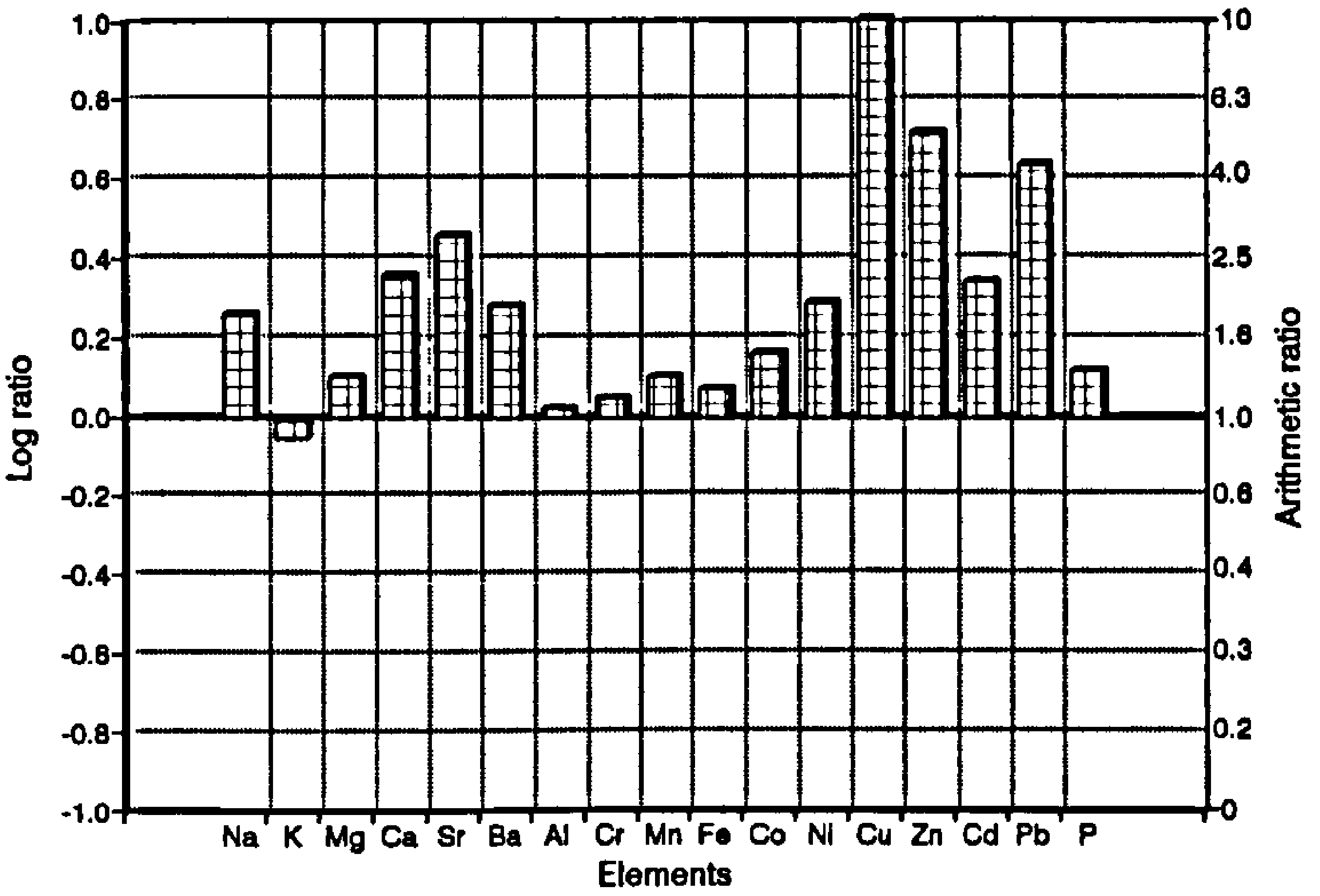


Fig. 9.19a Median concentrations of selected elements in topsoils (0-15cm) from industrial areas overlying made ground in Wolverhampton, normalised to median concentrations for soils in England and Wales (McGrath and Loveland, 1992) and expressed on a log-scale

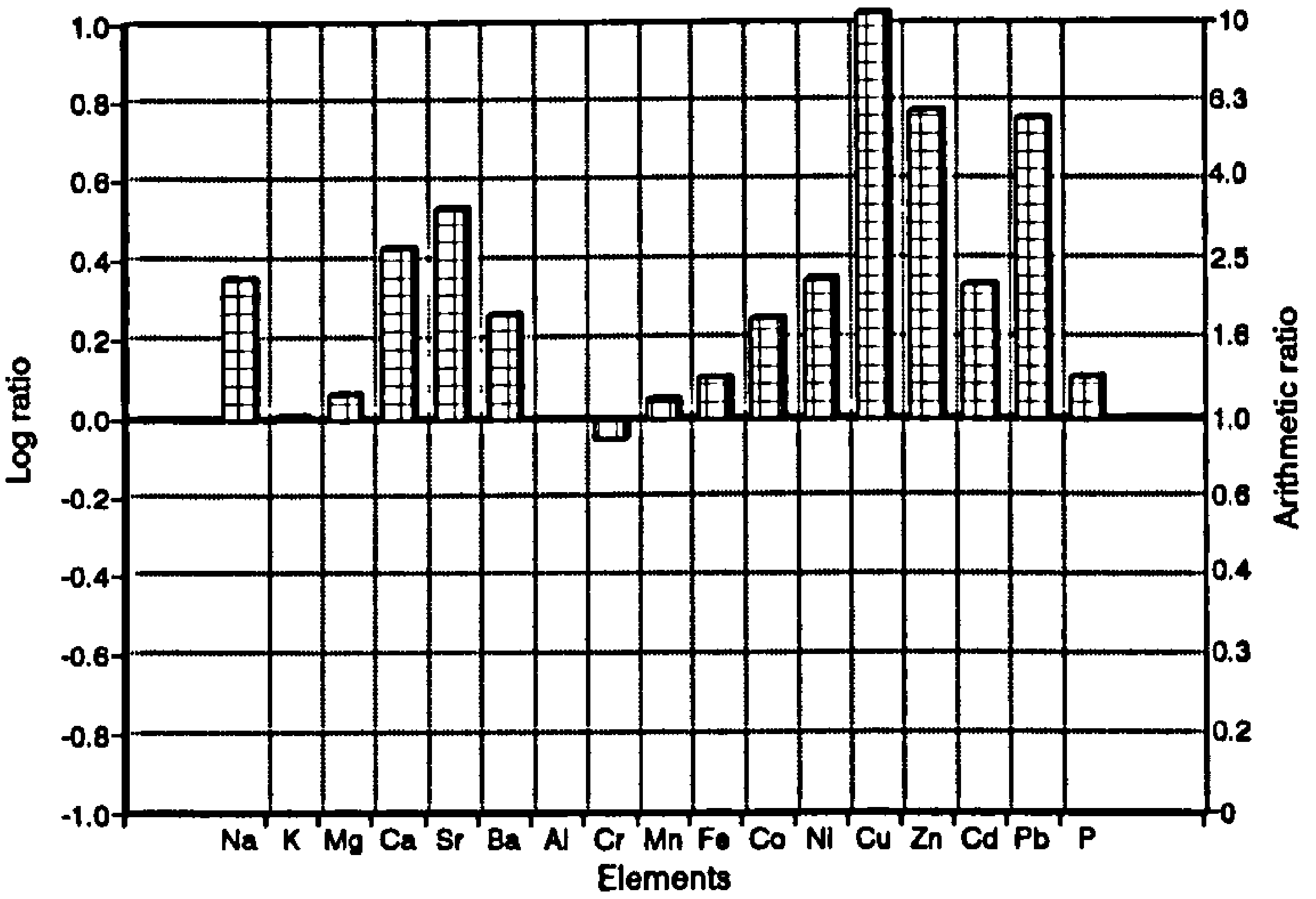


Fig. 9.19b Median concentrations of selected elements in subsurface soils (30-45cm) from industrial areas overlying made ground in Wolverhampton, normalised to median concentrations for soils in England and Wales (McGrath and Loveland, 1992) and expressed on a log-scale

Table 9.8 Ratios of elements in soils overlying made ground, as designated by land-use, after normalisation to median concentrations reported for soils in England and Wales (McGrath and Loveland, 1992)

	topsoils			subsurface soils		
	n=11	n=45	n=16	n=11	n=45	n=16
	OS	UG	IN	OS	UG	IN
Na	1.30	1.58	1.83	1.81	2.15	2.26
K	1.05	1.25	0.89	1.42	1.72	1.02
Mg	1.06	1.11	1.27	1.33	1.39	1.15
Ca	1.61	2.05	2.28	1.95	2.84	2.69
Sr	2.04	2.46	2.88	3.00	3.75	3.38
Ba	1.69	1.80	1.91	2.64	2.16	1.81
Al	0.87	1.05	1.05	1.21	1.44	1.00
Cr	0.65	0.75	1.12	0.82	0.63	0.89
Mn	1.05	1.03	1.27	1.35	1.17	1.12
Fe	0.79	0.81	1.18	1.24	1.04	1.26
Co	1.07	1.18	1.45	1.67	1.56	1.78
Ni	1.29	1.43	1.94	2.14	1.75	2.24
Cu	4.68	4.84	10.2	6.31	1.15	12.5
Zn	2.96	3.83	5.20	3.36	3.46	6.00
Cd	1.09	1.37	2.20	1.34	1.31	2.16
Pb	2.75	2.96	4.34	3.72	2.70	5.74
P	1.02	1.19	1.31	1.04	1.08	1.27

OS Soils in areas of open space UG Soils from urban gardens

IN Soils from industrial areas

9.2.40 Summary

In section 9.2 the data for Wolverhampton are normalised to data reported for the soils of England and Wales (McGrath and Loveland, 1992). The Wolverhampton data are designated by land-use and parent material, in an effort to assess the importance of these factors both individually and collectively and to discern if any geochemical signatures exist from the geology.

The importance of industrial activity in Wolverhampton has probably masked much of the natural geochemical signatures in the city, both locally though specific processes and emissions, and on a more widespread extent through large-scale burning of fossil fuels and small pockets of industrial activity away from the main body in the south-east. In general, industrial activity has resulted in high concentrations of metals in soils, particularly Cu, Zn, Pb and Cd, but also Ni and Co to a lesser extent. Ratios $>$ 2 are observed in most topsoil categories for Cu, Zn and Pb, irrespective of land-use and parent material. The highest ratios of Na, Ca, Sr, Mn, Fe and Co are also observed specifically in industrial areas, particularly those underlain by made ground. In general, most elements have higher ratios in industrial areas underlain by made ground than in industrial areas underlain by glacial-till. It is believed that although the nature of the industry may vary in these areas and the history of industrial activity may also differ, the most important factor accounting for this trend is the composition of the fill. The fill is known to contain by-products of industrial activity (see section 4.7.6).

In contrast, topsoils in agricultural areas very often have the lowest ratios of elements. Two important factors are the land-use and the location of these sites near the outskirts of the city, particularly in the north and west. Agricultural areas generally have the lowest ratios of Na, K, Mg, Ca, Al, Fe, Co, Ni, Cu, Zn, Cd, Pb and P.

The geological description of glacial-till (see section 4.7.5.2) states that this material is very homogenous and the ratios for K, Mg, Al and Mn in particular are very consistent in topsoils, irrespective of land-use, a trend which is not observed for any of the other parent materials in the city. This suite of elements possibly represents the clay fraction of the glacial-till, and in comparison with other topsoils in agricultural areas, those overlying till have higher ratios of Na, K, Ca, Sr, Ba, Al, Cr, Fe and Co than soils developed on alluvium and the Kidderminster Formation. The geological description of alluvium states that the deposit takes the form of silt and clay overlying coarser sand and gravel (see section 4.7.5.5), whilst the Kidderminster Formation is the oldest of the Triassic rocks and consists of medium to coarse grained sandstone (see section 4.7.4.1). Soils developed on the Clent Formation also have higher ratios of a number of elements than soils associated with other land-uses and parent materials, particularly those for K, Mg and Al, which suggests that this is a feature of the geochemical signature rather than anthropogenic inputs.

An examination of the data for areas of open space shows soils overlying Bromsgrove sandstone and, to a lesser extent, Wildmoor sandstone have lower ratios of a suite of elements than soils overlying glacial-till, alluvium and fluvio-glacial deposits. The location of these deposits near the outskirts of the city in the west, particularly Bromsgrove sandstone, is an important factor, with the industrial base located in the east and south-east. An examination of the geochemical maps for the city show that for most elements the lowest percentiles are often observed in these areas. This is also the case for elements such as K, Al, and Mn which do not have as many anthropogenic sources as the heavy metals. This suggests that the natural geochemical signature for these sandstones results in low concentrations of a suite of elements.

The metals Cu, Zn, Cd and Pb generally have lower ratios in subsurface soils reflecting the greater accumulation of these metals in the top 15cm of the profile, probably from anthropogenic inputs. The exceptions to this are soils overlying made ground in industrial areas and areas of open space, where ratios for these metals are higher at depths of 30-45cm compared to 0-15cm. This probably relates to the general disturbance of these soils and the composition of the fill material. Soils overlying glacial-till, irrespective of land-use have higher ratios of Na, K, Mg and Al in subsurface soils than in topsoils. This is probably due to natural variation of the geochemical signature which is apparent despite significant anthropogenic inputs to soils in the city. Very similar ratios of Na, K, Mg and Al are common for both sample depths in soils overlying a number other parent materials in Wolverhampton, reflecting the consistency of this component of the geochemical signature.

9.3 The influence of house-age on the concentrations of elements in garden soils

9.3.1 Introduction

In section 7.3.2 it is shown that house-age is an important factor influencing the concentration of a number of elements in garden soils from Richmond. Concentrations of

Pb, Ba, V and Fe in particular, are shown to increase significantly in soils with increasing age of property (houses < 50 years old, houses aged 50-100 years old and houses > 100 years old). That is, concentrations of Pb, for example are significantly higher in garden topsoils associated with housing > 100 years old, than in garden topsoils associated with housing of between 50-100 years old, which in turn are higher than those in garden topsoils associated with housing < 50 years old. Local government records only permitted the accurate ageing of 92 of the 176 houses sampled in Wolverhampton, the data from which are separated into three groups (as for Richmond; < 50 years old, 50-100 years old and > 100 years old) and summarised in Table 9.9.

9.3.2 Discussion

Copper, Pb and P are the only elements to show a numerical increase in concentration with increasing age of property across both of the age boundaries (using geometric means for comparison - see Table 9.9). These increases are, however, statistically insignificant (all $P > 0.05$). Beryllium, Mg, Ti, V, Cr, Fe, Co and Ni all have higher geometric means in garden soils associated with houses which exceed one hundred years in age than in garden soils associated with houses which are less than fifty years old. These increases in concentration, as with the trend observed for Cu, Pb and P, are statistically insignificant (all $P > 0.05$) and may represent minor anthropogenic additions of these elements over time or natural variation of the geochemical signature.

It is difficult to interpret why house-age would appear to be such an important influence on the concentration of a suite of elements in Richmond and yet statistically insignificant in Wolverhampton. It may relate to the importance of the industrial base as a source of a number of elements. It has been shown that soils in industrial areas have significantly higher concentrations of Mg, Ca, Cr, Fe, Cu and Cd than all the other land-uses in the city. No element was present at significantly higher concentrations in garden soils than in soils from industrial areas. The industrial base of Wolverhampton, both historically and today, is probably the most important source of metals in the city and this may reduce the significance of house-age as a factor influencing concentrations of metals in garden soils.

Table 9.9 Concentrations of elements in Wolverhampton garden topsoils (0-15cm) in relation to different ages property

Age	< 50 years		50-100 years		> 100 years	
n	23		51		18	
	GM	AM	GM	AM	GM	AM
Li	24	25	21	22	26	26
Na	336	366	306	356	328	335
K	5713	5814	4719	4782	5199	5230
Be	1.9	2.0	1.7	1.9	2.1	2.3
Mg	3761	3818	3086	3222	3788	3840
Ca	6752	8266	5681	7252	5772	5933
Sr	58	66	51	58	54	57
Ba	219	230	204	225	220	236
Al	2.56	2.63	2.19	2.24	2.5	2.5
La	21	21	19	19	21	21
Ti	571	584	560	592	579	582
V	45	47	41	43	48	49
Cr	26	27	26	28	27	28
Mn	476	531	445	499	448	460
Fe	2.08	2.14	1.91	2.03	2.3	2.4
Co	10	11	9.3	10	12	13
Ni	28	31	25	29	31	34
Cu	62	77	74	138	80	101
Zn	267	334	296	383	280	326
Cd	0.75	1.0	0.8	1.2	0.6	1.0
Pb	118	147	134	188	210	340
P	1135	1251	1175	1242	1618	1703

GM	geometric mean
AM	arithmetic mean

9.4 Comparison with the National Reconnaissance Survey

9.4.1 Introduction

The results for Pb, Zn, Cu and Cd were published for a National Reconnaissance Survey of urban soils and dusts in 100 towns/cities in Britain (see section 3.5.3 and Tables

3.17-3.21). The results for corresponding samples (25 sub-samples from exposed garden beds) taken in gardens from Wolverhampton are summarised in Tables 9.10 and 9.11.

9.4.2 Discussion

Unlike Richmond, Wolverhampton was not one of the cities sampled in the extensive urban study, so a comparison with data for Wolverhampton which pre-dates this study by more than 10 years is not possible. However, a comparison with the other cities in the study shows that the geometric mean for Pb in garden soils from Wolverhampton is much lower than that reported for all residential areas in Britain with the exception of the geochemical hotspots (135 μg/g, compared with 266 μg/g, respectively), whilst a geometric mean of 294 μg/g is reported for London parks (Culbard et al., 1983). Cadmium concentrations are also lower for garden soils in Wolverhampton (a geometric mean of 0.8 μg/g) compared with both London parks and all residential areas of Britain with the exception of the hotspots (1 μg/g and 1.2 μg/g, respectively). Comparisons are difficult, however, as concentrations of Cd which were below the detection limit were assumed to have a Cd concentration of 1 μg/g in the National Reconnaissance Survey (Moir, 1992).

For Zn and Cu, however, the geometric mean concentrations reported for Wolverhampton of 274 μg/g and 64 μg/g respectively, (see Table 9.10) are comparable with the results published for all the residential areas in Britain excluding the hotspots. Geometric mean concentrations of 278 μg/g and 56 μg/g are reported for Zn and Cu respectively, in this category (Culbard et al., 1983). The geometric mean concentrations for Zn and Cu in Wolverhampton are significantly higher than those reported for London parks (183 μg/g and 49 μg/g for Zn and Cu, respectively for soils in London parks). Geometric mean concentrations for Pb, Zn, Cu and Cd are all significantly lower in garden soils from Wolverhampton in comparison with data reported for 7 London boroughs, despite the industrial activity in Wolverhampton. The large population in London is an important factor influencing the metal content of soils (see Tables 3.17 and 9.10).

The results for the other elements analysed are summarised in Table 9.11. No results are reported for these elements in the National Reconnaissance Survey. Using geometric means for comparison, most elements are present at higher concentrations in soils from Wolverhampton at 0-5cm than at a depth of 0-15cm. However, only Pb, Zn, Ca and P have significantly higher concentrations at depths of 0-5cm (for Pb and Zn, $P < 0.05$; for Ca and P, $P < 0.001$). This suggests greater accumulation of these in the top 5cm from anthropogenic processes, relative to 0-15cm. For Ca and P, additions of fertilisers and lime and burial of building material may be responsible for this trend (see Table 3.21). In Richmond, Ca and P, along with Sr and Ba were observed at significantly higher concentrations in soils at depths of 0-5cm, relative to 0-15cm.

Table 9.10 Concentrations of selected metals (μg/g) in garden soils (0-5cm) in Wolverhampton

	Garden soil (n=176)			
	GM	AM	SD	Range
Pb	135	179	142	31-601
Zn	274	364	374	62-2650
Cu	64	90	109	15-722
Cd*	0.8	1.4	3.0	<0.2-22.3

GM	geometric mean
AM	arithmetic mean
SD	standard deviation

Table 9.11 Concentrations of selected elements ($\mu g/g$) in garden soils (0-5cm) from Wolverhampton

	topsoil (n=176)			
	GM	AM	SD	Range
Li	22	23	6	12-46
Na	316	345	167	142-1040
K	5188	5287	1102	362-9860
Be	1.7	1.89	0.8	0.7-4.7
Mg	3393	3488	805	1920-5380
Ca	6089	7273	4653	890-21400
Sr	52	58	29	18-165
Ba	224	244	117	95-836
Al	2.33	2.38	5167	1.48-4.44
La	19	19	3.4	13-32
Ti	548	562	146	408-1310
V	42	44	12	24-93
Cr	27	30	29	14-236
Mn	436	477	237	214-1410
Fe	1.96	2.04	5671	1.18-3.89
Co	9.5	10	4.6	4-27
Ni	27	30	15	10-90
P	1199	1305	589	387-3930

GM	geometric mean
AM	arithmetic mean
SD	standard deviation

9.5 Overall summary

A comparison has been made of the Wolverhampton data set (17 elements), as designated by land-use, geology and sample depths, with an overall data set for the soils of England and Wales (McGrath and Loveland, 1992). This normalisation technique has shown several trends:

1). Normalisation ratios of > 1 are observed in topsoils for Cu and Zn, irrespective of geology, land-use or location.

2). Topsoils overlying most parent materials, for most land-uses, have normalisation ratios of > 1 for Pb and P, in particular, but also Ca, Sr and Ba.

3). The highest ratios, in general, are associated with soils from industrial areas, particularly those overlying made ground.

4). The lowest ratios, in general, are associated with agricultural soils. This is a result of minimum anthropogenic inputs and their location near the outskirts of the city.

5). A consistent geochemical signature is observed for K, Mg, Al and Mn for soils overlying glacial-till, irrespective of land-use. The description of the geology states that the till is very homogenous (see section 4.7.5.2).

6). Subsurface soils overlying made ground in industrial areas have higher ratios of a suite of elements than topsoils, including, Cu, Zn and Pb. The disturbance of the soils in these areas and the composition of the fill material is probably responsible for this.

In contrast to Richmond, house-age is shown not to be a major influence on the concentration of elements in soils. Only Cu, Pb and P are present at numerically higher concentrations in garden soils associated with housing of between 50-100 years old than in soils associated with housing of < 50 years old, and also higher in garden soils associated with housing of > 100 years old than in soils associated with housing of between 50-100 years old (see Table 9.9). However, these increases are statistically insignificant ($P > 0.05$). Industrial activity in the city, both historically and today, is probably the most important factor influencing the distribution of a number of elements in soils in Wolverhampton.

In comparison with results from the National Reconnaissance Survey of metals in urban dusts and soils (Culbard *et al.,* 1983; Thornton *et al.,* 1985; Culbard *et al.,* 1988 and Thornton, 1989) concentrations of Pb and Cd are lower in garden soils from Wolverhampton (0-5cm) than for all residential areas of Britain with the exception of the hotspots. However, the geometric means for Zn and Cu are comparable with results for all the residential areas of Britain, with the exception of the hotspots. The geometric means for Cu, Zn, Cd and Pb are lower than the corresponding geometric means for seven London boroughs, despite the industrial activity in Wolverhampton.

Comparison of mean concentrations for elements at 0-5cm and 0-15cm, shows significantly higher concentrations of Pb, Zn, Ca and P at 0-5cm than 0-15cm ($P < 0.05$). This relationship is also observed for Ca and P in Richmond, and it is postulated that greater accumulation of P and Ca in the top 5cm of the profile probably results from additions of fertilisers and lime to garden soils, whilst higher concentrations of Pb and Zn probably result from industrial emissions.

CHAPTER TEN CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER STUDIES

10.1. Conclusions for Richmond-upon-Thames

10.1.1 Objective of research:

1. To investigate the spatial distribution of 21 elements in topsoils (0-15cm) in Richmond-upon-Thames.

10.1.2 Conclusions

Systematic sampling of soils on a grid basis in the study areas at a density of 4 samples per km^2, multi-element analysis by ICP-AES and the use of GIS mapping techniques has shown that the highest concentrations of Pb in topsoils, generally, occur close to roundabouts and major road junctions in Richmond (concentrations > 1094 μg/g). This suggests that emissions from cars are still important despite the reduction of Pb in petrol that has occurred since 1986, and that Pb has a long residence time in urban soils. The lowest concentrations of Pb, Zn and Cu are clearly shown in the large areas of open space in Richmond Park, Hampton Court and Bushy Park, and Kew gardens (generally $\leq$ 75 μg/g Pb, $\leq$ 60 μg/g Zn, and $\leq$ 17 μg/g Cu, respectively).

High concentrations of a number of elements are found in urban gardens in built-up parts of the borough, compared to areas of open space, particularly for Pb, Zn, Cu, Ni, Ca, Sr, Ba, V, Co and P. These elements have several anthropogenic sources in towns and cities which include:

1. Emissions from vehicles and wear of vehicle parts.
2. The burning of fossil fuels and disposal of ashes in the gardens.
3. The flaking of lead-rich paint.
4. The burial of building materials such as plaster, concrete, gypsum and pottery.
5. The applications of fertilisers and lime in gardens.

High concentrations are observed for several elements in soils close to the Thames, particularly in Petersham, Teddington, south of Hampton Court, and Kew (see Fig. 4.1). This trend may result from anthropogenic additions, or be a characteristic of soils overlying deposits of alluvium in these areas. The area close to Teddington, in particular, has been the site of past industrial activity, with an engineering works, an iron works, a sewage works and a gas works previously located in the area. Emissions from these industries and the application of sewage sludge to soils in this area may explain the relatively high concentrations of a number of elements. In addition, periodic flooding from the Thames in the past may have resulted in increased concentrations of a number of elements. A study of the local history has shown that areas close to the Thames in Richmond were prone to flooding from the river . Secondly, a number of these soils have developed on deposits of alluvium which have significantly higher concentrations of Cu, Ni, Ca, Sr and Co than soils overlying all the river terraces and London Clay. These may be the result of natural differences in the geochemical signature for these parent materials.

10.1.3 Objective

2. Assess the influence of anthropogenic factors, particularly land-use, on the distribution of 21 elements in Richmond-upon-Thames.

10.1.4 Conclusions

The data for Richmond were classified on the basis of land-use to assess the significance of any patterns that may result from anthropogenic activity. Samples were designated as either urban gardens or areas of open space, the latter comprising samples taken in the Richmond and Bushy Parks, Hampton Court, Kew gardens, sports grounds, golf courses, cemeteries and school playing fields. Most of the data have a log-normal distribution, so the data were log-transformed and compared using a students t-test. Results show significantly higher concentrations of a suite of elements in garden topsoils compared with topsoils in areas of open space at the following confidence intervals:

$P < 0.001$; Pb, Zn, Ca, Ba
$P < 0.01$; Cu, Ni, Na, Be, Sr, V, Cr, Mn, Fe, Co and P
$P < 0.05$; Al

As samples from urban gardens and areas of open space overlie the different geological parent materials in Richmond, it is suggested that differences in concentrations between these classes results from greater anthropogenic additions of these elements in urban gardens from a combination of vehicle emissions, wear of vehicle parts, burning of coal and the disposal of ashes from this process, the flaking of paint from houses, the use of fertilisers, the use of compost heaps and the burial of building materials and pottery.

Lead, Zn, Cu, Ni, Na, Be, Ca, Sr, Ba, Al, V, Cr, Mn, Fe, Co and P are also observed at significantly higher concentrations in subsurface garden soils relative to subsurface soils from areas of open space. With the exception of P ($P < 0.05$ for garden soils), there are no significant differences between the concentrations observed for elements in topsoils and those in subsurface soils, irrespective of land-use ($P > 0.05$). This may result from physical disturbance of the soils, particularly in urban gardens, consistent geochemical signatures, and possibly movement of elements from the top 15cm to depths of 30-45cm through leaching. Soils in Richmond are dominated by the sand-size fraction, which accounts for approximately 80% of the soil. This does not vary significantly for soils developed on different geological parent materials and different land-uses.

House-age is shown to be an important factor influencing the concentrations of a suite of elements in Richmond. The relationship is strongest for Pb, Ba, V and Fe which are shown present at significantly higher concentrations in garden soils associated with property of between 50-100 years old than in garden soils associated with property of < 50 years old. These metals have significantly higher concentrations in garden soils associated with property of > 100 years old than in garden soils associated with property of between 50-100 years old. Lead and Ba are associated with paints, particularly those manufactured pre-1913, whilst Fe and V probably represent additions to garden soils from the burning of fossil fuels and the disposal of ashes. Garden soils associated with older property have been exposed to anthropogenic processes for longer periods than soils associated with newer housing, whilst open-fires were more common and lead-rich paints used more extensively in the past.

Soils in urban gardens also have a significantly higher pH than soils from areas of open space ($P < 0.01$). It is suggested that this is the result of greater additions of fertilisers and lime to garden soils and the large amounts of building material and pottery which are found in garden soils. Percentages of sand, silt, clay and organic matter do not vary significantly with land-use. The pH and organic matter content of soils are important influences on the mobility of metals, and hence health considerations of metal contamination. Most metals having increased mobility at a low soil pH whilst organic matter influences the formation of stable organo-metallic complexes which greatly reduces the mobility of metals. Soil solution chemistry is a very complex system with parameters such as pH influencing, and in turn influenced, by many factors.

The geometric mean concentration for Pb in garden soils from Richmond is comparable with average concentrations reported for Liverpool and soils in the zone 4-10km from the centre of London (271 μg/g, 275 μg/g and 242 μg/g, respectively). Comparable results are also observed for Upper Silesia, Hong Kong and Seoul. American studies generally report higher concentrations of Pb in garden topsoils than observed in garden soils from Richmond. It is suggested that higher concentrations for Pb in soils from America are the result of differences in sampling techniques, sample depths or the result of a larger number of wooden houses in America. Paint is a source of Pb for garden soils, so a larger painted area is an important factor.

The geometric mean concentration for Zn in garden soils is similar to that reported for soils in a number of British towns and cities, whilst the corresponding measurement for Cu is generally lower than that reported for soils in other British cities. Concentrations of Zn and Cu in urban gardens, in general, are higher than those reported for garden soils in America and lower than for soils in more industrial cities such as Hamburg, Hong Kong and Seoul. Cadmium concentrations in Richmond soils are generally lower than those reported for other urban studies in Britain, America and other parts of Europe.

Samples were also taken from the top 5cm of exposed soils in urban garden to facilitate a comparison with results from National Reconnaissance Survey of metals in urban dusts and soils. In this extensive study samples were taken from one hundred gardens in fifty three towns and cities in Britain, one of which was the London borough of Richmond-upon-Thames. Sampling was undertaken in the early 1980's, which permits comparison of data for Pb, Zn, Cu and Cd in studies separated by approximately fifteen years. Geometric mean concentrations of Pb, Zn and Cd reported in the National Reconnaissance Survey for all residential areas of Britain, except the geochemical hotspots are higher than those observed for Richmond in the present study. Geometric mean concentrations of Cu are comparable for the two studies. Higher concentrations of Pb, Zn and Cd are probably the result of sampling older housing in the National Reconnaissance Survey and a reduction in important sources of metals that has occurred over the last fifteen years, particularly the reduction in the Pb content of petrol.

10.1.5 Objective

3. To investigate whether the underlying geology exerts an influence on the distribution of elements in soils in Richmond-upon-Thames.

10.1.6 Conclusions

The sand fraction is the dominant particle size in soils from Richmond, irrespective of parent material. In general, the sand fraction accounts for approximately 80 % of the soil with average clay and silt contents of approximately 5% and 10%, respectively. This sand dominance seems to be reflected in low concentrations of clay-associated elements such as K, Mg, Al and Mn. In comparison with other parent materials, soils overlying the high level terraces have the lowest concentrations of all elements (with the exception of Cr). This is probably a reflection of the natural geochemical signature for these soils and the location of these samples in the interior of Richmond Park where anthropogenic influence is small. Low concentrations of a suiteXofelements are also observed in soils overlying London Clay in Richmond park. Soils overlying London Clay are also dominated by the sand-size fraction, consistent with the geological description for the upper most part of this deposit which is a sandy facies.

Soils overlying alluvium in Richmond have significantly higher concentrations of Na, V, Mn and Fe than soils overlying London Clay and high level terraces. This may be a result of differences in the natural geochemical signatures for soils developed on these deposits, or a result of anthropogenic additions to soils overlying alluvium via periodic flooding and dumping of material in these areas, or both.

10.1.7 Objective

4. To compare and contrast multi-element data for soils in Richmond-upon-Thames with the large data set reported in The Soil Geochemical Atlas of England and Wales (McGrath and Loveland, 1992).

10.1.8 Conclusions

Normalisation of data of Richmond to those for the topsoils from England and Wales in general has shown that, with the exception of topsoils overlying high level terraces, ratios for Pb generally exceed 1, irrespective of land-use or parent material. The highest ratios of Pb are consistently observed in urban gardens, concentrations varying from 4.8-11.8 times higher than those reported as the median concentration for the topsoils of England and Wales in general. Urban gardens in Richmond generally have concentrations of Cu and Zn approximately two times higher than those observed for the topsoils of England and Wales. Calcium, Sr, Ba and P are also observed at higher concentrations in garden soils than in topsoils from England and Wales in general.

Concentrations of Na, K, Mg, Al and Mn, although generally higher in soils from urban gardens than areas of open space, are present at consistently lower concentrations in soils from Richmond than in the topsoils of England and Wales in General. This is probably the result of most soils in Richmond overlying glacial deposits which have a high sand content. Concentrations of Fe, Co and Ni although higher in garden soils than in soils from areas of open space, are similar to the median concentrations for these metals in soils from England Wales in general. This is probably a result of the minor anthropogenic additions of these metals to soils in Richmond, rather than natural variation of the geochemical signature.

10.1.9 Objective

5. To compare and contrast multi-element data for soils in Richmond-upon-Thames and Wolverhampton.

10.1.10 Conclusions

Most elements are present at higher concentrations in soils from Wolverhampton than those in Richmond. This is probably due to two main factors; most of Wolverhampton is underlain by a clay-rich glacial till which results in significantly higher concentrations of Na, K, Mg, Al, Li and Mn than in soils from Richmond which have developed, predominantly, over river terraces with a high sand content. Soils in Wolverhampton also have higher concentrations of Zn, Cu, Cd, Ni, Be, Sr, Ba, Cr and Co than soils in Richmond. It is suggested that this is due to the metal processing works in the city which dates back to the middle of the last century. The iron and steel industry was prevalent in the east of the city, which used a number of metals in galvanising techniques and involved the burning of extensive amounts of fossil fuel.

Concentrations of Pb are generally found at higher concentrations in Richmond than Wolverhampton, despite the lack of industry in the London borough. This suggests that traffic emissions may be the most important source of Pb in the study areas, with traffic densities probably higher in the Richmond. Wolverhampton has undergone a great deal of redevelopment in recent times which may also be an important factor. Concentrations of Ti are also generally higher in soils from Richmond. In both studies, the concentration of this metal is shown not to vary significantly with land-use, it is therefore suggested that differences in the geochemical signatures for study areas explains higher concentrations of Ti in soils from Richmond. Concentrations of Ca and P are similar for the two study areas, reflecting similar natural and anthropogenic inputs for the two areas.

Baseline concentrations of V and Fe are generally higher in Richmond than Wolverhampton, which may reflect the natural geochemical signature for the two areas. However, specific industrial areas of Wolverhampton have higher concentrations of V and Fe than any soils in Richmond. This is probably due to the extensive burning of fossil fuels in these areas and specific industrial processes involving the use of these metals.

10.2 Conclusions for Wolverhampton

10.2.1 Objective of research:

1. To investigate the spatial distribution of 21 elements in topsoils (0-15cm) in Wolverhampton.

10.2.2 Conclusions

Systematic sampling of soils on a grid basis in the study areas at a density of 4 samples per km^2, multi-element analysis by ICP-AES and the use of GIS mapping techniques has shown that the highest concentrations of a suite of elements are observed in areas of contemporary industrial activity. Concentrations of Pb > 1000 μg/g, Zn $>$ 1200 μg/g, Cu > 400 μg/g, Cd > 5.6 μg/g and Ni > 80 μg/g are observed in these areas, and the highest concentrations are generally observed for Mg, Ca, Cr, Mn, Fe and Co in industrial parts of the city.

High concentrations are also found for Pb, Zn, Cu, Cd, Ni, Ba, Cr and P in the residential areas of Bradmore and Merry Hill (see Fig. 4.3). This may be the result of past industrial activities in these areas or from sources of these elements which are more specific to the urban garden (e.g. the flaking of paint, the disposal of ashes from open fires and applications of fertilisers).

The lowest concentrations of most elements are generally found in the western outskirts of the city. In this region, Pb concentrations of ≤ 54 μg/g are found, in addition to Zn concentrations of ≤ 94 μg/g, Cu concentrations of ≤ 23 μg/g, Cd concentrations of ≤ 0.22 μg/g and Ni concentrations of ≤ 14 μg/g. The low concentrations of a suite of elements is the result of two main factors. This area is adjacent to agricultural land just outside the city and several kilometers from the industrial base in the east, which probably means deposition of metals from industrial emissions are much lower than for sites in the east of the city. Secondly, this area is underlain with Triassic sandstones (Bromsgrove and Wildmoor sandstones) which have naturally low concentrations of a suite of elements.

10.2.3 Objective

2. Assess the influence of anthropogenic factors, particularly land-use, on the distribution of 21 elements in Wolverhampton.

10.2.4 Conclusions

The data for Wolverhampton were separated on the basis of land-use to assess the significance of any patterns that may result from anthropogenic activity. Samples were designated as either originating from agricultural areas, areas of open space, urban gardens or industrial areas. Most of the data have a log-normal distribution, so the data were log-transformed and compared using a students t-tests. Soils from industrial areas have significantly higher concentrations of Pb, Zn, Cu, Cd, Ni, Mg, Ca, Cr and Fe than soils associated with the other land-uses in Wolverhampton. It is postulated that this is the result of processes using these metals in industrial areas, and also the composition of the made ground which underlies much of the industrial area.

Urban gardens have significantly higher concentrations of Pb, Zn, Na and Ba than soils in agricultural areas. It is suggested that this results from their greater proximity to industrial areas and/or sources of these metals in gardens which are more specific to urban gardens, such as the flaking of paint, the disposal of ashes from open fires and the salting of urban roads in winter. Garden soils also have significantly higher concentrations of Na, Mg, Ca, Ba and P than soils in areas of open space, which probably results from greater sources of these elements in gardens or differences in the geochemical signatures for these areas.

In subsurface soils, concentrations of Pb, Zn, Cu, Cd and Ni are significantly higher in industrial areas than for all other land-uses, a trend also observed for topsoils. Concentrations of Na, Be, Sr, V, Cr, and Co are also significantly higher in subsurface soils from industrial areas than for other land-uses. Made ground underlies many industrial areas, to depths of several metres. The fill contains some by-products of industrial activity which probably accounts for significantly higher concentrations of this suite of elements.

Subsurface soils from urban gardens have significantly higher concentrations of Be, Ca, Sr, Fe and P than subsurface soils in agricultural areas. It is postulated that this is the result of a greater number of sources of these elements in urban gardens, from the disposal of ashes from open fires, the burial of building material in garden soils and the application of fertilisers and lime to garden soils, and/or greater proximity of urban gardens to industrial areas, relative to many of the agricultural sites near the outskirts of the city.

In contrast to Richmond where, with the exception of P, elements were not observed to vary significantly in concentration with sample depth, a number of elements significantly vary in concentration with sample depth in Wolverhampton. In areas of open space and urban gardens, concentrations of Pb, Zn, Cu and Cd are significantly higher in topsoils than in subsurface soils, whilst in agricultural soils concentrations of Zn and Cd in topsoils are significantly higher than those for subsurface soils. A possible explanation for these differences is that mobility of the metals may vary between the study areas, with sand-rich soils common in Richmond compared with a clay-rich till which underlies most of Wolverhampton. Leaching of metals down the soil profile is probably greater in the sandy Richmond soils. A more detailed investigation of metal speciation and soil chemistry is necessary to interpret these differences accurately. The extent of profile disturbance, an important factor influencing the relationship between concentrations of elements at depths of 0-15cm and 30-45cm, may also differ for the two study areas.

Phosphorus, as in Richmond, is observed at significantly higher concentrations in topsoils than in subsurface soils, in agricultural areas, areas of open space and urban gardens. In urban gardens and industrial areas in particular, a number of elements have numerically higher concentrations, although not statistically significant, at depths of 30-45cm than at 0-15cm. In garden soils, Li, K, Mg, Sr, Al and La are present at significantly higher concentrations in subsurface soils than in topsoils, a trend which probably results from natural variation of the geochemical signature. Modern Wolverhampton is mainly a residential city and glacial-till is the deposit on which most soils have developed. Soils overlying glacial-till, irrespective of land-use, are observed to have higher concentrations of the clay associated elements such as K, Mg and Al at depths of 30-45cm relative to 0-15cm. In industrial areas, the numerically higher concentrations of all elements at depths of 30-45cm, although not statistically significant, is probably a result of the made ground which underlies much of the industrial area. This contains by-products of industrial processes to depths of several metres in places, and probably accounts for high concentrations of most elements at depths of 0-15cm and 30-45cm.

In contrast to Richmond, where house-age was shown to be an important factor influencing the concentrations of several elements in topsoils, no elements shows a statistically significant increase in concentration with increasing age of property in Wolverhampton. Copper, Pb and P are the only elements which show a numerical increase in concentration with increasing age of property (all $P > 0.05$) It is tentatively suggested that the importance of the industrial base as a source of metals in Wolverhampton may override the significance of house-age as a factor influencing multi-element concentrations. Soils in industrial areas have significantly higher concentrations of Pb, Zn, Cu, Cd and Ni than soils from all other land-uses in the city. In Richmond very little industry exists, so the major sources of elements are from cars or from processes occurring within the gardens themselves (the flaking of paint, the disposal of ashes, the burial of building material and the application of fertilisers) and processes which are more common in urbanised areas, relative to areas of open space, such as emissions from vehicles. This age of houses is therefore a more important factor in Richmond-upon-Thames, as this dictates the length of exposure to these sources, since older houses are more likely to have had open fires and been painted with Pb rich paint.

Comparisons with data reported for other urban studies shows that Pb concentrations in garden soils from Wolverhampton are generally lower than those reported for other British and American cities. This is observed when comparing samples at depths of 0-15cm and 0-5cm, the latter with results from the National Reconnaissance Survey of metals in dusts and soils. A geometric mean of 135 μg/g (0-5cm) is considerably lower than corresponding values reported for all the summarised categories in the National Reconnaissance Survey. The geometric mean concentration for Pb in industrial areas are similar to those reported for larger cities such as Birmingham and Leeds.

In contrast, the geometric mean concentration for Zn in urban gardens from Wolverhampton is generally higher than those observed for other British and American cities. This probably results from strong sources of this metal through specific industrial activities in the city and the burning of fossil fuels. The geometric mean concentration for Zn in industrial areas of Wolverhampton is comparable with those reported for the industrial cities of Hong Kong and Seoul. Comparable samples taken in this study and the National Reconnaissance Survey, shows good agreement for results in urban gardens and those for all residential areas of Britain, except the geochemical hotspots.

The geometric mean concentration for Cu in urban gardens in Wolverhampton is similar to mean concentrations reported for other British studies, including results from the National Reconnaissance Survey for all residential areas of Britain excluding the geochemical hotspots. Garden soils in Wolverhampton generally have higher concentrations of Cu than reported for studies based in the United States. As for Zn, Cu concentrations in industrial areas of Wolverhampton are similar to those reported for Hong Kong and Seoul. Cadmium concentrations in industrial areas of the city are similar to mean concentrations reported for larger cities such as London, Birmingham, Leeds and Liverpool, and Cd concentrations in garden soils from Wolverhampton are also similar to those reported for several studies in the United States.

10.2.5 Objective

3. To investigate whether the underlying geology exerts an influence on the distribution of elements in soils in Wolverhampton.

10.2.6 Conclusions

Most of Wolverhampton is underlain by a clay-rich glacial-till, with Triassic sandstones outcropping in the western part of the city and made ground located in the south-east. An examination of the geochemical maps for topsoils in Wolverhampton shows that the lowest percentiles for the majority of elements are generally located near the outskirts of the cities in the west. This is probably due to two main factors; these sites are several kilometres from the industrial base in the east, and deposition from industrial emissions is greatest in the immediate vicinity of the stacks. Secondly, most of the soils in this region have developed on Triassic sandstones (Wildmoor and Bromsgrove sandstones) which seem to have naturally low concentrations of a suite of elements as a feature of their geochemical signature.

The geological description of the glacial-till states that this material is very homogenous, and in this study the ratios of the clay-associated elements, K, Mg, Al and Mn are very consistent, irrespective of land-use. This trend is not observed for any of the other parent materials in Wolverhampton. In comparison with other agricultural areas, soils overlying glacial-till have higher concentrations of Na, K, Ca, Sr, Ba, Al, Cr, Fe and Co than soils overlying alluvium and the Kidderminster Formation. Soils overlying glacial-till also have higher concentrations of Na, K, Mg and Al at depths of 30-45cm, relative to depths of 0-15cm, irrespective of land-use. This is probably due to a natural variation of the geochemical signature.

Soils which have developed on the Clent Formation, a Permian age rock, comprising sandstones with thin beds of red mudstones, have high concentrations of a number of elements. Although these sites are close to the industrial base and therefore influenced by emissions from these works, elements less influenced by anthropogenic activity such as K, Mg, and Al also have high concentrations in these soils compared with soils overlying most parent materials in Wolverhampton. This suggests that the natural geochemical signature for these soils is an important factor influencing high concentrations of several elements.

10.2.7 Objective

4. To compare and contrast multi-element data for soils in Wolverhampton with the large data set reported in The Soil Geochemical Atlas of England and Wales (McGrath and Loveland, 1992).

10.2.8 Conclusions

Normalisation of data from Wolverhampton to those for the topsoils from England and Wales in general has shown that, on average, most topsoils have concentrations of Cu, Zn and Pb two times those reported as median for the topsoils of England and Wales, irrespective of land-use or parent material. In industrial areas concentrations of Pb, Zn and Cu are 3, 3 and 6 times higher, respectively for areas underlain with glacial-till and 4, 5 and 10 times higher, respectively in areas underlain with made ground. Soils in industrial areas underlain with made ground also have concentrations of Ca, Sr and Ba approximately two times higher than those observed for the soils of England and Wales.

Low concentrations of a suite of elements, relative to soils from England and Wales in general, are observed for soils overlying Bromsgrove and Wildmoor sandstones, particularly Al, Cr, Mn, Fe and Co. Soils overlying glacial-till, which most of the soils in Wolverhampton are, on average have concentrations of Na, K, Ca, Sr, Ba and P which are similar to median concentrations for the soils of England and Wales. Soils overlying glacial-till, Triassic sandstones, and alluvium have concentrations of Mg, Al, Cr, Mn, Fe and Co lower than those reported as median concentrations for the soils of England and Wales.

10.3 Recommendations for further studies

The present study has illustrated the spatial distribution of 21 elements in topsoils from Richmond and Wolverhampton and the importance of land-use and geology as factors influencing multi-element distribution in urban soils from these areas. The sampling scheme which was employed is shown to be a good technique for allowing a confident interpretation of spatial data sets, and the use of basic statistical techniques has confirmed many of the spatial trends observed in the geochemical maps. If this research was to be expanded, a number of investigations could be undertaken which will allow a better understanding of the specific processes which influence the multi-element geochemistry of urban soils.

1. The measurement of sampling error in urban gardens is an important feature which needs to be investigated to allow a more confident interpretation of data from urban soils. The present study has shown that the spatial distribution of most elements can be interpreted with confidence due to the small contribution of sampling errors to the overall estimate of variance. Most duplicate samples, however, were taken in areas of open space, to aid the speed of sampling, so it remains unclear if sampling urban gardens results in an equally low sampling error. Research in America has shown that concentrations of metals can vary greatly within a single urban garden, depending on where the sample is taken.

2. The present study has shown that in Richmond soils overlying alluvium have significantly higher concentrations of a number of elements than soils overlying the river terraces and London Clay. These sites flank the Thames, in some cases close to areas of past industrial activities, and it is postulated that direct emissions from these sources or past flooding of the Thames has resulted in higher concentrations of these elements. However, the differences may be a feature of the natural geochemical signature for these soils, despite the fact that soil texture, organic carbon and pH do not vary in soils as a function of parent material. A more detailed examination of the mineralogy of the soils, in relation to parent material, would aid the interpretation of the data. Where concentrations of metals are high enough SEM/EDX could also be

employed to aid the interpretation (see point 3).

3. Source apportionment - SEM/EDX has demonstrated considerable potential for apportioning sources of metals in urban dusts and soils. The present study has shown that urban soils have geometric mean concentrations of metals several times higher than those reported for areas of open space and the soils in England and Wales in general. Patterns within the data and a review of the literature has allowed potential sources to be suggested, and although the elevated concentrations in garden soils are likely to result from a combination of sources, the research would greatly benefit from an understanding of which sources are the most important.

4. Taking air and bulk deposition samples would allow an assessment of the current major sources of metals to urban areas. Sources of metals, and quantities of metals emitted into the environment have changed over the last 50 years in many urban areas with a reduction of the Pb content of petrol and the closing down of many heavy industries. Such an investigation will allow an estimation of metal inputs to soils in the future which will have important implications for the future development of urban land and the potential health risks to the urban population.

5. Operationally defined sequential extractions have been used to examine the partitioning of elements among the various geochemical phases of soils on the basis of their chemical reactivity. The technique provides information regarding the potential mobilization, migration and uptake of metals, which has implications for human health, particularly in areas of high metal concentrations where groundwater may be threatened and crops are grown for consumption in urban gardens.

4. Risk assessment - One of the most recent trends in environmental geochemistry is the concept of risk assessment. A number of models have been developed to assess the potential risk to human health of exposure to soil pollutants, particularly heavy metals. In addition, the CLEA model (Contaminated Land Exposure Assessment) has been developed for estimating the likely human exposures to contamination in soils. With this model, probability density functions are used which represent typical scenarios that

depend on a selected use of the land. Soil type and parameters such as pH and organic matter content can also be specified and used with a data set for a number of metals in a soils from a particular town or city to produce a risk or exposure value. The potential of these models for large urban data sets is great, particularly in light of any future development of contaminated land in cities for housing.

References

Adriano, D.C. 1986. Trace Elements in the Terestrial Environment. Springer-Verlag, New York.

