

Urban Geochemistry: research strategies to assist risk assessment and remediation of brownfield sites in urban areas.

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Abstract

Urban geochemical maps of Wolverhampton and Nottingham, based on multi-elements analysis of surface soils, have shown distribution patterns of “total” metals concentrations relating to past and present industrial and domestic land use and transport systems. Several methods have been used to estimate the solubility and potential bioavailability of metals, their mineral forms and potential risks to urban population groups. These include sequential chemical extraction, soil pore water extraction and analysis, mineralogical analysis by scanning electron microscopy, source apportionment by lead isotope analysis, and the development of models to predict metal uptake by home grown vegetables and to provide an estimate of risk from metal consumption and exposure. The results from these research strategies have been integrated by GIS to provide data for future land use planning.

Keywords

Urban geochemistry, Wolverhampton, Nottingham, risk assessment, brownfield, metals, chemical speciation, scanning electron microscopy, lead isotopes, predictive modelling of metal solubility and vegetable uptake.

Introduction

The discipline of urban geochemistry addresses the complex interactions and inter relationships between chemical elements and their compounds in the urban environment, the influence of past and present human and industrial activities on these, and the impacts or effects of geochemical parameters in urban areas