Aikawa, J.K. 1991. Magnesium. In: Metals and Their Compounds in the Environment, Occurrence, Analysis and Biological Relevance. E. Merian (Ed.). VCH publisher. 1025-1034.

Akhter, M.S. and Madary, I.M. 1993. Heavy metals in street and house dusts in Bahrain. Water, Air, Soil Pollut., 66: 111-119.

Albasel, N. and Cottenie, A. 1985. Heavy metal contamination near major highways, industrial and urban areas in Belgian Grassland. Water, Air and Soil Pollut., 24: 103-109.

Allen, S.E., Grimshaw, H.W., Parkinson, J.A. and Quarmby, C. 1974. Chemical Analysis of Ecological Materials. S.E. Allen (Ed.). Blackwell Scientific Publications, Oxford.

Alloway, B.J. and Davies, B.E. 1971. Trace-element content of soils affected by base metal mining in Wales. Geoderma 5: 197-208.

Alloway, B.J. 1990a. Soil processes and the behaviour of metals. In: Heavy Metals in Soils. B.J. Alloway (Ed.). Blackie, Glasgow, London; Halstead press, New York. 7-28.

Alloway, B.J. 1990b. The origins of heavy metals in soils. In: Heavy Metals in Soils. B.J. Alloway (Ed.). Blackie, Glasgow, London; Halstead press, New York. 29-39.

Alloway, B.J. 1990c Cadmium. In: Heavy Metals in Soils. B.J. Alloway (Ed.). Blackie, Glasgow, London; Halstead press, New York. 100-121.

Alloway, B.J. 1995. The origins of heavy metals in soils. In: Heavy Metals in Soils. 2nd edition. B.J. Alloway (Ed.). Blackie Academic and Professional. 38-57.

Analytical Methods Committee. 1989a. Robust statistics - how not to reject outliers. Part 1. Basic concepts. Analyst., 114: 1693-1697.

Analytical Methods Committee. 1989b. Robust statistics - how not to reject outliers. Part 2. Analyst., 114: 1732-1737.

Anden, A.W., Lindberg, S.E. and Bates, L.C. 1975. Atmospheric input and geochemical cycling of selected trace elements in the Walker Branch watershed. Oak Ridge National Laboratory. Environmental Science Division. Pub. No. 728.

Andersen, A., Hovmand, M.F. and Johnsen, I. 1980. Atmospheric metal deposition in the Copenhagen area. Environ. Pollut., 17: 133-151.

Andre, M., Joumard, R., Hickman, A.J. and Hassel, D. 1994. Actual car use and operating-conditions as emission parameters - derived urban driving cycles. Sci. Tot. Environ., 147: 225-233.

Archer, A. and Barratt, R.S. 1976. Lead levels in Birmingham dust. Sci. Tot. Environ. 6: 275-286.

Archer, F.H. and Hodgson, I.H. 1987. Total and extractable trace element contents of soils in England and Wales. J. Soil Sci., 38: 421-431.

Archer, J. and Curson, D. 1993. Nature Conservation in Richmond-upon-Thames. Ecology Handbook 21, London Ecology Unit.

Asami, T. and Kubota, M. 1995. Background levels of soil beryllium in several countries. Environ. Geochem. and Hlth., 17: 32-38.

Aubert, H. and Pinta, M. 1977. Trace elements in soils. Elsevier Publ. Co., Amsterdam. 1-395.

Avery, B.W. 1980. Soil Classification for England and Wales (Higher categories). Soil Survey Technical Monograph No. 14, Harpenden.

Baker, D.E. 1990. Copper. In: Heavy Metals in Soils. B.J. Alloway (Ed.). Blackie, Glasgow, London; Halstead press, New York. 151-176.

Ball, D.F. 1964. Loss-on-ignition as an estimate of organic matter and organic carbon in non-calcareous soils. J. Soil Sci., 15: 84-92.

Baltrop, D., Strehlow, C.D., Thornton, I. and Webb, J.S. 1975. The absorption of lead from dust and soil. Postgrad. Med. J., 51: 801-804.

Barcelona, M.J. 1988. Overview of the sampling process. In: Principles of Environmental Sampling . L.H. Keith (Ed.). American Chemical Society. 3-23.

Barratt, R.S. 1988. Cadmium in urban atmospheres. Sci. Tot. Environ., 72: 211-215.

Baxter, J.C., Aguilar, M. and Brown, K. 1983. Heavy metals and persistant organics at a sewage sludge disposal site. J. Environ. Qual., 12: 311-316.

Beavington, F. 1973. contamination of soil with zinc, copper, lead and cadmium in the Wollongong city area. Aust. J. Soil Res., 11: 27-31.

Beavington, F. 1975. Heavy metal contamination of vegetables and soil in domestic gardens around a smelting complex. Environ. Pollut., 9: 211-217.

Bell, M.P. 1987. Civil Engineering. Blackwell.

Berrow, M.L. and Reaves, G.A. 1984. Background levels of trace elements in soils. In: Proc. Int. Conf. Environmntal Contamination. London, 1984. CEP Consultants Ltd., Edinburgh. 333-340.

Best, R.H. 1981. Land-use and Living Space. Methuen.

Beyer, W.N., Miller, G.W. and Cromartie, E.J. 1984. Contamination of the O_2 soil horizon by zinc smelting and its effect on woodlouse survival. J. Environ. Qual,. 13: 247-251.

Birke, M. and Rauche, U. 1994. Geochemical Investigation of the Urban Area of Berlin. Federal Institute of Geosciences and Natural Resources, Branch Office Berlin, Germany.

Blake, P., Chamberlain, C.S., Chambers, D., Clarke, B. and Mendham, J. 1987. Heavy metal contamination near scrap metal yards and car breaker yards. Sci. Tot. Environ., 59: 9-18.

Bockheim, J.G. 1974. Nature and properties of highly disturbed urban soils, Philadelphia, Pennsylvania. Paper presented before Div. S-5, Soil Science Society of America, Chicago, Illinois.

Boon, D.Y. and Soltanpour, P.N. 1992. Lead, cadmium and zinc contamination of Aspen soils and vegetation. J. Environ. Qual., 21: 82-86.

Boswell, F.C. 1975. Municipal sewage sludge and selected element applications to soil: effects on soil and Fescue. J. Environ. Qual., 4: 267-273.

Boumans, P.W.J.M. 1978. Science and Eng., 12: 1.

Bouyoucos, G.J. 1927. The hydrometer as a new method for the mechanical analysis of soils. Soil Sci., 23: 343-348.

Bowen, H.J.M. 1966. Trace Elements in Biochemistry. Academic press, New York.

Bowen, H.J.M. 1979. Environmental chemistry of the elements. Academic press, London.

Bradley, R.I. 1980. Trace elements in soils around Llechryd, Dyfed, Wales. Geoderma, 24: 17-23.

Bradshaw, A.D. and Chadwick, M.J. 1980. The Restoration of Land. Studies in Ecology, Vol. 6. Blackwell Scientific Publications.

Brady, N.C 1990. The Nature and Properties of Soils. Tenth Edition, Macmillan Publishing Company.

Bridges, D., Brown, M.J. and Hucker, P.J. 1996. Wolverhampton Urban Environmental Survey - an Integrated Geoscientific Case Study. British Geological Survey, Technical Report WE/95/49.

Bridges, E.M. 1978. World soils. 2nd Edition. Cambridge University Press.

Bridges, E.M. 1991. Waste materials in urban soils. In: Soils in the Urban Environment. P. Bullock and P.J. Gregory (Ed.). Blackwell Scientific Publications. 24-46.

Bridges, E.M. 1993. Land-use and soil contamination in the city of Swansea. Land Contam. Reclam., 1: 83-91.

British Geological Survey. 1981. South London. Sheet 270, Solid and Drift edition.

Buchauer, M.J. 1973. Contamination of soil and vegetation near a zinc smelter by zinc, cadmium, copper and lead. Environ. Sci. Technol., 131-135.

Bullock, P. and Gregory, P.J. 1991. Soils - a neglected resource in urban areas. In : Soils in the Urban Environment. P. Bullock and P.J. Gregory (Ed.). Blackwell Scientific Publications. 1-4.

Burguera, J.L. and Burguera, M. 1988. Lead in roadside soils of Merida city, Venezuela. Sci. Tot. Environ., 77: 45-49.

Burkitt, A., Lester, P. and Nickless, G. 1972. Distribution of heavy metals in the vicinity of an industrial complex. Nature, 237-328.

Bushy Park - The Royal Parks. 1993. Published by the The Royal Parks, The Old Police House, Hyde Park, London.

Butler, J.R. 1954. Trace element distribution in some Lancashire soils. J. Soil Sci., 5: 156-166.

Byerrum, R. 1991. Vanadium. In: Metals and Their Compounds in the Environment, Occurrence, Analysis and Biological Relevance. E. Merian (Ed.). VCH Publisher. 1289-1297.

Byrd, D.S., Gilmore, J.T. and Lea, R.T. 1983. Effect of decreased use of lead in gasoline on the soil of a highway. Environ. Sci. Technol., 17: 121-123.

Cammarota, B. 1980. Production and uses of zinc. In: Zinc in the Environment - Part One, Ecological Cycling. J.O. Nriagu (Ed.). A Wiley-Interscience Publication. 1-38.

Cannon, H.L. and Bowles, J.M. 1962. Contamination of vegetation by tetraethyl lead. Science 137: 765-766.

Cawse, P.A. 1978. In: Inorganic Pollution and Agriculture. MAFF, HMSO.

Cawse, P.A. 1981. Deposition of trace elements from the atmosphere in the UK. In: Applied Environmental Geochemistry. I. Thornton (Ed.). Academic Press Inc. London. 35-51.

Cernuschi, S. and Giugliano, M. 1987. Trace elements emission factors from coal combustion. Sci. Tot. Environ., 65: 95-107.

Chaney, R.L., Sterret, S.B. and Mielke, H.W. 1984. The potential for heavy metal exposure from urban gardens and soils. In: Int. Symp. Heavy Metals in Urban Gardens. J.R. Preer (Ed.). Columbia University, Washington, D.C. 37-84.

Chang, A.C., Warneke, J.E., Page, A.L. and Lund, L.J. 1984. Accumulation of heavy metals in sewage sludge-treated soils. J. Environ. Qual., 13: 87-91.

Chen, J., Wei, F., Zheng, C., Wu, Y. and Adriano, D.C. 1991. Background concentrations of elements in soils of China. Water, Air, Soil Pollut., 57-58: 699-712.

Chon, H.T., Kim, K.W. and Kim, J.Y. 1995. Metal contamination of soils and dusts in Seoul Metropolitan city, Korea. Environ. Geochem. Hlth., 17: 139-146.

Church, S.E. 1981. Geostandards Newsletter 2, 133.

Cloake, J. 1993. The Growth of Richmond, 2nd edition, Richmond Local History Society, paper No. 8.

Coles, B.J. 1989. Improved accuracy in the analysis of trace metals in plant material by Inductively Coupled Plasma Atomic Emission Spectrometry using extended internal standard techniques. Unp. M.Sc Thesis, University of London.

Cotter-Howells, J. 1991. Lead minerals in soils contaminated by mine-waste: Implications for human health. Unp. Ph.D. Thesis, University of London.

Colbourn, P. and Thornton, I. 1978. Lead pollution in agricultural soils. J. Soil Sci., 29: 513-526.

Culbard, E., Thornton, I., Watt, J., Moorcroft, S., Brooks, K., and Thompson, M. 1983. A Nationwide Reconnaissance Survey to determine metal concentrations in urban dusts and soils. In: D.D. Hemphill (Ed.) Trace substances in environmental health, XVII. Univ. of Missouri, Columbia. 236-241.

Culbard E., Thornton I., Watt J., Wheatley M., Moorcroft S. and Thompson M. 1988. Metal contamination in British urban dusts and soils. J. Environ. Qual., 17: 226-234.

Daines, R.H., Motto, H. and Chilko, D.M. 1970. Atmospheric lead, its relationship to traffic volume and proximity to highways. Environ. Sci. Technol., 4: 318-322.

Davey, B.G. and Wheeler, R.C. 1980. Some aspects of the chemistry of lithium in soils. Pl. Soil, 5: 45-50.

Davies, B.E. and Holmes, P.L. 1972. Lead accumulation of roadside soil and grass in Birmingham, England, in relation to naturally occurring levels. J. Agric. Sci. Camb., 79: 479-484.

Davies, B.E. 1977. Heavy metal pollution of British agricultural soils with special reference to the role of lead and copper mining. In: Proc. Int. Semin. on Soil Environment and Fertility Management in Intensive Agriculture, Tokyo. 394-397.

Davies, B.E., 1978. Plant-available lead and other metals in British garden soils. Sci. Tot. Environ., 9: 243-262.

Davies, B.E., Conway, D., and Holts, S. 1979. Lead pollution of London soils: a potential restriction on their use for growing vegatables. J. Agric. Sci. Camb., 93: 749-752.

Davies, B.E. 1983. A graphical estimation of the normal lead content of some British soils. Geoderma., 29: 67-75.

Davies, B.E. and Houghton, N.J. 1984. Distance-decline patterns in heavy metal contamination of soils and plants in Birmingham, England. Urban Ecol., 8: 285-294.

Davies, B.E. and Paveley, C.F. 1985. Baseline survey of Welsh soils. Trace Substances in the Environmental Health - XIV, University of Missouri, Columbia. 87-93.

Davies, B.E. 1990. Lead. In: Heavy metals in soils. B.J. Alloway (Ed.). Blackie, Glasgow, London; Halstead press, New York. 177-196.

Davies, B.E. 1993. Lead in the urban and home evironments in Britain: an overview. In:

Davies, D.J.A. and Thornton, I. 1987. The influence of house age on lead levels in dusts and soils in Brighton, England. Environ. Geochem. Hlth., 9: 65-67.

Davies, D.J.A., Watt, J.M. and Thornton, I. 1987. Lead levels in Birmingham dusts and soils. Sci. Tot. Envir., 67: 177-185.

Davis, A., Ruby, M.V. and Bergstrom, P.D. 1992. Bioavailability of arsenic and lead in soils from the Butte, Montana, mining district. Environ. Sci. Technol., 26: 461-468.

Day, J.P., Hart, M. and Robinson, M.S., 1975. Lead in urban street dust. Nature, 253: 343-345.

Denton, D. 1988. Lead in London soils and vegetables - a further case study. London Environ. Suppl., 16: 1-11.

Department of the Environment. 1988. Problems arising from the redevelopment of gas works and similar sites, 2nd edition. London HMSO.

Department of the Environment. 1994. Sampling strategies for Contaminated land, CLR Report No. 4, UK DOE, London.

Duggan, M.J. and Williams, S. 1977. Lead in dusts in city streets. Sci. Tot. Environ., 7: 91-97.

Duggan, M.J. and Burton, M.A.S. 1983. Atmospheric metal deposition in London. Int. J. Environ. Stud., 21: 301-307.

Eldred, R.A. and Cahill, T.A. 1994. Trends in elemental concentrations of fine particles at remote sites in the United States of America. Atmos. Environ., 28: 1009-1019.

Hinshery, E.L. and Kumar, N.S. 1992. Lead levels in selected dusts of Tripoli, Libya. Sci. Tot. Environ., 119: 51-56.

Falahi-Ardakhani, A. 1984. Contamination of environment with heavy metals emitted from automotives. Ecotox. Environ. Safe., 8: 152-161.

Farmer, J.G. and Lyon, T.D.B., 1977. Lead in Glasgow street and soil. Sci. Tot. Environ., 8: 89-93.

Fassett, D.W. 1980. Cadmium. In: Metals in the Environment. H.A. Waldron (Ed.). Academic Press Inc, London. 61-110.

Fergusson, C.C. 1992. The statistical basis for spatial sampling of contaminated land. Ground Eng., 25: 34-38.

Fergusson, C.C. 1993. Designing sampling strategies for contaminated sites. A paper presented at the IBC conference on Site Investigations for Contaminated Sites, London September 1993.

Fergusson, J.E. and Ryan, D.E., 1984. The elemental composition of street dust from large and small urban areas related to city type, source and particle size. Sci. Tot. Environ., 34: 101-116.

Fergusson, J.E. 1986. The Heavy Elements. Pergamon, Oxford.

Fergusson, J.E. and Kim, N.D. 1991. Trace elements in street and house dusts - sources and speciation. Sci. of the Tot. Environ., 100: 125-150.

Final report of the departmental committee on ethyl petrol. 1930. HMSO, London.

FitzPatrick, E.A. 1971. Pedology - A Systematic Approach to Soil Science. Oliver and Boyd.

Fleming, G.A. and Parle, P.J. 1977. Heavy metals in soils, herbage and vegetables from an industrialised area west of Dublin city. Irish J. Agric. Res., 16: 35-48.

Frank, R., Ishida, K. and Suda, P. 1976. Metals in agricultural soils of Ontario. Can. J. Soil Sci., 56: 181-196.

Francek, M.A. 1992., Soil lead levels in a small town environment: a case study from Mt. Pleasant, Michigan. Environ. Pollut., 76: 251-257.

Francek, M.A., Makimaa, B., Pan, V. and Hanko, J.H. 1994 . Small town lead levels: a case study from the homes of pre-schoolers in Mt. Pleasant, Michigan. Environ. Pollut., 84: 159-166.

Friedland, A.J., Johnson, A.H. and Siccama, T.G., 1986. Zinc, Cu, Ni and Cd in the forest floor in the northeastern United states. Water, Air, Soil Pollut., 29: 233-243.

Fu, S.L., Hashimoto, H., Siegel, B.Z. and Siegel, S.M. 1989. Variations in plant and soil lead and mercury content in a major Honolulu park, 1972 to 1987, a period of significant source reduction. Water, Air, Soil Pollut. 43: 109-118.

Gale, W.K.V. 1979. The Black Country Iron Industry: a Technical History. The Metals Society.

Galloway, J.N., Thornton J.D., Nornton, S.A., Volchok, H.L. and McLean, R.A.N. 1982. Trace metals in atmospheric deposition: a review and assessment. Atmos. Environ., 16: 1677-1700.

Garcia-Miragaya, J., Castro, S. and Paolini, J. 1980. Lead and zinc levels and chemical fractionation in roadside soils of Caracus, Venezuela. Water, Air, Soil Pollut., 13: 285-297.

Garrett, R.G. 1969. The determination of sampling and analytical errors in exploration geochemistry. Econ. Geol., 64: 568-569.

Gatz, D.F. 1991. Urban precipitation chemistry - a review and synthesis. Atmos. Environ., Part B - Urban Atmosp., 25: 1-15.

Goering, P.L., Fisher, B.R. and Fowler, B.A. 1991. Lanthanum. In: Metals and Their Compounds in the Environment, Occurrence, Analysis and Biological Relevance. E. Merian (Ed.). VCH Publisher. 959-970.

Gibson, M.J. and Farmer, J.G. 1986. Multi-step sequential chemical extraction of heavy metals from urban soils. Environ. Pollut., (ser. B), 11: 117-135.

Goodroad, E.J. and Caldwell, C.J. 1979. Influence of phosphatic fertilisers on the concentrations of Pb and Cr in arable soils. Environ. Sci. Technol., 20: 234-237.

Griffiths, J.R. and Wadsworth, G.A. 1980. Heavy metal pollution of farms near an industrial complex. In: Inorganic Pollution and Agriculture. MAFF Reference Book 326. HMSO, London. 70-76.

Griffits, W.R. and Skilleter, D.N. 1991. In: Metals and Their Compounds in the Environment, Occurrence, Analysis and Biological Relevance. E. Merian (Ed.). VCH Publisher. 775-787.

Gzyl, J. 1990. Lead and cadmium contamination of soils and vegetables in the Upper Silesia region of Poland. Sci. Tot. Environ., 96: 199-209.

Habiba, K. 1970. Characterisation of particulate lead in vehicle exhaust - experimental techniques. Environ. Sci. Technol., 4: 239-248.

Hallsworth, E.G. and Adams, W.A. 1973. The heavy metal content of rainfall in the east midlands. Environ. Pollut., 4: 231-235.

Hallet, J.P., Lardinois, P., Ronneau, C. and Cara, J. 1982. Elemental deposition as a function of distance from an industrial zone. Sci. Tot. Environ., 25: 99-109.

Ham Lands. 1992. Richmond Local History Society, paper No. 6.

Harper, M., Sullivan, K.R. and Quinn, M.J. 1987. Wind dispersal of metals from smelter waste tips and their contribution to environmental contamination. Environ. Sci. Technol., 21: 481-484.

Harrison, R.M., Perry, R. and Wellings, R.A. 1975. Lead and cadmium in precipitation: their contribution to pollution. J. Air Pollut. Contr. Assoc., 25: 627-630.

Harrison, R.M. 1979. Toxic metals in street and household dusts. Sci. Tot. Environ., 11: 89-97.

Harrison, R.M., Laxen, D.P.H. and Wilson, S.J. 1981. Chemical associations of lead, cadmium, copper and zinc in street dusts and roadside soils. Environ. Sci. Technol., 15: 1378-1383.

Harrison, R.M. and Johnston, W.R. 1985. Deposition fluxes of lead, cadmium, copper, PAH's on the verges of a major highway. Sci. Tot. Environ., 46: 121-135.

Harrison, R.M., Johnston, W.R., Ralph, J.C. and Wilson, S.J. 1985. The budget of lead, copper and cadmium for a major highway. Sci. Tot. Environ., 46: 137-145.

Harrop, D.D., Mumby, M., Ashworth, J., Nolan J., Price, M and Pepper, K. 1990a. Air quality in the vicinity of urban roads. Sci. Tot. Environ. 93: 285-292.

Harrop, D.D., Mumby, M., Pepper, K. and Nolan, J. 1990b. Heavy metals in the near vicinity to roads in a north London borough. Sci. Tot. Environ. 93: 543-546.

Hernandez, L.M., Rico, C., Gonzalez, J. and Hernan, A. 1987. Environmental contamination by lead and cadmium in plants from the urban area of Madrid, Spain. Bull. Environ. Contam. Toxicol., 38: 203-208.

Hesse, P.J. 1971. Textbook of Soil Chemical Analysis. John Murray Ltd., London.

Heubers, H.A. 1991. Iron. In: Metals and Their Compounds in the Environment, Occurrence, Analysis and Biological Relevance. E. Merian (Ed.). VCH Publisher. 945-959.

Hewitt, C.N. and Candy, C.B.B., 1990. Soil and street dust heavy metal concentrations in and around Cuenca, Ecuador. Environ. Pollut., 63: 129-136.

Ho, Y.B. and Tai, K.M., 1988. Elevated levels of lead and other metals in roadside soil and grass and their use to monitor aerial metal depositions in Hong Kong. Environ. Pollut., 49: 37-51.

Ho, Y.B. 1990. The effect of Pb reduction in petrol on the Pb content of kerbside dust in Hong Kong. Sci. Tot. Environ., 93: 411-418.

Hollis, J.M. 1991. The classification of soils in urban areas. In: Soils in the Urban Environment. P. Bullock and P.J. Gregory (Ed.). Blackwell. 5-27.

Holmgren, G.G.S., Meyer, M.W., Chaney, R.L. and Daniels, R.B. 1993. Cadmium, lead, zinc, copper, and nickel in agricultural soils of the United States of America. J. Environ. Qual., 22: 335-348.

Hopke, P.K., Lamb, R. E. and Natusch, D.F.S. 1980. Multi-elemental characterisation of urban roadway dust. Environ. Sci. Technol., 14: 164-172.

House of Commons. 1990. Environment Committee. First Report: Contaminated Land, Vol. 1.

Hutton, M. and Symon, C. 1986. The quantities of cadmium, lead, mercury and arsenic entering the U.K. environment from human activities. Sci. Tot. Environ., 57: 129-150.

Hutton, M., Wadge, A. and Milligan, P.J. 1988. Environmental levels of cadmium and lead in the vicinity of a major refuse incinerator. Atmosp. Environ., 27: 411-416.

Interdepartmental Commitee on the Redevelopment of Contaminated Land (ICRCL). 1987. Guidance on the assesment and redevelopment of contaminated land. ICRCL Guidance note 59/83. Second Edition. July, 1987. Department of the Environment.

International Programme on Chemical Safety. 1990a. Environmental Health Criteria 106 Beryillium. WHO, Geneva.

International Programme on Chemical Safety. 1990b. Environmental Health Criteria 107 Barium. WHO, Geneva.

Jackson, K.W., Eastwood, I.W. and Wild, M.S. 1987. Stratified sampling protocol for monitoring trace metal concentrations in soil. Soil Sci., 143: 436-443.

Jenkins, D. A. and Jones, R.G. 1980. Trace elements in rocks, soils, plants and animals: introduction. In: Applied Soil Trace Elements. B.E Davies (Ed.). John Wiley and Sons, Chichester. 1-20.

Jenny, H. 1941. Factors of soil formation. McGraw-Hall. New York.

Jensen, H. 1992. Lead in household dust. Sci. Tot. Environ., 114: 1-6.

Jensen, R.A. and Laxen, D.P.H. 1985. Sources of lead in urban dust: identification of a contribution from newspaper printworks. Sci. Tot. Environ., 46: 19-27.

Jones, K.C., Johnston, A.E. and Symon, C.J. 1987. Retrospective analysis of an archived soil collection. Sci. Total. Environ., 61: 131-144.

Jones, K.C, Lepp, N.W. and Obbard, J.P. 1990. Other metals and metalloids. In: Heavy metals in Soils. B.J. Alloway (Ed.). Blackie, Glasgow, London; Halstead press, New York. 280-321.

Jones, K.C. and Johnston, A.E. 1991. Significance of atmospheric inputs of lead to grassland at one site in the United Kingdom since 1860. Environ. Sci. Technol., 25: 1174-1178.

Jones, R. and Burgesss, M.S.E. 1984. Zinc and cadmium in soils and plants near electrical transmission (hydro) towers. Environ. Sci. Technol., 18: 731-734.

Jones, R., Prohaska, K.A. and Burgess, S.E. 1988. Zinc and cadmium in corn plants growing near electrical transmission towers. Water, Air, soil Pollut., 37: 355-363.

Jordan, L.D. and Hogan, D.J. 1975. Survey of lead in Christchurch soils. New Zeal. J. Sci., 18: 253-260.

Kabata-Pendias, A. and Pendias, H. 1984. Trace Elements in Soils and Plants. CRC press, Inc., USA.

Kabata-Pendias, A. and Dudka, S. 1991. Baseline data for cadmium and lead in soils and some cereals of Poland. Water, Air, Soil Pollut., Special Issue International Conference on Metals in Soils, Waters, Plants and Animals. 57-58: 723-731.

Kelly, J.J.P. 1991. Heavy Metal Contamination in East and South-East London. Unpub. dissertation, University of London.

Kelly, J.J.P., Thornton, I, and Simpson, P.R. 1996. A study of the influence of anthropogenic activity on the heavy metal content of soils in traditionally industrial and non-industrial areas of Britain. App. Geochem., 11: 363-370.

Kenworth, J.R., Newman, P.W.G. and Lyons, T.J. 1983. A driving cycle for Perth. NERDD Council, Commonwealth Department of Resources and Energy. Canberra, A.C.T. 2600, Australia, report 79/9252.

Kim, K.W. 1993. Influence of uraniferous black shales on trace elements in soils and crops in Korea. Unpub. PhD thesis, University of London.

Kim, N. and Fergusson, J. 1993. Concentrations and sources of cadmium, copper, lead and zinc in house dust in Christchurch, New Zealand. Sci. Tot. Environ., 138: 1-21.

King, L.C. 1967. Morphology of the Earth. Oliver and Boyd, Edinburgh.

Kloke, A. and Riebartsch, K. 1964. Naturwiss., 51: 367-368.

Kraal, H. and Ernst, W. 1976. Influence of copper high tension lines on plants and soils. Environ. Pollut., 11: 131-135.

Krauskopf, K.B. 1967. Introduction to geochemistry. McGraw-Hill, New York.

Kretzschmar, J.G., Delesspaul, I. and Rijck, T.D. 1980. Heavy metals in Belgium: a five year survey. Sci. Tot. Environ., 14: 85-97.

Kreuger, A.J. and Duguay. 1989. Comparative analysis of lead in Maine urban soils. Bul. Environ. Contam. Tox., 42: 574-580.

Lagerwerff, J.V. 1967. Heavy metal contamination of soils. In: Agriculture and the Quality of our Environment. N.C. Brady (Ed.). Amer. Assoc. Adv. Sci. Pub., 85: 343-364.

Lagerwerff, J.V. and Specht, A.W., 1970. Contamination of roadside soil and vegetation with cadmium, nickel, lead and zinc. Environ. Sci. Technol., 4: 583-586.

Lagerwerff, J.V. 1972. Lead, mercury and cadmium as contaminants. In: Micronutrients in Agriculture. J.J. Mortvedt, P.M. Giordamo and W.L. Lindsay (Eds.). Soil Sci. Soc. Amer. Inc., Madison, Wis.

Langard, S. 1980. Chromium. In: Metals in the Environment. H.A. Waldron (Ed.). Academic Press Inc, London. 111-132.

Lantzy, R.J., Mackenzie, F.T. 1979. Atmospheric trace metals: global cycles and assessment of man's impact. Geochem. Cosmo. Acta., 43: 511-525.

Lazrus, A.L., Lorrange, E. and Lodge, J.P. jr. 1970. Lead and other metal ions in the United States precipitation. Environ. Sci. Technol., 4: 55-58.

Lee, D.S. and Longhurst, J.W.S. 1992. A comparison between wet and bulk deposition at an urban site in the UK. Water, Air, Soil Pollut., 64: 635-648.

Lee, D.S., Garland, J.A. and Fox, A.A. 1994. Atmospheric concentrations of trace elements in urban areas of the United Kingdom. Atmos. Environ., 28: 2691-2713.

Lester, J.N., Harrison, R.M. and Parry, R. 1979. The balance of heavy metals through a sewage treatment works. I. Lead, cadmium and copper. Sci. Tot. Environ., 12: 13-23.

Levinson, A.A. 1980. Introduction to Exploration Geochemistry. 2nd edition. Applied Publishing, Co. Calgary.

Levy, D.B., Barbarick, K.A., Siemer, E.G. and Sommers, L.E. 1992. Distribution and partitioning of trace metals in contaminated soils near Leadville, Colorado. J. Environ. Qual., 21: 185-195.

Li, X and Thornton, I., 1992. Multi-element contamination of soils and plants in old mining areas, U.K. App. Geochem., S2: 51-56.

Little, P. and Wiffen, R.D., 1977. Emission and deposition of petrol engine exhaust lead to plant and soil surfaces. Atmos. Environ., 11: 437-447.

Little, P. and Wiffen, R.D.., 1978. Emission and deposition of lead from motor exhausts - II: airborne concentrations, particle size and deposition of lead near motorways. Atmos. Environ., 12: 1331-1341.

Logan, T.J. and Miller, R.H. 1983. Background levels of heavy metals in Ohio farm soils, Research Circular 275. Ohio State University Agricultural Research and Development, Ohio.

Loranger, S. and Zayed, J. 1994. Manganese and lead concentrations in ambient air and emission rates from unleaded and leaded gasoline between 1981-1992 in Canada - A comparative study. Atmos. Environ., 28: 1645-1651.

Lowe, G.W. 1980. GLC development at Thamesmead; investigation and reclamation of contaminated land. In: Reclamation of Contaminated Land. Society of Chemical Industry, London.

Lukashev, V.K. 1988. Some scientific and applied problems of the supergene geochemistry in the U.S.S.R. App. Geochem., 1: 441-449.

Lux, W. 1991. Long-term heavy metal and As pollution of soils, Hamburg, Germany. App. Geochem., S2: 135-143.

Lyons, T.J., Kenworth, J.R. and Newman, P.W.G. 1990. Urban structure and air pollution. Atmos. Environ., 24B: 43-48.

McGrath, S.P., Cunliffe, C.H. and Pope, A.J. 1985. Cadmium, copper, nickel, and lead concentrations in topsoils of England and Wales. Proc. 1st Int. Sym. Geochem. Hlth. Science Review Ltd., London.

McGrath, S.P. and Smith, S. 1990. Chromium and nickel. In: Heavy Metals in Soils. B.J. Alloway (Ed.). Blackie, Glasgow, London; Halstead press, New York. 125-150.

McGrath, S.P. and Loveland, P.J. 1992. The Soil Geochemical Atlas of England and Wales. London, Blackie.

McInnes, G. 1979. Multi-element survey: analysis of the first 2 years results. Report No. LR 305 (AP). Warren Spring Laboratory, Stevenage.

Maessen, F.J., Balke, J. and De Boer, J.L. 1982. Preservation of accuracy and precision in the analytical practice of low-power ICP-AES. Spectrochim. Acta, 37B: 517-526.

Majdi, H. and Persson, H. 1989. Effects of road-traffic pollutants (lead and cadmium) on tree fine-roots along a major road. Plant and Soil., 119: 1-5.

Maskell, J and Thornton, I., 1993. Metal contamination at historical lead smelting sites. Land Contam. Reclam., 1: 92-96.

Mason, B. and Moore, C.B. 1980. Principles of Geochemistry, 3rd edition. John Wiley and Sons, New York.

Matzner, E. and Meiwes, K.J. 1994. Long term development of element fluxes with bulk precipitation and throughfall in 2 German forests; J. of Environ. Qual., 23: 162-166.
Mena, I. 1980. Manganese. In: Metals in the Environment. H.A. Waldron (Ed.). Academic Press Inc, London. 199-220.

Mielke, H.W. , Blake, B., Burroughs, S. and Hassinger, N. 1984. Urban lead levels in Minneapolis - the case of the Hmong children. Environ. Res., 34: 64-76.

Mielke, H.W. 1991. Lead in residential soils: Background and preliminary results of New Orleans. Water, Air, Soil Pollut., 57-58: 111-119.

Mielke, H.W. 1993. Lead dust contaminated U.S.A. communities: comparison of Louisiana and Minnesota. App. Geochem., S2: 257-261.

Mielke, H.W. 1994. Lead in New-Orleans soils - new images of an urbn environment. Environ. Geochem. and Health., 16: 123-128.

Milberg, R.P., Lagerwerff, J.V., Brower, D.L. and Biersdorf, G.T., 1980. Soil lead accumulation alongside a newly constructed roadway. J. Environ. Qual., 9: 6-9.

Miles, L.J. and Parker, G.R. 1979. DTPA soil extractable and plant heavy metal concentrations with soil-added cadmium treatments. Pl. Soil, 51: 59-68.

Miller, E.K. and Friedland, A.J. 1994. Lead migration in forest soils - response to changing atmospheric inputs. Environ. Sci. Technol., 28: 662-669.

Miner, B. 1969. Air Pollution Aspects of Barium and its compounds. Bethesda, Maryland, Litton Systems Inc., Environmental Systems Division.

Ministry of Agriculture, Fisheries and Food. 1986. Advice on Avoiding Pollution from Manures and other Slurry Wastes, MAFF Booklet 2200, MAFF Publications, London.

Mitchell, D.J., Wild, S.R. and Jones, K.C. 1992. Arrested municipal solid waste incinerator fly ash as source of heavy metals to the UK environment. Environ. Pollut., 76: 79-84.

Mitchell, R. L. 1964. Trace Elements in soils. In: Chemistry of the soil, 2nd edition. F.E Bear (Ed.). Reinhold, New York. p 320-368.

Moir, A.M., 1992. The influence of soil factors and atmospheric deposition on the cadmium and lead contents of vegetables. Unpub. Ph.D. thesis, University of London.

Moseholm, L., Larsen, E.H., Andersen, B. and Nielsen, M.M. 1992. Atmospheric deposition of trace elements around point sources and human health risk assessment. I: impact zones near a source of lead emissions. Sci. Tot. Environ., 126: 243-262.

Motto, H.L., Daines, R.H., Chilko, D.M. and Motto, C.K. 1970. Lead in soils and plants: its relationship to traffic volume and proximity to highways. Environ. Sci. Technol., 4: 231-238.

Mulla, D.J., Page, A.L. and Gange, T.J. 1980. Cadmium accumulation and bioavailability in soils from long-term phosphate fertilisation. J. Environ. Qual., 9: 408-412.

Mullins, C. E. 1991. Physical properties of soils in urban areas. In. Soils in the Urban Environment. P. Bullock and P.J. Gregory (Eds.). Blackwell Scientific Publications. 87-118.

Muskett, C.J. and Jones, M.P. 1980. The dispersal of lead, cadmium and nickel from motor vehicles and the effects on roadside invertebrate macrofauna. Environ. Pollut. (Ser. A), 23: 231-242.

Ndiokwere, C.L. 1984. A study of heavy metal pollution from motor vehicle emissions and its effects on roadside soil, vegetation and crops in Nigeria. Environ. Pollut. (Ser. B), 7: 35-42.

Nguyen, V.D., Merks, A.G.A. and Valenta, P. 1990. Atmospheric deposition of acid, heavy metals, dissolved organic carbon and nutrients in the Dutch delta areas in 1980-1986. Sci. Tot. Environ., 99: 77-91.

Nriagu, J.O. and Davidson, C.I. 1986. Toxic Metals in the Atmosphere. J. Wiley and sons Ltd., New York.

Nriagu, J.O. 1988. A silent epidemic of environmental metal poisoning. Environ. Pollut., 50: 139-161.

Nriagu, J.O and Pacyna, J.M. 1988. Quantitative assessment of worldwide contamination of air, water, and soils by trace metals. Nature, 333: 134-139.

Nriagu, J.O. 1990. The rise and fall of leaded gasoline. Sci. Tot. Environ., 92: 13-28.

Nriagu, J.O. 1992. Toxic metal pollution in Africa. Sci. Tot. Environ., 121: 1-37.

Nwanko, J.N. and Elinder, C.G. 1979. Cadmium, lead and zinc concentrations in soils and in food grown near a zinc and lead smelter in Zmbia. Bull. Environ. Contam. Toxicol., 22: 625-631.

O'Connor, B.H., Cameron, I. and Martin, D.J. 1990. Correlation between petrol lead additive consumption and atmospheric lead concentrations in Perth, Western Australia. 1990. Atmos. Environ., 24B: 413-417.

Ogunsola, O.J., Oluwole, A.F., Asubiojo, O.I., Durosinmi, M.A., Futusi, A.O. and Ruck, W. 1994. Traffic pollution in perliminary elemental characterisation of roadside dusts in Lagos, Nigeria. Sci. Tot. Environ., 147: 175-184.

Pacyna, J.M. 1986. Atmospheric trace elements from natural and anthropogenic sources. In: Toxic Metals in the Atmosphere. J.O. Nriagu and C.I. Davidson (Eds.). J. Wiley and Sons Ltd., New York. 33-52.

Page, A.L. and Ganje, T.J. 1970. Accumulation of lead in soils for regions of high and low motor vehicle traffic density. Environ. Sci. Technol., 4: 231-237.

Page, R.A., Cawse, P.A. and Baker, S.J. 1988. The effect of reducing petrol lead on airborne lead in Wales, U.K. Sci. Tot. Environ., 68: 71-77.

Panstwowy Instyut Geologiczny. 1992. Geochemical Atlas of Warsaw and Environs. Panstwowy Instyut Geologiczny.

Parry, G.D.R., Johnon, M.S. and Bell, R.M. 1981. Trace metal surveys of soil as a component of strategic and local planning policy development. Environ. Pollut. (ser. B), 2: 97-107.

Pattenden, N.J. 1974. Atmospheric concentrations and deposition rates of some trace elements measured in the Swansea/Neath/Port Talbot area. Environmental and Medical Science Division. AERE Rep. R - 7729. Her Majesty's Stationery Office, London.

Pauxbuam, H. 1991. Metal compounds in the atmosphere. In: Metals and Their Compounds in the Environment, Occurrence, Analysis and Biological Relevance. E. Merian (Ed.). VCH Publisher. 257-290.

Pawlowski, L. 1990. Chemical threat to the environment in Poland. Sci. Tot. Environ., 96: 1-21.

Peirson, D.H., Cawse, P.A., Salmon, L. and Cambray, R.S. 1973. Trace elements in the atmospheric environment. Nature, 241: 252-256.

Pedro, G. 1985. Grandes tendances des sols mondiaux. Cultivar, 84: 78-81.

Pierce, F.J., Dowdy, R.H. and Grigal, D.F. 1982. Concentrations of six trace metals in some major Minnesota soil series. J. Environ. Qual., 11: 416-421.

Plant, J. and Raiswell, R. 1983. Principles of environmental geochemistry. In: Applied Environmental Geochemistry. I. Thornton (Ed). Academic Press, London. 1-39.

Polemio, M., senesi, N. and Bufo, S.A. 1982. A survey in industrial and rural areas of southern Italy. Sci. Tot. Environ., 25: 71-79.

Pouyat, R.V. and McDonnell, M.J. 1991. Heavy metal accumulation in forest soils along an urban-rural gradient in southeastern New York, USA. Water, Air, Soil Pollut., 57-58: 797-807.

Preer, J.R. and Rosen, W.G. 1977. Lead and cadmium content of urban garden vegetables. In: Trace Substances in Environmental Health - XI. D.Hemphill (Ed.). University of Missouri, Columbia, Missouri. 399-405.

Preer, J.R., Akintoye, J.O. and Martin, M.L. 1984. Metals in downtown Washington, DC gardens. Biol. Trace Elem. Res., 6: 79-91.

Proceedings of the International Conference on Heavy Metals in the Environment. Geneva, 1989. CEP Consultants Ltd., Edinburgh

Purves, D. 1966. Contamination of urban garden soils with copper and boron. Nature, 210: 1077-1078.

Purves, D. 1967. Contamination of urban garden soils with copper, boron and lead. Pl. Soil., 26: 380-382.

Purves, D. and Mackenzie, E.J. 1969. Trace element contamination of parklands in urban areas. J. Soil Sci., 20: 288-290.

Quarles, H.D., Hanawalt, R.B. and Odum, W.E. 1974. Lead in small mammals, plants and soils at varying distances from a highway. J. Appl. Ecol., 11: 937-949.

Ragaini, R.C., Raiston, H.R. and Roberts, N. 1977. Environmental trace metal contamination in Kellogg, Idaho, near a lead smelting complex. Environ. Sci. Technol., 11: 773-781.

Ramsey, M.H., Thompson, M. and Banerjee, E.K. 1987. A realistic assessment of analytical data quality from inductively coupled plasma atomic emission spectrometry. Anal. Proc., 24: 260-265.

Ramsey, M.H., Thompson, M. and Hale, M. 1992. Objective evaluation of precision requirements for geochemical analysis using robust analysis of variance. J. Geochem. Explor., 44: 23-36.

Ramsey, M.H. 1993a. Appropriate precision: matching analytical specifications to the particular application. Anal. Proc., 30: 110-112.

Ramsey, M.H. 1993b. Sampling and analytical quality control (SAX) for improved error estimation in the measurement of Pb in the environment using robust analysis of variance. Appl. Geochem., S2: 149-153.

Ramsey, M.H., Argyraki, A. and Thompson. M. 1995a. On the collaborative trial in sampling. Analyst, 120: 2309-2312.

Reaves, G.A. and Berrow, M.L. 1984. Total lead concentrations in Scottish soils. Geoderma. 32: 1-8.

Ribas, B. 1991. Lithium. In: Metals and Their Compounds in the Environment, Occurrence, Analysis and Biological Relevance. E. Merian (Ed.). VCH Publisher. 1015-1024.

Rice, J.A., Brown, D.G. and Klusman, R.W. 1984. A baseline geochemical description of surficial materials in the southeastern Uinta basin, Utah. Environ. Geol. Water Sci., 6: 229-236.

Richmond Park - The Royal Parks. 1993. Published by the Royal Parks, the Old Police House, Hyde Park, London.

Ritter, C.J. and Rinefierd, S.M. 1983. Natural background and pollution levels of some heavy metals in soils from the area of Dayton, Ohio. Environ. Geol., 5: 73-78.

Rodriguez-Flores, M. and Rodriguez-Castellon, E. 1982. Lead and cadmium levels in soil and plants near highways and their correlation with traffic density. Environ. Pollut., Ser.B. 4: 281-290.

Romero, F., Elejalde, C. and Azpiazu, M.N. 1987. Metal plant and soil pollution indexes. Water, Air Soil Pollut., 34: 347-352.

Rose, A.W., Hawkes, H.E. and Webb, J.S. 1979. Geochemistry in mineral exploration, 2nd edition. Academic Press, London.

Rundle, S.A. and Duggan, M.J. 1986. Lead pollution from the external redecoration of old buildings. Sci. Tot. Environ., 57: 181-190.

Sadiq, M., Alam, I., El-Mubarek, A. and Al-Mohdhar, H.M. 1989. Preliminary evaluation of metal pollution from wear of auto tires. Bull. Environ. Contam. Toxicol., 42: 743-748.

Saltzman, B.E., Cholak, J., Schafer, L.J., Yeager, D.W., Yeager, R., Meiners, B.G. and Svetlik, J. 1985. Concentrations of six metals in the air of eight cities. Environ. Sci. Technol., 19: 328-333.

Sanchez-Camazano, M., Sanchez-Martin, M.J. and Lorenzo, L.F. 1994. Lead and cadmium in soils and vegetables from urban gardens of Salamanca (Spain), Sci. Tot. Environ., 146: 163-168.

Schiele, R. 1991. Manganese. In: Metals and Their Compounds in the Environment, Occurrence, Analysis and Biological Relevance. E. Merian (Ed.). VCH Publisher. 1035-1044.

Schlesinger, W., Reiners, W.A. and Knopman, E.S. 1974. Heavy metal concentrations and deposition in bulk deposition in montane ecosystems of New Hampshire, USA. Environ. Pollut., 6: 39-47.

Schmitt, M.D.C., Trippler, D.J., Wachtler, J.N. and Lund, G.V. 1988. Soil lead concentrations in residential Minnesota as measured by ICP-AES. Water, Air, Soil Pollut., 39: 157-168.

Schrauzer, G. 1991. Cobalt. In: Metals and their Compounds in the Environment, Occurrence, Analysis and Biological Relevance. E. Merian (Ed.). VCH Publisher. 879-892.

Schuuring, C. 1981. Dutch Dumps. Nature, 289, 340.

Schwar, M.J.R., Moorcroft, J.S., Laxen, D.P.H., Thompson, M. and Armorgie, C. 1988. Baseline metal-in-dust concentrations in Greater London. Sci. Tot. Environ., 68: 25-43.

Schwar, M.J.R. and Alexander, D.J. 1988. Redecoration of external leaded paintwork and lead-in-dust concentrations in school playgrounds. Sci. Tot. Environ., 68, 45-59.

Seki, M. 1987. Metal concentrations in urban housedust, road dust and soil with particular reference to the London Boroughs of Richmond and Westminster. Unpub. M.Sc thesis, University of London.

Sevin, I.F. 1980. Nickel. In: Metals in the Environment. H.A. Waldron (Ed.). Academic Press Inc, London. 263-292.

Shell International Petroleum Company Limited. 1985. Lead in gasoline - an environmental brief. PAC/3 July.

Simpson, R.W. and Hongchang, X. 1994. Atmospheric lead pollution in an urban area - Brisbane, Australia. Atmos. Environ., 28: 3073-3082.

Sims, D.L. and Morgan, H. 1988. Sci. Total Environ., 75: 1-10.

Smith, R.T. and Atkinson, K. 1975. Techniques in pedology: A Handbook for Environmental and Resource Studies. Elek, London. 113-120.

Smith, I.C. and Carson, B.L. 1981. Trace Metals in the Environment, Vol. 6, Ann Arbor Scientific Publications.

Smith, K.A. 1990. Manganese and Cobalt. In: Heavy Metals in Soils. B.J. Alloway (Ed.). Blackie, Glasgow, London; Halstead press, New York. 197-221.

Solomon, R.L. and Hartford, J.W. 1976. Lead and cadmium in a small urban community. Environ. Sci. Technol., 10: 773-777.

Spittler, T.M. and Feder, W.A. 1979. A study of soil contamination and plant lead uptake in Boston urban gardens. Comm. Soil Sci. Pl. Anal., 10: 1195-1210.

Sposito, G. and Page, A.L. 1981. Circulation of metals in the environment. In: Metal Ions in Biological Systems, Vol. 18. S.H. Marcel Dekker (Ed.). New York.

Sposito, G. 1983. Soil chemistry. In: Applied Geochemistry. I.Thornton (Ed.). Academic Press, London. 123-170.

Steinnes, E., Solberg, W., Petersen, H.M. and Wren, C.D. 1989. Heavy metal pollution by long range atmospheric transport in natural soils of Southern Norway. Water, Air, Soil Pollut., 45: 219-243.

Stiglliani, W.M., Jaffe, P.R. and Anderberg, S. 1993. Heavy metal pollution in the Rhine Basin. Environ. Sci. Technol., 27: 786-793.

Tam, N.F.Y., Liu, W.K. and Wong, Y.S. 1987. Heavy metal pollution in roadside urban parks and gardens in Hong Kong., Sci. Tot. Environ., 59: 325-328.

Teixeira, E.C, Samama, J.C. and Brun, A. 1992. Study of the concentration of trace elements in fly-ash resulting from coal combustion. Environ. Technol., 13: 995-1000.

Thompson, M. and Howarth, R.J. 1976. A new approach to the estimation of analytical precision. J. Geochem. Explor., 9: 23-30.

Thompson, M. and Howarth, R.J. 1980. The frequency distribution of analytical error. Analyst, 105: 1188-1195.

Thompson, M. 1983. Control procedures in geochemical analysis. In: Handbook of Exploration Geochemistry. Vol. 2. R.J. Howarth (Ed.). Elsevier Scientific Publishing Co., Amsterdam. 39-58.

Thompson, M. and Walsh, J.N. 1988. A Handbook of Inductively Coupled Plasma Spectrometry, 2nd editionn. Blackie, London.

Thompson, M. and Maguire, M. 1993. Estimating and using sampling precision in surveys of trace constituents in soils. Analyst, 118: 1107-1110.

Thompson, M. and Ramsey, M.H. 1995. Quality concepts and practices applied to sampling - an exploratory study. Analyst, 120: 261-270.

Thornton, I. 1980. Geochemical aspects of heavy metal pollution and agriculture in England and Wales. In: Inorganic Pollution and Agriculture. MAFF Reference Book No. 326. HMSO, London.

Thornton, I. and Jones, T.H. 1984. Sources of lead and associated metals in vegetables grown in British urban soils: uptake from the soil versus air deposition. Trace Subs. Environ. Hlth., XVIII.

Thornton, I., Culbard, E., Moorcroft, S., Watt, J., Wheatley, M. and Thompson, M. 1985. Metals in urban dusts and soils. Environ. Technol. Lett., 6: 137-144.

Thornton, I. 1986. Metal contamination of soils in UK gardens: implications to health. In: Contaminated Soil. J.W. Assink and W.J. Van der Brink (Eds.). Martinus Nijhoff Publishers, Dordrecht, Netherlands. 203-209.

Thornton, I. 1989. A survey of lead in the British urban environment: An example of research in urban geochemistry. Element Concen. Cadasters in Ecosyst: Methods of assessment and evaluation. H. Lieth and B. Markert (Eds.). 221-233.

Thornton, I. 1990. Soil contamination in urban areas. Palaeogeo. Paleoclim. Palaeoecol. (global and planetary change section)., 82: 121-140.

Thornton, I. 1991. Metal contamination of soils in urban areas. In: Soils in the Urban Environment. P. Bullock and P.J. Gregory (Eds.). Blackwell Scientific Publication. 47-75.

Tjell, J.C. and Christensen, T.H. 1985. Evidence of increasing cadmium contents of agricultural soils. In: Proc. Int. Conf. Heavy Metals in the Environment. Vol. 2. Athens, 1985. CEP Consultants Ltd., Edinburgh. 391-393.

Tong, S.T.Y. and Marrell, P.M. 1991. The concentration profile of heavy metals in an urban forest. Environ. Technol., 12: 79-85.

Trescases, J.J. 1992. Chemical weathering. In. The Handbook of Exploration Geochemistry, Vol. 4 - Regolith Exploration Geochemistry in Tropical and Subtropical Terrains. C.R.M Butt and H. Zeegers (Eds.). Elsevier Science Publishers. 25-40.

Trindale, H.A., Pfeiffer, W.C., Londres, H., and Costa-Ribeiro, C.L. 1981. Atmospheric concentrations of metals and total suspended particulates in Rio de Janeiro. Environ. Sci. and Technol., 15: 84-89.

Tripathi, A. 1994. Airborne lead pollution in the city of Varansi, India. Atmos. Environ., 28: 2317-2323.

Turner, A.C. 1973. Warren Spring laboratory report., LR189 (AP), Stevenage, England.

Turekian, C. and Wedepohl, K.H. 1961. Distribution of the elements in some major units of the earth's crust. Geol. Soc. Amer. Bull., 72: 175-192.

Ure, A.M. 1990. Methods of analysis for heavy metals in soils. In: Heavy Metals in Soils. B.J. Alloway (Ed.). Blackie, Glasgow, London; Halstead press, New York. 40-80.

USDA. 1975. Soil Taxonomy. Agricultural handbook, No. 436.

US EPA. 1987. Health Assessment document for Be. North Carolina US Environmental Protection Agency, Office of Research and Development (EPA report No. 600/8-84-026F).

Valerio, F., Brescianini, C., Pala, M., Lazzarotto, A., Balducci, D. and Vincenzo, F. 1992. Sources and atmospheric concentrations of polycyclic aromatic hydrocarbons and heavy metals in two Italian towns (Genoa and La Spezia). Sci. Tot. Environ., 114: 47-57.

Vazquez-Duhalt, R. 1989. Environmental impact of used motor oil. Sci. Tot. Environ., 79: 1-23.

Vinagradov, A.P. 1959. The Geochemistry of Rare and Dispersed Chemical Elements in Soils, 2nd edition. Consultants Bureau Inc., New York.

Wadge, A. and Hutton, M. 1987. The cadmium and lead content of suspended particulate matter emitted from a UK refuse incinerator. Sci. Tot. Environ., 67: 91-95.

Waldron, H.A. 1980. Lead. In: Metals in the Environment. H.A. Waldron (Ed.). Academic Press Inc, London. 155-198.

Walsh, J.N. and Howie, R.A. 1980. Min. Mag. 43: 967-490.

Ward, N.I., Reeves, R.D. and Brooks, R.R. 1975. Lead in soil and vegetation along a New Zealand state highway with low traffic volume. Environ. Pollut., 9: 243-251.

Ward, N.I., Brooks, R.R., Roberts, E. and Boswell, E. 1977. Heavy-metal pollution automotive emissions and its effect on roadside soils and pasture species in New Zealand. Environ. Sci. Technol., 11: 917-920.

Ward, N.I. 1990a. Lead contamination of the London orbital motorway (since its opening in 1986). Sci. Tot. Environ., 93: 277-283.

Ward, N.I. 1990b. Multielement contamination of British motorway environments. Sci. Tot. Environ., 93: 393-401.

Warren, H.V., Delavault, R.E. and Fletcher, K.W. 1971. Metal pollution - a growing problem in industrial and urban areas. Can. Min. Metall. Bull., 64: 1-12.

Warren, R.S. and Birch, P. 1987. Heavy metal levels in atmospheric particulates, roadside dust and soil along a major urban highway. Sci. Tot. Environ., 59: 253-256.

Webb, J.S., Thornton, I., Thompson, M., Howarth, R.J. and Lowenstein, P.L. 1978. The Wolfson Geochemical Atlas of England and Wales. Oxford University Press.

Webster, R. 1977. Quantitative and Numerical Methods in Soil Classification and Survey. Clarendon Press, Oxford.

Wedepohl, K.H. 1971. Geochemistry. Holt, Rinehart and Winston, Inc.

Wedepohl, K.H. 1991. The composition of the upper earth's crust and the natural cycles of selected metals. Metals in natural raw materials. Natural resources. In: Metals and their compounds in the environment. E. Merian (Ed.). VCH Publisher.

West, T.S. 1981. Soil as the source of trace elements. Phil. Trans. R. Soc. Lond. B 294: 19-31.

Wheeler, G.L. and Rolfe, G.L. 1979. The relationship between daily traffic volume and the distribution of lead in roadside soils. Environ. Pollut., 18: 265-274.

Wilkins, C. 1978. The distribution of lead in the soils and herbage of west Pembrokeshire. Environ. Pollut., 15: 23-30.

Wong, M.H. and Tam, F.Y. 1978. Lead contamination of soil and vegetables grown near motorways in Hong Kong. J. Environ. Sci., A13: 13-22.

Woodcock, N.H. 1994. Geology and environment in Britain and Ireland. Academic Press Inc.

Xuelin, Z. and Ke, M. 1989. Levels of lead in urban soils in China.

Yassoglou, N., Kosmas, C., Asimakopoulos, J. and Kallianou, C. 1987. Heavy metal contamination of roadside soils in the Greater Athens area. Environ. Pollut., 47: 293-304.

Yim, W.W.S. and Nau, P.S. 1987. Distribution of lead, zinc, copper and cadmium in dusts from selected urban areas of Hong Kong. Hong Kong Eng. Jan: 7-14.

Yingming, L. and Corey, R.B. 1993. Redistribution of sludge-borne cadmium, copper and zinc in a cultivated plot. J. Environ. Qual., 22: 1-8.

Zimdahl, R.L. and Skogerboe, R.K. 1977. Behaviour of lead in soil. Environ. Sci. Technol., 11: 1202-1207.

APPENDIX ONE

ANALYTICAL METHODS

APPENDIX ONE ANALYTICAL METHODS

Appendix 1.1 Acid digestion of soils for multi-element analysis

1. APPARATUS

1) test tube; 2) wire test tube rack(plastic coated); 3) stainless steel test tube rack; 4) aluminium heating block(deep, 252 holes); 5) shallow aluminium heating block(315 holes); 6) Oxford dispenser; 7) centrifuge tube; 8) vortex tube mixer; 9) balance(top pan); 10) centrifuge

2. REAGENTS

1) deionised water; 2) nitric acid(A.R. 70% w/w); 3) perchloric acid(A.R. 60% w/w); 4) hydrochloric acid 5M(A.R.): dilute 430ml conc. HCl(36% w/w) to 1,000ml with DIW

3. PROCEDURE

1) Weigh 0.250g (± 0.001) of sample using the top-pan balance into a clean dry test tube

2) Add 4.0ml nitric acid into each tube from an Oxford dispenser

3) Add 1.0ml perchloric acid into each tube from the dispenser

4) place tubes in the aluminium heating block and switch programmer to 'MANUAL' mode, set programmer as follows:

rise rate (sec/deg)	dwell time (hrs)	dwell temperature (°C)
001	3.0	50
001	3.0	150
001	18.0	190
001	0.1	195

5) Turn on the fume cupboard and switch programmer to 'AUTO'

6) The attack cycle is complete when the residue in each tube is dry

7) Transfer tubes to the stainless steel racks and when cool, add 2.0ml hydrochloric acid(5M) to each tube from an Oxford dispenser and heat at 60°C for 1hr.
8) Transfer tubes to wire racks and allow to cool

9) Add 8.0ml of deionised water from an Oxford dispenser and mix each tubes using a vortex
mixer

10) Decant into polystyrene tubes and cap. If necessary, centrifuge at 2,000rpm for 2 minutes

11) Chemical analysis for general elements using ICP-AES

Appendix 1.2 Determination of soil pH

1. APPARATUS

1) deionised water; 2) 15ml disposable polystyrene test tube; 3) balance; 4) box shaker

2. PROCEDURE

1) Weigh 4g of soil which is a dried and sieved through a 2mm aperture(10 mesh) into a 15ml disposable polystyrene test tube

2) Add 10ml of deionised water

3) Shake for 1 hour using a box shaker

4) Stand the samples for 15-30 mins to clear the supernatant

5) Calibrate the Orion Research 701A pH meter using buffer solutions of 4, 7 and 9

6) Insert the probe into the solution, keeping the probe in motion until a stable reading is obtained

7) Quality control involves regular calibration using the buffer solutions and duplicate samples

Appendix 1.3 Determination of soil organic matter content of soils

1. APPARATUS

1) deionised water; 2) balance; 3) crucible: washed in 90% Decon solution; 4) china graphed pencil; 5) oven (105°C) and muffle furnace (450°C); 6) desiccator

2. PROCEDURE

1) Weigh empty crucible (A)

2) Weigh crucible + sample (B)

3) Dry overnight in an oven at 105°C

4) Cool in a desiccator (2 or 3 hours) and weigh(C)

5) Ignite the sample in a muffle furnace at 450°C

6) Cool in the desiccator (4 or 5 hours) and weigh (D)

3. CALCULATION

$$\mathrm{LOI}(\%) = \frac{\text{[mass of oven-dried soil] - [mass of ignited soil]}}{\text{[sample mass of oven-dried soil]}} \times 100$$

or,

$$\mathrm{LOI}(\%) = \frac{C - D}{C - A} \times 100$$

Appendix 1.4 Determination of soil texture

1. APPARATUS

1) deionised water; 2) balance; 3) hydrometer; 4) 1000ml measuring cylinder; 5) thermometer
6) 800ml measuring beaker; 7) ruler; 8) stop clock; 9) oven; 10) mechanical stirrer

2. REAGENTS

1) hydrogen peroxide (30 vol.)
2) calgon (50g sodium hexametaphosphate + 5.724g sodium carbonate in 1000ml DIW

3) amyl alcohol or capryl

3. PROCEDURE

1) Approximately 50g of soil sample, dried and sieved through a 2mm aperture, are weighed into an 800ml beaker

2) 60ml of 30 vol. hydrogen peroxide added to remove any organic matter

3) The beaker is gently warmed until all frothing has ceased, and then gently boiled for a few minutes to destroy excess peroxide solution

4) Excessive frothing during the hydrogen peroxide treatment can be controlled by adding a few drops of capryl or amyl alcohol

5) When cool, 10ml of calgon are added, the suspension washed into the cup of a mechanical stirrer and stirred for 15 minutes

6) The soil suspension is then washed into a 1000ml measuring cylinder and made up to volume with deionised water

7) Any remaining froth on the liquid can be dampened by one drop of capryl or amyl alcohol

8) The temperature of the suspension is taken, and the cylinder shaken end over end for about 1 minute, the end being stoppered with a bung or the palm of the hand

9) The cylinder is placed on the bench, a stop clock started and the hydrometer gently inserted to take the readings

10) The first reading is taken after 40 seconds, and this gives the percentage of silt and clay (USDA limit). The hydrometer is withdrawn and the cylinder shaken again and allowed to stand for 2 hours

11) Prior to 2 hours the hydrometer is re-introduced and a reading is taken which gives the percentage of clay in the sample

12) To determine the content of coarse and fine sand, the supernatant suspension is then discarded and the sediment washed into an 800ml beaker with deionised water to a volume of 10cm

13) The suspensions are stirred and allowed to stand for the appropriate time for the sand to settle out, as defined by temperature, after which the supernatant is discarded and these processes are repeated until the supernatant is clear

14) The sand residues are then dried at 105°C and weighed to give the percentage sand

4. CALCULATION

The results for sand(coarse and fine), silt and clay are expressed as a percentage weight of the soil sample, and are obtained by correcting the weight of mineral material in suspension(g/l) for temperature and the density of calgon. In addition, the results presented as a percentage of the mineral weight are subsequently corrected for organic matter content, which is determined separately by LOI (loss on ignition - see Appendix 2-3). The correction of the size fraction is possible using the following equation:

$$\text{corrected}(\%) = \text{determined}(\%) \times \frac{[100]}{[100 - \text{organic matter}(\%)]}$$

APPENDIX TWO

ANALYTICAL DATA FOR RICHMOND AND WOLVERHAMPTON

Appendix 2.1 Data for Richmond topsoils
Geochemical data in µg/g unless otherwise stated

ID	East	North	Li	Na	K	Rb	Be	Mg	Ca	Sr	Ba	Al%	La	Ti	V	Cr	Mo	Mn	Fe%	Co	Ni	Cu	Ag	Zn	Cd	Pb	P	pH	LOI %
10001	2125	7225	12.50	113	2080	20	0.66	1420	2570	20.3	95.3	1.300	12.2	489	39.0	18.4		202.0	1.730	4.2	13.6	27.3		111.0	0.3	174	777	5.77	9.6
10002	2125	7275	25.90	233	6220	40	1.13	4430	3900	31.6	114.0	2.960	19.6	929	65.8	35.8		250.0	2.550	8.6	25.0	22.8		74.2		86	580		
10003	2075	7225	13.20	53	1350	16	0.24	802	223	9.5	33.3	0.926	7.8	485	29.6	19.0		32.1	0.881	1.8	6.6	8.6		25.2		38	280	3.77	6.1
10004	2025	7225	14.50	157	5120	60	0.73	2700	445	19.7	82.8	2.520	18.2	1050	51.2	47.6	2.6	124.0	2.400	5.6	14.2	12.2		50.0		46	504		
10005	2025	7275	4.80	53	1480	8	0.31	824	180	8.4	27.7	0.869	9.6	645	32.8	26.2	1.0	33.6	1.320	2.8	8.0	8.5		17.0		55	270	4.27	6.1
10006	2075	7275	7.50	89	2660	28	0.49	1270	400	13.3	55.5	1.300	12.2	715	41.4	34.6		195.0	1.920	4.4	11.4	13.7		36.0		79	778		
10007	2025	7325	9.00	82	2100	32	0.38	1130	278	11.5	44.3	1.240	12.0	712	38.4	35.4		84.6	1.810	3.6	8.4	6.1		26.6		26	329	4.03	5.6
10008	2075	7325	9.60	129	2770	32	0.51	1390	835	15.2	64.1	1.420	14.0	772	39.8	35.2	1.8	121.0	1.850	5.0	11.8	14.2		36.6		114	449	4.44	
10009	2125	7325	16.60	183	3100	28	0.86	1990	2640	25.6	100.0	1.710	16.4	822	48.8	34.4		222.0	1.810	6.2	17.6	22.4		83.8	0.2	83	598		
10010	2125	7375	14.30	154	3310	24	0.83	1970	6560	29.6	105.0	1.810	15.4	807	51.4	31.6	0.4	236.0	2.290	7.4	19.0	19.2		70.8		84	586		
10011	2075	7375	27.80	174	4830	44	1.00	3190	2090	28.9	97.1	2.690	20.4	961	56.4	41.6		160.0	2.180	6.0	17.4	13.1	0.4	61.6		38	489		6.6
10012	2025	7375	23.50	151	3750	36	0.87	2470	1000	22.4	91.7	2.340	19.8	1020	52.7	40.4		86.1	2.100	5.2	14.6	19.9	0.4	59.8		53	579		
10013	2025	7425	11.20	126	3030	20	0.78	1700	3110	27.9	107.0	1.610	15.2	819	44.7	34.4	0.8	218.0	2.070	6.6	17.6	30.5	0.6	79.8		62	686		
10014	2075	7425	4.98	63	1110	16	0.52	684	970	12.9	73.6	0.749	10.6	470	37.0	34.2	1.8	225.0	2.090	4.6	14.6	33.1	1.0	76.8		88	969		
10015	1875	7375	5.88	90	1730	20	0.43	880	461	10.1	41.2	1.050	11.2	676	29.1	34.4	1.4	117.0	1.360	3.6	8.4	17.1		33.0		581	417		
10016	1925	7375	6.66	69	1520	16	0.37	834	583	12.0	49.3	1.030	13.0	771	30.6	36.4		160.0	1.430	4.8	7.4	5.9		30.2		31	311	4.84	5.0
10017	1925	7425	12.80	123	3050	32	0.62	1710	481	18.0	70.3	1.920	17.0	855	44.4	37.2	1.2	61.8	1.690	3.8	11.2	9.8		37.8		57	330		
10018	2025	7175	5.22	50	928	12	0.43	450	138	7.8	25.6	0.713	8.2	635	20.8	24.4	2.0	20.4	0.278	1.8	3.4	3.8		11.4		26	247	4.00	6.6
10019	1975	7175	17.30	116	2390	32	0.55	1540	254	14.9	57.3	1.730	15.0	879	40.0	38.6	1.0	54.9	1.480	3.6	10.8	7.8		37.6		52	251		
10020	1975	7125	10.00	140	3300	24	0.67	1400	5190	28.9	123.0	1.550	17.2	761	23.1	62.8		140.0	1.690	5.6	12.8	17.4		85.4		44	222		
10021	1925	7125	4.38	55	1590	24	0.37	752	206	9.2	55.5	0.829	10.8	691	30.6	31.0		507.0	1.760	3.8	7.4	12.8		34.8		30	1100		
10022	1925	7175	5.76	91	1860	28	0.46	926	368	11.0	63.4	0.976	13.4	752	46.6	40.0		184.0	2.310	4.4	13.2	16.2		38.0		87	881		
10023	1875	7275	14.00	167	4390	32	0.82	2870	574	19.2	79.8	2.420	16.0	829	45.0	31.8	1.8	96.0	2.170	6.6	15.8	11.7		57.8		76	337		
10024	1925	7225	4.92	63	1570	24	0.26	734	350	9.1	34.8	0.849	11.4	652	31.1	26.8	0.8	75.3	1.330	3.0	6.8	7.2		25.8		35	432	3.96	7.1
10025	1975	7425	11.90	131	2800	20	0.75	1700	3020	22.3	85.9	1.870	16.4	851	43.9	42.8	2.0	99.3	1.570	5.0	19.2	23.0	0.8	65.2	0.3	81	661	6.13	
10026	1975	7375	17.80	115	3000	20	0.52	1830	354	15.0	64.8	1.800	14.8	883	42.5	35.2		81.3	1.810	4.2	11.2	9.0		43.2		33	241	4.05	6.1
10027	1975	7325	15.60	96	1900	28	0.37	1290	384	13.0	56.3	1.440	15.8	803	36.2	27.6	1.2	48.9	1.350	2.8	8.4	8.4		35.8		33	212		
10028	1975	7275	9.06	77	1720	28	0.36	1000	756	13.6	40.7	1.110	11.2	730	35.4	23.2	0.6	71.7	1.260	2.8	8.2	11.1		28.2		37	329		
10029	1975	7225	4.74	67	1070	12	0.16	546	156	9.2	32.5	0.704	9.4	826	24.1	39.2	1.8	90.0	0.890	2.0	4.8	7.1		21.8		46	318	3.72	
10030	1875	7325	13.00	177	3770	32	0.71	2260	355	16.7	75.5	2.130	16.2	857	44.2	35.0	2.6	39.6	1.880	4.4	14.6	12.4		40.4		54	298		
10031	1925	7325	4.62	100	1390	16	0.21	628	286	10.0	38.5	0.826	12.2	788	31.5	31.8		120.0	1.380	2.4	6.2	9.3		27.8		43	497		
10032	1925	7275	13.90	66	994	8	0.33	754	438	9.1	32.4	0.854	9.2	563	28.4	23.8	0.8	26.4	0.959	2.2	6.8	6.9		22.8		54	261		
10033	1875	7225	22.50	295	7560	64	1.10	4030	1410	30.5	128.0	3.550	22.0	1200	62.9	46.4	2.4	360.0	2.950	10.2	19.6	14.7		76.4		103	550		
10034	1825	7325	16.40	242	5170	40	1.35	3390	3740	33.2	112.0	2.590	19.6	974	61.7	41.8	3.2	420.0	2.740	12.2	28.2	25.7		124.0		183	650	5.45	10.3
10035	1875	7175	8.46	197	2490	24	0.84	1610	2350	28.3	75.3	1.380	15.0	779	39.6	35.4	1.8	275.0	2.120	7.0	13.4	17.2		55.8		67	690		
10036	1825	7375	17.30	400	3980	20	1.64	3980	10200	58.5	458.0	2.100	16.2	905	65.4	27.6	3.0	313.0	2.590	11.4	33.8	45.0		132.0		248	974		
10037	1825	7225	19.60	188	4060	36	1.02	1960	785	25.3	126.0	2.760	21.0	745	62.9	39.6	7.4	344.0	2.900	9.2	18.8	16.6		48.2		96	658		
10038	1825	7275	4.26	93	1330	20	0.92	832	2580	18.9	90.2	0.730	9.8	365	43.2	17.4	2.0	281.0	2.270	7.0	20.6	39.1		114.0		406	1140	5.34	7.6
10039	1725	7475	7.56	197	2110	12	1.09	1420	7370	37.3	153.0	1.130	12.8	356	30.8	43.0		271.0	1.860	7.0	26.6	71.4		223.0		515	1180	7.03	8.6
10040	1725	7425	9.78	219	3040	28	1.00	1910	13800	60.3	246.0	1.510	16.2	738	51.8	37.2	1.6	418.0	2.640	9.0	23.6	40.4		226.0		390	1450	7.56	5.6
10041	1775	7425	13.00	155	3340	24	1.19	2140	8260	32.8	141.0	1.840	19.0	634	55.8	39.4		582.0	3.030	10.0	28.0	60.2	0.4	109.0		163	1120		
10042	1825	7425	17.60	224	3340	32	1.63	2170	4630	37.8	302.0	2.170	17.8	784	58.3	44.2		232.0	2.770	9.4	26.0	56.6	0.8	269.0	0.2	573	1160	6.26	9.2
10044	1825	7475	12.20	178	2760	32	1.26	1910	7000	46.4	372.0	1.550	16.2	514	54.4	47.4		451.0	3.040	10.6	28.4	231.0	1.6	1810.0	2.6	473	2040		8.2
10045	1875	7475	7.74	106	1680	12	0.76	1230	1410	19.0	112.0	1.090	14.6	698	45.0	40.2		376.0	2.380	7.6	15.4	33.4		60.4		146	758	5.20	4.5
10046	1925	7475	9.36	124	2070	24	0.83	1190	1090	15.8	101.0	1.130	13.0	702	46.6	42.8		221.0	2.380	7.4	18.6	30.4	0.4	95.6		196	978		
10047	1975	7475	9.96	198	1810	12	1.30	1140	4720	33.7	204.0	1.220	16.2	652	50.4	36.2		322.0	2.530	8.8	25.0	82.8	1.0	277.0		368	1850	6.18	
10048	1875	7425	15.70	159	2650	28	0.81	1940	3560	26.2	72.7	1.810	16.2	670	41.5	27.4		126.0	1.770	6.2	13.8	14.6		36.6		136	467		
10049	1625	7425	26.30	3440	4040	16	7.18	3550	25100	182.0	304.0	2.520	24.6	626	90.7	60.2	7.0	985.0	6.240	33.6	110.0	497.0	1.8	839.0	1.4	1690	3350	4.15	9.7
10050	1575	7425	25.70	203	3290	28	1.43	2620	3540	36.4	182.0	2.960	23.2	858	99.6	36.2	9.6	260.0	2.770	9.4	22.8	41.8		136.0		150	979	5.18	6.6
10051	1525	7425	11.00	165	3300	24	0.92	1830	2530	24.5	104.0	1.740	18.4	811	46.9	34.4	1.8	280.0	2.800	8.6	21.2	22.8	0.6	244.0		93	808		
10052	1525	7375	15.20	215	3430	28	1.02	2030	4110	34.2	174.0	1.980	20.6	891	46.1	34.8		190.0	2.150	7.2	19.4	29.7	0.8	109.0		135	1250		
10053	1625	7325	12.80	181	2880	16	1.04	1690	6280	37.8	211.0	1.580	16.4	702	47.5	37.2	5.2	297.0	2.110	7.4	19.8	88.1	0.6	222.0	0.9	244	1340		

Appendix 2.1 Data for Richmond topsoils
Geochemical data in µg/g unless otherwise stated

ID	East	North	Li	Na	K	Rb	Be	Mg	Ca	Sr	Ba	Al%	La	Ti	V	Cr	Mo	Mn	Fe%	Co	Ni	Cu	Ag	Zn	Cd	Pb	P	pH	LOI %
10054	1675	7325	9.06	177	2530		1.06	1740	23300	51.0	84.2	1.150	15.4	407	64.4	29.0	3.4	320.0	3.760	10.2	29.4	27.4		103.0		123	1400		
10055	1575	7275	10.90	145	2750	28	1.13	1710	3360	29.0	309.0	1.560	19.2	752	49.6	37.6		413.0	2.510	9.2	21.6	44.3	1.0	145.0		589	1140	6.47	4.6
10056	1525	7275	13.00	147	2390	20	1.11	1720	2750	26.2	139.0	1.900	20.4	759	45.2	37.6		256.0	2.180	8.4	20.0	29.7	0.8	113.0	0.4	187	633	6.14	5.1
10057	1525	7325	12.20	324	2800	20	2.19	1720	6190	48.9	337.0	1.710	20.2	780	51.6	44.2	3.6	450.0	2.770	11.8	33.0	121.0	0.8	472.0	0.4	533	1560		
10058	1575	7375	15.10	268	3370	32	1.52	1930	3870	65.3	205.0	2.060	21.2	880	52.9	43.8	2.8	273.0	2.550	12.2	28.8	53.8	0.6	200.0		215	1780		
10059	1575	7325	9.90	194	3280	20	1.59	1640	3380	30.8	297.0	1.630	18.6	690	52.0	38.2	3.2	341.0	2.810	10.6	26.8	70.0	0.4	193.0		312	1350	6.39	
10060	1625	7360	12.70	194	3180	24	1.02	1700	4010	33.0	255.0	1.750	18.0	843	49.9	36.8	2.0	466.0	2.540	10.2	22.8	93.0		332.0	0.6	302	1050	7.06	
10061	1675	7375	14.50	348	2840	16	1.62	1680	13800	57.9	256.0	1.530	18.2	694	58.7	37.0		450.0	3.080	11.6	35.8	69.5	0.4	200.0	0.3	1100	1730	7.67	14.3
10062	1675	7425	10.90	206	3010	24	0.99	1740	9410	37.2	141.0	1.540	17.0	699	48.7	41.4	1.8	339.0	2.680	9.6	23.2	27.8		119.0		318	534		
10063	1575	7225	7.56	144	2640	16	0.76	1410	14700	41.9	124.0	1.200	15.6	504	42.9	31.6		433.0	2.340	7.4	17.6	26.2		126.0		225	789	7.82	
10064	1475	7225	13.30	228	2410	16	1.22	1390	13300	54.9	192.0	1.500	16.8	689	46.7	33.6		298.0	2.220	8.0	22.4	37.8		165.0		371	1110		
10065	1425	7225	10.30	173	2500	20	0.78	1520	1010	18.1	88.8	1.720	18.2	797	34.7	34.2	1.6	150.0	1.690	5.4	13.0	23.1		52.6		185	362	4.80	4.0
10066	1425	7275	10.00	679	3440	16	0.98	2970	43500	117.0	280.0	1.720	15.6	833	42.2	24.2	2.8	517.0	2.240	9.2	22.8	52.6	0.8	330.0	11.1	218	1290		
10067	1475	7275	18.00	577	3960	20	3.49	2290	13900	109.0	473.0	2.250	19.8	742	65.0	42.6	4.2	461.0	3.560	18.4	47.0	86.7	0.8	509.0	0.3	1350	1970	7.54	9.2
10068	1525	7225	12.10	234	1900	12	0.84	1420	3490	23.8	93.1	1.550	17.4	788	39.0	34.6	1.6	185.0	1.940	6.0	15.8	18.7		60.8		73	519		
10069	1425	7325	9.42	130	2140	16	0.96	1290	2290	23.7	135.0	1.370	17.6	621	39.5	28.2		298.0	2.080	6.8	17.2	29.8		99.6		145	816	5.86	
10070	1475	7325	12.10	117	2280	24	0.87	1440	1390	20.7	98.5	1.540	16.4	730	42.6	32.8		458.0	2.230	7.2	16.2	21.8		67.8		103	934	4.97	
10071	1425	7375	16.10	205	2390	20	1.21	1760	4430	45.2	245.0	1.950	20.6	875	46.6	45.0		270.0	2.080	8.0	20.0	39.1	1.0	229.0	0.5	352	1600		
10072	1475	7375	13.50	185	3330	32	1.22	1750	4010	36.2	165.0	1.770	20.4	727	48.3	38.0		481.0	2.510	9.6	22.6	35.8		161.0		133	1150	6.59	5.1
10073	1875	7525	10.30	250	2380	72	1.91	1450	6330	48.9	367.0	1.330	16.0	593	55.3	64.4	0.6	384.0	3.360	10.4	32.8	133.0	1.0	609.0	0.7	789	2520	6.57	5.1
10074	1925	7525	9.42	143	1990	20	0.86	1430	4680	34.0	173.0	1.190	14.8	660	46.1	40.6		262.0	2.430	6.4	17.6	54.2	0.4	180.0		307	1620		
10075	1975	7525	11.60	263	2320	16	1.56	1640	11800	50.6	291.0	1.450	16.4	654	55.7	40.8	2.6	285.0	3.000	10.0	28.4	47.4		281.0		1440	1200	7.57	8.6
10076	1975	7575	14.80	311	4090	36	1.35	2790	11300	54.1	216.0	2.080	17.8	710	62.1	31.0	2.0	344.0	2.930	10.6	27.8	72.0	2.6	240.0		473	1660	7.15	9.7
10077	1975	7625	8.94	214	2970	28	1.08	1640	6920	37.1	155.0	1.310	16.2	674	51.0	36.0	2.4	379.0	2.630	9.4	24.6	72.3	1.0	169.0		467	1650		
10078	1925	7625	9.42	170	2150	16	0.97	1250	3640	27.1	158.0	1.290	14.2	654	50.0	33.8	2.8	349.0	2.560	8.6	21.6	62.9	0.8	143.0	0.3	351	1130	6.17	
10079	1925	7575	8.34	204	2430	20	1.27	1160	5490	55.7	504.0	1.140	14.0	540	48.2	44.0	2.6	349.0	2.680	10.4	29.2	126.0	0.6	495.0	0.9	538	3350	6.07	8.1
10080	1875	7575	13.60	242	2650	24	1.47	1620	5260	36.8	176.0	1.690	17.4	773	63.8	43.4	2.8	235.0	2.820	10.2	30.4	48.9		125.0		320	1300	6.60	
10081	1875	7625	13.10	217	2950	28	1.01	1850	15300	68.8	171.0	1.650	15.2	667	47.9	30.8	1.8	242.0	2.000	7.4	20.8	49.7		154.0		274	1940		
10082	1925	7725	12.80	394	3160	32	2.60	1860	15400	83.8	480.0	1.790	18.6	561	62.7	41.4	3.0	496.0	3.380	14.4	39.2	112.0	0.8	784.0	0.4	921	4120		
10083	1975	7675	17.90	361	4230	32	1.66	2800	16200	72.5	255.0	2.450	19.2	771	59.9	38.0	2.6	396.0	2.930	12.4	33.4	81.1	1.8	246.0		345	1940		
10084	1925	7675	6.30	125	1560		0.83	956	4830	49.1	507.0	0.845	8.8	370	38.7	66.0		273.0	2.300	7.8	19.8	89.1		415.0		1840	1690	6.50	7.1
10085	1375	7375	14.60	178	3640	20	1.27	1850	3810	31.1	155.0	1.900	17.4	718	46.0	34.8		301.0	2.610	8.2	20.4	32.4		218.0		237	1440	6.28	
10086	1375	7425	13.00	162	2960	28	0.82	1830	1510	22.0	145.0	1.960	20.6	891	44.1	37.2	1.4	192.0	2.340	7.0	17.0	23.1	0.6	101.0		89	787		
10087	1375	7325	23.60	232	7280	48	1.65	4500	2710	35.4	137.0	3.650	25.6	905	85.2	42.0	2.4	374.0	4.850	13.8	40.4	15.9		63.6		40	491	6.08	4.6
10088	1375	7275	15.10	198	2600	16	1.37	1430	3740	33.1	157.0	1.580	16.2	415	48.6	38.8		334.0	2.610	8.2	24.6	49.3		160.0		1210	1220	6.00	
10089	1375	7225	10.90	137	2200	20	0.78	1380	2370	22.3	92.4	1.540	16.4	731	38.5	33.4		342.0	1.880	6.8	14.2	22.4		67.0		166	1060	5.33	12.8
10090	1325	7325	2.94	47	862		0.28	458	835	7.9	42.2	0.580	5.0	228	16.6	37.6	0.6	42.9	0.868	2.6	23.6	8.0		37.8		35	384	5.70	8.6
10091	1325	7375	13.70	205	3970	40	0.92	2270	4980	39.8	259.0	2.180	20.8	812	43.3	68.4	2.4	244.0	2.080	7.6	22.4	70.0	4.6	210.0	3.5	181	1920	6.54	
10092	1325	7425	15.10	280	3850	32	1.28	2120	10500	69.7	479.0	1.910	19.2	780	45.5	46.2		378.0	2.400	10.0	27.2	92.1	0.8	848.0	0.9	315	2980		
10093	1275	7375	13.30	219	4230	32	0.87	2050	5240	35.4	142.0	2.150	20.6	942	43.6	43.6	1.4	265.0	2.110	6.8	17.0	27.9		243.0	0.4	113	10105		
10094	1275	7325	11.20	187	2420	20	1.02	1740	6790	45.2	241.0	1.500	16.6	687	42.6	34.6		335.0	2.220	8.2	20.4	42.9		163.0		212	1040		
10095	1325	7175	12.10	156	2560	20	0.88	1580	3050	30.0	158.0	1.730	18.2	686	40.4	38.6		262.0	2.060	8.2	17.8	27.1	0.8	180.0	0.6	187	1250		
10096	1375	7125	16.60	238	3530	28	1.71	1800	4600	46.3	276.0	2.060	21.8	759	49.8	42.2		287.0	2.880	10.4	28.2	47.8	0.8	229.0	0.4	604	1680		10.3
10097	1325	7125	12.80	150	3350	20	0.91	1580	3290	28.1	128.0	1.850	18.4	710	40.4	31.0		190.0	1.910	5.8	16.2	24.8		97.2		116	1080		
10098	1275	7125	18.70	216	3590	24	1.09	1920	7370	51.5	253.0	2.410	22.6	917	50.1	36.6		251.0	2.220	8.0	21.2	41.3	1.0	143.0	0.3	295	1580		
10099	1275	7175	12.80	171	3270	28	0.66	1930	3540	33.6	88.7	1.820	17.8	812	36.6	83.0		196.0	1.740	5.4	14.0	13.1		70.8		58	1030		
10100	1375	7175	13.10	141	2720	24	0.68	1550	1500	20.8	84.5	1.870	19.0	891	35.1	33.2		103.0	1.650	4.8	12.2	12.4		45.2		64	455	5.14	
10101	1375	7075	18.30	298	3090	24	1.48	1820	7440	77.5	297.0	1.890	20.8	802	57.5	45.4	1.4	321.0	3.340	12.4	35.0	47.5	0.6	389.0	0.6	770	1140	7.21	8.1
10102	1375	7025	20.80	468	2990	20	1.82	1890	5460	76.5	273.0	2.030	20.2	910	63.1	48.6	3.6	268.0	2.920	14.2	38.6	50.7		125.0		357	1650		
10103	1375	6975	11.20	244	2680	20	1.30	1620	9710	74.3	231.0	1.220	16.0	619	45.4	28.8		484.0	2.510	10.0	28.0	48.1	0.8	295.0	0.5	490	2300	7.26	8.1
10104	1325	6975	14.50	211	2620	24	1.42	1800	7310	70.0	166.0	1.770	20.2	722	49.6	40.4		298.0	2.660	10.8	28.8	50.3		124.0		247	1010	6.88	
10105	1275	6975	13.00	247	3090	28	1.24	2090	20300	70.5	177.0	1.700	18.8	710	56.6	34.8	1.8	451.0	3.250	11.2	33.4	38.8	1.4	159.0		125	814		

Appendix 2.1 Data for Richmond topsoils

Geochemical data in µg/g unless otherwise stated

ID	East	North	Li	Na	K	Rb	Be	Mg	Ca	Sr	Ba	Al%	La	Ti	V	Cr	Mo	Mn	Fe%	Co	Ni	Cu	Ag	Zn	Cd	Pb	P	pH	LOI %
10106	1275	7025	11.90	224	3030	32	1.23	1650	2990	39.4	524.0	1.910	20.0	779	45.5	42.2	3.4	222.0	2.430	10.2	22.6	74.3		461.0	0.9	863	1300		
10107	1325	7025	13.80	199	4080	36	1.16	1920	5290	37.2	206.0	2.080	19.6	682	56.1	49.0	1.6	304.0	3.000	9.8	30.8	109.0	2.8	287.0	1.2	229	1810		
10108	1325	7075	14.80	217	3690	36	0.96	1700	1750	27.8	120.0	2.310	20.0	742	50.6	33.8	3.4	196.0	2.170	8.2	19.2	20.8		66.2		101	748		
10109	1275	7075	14.30	251	3540	32	1.05	2210	8590	61.6	145.0	2.010	18.6	863	52.9	40.6	2.6	274.0	2.580	9.0	23.0	25.9		97.2		237	877		
10110	1225	7025	12.20	142	2550	24	0.89	1500	1340	26.3	105.0	1.690	19.4	842	40.6	40.4		233.0	1.850	6.6	15.2	16.2		58.8		76	858		
10111	1225	7125	14.30	178	3640	28	1.01	1580	3780	31.8	132.0	2.170	20.6	751	46.9	38.4	1.8	346.0	2.210	7.4	19.0	27.2		91.0		195	1520	5.70	
10112	2025	7525	10.40	183	2740	28	0.97	1650	6310	33.3	202.0	1.520	16.6	650	49.8	45.4	2.8	295.0	2.600	8.6	21.2	54.6		297.0	0.5	380	886	7.35	
10113	2025	7475	6.66	146	1470	20	1.11	906	3190	22.5	131.0	0.960	13.2	491	45.3	37.4	2.4	280.0	2.350	8.0	20.8	38.2		164.0		396	1090		
10114	2075	7475	8.22	145	1640	16	0.88	1020	2260	21.2	109.0	1.140	14.8	653	55.1	38.2	2.8	218.0	2.720	7.0	19.8	34.3	0.6	114.0	0.6	238	1180		
10115	2075	7525	9.96	131	1900		0.88	1440	2210	19.8	111.0	1.380	15.0	690	47.0	32.4	0.6	190.0	2.260	6.8	18.2	33.4		124.0		195	658		
10116	2125	7525	12.50	285	3160	24	1.30	3280	8850	52.8	323.0	1.520	14.6	527	53.8	30.6	2.4	289.0	2.830	11.6	36.4	97.8	3.0	406.0	0.4	645	1760	6.50	8.6
10117	2175	7575	13.00	296	3450	24	1.32	2520	7920	49.2	219.0	1.750	16.2	786	58.1	29.0	1.0	301.0	2.590	10.4	28.0	58.3		218.0		434	1300	6.59	10.2
10118	2225	7575	5.16	168	1420	16	0.64	1270	2270	21.9	112.0	0.961	13.0	765	44.6	29.0	2.6	103.0	1.740	6.8	19.4	60.5		52.2		195	673		
10119	1625	6825	6.78	86	1970	20	0.69	1170	1100	13.1	58.5	1.060	14.2	699	44.4	44.2		437.0	2.460	7.4	15.6	10.0		49.8		50	798		
10120	1625	6775	6.66	131	1840	20	0.90	1160	858	14.0	101.0	1.160	14.2	593	45.6	36.0	2.4	502.0	2.380	8.6	18.6	61.0		83.6		244	584		
10121	1675	6725	9.30	137	1630	20	0.68	1490	62700	78.5	73.1	1.170	12.0	479	32.4	19.4		556.0	1.930	6.2	15.8	12.5		57.0		49	798		
10122	1675	6775	9.24	67	2160	20	0.86	1450	983	13.9	64.9	1.520	13.4	540	50.2	27.2		278.0	2.820	6.0	19.4	12.8		68.2		57	814		
10123	1725	6775	43.10	313	10100	64	1.65	7630	22800	68.9	155.0	4.260	25.6	922	88.1	33.0		286.0	3.860	13.6	38.8	25.2		84.8	0.4	44	957		
10124	1725	6825	6.72	69	1400	28	0.70	960	601	12.2	70.1	1.050	12.4	571	43.4	26.2	1.0	392.0	2.520	7.2	15.6	12.6		66.0		59	704	4.78	
10125	1675	6825	5.76	96	2210	24	0.89	1180	1100	13.4	69.8	1.080	17.4	472	57.6	30.0	2.0	336.0	3.390	8.4	24.2	15.8		69.6		71	1030		
10126	1575	6825	6.60	120	2470	20	0.89	1380	2030	16.2	63.7	1.200	14.8	601	55.0	33.4	1.0	390.0	3.210	8.8	23.4	11.4		60.0		116	576	6.09	
10127	1575	6875	4.86	57	1640		0.46	974	906	10.2	45.5	0.902	9.6	506	35.9	25.6		278.0	2.030	4.4	7.8	9.9		36.4		45	698		
10128	1575	6925	13.70	159	2800	20	0.80	2180	75400	103.0	142.0	1.720	15.2	589	42.4	32.4		265.0	1.930	6.4	17.6	24.1	0.8	89.6		88	685		
10129	1575	6975	5.70	101	1970	16	0.52	1180	920	14.2	57.3	1.010	13.6	642	39.3	29.8	1.6	242.0	2.090	5.4	13.6	15.5		41.6		62	739	4.69	
10130	1575	7025	8.34	129	2860	24	0.82	1630	1920	18.7	92.9	1.420	17.4	800	45.4	35.4	1.2	310.0	2.450	8.2	19.4	42.4		82.6		55	632		
10131	1625	7025	8.16	147	2450	16	1.00	1430	21800	45.7	102.0	1.230	15.4	566	50.8	29.8	1.8	419.0	2.770	9.6	26.6	60.4		97.0	0.2	446	849	7.10	6.1
10132	1625	6975	6.12	98	2030	16	0.40	1120	533	12.5	52.2	1.120	16.2	827	37.7	49.0	1.4	90.9	1.790	3.6	11.0	10.2		31.8		54	714		
10133	1625	6925	6.06	87	1900	24	0.51	1060	404	12.2	53.4	1.060	16.4	753	41.6	51.2	0.8	185.0	2.200	4.8	13.6	14.0		36.8		54	663	4.08	
10134	1675	6925	5.76	122	1530	20	0.54	964	1770	12.9	55.1	0.959	12.6	676	38.8	34.8	1.2	284.0	2.010	5.8	13.2	29.5		47.0		46	476		
10135	1725	6925	2.82	43	1160		0.52	664	431	6.6	34.5	0.560	7.8	404	37.1	26.2	1.0	250.0	2.110	5.0	13.6	8.1		38.8		32	513		
10136	1675	6975	7.38	154	1630	12	0.54	1090	2610	18.7	52.2	1.150	12.6	631	35.8	27.4	1.8	63.9	1.470	3.8	13.6	10.1		42.0		40	502	6.13	
10137	1675	7025	7.38	141	1960	12	0.84	1180	3920	34.4	398.0	0.974	13.0	530	46.9	38.0		295.0	2.400	7.6	22.4	27.4		141.0		147	774	6.48	8.1
10138	1525	7025	6.48	90	2050	24	0.58	1140	506	12.4	66.0	1.090	14.2	696	37.0	31.4	3.8	220.0	1.760	4.4	11.0	13.4		33.8		49	1000	4.40	
10139	1475	7075	8.46	139	2850	32	0.52	1510	734	15.9	73.7	1.510	17.6	954	38.9	43.6	2.0	283.0	1.850	5.4	12.2	11.6		46.6		47	773		
10140	1425	7075	11.30	198	2560	24	0.70	1460	6720	27.8	100.0	1.520	18.2	882	38.7	34.4	3.0	179.0	1.700	6.0	15.8	31.7		91.0	0.4	155	802	6.80	11.3
10141	1475	7025	9.24	158	2260	20	0.71	1520	2590	21.2	88.0	1.430	17.8	804	39.8	40.4	1.4	328.0	1.840	6.2	14.2	13.1		56.6		47	699	5.96	5.6
10142	1525	6975	4.74	102	1410	8	0.53	822	1540	12.1	64.0	0.865	11.2	560	37.5	27.8	1.2	120.0	2.120	4.2	13.0	14.7		49.2		84	1100		
10143	1475	6975	8.76	136	2850	20	0.69	1510	9640	25.1	108.0	1.370	17.4	771	38.3	45.2	0.8	521.0	2.120	7.4	15.6	15.8		153.0		52	824		
10144	1425	7025	12.40	150	2260	16	0.77	1680	2410	21.8	98.5	1.750	19.2	736	40.9	33.0	1.2	145.0	1.820	5.2	16.6	20.5		60.8		54	763		
10145	1475	6925	6.30	126	2320	20	0.79	1380	1450	15.7	84.0	1.190	17.4	632	47.0	45.4	1.0	626.0	2.640	8.0	18.2	32.6		79.4		132	997	5.20	
10146	1525	6925	5.58	104	1920	20	0.57	1020	588	12.0	52.6	0.983	15.0	716	50.4	43.4	1.6	289.0	2.510	5.4	15.4	12.6		44.8		63	935	4.26	
10147	1625	6875	6.36	93	2390	20	0.73	1320	2320	16.3	74.4	1.080	14.0	628	46.7	30.6	1.4	348.0	2.380	7.6	18.0	20.8		65.2		94	1020		
10148	1675	6875	11.00	172	4040	36	0.90	2000	1890	19.3	87.5	1.860	19.0	807	47.8	34.4	1.0	580.0	2.500	8.8	20.0	16.0		72.6		72	724		
10149	1725	6875	9.60	150	3180	20	0.65	1680	644	16.4	81.0	1.700	13.4	602	53.0	24.4	1.4	77.7	2.210	4.4	15.0	20.4		53.0		93	921		
10150	1525	7175	8.34	125	2210	16	0.94	1560	2510	29.1	95.5	1.370	16.4	657	41.9	27.0	1.8	287.0	2.090	7.4	16.6	25.7		71.8		117	650		
10151	1475	7175	11.30	269	2730	32	1.13	2030	6760	48.6	342.0	1.690	19.0	867	45.8	38.6	2.2	326.0	2.510	9.2	22.6	72.5		450.0	0.7	314	1320		
10152	1525	7125	9.60	147	2620	24	0.98	1570	4590	35.0	138.0	1.620	20.2	802	45.5	38.6	2.0	655.0	2.350	8.6	19.6	20.7		120.0		133	1180		
10153	1575	7125	13.90	216	3050	28	1.36	2010	6030	44.8	263.0	1.890	20.2	760	51.1	43.6		421.0	2.790	9.8	26.4	58.1	3.0	279.0	1.0	330	1380		
10154	1625	7125	8.58	131	2830	16	0.87	1490	5640	29.4	209.0	1.270	17.8	684	45.1	34.0	3.6	346.0	2.370	7.8	18.0	22.0		137.0		206	943	7.13	
10155	1625	7175	16.60	222	3630	28	1.14	2600	23400	65.9	135.0	2.120	20.0	747	54.0	44.6		416.0	2.630	9.2	24.0	33.5	0.4	125.0	0.3	163	820	7.00	
10156	1675	7125	10.40	103	2430	28	0.98	1550	1980	18.7	106.0	1.410	14.2	526	50.9	26.6		367.0	2.630	7.4	21.2	23.8		150.0		149	956		
10157	1725	7075	12.20	280	3290	24	2.13	1790	6370	52.4	469.0	1.790	17.6	534	57.5	55.0	2.6	460.0	3.450	12.0	38.4	114.0	1.0	574.0	0.5	751	1520		

Appendix 2.1 Data for Richmond topsoils

Geochemical data in µg/g unless otherwise stated

ID	East	North	Li	Na	K	Rb	Be	Mg	Ca	Sr	Ba	Al%	La	Ti	V	Cr	Mo	Mn	Fe%	Co	Ni	Cu	Ag	Zn	Cd	Pb	P	pH	LOI %
10158	1675	7075	8.10	168	2190	16	1.10	1280	10400	47.3	272.0	1.080	12.8	519	40.6	30.8		367.0	2.320	8.0	23.4	233.0	0.6	437.0	0.6	226	1220		
10159	1575	7075	9.84	157	2380	32	1.12	1590	2590	23.6	132.0	1.610	19.0	819	48.0	36.4	2.4	242.0	2.440	8.4	20.8	38.1		111.0		255	942		
10160	1625	7075	5.28	86	2110	20	0.69	1040	1910	13.9	78.2	0.934	13.8	556	36.8	22.6	1.0	341.0	2.060	6.8	15.0	20.9		65.4		83	1150		
10161	1475	7125	10.40	249	2380	20	1.67	1430	5260	42.5	238.0	1.440	15.4	617	46.3	31.8	3.0	229.0	2.600	10.0	28.0	48.3		283.0	0.3	362	884	7.42	
10162	1525	7075	12.60	179	2510	28	1.36	1640	2700	33.5	213.0	1.630	20.6	736	47.6	44.2		309.0	2.530	8.8	24.8	46.9	0.6	227.0	0.4	307	1590	5.57	
10163	1425	7125	8.52	247	2430	12	1.16	1450	15600	75.9	236.0	1.190	14.8	572	48.8	33.8	2.2	283.0	2.900	9.4	25.8	32.2		270.0		365	918		
10164	1425	6975	9.60	872	2300	24	1.03	1470	2240	25.1	117.0	1.400	17.0	611	44.9	30.2		444.0	2.290	8.0	19.4	26.2		84.8		206	1400		
10165	1575	7175	8.16	129	2280	24	0.78	1180	4040	25.0	123.0	1.090	12.0	540	37.3	22.8	2.8	202.0	1.890	6.6	17.8	29.7		132.0	0.2	172	562	7.03	
10166	2025	7675	9.96	173	3280	24	1.21	1770	6070	34.6	170.0	1.720	17.6	693	55.4	31.6	1.8	310.0	2.840	9.2	24.8	35.5		123.0		214	1160	7.03	
10167	2025	7575	10.30	201	2440	28	1.20	1340	4610	36.5	200.0	1.390	16.8	613	58.8	45.4	3.2	328.0	3.160	10.0	27.8	61.2	0.8	213.0	0.3	436	1340	6.65	7.1
10168	2075	7575	13.50	391	3210	20	1.82	1890	11300	67.7	260.0	1.530	18.0	595	68.7	30.6	0.6	385.0	2.950	12.6	37.6	92.0	0.6	177.0	0.4	428	1780		
10169	2125	7575	12.70	138	3340	24	0.90	1890	2430	20.9	86.0	1.760	15.2	810	50.8	35.0	1.8	340.0	2.530	9.8	22.4	19.0		71.4		69	724	5.74	
10170	1825	7725	9.12	133	2540	20	1.10	1450	4190	24.9	112.0	1.350	13.8	653	62.4	35.8	1.0	410.0	3.120	9.2	26.2	33.8		115.0		303	1120	6.58	
10171	1775	7625	4.14	84	1840	24	0.76	996	590	12.7	51.8	0.870	12.2	456	64.5	28.6	1.8	270.0	3.700	7.2	26.6	17.2		56.6		95	686		
10172	1825	7625	4.14	93	1430	12	0.53	758	1170	11.2	47.8	0.894	9.0	530	41.9	28.2		175.0	2.190	4.4	15.6	25.6		40.4		101	713	4.52	
10173	1825	7675	17.60	204	5580	48	1.33	3220	2300	27.7	121.0	2.940	20.2	972	74.7	43.2	1.2	339.0	3.660	12.4	28.0	19.6		84.8		70	656		
10174	1875	7675	6.54	79	2050	16	0.88	1220	1080	14.9	64.9	1.050	13.4	538	56.2	30.0		423.0	3.070	8.8	22.8	19.0		61.8		83	762	5.22	
10175	1875	7725	10.40	109	2680	20	0.97	1660	2430	22.3	111.0	1.500	15.6	694	55.2	32.0		269.0	2.780	9.0	22.6	29.4		89.2		124	934		
10176	1875	7775	13.60	212	3820	28	1.33	2010	7110	34.6	151.0	1.900	17.0	695	68.7	41.6	2.6	457.0	3.450	11.6	31.8	38.2		141.0		359	1120	6.98	
10177	1775	7525	6.36	103	2400	12	0.68	1290	4630	20.3	101.0	1.040	13.8	655	46.1	45.6	4.8	365.0	2.620	6.8	17.2	23.7		78.0		112	911		
10178	1725	7525	11.00	138	3360	36	1.12	2030	4980	30.5	108.0	1.800	17.0	638	60.8	34.4	3.0	765.0	3.760	11.4	31.2	20.7		99.0	0.3	122	910		
10179	1725	7575	7.14	658	1590		1.48	1900	10400	55.4	251.0	0.965	8.0	477	35.3	18.0		294.0	2.410	8.6	24.0	116.0		149.0		309	1200		
10180	1775	7575	27.30	225	7680	60	1.39	4270	1240	28.2	125.0	3.600	20.0	1070	81.0	45.0		211.0	3.400	9.4	29.8	22.2	0.4	76.6		64	687		
10181	1825	7575	4.20	63	1910		0.66	960	1170	11.6	51.1	0.803	11.2	457	49.6	28.6	1.2	295.0	2.750	6.8	20.2	12.6		52.8		76	666		
10182	1625	7225	22.00	191	5410	40	1.28	3310	3820	35.6	140.0	2.520	20.2	932	62.5	42.0		358.0	2.760	10.6	27.2	32.7	0.6	97.8		167	868	6.34	6.6
10183	1625	7275	17.20	224	4640	32	1.33	3670	10100	41.9	120.0	2.530	20.4	757	70.9	33.8	2.6	377.0	3.800	12.0	38.0	28.5		158.0		129	982	6.90	
10184	1675	7275	7.20	97	2290	16	0.75	1110	2070	18.4	85.9	1.180	15.6	687	43.9	48.0	1.8	301.0	2.380	6.4	17.0	23.0		90.0		114	886		
10185	1675	7225	12.80	198	4680	36	1.16	2330	7480	32.9	129.0	2.100	18.8	841	57.1	43.6	2.2	457.0	3.010	10.4	31.4	31.6		103.0		105	722	6.99	
10186	1725	7225	10.70	161	4230	52	1.02	1930	2060	21.9	121.0	1.920	19.0	820	51.6	35.8	2.4	552.0	2.490	10.4	20.8	21.2		97.8		100	1070		
10187	1775	7225	5.70	95	1910		0.57	978	6850	24.7	98.8	1.020	8.4	395	33.8	26.4		278.0	1.850	4.6	9.6	19.7		87.4		194	824		
10188	1775	7275	10.90	481	3120	20	1.79	1320	5600	55.7	181.0	1.340	14.4	529	54.9	37.0	2.6	369.0	2.310	13.4	33.8	54.4		146.0		127	1590		
10189	1725	7275	8.94	185	3670	36	1.25	1750	11500	50.8	158.0	1.590	18.0	543	52.5	32.6	1.4	397.0	2.820	9.8	27.4	40.6		167.0		361	2460		
10190	1725	7325	14.60	270	4180	40	1.07	2480	16900	66.4	131.0	2.150	17.0	710	54.3	45.8	2.6	542.0	2.800	10.2	36.8	43.6	1.6	186.0	1.6	151	1950	7.10	9.3
10191	1775	7325	8.40	241	2770	24	0.73	2400	4030	26.8	83.5	1.400	14.0	816	46.6	21.8	2.8	486.0	2.360	8.6	17.4	21.5		75.6		188	1010		
10192	2275	7775	18.40	445	3820	32	1.96	2450	8390	54.8	321.0	2.180	22.4	872	79.7	38.0	3.8	405.0	3.270	15.2	42.4	73.6	0.8	226.0	0.5	455	1250	7.21	7.1
10193	2225	7775	8.70	190	2250	28	1.30	1330	8810	44.8	192.0	1.180	14.4	469	57.5	27.2	3.2	400.0	2.870	10.0	28.8	123.0	0.6	199.0	0.4	439	1710		
10194	2175	7725	10.30	188	2530	20	1.24	1790	22600	41.8	139.0	1.530	13.8	491	66.5	25.8	2.2	484.0	3.380	10.8	31.2	52.6		132.0	0.4	205	1410		
10195	2175	7675	14.80	243	4520	32	1.28	2800	21000	55.4	260.0	2.080	18.2	645	62.8	29.0	1.4	389.0	2.940	10.6	30.8	50.7		240.0		328	1780		
10196	2225	7675	12.40	218	3180	32	1.25	1860	7460	41.7	249.0	1.840	18.8	675	59.2	31.8	2.8	291.0	2.810	10.8	26.4	74.9	0.6	183.0	0.3	644	1620	6.90	8.2
10197	2225	7725	11.60	195	3850	36	1.30	2100	11500	42.4	177.0	1.770	19.0	748	61.0	36.8	1.6	396.0	2.760	11.0	28.4	62.8	0.8	164.0		249	1350		
10198	1825	7525	10.20	143	1920	16	1.32	1340	3600	34.5	465.0	1.310	17.4	551	59.5	41.4		350.0	3.030	10.0	26.0	67.3		410.0	0.3	1210	1540		
10199	2275	7675	3.84	59	1480		0.53	750	3860	13.1	39.6	0.601	10.4	438	36.4	26.8	1.2	281.0	2.200	5.8	17.0	15.6		55.4		34	506	6.80	4.0
10200	2275	7725	11.10	173	3500	20	1.08	1840	12600	35.4	127.0	1.650	16.8	666	56.8	32.6	1.6	397.0	2.650	9.6	26.0	41.7		99.4		197	941		
10201	1425	7425	12.20	176	3240	32	0.84	1720	1220	19.1	119.0	1.820	19.8	841	46.8	36.2	2.2	200.0	2.200	6.0	17.2	22.4		60.6		106	1050	4.90	
10202	1475	7425	7.50	179	2470	24	0.90	1590	2400	18.8	107.0	1.410	16.8	702	47.5	35.0	1.4	504.0	2.380	8.8	18.8	35.0		81.4		134	843		
10203	1725	7375	7.02	123	2350	24	0.86	1500	875	15.6	95.7	1.390	17.0	785	47.7	41.6	2.2	498.0	2.450	9.0	16.6	23.4		63.0		101	731	4.50	5.1
10204	1775	7375	30.60	314	5300	52	1.82	4260	28800	74.9	228.0	4.030	29.6	741	72.8	38.0		1310.0	4.350	17.6	44.4	39.4		137.0	0.3	121	1060		
10205	1775	7175	8.22	105	2390	36	0.84	1220	263	13.2	71.9	1.450	15.4	728	53.1	34.0	2.2	332.0	2.750	8.2	17.8	18.0		52.8		157	725	4.15	6.1
10206	1725	7175	9.00	136	2850	32	1.03	1500	3090	25.7	215.0	1.490	16.8	749	51.4	42.0	1.8	568.0	2.840	10.6	22.8	63.0	0.6	217.0		208	975		
10207	1875	7125	23.80	331	5710	44	1.45	3280	7310	48.1	187.0	3.280	25.2	873	61.9	34.4	0.6	255.0	2.650	10.0	25.8	54.3		137.0		208	746		
10208	1825	7175	9.78	165	2870	28	0.77	1430	355	14.3	73.0	1.690	17.4	708	68.0	38.0	2.2	157.0	3.310	6.6	23.4	19.9		46.4		97	1080		
10209	1725	6975	8.40	191	2610	20	1.19	1640	9390	57.2	225.0	1.320	15.4	582	51.3	32.2	1.2	351.0	2.910	8.8	24.6	41.0		216.0		315	1090		

Appendix 2.1 Data for Richmond topsoils
Geochemical data in µg/g unless otherwise stated

ID	East	North	Li	Na	K	Rb	Be	Mg	Ca	Sr	Ba	Al%	La	Ti	V	Cr	Mo	Mn	Fe%	Co	Ni	Cu	Ag	Zn	Cd	Pb	P	pH	LOI %
10210	1725	7025	5.64	67	1720	16	0.76	1140	1610	12.9	52.2	0.948	13.4	230	52.0	32.2		252.0	3.060	7.2	20.0	14.2	1.0	54.6		1100	778		
10211	1775	7025	6.30	94	2150	20	0.73	1150	5050	21.3	82.0	1.120	15.0	510	45.6	24.2		269.0	2.600	7.2	19.4	13.4		76.0		92	646		
10212	1775	7075	25.00	870	3340	12	5.14	1990	10900	126.0	323.0	2.200	23.4	619	86.5	47.0	2.0	471.0	3.920	23.2	74.0	164.0	0.8	657.0	1.2	690	1850		
10213	1425	7175	7.26	125	2210	24	0.96	1330	4550	26.5	123.0	1.200	16.2	553	46.1	29.8	0.8	472.0	2.500	8.0	21.6	26.2		123.0		167	938		
10215	2225	7625	31.90	894	7060	40	2.39	4450	21100	112.0	608.0	3.910	26.0	801	80.3	48.8	1.2	756.0	4.300	17.4	52.6	192.0	1.2	899.0	1.8	857	2160	7.42	11.5
10216	1325	6925	17.90	732	3390	16	3.47	1910	9330	92.4	388.0	2.000	19.8	503	69.5	44.0	6.8	443.0	4.010	20.2	69.2	1130	0.6	892.0	6.1	631	1560	7.38	13.8

Appendix 2.2 Data for Richmond subsurface soils
Geochemical data in μg/g unless otherwise stated

No.	East	North	Li	Na	K	Rb	Be	Mg	Ca	Sr	Ba	Al%	La	Ti	V	Cr	Mo	Mn	Fe%	Co	Ni	Cu	Ag	Zn	Cd	Pb	P	pH
10001	2125	7225	13.50	132	2230	20	0.68	1480	2660	21.5	100.0	1.360	13.0	607	40.9	24.2		206.0	1.800	4.4	14.6	28.3		114.0	0.5	177	819	5.86
10002	2125	7275	12.70	96	2230	16	0.47	1630	1530	15.1	54.7	1.250	11.6	651	37.9	37.6	3.6	102.0	1.500	3.6	10.4	9.9		34.8		44	350	
10003	2075	7225	16.90	54	1210	12	0.26	920	179	9.7	35.2	1.080	8.2	530	27.2	24.6		45.0	0.814	2.0	5.6	3.0		21.4		10	170	3.89
10004	2025	7225	20.20	166	5150	44	0.88	2970	559	22.2	79.5	2.610	18.2	1150	55.1	51.4		353.0	2.560	9.0	14.0	9.5		40.6		19	402	
10005	2025	7275	5.88	54	1580	8	0.39	842	174	7.7	28.1	0.821	8.0	545	30.9	29.8	1.4	112.0	1.770	6.0	11.6	7.7		18.2		391	175	4.62
10006	2075	7275	7.68	103	2810	24	0.58	1350	269	12.6	61.7	1.390	11.8	766	38.0	37.0	1.8	342.0	1.930	6.8	10.8	10.6		39.2		43	561	
10007	2025	7325	10.50	106	2300	32	0.45	1310	269	12.2	47.7	1.420	13.2	783	39.1	37.8	2.2	163.0	1.970	5.2	9.0	4.3		27.8		16	194	4.11
10008	2075	7325	9.60	99	2470	32	0.55	1250	497	13.6	55.1	1.330	13.8	740	35.7	31.8	1.4	211.0	1.800	7.6	10.2	5.8		33.0		28	279	4.62
10009	2125	7325	7.02	98	1700	12	0.57	1030	1390	17.0	62.1	0.990	12.8	790	39.2	36.6		371.0	2.070	7.0	12.4	14.5		42.6		64	597	
10010	2125	7375	16.00	116	2472	26	0.62	1603	4426	24.0	73.0	1.655	16.0	745	43.0	34.0	0.4	156.0	0.904	5.0	13.0	12.0		47.0		45	460	
10011	2075	7375	29.00	169	4490	44	0.96	2980	1740	28.3	94.2	2.560	20.4	991	53.5	40.0		145.0	2.230	5.8	15.6	10.2	0.4	46.6		28	386	
10012	2025	7375	19.90	149	3590	36	0.93	2270	1190	24.7	85.2	2.190	20.0	982	46.2	41.0	1.8	181.0	2.280	6.8	13.6	16.1		43.2		44	312	
10013	2025	7425	13.90	151	3370	32	0.81	1920	7750	26.4	103.0	1.750	16.2	844	43.2	34.2	2.2	259.0	2.190	7.4	15.8	29.5		62.0		55	410	
10014	2075	7425	4.74	67	1090		0.44	648	678	10.2	48.7	0.723	8.6	498	34.3	31.8	1.0	258.0	2.170	5.2	11.6	16.1		57.0		38	657	
10015	1875	7375	5.16	67	1670	16	0.49	768	361	9.3	50.1	0.908	10.6	602	27.3	25.2	1.2	99.6	1.460	5.0	8.2	15.1		29.4		300	311	
10016	1925	7375	7.44	85	1580	16	0.36	828	922	12.3	46.3	1.020	12.6	873	27.5	39.4		268.0	1.380	6.2	6.8	2.8		22.8		11	246	4.92
10017	1925	7425	13.60	103	2790	28	0.60	1550	572	15.5	65.4	1.770	15.2	881	37.4	36.8		119.0	1.760	4.8	8.8	9.5		27.4		17	203	
10018	2025	7175	3.54	48	764		0.16	368	70.8	4.9	17.6	0.478	4.8	426	17.4	12.6	0.6	34.8	0.466	1.2	2.4	2.4		6.0		8	81.6	4.56
10019	1975	7175	21.70	109	2330	24	0.48	1590	376	15.9	62.6	1.710	13.4	850	36.5	36.0		89.7	1.340	4.2	9.0	5.0		29.8		20	210	
10020	1975	7125	16.00	182	6712	52	1.00	3240	2529	29.0	98.0	3.288	21.0	910	54.0	73.0	1.5	92.0	2.878	8.0	18.0	12.0		53.0		49	106	
10021	1925	7125	3.90	67	1660	20	0.42	756	400	9.6	65.6	0.885	11.6	602	29.8	35.8		1320.0	1.680	6.4	6.4	14.8		40.2		13	1120	
10022	1925	7175	5.10	83	1800	16	0.47	896	238	10.4	51.1	0.964	11.4	828	43.1	40.8	1.4	306.0	2.560	5.0	11.0	8.8		34.8		34	954	
10023	1875	7275	7.02	61	1390		0.66	772	218	8.9	30.3	1.000	12.0	648	35.3	31.2		273.0	2.950	10.6	7.0	3.8		16.8		11	266	
10024	1925	7225	6.18	91	1380	16	0.30	778	205	9.0	33.0	0.929	11.8	699	29.3	31.6	1.0	170.0	1.470	3.8	6.4	5.5		24.6		15	330	4.13
10025	1975	7425	13.00	100	2530	28	0.76	1470	1630	17.3	63.7	1.710	15.2	910	44.2	39.0		71.1	1.960	4.0	10.0	8.2	0.4	32.0		23	276	6.32
10026	1975	7375	19.80	123	2680	24	0.84	1720	545	16.5	68.8	1.660	17.0	841	39.4	34.4	1.4	221.0	1.840	6.8	11.6	7.2		39.2		21	173	4.22
10027	1975	7325	22.90	117	2250	28	0.76	1690	758	16.3	65.7	1.680	18.6	881	39.8	32.4	2.2	126.0	2.150	4.8	12.8	6.0		46.6		18	146	
10028	1975	7275	11.00	79	1770	16	0.44	1120	665	13.1	44.3	1.200	11.2	592	32.1	19.4		82.2	1.290	3.0	7.4	5.0		24.4		10	222	
10029	1975	7225	6.06	45	964		0.17	604	128	8.3	28.5	0.822	12.0	731	23.0	38.4	0.4	35.7	0.906	1.8	5.0	3.6		20.0		15	252	3.89
10030	1875	7325	7.00	72	2884	20	0.80	1550	567	14.0	44.0	1.323	15.0	533	37.0	26.0		74.0	2.019	7.0	17.0	6.2		31.0		14	207	
10031	1925	7325	6.54	78	1440	16	0.32	732	278	10.5	42.8	0.956	13.4	755	29.2	37.4		372.0	1.510	4.0	6.2	5.8		28.8		15	417	
10032	1925	7275	13.30	52	1070	8	0.44	898	601	10.4	34.9	0.870	9.0	511	30.4	24.8		90.0	1.300	3.4	6.8	2.7		17.2		16	165	
10033	1875	7225	30.40	293	9670	72	1.46	5770	1900	39.5	142.0	4.630	23.8	1160	72.9	37.8		200.0	3.740	12.4	25.8	14.3		58.0		23	267	
10034	1825	7325	28.70	235	7190	64	1.36	4870	2840	38.4	139.0	3.530	23.8	1170	71.5	47.2		265.0	3.010	12.6	28.0	19.7	0.8	62.6		107	514	5.63
10035	1875	7175	10.30	171	2630	28	0.80	1710	1480	21.5	75.1	1.440	15.6	685	40.7	32.4	1.8	555.0	2.280	9.6	16.0	9.5		47.6		32	602	
10036	1825	7375	23.60	357	5210	28	1.51	7300	18400	70.5	676.0	2.500	18.6	808	64.9	29.8	8.4	373.0	2.600	11.4	29.8	42.0		115.0		302	898	
10037	1825	7225	23.20	205	4660	40	1.17	2210	736	26.5	147.0	3.170	21.6	971	67.6	42.0		589.0	3.270	13.4	20.6	13.9		53.2		62	501	
10038	1825	7275	5.82	107	1720	16	0.87	924	6330	30.1	90.0	0.817	11.6	407	44.9	24.6		328.0	2.570	8.4	20.8	39.8	0.4	68.2		237	1160	5.65
10039	1725	7475	22.00	1488	3645	28	5.53	3510	24050	132.0	288.0	2.270	25.0	613	80.0	52.0	4.2	762.0	5.140	25.0	78.0	255.0	1.6	601.0	1.1	1100	2350	7.12
10040	1725	7425	11.00	263	3204	19	1.00	2671	20752	104.0	323.0	1.599	15.0	587	51.0	43.0	2.0	913.0	2.985	10.4	44.4	153.0	0.7	1128.0	3.6	1027	1735	
10041	1775	7425	23.60	451	3440	24	2.02	2730	22200	94.1	221.0	2.090	19.8	538	61.3	44.0	0.6	860.0	5.590	16.0	52.2	1420.0	0.6	614.0	1.4	338	925	
10042	1825	7425	20.10	276	5030	44	1.44	2970	3300	32.9	176.0	2.920	19.2	985	63.2	34.6	2.0	159.0	2.770	9.0	23.0	32.3		178.0		232	637	6.18
10044	1825	7475	10.90	173	2550	28	1.02	1630	5850	35.6	218.0	1.400	15.0	689	49.6	41.0	3.2	594.0	2.690	9.4	21.8	55.2	0.6	376.0	0.6	339	1800	
10045	1875	7475	15.50	143	2820	24	0.60	1570	997	18.3	69.5	1.580	15.4	846	39.7	37.6	4.0	134.0	1.460	4.2	9.2	11.8		40.4		38	375	5.36
10046	1925	7475	7.80	110	1980	16	0.72	1100	854	14.3	84.1	1.050	12.2	624	39.9	27.8		145.0	2.190	5.8	15.2	21.0		93.2		147	794	4.59
10047	1975	7475	8.34	132	1770	12	0.97	1000	2960	23.6	119.0	1.130	13.6	555	45.2	30.6		265.0	2.290	7.2	18.8	50.8	0.4	151.0		225	1200	6.15
10048	1875	7425	16.60	148	2800	24	0.85	1940	3150	25.6	73.1	1.930	16.6	829	44.9	28.2	0.6	187.0	2.000	9.4	14.2	15.0		35.6		95	460	
10049	1625	7425	17.00	205	3540	32	1.24	2210	3440	50.2	162.0	2.190	22.2	835	51.8	41.4		362.0	2.600	10.4	24.8	42.6	0.6	115.0		230	1320	
10050	1575	7425	25.00	217	3157	26	1.31	2811	5033	41.0	175.0	3.204	24.0	957	57.0	32.0	1.7	213.0	2.791	9.0	23.0	26.0	0.3	111.0		109	751	5.32
10051	1525	7425	12.40	168	3420	32	0.86	2090	2570	24.7	97.9	2.030	21.6	991	46.2	36.6	2.0	316.0	2.480	7.8	17.8	11.2		65.2		28	531	6.56
10052	1525	7375	14.30	236	3580	28	1.09	2110	4190	32.3	169.0	2.080	21.4	981	49.0	42.4	2.6	223.0	2.430	8.0	20.6	31.6	0.6	117.0		145	1160	6.55
10053	1625	7325	16.40	249	4790	32	1.20	3390	14800	53.4	191.0	2.280	19.4	698	59.1	31.6	2.0	296.0	2.850	9.6	27.0	51.8		185.0	1.0	256	1180	
10054	1675	7325	9.42	174	3040	12	1.08	2110	28100	56.2	85.7	1.400	15.0	422	68.4	29.0	1.2	341.0	4.260	10.4	31.2	28.5		117.0		145	1280	

Appendix 2.2 Data for Richmond subsurface soils

Geochemical data in μg/g unless otherwise stated

No.	East	North	Li	Na	K	Rb	Be	Mg	Ca	Sr	Ba	Al%	La	Ti	V	Cr	Mo	Mn	Fe%	Co	Ni	Cu	Ag	Zn	Cd	Pb	P	pH
10055	1575	7275	9.36	160	2850	36	1.00	1680	2910	25.2	162.0	1.560	18.8	785	44.8	32.8	2.0	361.0	2.310	8.6	21.2	37.3		94.0		225	797	6.68
10056	1525	7275	12.40	161	2610	24	0.89	1750	2300	24.2	112.0	2.010	20.6	794	35.0	35.0	0.8	268.0	2.100	10.4	16.2	87.5		62.0		74	313	6.46
10057	1525	7325	13.30	281	2690	28	2.14	1670	5330	47.9	235.0	1.650	19.6	701	48.4	45.8	0.6	487.0	2.620	10.6	28.8	71.4	1.0	234.0	0.2	329	1410	
10058	1575	7375	27.20	299	3690	28	1.56	2510	5460	37.5	127.0	2.020	16.6	642	56.2	23.8		497.0	2.930	9.8	30.8	38.1		101.0		128	864	
10059	1575	7325	10.30	160	3310	28	1.42	1760	1840	25.4	253.0	1.690	18.0	522	48.9	34.0		411.0	2.700	10.0	23.2	59.7		143.0		337	1200	5.36
10060	1625	7360	10.00	178	2758	27	1.10	1564	5360	35.0	168.0	1.465	17.0	648	49.0	31.0	1.4	519.0	2.530	9.9	23.3	40.0		162.0	0.2	270	1274	6.35
10061	1675	7375	15.10	393	3070	20	1.76	1860	30400	72.6	273.0	1.680	16.8	704	61.6	31.0	2.4	402.0	3.120	12.8	38.6	58.9		140.0		503	1190	7.85
10062	1675	7425	7.92	245	2780	24	0.91	1640	8660	33.3	95.3	1.420	18.0	723	43.5	33.0	1.2	340.0	2.570	9.0	20.6	24.1		62.8		158	487	
10063	1575	7225	6.42	193	2130	8	0.71	1280	38000	78.2	92.0	0.963	12.2	477	44.3	27.2		350.0	2.500	6.6	17.0	21.6		92.6		274	638	7.65
10064	1475	7225	11.80	165	2320	20	1.38	1420	9060	48.2	140.0	1.500	17.4	654	44.9	33.2		301.0	2.240	9.4	22.8	33.3		96.6		290	887	
10065	1425	7225	12.50	141	3070	28	0.79	1820	1240	21.4	94.4	1.940	20.0	854	37.1	35.6		455.0	1.880	10.0	12.8	9.2		36.2		34	249	5.11
10066	1425	7275	12.30	564	3190	12	1.10	2890	49000	136.0	261.0	1.700	17.2	651	45.4	28.8		442.0	2.270	9.0	28.2	80.9	2.6	257.0	3.1	225	1370	
10067	1475	7275	16.90	342	3450	24	2.55	2040	9090	62.6	336.0	2.060	20.0	660	60.2	37.4		340.0	3.250	13.4	35.2	67.6	0.6	272.0	1.1	887	1680	7.82
10068	1525	7225	11.90	170	2000	12	0.81	1540	3140	24.1	95.4	1.710	19.2	832	40.1	31.4		148.0	2.000	5.8	14.0	15.1		49.0		49	470	
10069	1425	7325	9.66	173	2150	20	0.81	1220	2180	20.5	112.0	1.300	16.2	727	36.5	37.4	2.0	341.0	1.970	6.6	15.2	25.0	0.4	78.8		131	678	6.01
10070	1475	7325	11.00	109	2213	22	0.75	1353	1608	19.0	93.0	1.438	16.0	721	40.0	36.0		425.0	2.156	7.0	15.0	24.0		58.0		70	846	5.12
10071	1425	7375	11.70	171	2110	20	0.86	1450	3860	30.7	126.0	1.740	19.0	806	38.3	35.8	1.0	174.0	1.680	5.6	15.0	23.4		107.0		147	1130	
10072	1475	7375	13.70	199	3190	24	1.48	1640	4020	39.8	190.0	1.730	19.8	752	46.4	44.4	2.6	449.0	2.500	9.8	23.6	37.3		183.0		158	1170	7.14
10073	1875	7525	9.42	232	2280	16	1.65	1320	6080	42.9	263.0	1.240	14.2	608	49.0	65.2	3.6	377.0	3.080	9.6	28.4	93.1	0.6	497.0	0.7	579	1990	6.77
10074	1925	7525	8.82	137	1870	16	0.75	1340	4580	31.5	132.0	1.140	17.6	673	43.7	40.4		246.0	2.380	5.6	14.6	40.8		130.0		234	1540	
10075	1975	7525	11.00	206	2170	20	1.33	1420	10700	49.3	168.0	1.350	19.6	581	50.2	36.4		253.0	2.680	8.4	22.6	36.4		203.0		332	1230	7.65
10076	1975	7575	15.80	308	3650	28	1.28	2980	13200	61.0	194.0	1.990	18.0	651	58.1	26.4		373.0	2.870	10.6	26.6	84.0	0.6	171.0		685	1430	
10077	1975	7625	8.82	180	2660	20	0.96	1410	6000	30.6	130.0	1.250	14.8	574	48.1	30.4	2.0	315.0	2.430	8.2	26.2	63.6	0.6	118.0		196	1260	
10078	1925	7625	8.04	159	2140	28	0.86	1140	5500	27.4	121.0	1.190	13.8	652	48.3	31.4	1.4	286.0	2.530	7.6	19.4	62.1	0.8	97.2		285	1200	6.33
10079	1925	7575	9.12	196	2530	16	1.27	1270	5700	44.2	265.0	1.230	14.4	615	47.1	42.4	3.2	393.0	2.640	9.6	25.4	143.0	0.6	346.0	0.5	370	2540	6.04
10080	1875	7575	13.00	233	2899	29	1.22	1685	6044	38.0	164.0	1.645	17.0	780	56.0	41.0	3.4	310.0	2.690	10.0	26.0	45.0	0.6	151.0	0.1	389	1364	6.62
10081	1875	7625	11.20	185	2340	12	0.89	1480	20800	126.0	136.0	1.220	13.6	612	43.0	31.0		257.0	2.140	7.0	19.0	37.2		100.0		268	1460	
10082	1925	7725	12.80	348	3040	28	2.07	1760	11500	61.3	313.0	1.760	17.2	587	56.1	40.6	3.8	496.0	3.070	12.6	33.2	71.7	0.6	433.0	0.8	492	3080	
10083	1975	7675	19.90	353	4530	32	1.65	3320	14100	65.6	214.0	2.950	19.2	726	65.0	29.2	2.0	311.0	3.130	12.2	32.4	78.8		186.0		310	1500	
10084	1925	7675	4.92	111	1600	8	0.71	852	4080	31.4	342.0	0.806	9.8	335	35.4	33.6	1.4	211.0	2.060	6.8	16.4	163.0		241.0		772	1250	6.75
10085	1375	7375	14.10	129	4120	32	0.97	2210	1980	21.8	94.1	2.110	14.0	676	47.3	33.4		157.0	2.870	6.8	16.2	14.3		76.2		56	507	6.32
10086	1375	7425	17.80	162	2460	16	0.83	1820	2640	26.6	131.0	2.060	20.8	888	44.3	36.6		213.0	3.000	7.6	15.4	16.8	0.4	80.4		58	820	
10087	1375	7325	24.00	230	5910	40	1.47	3640	3870	38.7	143.0	3.080	24.2	905	73.9	43.0		394.0	4.110	13.0	35.0	20.4		92.0		73	715	6.22
10088	1375	7275	22.80	1210	3020	20	4.61	1850	8850	107.0	346.0	2.160	22.4	551	73.4	53.6	4.2	655.0	4.780	21.8	74.2	210.0	1.0	578.0	0.6	632	1650	5.88
10089	1375	7225	11.20	142	2430	20	0.71	1510	2850	25.4	81.5	1.640	18.0	802	36.9	35.6		410.0	1.890	7.6	12.2	14.4		43.0		81	796	5.62
10090	1325	7325	12.00	212	2779	35	0.83	1614	5303	34.0	129.0	1.719	18.0	735	42.0	36.0	1.9	228.0	1.962	6.1	16.2	28.0	0.5	119.0		142	1238	5.88
10091	1325	7375	14.30	186	4730	44	0.93	2570	3020	27.2	135.0	2.540	17.4	873	50.5	38.0	1.8	151.0	2.890	6.8	17.8	28.4	1.8	83.4	0.6	58	778	6.42
10092	1325	7425	10.30	234	2960	28	0.94	1600	6870	49.7	329.0	1.550	15.2	783	35.7	38.0	2.6	252.0	1.810	7.4	19.4	49.8	0.4	529.0	0.3	201	1980	
10093	1275	7375	15.10	200	4630	28	0.83	2370	2280	28.4	116.0	2.480	21.2	945	43.7	41.6	0.6	192.0	2.210	5.8	16.2	15.0		102.0		52	575	
10094	1275	7325	10.40	187	2470	36	0.85	1570	6270	42.1	153.0	1.520	16.4	778	41.6	33.8	1.8	271.0	2.150	7.4	17.4	30.6		106.0		146	736	
10095	1325	7175	13.10	226	3450	28	1.00	2000	3430	34.3	148.0	2.190	23.2	884	45.5	37.4	2.4	299.0	2.370	10.0	18.6	28.9		155.0	0.4	149	1000	
10096	1375	7125	15.70	260	3690	32	1.61	1840	5840	56.3	236.0	2.080	21.4	691	49.1	40.0	3.2	256.0	2.920	9.8	27.6	40.4		365.0	0.4	873	1620	
10097	1325	7125	13.30	194	3640	36	0.81	1660	2580	26.2	114.0	1.940	18.0	884	38.6	39.4	2.4	160.0	1.880	5.6	15.0	21.4	0.4	79.4		91	614	
10098	1275	7125	15.10	216	3610	32	0.92	2060	5220	35.1	132.0	2.600	22.8	942	45.4	31.4	2.6	115.0	2.210	7.0	16.6	20.2		75.6		79	680	
10099	1275	7175	13.00	216	4090	48	0.69	2540	2800	31.6	89.0	2.110	18.2	949	39.2	53.4	1.2	163.0	2.010	5.0	12.4	10.7		52.6		37	735	
10100	1375	7175	12.00	182	3044	29	0.69	1620	2000	23.0	89.0	2.049	20.0	921	39.0	34.0	1.1	122.0	1.712	6.0	13.0	14.0		47.0		56	308	5.44
10101	1375	7075	13.40	202	2940	20	0.83	1680	4360	35.9	138.0	1.710	20.0	978	40.4	40.0		271.0	2.100	7.8	16.6	20.5	0.6	104.0		215	870	7.36
10102	1375	7025	24.20	389	2870	20	1.56	1880	4810	116.0	281.0	2.070	22.6	955	57.4	43.8		253.0	2.750	13.0	34.2	41.5	0.4	93.4		209	1570	
10103	1375	6975	10.50	226	2330	20	1.01	1830	17500	59.5	144.0	1.000	15.6	997	37.2	25.4	0.4	426.0	2.500	8.4	21.6	41.5	0.4	142.0		220	1730	7.16
10104	1325	6975	13.10	172	2700	24	0.99	1830	4020	40.3	122.0	1.900	21.8	845	42.9	37.8		207.0	2.180	7.6	17.6	29.8		66.2		105	651	7.11
10105	1275	6975	15.10	252	3090	20	1.24	2060	21500	74.8	176.0	1.690	17.6	997	60.8	35.8		551.0	3.710	11.6	34.2	34.2	0.6	106.0		93	939	
10106	1275	7025	12.10	196	2910	24	1.00	1640	2960	40.7	613.0	1.920	20.2	873	41.8	46.8	2.6	310.0	2.230	8.0	18.8	60.1		445.0	0.5	1130	1390	
10107	1325	7025	10.50	605	2950	16	2.37	2580	16100	85.2	247.0	1.410	15.2	498	55.0	44.0	3.0	420.0	3.090	14.0	39.8	129.0	0.6	521.0	1.5	1940	3810	

Appendix 2.2 Data for Richmond subsurface soils
Geochemical data in µg/g unless otherwise stated

No.	East	North	Li	Na	K	Rb	Be	Mg	Ca	Sr	Ba	Al%	La	Ti	V	Cr	Mo	Mn	Fe%	Co	Ni	Cu	Ag	Zn	Cd	Pb	P	pH
10108	1325	7075	14.50	188	3140	32	0.92	1780	1380	26.5	113.0	2.230	21.2	916	43.8	40.0	1.2	175.0	2.180	7.6	16.6	13.8		53.4		94	492	
10109	1275	7075	19.70	247	4230	24	1.12	2560	7690	71.9	167.0	2.310	20.4	918	57.3	41.2		258.0	2.720	8.8	24.4	23.4		81.6		197	869	
10110	1225	7025	15.00	418	2610	16	2.00	1976	10168	90.0	237.0	1.891	22.0	742	48.0	40.0	2.6	290.0	2.243	13.0	32.0	52.0		136.0		150	959	
10112	2025	7525	9.72	175	2370	20	0.91	1460	10500	43.0	205.0	1.450	16.4	672	48.8	42.6	0.8	261.0	2.440	8.4	18.2	28.4		168.0		461	685	7.62
10113	2025	7475	6.84	115	1460	12	0.92	880	2630	20.6	96.2	0.916	11.8	523	39.3	29.6		289.0	2.120	6.6	16.4	36.1	0.4	101.0		286	958	
10114	2075	7475	7.86	105	1570	12	0.76	892	2310	19.3	89.3	1.000	13.8	564	48.0	34.6		313.0	2.510	5.6	16.4	48.9		69.0		164	1130	
10115	2075	7525	11.30	147	1960	24	0.78	1350	1990	18.3	84.1	1.390	15.0	743	43.7	32.4	2.6	165.0	2.180	6.2	15.8	27.4	0.8	82.0		147	468	
10116	2125	7525	15.70	326	3210	20	1.43	2810	8900	62.6	290.0	1.640	15.6	580	53.4	39.4	3.4	366.0	2.860	12.2	36.2	83.7	2.6	345.0	0.9	503	1670	6.87
10117	2175	7575	13.10	326	3510	28	1.42	2580	13700	57.7	216.0	1.890	18.0	787	56.8	25.6	1.8	280.0	2.690	11.6	31.0	55.5		180.0		433	1120	6.45
10118	2225	7575	4.38	77	978		0.26	576	612	10.9	42.5	0.740	10.2	721	26.3	35.6	1.2	44.4	0.942	2.6	6.4	15.9		19.0		87	375	
10119	1625	6825	5.64	97	2030	24	0.63	1080	787	12.4	51.8	1.030	12.8	630	40.4	26.8	1.6	329.0	2.430	6.8	15.0	7.8		43.6		33	628	
10120	1625	6775	8.00	71	2305	18	0.82	1454	1117	14.0	56.0	1.206	16.0	554	55.0	33.0		282.0	3.310	8.2	21.8	7.8		40.2		1420	607	
10121	1675	6725	7.80	133	1520		0.59	1420	78400	86.3	64.9	1.170	10.4	466	29.1	17.0		468.0	1.860	5.8	13.4	7.0		39.4		22	566	
10122	1675	6775	8.58	77	1870	16	0.76	1370	936	13.0	61.7	1.460	13.4	606	47.0	27.8	1.8	350.0	2.850	6.8	18.2	6.9		55.8		23	504	
10123	1725	6775	51.70	453	13200	92	2.03	10600	21500	78.1	193.0	5.850	31.4	1050	101.0	32.6	1.4	321.0	4.370	16.8	45.8	25.8		89.6		40	706	
10124	1725	6825	7.32	64	1480	16	0.68	1000	920	14.2	70.7	1.070	12.8	561	43.2	26.8	2.8	572.0	2.540	7.2	14.6	8.0		48.2		20	680	5
10125	1675	6825	8.46	107	2900	36	1.08	1650	844	15.3	75.3	1.500	16.8	615	66.6	38.8	2.0	627.0	4.090	11.2	28.8	11.7		70.6		40	864	
10126	1575	6825	7.44	133	2680	16	0.85	1550	13500	27.0	65.7	1.280	16.0	660	54.8	34.0	0.4	411.0	3.330	9.0	24.2	9.3		46.8		83	611	6.23
10127	1575	6875	7.20	86	2410	24	0.76	1380	629	14.9	55.8	1.250	16.0	704	50.3	33.6	0.6	311.0	2.940	8.2	19.4	10.0		45.0		44	537	4.73
10128	1575	6925	9.96	136	2100	24	0.62	1410	46300	61.4	107.0	1.260	14.8	707	38.1	33.2	1.8	189.0	2.070	6.2	15.2	16.5	0.6	72.8		61	492	
10129	1575	6975	6.48	106	2070	20	0.44	1130	626	12.5	51.6	1.070	14.8	860	33.6	38.0	1.8	211.0	1.890	4.8	11.6	9.0		34.8		29	542	4.59
10130	1575	7025	9.00	123	2599	23	0.60	1419	1561	17.0	74.0	1.329	18.0	856	39.0	40.0	0.9	463.0	2.144	7.2	14.0	15.0		44.0		26	514	
10131	1625	7025	8.46	110	2350		0.88	1460	14600	35.1	84.9	1.160	17.6	561	48.2	28.4	3.8	333.0	2.850	9.0	23.2	27.1		58.6		47	592	7.13
10132	1625	6975	7.20	92	1980	24	0.45	1160	365	12.6	49.3	1.220	15.8	854	37.6	37.2	0.4	156.0	1.900	4.4	10.8	5.0		27.0		23	509	
10133	1625	6925	6.42	87	1990	28	0.58	1130	337	12.7	57.5	1.160	17.0	825	39.1	41.2	1.4	286.0	2.270	7.4	12.4	6.7		33.2		24	533	3.92
10134	1675	6925	5.10	71	1500	16	0.47	876	1720	12.7	46.8	0.918	13.2	629	35.6	31.4	0.6	233.0	2.050	6.0	11.6	5.6		32.6		22	387	
10135	1725	6925	4.26	70	1560	16	0.64	912	757	11.1	52.6	0.785	11.0	494	44.0	33.4	2.0	411.0	2.430	6.8	15.8	11.2		48.2		42	654	
10136	1675	6975	7.20	134	1790	20	0.58	1160	1500	15.4	54.4	1.260	13.4	726	34.5	27.0	1.4	66.3	1.810	4.2	11.8	5.6		31.4		20	317	6.23
10137	1675	7025	3.30	81	1240	12	0.46	638	1100	12.2	82.2	0.588	9.2	454	34.9	28.8	1.6	149.0	2.080	4.6	13.0	9.8		51.4		59	374	6.5
10138	1525	7025	4.20	90	1870	28	0.47	926	326	10.1	61.5	0.907	11.6	593	26.6	25.8	1.8	348.0	1.530	5.2	8.8	8.3		31.4		20	862	4.85
10139	1475	7075	9.30	121	2900	32	0.60	1550	604	16.0	77.3	1.580	19.6	921	37.7	32.8	1.0	437.0	1.920	7.0	11.6	8.5		41.0		22	614	
10140	1425	7075	10.00	165	2455	20	0.66	1427	6379	27.0	87.0	1.626	20.0	881	37.0	37.0	1.4	242.0	1.786	6.5	13.0	15.0		44.0		56	555	6.88
10141	1475	7025	7.80	141	2300	24	0.64	1430	1870	18.0	80.2	1.350	16.6	820	32.9	34.2	0.8	425.0	1.820	6.4	13.0	8.9		40.8		40	563	6.12
10142	1525	6975	5.04	90	1440		0.52	842	1920	14.6	102.0	0.857	11.8	575	39.0	26.0		124.0	2.160	4.0	12.4	14.6		48.8		115	1070	
10143	1475	6975	8.22	151	2730	40	0.68	1520	8000	25.0	86.6	1.340	20.2	726	36.9	34.8	1.4	519.0	1.900	7.4	14.6	16.6		97.4		37	630	
10144	1425	7025	12.70	152	2730	20	0.78	1810	1800	21.2	96.5	1.970	20.6	898	36.7	36.4		99.9	1.970	5.2	14.6	7.2		34.2		20	359	
10145	1475	6925	6.78	100	2730	36	0.87	1560	1350	15.8	79.8	1.320	18.8	695	51.8	43.8	1.6	603.0	3.100	9.4	21.2	28.1		64.2		73	862	5.66
10146	1525	6925	6.18	86	1950	16	0.70	1060	344	11.3	58.7	1.040	15.8	760	47.0	40.6	1.6	421.0	2.940	7.4	16.6	6.5		42.0		27	754	5.12
10147	1625	6875	6.48	93	2660	36	0.76	1430	2260	16.1	66.1	1.200	16.2	705	45.3	35.0	1.4	391.0	2.560	8.0	18.4	16.0		48.0		56	687	
10148	1675	6875	9.96	139	3840	40	0.85	1950	1430	17.8	83.5	1.870	20.0	785	44.7	29.4	1.2	383.0	2.430	9.0	19.2	10.6		53.2		39	483	
10149	1725	6875	14.00	186	4140	40	0.74	2360	959	20.5	92.7	2.410	19.0	835	58.0	31.8	1.8	69.3	2.250	5.4	16.0	18.3		57.4		48	599	
10150	1525	7175	9.00	150	2441	29	0.80	1494	1732	20.0	102.0	1.480	19.0	783	41.0	39.0	2.3	332.0	2.070	7.6	16.0	34.0	0.3	74.0		115	729	
10151	1475	7175	11.90	206	2580	24	0.87	1830	4940	36.0	182.0	1.650	19.2	821	39.9	32.6		277.0	2.130	6.8	17.0	38.5	0.4	206.0		163	841	
10152	1525	7125	11.40	192	2630	20	1.02	1870	16000	113.0	185.0	1.490	18.6	710	43.7	36.8		521.0	2.340	8.6	22.6	42.6		171.0		245	1450	
10153	1575	7125	14.60	183	2640	32	1.31	1790	5210	39.0	278.0	1.790	20.4	814	49.7	40.2		297.0	2.560	8.6	24.2	43.0	1.4	508.0	0.3	414	940	
10154	1625	7125	8.46	141	2670	24	0.88	1410	5110	27.4	143.0	1.260	17.4	736	42.3	41.0		378.0	2.430	7.2	17.4	20.7	0.4	157.0		166	894	7.35
10155	1625	7175	17.40	173	3280	28	1.08	2160	11600	40.3	117.0	2.120	22.4	786	49.2	38.8		391.0	2.290	8.2	22.6	27.7	0.6	68.8		75	650	7.56
10156	1675	7125	27.10	335	3580	40	1.48	2490	5390	34.8	117.0	2.000	17.4	712	51.7	24.6	5.0	469.0	2.770	9.8	30.4	37.9	0.8	106.0	0.3	135	778	
10157	1725	7075	9.54	200	2340	20	1.70	1400	4020	37.6	253.0	1.340	15.8	436	51.1	40.2	0.4	403.0	3.130	10.0	28.4	99.7	0.6	252.0	0.4	276	1130	
10158	1675	7075	8.52	194	2750	16	1.04	1530	13700	52.0	233.0	1.290	14.0	573	43.0	36.2	1.4	352.0	2.480	8.2	22.8	47.9		265.0		208	1060	
10159	1575	7075	10.40	132	2460	20	0.94	1560	3690	25.9	105.0	1.600	19.4	720	44.0	34.8	1.4	260.0	2.270	7.4	16.8	36.4		80.4		153	714	
10160	1625	7075	6.00	99	2125	22	0.70	1066	1630	15.0	88.0	0.979	14.0	616	37.0	31.0	1.8	366.0	2.107	7.0	16.0	22.0		82.0		103	889	
10161	1475	7125	9.30	192	2560	20	1.19	1560	6250	39.3	214.0	1.430	16.0	689	49.0	37.6	2.4	401.0	3.020	10.0	24.0	33.6		236.0		336	842	7.42

Appendix 2.2 Data for Richmond subsurface soils

Geochemical data in μg/g unless otherwise stated

No.	East	North	Li	Na	K	Rb	Be	Mg	Ca	Sr	Ba	Al%	La	Ti	V	Cr	Mo	Mn	Fe%	Co	Ni	Cu	Ag	Zn	Cd	Pb	P	pH
10162	1525	7075	9.54	166	2490	24	0.99	1500	1620	21.1	144.0	1.560	19.2	862	42.8	37.6	1.6	259.0	2.300	7.2	18.4	31.5		150.0		180	1070	5.59
10163	1425	7125	7.68	237	2280	16	0.95	1210	14400	58.9	150.0	1.090	14.0	512	45.6	26.0	1.2	281.0	2.690	8.6	22.0	22.4		346.0		298	714	
10164	1425	6975	9.54	716	2490	24	0.94	1500	2540	26.1	113.0	1.430	16.6	740	43.2	38.2	2.2	474.0	2.240	8.2	20.0	25.3		86.6		157	1240	
10165	1575	7175	13.00	238	3320	24	1.05	1920	11700	45.2	219.0	1.630	16.2	671	45.8	36.4	2.4	342.0	2.460	8.6	24.2	53.5		241.0	0.4	294	750	7.13
10166	2025	7675	10.60	142	3040	28	1.13	1580	6420	33.5	192.0	1.570	23.4	719	55.5	39.2		466.0	2.840	9.4	23.0	37.0	0.8	89.8		212	1460	7.53
10167	2025	7575	9.60	193	2570	16	1.22	1330	6540	40.0	188.0	1.380	16.4	577	59.6	39.2	2.2	370.0	3.250	9.8	27.8	58.8	0.4	160.0		336	1210	6.56
10168	2075	7575	14.00	446	3260	20	1.99	2040	12000	76.9	278.0	1.640	18.8	640	69.8	31.0	0.6	420.0	3.120	13.8	40.6	109.0	0.6	187.0	0.4	468	2040	
10169	2125	7575	11.70	131	3050	28	0.95	1840	1950	19.1	88.3	1.730	16.0	613	51.7	29.6	1.8	414.0	2.550	9.6	21.0	18.3		61.0		64	580	5.87
10170	1825	7725	9.00	156	2639	20	1.00	1500	12779	38.0	138.0	1.360	15.0	608	60.0	40.0	1.4	457.0	3.381	9.0	26.0	41.0		81.0		432	1233	6.59
10171	1775	7625	6.36	100	2810	28	0.64	1370	294	11.8	59.2	1.250	15.0	781	46.0	49.2	1.4	348.0	2.460	6.8	15.4	14.0		42.6		42	505	4.26
10172	1825	7625	2.88	53	1200	16	0.37	538	210	7.1	30.8	0.568	8.2	513	33.1	27.8	1.2	156.0	1.920	3.6	10.6	6.2		24.8		50	426	4.44
10173	1825	7675	18.70	219	6010	52	1.30	3460	2340	29.2	124.0	3.170	20.2	1030	73.4	43.0	1.6	352.0	3.690	12.2	26.4	16.5		69.8		45	538	
10174	1875	7675	5.34	71	1820	8	0.70	986	589	11.3	53.6	0.924	13.2	650	45.7	32.4	1.2	280.0	2.780	7.2	18.8	11.4		44.6		155	543	5.04
10175	1875	7725	8.64	81	2500	16	0.79	1490	1800	18.4	63.4	1.290	13.2	557	46.3	27.6		264.0	2.530	8.4	18.6	14.2		54.0		45	630	
10176	1875	7775	11.60	188	3010	24	1.32	1780	7280	36.3	144.0	1.660	16.8	665	67.2	33.4	2.6	536.0	3.780	11.6	32.0	35.6		141.0		239	1010	7.23
10177	1775	7525	8.22	142	2460	28	0.83	1590	11200	33.1	111.0	1.230	18.8	618	50.8	38.0	1.2	404.0	2.920	8.0	21.8	29.6		99.0		113	989	
10178	1725	7525	9.18	124	2730	20	0.98	1720	3760	24.9	88.2	1.520	14.6	598	57.7	60.6	2.8	666.0	3.720	10.2	27.8	13.3		66.8		61	707	
10179	1725	7575	14.30	162	3220	32	1.14	2130	6080	37.1	152.0	2.090	20.6	754	57.5	36.4		497.0	3.050	10.8	23.4	27.2		82.6		190	733	
10180	1775	7575	19.00	199	6550	53	1.24	3640	2862	25.0	112.0	3.114	21.0	916	71.0	41.0	1.3	245.0	3.332	11.0	28.0	19.0	0.4	69.0		55	558	
10181	1825	7575	4.80	57	1500	8	0.59	762	445	10.1	51.3	0.729	10.2	530	41.5	28.6		168.0	2.430	5.2	15.2	14.6		36.4		120	673	
10182	1625	7225	17.40	148	3570	28	0.98	2200	3990	32.8	127.0	1.860	17.4	839	50.3	45.2		241.0	2.260	8.4	19.8	37.6		78.6		141	694	6.22
10183	1625	7275	22.00	251	3740	28	1.37	3320	26100	63.1	155.0	2.780	21.4	651	61.4	34.0		1000.0	3.670	12.8	34.4	29.4	0.4	115.0		87	885	7.45
10184	1675	7275	5.82	70	1970	16	0.68	898	2160	15.4	72.6	0.924	11.8	538	41.6	30.8		375.0	2.330	6.2	16.2	33.8		59.2		74	982	
10185	1675	7225	14.40	213	4060	28	1.27	2290	10500	41.4	181.0	2.080	20.0	725	58.6	44.6		472.0	2.980	11.0	29.0	42.6		107.0		122	666	7.34
10186	1725	7225	11.50	135	3430	32	0.96	1700	1740	20.8	114.0	1.750	17.4	732	48.3	32.8	5.2	511.0	2.380	9.4	18.2	36.7		68.2		72	1060	
10187	1775	7225	12.70	198	3250	24	1.33	1530	9110	40.4	186.0	1.700	17.6	619	60.3	38.0		544.0	3.040	10.2	26.2	35.2		128.0		309	1360	
10188	1775	7275	7.02	140	2450	28	0.88	1180	3420	36.3	108.0	1.150	13.6	550	42.5	23.2	1.8	316.0	2.150	8.2	19.6	26.4		75.0		83	960	
10189	1725	7275	9.48	181	3630	32	1.25	1750	14300	53.7	158.0	1.550	18.6	698	55.7	38.0	2.0	498.0	2.930	9.8	27.6	44.4	0.4	335.0		340	2750	
10190	1725	7325	16.00	270	3931	35	1.11	2542	31295	77.0	259.0	2.279	19.0	712	51.0	45.0	1.2	478.0	2.928	10.0	36.0	32.0	0.9	160.0	0.9	105	1358	7.44
10191	1775	7325	9.12	155	2790	24	0.72	1940	2100	20.3	77.4	1.380	14.6	742	43.0	27.6		443.0	2.310	7.6	15.0	15.3		53.0		66	789	
10192	2275	7775	14.70	290	3420	20	1.72	1940	5340	39.7	234.0	1.930	20.8	817	75.9	39.2	1.4	402.0	2.960	12.6	34.8	69.9		133.0		308	1090	7.23
10193	2225	7775	8.94	212	2230	16	1.16	1310	9470	46.3	171.0	1.160	13.2	549	56.9	29.2	2.4	381.0	2.840	9.0	24.8	248.0	1.0	129.0		360	1690	
10194	2175	7725	9.30	133	2190	16	1.14	1460	8690	26.1	119.0	1.430	15.4	519	69.6	30.8	2.2	398.0	3.980	10.2	30.0	46.9		84.8		132	1070	
10195	2175	7675	14.90	310	4480	28	1.33	2800	15800	52.5	207.0	2.120	18.2	691	69.0	31.8	3.2	335.0	3.290	11.0	32.8	56.9		225.0	0.5	299	1780	
10196	2225	7675	12.20	238	3400	32	1.18	1880	13400	50.0	173.0	1.800	17.6	684	55.4	33.6	1.4	404.0	2.780	10.6	24.0	89.0	1.0	140.0		486	1810	7.12
10197	2225	7725	10.40	163	3490	24	1.13	1800	9070	33.4	155.0	1.650	18.0	730	55.6	39.2	1.6	447.0	2.630	9.8	24.0	59.1	0.6	102.0		231	1230	7.63
10198	1825	7525	9.24	125	1960	20	1.10	1230	3620	32.5	363.0	1.270	16.0	583	56.9	41.0		383.0	2.900	8.6	21.4	41.0	0.4	219.0		854	1470	
10199	2275	7675	3.42	60	1770	12	0.66	898	10800	24.8	50.1	0.711	11.4	465	43.3	29.4	0.8	376.0	2.660	6.8	20.2	24.3		65.0		28	696	6.55
10200	2275	7725	9.00	177	2876	20	1.05	1608	10144	43.0	144.0	1.399	15.0	673	51.0	32.0	2.0	355.0	2.710	9.0	26.0	45.0		101.0		205	781	
10201	1425	7425	11.70	148	3420	28	0.88	1790	863	18.5	111.0	1.940	20.2	849	45.3	35.2	1.4	325.0	2.360	8.0	16.0	13.4		49.0		59	728	5.12
10202	1475	7425	8.76	144	2480	24	0.88	1500	2320	19.3	116.0	1.430	17.8	713	47.0	39.2	1.4	446.0	2.350	8.8	18.8	40.1		75.2		116	649	
10203	1725	7375	7.98	129	2690	32	0.89	1510	952	15.8	99.8	1.500	18.8	726	47.6	36.0	2.4	382.0	2.530	9.4	18.2	20.5		59.8		70	692	4.69
10204	1775	7375	27.20	291	4340	44	1.65	4060	48100	91.1	246.0	3.890	30.2	762	62.4	28.4		1820.0	4.300	18.6	43.4	21.1		93.6		44	678	
10205	1775	7175	8.28	107	2490	20	0.71	1180	208	12.8	65.2	1.450	13.4	610	48.8	34.4	1.0	510.0	2.720	9.0	14.8	14.6		43.0	0.5	54	694	4.56
10206	1725	7175	8.10	140	2780	28	1.00	1430	5580	34.8	252.0	1.460	18.8	668	50.2	37.6	2.8	449.0	2.690	10.2	21.4	47.5		215.0	0.2	196	940	
10207	1875	7125	27.10	230	4900	48	1.48	2890	4290	39.0	156.0	3.290	24.2	837	68.0	38.6		223.0	2.950	9.4	26.2	31.2	0.4	96.6		165	703	
10208	1825	7175	7.38	112	2710	20	0.98	1360	179	11.5	52.2	1.380	16.8	594	70.0	38.8	2.8	188.0	4.340	8.2	26.8	10.4		44.2		27	768	
10209	1725	6975	8.88	219	3010	20	1.03	1960	12400	82.9	194.0	1.430	15.0	604	51.2	30.6	2.4	389.0	2.860	8.6	24.2	56.3		224.0		410	1220	
10210	1725	7025	7.00	103	2379	19	0.80	1325	997	15.0	98.0	1.331	16.0	658	44.0	35.0	1.0	543.0	2.416	8.0	18.0	26.0		62.0		103	508	
10211	1775	7025	7.02	99	1780	12	0.82	1140	10100	39.0	108.0	0.945	12.4	464	47.1	28.0		326.0	2.830	7.6	21.8	20.4		153.0		208	711	
10212	1775	7075	12.10	634	2460	8	2.87	1710	18800	93.6	456.0	1.460	18.0	411	72.7	44.0	4.6	472.0	4.850	16.8	57.8	246.0	0.4	1020.0	1.4	707	1430	
10213	1425	7175	5.70	104	2020	24	0.78	1160	4070	24.5	89.4	1.040	13.8	561	39.8	23.8	0.8	349.0	2.280	7.2	18.0	20.0		76.0		99	755	
10215	2225	7625	33.80	1800	5940	24	3.14	3880	26100	158.0	294.0	3.380	24.8	579	83.2	79.4	2.4	1300.0	5.960	24.0	97.0	427.0	2.1	1910.0	3.4	1250	2910	

Appendix 2.2 Data for Richmond subsurface soils
Geochemical data in μg/g unless otherwise stated

No.	East	North	Li	Na	K	Rb	Be	Mg	Ca	Sr	Ba	Al%	La	Ti	V	Cr	Mo	Mn	Fe%	Co	Ni	Cu	Ag	Zn	Cd	Pb	P	pH
10216	1325	6925	32.90	2720	4310	12	6.13	2240	23200	251.0	271.0	2.890	23.0	592	95.2	90.0	10.4	763.0	5.770	36.4	117.0	1520.0	4.2	2650.0	4.0	5290	3340	7.89

Appendix 2.3 Data for Wolverhampton topsoils
Geochemical data in µg/g unless otherwise stated

No.	East	North	Li	Na	K	Rb	Be	Mg	Ca	Sr	Ba	Al%	La	Ti	V	Cr	Mo	Mn	Fe%	Co	Ni	Cu	Ag	Zn	Cd	Pb	P	pH
990004	39375	30325	24.80	244	5770	44	1.30	3920	2420	31.0	145.0	2.530	20.2	542	44.5	24.4		283.0	1.690	7.5	18.2	35.1		113.0	0.4	47	634	5.90
990008	39024	30075	37.30	289	5010	36	1.52	4130	6530	44.1	248.0	3.500	23.8	700	54.9	36.2		247.0	2.050	7.7	21.0	28.8		171.0	0.7	70	784	6.40
990010	39417	30176	22.00	226	5520	40	1.12	4020	1420	26.7	133.0	2.380	17.8	513	35.7	24.0		278.0	1.610	6.6	17.4	23.1		101.0	0.2	41	517	
990011	39374	30121	20.10	217	4640	36	1.44	3050	2900	32.9	128.0	2.180	17.2	480	35.8	22.0		319.0	1.650	7.4	21.0	39.6		169.0	0.6	71	803	5.75
990017	39277	30374	23.30	221	6450	44	1.11	5280	3460	25.6	134.0	2.440	18.4	525	36.9	22.8		352.0	1.790	7.3	18.2	19.6		80.8		28	644	6.89
990018	39275	30325	16.90	149	4400	32	1.13	2740	1390	23.0	111.0	1.950	16.8	467	31.7	21.6		418.0	1.670	6	15.4	28.7		96.6	0.3	38	705	5.43
990019	39125	30375	9.84	149	2690	16	0.84	1840	1980	25.1	88.1	1.230	10.8	352	25.1	14.2		224.0	1.100	4.4	14.6	24.0		86.8		46	486	5.77
990025	39176	30075	33.10	422	7200	44	2.17	5530	4030	54.0	215.0	2.960	20.4	548	54.8	41.2	1.0	453.0	3.440	13.3	41.0	90.6		290.0	1.3	225	737	5.92
990029	39275	30225	19.60	254	6630	44	1.47	2360	2440	36.7	122.0	2.720	20.6	476	49.7	18.2		505.0	2.540	10.6	19.0	90.6		103.0		44	415	6.10
990034	39325	30275	23.00	237	5810	44	1.17	3830	1330	28.0	142.0	2.340	17.8	516	36.0	20.6		386.0	1.770	7.5	19.0	29.8		130.0	0.3	53	587	
990038	39377	30233	21.40	474	4800	36	2.09	3760	7610	61.8	256.0	2.240	18.2	671	39.8	22.8		482.0	2.010	11.1	30.6	59.6		357.0	1.0	151	2110	6.60
990040	39025	30325	19.80	212	4700	32	1.05	3040	2050	32.3	146.0	2.250	19.6	503	34.3	20.6		171.0	1.560	5.7	17.2	31.6		150.0	0.4	43	644	5.82
990042	39225	30285	19.40	217	5580	44	1.32	3340	1670	28.7	140.0	2.190	20.2	570	36.4	22.0		329.0	1.560	6.9	18.0	32.3		138.0	0.6	66	685	5.34
990043	39024	30270	20.30	205	4330	40	1.37	1890	3280	30.7	131.0	1.950	16.4	400	35.9	20.2		613.0	1.570	7.7	18.8	21.9		229.0	1.1	169	630	6.63
990045	39175	30325	25.80	302	6410	40	1.58	5630	5370	46.6	264.0	2.640	18.0	542	43.1	21.8		425.0	1.990	8.9	25.4	42.6		132.0	0.2	69	634	6.58
990046	39125	30325	20.90	253	5240	44	1.37	3000	4330	47.1	229.0	2.200	19.2	550	35.3	28.0		223.0	1.380	6.1	17.2	25.1		173.0	0.6	63	1160	6.34
990048	39325	30225	21.10	370	5070	40	1.99	3050	8180	71.8	311.0	2.200	19.0	577	41.2	31.6		438.0	2.050	10.9	28.0	84.1		369.0	1.4	183	1230	
990051	39325	30175	31.70	456	7950	52	2.16	6560	9300	80.2	213.0	3.090	23.4	603	52.6	25.2		689.0	2.860	12.5	33.6	45.1		120.0	0.4	56	570	7.45
990053	39324	30127	20.10	236	5030	36	1.27	3070	1710	29.0	146.0	2.360	18.2	506	36.2	27.2		284.0	1.610	7	21.0	52.6		162.0	0.4	70	838	5.08
990054	39225	30325	27.40	271	6120	44	1.45	4320	1130	28.4	169.0	2.600	19.8	566	43.5	27.8		442.0	1.810	9.2	21.4	43.6		126.0	0.3	60	494	
990055	39075	30272	34.10	356	3860	28	1.80	3270	3780	49.5	191.0	2.670	18.2	616	45.4	26.6	0.6	397.0	2.110	11.5	31.2	38.9		170.0	0.5	59	1020	5.73
990056	39175	30375	15.80	177	3760	36	0.90	2750	1330	21.7	121.0	1.790	14.8	427	28.9	15.0		255.0	1.520	6.1	15.0	27.4		181.0	0.3	74	728	5.15
990057	39075	30325	14.80	189	3540	24	1.02	2760	4510	39.8	120.0	1.720	14.0	492	30.4	21.0		424.0	1.300	4.7	13.0	19.1		129.0	0.3	68	732	5.82
990058	39233	30225	23.30	363	5250	36	2.02	3710	4890	51.0	173.0	2.420	19.8	597	45.2	24.0		511.0	2.250	10.3	31.2	48.7		204.0	0.6	108	1270	6.00
990059	39126	30076	27.70	295	5280	32	2.03	3970	5950	49.2	195.0	2.560	19.6	548	45.6	25.4		663.0	2.250	11.3	30.8	56.6		432.0	1.9	130	1260	6.44
990063	39275	30127	18.50	226	4490	32	1.40	2980	3610	33.3	148.0	2.070	16.0	478	35.7	24.2		393.0	1.510	7	19.4	48.2		158.0	0.4	78	620	
990064	39075	30075	16.50	241	4690	36	1.66	2380	4030	54.8	172.0	1.850	17.0	466	34.6	22.2		485.0	1.860	11.2	24.2	73.1		287.0	0.9	152	1270	6.52
990065	39325	30324	15.30	171	3660	32	0.87	3000	2150	21.2	97.0	1.700	14.6	460	31.8	22.2		594.0	1.370	5.7	12.6	25.6		108.0	0.3	64	884	6.00
990067	39375	30275	25.30	253	5990	44	1.15	3930	3580	32.7	135.0	2.510	18.6	532	41.0	24.8		327.0	1.860	7.1	18.2	26.1		117.0	0.4	38	887	6.48
990068	39428	30125	24.10	242	4690	36	1.55	3340	1770	32.7	149.0	2.490	19.4	597	43.5	26.2	0.6	248.0	1.790	8.7	23.8	51.6		181.0	0.7	83	804	4.97
990069	39375	30375	13.30	131	3790	32	0.70	2490	1360	17.2	92.8	1.610	14.2	364	26.6	12.8		445.0	1.210	5	10.4	18.9		66.8	0.2	37	781	6.00
990074	39274	30171	18.50	226	4070	32	1.20	1860	1650	34.6	129.0	1.960	18.6	455	34.0	19.6		299.0	1.570	7.4	18.6	35.8		118.0	0.3	63	690	5.14
990077	39024	30226	22.50	261	4540	32	1.08	3270	10800	38.3	219.0	2.100	17.2	422	33.7	70.2		346.0	1.860	7.4	39.0	118.0	0.8	852.0	6.0	104	1720	6.65
990080	39224	30375	25.40	260	6110	36	1.15	4830	4440	34.1	192.0	2.590	17.6	484	39.4	22.2		411.0	1.880	7.4	19.0	24.4		72.0		27	514	6.65
990083	39275	30275	11.60	179	4630	32	0.81	1960	4060	29.0	87.0	1.440	14.8	334	25.5	12.2		447.0	1.400	4.1	10.8	36.7		125.0	0.3	35	1820	6.90
990084	39025	30375	19.50	194	4980	44	0.97	3420	1300	25.6	131.0	1.960	17.2	486	35.9	26.4		303.0	1.410	5.8	15.8	25.9		157.0	0.6	49	672	
990086	39224	30078	25.70	337	4650	32	2.82	3440	6070	55.7	385.0	2.270	19.4	495	49.3	40.6	0.4	484.0	2.320	12.7	47.0	99.4		723.0	1.3	256	1290	6.72
990087	39227	30175	19.00	239	4860	28	1.23	3120	3110	32.2	141.0	2.150	17.0	518	34.8	23.4		445.0	1.630	6.2	17.2	44.9		143.0	0.4	56	732	6.00
990092	39226	30123	27.20	357	5630	40	2.10	4030	5810	59.2	322.0	2.490	20.4	561	44.6	32.2		465.0	2.260	11	32.8	106.0		470.0	2.0	216	1240	
990095	39075	30375	16.10	184	4110	32	1.28	2370	3730	29.0	159.0	1.820	15.8	401	34.0	41.4		216.0	1.370	6.6	22.2	99.4		1050.0	2.1	137	1280	6.50
990099	39325	30375	14.40	157	3330	32	0.86	1830	814	18.2	88.2	1.600	15.2	473	31.0	20.8		540.0	1.380	5.4	11.0	35.5		87.4	0.1	56	562	4.76
990100	39027	30174	41.90	292	5790	36	2.09	4580	5360	46.9	291.0	3.300	23.8	548	53.1	35.0		369.0	2.310	9.7	30.8	52.7		253.0	0.7	94	1150	5.86
990101	39427	30227	23.00	235	4930	40	1.51	3480	4110	30.4	147.0	2.440	19.4	481	61.0	34.8		497.0	1.470	7.1	19.4	36.1		200.0	0.7	96	926	5.83
990107	38827	30122	18.40	299	4280	32	0.94	2620	3580	32.2	109.0	1.970	18.6	412	30.5	16.4		332.0	1.260	4.8	12.6	17.1		92.0	0.6	48	1190	
990111	39380	30177	24.10	402	3620	28	2.51	4190	6880	58.0	195.0	2.370	18.6	708	56.4	26.0		721.0	2.960	15.8	35.4	128.0		429.0	1.5	164	1980	5.91
990112	39025	30022	25.00	291	6880	44	1.40	5790	11600	50.1	197.0	2.750	20.0	489	38.8	18.4		369.0	2.000	8.2	23.8	33.0		277.0	0.3	64	700	
990113	38863	30091	11.20	215	3320	24	0.71	1700	683	16.7	75.9	1.330	12.2	422	30.0	20.4		171.0	1.210	4.4	16.6	48.0		108.0	0.3	108	773	3.74
990114	38721	30021	17.10	191	4270	40	1.09	2730	1910	26.1	111.0	1.900	16.6	455	32.1	16.4		192.0	1.310	5.9	14.8	17.4		99.2	0.3	45	682	5.63
990122	39177	30177	28.30	425	5290	40	2.88	3750	5300	76.6	499.0	2.730	23.6	627	57.7	40.6		329.0	2.370	14.2	44.4	213.0	0.4	656.0	1.7	207	1020	6.37
990123	38915	30219	18.40	251	4270	32	0.98	2760	1860	25.3	176.0	1.960	16.6	421	31.5	42.4		311.0	1.500	6.3	20.0	74.7	0.4	467.0	1.7	115	1130	
990124	38832	30077	26.00	737	3110	16	4.80	2760	18500	132.0	258.0	1.300	21.0	523	54.9	25.2	12.8	631.0	2.530	20.5	69.6	89.2		601.0	2.2	678	1080	
990126	38923	30076	16.30	255	4710	36	1.18	2500	1790	29.3	122.0	2.010	16.0	461	34.3	22.4		449.0	1.640	6.4	16.8	69.7		202.0	0.8	77	783	5.01
990127	39175	30283	20.90	265	4920	40	1.41	3200	2330	35.6	137.0	2.090	18.8	492	37.0	19.6		260.0	1.710	7.6	20.6	58.3		148.0	0.3	56	856	

Appendix 2.3 Data for Wolverhampton topsoils
Geochemical data in µg/g unless otherwise stated

No.	East	North	Li	Na	K	Rb	Be	Mg	Ca	Sr	Ba	Al%	La	Ti	V	Cr	Mo	Mn	Fe%	Co	Ni	Cu	Ag	Zn	Cd	Pb	P	pH
990128	38778	30025	20.80	353	4860	36	1.13	2520	3010	34.1	164.0	2.220	17.6	490	32.7	19.0		262.0	1.260	6	14.8	37.0		164.0	0.5	85	882	5.85
990129	39176	30425	24.40	267	5650	36	1.25	3810	4200	34.3	161.0	2.510	20.4	535	39.1	23.4		236.0	1.730	7.3	21.8	59.8		156.0	0.6	66	694	6.72
990130	38925	30175	20.50	313	5490	40	1.74	3120	3300	40.1	195.0	2.100	18.0	472	43.0	36.2		535.0	2.000	9.1	25.4	70.4		383.0	0.9	151	1870	5.74
990131	38972	30028	24.60	470	4640	24	2.59	4190	18100	118.0	255.0	2.190	21.0	538	51.2	55.4		604.0	2.990	14.5	52.0	186.0		638.0	1.6	231	1480	7.03
990132	39125	30276	19.10	215	4740	36	1.14	3090	1840	29.7	141.0	2.110	17.4	473	34.7	22.4		323.0	1.460	5.9	23.8	78.0		143.0	0.3	57	718	5.54
990133	38874	30026	19.60	244	5870	40	1.71	2850	1400	33.8	115.0	2.170	16.2	501	36.0	16.8		368.0	1.710	8.1	22.4	30.3		135.0	0.4	111	930	5.11
990135	38974	30126	21.20	349	4220	36	2.45	2810	5250	74.6	241.0	2.030	18.8	460	41.6	24.2	0.6	325.0	1.790	10.3	31.8	47.2		400.0	1.1	316	1410	6.54
990136	39124	30434	31.90	413	7420	44	1.66	4650	3250	48.7	183.0	2.890	19.4	469	43.4	15.4		320.0	2.060	10.2	30.2	27.9		170.0	0.5	42	394	
990138	39075	30125	16.90	195	3930	36	1.12	2590	499	25.1	135.0	1.730	16.2	473	36.7	21.0	0.4	145.0	1.390	6.5	20.8	50.5		87.8	0.3	95	882	
990139	38177	30177	28.60	385	5690	44	2.61	3800	4620	64.6	288.0	2.780	23.2	642	52.9	33.2		318.0	2.110	12.1	37.4	131.0		383.0	1.0	169	1250	5.88
990140	39127	30019	14.90	217	5430	32	1.11	4450	24200	71.9	135.0	1.800	16.6	456	29.2	17.8		372.0	1.710	6.5	17.2	73.7		141.0	0.7	60	438	
990141	39133	30115	23.80	925	4520	28	3.33	4430	18900	130.0	657.0	2.390	20.4	802	52.9	51.2		829.0	3.270	17.8	52.4	198.0	0.8	756.0	2.5	14900	1280	
990143	38830	30027	24.30	402	6120	40	2.50	3950	7190	64.5	278.0	2.500	19.8	603	42.5	24.8		487.0	2.080	11.8	35.2	55.9		260.0	0.7	218	1370	
990144	38923	30113	19.90	291	4580	32	1.84	3130	5690	46.0	208.0	2.060	18.0	477	37.8	23.4		432.0	1.820	8.4	25.8	66.6		353.0	1.0	201	1520	
990151	38872	30191	17.20	236	4550	40	0.99	2830	2470	32.4	136.0	1.800	17.4	497	31.1	23.8		525.0	1.520	6.3	16.2	27.6		139.0	0.3	53	954	
990154	39176	30222	25.90	351	5850	40	2.24	3810	8530	70.9	311.0	2.430	20.0	491	40.4	31.4		273.0	1.850	10	33.4	96.7		501.0	2.2	148	1800	
990155	38976	30026	16.10	202	5050	36	1.46	2440	3220	45.6	138.0	1.880	17.4	446	31.6	17.6		492.0	1.560	6.7	17.6	38.0		137.0	0.3	62	876	7.20
990156	38866	30129	8.52	134	3410	24	0.88	1530	1570	21.5	74.4	1.160	12.2	335	23.5	13.2		378.0	1.030	4.2	12.4	21.3		101.0	0.5	63	586	
990160	38924	30271	12.50	133	3580	28	0.71	1930	1840	21.7	103.0	1.360	12.6	357	22.6	23.2		158.0	1.120	4.2	14.8	35.3		367.0	0.9	46	718	6.21
990163	39075	30224	37.70	428	5430	36	2.53	4860	5330	55.8	304.0	3.360	22.0	637	53.5	45.0		523.0	2.780	14.2	41.0	128.0	0.8	763.0	1.7	235	1720	5.86
990168	39075	30176	18.10	184	4320	36	0.88	2970	882	23.4	110.0	2.060	16.0	473	33.5	19.2		111.0	1.280	4.2	13.8	22.9		58.6		52	683	4.18
990169	39016	30124	20.00	239	4440	36	1.82	3440	4370	44.9	387.0	2.020	18.6	413	37.0	128.0		403.0	2.230	14	64.4	387.0	2.0	2950.0	10.7	492	3170	
990170	39125	30175	20.40	214	4600	36	1.24	3150	1250	26.1	128.0	2.120	17.4	496	35.0	17.4		265.0	1.370	6.3	18.2	43.7		127.0	0.4	86	676	4.69
990172	38985	30230	24.30	208	4870	36	1.12	3820	6360	32.0	157.0	2.240	17.0	483	40.1	26.2		265.0	1.210	6	17.0	25.2		86.8	0.5	44	756	6.30
990175	39074	30025	23.40	455	5560	36	3.54	3100	10900	89.7	417.0	2.410	21.0	528	46.3	36.0		463.0	2.840	14.9	53.4	121.0		966.0	2.8	314	1510	7.20
990184	38916	30032	10.60	125	3780	24	1.20	1600	4440	39.2	89.5	1.490	12.0	353	22.9	15.2		301.0	1.100	5.6	13.6	32.1		137.0	0.4	81	1280	
990185	39132	30210	19.00	266	4530	32	1.70	3140	3940	40.9	154.0	2.070	17.0	499	36.7	16.8		294.0	1.550	7.7	22.6	42.9		160.0	0.5	104	695	5.90
990190	39170	30017	12.50	363	2780	12	1.36	3340	12600	113.0	243.0	1.370	11.6	564	30.2	19.8		889.0	1.990	11.5	32.4	174.0		286.0	1.6	161	856	
990195	39182	30119	30.70	504	6020	40	3.66	3890	11000	91.7	505.0	2.960	21.6	700	53.8	44.0		555.0	2.830	16.9	51.2	366.0		959.0	1.8	370	1480	
990199	38974	30274	19.70	224	4230	24	1.38	4040	8480	45.2	168.0	1.830	17.4	410	32.0	16.6		297.0	1.440	7	24.6	70.4		309.0	1.0	113	910	
990201	39325	29975	35.20	354	5040	40	2.23	4500	3780	46.6	252.0	3.680	25.0	694	54.0	27.4		344.0	2.050	11.3	31.2	77.8		261.0	0.9	113	1060	
990204	39419	29975	20.80	426	3910	12	3.32	2170	6300	85.9	226.0	1.970	19.4	462	41.9	41.8		485.0	4.120	13.4	57.2	610.0		412.0	0.9	226	653	
990205	39523	29771	50.70	859	7850	44	4.25	5430	30600	153.0	345.0	4.840	32.4	865	81.2	31.2		1730.0	2.680	19	49.4	167.0		501.0	2.1	284	2020	
990206	39520	29925	63.30	750	7790	40	3.97	3050	5990	155.0	185.0	4.560	26.8	770	117.0	40.6	2.0	802.0	5.200	31.5	72.0	174.0		470.0	2.3	133	1360	6.08
990208	39381	29931	81.50	551	10300	60	2.38	3440	6130	164.0	280.0	6.340	26.8	740	83.2	21.2		389.0	2.310	18.8	42.4	153.0		257.0	0.8	94	813	
990209	39528	30079	23.60	269	4160	36	1.52	3730	2700	32.9	155.0	2.270	18.2	612	41.4	25.2		356.0	1.860	9	23.2	66.3		227.0	0.8	114	741	
990212	39472	29981	19.40	233	4330	32	1.33	3350	5660	40.6	153.0	1.890	16.0	450	34.2	26.0		454.0	1.980	8.1	35.8	72.2		186.0	1.0	55	797	
990215	39626	30122	42.50	304	6690	44	1.42	4090	3630	34.8	198.0	3.300	19.8	672	45.7	23.8		340.0	1.750	8.8	23.8	36.3		143.0	0.4	45	628	6.18
990219	39430	30076	27.30	303	4570	36	2.58	3500	2520	41.6	172.0	2.680	21.2	710	54.3	31.8		402.0	2.180	13.1	34.6	192.0		380.0	1.2	189	1340	
990220	39675	30225	10.40	135	3320	28	0.74	1190	906	20.6	84.4	1.570	14.8	436	23.8	17.0		113.0	0.918	3	9.8	21.6		105.0	0.5	50	470	5.13
990222	39625	30275	28.00	397	6560	40	1.94	4160	7980	59.3	203.0	2.910	21.4	695	49.0	29.0		463.0	2.240	10.7	31.8	68.7		278.0	0.8	93	837	
990223	39278	30026	25.10	368	5100	40	2.31	3710	5820	56.6	249.0	2.510	19.2	617	45.7	27.0		498.0	2.140	11.3	34.4	79.2		743.0	1.3	204	1030	
990225	39475	30179	25.40	261	4820	32	1.53	3260	4960	41.7	162.0	2.360	19.0	507	62.5	37.6		611.0	1.790	8.1	21.8	38.2		170.0	0.7	60	1150	6.64
990226	39475	30179	19.30	213	4280	32	1.11	3000	3390	30.7	117.0	2.050	15.0	516	43.9	26.8		409.0	1.660	6.6	17.2	20.8		94.6	0.2	31	774	
990232	39472	30127	20.20	231	3490	28	1.19	3020	2790	29.5	126.0	2.100	17.0	555	36.5	25.2		313.0	1.590	6.7	17.6	44.5		161.0	0.5	67	812	5.72
990235	39625	30075	23.00	220	3920	32	1.10	3020	1660	26.3	123.0	2.340	17.8	470	36.9	19.8		169.0	1.590	6.7	17.6	32.1		153.0	0.6	52	801	
990237	39325	29975	36.10	503	5920	40	2.82	4530	7570	72.6	314.0	3.460	23.2	859	60.6	35.0		869.0	2.530	13.2	46.0	130.0		526.0	1.6	200	1170	
990238	39627	30224	23.60	297	4910	28	1.86	4400	7990	60.7	203.0	2.180	18.6	583	48.0	36.2	9.0	620.0	2.220	10.1	29.2	115.0		325.0	1.0	121	1020	
990239	39375	30022	118.00	784	17700	100	3.31	6350	3270	114.0	431.0	8.140	34.6	722	85.9	21.6		504.0	2.790	23.1	50.0	43.6		203.0	1.3	70	466	5.57
990242	39575	30075	48.20	329	5700	40	1.90	4210	2770	47.3	222.0	3.560	22.0	653	57.8	32.0		517.0	2.130	12.7	30.4	61.9		261.0	1.0	108	823	5.32
990246	39626	30223	23.90	212	4850	36	1.09	2600	1860	28.4	161.0	2.320	17.6	468	39.5	20.6		380.0	1.750	6.9	16.0	31.3		163.0	0.6	98	945	
990247	39375	29975	19.90	219	3520	28	1.62	2500	864	25.1	123.0	2.000	17.0	523	40.7	23.6		368.0	1.660	9.4	22.0	94.3		198.0	1.0	103	1010	4.95
990248	39377	30077	24.60	302	5380	40	1.96	4590	3670	42.2	178.0	2.520	19.2	653	43.1	24.0		402.0	1.990	10.3	27.4	74.0		233.0	0.7	100	777	

Appendix 2.3 Data for Wolverhampton topsoils
Geochemical data in µg/g unless otherwise stated

No.	East	North	Li	Na	K	Rb	Be	Mg	Ca	Sr	Ba	Al%	La	Ti	V	Cr	Mo	Mn	Fe%	Co	Ni	Cu	Ag	Zn	Cd	Pb	P	pH
990251	39215	29924	21.80	418	4590	32	2.24	3420	9360	76.6	378.0	2.360	18.0	635	42.8	51.6		606.0	2.630	12	38.2	208.0		869.0	2.4	383	1480	6.77
990253	39571	30126	17.80	189	4240	36	1.20	2980	2160	28.8	129.0	2.010	17.2	485	35.4	25.2		426.0	1.670	6.5	18.2	57.7		178.0	0.5	84	753	
990255	39575	30228	28.00	339	5830	40	1.41	3530	3790	47.5	161.0	2.590	19.4	595	40.3	20.6		234.0	1.660	8.1	22.6	31.9		165.0	0.4	35	416	7.30
990256	39677	30174	56.20	279	5150	40	2.05	2860	3630	53.4	292.0	3.680	21.4	599	54.9	33.0		3570.0	3.650	24.9	37.0	42.0		332.0	1.1	66	1440	5.86
990258	39584	30027	23.90	310	5730	32	1.16	5900	8490	48.8	186.0	2.230	17.4	435	33.3	18.4		530.0	1.910	7.8	30.4	31.1		132.0	0.3	64	610	6.92
990259	39622	30031	25.40	357	5100	36	1.59	3230	1680	40.7	355.0	2.880	19.6	531	42.3	23.4		180.0	1.440	7.5	21.2	55.0		188.0	0.8	89	644	
990261	39575	29975	39.20	248	4290	36	1.96	3570	1350	28.1	169.0	2.910	20.2	615	50.8	33.4		191.0	2.180	10.8	28.6	117.0		313.0	1.5	155	1080	
990264	39475	29829	29.00	405	8780	52	1.68	4050	5820	59.4	269.0	3.550	22.2	573	51.2	27.6		441.0	2.000	10.6	26.8	87.2		235.0	0.6	97	766	
990266	39323	30029	24.70	324	7030	44	1.51	2930	2250	44.3	183.0	2.830	19.2	535	43.1	13.8		281.0	2.030	8.7	22.0	32.6		143.0	0.3	76	578	6.25
990269	39274	30072	27.60	341	6980	44	2.06	4420	6790	53.8	247.0	2.890	22.2	577	48.1	28.2		357.0	2.190	11.2	30.8	66.8		303.0	1.2	123	990	7.10
990272	39475	29775	25.50	298	6740	48	1.45	2820	2220	43.3	195.0	2.970	18.4	496	44.8	15.8		462.0	1.750	9.8	24.0	51.0		205.0	0.8	64	578	6.00
990274	39470	30026	16.80	238	3130	28	1.62	2580	7410	55.5	189.0	1.700	16.2	630	37.9	25.6		641.0	2.230	9.5	26.2	128.0		409.0	1.3	150	1300	
990275	39570	30180	17.00	191	3860	24	0.84	2540	2680	30.1	100.0	1.830	14.4	460	28.6	13.8		182.0	1.240	4.8	14.2	27.6		135.0	0.4	42	430	6.07
990278	39628	30176	22.40	240	4950	40	1.13	2940	2240	31.0	142.0	2.340	16.2	496	36.1	20.4		365.0	1.780	7	17.4	31.9		155.0	0.5	56	974	5.10
990285	39476	30076	29.20	372	5750	40	2.51	4350	4360	58.3	302.0	2.820	20.6	701	50.8	27.2		444.0	2.240	12.5	35.4	143.0		638.0	1.3	171	988	5.94
990286	39225	30025	27.80	293	5540	44	2.03	3930	2740	39.8	233.0	2.860	21.6	560	46.7	27.8		693.0	1.920	9.8	29.2	94.6		268.0	1.2	167	865	5.43
990287	39524	30125	21.10	234	4510	32	1.44	3930	4440	36.7	159.0	2.120	17.0	551	40.7	23.6		428.0	1.840	7.6	22.2	94.5		218.0	0.8	71	907	
990289	39541	29971	63.00	648	11000	48	2.99	5940	12400	112.0	325.0	4.860	26.8	550	83.9	431.0		1220.0	8.410	27.7	142.0	353.0		586.0	2.9	149	997	
990290	39675	30125	17.20	250	4250	20	1.99	2470	11600	120.0	156.0	1.610	16.4	356	38.3	19.4	0.4	497.0	3.900	15.2	41.0	420.0		350.0	1.2	268	643	
990294	39326	30080	24.00	281	5990	44	1.84	3860	3610	39.0	229.0	2.580	20.6	538	44.9	31.0		230.0	1.870	9.2	27.0	106.0		324.0	1.4	135	1690	5.77
990295	39482	29865	26.80	515	4160	20	3.50	3300	12500	98.0	316.0	2.400	23.0	640	53.5	35.2	1.4	559.0	2.870	15.7	52.0	243.0		525.0	1.4	188	1160	7.23
990298	39414	29930	43.40	512	11000	64	1.86	4930	5090	62.5	300.0	4.760	23.4	654	58.8	16.6		605.0	2.380	12.2	30.2	42.2		131.0	0.4	42	636	
990299	39466	29928	36.20	455	5730	44	2.04	4180	3420	57.5	218.0	2.950	21.4	743	53.1	28.2	0.6	353.0	2.180	12.8	35.8	97.0		380.0	1.3	95	741	
990301	38759	29823	20.00	197	6630	40	1.53	3920	2040	30.9	117.0	2.310	18.2	484	30.9	17.2		242.0	1.510	6.5	19.2	25.8		72.2	0.2	32	452	6.05
990302	38712	29826	21.70	247	6030	32	1.28	4570	4050	34.0	149.0	2.270	17.4	451	34.7	17.8		378.0	1.700	8	21.6	24.9		99.0	0.3	298	658	
990304	39319	29930	23.00	281	5200	32	1.59	3430	3310	38.1	181.0	2.430	17.4	493	40.7	21.6		346.0	2.090	9.2	25.8	88.6		276.0	0.7	135	718	6.20
990305	38875	29975	34.10	2090	3860	20	9.66	2720	18400	493.0	182.0	2.880	29.0	814	79.5	90.8	6.2	784.0	3.530	41.6	160.0	601.0	1.2	1220.0	5.1	520	2220	6.78
990306	39334	29778	52.20	830	8310	44	4.67	3440	38800	203.0	340.0	4.920	28.6	857	70.9	27.6		2150.0	2.810	20.7	62.2	172.0		357.0	1.2	597	794	
990307	38675	29832	12.10	167	3540	32	0.89	2080	2590	27.0	109.0	1.570	13.2	469	26.6	19.0		523.0	1.280	5	11.0	20.2		104.0	0.2	55	715	5.66
990309	39272	29926	14.80	729	3800	24	1.72	3940	9670	65.8	180.0	1.920	15.8	1020	41.3	25.4		715.0	2.100	9.1	25.0	94.8		238.0	0.5	112	794	6.54
990311	38677	29875	13.90	160	4340	28	0.83	2580	1770	22.9	104.0	1.730	14.2	403	27.0	16.4		559.0	1.330	5	11.4	14.6		84.6		29	562	
990314	38775	29924	16.40	265	4340	24	1.84	3010	13700	71.2	169.0	1.810	16.4	451	33.9	25.8		353.0	1.560	9.2	24.8	42.3		195.0	0.6	147	1020	7.03
990316	38628	29874	10.60	143	3190	28	0.74	1840	1000	17.9	85.7	1.370	12.6	375	22.1	14.0		557.0	1.080	4.4	9.6	16.2		72.6	0.2	40	526	
990318	39271	29725	13.40	169	3490	28	1.02	1600	2430	27.2	112.0	1.740	14.0	438	33.9	20.4		427.0	1.650	6.2	14.6	62.4		168.0	0.5	58	654	
990328	38976	29975	25.70	443	3920	24	2.64	3140	7270	69.8	208.0	2.270	20.4	642	56.0	22.2		447.0	2.520	14.3	38.8	87.0		341.0	1.0	266	1680	6.47
990331	38880	29936	18.40	183	4860	36	1.23	3050	1860	27.0	123.0	2.060	16.6	455	33.2	18.0		469.0	1.560	6.7	16.0	25.8		77.8	0.2	38	501	6.00
990332	39422	29814	26.50	475	4420	24	1.82	3410	9670	52.1	221.0	2.380	18.0	628	39.9	25.4		350.0	1.700	9.3	24.6	54.4		212.0	0.8	94	625	
990333	38876	29875	16.00	178	4140	36	1.35	2720	1780	26.1	144.0	1.760	17.0	379	31.6	19.0		453.0	1.620	7.2	19.2	51.3		202.0	0.6	174	855	
990336	39268	29835	29.60	567	3710	16	4.21	4960	16800	132.0	212.0	2.920	20.6	645	83.4	64.2	3.8	1010.0	5.440	28.4	89.0	2750.0		3040.0	9.8	1400	1480	7.63
990338	39324	29824	35.30	523	5460	32	3.45	3580	11400	99.0	245.0	3.230	22.2	759	102.0	33.0		854.0	4.220	23.9	52.2	218.0		385.0	1.7	192	1740	6.95
990339	38927	29930	23.80	284	5700	40	1.81	3740	3210	40.3	148.0	2.520	18.2	584	47.9	30.4		408.0	1.880	9.2	24.0	54.5		162.0	0.5	89	836	
990341	39425	29875	17.30	285	3470	24	2.63	1750	3500	57.1	209.0	2.110	20.4	555	41.0	30.8		543.0	2.000	11.2	37.6	93.6		669.0	1.5	230	776	
990342	39425	29720	45.20	555	10100	56	2.63	5120	5850	87.1	358.0	4.470	25.6	696	77.3	31.0		904.0	3.020	18.4	43.2	93.9		441.0	1.5	124	1010	
990346	39378	29728	21.20	234	5590	36	1.16	3280	29900	58.8	168.0	2.600	23.2	548	44.6	26.0		710.0	1.930	8.9	20.6	47.4		141.0	0.7	45	900	7.84
990347	38785	30073	16.20	189	3990	36	1.24	2480	2850	27.1	122.0	1.830	16.6	425	37.4	21.0		421.0	1.530	6.9	16.6	39.3		131.0	0.5	157	750	
990349	39323	29877	25.30	512	4710	36	2.59	3640	11900	91.9	285.0	2.380	21.4	687	50.8	28.2		936.0	2.560	13	40.6	184.0		468.0	1.7	212	1240	6.67
990353	39227	29972	50.70	428	6920	56	3.15	5680	6240	56.6	309.0	3.950	25.4	842	65.8	39.2		883.0	3.890	17.1	72.0	155.0	0.8	412.0	1.5	248	1640	6.04
990355	39528	29834	18.30	244	4500	32	1.25	2730	5070	39.9	155.0	2.080	16.6	498	41.2	30.6		458.0	1.670	7.5	18.4	39.8		169.0	0.6	74	770	6.68
990356	39378	29826	37.30	475	11800	72	2.04	5020	2540	62.8	313.0	4.850	25.4	627	60.9	15.2		354.0	2.170	13.1	33.6	71.2		183.0	0.6	56	597	
990359	39596	29786	29.20	329	7130	32	1.60	4280	16300	78.2	232.0	3.080	20.6	461	44.0	31.0		456.0	1.840	9.2	30.0	177.0		328.0	0.2	59	404	7.56
990361	39324	29726	22.40	246	4380	36	1.52	1740	3450	47.9	172.0	2.360	15.8	494	41.7	18.0		449.0	1.650	7.8	23.2	169.0		598.0	1.7	107	831	5.74
990363	38920	29975	36.10	863	5820	32	5.69	3960	10300	116.0	310.0	2.910	24.8	748	61.9	32.2	1.2	581.0	2.980	23.7	79.6	107.0		518.0	1.4	243	1900	6.43
990365	39375	29775	70.00	475	5350	28	2.65	3320	4060	90.0	217.0	5.270	23.6	740	77.1	23.2		610.0	2.340	15.2	40.4	163.0		607.0	2.5	193	996	

Appendix 2.3 Data for Wolverhampton topsoils

Geochemical data in μg/g unless otherwise stated

No.	East	North	Li	Na	K	Rb	Be	Mg	Ca	Sr	Ba	Al%	La	Ti	V	Cr	Mo	Mn	Fe%	Co	Ni	Cu	Ag	Zn	Cd	Pb	P	pH
990366	39378	29826	29.80	350	7970	52	1.81	3970	1850	47.1	219.0	3.600	21.6	668	53.4	22.6		326.0	1.900	10.6	27.8	77.0		260.0	0.7	73	700	
990368	39209	29827	31.20	312	5720	36	1.53	4270	5850	47.1	208.0	2.620	20.8	632	43.4	31.0		325.0	2.150	8.3	25.4	80.0	0.4	271.0	0.6	136	756	7.34
990376	39477	29721	48.60	969	9150	44	7.15	5000	20100	221.0	362.0	4.560	32.4	951	97.3	38.2	1.0	1040.0	3.660	40.8	94.2	289.0	0.6	732.0	3.8	380	2800	6.84
990378	38725	30067	12.10	140	3350	28	0.81	1760	2470	27.5	93.6	1.430	13.4	446	25.4	20.6		409.0	1.160	4.6	10.4	17.3		74.2	0.3	34	825	
990380	39371	29875	33.40	384	7560	52	2.60	4110	4420	72.2	256.0	3.490	23.4	622	66.3	28.0	0.8	435.0	2.730	15.8	38.6	173.0		420.0	1.1	163	1670	
990382	38773	29975	21.10	250	4160	28	1.38	3040	2670	31.6	144.0	2.210	17.2	552	35.4	25.6		312.0	1.480	7.2	19.0	27.2		124.0	0.4	59	638	
990383	39225	29887	27.90	1090	3910	20	3.35	5920	32200	180.0	322.0	2.600	20.6	1090	64.5	116.0	6.0	1420.0	4.780	22.5	101.0	615.0	1.8	2340.0	12.6	977	1870	
990386	38775	29877	9.48	114	3480	24	0.73	1860	1040	17.8	66.2	1.450	13.2	345	19.1	13.6		271.0	0.930	3.3	8.4	9.7		54.6		24	474	5.52
990390	38830	29936	12.70	184	4890	36	0.98	2770	1110	25.2	101.0	1.800	15.2	407	28.4	11.2		608.0	1.400	5.4	13.4	13.7		56.6		29	437	
990393	39289	29875	24.50	316	4960	40	1.93	2550	5250	59.2	290.0	2.590	19.2	599	59.8	30.6	0.8	697.0	2.800	12.1	31.0	88.3		251.0	0.7	117	942	
990396	39421	29781	16.50	185	4310	36	0.90	2480	2260	27.7	124.0	1.900	15.6	450	30.3	20.4		509.0	1.440	5.7	13.8	29.0		151.0	0.4	47	734	6.52
990397	39282	29971	29.30	573	3440	16	3.72	2680	9340	101.0	234.0	2.370	20.4	780	70.5	56.4		1290.0	6.370	25.7	111.0	213.0		851.0	4.1	404	1110	
990404	38968	29925	26.30	386	5150	36	1.86	4040	3550	45.1	183.0	2.840	20.4	805	54.3	25.8		366.0	1.970	10.1	27.0	68.2		228.0	0.8	99	873	5.70
990407	38827	29777	27.60	336	7500	48	1.51	5930	3730	41.5	211.0	2.970	20.2	560	43.8	19.2		375.0	2.080	9.4	26.6	24.3		86.2	0.2	31	388	
990410	38776	29785	27.00	267	7010	48	1.46	4810	1620	33.2	173.0	2.970	20.2	540	44.5	30.4		346.0	1.980	8.7	20.4	29.1		118.0	0.2	57	634	
990413	39024	29877	27.80	326	4610	36	3.13	3130	4510	56.0	243.0	2.600	20.6	665	54.5	32.0		307.0	2.230	15	41.0	105.0		325.0	1.7	278	2560	5.20
990415	39228	29878	29.20	392	6720	44	2.28	5160	7860	66.9	303.0	2.770	20.2	671	53.2	38.2		523.0	2.370	12.6	33.4	91.6		423.0	0.9	587	1740	6.55
990416	39121	29972	26.40	267	5790	44	1.59	3870	4360	47.4	178.0	2.810	19.8	566	45.5	28.8		353.0	2.040	9.8	24.0	59.5		184.0	0.4	68	667	
990417	39076	29977	14.50	226	4220	28	1.24	2870	7090	56.5	196.0	1.580	18.0	490	31.1	23.6		404.0	1.380	6.2	17.8	35.7		146.0	0.4	74	885	7.15
990419	39223	29779	25.50	433	4300	24	2.07	4330	19400	85.8	199.0	2.410	21.6	831	54.2	22.0		1220.0	2.080	10.7	25.6	60.0		275.0	1.6	68	713	
990420	38824	29970	21.80	236	6910	44	1.24	4530	2400	32.7	142.0	2.420	17.4	450	35.2	15.4		445.0	1.700	6.9	19.2	19.2		74.6	0.2	78	467	
990421	39226	29725	23.20	185	5360	36	1.51	2980	4000	34.4	182.0	3.090	20.4	472	37.2	16.8		499.0	2.260	9.3	19.6	80.8		186.0	0.6	74	497	
990423	39362	29585	42.70	652	13800	72	2.21	7020	16700	119.0	305.0	5.290	28.8	532	81.2	33.6		1440.0	3.340	13.9	39.0	41.2		236.0	1.0	85	778	7.55
990424	38830	29829	25.70	273	6580	44	1.53	4870	3800	35.3	176.0	2.560	19.8	485	39.7	22.0		354.0	1.800	8.1	22.4	36.8		157.0	0.6	68	642	
990426	39479	29573	19.00	255	4010	32	1.69	2010	4760	45.3	204.0	2.090	15.6	543	42.6	30.6		618.0	2.410	9.8	27.6	155.0		354.0	1.2	104	558	
990428	38721	29777	28.40	331	6640	40	1.88	4440	6720	60.2	240.0	2.690	20.0	601	42.9	22.4		347.0	2.140	11.8	33.6	42.2		239.0	0.7	116	782	7.16
990430	38718	29877	13.60	177	5740	40	1.24	2550	426	28.5	130.0	2.120	17.6	457	31.0	14.2		322.0	1.480	6.8	29.2	22.0		95.4		60	591	4.20
990434	39428	29673	29.10	416	6620	40	2.34	4310	9060	85.0	279.0	3.090	24.6	735	63.8	39.6	0.8	940.0	2.760	13.6	40.6	104.0	0.8	608.0	1.4	157	1270	
990436	39121	29816	27.10	731	6330	36	2.56	3980	11900	94.6	281.0	3.080	23.8	655	61.3	28.2		845.0	3.170	15.4	45.8	305.0		491.0	4.3	290	1160	7.46
990438	39426	29521	15.60	171	4090	32	1.04	2550	2860	26.1	110.0	1.800	14.4	457	34.1	38.6		608.0	1.510	5.8	14.4	31.0		108.0	0.3	62	714	6.15
990440	39177	29821	22.10	351	5920	36	1.58	4760	7430	52.0	158.0	2.420	18.4	606	41.9	27.4		472.0	2.000	8.8	25.0	46.3		143.0	0.3	77	710	7.02
990443	39021	29829	16.60	329	3850	32	1.68	3000	6010	48.1	193.0	1.890	17.0	616	36.1	25.2		487.0	2.030	8.6	24.8	85.8		268.0	0.6	297	905	6.70
990445	39478	29677	33.80	659	7130	36	3.27	6070	29700	184.0	362.0	3.480	24.8	1060	74.5	37.4		1290.0	2.940	21.4	46.0	153.0		659.0	2.9	1840	1680	7.25
990447	39163	29925	20.10	253	5080	36	1.37	3970	6040	43.9	157.0	2.240	17.8	526	40.4	21.0		591.0	1.890	9.2	20.8	59.1		162.0	0.5	92	781	6.90
990449	39426	29870	39.50	632	6570	40	3.24	7620	38700	162.0	375.0	3.410	26.2	707	143.0	94.6		3280.0	4.150	13	42.0	83.2		358.0	2.5	102	1550	7.42
990452	39020	29928	18.40	201	4860	36	1.26	3150	4080	29.7	144.0	2.110	16.8	464	34.8	20.4		314.0	1.470	6	15.4	25.5		90.4	0.3	58	583	6.27
990454	38924	29824	22.30	253	4600	36	1.55	3220	3440	38.1	208.0	2.230	17.2	536	39.0	24.2		366.0	1.800	8.6	23.0	53.1		208.0	0.6	143	986	6.00
990456	39277	29777	17.20	235	3700	28	1.15	2370	3500	35.3	180.0	1.850	17.2	476	33.6	26.6		554.0	1.890	7.9	22.4	1030.0		877.0	1.7	165	692	6.95
990459	39023	29978	16.00	180	4420	28	1.16	2640	2720	27.2	126.0	1.800	16.0	405	30.3	19.4		229.0	1.380	7	16.2	38.3		121.0	0.4	61	549	6.58
990464	39076	29925	30.50	387	7350	52	2.20	4550	5230	70.2	281.0	3.020	21.4	656	51.9	30.0		546.0	2.420	12	31.8	108.0		256.0	0.7	235	1630	
990466	39423	29628	69.60	748	13300	84	3.48	3760	12300	275.0	347.0	6.100	30.2	688	88.3	28.6		959.0	2.850	17.9	51.4	92.4		480.0	1.6	204	1710	
990467	39126	29885	10.30	158	2510	20	1.04	1470	3680	27.8	84.9	1.290	13.6	333	26.4	11.6		286.0	1.180	5.5	11.0	23.0		123.0	0.3	72	606	
990471	39076	29825	29.20	541	3900	24	3.52	2630	15400	123.0	220.0	2.660	21.6	664	56.3	25.4		331.0	2.440	14.2	53.4	109.0		521.0	1.6	256	1220	6.86
990472	39179	29982	10.00	125	2210	16	0.75	1590	2830	22.1	77.7	1.110	10.0	272	22.7	9.6		289.0	1.160	4.5	12.4	118.0		130.0	0.3	46	426	7.36
990473	39172	29878	20.50	284	5320	40	1.05	2400	5120	35.7	140.0	2.170	16.4	450	35.1	21.0		577.0	1.670	7	16.0	17.8		119.0	0.6	46	690	7.00
990476	38982	29872	32.40	402	7970	44	2.08	5140	6500	66.6	235.0	3.180	22.8	586	49.8	25.6		557.0	2.530	12.2	31.4	62.5		225.0	0.8	294	845	
990478	38822	29888	9.78	124	3570	24	0.93	2240	2630	20.0	99.7	1.460	12.6	354	19.0	14.4		191.0	1.060	3.5	9.2	12.1		54.2		36	474	6.42
990480	38928	29878	28.00	361	5160	36	2.49	4650	7730	70.1	377.0	2.570	20.6	655	52.2	32.4		502.0	2.760	15.1	38.2	118.0		440.0	2.0	426	1440	6.85
990481	39072	29881	21.50	282	4570	36	1.93	2860	2890	43.7	185.0	2.200	18.6	564	45.0	25.6		344.0	2.260	10.7	27.4	99.8	0.4	184.0	0.4	225	1500	
990487	38996	30167	26.70	414	5100	32	2.11	4390	15800	74.1	421.0	2.410	17.6	566	46.1	94.2		514.0	2.960	13.6	62.0	303.0	2.6	1430.0	5.6	317	3260	7.17
990490	39474	29621	19.10	306	3650	28	1.43	3970	17000	67.0	223.0	1.660	18.2	464	40.4	21.8	0.4	501.0	2.960	9.9	28.0	100.0		263.0	0.9	237	966	7.61
990491	39133	29927	14.40	214	4200	20	0.93	3840	25100	57.7	141.0	1.540	15.2	368	26.1	11.8		268.0	1.580	5.7	15.6	48.5		126.0	0.4	43	533	
990492	38882	29826	32.50	519	8410	48	2.36	5140	6820	136.0	285.0	3.220	24.0	671	58.1	31.6		790.0	2.970	15.4	42.0	247.0		178.0	0.7	127	770	

Appendix 2.3 Data for Wolverhampton topsoils
Geochemical data in µg/g unless otherwise stated

No.	East	North	Li	Na	K	Rb	Be	Mg	Ca	Sr	Ba	Al%	La	Ti	V	Cr	Mo	Mn	Fe%	Co	Ni	Cu	Ag	Zn	Cd	Pb	P	pH
990501	39278	29426	37.50	367	22000	116	2.66	14800	5270	53.7	322.0	5.980	37.6	631	74.6	18.4		555.0	3.790	17.2	60.0	32.9		98.6	0.4	23	424	7.57
990502	39225	29469	9.30	128	4980	32	0.89	2940	1390	15.9	110.0	1.640	14.0	379	28.2	24.4		375.0	1.470	5.1	14.2	29.8		80.4		34	1220	5.08
990503	39280	29474	23.70	261	11900	76	2.23	4900	3580	40.9	301.0	4.090	27.6	662	60.6	27.8	0.8	826.0	2.920	14.3	36.0	40.4		190.0	0.5	73	747	
990504	39223	29526	23.50	273	5370	44	1.48	3060	4120	33.9	179.0	2.970	20.0	655	49.5	27.4		615.0	1.960	10.7	22.2	43.8		206.0	0.8	112	774	6.39
990505	39224	29571	26.50	293	6350	40	1.43	4250	5070	44.0	192.0	3.010	19.2	602	44.7	29.4		600.0	2.540	9.4	25.2	45.6		122.0	0.3	115	634	7.14
990508	39627	29721	45.90	550	7870	48	3.28	4000	7440	91.5	278.0	3.940	23.6	976	69.2	35.6		454.0	2.770	18.5	48.8	297.0		652.0	1.7	178	1060	
990510	39124	29762	26.60	509	4000	28	2.90	3390	8730	67.5	239.0	2.270	20.0	639	59.6	46.2	0.8	807.0	2.520	15.7	54.8	209.0		526.0	1.5	265	1040	
990513	39618	29682	23.90	253	5370	36	1.31	2310	4080	41.2	161.0	2.720	16.4	498	42.4	43.4		557.0	1.710	7.2	21.6	71.5		199.0	0.6	65	686	
990515	38894	29787	22.30	219	4320	36	1.59	3500	1470	29.2	150.0	2.340	17.8	512	39.8	23.2		247.0	1.660	8.7	22.4	35.7		136.0	0.4	83	502	5.09
990520	39319	29682	20.40	253	4870	40	1.41	3090	15900	50.1	164.0	2.280	18.6	540	34.3	23.6		450.0	1.530	7.5	21.8	40.1		143.0	0.6	100	639	
990522	39524	29474	36.80	329	7530	56	1.62	3870	4290	41.3	225.0	4.200	25.2	645	53.2	16.8		691.0	2.100	10.4	24.8	29.2		109.0	0.4	46	502	
990526	39577	29729	58.00	626	15200	88	3.45	5420	9430	113.0	418.0	6.940	33.2	711	84.0	17.6		636.0	2.340	19.6	53.4	153.0		418.0	1.2	102	1050	
990527	39275	29575	29.30	665	5040	36	2.24	3860	8180	58.9	192.0	2.800	20.4	614	56.5	25.2		655.0	2.100	14.4	31.0	68.9		844.0	2.8	183	872	6.77
990528	39531	29725	32.60	373	7350	52	2.52	4320	6350	77.8	260.0	3.440	23.6	628	54.6	26.0		518.0	2.620	14.7	36.6	145.0		384.0	1.0	153	1340	6.43
990535	39380	29517	17.90	230	7270	36	1.72	3530	3230	30.6	110.0	2.510	19.6	520	30.7	17.2		316.0	1.870	5.4	15.0	20.0		76.2		22	570	7.15
990536	39325	29475	28.50	303	7470	56	2.17	2420	2990	61.4	213.0	4.060	23.6	581	61.0	17.6		536.0	2.200	17.4	33.2	47.3		232.0	1.0	86	851	5.38
990539	39326	29572	43.60	509	6610	44	2.63	3950	11300	96.3	303.0	3.790	24.0	726	69.4	37.4	0.8	473.0	3.030	15.4	47.4	152.0		602.0	1.9	235	1180	7.40
990540	39329	29528	10.10	130	3540	20	0.74	2360	3550	20.8	75.8	1.200	10.8	323	21.4	42.4		222.0	0.956	3.7	11.4	19.6		71.6		16	192	8.33
990541	39041	29783	32.90	393	8550	56	1.97	5480	2910	41.9	214.0	3.360	20.6	570	48.9	24.8		392.0	2.440	10.5	29.6	63.0		191.0	0.5	214	675	5.84
990543	39196	29728	12.80	156	4050	32	1.52	2040	2530	27.3	150.0	1.560	14.8	464	27.3	16.6		529.0	1.470	7	17.0	47.8		125.0	0.3	101	1360	6.24
990552	39618	29468	14.60	176	3640	28	1.01	1980	2610	34.7	121.0	1.650	13.2	478	32.4	20.6		482.0	1.790	6.9	16.2	47.6		140.0	0.3	60	773	
990555	38978	29778	26.30	394	4980	36	3.20	3710	4060	49.5	195.0	2.680	21.2	781	48.9	24.6		402.0	2.150	14.3	40.2	107.0		300.0	0.9	191	1060	5.75
990558	39134	29724	28.80	585	5630	32	3.68	4090	12400	128.0	319.0	2.820	23.2	749	60.7	26.6	0.6	635.0	2.750	20.6	50.4	114.0		487.0	1.4	359	1250	
990559	39082	29778	14.60	241	4610	28	0.87	2820	3360	35.8	115.0	1.820	20.0	458	31.1	13.4		312.0	1.510	5.3	13.2	27.1		118.0	0.2	38	703	6.54
990560	39177	29770	28.90	1040	4180	20	3.40	5480	21900	148.0	345.0	2.690	23.2	1270	69.1	37.0		1440.0	3.790	20.7	61.2	295.0		706.0	2.3	322	1910	7.05
990563	39575	29525	22.10	288	5550	36	1.76	2350	1960	49.1	165.0	2.540	18.6	441	63.7	23.0		1340.0	3.070	14.5	32.4	95.9		247.0	1.0	143	1010	5.71
990564	39372	29634	16.20	356	4780	40	1.32	3510	5270	42.9	157.0	2.800	23.4	895	44.6	38.6		742.0	2.220	9.1	20.0	55.7		187.0	0.4	59	949	
990565	39371	29679	37.90	1040	5230	28	10.50	3530	15600	196.0	197.0	3.730	33.2	910	104.0	66.4	2.8	1170.0	4.390	39.3	115.0	259.0		1020.0	3.2	623	2340	
990566	39278	29623	27.10	293	6340	44	1.40	3280	5500	45.9	183.0	2.850	20.6	564	50.2	23.2		574.0	1.980	10.6	23.0	36.7		159.0	0.4	129	591	7.27
990567	39576	29475	32.20	602	3170	20	1.21	1920	37800	111.0	543.0	2.080	14.8	810	61.1	30.6		3310.0	1.990	6.6	15.8	35.9		875.0	0.5	79	265	
990569	39224	29674	28.80	290	7980	52	1.55	3370	1490	53.8	270.0	3.490	21.8	538	39.0	16.4		273.0	1.530	10	24.0	38.2		133.0	0.5	51	603	
990573	39324	29638	15.80	196	4170	28	1.14	2110	3250	32.4	142.0	2.150	16.6	465	37.7	20.4		626.0	2.170	8.5	19.6	111.0		199.0	1.0	504	601	
990577	38935	29785	23.10	250	5000	40	1.69	3410	929	26.3	168.0	2.390	18.0	508	37.8	22.0		321.0	1.680	8.8	22.0	48.5		140.0	0.5	99	738	5.04
990579	39524	29528	31.70	432	4870	28	2.75	3260	11700	109.0	220.0	3.090	22.0	709	74.4	32.4		1190.0	3.760	19.8	51.0	92.3		318.0	1.4	165	1840	
990581	39587	29670	39.40	610	5490	32	3.35	5100	21200	116.0	371.0	4.070	25.2	768	94.0	151.0		1000.0	3.360	21	147.0	542.0	4.4	978.0	7.4	279	3450	
990586	39365	29481	27.30	331	7360	48	1.41	3410	6390	67.0	182.0	3.180	20.8	539	46.7	21.4		524.0	2.170	9.4	23.4	39.1		152.0	0.3	52	755	
990587	39328	29428	35.70	207	5110	40	1.67	2600	1860	36.5	143.0	3.400	19.4	627	57.5	17.6		203.0	1.570	9.5	22.8	45.1		167.0	0.7	89	726	
990588	39572	29636	26.80	344	5750	40	1.97	3040	5800	63.0	201.0	2.690	20.4	523	46.0	35.4		467.0	1.950	10	29.4	91.8		294.0	1.0	126	658	6.52
990589	39522	29622	46.10	1340	6720	36	3.60	5230	37900	251.0	432.0	4.350	25.0	1430	83.6	86.0		2930.0	4.510	18.4	76.4	175.0		640.0	2.6	274	1150	
990590	39273	29529	21.70	240	3330	24	2.40	1950	6790	61.3	192.0	2.460	18.6	525	49.3	27.2		683.0	2.390	13.5	28.2	56.2		408.0	1.0	127	990	6.51
990594	39528	29673	30.60	303	5910	44	1.87	3960	5350	60.1	178.0	2.860	22.4	605	50.0	25.6		349.0	2.120	10.5	29.4	60.8		202.0	0.7	91	709	6.42
990595	38977	29726	27.20	278	6190	44	1.57	5100	3060	35.0	199.0	2.800	22.4	527	43.0	23.0		376.0	2.000	8.8	24.4	40.8		147.0	0.4	95	510	6.20
990601	39571	29581	28.10	390	5450	36	2.10	3600	13300	78.8	205.0	2.630	20.0	622	50.3	24.2		502.0	2.030	10.8	28.6	93.8		272.0	0.8	100	842	7.10
990602	39172	29573	29.80	222	5930	48	1.54	2650	2710	40.0	232.0	3.710	27.4	666	56.6	26.0		538.0	2.080	9.2	20.0	34.3		175.0	0.7	90	970	5.80
990604	39077	29574	33.70	288	6240	56	1.70	3160	2300	42.4	201.0	3.270	21.4	611	57.2	26.2		395.0	1.860	10.4	23.0	43.1		177.0	0.7	99	948	
990606	38875	29574	16.90	200	4610	40	0.96	3130	2270	27.3	255.0	2.010	15.8	419	31.0	15.4		344.0	1.500	6.3	15.6	22.0		198.0	0.4	137	613	
990608	39026	29532	26.20	324	5890	40	2.05	4140	6080	58.5	208.0	2.930	19.6	703	56.9	30.4		808.0	2.690	12.2	29.6	63.0		280.0	0.9	100	1170	6.81
990629	38880	29677	18.30	243	4550	32	1.38	2980	3720	34.6	142.0	2.090	15.8	487	38.1	27.8		504.0	1.720	7.8	20.0	39.1		146.0	0.3	75	714	6.38
990630	39624	29526	42.50	588	11300	64	2.63	4270	7720	137.0	307.0	5.100	26.2	656	77.5	24.8		1050.0	4.740	19.9	49.0	114.0		237.0	1.3	94	918	
990633	39130	29532	29.90	253	7330	52	1.51	3970	3340	37.8	292.0	3.260	23.2	550	59.0	25.4		575.0	2.110	9.5	20.6	25.8		105.0	0.4	44	618	6.78
990637	39022	29625	15.00	136	4050	32	1.02	2390	2060	19.2	105.0	1.940	12.2	355	27.6	8.2		201.0	1.370	4.7	12.2	18.9		113.0		57	575	
990638	38976	29679	16.70	225	3870	28	1.33	2810	4670	37.8	410.0	1.880	16.4	524	33.8	23.2		336.0	1.420	7.3	19.0	48.0		518.0	1.1	386	952	6.90
990639	38824	29573	16.00	193	4440	32	0.99	2760	10500	61.2	685.0	1.710	15.6	619	28.3	23.2		325.0	1.540	9	16.0	28.9		593.0	0.7	579	1060	6.83

Appendix 2.3 Data for Wolverhampton topsoils
Geochemical data in µg/g unless otherwise stated

No.	East	North	Li	Na	K	Rb	Be	Mg	Ca	Sr	Ba	Al%	La	Ti	V	Cr	Mo	Mn	Fe%	Co	Ni	Cu	Ag	Zn	Cd	Pb	P	pH
990641	38874	29725	13.90	164	3500	24	1.00	2210	1580	23.0	91.7	1.500	13.2	371	25.3	18.4		208.0	1.180	5.4	15.6	22.4		152.0		44	659	
990642	38920	29532	30.70	431	8090	56	3.07	3060	3530	61.2	330.0	3.380	21.4	564	54.6	26.4		427.0	2.400	12.2	35.2	74.7		420.0	1.2	226	2060	
990643	39218	29624	25.80	421	4320	32	1.84	3040	5090	43.4	420.0	2.320	18.6	745	44.4	25.6		457.0	2.080	10.4	34.8	68.1		268.0	1.1	92	815	
990646	39522	29581	11.50	158	2830	24	0.75	1860	2320	22.9	85.0	1.390	14.4	438	25.9	18.6		532.0	1.420	4.9	12.8	18.2		65.6		28	572	
990648	38821	29532	13.50	142	3690	16	0.99	2660	3350	25.4	215.0	1.580	13.8	368	25.7	14.8		432.0	1.370	4.9	13.0	31.2		217.0	0.6	63	644	
990652	38918	29725	27.90	663	4900	28	2.72	3710	9650	75.9	278.0	2.650	21.2	626	49.6	21.4		581.0	2.090	12.9	40.8	74.7		246.0	0.6	111	686	
990653	39178	29674	18.40	245	2930	20	1.80	1330	3540	50.2	135.0	1.780	15.4	501	37.0	14.8		283.0	1.670	9.3	29.2	60.5		157.0	0.6	82	826	5.83
990654	39173	29623	27.70	254	4700	40	1.47	2680	2370	35.9	176.0	2.640	18.4	584	44.3	28.2		339.0	1.760	8.8	20.6	33.4		168.0	0.4	70	750	
990655	39122	29624	22.10	236	4450	32	1.25	1940	2980	34.4	188.0	2.420	17.2	453	42.7	39.8		493.0	1.850	8.5	22.6	76.0	0.4	666.0	1.5	113	1380	
990659	38828	29673	23.60	257	5750	36	1.26	5110	6220	39.5	329.0	2.350	18.6	530	46.7	121.0	0.8	676.0	2.070	8.1	26.2	98.3	1.4	396.0	1.1	154	1810	6.70
990663	38875	29528	15.10	180	4050	32	1.18	2150	4220	35.7	125.0	1.790	14.4	448	30.6	18.2		523.0	1.480	6.2	17.4	29.1		161.0	0.5	80	1410	6.00
990664	38984	29525	22.40	265	5870	40	1.33	3850	1890	31.5	147.0	2.540	20.2	536	39.2	20.8		484.0	1.770	7.8	18.8	26.8		117.0	0.2	54	653	5.40
990666	39069	29625	21.40	407	4260	28	2.08	3000	14700	71.6	204.0	2.320	18.2	606	48.1	35.4		808.0	2.040	9.1	27.2	71.9		267.0	0.9	148	2050	6.79
990667	39080	29671	23.10	252	4980	36	2.11	2830	4630	58.5	208.0	2.610	17.8	523	46.5	24.6		532.0	2.590	12.3	31.2	111.0		592.0	1.1	251	2480	
990668	38870	29633	20.20	473	3930	28	2.08	2860	5300	50.8	211.0	1.960	16.0	379	36.3	27.0		375.0	2.030	10.3	47.0	431.0	0.8	541.0	3.2	315	941	6.23
990669	38924	29630	21.20	264	5340	40	1.24	3490	2180	35.1	523.0	2.430	16.8	528	38.7	22.6		383.0	1.730	7.3	19.6	34.7		148.0	0.5	85	683	5.55
990670	38980	29623	21.60	262	5320	36	1.46	3260	2380	32.9	158.0	2.280	17.4	519	40.2	22.8		391.0	1.750	8.4	22.4	38.6		162.0	0.5	99	972	5.90
990671	38923	29679	26.50	346	4660	36	1.30	5430	26700	108.0	291.0	2.210	15.4	485	34.7	552.0		463.0	2.840	14	178.0	841.0	10.2	6740.0	54.7	345	7410	6.75
990675	39131	29577	39.80	335	11600	72	2.07	7420	3380	35.9	335.0	4.310	21.4	621	76.2	17.6		862.0	3.490	15.8	26.0	39.3		139.0	0.5	54	552	6.45
990676	39275	29675	24.80	340	4990	32	2.01	3460	14800	94.8	420.0	2.950	20.8	544	63.7	60.6		1400.0	2.470	11.5	32.8	170.0		436.0	1.2	473	1030	6.88
990678	38924	29569	12.40	151	3620	28	0.98	1870	1270	21.1	111.0	1.570	16.6	363	29.6	13.0		317.0	1.520	5.4	13.2	28.6		74.4	0.2	65	698	5.40
990680	38822	29624	17.90	190	4730	36	0.83	2920	1120	22.6	108.0	2.050	15.0	494	28.5	19.2		361.0	1.420	5.5	12.8	12.7		67.8		18	386	
990683	39025	29578	9.84	74	2820	8	0.68	1790	1150	15.2	79.1	1.170	9.6	282	19.2	7.6		267.0	0.883	4	10.0	20.0		58.4		18	314	5.98
990688	38979	29576	22.40	281	6340	40	1.57	4870	4120	37.7	150.0	2.510	19.0	514	39.9	16.0		426.0	1.990	9.3	24.4	37.6		131.0	0.3	58	690	6.30
990691	39018	29671	24.90	665	3480	24	2.92	3520	15000	95.4	447.0	2.300	19.0	726	57.8	40.8		836.0	3.150	15.8	49.6	130.0		447.0	1.6	272	1730	7.03
990692	38918	29725	23.80	535	3860	28	2.78	3440	9890	76.3	238.0	2.320	19.2	578	49.1	21.2		632.0	2.080	11.8	42.4	73.0		327.0	0.9	210	1070	6.56
990693	38821	29723	19.00	254	4730	36	1.34	3530	4510	36.2	203.0	2.100	17.0	476	34.2	17.8		365.0	1.700	7.9	22.2	40.3		186.0	0.5	115	678	6.51
990695	39076	29725	24.30	295	5930	40	2.19	4110	7920	61.4	290.0	2.800	20.8	547	49.3	23.4		650.0	2.470	12	31.4	141.0		302.0	0.8	176	1180	6.75
990699	39031	29722	16.80	178	3560	32	1.22	2450	1830	24.3	132.0	1.810	16.0	427	33.9	15.6		388.0	1.520	6.7	18.0	95.7		186.0	0.7	109	713	5.67
990700	39131	29671	21.40	374	4870	36	1.72	2990	11400	79.2	405.0	2.280	21.2	573	45.6	38.2		501.0	1.860	10.5	27.0	103.0		728.0	1.8	405	1700	

Appendix 2.4 Data for Wolverhampton subsurface soils
Geochemical data in µg/g unless otherwise stated

No.	East	North	Li	Na	K	Rb	Be	Mg	Ca	Sr	Ba	Al%	La	Ti	V	Cr	Mo	Mn	Fe%	Co	Ni	Cu	Zn	Cd	Pb	P	pH
990001	39375	30375	23.80	231	6860	44	1.09	4970	1400	22.4	139.0	2.510	16.6	523	35.2	17.4		438.0	1.710	7.8	18.0	17.4	57.4		24.0	478	
990002	39226	30123	26.90	320	7040	48	1.64	4450	3780	42.2	229.0	2.940	18.6	523	41.8	22.2		289.0	2.280	8.7	25.6	82.0	270.0	0.7	82.0	662	6.67
990003	39325	30375	12.80	136	3340	36	0.66	1800	656	17.0	77.1	1.470	14.0	383	24.1	15.2		533.0	1.230	4.3	8.6	21.0	48.8		20.0	414	
990006	39227	30175	21.50	206	5130	36	1.39	2830	4080	33.5	174.0	2.300	15.8	496	36.7	15.8		483.0	1.870	6.6	16.6	28.9	122.0	0.3	45.0	579	7.21
990007	39375	30275	28.40	282	7750	44	1.20	5070	1890	31.0	139.0	2.990	18.4	576	41.9	18.6		295.0	2.220	8.5	19.2	17.4	65.2		20.0	392	6.57
990014	39075	30272	32.70	328	4210	32	1.61	3530	4710	45.5	181.0	2.700	21.0	493	42.9	20.0		377.0	2.210	10.6	25.6	28.2	123.0	0.5	46.0	854	
990015	39175	30375	16.60	170	3620	32	0.90	2630	1450	22.8	113.0	1.740	15.4	409	29.4	17.8		251.0	1.320	5.8	13.8	24.4	126.0	0.3	61.0	642	
990016	39224	30375	27.20	351	6000	32	1.32	4730	9270	56.3	195.0	2.710	19.0	549	42.6	26.4		475.0	2.200	8.5	22.4	26.3	68.8	0.2	27.0	543	7.14
990020	39225	30285	19.00	211	5770	44	1.23	3310	2030	29.0	133.0	2.200	18.8	591	34.4	24.0		589.0	1.610	7.0	16.4	25.8	136.0	0.6	53.0	566	5.99
990021	39075	30375	18.10	200	4550	32	1.14	2440	3300	28.5	147.0	1.890	19.2	432	33.6	38.2		225.0	1.260	6.1	20.0	73.4	799.0	1.9	100.0	1050	
990022	39428	30125	21.00	241	4300	32	1.68	3160	3570	47.2	155.0	2.450	19.2	537	42.2	24.4		287.0	1.830	9.2	21.4	45.9	117.0		73.0	611	6.02
990023	39274	30171	14.60	173	4090	36	0.84	1580	1150	29.5	96.7	1.820	16.6	434	29.3	15.0	0.4	439.0	1.380	6.0	11.4	20.0	82.4	0.3	32.0	476	5.64
990024	39027	30174	49.00	295	5820	36	2.29	5080	5260	49.7	228.0	3.740	25.8	570	60.2	34.6		340.0	2.420	10.5	33.4	63.4	304.0	1.0	98.0	1150	
990027	39324	30127	33.70	323	8860	48	1.44	5050	1660	39.9	167.0	3.560	21.0	555	47.3	21.2		233.0	2.410	7.5	21.0	24.7	97.8	0.2	28.0	429	
990031	39275	30127	19.00	214	4190	32	1.46	2810	5410	45.1	137.0	2.120	17.4	443	37.8	16.4		246.0	1.470	7.2	19.4	37.4	122.0	0.4	62.0	585	
990033	39275	30275	11.30	156	4180	36	0.69	1790	2390	20.8	81.9	1.420	14.4	421	25.6	19.0		538.0	1.380	3.7	9.2	29.6	82.4		21.0	1160	
990035	39325	30225	20.10	296	4750	40	1.82	2630	5270	55.8	289.0	2.060	21.4	450	38.2	29.6		554.0	1.970	10.1	26.6	85.2	399.0	1.7	168.0	1050	
990037	39325	30324	16.40	158	3650	32	0.84	2800	1550	22.6	99.1	1.630	16.0	474	30.3	18.8		551.0	1.420	5.3	11.4	19.4	70.2		45.0	569	6.01
990039	39125	30375	14.70	251	3940	28	1.07	2710	2890	34.7	116.0	1.700	16.0	486	29.4	14.6		224.0	1.480	6.1	18.2	29.6	96.0		51.0	573	
990041	39125	30325	19.80	240	5670	44	1.25	3170	2910	39.7	143.0	2.300	19.0	477	34.6	19.2		224.0	1.460	5.0	14.2	15.1	94.6		31.0	690	
990044	39233	30225	23.50	360	4840	32	1.80	3560	5380	56.6	156.0	2.300	20.6	573	49.0	23.8		922.0	3.190	9.6	26.0	73.8	144.0	0.2	68.0	971	
990047	39176	30075	45.10	488	8350	52	2.33	6700	4080	61.6	258.0	3.700	22.8	717	59.1	26.4		407.0	4.170	16.0	51.2	74.5	217.0	0.9	200.0	542	
990049	39275	30325	17.60	178	4530	32	1.08	2800	1560	24.6	113.0	1.990	17.4	490	31.7	22.6		662.0	1.690	6.2	14.8	25.1	76.2	0.2	28.0	572	5.89
990050	39275	30275	9.48	139	3720	32	0.59	1580	1730	18.5	69.7	1.260	14.8	381	22.7	15.0		499.0	1.270	3.3	7.6	22.3	68.6		18.0	1030	7.20
990052	39075	30075	23.00	276	5980	40	1.68	3770	4370	49.2	193.0	2.320	19.8	512	37.8	20.6		434.0	1.920	8.6	23.8	46.0	194.0	0.5	71.0	805	6.71
990061	39075	30325	14.90	190	3500	28	1.07	2870	4770	44.9	138.0	1.710	17.6	411	29.2	15.0		346.0	1.350	5.5	13.8	25.0	186.0	0.6	67.0	729	
990062	39225	30325	22.80	232	5470	44	1.25	3630	1650	27.5	152.0	2.370	18.6	546	36.5	20.0		384.0	1.620	7.5	17.0	36.9	103.0		51.0	414	
990071	39025	30325	20.20	199	4880	32	1.03	3140	2560	32.9	138.0	2.210	17.6	505	34.2	28.4		296.0	1.600	5.6	16.8	29.5	129.0	0.3	46.0	607	5.99
990072	39277	30374	23.80	226	6540	44	1.09	5400	2430	22.9	128.0	2.480	16.0	504	35.0	17.0		264.0	1.870	7.3	18.0	15.3	66.6		21.0	486	6.90
990073	39275	30225	17.20	215	6870	36	1.04	2240	864	32.6	104.0	2.610	15.8	427	53.4	12.4		472.0	2.770	9.7	14.6	102.0	40.2		11.0	164	
990075	39417	30176	20.80	261	5930	40	1.06	4440	1980	29.4	139.0	2.580	18.4	551	35.4	19.8		314.0	1.730	7.0	17.4	18.0	68.6		27.0	387	6.28
990076	39374	30121	23.30	261	6210	40	1.26	4000	1960	32.2	138.0	2.580	17.0	535	36.0	17.4		238.0	1.750	7.3	19.6	17.7	63.2		24.0	245	
990078	39224	30078	24.70	311	4440	28	2.26	3310	4620	47.9	282.0	2.260	18.2	489	41.6	28.6		350.0	1.770	9.6	38.4	65.1	341.0	0.5	115.0	827	6.81
990082	39024	30270	17.90	225	4460	32	1.13	2250	29500	46.5	116.0	1.910	16.0	425	31.2	20.2	0.5	553.0	1.520	6.9	17.0	24.3	186.0	1.4	68.0	589	
990088	39126	30076	23.30	366	5790	44	1.78	3820	7630	66.5	180.0	2.380	17.8	605	38.7	22.0		587.0	1.950	9.3	24.8	40.2	190.0	0.4	88.0	711	
990089	39325	30275	27.30	253	7280	48	1.31	4600	1620	34.6	152.0	2.890	19.8	525	43.7	25.0	0.6	279.0	2.080	7.4	18.8	68.8	85.6		40.0	474	5.53
990090	39375	30325	32.80	315	8530	56	1.28	5170	1890	34.2	162.0	3.360	19.8	592	46.6	27.2		217.0	2.250	7.0	18.6	19.4	58.6		19.0	283	6.29
990091	39377	30233	21.80	437	5000	36	1.98	3880	6920	57.7	179.0	2.310	19.2	736	37.8	21.0		504.0	1.940	10.6	27.8	41.5	211.0	0.6	84.0	1640	
990094	39175	30325	25.10	308	6480	40	1.39	4590	13200	64.9	219.0	2.490	19.4	544	37.7	19.4		449.0	1.810	8.0	21.6	30.1	92.8		48.0	527	
990096	39024	30075	28.90	231	4030	28	1.04	3140	2160	30.7	177.0	2.760	23.4	617	43.7	39.4		169.0	1.670	4.9	13.4	12.9	87.6		29.0	455	
990102	38874	30026	19.30	204	6210	40	1.39	3140	1000	32.7	111.0	2.220	17.6	439	39.7	14.0		1730.0	2.140	10.4	19.0	15.1	65.8		22.0	647	
990103	38974	30126	19.70	297	4500	36	2.12	2660	6260	62.4	222.0	1.940	18.8	428	41.4	29.2		501.0	1.690	9.1	28.2	48.5	422.0	1.2	282.0	1720	6.44
990104	39175	30283	25.80	335	6880	44	1.22	4190	1340	30.5	132.0	2.740	18.8	468	38.4	21.0		269.0	2.000	7.3	18.0	19.7	49.6		18.0	317	6.24
990105	39124	30434	27.00	381	7070	40	1.42	4470	3790	44.1	140.0	2.620	18.0	450	35.6	14.8		244.0	1.880	8.5	25.2	20.1	126.0	0.3	26.0	310	7.60
990108	39176	30425	23.00	300	5020	36	1.43	4610	6230	47.1	248.0	2.380	19.8	682	42.4	40.0		380.0	2.200	9.9	47.2	294.0	384.0	2.4	214.0	1010	
990109	38924	30271	12.80	139	3350	28	0.85	1990	2550	27.7	117.0	1.400	14.4	324	24.5	29.2		169.0	1.260	5.0	22.2	64.0	633.0	1.7	69.0	993	
990115	39176	30425	27.30	287	7050	44	1.33	4890	3270	36.5	171.0	2.930	20.2	541	41.5	23.8		311.0	2.070	8.8	23.6	67.6	117.0	0.5	51.0	510	
990116	39074	30025	23.90	402	6090	44	2.47	3350	7450	79.7	593.0	2.650	21.2	519	42.8	28.4		336.0	2.450	11.3	33.0	58.3	517.0	0.8	151.0	886	
990118	39025	30022	29.70	313	8430	52	1.48	6820	7630	47.5	210.0	3.210	21.4	548	41.5	20.2		427.0	2.300	10.3	25.2	26.2	172.0		40.0	445	
990119	38974	30274	15.80	183	4120	20	1.05	3840	8190	37.4	140.0	1.570	15.0	361	26.5	16.6		376.0	1.290	6.0	21.4	53.6	216.0	0.8	68.0	824	
990120	38976	30026	31.20	448	6890	44	2.30	5240	8630	65.1	220.0	2.820	22.2	597	45.4	23.6		477.0	2.320	12.0	37.2	234.0	271.0	0.6	123.0	608	7.72
990125	39075	30125	17.40	186	4700	40	0.90	2890	365	22.6	109.0	1.920	14.8	444	29.5	15.0		299.0	1.320	5.4	12.4	18.0	62.2		55.0	590	
990134	39177	30177	23.50	288	5110	36	1.71	3480	3420	50.0	244.0	2.450	21.4	559	42.8	28.4	0.6	271.0	1.720	8.7	24.0	66.5	252.0	0.6	79.0	632	6.78

Appendix 2.4 Data for Wolverhampton subsurface soils
Geochemical data in µg/g unless otherwise stated

No.	East	North	Li	Na	K	Rb	Be	Mg	Ca	Sr	Ba	Al%	La	Ti	V	Cr	Mo	Mn	Fe%	Co	Ni	Cu	Zn	Cd	Pb	P	pH
990142	39016	30124	23.90	262	6290	48	1.27	4800	3150	33.7	216.0	2.480	18.0	455	35.9	45.0		311.0	1.970	9.2	33.0	118.0	937.0	2.7	140.0	1060	
990146	39132	30210	22.90	345	5940	36	1.99	3610	4620	53.7	189.0	2.540	18.4	590	41.6	23.6		496.0	1.860	9.8	25.0	36.5	142.0	0.4	81.0	534	
990148	39176	30222	22.80	293	5770	44	1.48	3310	4670	47.5	199.0	2.540	20.8	479	36.4	22.0		178.0	1.410	6.5	20.6	43.7	232.0	0.8	63.0	1060	
990149	39125	30276	20.70	222	5080	36	1.01	3410	1790	29.4	128.0	2.270	17.2	470	35.3	23.4	1.0	313.0	1.640	6.4	15.8	22.5	86.6		32.0	529	
990152	38863	30091	14.00	164	3730	36	1.20	2140	1000	24.1	113.0	1.600	17.2	425	28.0	22.4		619.0	1.380	6.6	15.4	26.2	130.0	0.2	55.0	530	5.09
990153	38923	30076	18.30	237	5090	40	0.96	2630	1370	27.9	110.0	2.080	20.6	444	29.6	14.6		508.0	1.470	5.4	12.2	44.7	76.4	0.5	24.0	501	
990157	38872	30191	16.80	210	4470	40	1.01	2630	2620	33.2	128.0	1.750	21.8	479	29.8	22.4		631.0	1.500	6.1	14.8	29.2	152.0	0.3	53.0	718	
990159	38974	30126	18.70	286	4680	32	1.57	2680	4380	55.9	158.0	1.940	17.4	425	36.3	20.6		497.0	1.570	7.0	21.0	41.9	234.0	0.6	112.0	1180	
990161	38976	30026	27.60	359	6840	40	1.87	4910	5270	54.7	205.0	2.680	21.0	560	43.0	25.8		422.0	2.090	9.9	30.0	60.2	236.0	0.7	79.0	702	
990164	39125	30175	20.90	266	4990	44	1.27	2870	1260	27.3	129.0	2.170	16.8	513	35.3	21.8		241.0	1.330	6.3	19.0	46.8	143.0	0.5	74.0	838	
990166	38832	30077	36.70	2000	3640	16	10.40	3260	24400	176.0	279.0	2.690	23.2	756	73.9	26.2		760.0	3.910	35.7	128.0	124.0	655.0	2.9	520.0	1100	
990167	39182	30119	36.00	402	6300	48	2.78	4190	5620	72.0	452.0	3.070	22.8	546	50.8	30.0		435.0	2.740	13.1	38.2	147.0	509.0	1.0	187.0	896	7.01
990171	39427	30227	22.00	231	5330	44	1.17	3410	2420	30.4	141.0	2.470	18.4	472	40.8	21.0		200.0	1.520	6.1	16.0	19.5	67.2		49.0	478	
990173	39075	30176	21.10	205	4470	40	0.96	3110	480	22.3	121.0	2.160	17.6	456	32.2	20.2		250.0	1.390	5.6	13.0	11.0	54.0		20.0	406	4.53
990174	38827	30122	23.90	404	5370	44	1.01	2880	1470	28.4	127.0	2.400	21.0	473	34.1	21.4		316.0	1.400	5.3	12.6	13.8	60.4	0.3	38.0	708	
990176	39380	30177	27.20	623	4830	32	2.59	3950	7980	77.4	229.0	2.610	20.4	808	49.4	27.4		594.0	2.360	13.6	37.4	96.0	356.0	1.7	120.0	1330	
990177	38830	30027	24.20	337	6590	36	1.93	4280	5140	52.0	196.0	2.590	18.6	585	40.1	24.2		413.0	2.000	10.1	28.8	37.4	167.0	0.4	109.0	1060	
990178	38915	30224	20.40	273	4440	36	0.95	2750	1950	27.5	181.0	2.060	17.8	459	31.8	52.8		286.0	1.590	6.4	24.2	84.4	663.0	2.4	104.0	1100	
990179	39075	30224	44.50	367	4890	40	1.77	4700	4800	46.3	264.0	3.440	21.8	577	46.3	28.6		599.0	2.290	11.2	30.6	75.0	295.0	0.6	80.0	938	6.92
990180	38778	30025	18.50	347	4690	32	1.05	2340	2640	30.6	130.0	2.130	18.2	459	30.5	15.8		226.0	1.100	4.8	13.0	20.8	99.2	0.2	49.0	630	
990181	38925	30175	21.40	258	5240	36	1.44	3190	2860	37.2	169.0	2.130	19.2	523	38.9	30.6		425.0	1.870	7.9	20.4	70.6	332.0	0.5	109.0	1330	
990182	39125	30175	22.30	235	5580	44	1.03	3070	679	25.5	119.0	2.300	17.4	534	33.3	23.2		546.0	1.520	7.6	13.8	19.0	78.0	0.4	30.0	463	5.22
990183	38916	30032	10.70	131	3720	24	1.23	1590	3340	35.9	89.2	1.530	12.8	362	23.1	14.4		268.0	1.090	5.1	12.4	24.7	90.8		49.0	1170	
990186	39176	30425	23.80	266	5790	40	1.22	3820	4290	34.5	153.0	2.550	19.2	537	38.5	21.0		225.0	1.730	7.1	18.6	32.8	103.0	0.3	43.0	639	6.74
990187	38923	30113	20.80	289	5010	36	1.49	3260	6290	43.6	181.0	2.240	18.8	490	39.9	20.2		463.0	1.820	7.4	21.6	51.6	249.0	0.7	114.0	1050	6.92
990189	38866	30129	8.88	103	3340	32	0.81	1520	799	20.4	73.5	1.240	14.0	310	20.5	8.0		439.0	1.040	3.8	10.4	12.8	67.2		27.0	390	
990192	38978	30072	30.80	623	4530	20	2.96	4110	14700	124.0	259.0	2.550	21.6	681	71.0	31.8		680.0	3.470	17.6	49.6	106.0	362.0	1.5	184.0	1310	
990193	38985	30230	18.10	195	4590	28	0.92	3400	5050	27.0	140.0	1.950	15.2	427	32.3	27.2		231.0	1.330	5.2	14.6	36.0	122.0	0.2	60.0	475	
990202	39622	30031	18.90	265	3960	24	0.96	2360	1380	27.8	117.0	2.100	15.8	485	29.8	19.0		119.0	1.040	4.4	13.4	25.6	94.2		32.0	381	
990203	39326	30080	25.60	281	6020	48	1.59	3590	2220	35.6	174.0	2.740	21.0	548	43.3	31.2	0.7	289.0	1.690	8.0	21.2	48.9	168.0	0.8	119.0	893	
990207	39626	30122	40.90	298	6280	40	1.27	3910	3090	35.9	176.0	3.280	19.8	584	41.7	19.2		287.0	1.690	7.9	19.4	19.9	61.6		21.0	335	
990210	39628	30176	27.80	300	6850	44	1.31	4150	4310	45.5	166.0	2.820	23.0	501	40.9	15.6		370.0	1.950	8.6	20.2	24.3	75.4	0.2	30.0	422	7.40
990211	39325	29975	38.20	541	6080	44	2.75	5030	7430	68.9	302.0	3.740	23.4	818	60.2	36.0		684.0	2.450	12.5	38.0	75.2	301.0	0.8	117.0	783	6.47
990213	39528	30079	26.70	292	6210	40	1.31	4310	2760	36.8	157.0	2.580	19.6	649	39.0	20.4		429.0	1.960	8.7	20.6	31.1	105.0		83.0	637	
990216	39472	30127	19.70	228	3570	24	0.98	2820	2840	29.3	114.0	2.180	16.8	543	31.7	23.8		250.0	1.520	5.7	15.0	28.8	78.6		31.0	614	6.39
990217	39571	30126	27.70	286	7600	48	1.30	4680	2620	37.1	142.0	3.090	19.6	527	41.1	19.2		221.0	2.370	7.3	20.2	21.3	66.8		21.0	326	7.05
990221	39677	30174	53.30	248	4590	40	1.99	2710	3000	48.6	284.0	3.430	22.4	479	52.3	28.0		3350.0	3.610	26.5	37.8	34.4	283.0	0.9	64.0	1080	
990224	39427	30024	21.20	290	4150	32	1.74	3200	9270	57.9	169.0	2.000	17.8	659	41.3	31.4		489.0	2.270	9.6	24.0	137.0	240.0	0.6	98.0	785	
990229	39278	30026	23.70	296	5040	32	1.50	3720	6970	55.0	160.0	2.450	20.0	592	38.1	19.6		327.0	1.760	8.5	22.0	52.2	238.0		76.0	596	7.70
990233	39414	29930	78.60	758	10800	68	3.19	4650	9330	101.0	307.0	5.930	31.4	724	84.7	21.8		629.0	3.000	21.3	54.2	85.6	240.0	1.0	77.0	634	
990236	39625	30075	23.70	249	4790	32	0.92	3630	2850	31.0	116.0	2.510	17.6	515	33.7	23.2		141.0	1.690	6.0	15.6	13.8	67.0		14.0	379	
990240	39325	29975	39.30	433	9230	48	2.06	11500	15400	60.3	291.0	3.740	23.6	628	53.8	25.0		524.0	2.370	11.6	30.2	40.0	107.0	0.4	46.0	680	
990243	39225	30025	27.10	254	5540	40	1.42	3820	1870	36.7	195.0	2.760	19.8	513	39.4	21.6		352.0	1.830	7.8	18.6	27.0	87.8		42.0	385	5.67
990244	39524	30125	27.80	276	7500	44	1.39	6840	8720	44.7	180.0	2.850	22.0	503	39.9	18.8	0.5	398.0	2.050	8.5	22.4	23.4	75.0		23.0	416	
990250	39377	30077	24.20	312	5450	36	1.88	3860	4170	51.9	176.0	2.570	21.2	619	43.6	21.6		375.0	1.970	10.0	25.6	57.3	149.0	0.5	79.0	587	
990252	39475	29775	59.60	674	16700	100	2.75	4860	3570	126.0	353.0	7.320	32.2	648	82.8	12.2		414.0	2.680	19.1	44.4	57.0	154.0	0.8	50.0	582	
990257	39274	30072	28.40	371	7130	40	2.11	4560	6360	53.7	277.0	2.990	23.0	596	50.3	30.6		385.0	2.350	11.5	31.2	76.9	331.0	1.2	129.0	919	7.14
990260	39475	29829	31.70	474	9100	48	1.99	4200	15700	108.0	318.0	3.710	23.6	482	52.7	19.8		485.0	2.510	13.4	36.2	155.0	361.0	0.7	130.0	829	
990262	39419	29975	25.90	541	3980	20	3.89	2400	9170	114.0	227.0	2.140	21.4	472	47.0	35.6		439.0	4.090	14.8	63.6	428.0	408.0	0.8	312.0	680	
990267	39625	30275	31.30	444	8120	48	1.95	5590	12100	74.5	229.0	3.290	24.0	665	50.3	23.4		473.0	2.360	11.1	32.4	98.2	249.0	0.6	89.0	698	7.30
990268	39523	29771	65.60	1050	10900	60	3.24	4690	17700	157.0	390.0	5.990	29.0	747	89.7	24.8		914.0	3.050	21.9	52.2	104.0	300.0	1.2	185.0	1200	
990270	39470	30026	25.90	376	4300	24	2.25	4020	13900	92.8	247.0	2.230	20.0	700	49.8	34.0		893.0	2.910	12.9	34.0	146.0	409.0	1.4	153.0	1480	7.22
990271	39570	30180	17.20	186	4160	28	0.68	2490	2630	26.6	90.5	1.850	15.2	480	27.9	21.0		186.0	1.300	4.3	11.6	16.4	81.0		24.0	277	

Appendix 2.4 Data for Wolverhampton subsurface soils
Geochemical data in μg/g unless otherwise stated

No.	East	North	Li	Na	K	Rb	Be	Mg	Ca	Sr	Ba	Al%	La	Ti	V	Cr	Mo	Mn	Fe%	Co	Ni	Cu	Zn	Cd	Pb	P	pH
990273	39675	30225	16.90	186	5480	36	0.93	1920	812	25.1	106.0	2.310	16.8	475	34.1	14.2		80.4	1.650	3.8	11.6	12.8	55.6		20.0	175	
990279	39482	29865	28.00	2430	2490	12	20.30	2050	34300	312.0	143.0	3.110	38.6	798	113.0	71.8		888.0	7.550	50.8	224.0	1580.0	1040.0	3.5	1040.0	1980	
990280	39466	29928	30.80	371	4800	40	2.20	3730	3130	68.7	234.0	2.670	21.6	632	52.3	25.4		500.0	2.260	12.9	33.0	106.0	280.0	1.5	99.0	892	5.35
990281	39375	30022	16.90	445	2530	20	1.10	9230	5030	45.7	226.0	3.090	13.8	2070	69.1	42.2		922.0	4.140	21.9	51.0	41.5	135.0	0.7	29.0	726	6.24
990282	39520	29925	79.70	593	4830	20	3.71	1750	5150	119.0	111.0	3.550	22.6	762	105.0	26.4		362.0	2.590	30.4	63.6	99.7	228.0	0.9	49.0	982	5.85
990283	39575	29975	32.80	218	4870	40	1.58	3740	1330	29.1	176.0	2.740	18.8	505	48.8	26.4		763.0	3.620	16.8	21.2	24.1	178.0	0.4	39.0	487	5.24
990284	39323	30029	46.90	845	11500	72	3.24	5100	8080	109.0	369.0	4.720	26.2	651	67.0	23.0		592.0	3.020	16.9	56.6	96.3	549.0	1.4	228.0	792	
990291	39375	29975	20.60	238	3750	32	1.62	2610	1130	29.8	131.0	2.080	18.0	568	39.5	21.0		271.0	1.650	9.0	22.2	68.4	221.0	0.7	95.0	854	
990293	39476	30076	29.60	386	5440	40	2.70	3980	5850	70.8	256.0	2.900	22.4	703	51.6	22.0		481.0	2.380	13.4	36.0	144.0	411.0	0.7	97.0	766	6.84
990297	39626	30223	22.40	224	5430	40	0.76	2800	953	25.4	115.0	2.510	17.0	524	33.8	20.8		133.0	1.840	3.6	9.8	10.3	59.4		18.0	234	
990300	39575	30075	23.80	491	2670	20	2.44	6500	4610	51.3	239.0	2.740	17.2	1780	73.2	39.0		911.0	3.440	21.7	55.6	86.3	389.0	1.5	115.0	961	
990303	39425	29720	54.10	711	10500	60	3.30	5890	12200	129.0	415.0	4.840	29.6	834	116.0	32.8		1480.0	4.590	23.0	53.8	98.4	297.0	1.5	135.0	1120	
990308	39378	29728	65.80	589	15800	92	2.43	4820	12700	117.0	384.0	7.310	32.6	697	82.7	13.6		829.0	2.760	17.5	38.8	48.6	119.0	0.6	38.0	586	
990310	39425	29875	32.90	1010	4090	20	6.45	2340	10600	184.0	242.0	3.070	27.4	597	65.4	68.4		738.0	4.850	26.2	120.0	540.0	1430.0	4.2	645.0	1410	
990313	39272	29926	27.10	2280	4190	20	4.87	8560	39800	209.0	367.0	3.110	25.4	2720	75.2	28.8		1900.0	3.820	22.2	56.2	150.0	331.0	1.5	217.0	1240	
990315	39323	29877	27.50	1010	4830	28	3.33	6140	23900	162.0	259.0	2.780	22.4	1280	64.1	45.4		1390.0	3.730	16.7	56.8	779.0	916.0	2.8	439.0	1400	7.63
990317	38976	29975	33.50	488	5570	32	2.01	3360	5020	59.3	291.0	2.640	22.4	805	49.2	25.8		467.0	2.220	13.3	32.0	61.4	160.0	0.5	95.0	867	
990319	39596	29786	38.60	446	10300	60	1.75	4950	9360	73.0	263.0	4.270	23.4	644	57.7	26.0		301.0	2.140	11.4	32.6	64.1	169.0	0.3	41.0	466	
990320	39289	29875	56.30	528	13700	84	3.84	4570	5210	125.0	543.0	6.340	32.4	670	105.0	20.8	0.6	844.0	4.510	26.8	58.0	134.0	282.0	1.2	154.0	1260	
990321	39422	29824	36.20	481	6230	40	2.31	5370	21700	115.0	368.0	3.450	24.8	662	54.6	34.4		969.0	2.170	11.5	30.4	80.9	228.0	0.8	83.0	605	
990323	38773	29975	17.50	194	4570	28	1.04	3000	1320	22.5	118.0	1.970	15.6	431	31.0	19.4		334.0	2.070	7.3	15.2	12.6	43.0		18.0	230	6.60
990325	38675	29832	13.30	179	3250	32	0.90	1910	1730	28.8	96.0	1.540	14.6	414	28.3	17.8		736.0	1.260	5.1	10.2	13.8	64.8		26.0	514	6.06
990329	39477	29721	58.10	876	12700	64	4.86	5590	18300	208.0	376.0	5.650	33.4	776	90.0	28.4		1240.0	3.310	32.3	68.2	136.0	1050.0	2.7	248.0	1990	
990330	38628	29874	12.70	158	3760	28	0.73	2080	1180	19.6	93.7	1.530	12.2	428	22.8	15.4		468.0	1.210	4.4	9.4	11.8	54.2		25.0	556	
990334	39378	29826	53.20	747	17900	104	2.81	6190	3770	104.0	506.0	7.670	34.4	646	80.8	9.0		408.0	2.390	19.6	47.0	87.0	161.0	0.5	47.0	516	
990335	38775	29877	8.64	96	3270	24	0.73	1660	979	15.2	59.8	1.380	11.4	292	17.4	8.0		204.0	0.955	3.2	7.4	7.9	42.6		19.0	353	
990337	39225	29887	27.00	1830	3460	24	3.91	6880	24800	207.0	467.0	2.880	23.2	1080	70.5	30.2		1550.0	4.140	22.9	63.4	297.0	858.0	3.3	416.0	1620	
990343	39319	29930	29.50	393	5540	32	2.17	3640	8140	69.5	202.0	2.700	18.4	500	48.6	19.8		463.0	3.200	13.5	34.6	174.0	307.0	0.4	106.0	672	
990344	38775	29924	16.30	275	4090	24	1.68	3080	12500	70.3	177.0	1.710	15.4	454	32.5	17.0		387.0	1.590	9.0	23.8	47.8	230.0	0.5	149.0	1050	
990345	38785	30073	19.40	207	5160	40	0.94	3360	1590	25.2	110.0	2.030	15.4	490	30.3	17.0		362.0	1.550	6.0	14.4	14.5	48.0		22.0	422	
990348	38759	29823	19.60	232	6300	40	1.42	4100	4110	36.2	119.0	2.340	17.8	354	30.9	14.0		312.0	1.590	7.1	18.6	20.5	62.4		137.0	381	
990350	39375	29775	89.20	594	12000	72	2.54	3170	3150	93.1	333.0	7.710	27.2	820	87.5	25.8		335.0	1.710	14.3	36.2	73.3	236.0	0.9	57.0	483	
990351	38677	29875	14.30	170	4170	32	0.85	2360	1980	23.3	108.0	1.740	15.6	425	27.1	16.4		572.0	1.370	5.0	11.2	12.0	67.0		27.0	459	
990352	38725	30067	10.70	131	2940	32	0.72	1500	1890	28.7	83.6	1.310	13.2	350	23.5	13.8		414.0	1.080	4.1	10.0	10.7	55.8		25.0	559	
990354	39271	29725	33.20	414	6060	36	2.39	2560	7280	88.9	272.0	3.810	22.2	733	69.6	24.4		570.0	3.310	15.2	36.6	106.0	266.0	0.7	76.0	738	
990357	39209	29827	25.70	453	5110	24	1.76	4880	19300	98.7	233.0	2.380	20.4	562	45.8	36.2		754.0	2.340	10.2	27.8	115.0	466.0	1.0	175.0	728	
990358	39227	29972	45.50	353	7360	64	1.80	5930	4950	50.0	261.0	4.050	23.2	694	53.1	28.8		481.0	2.670	11.0	28.2	47.2	155.0	0.2	71.0	734	
990362	39324	29824	33.40	450	7930	52	2.76	2970	7840	89.0	262.0	3.840	22.6	589	75.0	17.8		611.0	3.360	16.6	40.8	128.0	266.0	0.9	167.0	959	
990367	39371	29875	65.90	860	21600	128	3.06	6850	3270	126.0	543.0	8.900	35.8	783	85.6	8.2		453.0	2.650	20.5	47.6	62.2	168.0	0.5	56.0	764	7.00
990369	38927	29930	34.80	431	10300	60	1.66	6290	2590	41.6	180.0	3.650	19.4	583	60.2	20.2		1410.0	3.030	14.9	27.4	37.4	73.0		35.0	485	
990370	39421	29781	26.50	451	5840	40	2.04	4000	6290	54.0	196.0	2.650	20.0	641	45.2	21.0		421.0	2.170	11.2	30.6	74.0	160.0	0.4	89.0	679	
990371	38875	29975	23.90	807	3340	20	4.54	2710	13100	370.0	224.0	2.030	23.6	576	52.5	61.8		793.0	2.230	26.0	80.4	102.0	302.0	1.4	180.0	1580	
990372	38876	29875	14.00	148	4000	32	0.87	2220	824	18.9	93.5	1.610	16.8	401	24.3	17.8		459.0	1.160	4.9	10.6	18.5	63.8		46.0	519	5.10
990375	38920	29975	27.10	342	5720	40	2.08	3960	4130	46.8	178.0	2.510	20.6	542	41.6	25.6		331.0	1.930	9.7	30.2	39.9	140.0		62.0	809	
990377	38830	29936	3.90	52	2230	16	0.36	862	340	10.9	35.9	1.090	4.8	190	11.6	6.4		137.0	0.613	1.7	5.6	3.3	9.8			78.4	6.97
990379	39268	29835	25.20	520	3750	16	3.45	5030	17400	115.0	185.0	2.630	18.4	582	76.7	68.0		1100.0	6.230	54.1	89	4380	6070	14.2	3330	1400	
990384	39209	29827	27.60	505	5840	32	1.85	5120	20500	105.0	260.0	2.620	20.4	654	59.6	106.0		786.0	2.860	12	33.4	187	621	1.4	215	874	
990385	39334	29778	65.20	636	14500	80	2.57	4770	13900	176.0	351.0	6.880	29.4	774	81.5	31.8		646.0	2.510	18.6	56.8	185	1310	6	209	1610	
990388	39282	29971	36.40	403	3890	20	3.16	2860	9680	107.0	223.0	2.470	20.8	641	58.4	24.8		575.0	2.880	18.6	49.8	117	571	1.1	284	1040	
990389	38721	30021	24.60	237	6280	40	1.06	4480	1300	25.3	122.0	2.490	19.0	532	36.6	20.4		425.0	1.800	8.8	20.6	11.3	55.8		14	398	
990391	39528	29834	29.30	482	7630	48	1.91	4020	7420	69.7	223.0	3.390	23.2	626	55.2	21.4		562.0	2.570	12.9	35	72	236	0.8	71	788	
990392	38880	29936	20.60	210	6000	36	1.33	4240	2660	28.8	123.0	2.330	18.2	401	31.0	15.8		341.0	1.740	6.7	19.4	16.3	45.2		16	339	
990395	38712	29826	24.30	248	7520	40	1.34	5720	3040	33.1	144.0	2.550	20.2	426	35.0	13.4		520.0	1.790	8.7	24.4	16.3	59.8		93	471	7.23

Appendix 2.4 Data for Wolverhampton subsurface soils
Geochemical data in µg/g unless otherwise stated

No.	East	North	Li	Na	K	Rb	Be	Mg	Ca	Sr	Ba	Al%	La	Ti	V	Cr	Mo	Mn	Fe%	Co	Ni	Cu	Zn	Cd	Pb	P	pH
990399	39324	29726	63.00	760	17200	100	2.95	4640	7980	141.0	419.0	7.380	32.4	690	85.3	11.8		497.0	3.050	19.1	50.8	83.8	248	0.9	66	638	
990400	39215	29924	26.90	503	4670	40	2.74	3780	11400	101.0	430.0	2.570	22.4	733	50.3	60.6		686.0	2.530	14.3	43.2	303	997	2.9	489	1490	7.49
990402	39023	29978	19.70	273	4720	32	1.14	3250	10100	59.7	232.0	2.290	19.4	440	32.6	17.0		201.0	1.370	6	15.4	18.8	118		66	498	8.04
990405	39426	29870	32.60	545	6180	32	3.03	7670	42200	155.0	334.0	3.160	22.6	694	146.0	57.2		2860.0	3.570	11.1	34.2	66.8	213	0.9	60	1640	
990408	38968	29925	27.10	363	6150	44	1.33	4210	2830	44.1	162.0	3.050	21.8	670	40.7	23.4		214.0	1.670	7	20	23.6	86.8		23	436	
990409	38822	29888	9.84	104	3700	20	0.93	1930	1560	20.5	64.3	1.520	14.4	339	18.5	12.2		160.0	1.070	3.2	8.6	8.6	38.4		29	376	6.40
990411	39423	29628	94.00	791	17200	108	3.14	3860	7980	315.0	341.0	7.870	34.4	722	92.9	33.6		693.0	2.470	18.2	43.2	62	208	0.9	89	1370	
990412	39428	29673	28.70	335	8450	48	1.53	6360	4120	49.5	280.0	3.230	22.6	595	47.2	18.4		1240.0	2.520	10.9	29	26.8	109	0.2	30	511	
990418	39024	29877	41.50	415	5280	28	3.22	3290	4060	72.4	209.0	3.020	21.6	892	61.2	27.2		463.0	2.240	16.7	46.2	90.5	306	0.9	156	1490	5.70
990422	39076	29825	21.70	418	3650	20	2.13	2680	15900	95.4	141.0	1.970	18.6	536	44.6	16.0		364.0	2.040	10.6	35	87.6	194	0.4	104	630	
990427	39426	29521	18.20	220	4030	32	1.45	2470	4550	41.1	133.0	1.930	16.6	490	37.6	77.0		474.0	1.650	7.1	20.2	45.2	131	0.4	75	662	
990429	39163	29925	24.10	367	5820	32	1.90	3450	20100	106.0	200.0	2.520	21.8	584	48.2	24.2		617.0	2.680	12.4	28.8	184	280	0.9	136	768	
990431	38996	30167	35.00	407	8820	52	1.82	6610	7190	49.0	252.0	3.230	20.8	575	47.5	34.2		303.0	2.570	12.1	36.2	94.5	389	1.2	132	832	7.20
990433	39076	29977	13.60	228	4620	28	1.15	3060	6450	55.7	166.0	1.570	16.8	449	28.5	18.6		362.0	1.350	5.8	16.6	52.5	139	0.4	71	861	
990435	39076	29825	25.10	468	4040	16	2.24	4270	1e+05	177.0	183.0	2.080	19.0	444	40.3	21.0		424.0	2.410	11.2	35.6	88.9	467	1.8	190	802	
990437	39021	29829	32.20	524	8730	48	2.16	6760	7390	70.9	286.0	3.230	22.0	662	47.7	23.8		657.0	2.750	12.5	35.8	75.9	197	0.3	157	771	7.82
990439	38982	29872	33.50	416	7940	52	2.16	5500	5950	59.5	226.0	3.460	23.2	694	54.5	28.2		437.0	2.480	12.9	31.4	97.7	262	0.9	168	794	
990448	39121	29972	16.20	213	4820	28	1.08	3440	4670	48.6	108.0	1.740	14.2	441	26.1	15.6		305.0	1.290	5.4	16	21.9	70.2		24	341	
990450	39121	29816	24.70	748	5040	28	3.09	4630	17300	109.0	316.0	2.750	22.6	814	59.6	28.4		1160.0	3.570	15.7	49	779	901	4.4	447	1190	7.60
990453	39133	29927	17.00	260	4610	28	1.19	3570	27000	78.9	175.0	1.910	17.2	471	31.4	19.4		300.0	1.680	7	19.2	60.2	139	0.3	177	526	7.80
990455	38824	29970	20.50	285	6050	40	1.53	4070	15700	78.2	170.0	2.230	18.8	478	34.9	13.8		639.0	1.730	7.7	19.8	24.6	59.6		139	506	
990457	39223	29779	21.50	229	4840	32	1.09	3330	2180	26.1	119.0	2.170	17.2	473	46.2	25.6		525.0	2.050	7.6	18.6	26.1	91.2	0.2	30	670	6.31
990458	39177	29821	22.70	312	6110	40	1.74	5480	8570	57.3	167.0	2.400	18.6	565	40.6	44.2		713.0	2.050	9.1	25.4	33.1	118	0.3	70	630	7.90
990460	38968	29925	25.10	367	4990	36	1.80	3830	3130	42.1	174.0	2.730	19.2	719	49.3	27.4		392.0	1.870	10.1	26.6	57.7	246	1	89	792	
990463	39020	29928	26.90	339	6630	40	1.87	5700	7680	48.5	177.0	2.820	18.6	587	43.0	22.6		313.0	2.150	10.5	27.8	48.9	131		92	570	7.25
990465	39076	29925	35.50	403	6890	48	2.73	4560	4680	90.0	283.0	3.150	23.0	650	59.5	26.6		591.0	2.950	16.8	41.6	112	278	0.9	151	1740	
990468	38882	29826	28.10	341	8320	48	1.41	6490	6460	59.8	187.0	3.040	21.0	577	42.1	23.2		423.0	2.210	9.3	24.6	24.8	84	0.3	27	378	
990469	38924	29824	20.50	209	4730	32	1.15	3490	2720	32.7	126.0	2.290	17.0	455	34.7	17.2		217.0	1.530	6.2	17.2	21.8	74		52	664	
990470	39277	29777	21.40	385	3560	24	2.22	2710	7740	87.1	325.0	2.050	20.8	554	42.1	27.2		732.0	3.070	13.5	42.6	1130	1040	2.4	278	736	
990477	38718	29877	12.60	158	5350	44	1.39	2420	1490	30.5	120.0	2.010	15.6	416	27.4	15.8		981.0	1.400	7.8	12.4	14.1	68.2		32	443	5.49
990479	39072	29881	20.30	226	4560	36	1.64	2840	1450	34.2	160.0	2.210	18.6	504	40.5	23.2		307.0	1.920	9	20.2	94.3	140	0.3	130	1340	4.83
990482	39076	29925	29.60	372	7110	48	2.24	4300	4990	66.6	281.0	2.890	21.0	599	50.5	26.8		580.0	2.560	12.6	34.4	115	360	1.2	163	1670	6.10
990484	38776	29785	24.50	256	6380	44	1.35	4020	1880	35.4	147.0	2.740	18.4	533	40.3	25.6		278.0	2.000	7.9	18.6	40.4	84.8		42	385	5.80
990485	39127	29885	17.10	267	3820	24	1.50	2020	8010	51.9	147.0	1.960	13.6	468	36.8	17.8		451.0	1.640	7.9	17.6	32.5	127	0.3	67	598	
990489	38981	29826	20.50	267	4810	32	1.62	3450	9600	52.8	191.0	2.210	17.2	490	37.1	20.2		350.0	1.790	8.4	23	48.4	280	0.5	101	626	
990493	38721	29777	39.60	351	10100	60	1.63	7800	2610	43.3	185.0	3.870	21.6	664	48.9	24.8		397.0	2.610	11.1	28.2	25.5	94.2		25	358	7.13
990494	39172	29878	20.10	277	5440	40	1.00	2360	4060	31.8	132.0	2.230	16.4	410	34.0	17.4		405.0	1.710	6.8	15.8	18.8	104		33	562	
990495	39474	29621	19.70	338	3920	24	1.48	4060	18900	76.5	256.0	1.780	17.8	528	40.4	27.2		556.0	2.900	10.6	29.2	139	272	0.7	173	971	
990496	38830	29829	23.80	260	6290	40	1.45	4200	5190	40.7	167.0	2.580	19.2	523	40.1	22.8		286.0	1.760	7.7	20.4	34.5	129	0.3	49	557	
990498	39479	29573	27.90	1260	3630	16	5.40	2400	24200	183.0	249.0	2.660	24.6	698	78.5	90.2		1260.0	5.240	28.4	107	525	1370	5.3	504	1410	
990500	39226	29725	40.90	460	7910	48	2.65	3260	10300	103.0	351.0	4.190	25.4	602	58.1	21.6		616.0	2.960	16.1	43	468	431	1.2	161	741	
990507	39329	29528	22.40	309	4960	24	1.34	3470	12500	57.8	153.0	2.240	16.2	486	48.1	166.0		822.0	1.820	7.1	25	44.8	234	0.7	73	386	
990509	39577	29729	67.00	717	17600	108	3.18	5430	6970	112.0	493.0	8.840	36.4	734	93.8	7.6		498.0	2.130	26.8	57.4	61.5	256	1	50	390	
990511	39365	29481	47.20	637	10500	64	2.40	4050	29900	203.0	278.0	4.640	27.0	600	72.0	21.6		817.0	3.270	15.6	41.2	91.8	322	1.2	99	827	
990512	39587	29670	32.50	1100	4820	24	3.64	3870	20700	122.0	294.0	3.310	23.0	779	94.2	90.4		971.0	4.040	22.4	103	574	1100	5.8	400	1980	
990514	39134	29724	32.40	684	4540	24	4.99	3520	18700	165.0	340.0	2.700	25.6	745	67.0	61.8		905.0	3.780	23.7	66.8	251	1100	4	446	2100	
990516	39575	29525	31.20	383	5370	32	2.71	2370	3230	85.3	178.0	3.020	21.4	612	114.0	38.6		1810.0	6.180	22.6	52	151	285	1.7	398	1480	
990518	39627	29721	71.50	860	17800	100	3.33	5370	4510	135.0	364.0	7.890	32.2	797	92.3	20.8		645.0	3.020	23.9	57.6	243	435	1.5	229	671	
990519	39328	29428	61.60	423	8820	56	3.40	2860	6070	94.5	251.0	5.950	29.2	726	90.2	23.0		713.0	2.850	22.6	42.8	75.1	175	0.5	83	924	
990521	39124	29762	29.10	426	4660	32	2.58	3520	6060	62.8	244.0	2.550	21.2	680	52.3	25.8		551.0	2.130	15	39.8	135	341	1	177	979	6.40
990523	39371	29679	37.80	481	10200	52	2.87	13100	17500	76.1	283.0	3.500	24.6	565	53.3	23.2		625.0	2.520	14.2	39.6	77.9	199	0.5	83	749	7.71
990524	39374	29634	16.40	200	4330	40	0.97	2690	2760	28.5	114.0	1.960	16.8	505	31.8	19.4		419.0	1.380	5.6	13.8	24.5	96.8	0.3	37	601	
990525	39326	29572	31.60	472	5750	32	2.27	3520	12600	83.5	285.0	3.020	20.8	619	52.7	28.2		484.0	2.820	13.3	38.8	113	491	1.4	159	1260	

Appendix 2.4 Data for Wolverhampton subsurface soils
Geochemical data in µg/g unless otherwise stated

No.	East	North	Li	Na	K	Rb	Be	Mg	Ca	Sr	Ba	Al%	La	Ti	V	Cr	Mo	Mn	Fe%	Co	Ni	Cu	Zn	Cd	Pb	P	pH
990529	39223	29526	43.20	343	7570	52	2.89	3440	7020	87.5	217.0	5.740	22.6	721	91.1	21.2		931.0	4.280	21.2	38.4	77.6	241	0.6	103	1200	6.50
990530	39082	29778	15.00	467	4030	28	1.09	2740	11500	68.1	201.0	1.650	16.8	505	27.8	20.4		312.0	1.520	6.9	17	147	525	0.5	94	558	
990531	39324	29638	18.00	256	4430	28	1.36	2150	6190	46.6	216.0	2.300	20.0	464	44.8	24.8		658.0	2.750	11.5	29.4	536	821	4.5	785	663	
990532	39225	29469	24.80	276	14700	84	1.78	10400	17100	70.9	253.0	3.890	31.0	550	50.9	14.6		539.0	2.690	11.9	35.2	18.4	76.6	0.3	34	561	7.70
990533	39618	29682	51.90	486	10300	72	2.42	3770	3900	87.8	249.0	5.100	26.2	623	72.4	23.6	0.4	489.0	2.290	14.5	37.2	89.1	262	1.1	110	838	
990534	39572	29636	33.80	545	8350	48	2.60	3650	10400	107.0	279.0	3.820	23.6	587	58.2	26.0		503.0	2.440	12.9	37.4	105	391	1.1	168	761	
990537	39325	29475	39.10	559	14000	88	2.41	3790	2380	83.9	287.0	6.470	30.8	650	68.8	8.6		356.0	2.050	18.5	34.6	38.6	169	0.7	57	584	
990542	38977	29726	22.70	243	5010	36	1.52	3760	3250	32.5	158.0	2.500	18.8	535	40.8	21.6		356.0	1.880	8.5	21.8	41.6	114	0.3	69	484	6.53
990544	39618	29468	38.20	561	9870	60	2.33	3890	11800	107.0	272.0	4.860	24.2	644	63.6	12.8		674.0	2.540	14.4	35.6	65.9	169	0.4	53	538	7.62
990547	39528	29673	37.60	431	8700	52	2.14	5100	14500	140.0	249.0	3.680	24.4	523	54.8	20.0		620.0	2.860	13.2	32.6	46.6	156	0.5	80	1040	
990549	39380	29517	17.40	242	7740	36	1.94	4030	6190	39.6	112.0	2.550	21.2	478	34.1	37.8		394.0	2.070	5.9	19.6	25.9	165	0.3	37	625	
990550	39280	29474	22.00	265	13600	84	2.01	7780	2490	40.0	321.0	4.440	28.4	668	55.6	20.0		913.0	3.100	13.7	34.4	27	132	0.5	40	483	
990553	39273	29529	19.10	192	2540	20	1.72	1230	5560	39.7	163.0	2.260	18.0	489	44.8	21.6		939.0	2.790	15.2	18.2	29.3	194	0.3	60	715	
990557	38935	29785	22.90	229	5540	44	1.22	3720	1150	27.5	129.0	2.450	18.0	482	35.5	20.0		289.0	1.680	6.9	17.4	17	79	0.2	30	414	5.34
990561	38894	29787	24.20	240	5400	40	1.34	4230	1890	35.0	140.0	2.630	19.4	537	37.6	18.8		174.0	1.810	7.8	20.8	21.5	67.8		35	325	
990562	39478	29677	39.50	656	7910	44	3.84	5880	26900	194.0	370.0	4.060	30.0	881	85.9	27.6		1300.0	3.070	24.9	53	157	544	2.5	710	1530	
990568	39224	29571	29.90	322	7990	44	1.56	5360	9270	58.0	239.0	3.610	21.4	515	49.5	44.2		814.0	3.440	11.6	35.4	64.8	200	0.8	124	708	
990570	39224	29674	66.10	639	17200	100	3.03	5860	3080	127.0	517.0	8.050	33.6	724	86.1	11.4		376.0	2.130	19.2	46.6	48.1	134	0.8	47	547	6.30
990572	39278	29426	37.70	361	21300	112	2.67	14400	4220	49.8	322.0	5.810	37.8	607	71.9	18.8		568.0	3.750	17	59	30.8	95.2	0.5	29	429	
990575	39177	29770	30.40	1020	3610	20	4.27	4200	24900	186.0	250.0	2.640	24.2	1270	76.8	25.4		876.0	4.310	29	67.6	237	384	2	286	1320	7.81
990576	38827	29777	34.80	372	9120	56	1.65	7290	3030	40.9	199.0	3.400	23.4	575	46.7	19.8		414.0	2.340	10.9	29.4	22.1	61.2	0.2	23	347	7.38
990578	39196	29728	23.80	432	5090	36	2.76	3250	17300	91.8	273.0	2.450	21.4	612	45.9	24.2		499.0	2.150	13.3	40.2	110	405	1.1	183	1090	
990580	39531	29725	65.70	567	17400	112	2.99	6860	4250	95.7	411.0	7.600	34.4	735	85.0	11.2		362.0	2.520	22.1	48	80.4	201	0.7	74	874	
990585	38978	29778	25.50	358	5120	40	3.11	3660	5250	66.5	197.0	2.730	23.4	637	50.4	23.6		424.0	2.010	14.4	36.2	110	211	0.7	195	793	6.20
990591	39576	29475	32.90	377	5200	36	1.59	3110	23100	134.0	119.0	2.610	20.2	561	46.3	25.8		867.0	2.430	10.9	26.8	55.5	397	0.6	75	684	
990592	39524	29474	42.20	311	10500	76	2.57	4790	3990	56.8	221.0	6.930	27.4	694	103.0	16.0		1040.0	4.600	17.7	30.2	63.1	121	0.8	45	582	6.62
990593	39319	29682	30.50	320	6400	40	1.80	3310	15000	72.3	234.0	3.530	22.2	515	56.0	21.8		798.0	2.470	13.4	31.2	83	300	1	81	710	
990597	39524	29528	37.50	463	5050	32	3.24	3220	19300	173.0	217.0	3.430	23.0	816	80.4	29.0	0.5	1060.0	5.770	26	53	98.6	219	2.1	116	2040	
990598	39275	29575	31.90	414	8400	48	1.80	2950	9740	55.2	237.0	5.060	22.4	860	64.7	14.4		505.0	2.760	13.3	27.4	64.3	1510	1.8	92	530	
990599	39278	29623	35.20	328	8560	52	1.64	4300	10600	69.7	273.0	4.360	21.6	622	60.7	10.8		461.0	2.100	11.5	26.4	51.7	168	0.3	69	402	
990600	39328	29428	34.50	229	5740	36	1.71	2780	2160	39.3	152.0	3.460	19.8	574	58.0	18.8		362.0	1.730	10.5	24.2	45.9	176	0.6	82	790	
990603	39077	29574	29.20	292	6870	56	1.14	2840	1590	37.4	177.0	3.220	20.4	602	45.7	21.4		229.0	1.610	6.8	15.4	30	71.4		36	430	
990605	38875	29528	13.90	142	4110	32	0.84	1930	1810	25.5	119.0	1.660	15.4	353	25.7	8.2		564.0	1.370	4.9	10.4	14.2	51.2		24	634	6.56
990607	39218	29624	15.10	264	4000	24	1.34	2170	5420	41.9	199.0	1.920	15.0	497	34.9	24.8		440.0	2.070	8.9	42	49.2	176	0.5	155	514	
990610	38924	29569	13.90	144	3700	36	0.90	1950	524	17.2	89.0	1.780	14.4	432	26.9	16.6		692.0	1.410	5.2	10	15.8	52.4		23	452	4.84
990611	39571	29581	44.00	861	5740	24	4.75	7140	48900	300.0	300.0	4.260	28.4	1260	131.0	39.6		2440.0	5.160	22.8	49.6	120	327	1.9	192	2010	
990612	39076	29725	23.40	268	5410	36	2.24	3480	7170	59.2	249.0	2.970	19.6	591	48.3	19.4		684.0	2.520	11.8	30	199	269	0.7	193	1170	6.82
990615	38874	29725	21.00	238	5350	32	1.28	3700	1970	32.3	125.0	2.240	15.6	424	33.4	16.0		241.0	1.690	7.8	20.4	21	108		34	470	
990616	39624	29526	55.10	818	16400	92	2.95	5940	7540	138.0	373.0	6.620	30.4	707	91.4	24.6		1540.0	4.860	20.9	57	75.7	185	1.4	62	918	
990617	38870	29633	23.60	329	5100	40	1.58	3460	3420	39.7	174.0	2.260	18.4	484	38.2	24.2		394.0	1.770	8.7	26.2	124	252	1.2	119	629	6.75
990618	38880	29677	21.80	256	5270	36	1.33	3640	2960	35.9	149.0	2.200	17.8	543	36.5	25.0		364.0	1.710	8	21.2	33.3	126	0.3	60	484	
990621	39130	29532	26.60	238	6530	48	1.15	3600	2210	31.2	290.0	3.040	21.0	588	45.3	22.6		738.0	2.200	9.4	17	16.8	61		21	346	
990622	39173	29623	29.80	178	3890	40	1.15	2190	2080	31.8	207.0	2.440	17.6	421	36.2	20.8		571.0	1.940	8.3	15.6	15.8	76.6		31	362	
990624	38821	29532	14.30	233	4000	28	0.92	2110	4830	38.5	400.0	1.640	14.0	418	24.7	31.8		433.0	1.530	6	16.6	79	443	2.7	305	1060	7.00
990626	38875	29574	17.30	193	4360	40	0.96	2810	1880	24.4	131.0	1.920	17.8	427	29.7	17.4		327.0	1.340	5.5	13.2	39.5	74		40	429	6.30
990627	38821	29723	17.80	234	4980	36	1.15	3440	4110	32.6	151.0	2.030	16.4	466	31.2	16.8		450.0	1.500	7.7	18.2	27.3	94		125	427	7.10
990628	38824	29573	15.10	163	4980	28	0.98	2680	8810	41.4	113.0	1.900	16.8	421	26.5	16.6		397.0	1.350	5.1	12	11.2	115		38	502	7.31
990631	39522	29622	35.50	507	11600	56	1.57	12600	17000	65.5	260.0	3.450	24.2	601	45.5	21.4		657.0	2.550	11	31	46	234	0.6	166	616	
990635	39026	29532	20.00	221	5840	40	1.19	3850	6650	43.0	138.0	2.510	19.8	506	40.5	20.4		524.0	2.000	7.4	17.2	29.2	88.8	0.2	37	529	7.62
990636	38979	29576	21.80	296	4880	36	1.80	3860	3970	41.1	151.0	2.200	20.0	572	38.5	21.4		429.0	1.880	9.3	24.4	41.8	123	0.3	65	798	6.57
990640	39031	29722	26.30	288	5190	44	1.79	3800	3830	41.9	251.0	2.630	21.2	529	42.5	20.6		361.0	1.790	9.2	24.2	64.1	209	0.6	96	674	6.23
990645	39131	29577	46.50	344	15900	80	2.12	10400	2850	31.3	348.0	5.320	22.8	616	84.0	11.6		1180.0	4.280	18.1	25.4	33.3	99.8	0.6	32	305	6.94
990650	39122	29624	45.00	433	9830	64	1.67	3860	2070	51.2	217.0	4.350	22.6	481	58.1	17.6		397.0	3.190	11.2	29.4	32.1	223	0.4	44	514	6.60

Appendix 2.4 Data for Wolverhampton subsurface soils
Geochemical data in µg/g unless otherwise stated

No.	East	North	Li	Na	K	Rb	Be	Mg	Ca	Sr	Ba	Al%	La	Ti	V	Cr	Mo	Mn	Fe%	Co	Ni	Cu	Zn	Cd	Pb	P	pH
990651	38976	29679	17.50	225	4060	28	1.86	3150	4440	40.6	370.0	2.080	17.4	469	37.8	22.0		295.0	1.580	8.8	23.4	43	153	0.4	111	531	6.94
990656	39069	29625	23.40	487	4000	32	2.40	3200	18600	99.4	218.0	2.300	19.2	603	56.6	34.6		1020.0	2.280	10.8	32.6	91.4	304	1.1	180	1740	
990657	39080	29671	24.00	187	5280	36	1.49	2980	3770	42.6	145.0	2.900	14.0	470	41.5	12.8		463.0	2.350	8.7	19.2	78.9	256	0.3	87	1290	
990658	38923	29679	26.50	364	5270	36	1.62	3840	7050	54.1	182.0	2.390	20.2	554	39.5	30.6		423.0	1.820	9.2	26.8	51.7	261	1.5	57	610	7.51
990661	39275	29675	40.40	377	10100	64	2.39	3720	5180	105.0	530.0	5.450	27.6	600	71.6	17.6		521.0	2.770	17.2	40.6	103	392	0.6	865	782	
990662	39025	29578	11.80	125	4320	24	0.82	2620	834	14.8	83.7	1.420	11.8	336	21.0	10.2		190.0	1.060	5.1	12	17.9	32.4		9	164	7.05
990672	38822	29624	19.20	184	4120	40	0.88	2620	1100	22.9	104.0	2.120	14.8	463	27.7	17.4		353.0	1.230	5.5	11.2	5.1	33		10	274	5.95
990674	39522	29581	13.80	175	3100	28	1.10	2000	2530	29.2	97.7	1.550	16.4	461	39.7	31.4		576.0	1.830	6.6	16.6	23.2	84.4		46	654	
990677	39018	29671	32.60	543	4690	32	3.20	3540	9660	86.0	283.0	2.480	21.0	576	58.2	30.6		448.0	2.760	17.7	49.2	150	251	0.5	161	1180	7.28
990679	38980	29623	21.60	235	4610	36	1.37	3110	2100	35.0	140.0	2.120	19.0	498	39.3	20.2		266.0	1.540	7.8	20.4	30.2	118	0.3	68	608	5.93
990681	39172	29573	28.80	193	5190	48	1.43	2450	1720	35.8	212.0	3.550	25.0	621	49.2	24.8		490.0	1.820	7.9	17	19.5	146	0.7	51	589	5.36
990684	38984	29525	23.00	219	5130	44	1.29	3400	2010	31.1	145.0	2.370	18.2	465	37.3	18.2		516.0	1.630	7.3	17.8	22.1	79.8	0.2	39	540	6.20
990685	39131	29671	16.70	258	4180	32	0.86	2410	4540	36.7	163.0	1.880	15.0	501	29.8	33.0		254.0	1.170	5.2	13.6	35.1	214	0.4	97	685	
990686	38920	29532	37.90	454	10400	68	1.72	3630	1830	49.1	228.0	3.900	22.4	585	51.7	23.0		345.0	2.540	8.2	21.8	111	161		58	1060	5.51
990687	39022	29625	24.40	300	5290	36	1.48	3350	7840	48.0	189.0	2.390	18.8	531	39.2	17.0		227.0	1.660	7.9	25	32	191	0.3	122	392	7.57
990689	38828	29673	22.60	298	5310	32	1.23	6260	13300	42.7	207.0	2.310	18.2	508	71.3	363.0	0.8	1500.0	2.500	8.4	29.6	53.5	344	1.1	92	910	
990690	39178	29674	37.70	679	3350	12	3.73	1710	9590	139.0	404.0	2.360	19.0	721	70.0	117.0		797.0	8.510	31.9	212	1010	493	2.9	212	705	
990697	38874	29725	25.00	277	6380	40	1.50	4490	2330	35.5	164.0	2.580	19.4	487	38.9	18.8		334.0	1.960	9	24.8	27.6	130	0.2	36	579	6.50
990698	38924	29630	24.30	317	6030	52	1.32	4250	2180	52.8	1050.0	2.630	19.2	608	40.5	19.2		355.0	1.840	7.7	19.4	23.7	97.6	0.4	79	467	5.94

APPENDIX THREE

PRINCIPAL COMPONENTS ANALYSIS
OF
RICHMOND TOPSOIL DATA

Appendix 3-1 Identification of processes influencing the concentrations of elements in Richmond soils

Through the use of multivariate statistics it is possible to infer which processes are important factors in influencing the distribution of elements in soils. In section 6.3 it was shown that a number of elements were present at higher concentrations in urban gardens than in areas of open space, and it was postulated that this was the result of anthropogenic activity. Other elements such as Li and La were believed to be unaffected by anthropogenic activity, having similar concentrations in areas of open space and urban gardens. For these elements, the underlying geology and pedogenic processes are postulated to be the most important factors influencing their concentrations in soils. Principal components analysis can be used, initially, to identify multi-element associations within the data set. These element associations can then be defined either anthropogenic or geological and pedogenic through a study of the literature.

1. Principal Components Analysis

Principal components Analysis (PCA) aims to separate element associations in the structure of a correlation matrix into a number of groups of elements that together account for the greater part of the observed variability of the original data (Howarth, 1983). By applying PCA to the data set for Richmond, the 20 elements analysed for can be represented by 20 components which are linear functions (transformation) of element concentrations. Each component maximizes the common variance. This results in element associations for each component (component loadings) which may be accounted for in terms of anthropogenic activity or geological/pedogenic processes. Principal component scores are subsequently calculated, based on the component loadings, which allows an assessment of a particular component on the individual sample. The first 5 components are discussed and these account for 80% of the variance in the data set.

2. Principal Component 1

The first PC, which accounts for 46.2% of the total data variance, provides very little information regarding the processes influencing the geochemistry of soils in Richmond. The 21 elements have very similar loadings, with no antipathetic relationships apparent.

3. Principal component 2

The second PC illustrates 2 different processes operating in Richmond soils. This component accounts for 17.3 % of the total data variance, and from the high positive loadings of Pb, Zn and P and the high negative loadings of Ti, Al, K and Mg, 2 distinct processes can be separated. An examination of the scores for PC 2, which are calculated from the loadings for this component, allows a more detailed investigation of the spatial distribution of the samples which have high positive scores. High positive scores (indicating high concentrations of Pb, Zn and P) are only found for samples taken in urban gardens. This represents anthropogenic additions via the burning of fossil fuel and the disposal of resulting residues, and possibly the application of phosphatic fertilisers. This confirms the observations already made in this report from the mapping process and the very basic statistical analysis. This multi-variate approach has illustrated the importance of anthropogenic activity to concentrations of Pb, Zn and P in urban gardens. An investigation of the high negative scores for PC 2 shows that sample sites located in areas of open space are responsible for coincident high concentrations of Ti, Al, K and Mg. Concentrations of these elements were found not to vary significantly as a result of anthropogenic activity (see sections 6.3 and 6.4) and this represents the importance of geology and pedogenic processes.

4. Principal component 3

This PC accounts for 7.1% of the total data variance, with 2 processes occurring antipathetically. High positive loadings are observed for Cr, Zn, Pb and Ba whilst high negative loadings are observed for Mn, Fe and V. An examination of the scores for the samples shows that the high positive scores (Cr, Zn, Pb and Ba) all occur in urban garden samples and are clearly a result of anthropogenic activity. These four elements are diagnostic of a paint source, with Cr used for road markings (see section 3.6.7) and Zn, and Pb and Ba all associated with paint (see table 3.x). This confirms the observations of section 6.3 and 6.4 and the investigation into the influence of house age on garden soil geochemistry (see section 7.5). In this Pb and Ba were found to increase significantly with an increase in the age of the property (across 3 age categories) and this was believed to be a result of the importance of leaded paints in the last century and the early part of this century. Zinc was also a component of paints.

An examination of the high negative scores for Mn, Fe and V shows that these samples occur in areas of open space. This seems to be a product of the natural geochemistry in Richmond through a process such as co-precipitation of Mn and V with hydrous Fe oxides.

5. Principal Component 4

This PC accounts for 5.1% of the total data variance, with high positive loadings for Cr, Mn and Fe and high negative loadings for Li, Na and Cu. An examination of the high positive scores for PC 4 shows that the sites are located in both urban gardens and areas of open space. This appears to be a feature of the natural geochemistry in Richmond soils, with the co-precipitation of Cr, Mn and Fe, geochemically similar elements which occur in a sequence within the periodic table, with clay minerals. The high negative scores for PC 4 occur for samples located in areas of open space, and have a strong association with soils developed on an alluvial parent material. Section 7.4 illustrated that soils developed over alluvium in Richmond generally have higher concentrations of a number of elements. It was suggested that this may be a result of natural differences in the soil texture, alluvial deposits having a higher clay content, and therefore higher concentrations of clay associated elements. Another possibility is that as the most recent deposit in Richmond anthropogenic activity may have increased the concentration of a number of elements, particularly the trace metals, with flooding of this river side soils a possibility prior to the development of the Thames barrier. These samples have high loadings of Li, Na and Cu. It is difficult to ascribe these this trend to a specific geological/pedogenic processes.

6. Principal Component 5

This PC accounts for 4.4% of the total data variance with high positive loadings for Ca, Sr and P and high negative loadings for Cu. An examination of the high positive scores associated with PC 5 shows that the samples are located in areas of open space, and this element pattern appears to be a result of natural geological/pedogenic processes with Ca and Sr being geochemically similar and likely to substitute for one another isomorphously. These elements are probably in the form of phosphates.

The negative loadings for PC 5 shows the domination of a single element, Cu, and the scores for the samples indicates that these are all residential sites, generally urban gardens which are associated with property which is > 100 years old. This single element pattern may be as a consequence of a specific anthropogenic process at these locations, although is difficult to suggest what this is.

7. Summary

The use of multi-variate statistics has helped to confirm the importance of anthropogenic and geological/pedogenic processes in influencing the multi-element trends in soils from Richmond. Principal components 2 and 3 separated out processes which generally grouped together associations of trace metals (with Ba and P as well) which occur in soils from urban gardens. In the second component, Pb, Zn and P were observed as a grouping and although difficult to interpret as a single anthropogenic process, this does in many ways represent anthropogenic activities in general. Several sources of trace metals occur to soils in urban gardens, and very often these are the source of more than one trace metal. These include emissions from vehicles, the wearing of various vehicle components, the burning of fossil fuel and subsequent disposal of residues, the use of leaded paints and the application of fertilisers. This results in a cocktail of trace metals in garden soils, the identify and concentration of dependant on the location of the site, the age of the property and the individual householders activities. This often results in complex data patterns which are difficult to interpret. However, principal component 3 separates out a group of elements which has the signature of a paint source. These elements are Pb, Ba, Zn and Cr, the first three being components of paint used on external and internal surfaces of the house and Cr used for road markings.

The use of this multi-variate statistical technique has also highlighted a number of natural geochemical processes, often occurring in an antipathetic relation to the anthropogenic processes. Most of these are observed in soils from areas of open space, but not exclusively. Anthropogenic activity has not masked or prevented the detection of various geochemical associations associated with geological and pedogenic processes. This is observed in the third principal component with the grouping of Mn, Fe and V, particularly in soils from areas of open space, which may be a result of the co-precipitation of Mn and V with hydrous iron oxides. The fourth principal component groups together Cr, Mn and Fe, particularly for soils overlying deposits of Alluvium. This probably represents the co-precipitation of these elements with clay minerals (see table 3.x), field soil analysis along with the normalisation technique (see section 7.2) suggested that the clay content of soils developed over Alluvium had a higher clay content than soils developed over River Terraces and London Clay.

Appendix Table 3.1 Summary of element associations determined by Principal components analysis of Richmond topsoil (0-15cm) data.

Loadings	PC1	PC2	PC3	PC4	PC5
Positive	-	Pb Zn P	Cr Zn Pb Ba	Cr Mn Fe	Ca Sr P
Negative	-	Ti Al K Mg	Mn Fe V	Li Na Cu	Cu
% of variance	46.2	17.3	7.1	5.1	4.4

Pergamon

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Urban Geochemistry: A study of the influence of anthropogenic activity on the heavy metal content of soils in traditionally industrial and non-industrial areas of Britain

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Abstract—Heavy metal concentrations have been determined in topsoils (0–15cm) in the London Borough of Richmond-upon-Thames, a non-industrial, mainly residential area of approximately 56 km^2, and Wolverhampton an industrial city in the West Midlands of 70 km^2. Soil samples were taken on a grid basis at a density of four per km^2 and analysis for 25 elements was carried out by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). Topsoils in Richmond were found to have significantly higher concentrations of heavy metals in developed locations compared to areas of open space, whilst in Wolverhampton topsoils a greater degree of contamination with Zn was found than with Pb.

GIS-based mapping techniques used in conjunction with statistical analysis of the data have highlighted the influence of land-use on the heavy metal content of topsoils in these two urban areas. The highest concentrations of Pb in Richmond-upon-Thames (> 1000 μg/g) tend to occur close to major road junctions on roads with high traffic densities. High levels of Pb (approx. 500 μg/g) also occur in the areas where the oldest housing is located (> 100 a). In Wolverhampton the highest concentrations of heavy metals, Zn in particular, are generally located to the east of the city in areas of both historical and contemporary industrial activity. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

The urban environment is affected by a wide variety of anthropogenic activities. Road networks, housing and the metal processing and manufacturing industries will tend to increase the heavy metal content of soils (Rodriguez-Flores and Rodriguez-Castellon, 1982; Davies and Thornton, 1987; Davies, 1990). Previous soil surveys have designated urban soils as 'built-up' (Hollis, 1991). Various soil 'types' are found within towns and cities (Bridges, 1991) ranging from relatively undisturbed soils, similar in some respects to their rural counterparts (Hollis, 1991), to completely man-made soils (Bockheim, 1974). Wolverhampton has been extensively redeveloped over the last century during a period of industrial decline, with made ground and imported topsoil a common feature within the city area.

Investigations of heavy metal concentrations in urban soils commenced in the late 1960s (Purves, 1966, 1967; Purves and Mackenzie, 1969), and indicated that urban gardens had significantly higher levels of Cu and B than rural gardens (Purves, 1967) and greater heavy metal contamination in urban parks than in rural parks (Purves and Mackenzie, 1969). Later studies undertaken on urban soils include those by Warren *et al.* (1971), Wilkins (1978), Davies (1978) and Gibson and Farmer (1986). The National Survey of Metals in Urban Dusts and Soils (Culbard *et al.*, 1983, 1988; Thornton *et al.*, 1985; Thornton, 1991) was based on 53 towns and cities in Britain. These were selected on the basis of geographical location, population size and the presence or absence of industrial activity, with 100 households being sampled in each. This comprehensive study showed that concentrations of Pb in garden soils from London are generally higher than for other towns and cities in Britain. The work presented in this study aims to assess the influence of urbanisation and industrial activity in Britain on the heavy metal content of topsoils. A similar study has been undertaken recently in Berlin (Birke and Rauche, 1994). A more comprehensive set of data are presented in the PhD thesis of the senior author (Kelly) and is held on open file at the British Geological Survey and Imperial College.

STUDY AREAS AND METHODS

Richmond-upon-Thames is one of 32 Boroughs within the Greater London area. It lies 17.5 km to the SW of the city centre, covering an area of approximately 56 km^2. It is a residential suburb with a population of approximately 160,000 and has very little history of industrial activity. The majority of Richmond is underlain by River Terrace deposits which vary in age and thickness, and consist mainly of gravels and sands. Outcrops of London Clay occur mainly in Richmond Park. Richmond is unique as a London Borough since it has large areas of relatively undisturbed open space in Richmond Park, Bushy Park and Hampton Court. The amenity areas comprise 2/3 of the land area in the Borough. These open spaces have been used to establish baseline concentrations of heavy metals, with a view to comparing these with concentrations in soils in the built part of the Borough which are affected by anthropogenic contamination.

Wolverhampton is located in the West Midlands approximately 72 km to the W of Birmingham, with an area of 70 km^2 and a population of 175,000. The city has a long history of industrial activity, with the Fe industry growing rapidly from the mid-18th century until it declined during the mid-19th century. Peak Fe production occurred from 1850 to 1860 (Gale, 1979). Figure 1a shows the locations of London and Wolverhampton in Britain; both study areas are shown in detail in Figs 1b and 1c. The majority of Wolverhampton is covered with periglacial deposits, in the form of a widespread till sheet with subordinate sands, gravels and laminated clays.

A systematic sampling strategy was developed in Richmond and then also applied to Wolverhampton. Samples were taken from household gardens, public and derelict land, and parkland. Four samples were collected per km^2 at regular intervals, with topsoil samples (0–15 cm) comprising a composite of 9 subsamples collected from a 4 m^2 grid. Sub-surface samples (30–45 cm) were also collected, but these results will be published elsewhere. Duplicates were collected at 10% of sites to enable an estimate of sampling and analytical precision. All soils were dried at 20°C, disaggregated and sieved. Multi-element analysis of the <2 mm fraction was carried out by ICP-AES, following digestion in concentrated HNO_3 and $HClO_4$ (4:1) and leaching with HCl (Thompson and Walsh, 1988). A complete sampling and analytical control scheme was implemented with sampling and

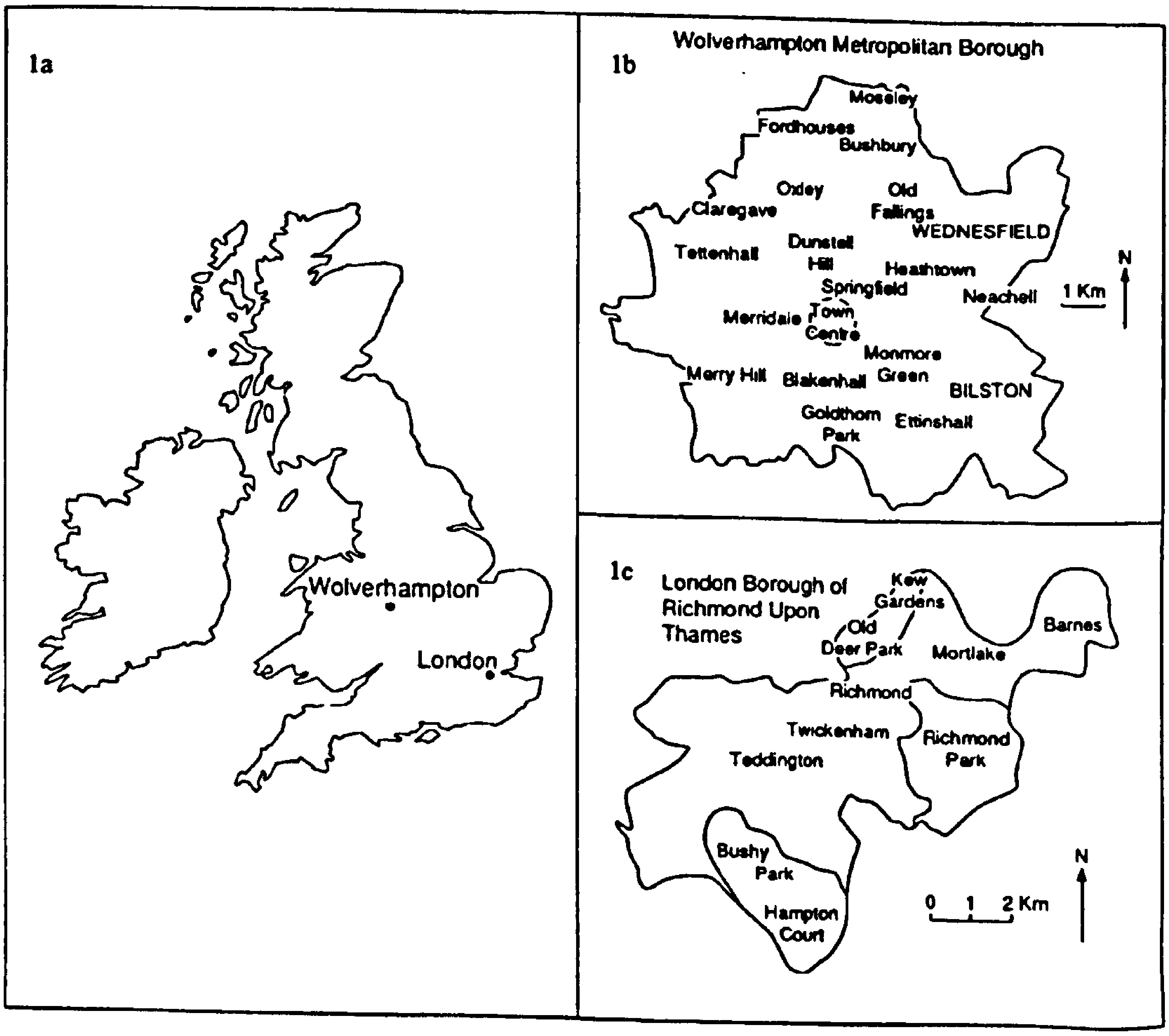

Fig. 1. (a) British location map of the two study areas. (b) The Metropolitan Borough of Wolverhampton. (c) The London Borough of Richmond-upon-Thames.

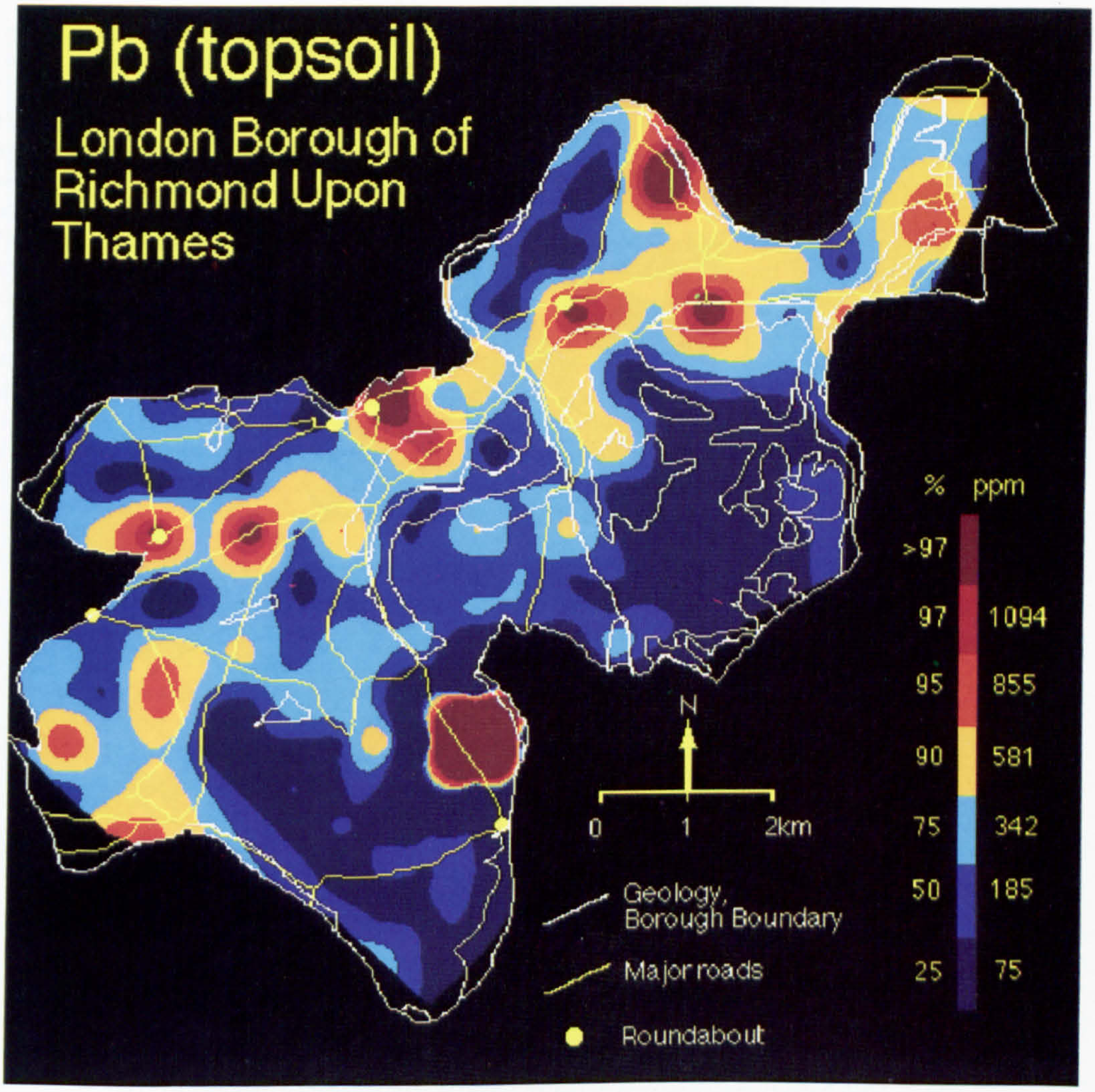

Fig. 2. Geochemical map of Pb concentrations (ppm) in Richmond-upon-Thames topsoils (0–15 cm).

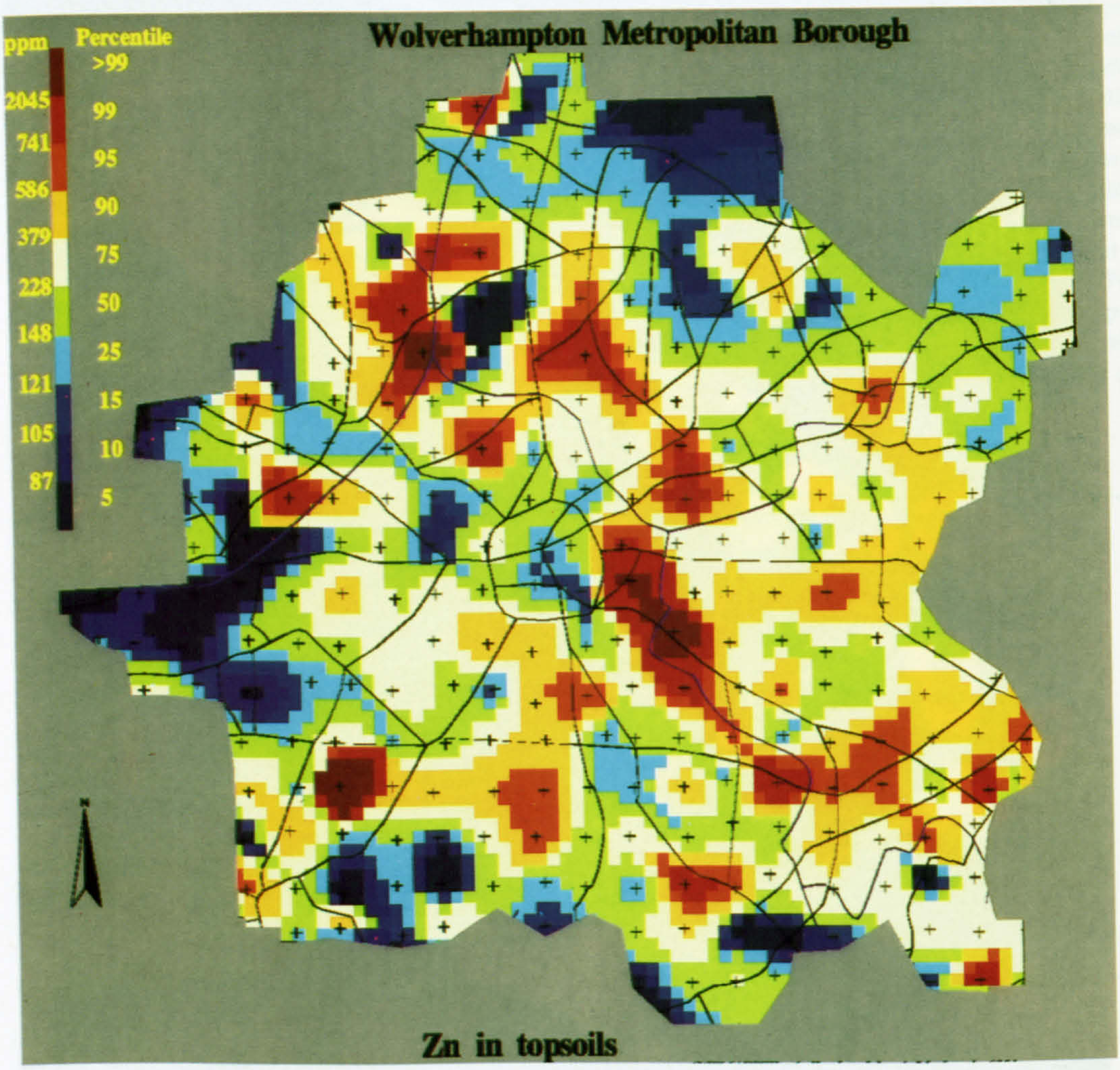

Fig. 3. Geochemical map of Zn concentrations (ppm) in Wolverhampton topsoils (0–15 cm).

analytical duplicates, reference materials and reagent blanks (Ramsey *et al.*, 1987). The technical variance, a combination of sampling and analytical variance, was found to contribute less than 20% of the total variance for the heavy metals. This is within the suggested threshold, allowing a confident interpretation of the geochemical variability (Ramsey *et al.*, 1992).

RESULTS AND DISCUSSION

The results from the urban soil surveys are shown as geochemical maps in Figs 2 and 3. These maps were generated at the British Geological Survey using an Interactive Surface Modelling griding algorithm for the Richmond-upon-Thames data. The map for Wolverhampton was produced by griding with a triangular algorithm on a G-MAP which is based on an Arc Info GIS. Both maps employ a colour classification applied to grey scale, density-sliced class intervals presented as percentiles. This facilitates the comparison between different elements in the two study areas and baseline values for the U.K. which are reported in geochemical atlases based on stream sediment samples (Webb *et al.*, 1978 and British Geological Survey, 1991) and soil samples (McGrath and Loveland, 1992).

The lowest concentrations of Pb (≤ 75 μg/g) for Richmond shown in Fig. 2 tend to occur in the 3 main areas of open space: Richmond Park, Hampton Park/Bushy Park and Kew Gardens. This is clearly seen in Fig. 1b which shows the layout of the Borough in detail. Soils at the centres of Richmond and Bushy Parks, over 1km from any major roads, have concentrations of Pb between 20 and 30 μg/g. Soils developed from individual geological units, in areas unaffected by development, show a range of metal concentrations. The concentrations of Pb found at the centre of the parks in Richmond are lower than the median value quoted in the Soil Geochemical Atlas of England and Wales of 40 μg/g (McGrath and Loveland, 1992) and are in the range quoted by Davies (1990) of 10–30 μg/g Pb for remote regions.

The sites which show the highest concentrations of Pb generally occur close to major junctions or roundabouts on main roads with a high traffic density. This is particularly the case in the N of the Borough, both E and W of Richmond town centre. A busy road here carries 10,000 vehicles eastwards towards Mortlake (see Fig. 1b) and 20,000 westwards through Twickenham towards Heathrow airport each day. Most of the Pb deposited from traffic sources occurs where the traffic density is high and vehicles are required to stop and accelerate (Lyons *et al.*, 1990). Concentrations of lead are also seen to be high, from 342–581 μg/g, in locations parallel to busy roads, as seen in Fig. 2, along a major road in the N of the Borough. However, the levels of Pb found here are not as high as those found at the major road junctions. Similar patterns are also seen along the busier roads throughout the London Borough. Lead in roadside soils typically decreases exponentially, with most of the metal deposited within 30–50 m of the road (Davies, 1990).

As many of the samples were taken from household gardens along busy roads, it is unlikely that vehicle emissions are the only source of Pb. The oldest housing in the Borough (> 100 a old) tends to occur close to the town centre and along the road leading out to Mortlake (see Figs 1b and 2). The houses are also of a similar age to the E of Kew gardens where Pb concentrations are comparable. A number of studies have shown the influence of house age on the Pb content of garden soil (Davies and Thornton, 1987; Davies *et al.*, 1987). Lead was an important component of paint until recently (Rundle and Duggan, 1986; Schwar and Alexander, 1988; Davies, 1990). An additional source of heavy metals results from the once common practice of disposing of ash from open fires in garden soils (Thornton, 1991). The distribution of Zn and Cu is similar to that of Pb (Fig. 2). This is in agreement with a number of studies which show Zn and Cu to be present in elevated concentrations in roadside soils (Lagerwerff and Specht, 1970; Albasel and Cottenie, 1985; Muskett and Jones, 1990).

Figure 3 shows Zn concentrations in Wolverhampton topsoils; these are generally higher than those for Pb in the city area (see Table 1). Highly anomalous levels of Zn, ranging from 586 to 2045 μg/g, are generally associated with areas of contemporary industry located to the E of the major road which bisects the city N–S. This is illustrated by the area around Monmore Green following a path S-eastwards towards Bilston (see Figs 1c and 3). This region retains Fe-related industries which have been established for over a 100 a. To the NE, an anomalous area is attributed to metal workings, and to the NW an anomalous concentration of Zn can be found near the Goodyear plant associated with engineering work. Some soils in the NW and SW of the city have concentrations of Zn ranging from 586 μg/g to 2045 μg/g. These occur in industrial areas, although the largest of these, in the NW, coincides with a sewage works. The lowest Zn class shown in Fig. 3 (≤ 87 μ/g), is most commonly present at the outskirts of the city which coincides with the change to a more rural environment, particularly in the W where farmland is several kilometres from the industrial centre.

COMPARISON OF THE TWO URBAN AREAS

Table 1 presents a comparison of the heavy metal concentrations in topsoils from Richmond-upon-Thames and Wolverhampton as geometric means, due to the log-normal distribution of the data. They have been calculated using all the topsoil samples taken in both locations. In Wolverhampton, topsoils generally have higher concentrations of Zn (× 2), Cu (× 2) and Cd than those from Richmond. Seventy-

Table 1. Concentrations of metals in topsoils (0–15 cm) in Richmond and Wolverhampton (μg/g)

	Pb range (g.m)[1]	Zn range (g.m)	Cd range (g.m)	Cu range (g.m)	*N*
Richmond[2]	20–1840 (158)	11.4–1810 (108)	<0.2–11.1 (<0.2)	3.8–1130 (30)	214
Wolverhampton	16–14,900 (106)	54.2–6740 (231)	<0.2–54.7 (0.80)	9.7–2750 (62)	295

[1] Geometric mean.
[2] Refers to results for the London Borough of Richmond-upon-Thames.

Table 2. Concentrations of metals in topsoils (0–15 cm) relating to land-use in the London Borough of Richmond-upon-Thames (μg/g)

	Pb range (g.m)[1]	Zn range (g.m)	Cd range (g.m)	Cu range (g.m)	*N*
Residential[2]	34–1840 (271)	36.6–1810 (179)	<0.2–11.1 (<0.2)	13.1–1130 (48)	106
Recreational[3]	20–1210 (93)	11.4–657 (66)	<0.2–1.2 (<0.2)	3.8–164 (19)	108

[1] Geometric mean.
[2] Refers to samples taken in back gardens.
[3] Refers to samples taken elsewhere, i.e. parks and sports grounds.

Table 3. Concentrations of metals in topsoils (0–15 cm) relating to land-use in Wolverhampton (μg/g)

	Pb range (g.m)[1]	Zn range (g.m)	Cd range (g.m)	Cu range (g.m)	*N*
Residential[2]	16–14,900 (111)	54.6–6740 (240)	<0.2–54.7 (0.7)	10–841 (62)	178
Recreational[3]	23–687 (96)	54.2–2950 (205)	<0.2–10.7 (0.7)	12–387 (55)	58
Industrial[4]	28–1400 (144)	66–3040 (368)	<0.2–12.6 (1.2)	18–2750 (139)	25
Agricultural[5]	23–129 (51)	80.8–200 (125)	<0.2–0.7 (0.3)	20–60 (32)	15

[1] Geometric mean.
[2] Refers to samples taken in back gardens.
[3] Refers to samples taken in areas of open space such as small parks or sports grounds.
[4] Refers to samples taken on industrial sites or within 50 m of industrial activity.
[5] Refers to samples taken on agricultural land.

five percent of the soils in Richmond have Cd concentrations below the ICP-AES detection limit of 0.2 μg/g, and this is reflected in the calculation of the geometric means presented in Tables 1 and 2. Wolverhampton topsoils generally have lower concentrations of Pb than those in Richmond, see Table 1. This contrasts with other heavy metals listed in Table 1, although traffic densities are not higher and the houses not older in Richmond.

It is suggested that this difference relates to the changes that have occurred in Wolverhampton over the last 100 a. As an industrially declining city, redevelopment has occurred with many industrial locations now being re-used for housing or leisure facilities. Much of the topsoil is now made ground or has been imported from elsewhere. The heavy metal concentrations reported here are probably much lower than in the recent past. It is considered that anthropogenic Pb has only recently accumulated in surface soils in Wolverhampton.

The important influence of land-use in the 2 locations is shown in Tables 2 and 3. In Richmond the sample sites are classified as either residential or open space, the latter including golf courses and sports grounds as well as the large parks. In contrast to developed areas, the soils in the middle of the parks in Richmond are over 1 km from major roads. The residential or garden soils have significantly higher concentrations of all the heavy metals than soils in areas of open space. These are shown to be statistically significant by means of a t-test, $p<0.001$, using both log-transformed and raw data.

A similar land-use classification for sample sites in Wolverhampton is shown in Table 3. The geometric mean values for heavy metals do not differ significantly between residential locations and open spaces. The amount of open space is very limited and small in comparison to Richmond, and this coupled with the industrial activity in the city has resulted in the widespread dispersal of heavy metals. The industrial locations in Wolverhampton have significantly higher levels of heavy metals than the other locations shown in Table 3. Zinc is generally highest with a geometric mean of 368 μg/g. This relates to the prevalence of the

Fe and steel industry and Zn's association with Fe ores and galvanizing techniques. Cadmium is also present in higher concentrations at industrial sites, at levels almost twice that found in soils in residential locations and areas of open space. Cadmium has a close geochemical association with Zn (Alloway, 1990), and in Wolverhampton topsoil concentrations of Zn and Cd are significantly correlated ($r = >0.90$, $p<0.001$) suggesting a similar source for the 2 metals. In general all heavy metals are elevated at industrial locations; this is probably also a reflection of the extensive burning of fossil fuel at these sites.

In contrast, agricultural land in Wolverhampton has significantly lower concentrations of heavy metals, as it is only present on the outskirts of the city, especially on the W side of Wolverhampton.

CONCLUSIONS

The present study has shown that heavy metal concentrations in urban topsoils are strongly influenced by land-use. In Richmond-upon-Thames, a non-industrial London Borough, busy road junctions and old housing result in concentrations of Pb in topsoil in excess of 1000 μg/g. Concentrations of Pb in topsoils in general are higher than those in the more industrial city of Wolverhampton (a geometric mean for topsoils of 158 μg/g compared to 106 μg/g in Wolverhampton). The large areas of open space, which are isolated from major roads, result in concentrations of heavy metals at the centres which provide a local baseline of: Pb < 30 μg/g, Zn < 20 μg/g, Cu < 10 μg/g and Cd < 0.2 μg/g). In Wolverhampton contamination from the Fe industry has resulted in higher concentrations of Zn than Pb in topsoils. However, the redevelopment over the previous 30–40 a has led to changes to the surface layer of soil which is now largely made ground or imported topsoil. This has been exposed to further heavy metal contamination during only a few years of declining industrial activity. Hence the concentrations of heavy metals reported here are probably now much lower than during the early 19th century when industry was at its peak. The highest concentrations of heavy metals, and Zn in particular (over 2000 μg/g), are found close to the much reduced industrial base that remains.

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REFERENCES

Albasel N. and Cottenie A. (1985) Heavy metal contamination near major highways, industrial and urban areas in Belgian grassland. *Water, Air and Soil Pollut.* **24**, 103–109.

Alloway B. J. (1990) Cadmium. In *Heavy Metals in Soils* (ed. B. J. Alloway), Chap. 6, pp. 100–121. Blackie and Son.

Birke M. and Rauche U. (1994) Geochemical investigation of the urban area of Berlin. *Federal Institute of Geosciences and Natural Resources, Branch Office Berlin, Germany.*

Bockheim J. G. (1974) Nature and properties of highly disturbed urban soils, Philadelphia, Pennsylvania. *Paper presented before Div. S-5, Soil Science Society of America, Chicago, Illinois.*

Bridges E. M. (1991) Waste materials in urban soils. In *Soils in the Urban Environment* (ed. P. Bullock and P. J. Gregory), Chap. 3, pp. 28–46. Blackwell.

British Geological Survey (1991) *Regional geochemistry of the East Grampians area.* (British Geological Survey, Keyworth, Nottingham).

Culbard E., Thornton I., Watt J., Moorcroft S. Brooks K., and Thompson M. (1983) A nationwide reconnaissance survey to determine metal concentrations in urban dusts and soils. In *Trace Substances in Environmental Health,* **XVII** (ed. D. D. Hemphill), pp. 236–241. Univ. of Missouri, Columbia.

Culbard E. B., Thornton I., Watt J., Wheatley M., Moorcroft S. and Thompson M. (1988) Metal contamination in British urban dusts and soils. *J. Environ. Qual.* **17**(2), 226–234.

Davies B. E. (1978) Plant available lead and other metals in British garden soils. *Sci. Tot. Environ.* **9**, 243–262.

Davies B. E. (1990) Lead. In *Heavy Metals in Soils* (ed. B. J. Alloway), Chap. 9, pp. 177–194. Blackie and Son.

Davies D. J. A. and Thornton I. (1987) The influence of house age on lead levels in dusts and soils in Brighton, England. *Environ. Geochem. Health.* **9**, 65–67.

Davies D. J. A., Watt J. and Thornton I. (1987) Lead levels in Birmingham dusts and soils. *Sci. Tot. Environ.* **67**, 177–185.

Gale W. K. V. (1979) *The Black Country Iron Industry: a Technical History.* The Metals Society.

Gibson M. J. and Farmer J. G. (1986) Multi-step sequential chemical extraction of heavy metals from urban soils. *Environ. Pollut.* Ser. **B 11**, 117–135.

Hollis J. M. (1991) The classification of soils in urban areas. In *Soils in the Urban Environment* (eds P. Bullock and P. J. Gregory), Chap. 2, pp. 5–27. Blackwell.

Lagerwerff J. V. and Specht A. W. (1970) Contamination of roadside soil and vegetation with cadmium, nickel, lead and zinc. *Environ. Sci. Technol.* **4**, 583–586.

Lyons T. J., Kenworth J. R. and Newman P. W. G. (1990) Urban structure and air pollution. *Atmos. Environ.* Vol. **24B**(1), 43–48.

McGrath S. P. and Loveland P. J. (1992). *The Soil Geochemical Atlas of England and Wales.* London: Blackie Academic.

Muskett C. J. and Jones M. P. (1990) The dispersal of lead, cadmium and nickel from motor vehicles and the effects on roadside invertebrate macrofauna. *Environ. Pollut.* ser. **A 23**, 231–242.

Purves D. (1966) Contamination of urban garden soils with copper and boron. *Nature* **210**, 1077–1078.

Purves D. (1967) Contamination of urban garden soils with copper, boron and lead. *Plant and Soil* **26**, 380–382.

Purves D. and Mackenzie E. J. (1969) Trace element contamination of parklands in urban areas. *J. Soil Sci.* **20**, 288–290.

Ramsey M. H., Thompson M. and Banerjee E. K. (1987) Realistic assessment of analytical data quality from Inductively Coupled Plasma Atomic Emission Spectrometry. *Anal. Proc.* **24**, 260–265.

Ramsey M. H., Thompson M. and Hale M. (1992) Objective evaluation of precision requirements for geochemical analysis using robust analysis of variance. *J. Geochem. Explor.* 44, 23–36.

Rodriguez-Flores M. and Rodriguez-Castellon E. (1982) Lead and cadmium levels in soil and plants near highways and their correlation with traffic density. *Environ. Pollut.* ser. B. 4, 281–290.

Rundle S. A. and Duggan M. J. (1986) Lead pollution from the external redecoration of old buildings. *Sci. Tot. Environ.* 57, 181–190.

Schwar M. J. R. and Alexander D. J. (1988) Redecoration of external leaded paintwork and lead-in-dust concentrations in school playgrounds. *Sci. Tot. Environ.* 68, 45–59.

Thompson M. and Walsh J. N. (1988) *A Handbook of Inductively Coupled Plasma Spectrometry*, 2nd Edn. Blackie, London.

Thornton I., Culbard E., Moorcroft S., Watt J., Wheatley M., Thompson M and Thomas J. F. A. (1985) Metals in urban dusts and soils. *Environ. Technol. Lett.* 6, 137–144.

Thornton I. (1991) Metal contamination of soils in urban areas. In *Soils in the Urban Environment* (eds P. Bullock and P. J. Gregory), Chap. 4, pp. 47–75. Blackwell.

Warren H. V., Delavault R. E. and Fletcher K. W. (1971) Metal pollution—a growing problem in industrial and urban areas. *Can. Min. Metall. Bull.* 64, 34–45.

Webb J. S., Thornton I., Thompson M., Howarth R. J. and Lowenstein P. L. (1978) *The Wolfson Geochemical Atlas of England and Wales.* Oxford University Press.

Wilkins C. (1978) The distribution of lead in the soils and herbage of west Pembrokeshire. *Environ. Pollut.* 15, 23–30.

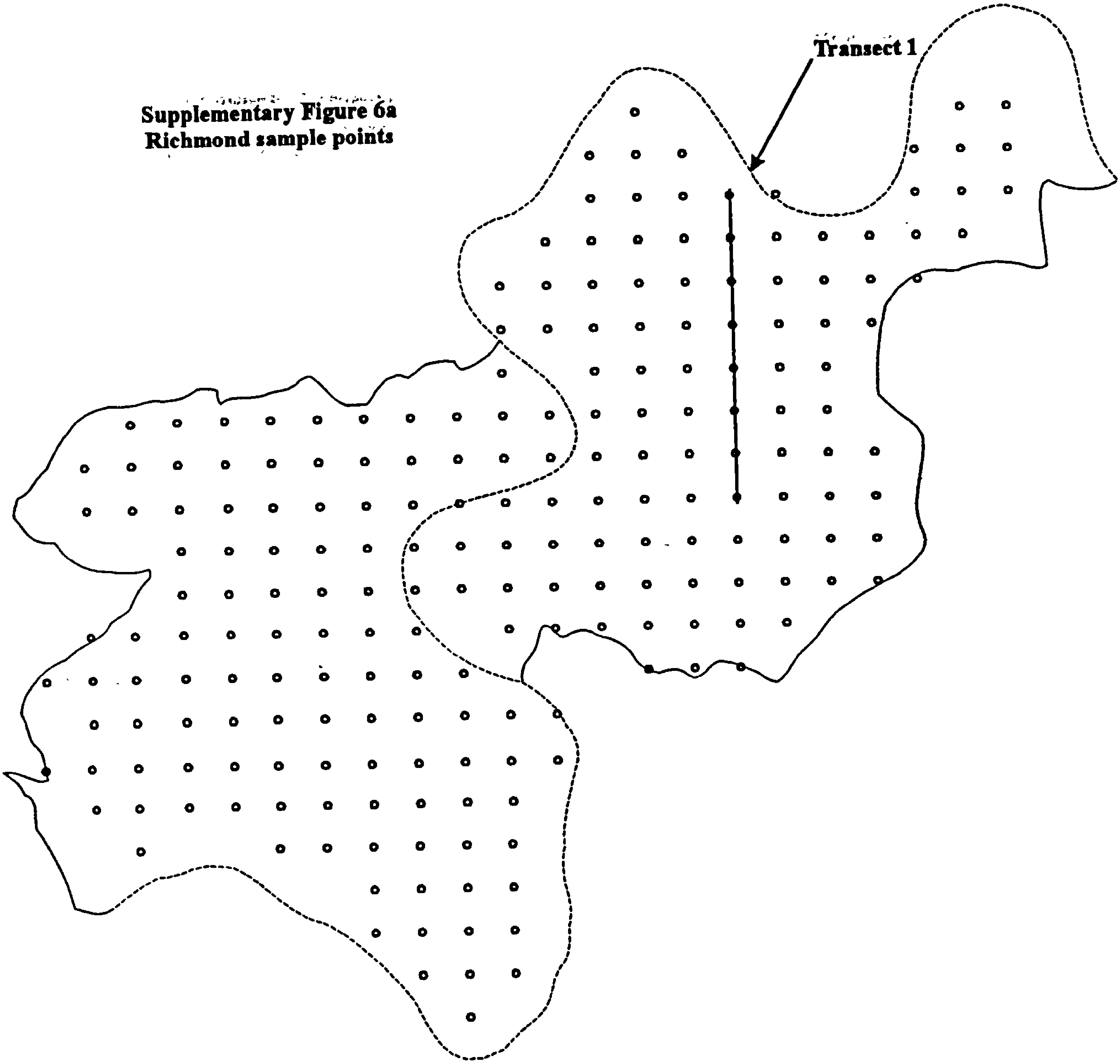
UK Department of the Environment ICRCL 'trigger' concentrations for metals in contaminated land which is to be redeveloped for the uses specified

Metal	Proposed use	Threshold trigger concentration (mg/kg)
Contaminants which pose hazards to human health		
As	Gardens, allotments	10
	Parks, playing fields, open space	40
Cd	Gardens, allotments	3
	Parks, playing fields, open space	15
Cr (hexavalent)*	Gardens, allotments	25
	Parks, playing fields, open space	–
Cr (total)	Gardens, allotments	600
	Parks, playing fields, open space	1000
Pb	Gardens, allotments	500
	Parks, playing fields, open space	2000
Hg	Gardens, allotments	1
	Parks, playing fields, open space	20
Se	Gardens, allotments	3
	Parks, playing fields, open space	6
Phytotoxic contaminants not normally hazardous to human health		
B (water soluble)	Any uses where plants grown	3
Cu (total)	Any uses where plants grown	130
Cu (extractable)†		50
Ni (total)	Any uses where plants grown	70
Ni (extractable)†		20
Zn (total)	Any uses where plants grown	300
Zn (extractable)†		130

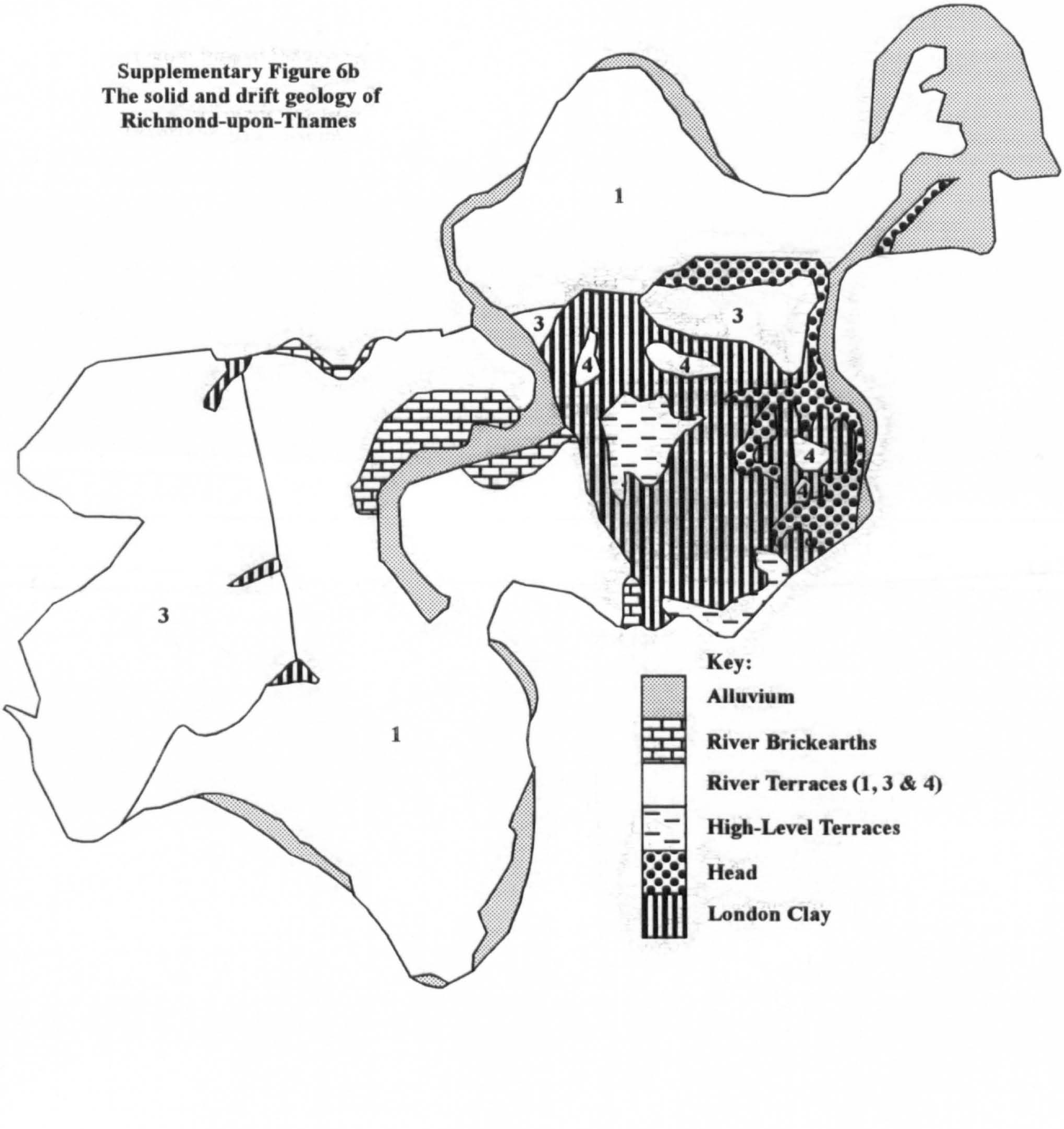
*Hexavalent Cr extracted by 0.1MHCl adjusted to pH at 37.5°C.
†Cu, Ni and Zn extracted in 0.05M EDTA (ethylenediaminetetraacetic acid).

Ref. Interdepartmental Committee on the Redevelopment of Contaminated Land, Guidance on the assessment and redevelopment of contaminated land, Guidance Note 59/83, Department of the Environment, London, 1987.

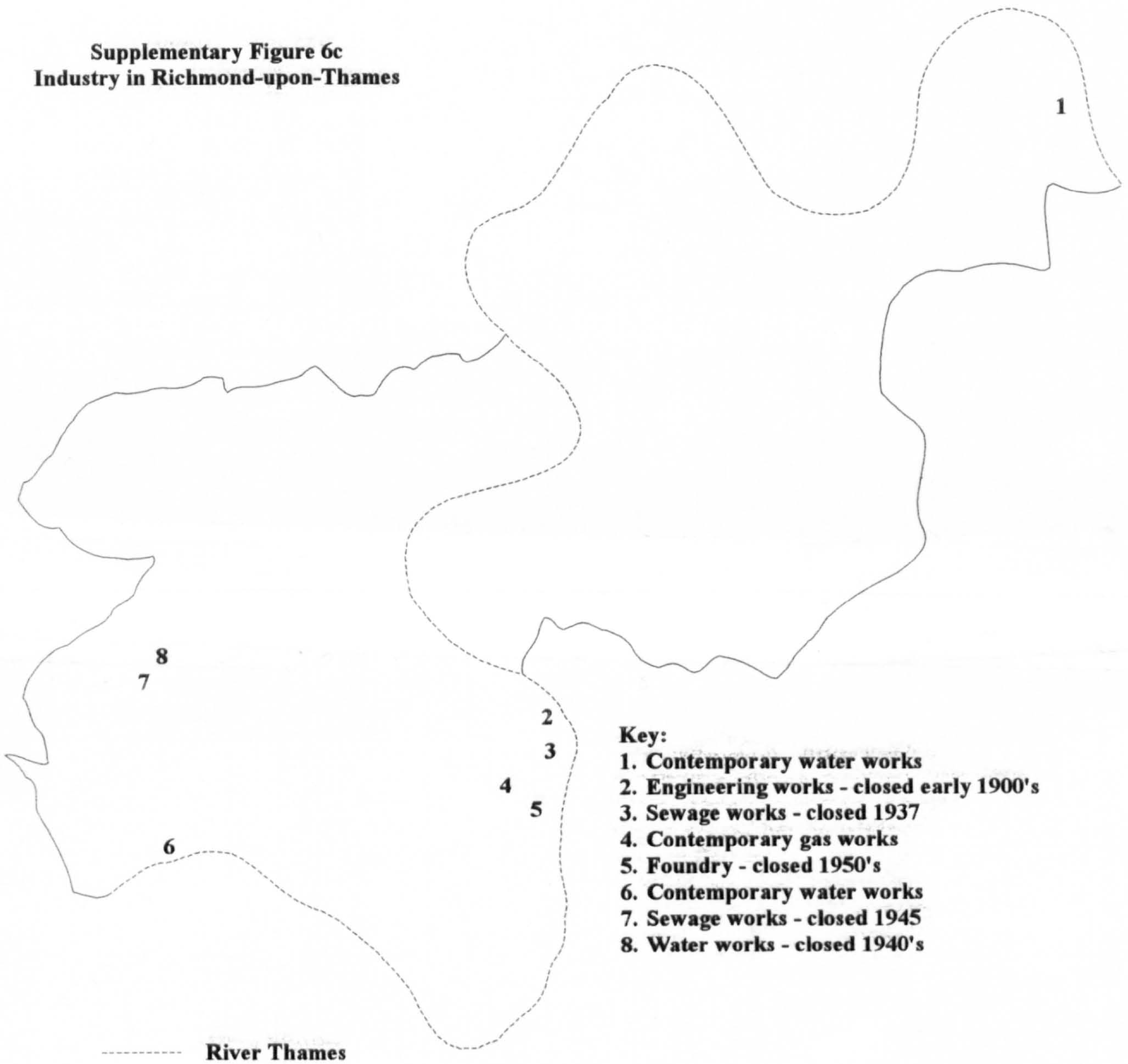
Supplementary Figure 6a
Richmond sample points



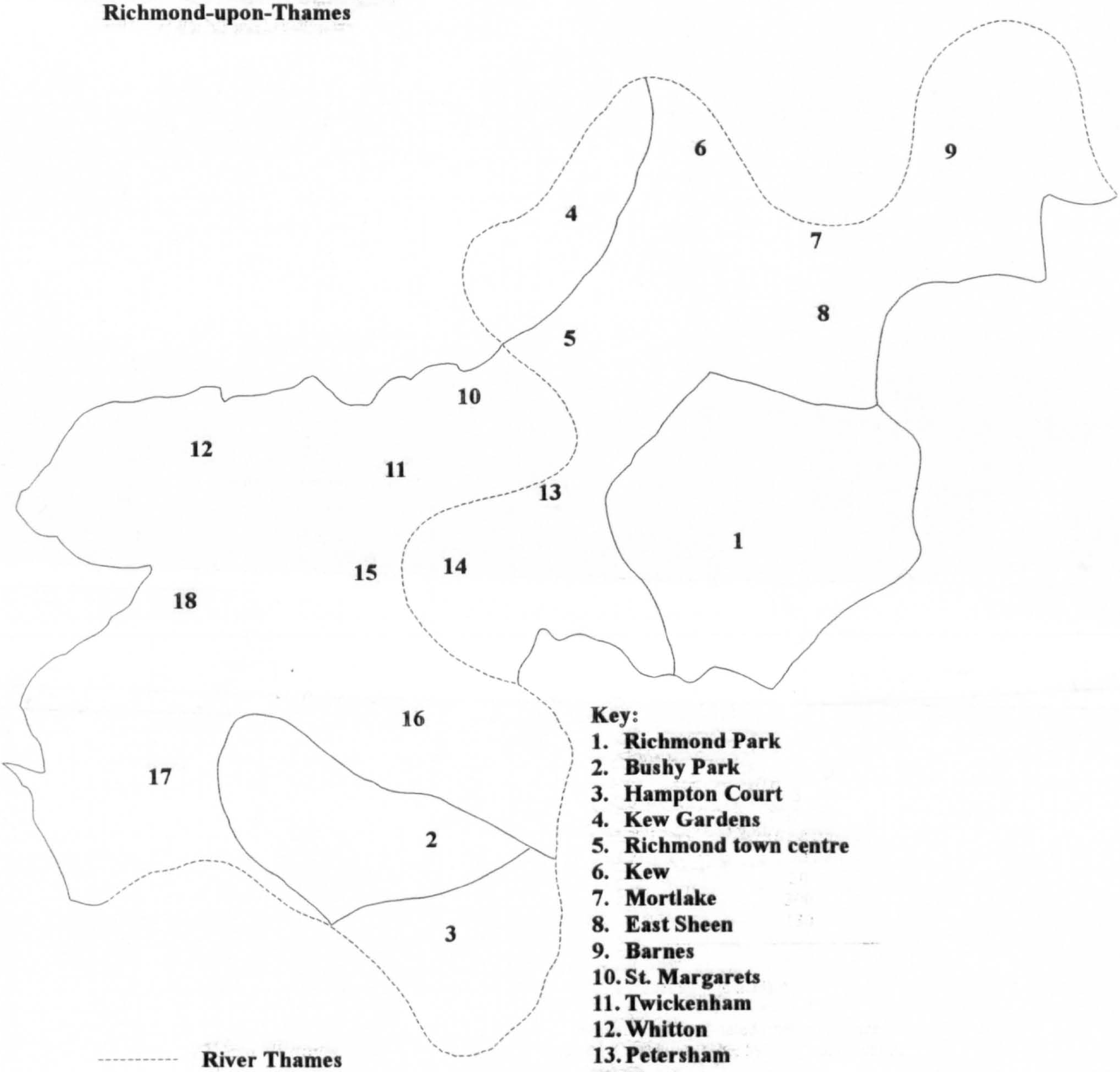
Supplementary Figure 6b
The solid and drift geology of Richmond-upon-Thames



Supplementary Figure 6c
Industry in Richmond-upon-Thames

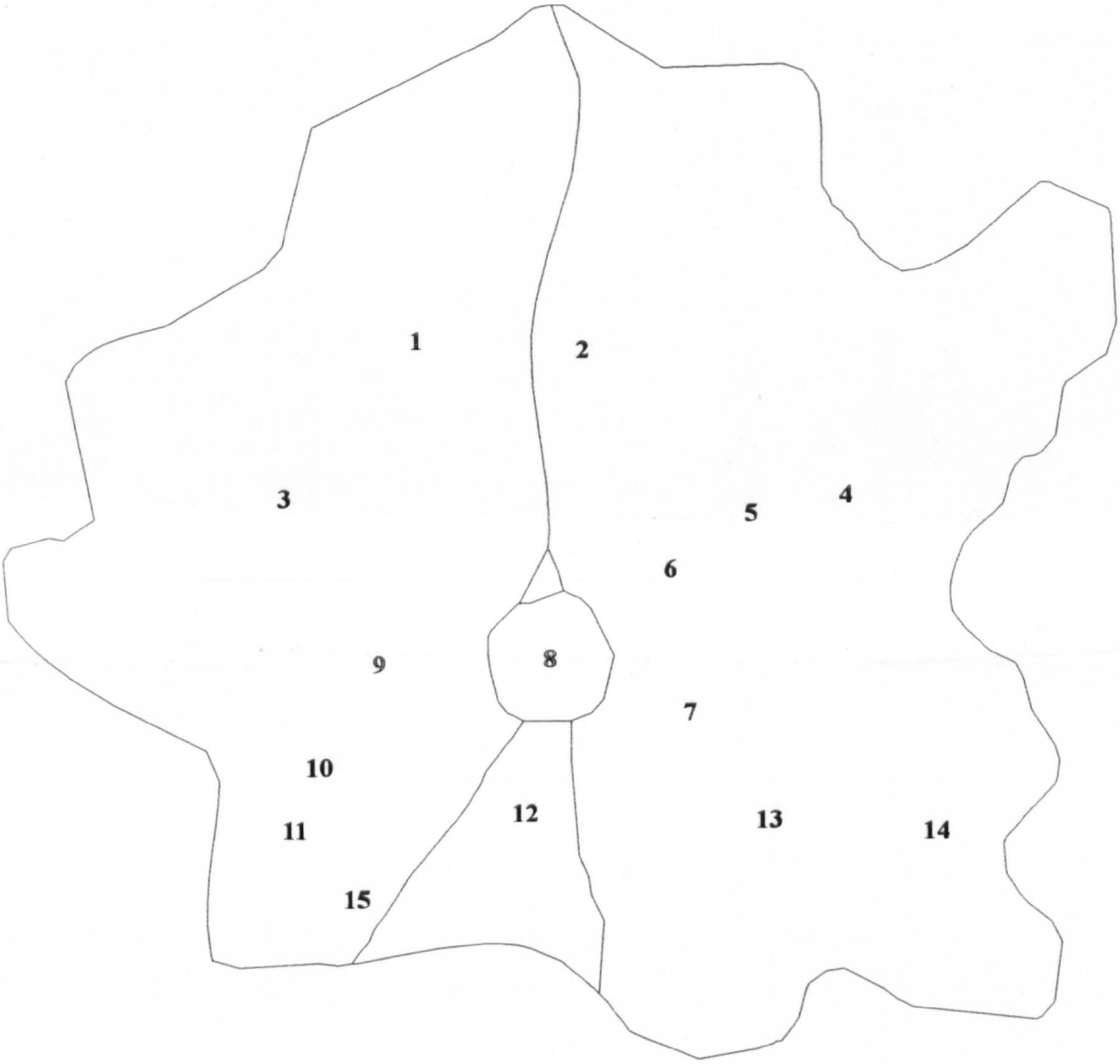


Supplementary Figure 6d
locations in the London borough of
Richmond-upon-Thames



Key:
1. **Richmond Park**
2. **Bushy Park**
3. **Hampton Court**
4. **Kew Gardens**
5. **Richmond town centre**
6. **Kew**
7. **Mortlake**
8. **East Sheen**
9. **Barnes**
10. **St. Margarets**
11. **Twickenham**
12. **Whitton**
13. **Petersham**
14. **Ham**
15. **Strawberry Hill**
16. **Teddington**
17. **Hampton**
18. **Fulwell Park**

Supplementary Figure 8
Locations in Wolverhampton



Key:

1. Sewage works
2. Goodyear Engineering plant
3. Tettenhall
4. Wednesfield
5. Heath town
6. Springfield
7. Monmore Green
8. City centre
9. Merridale
10. Bradmore
11. Merry Hill
12. Blakenhall
13. Priestfield
14. Bilston
15. Penn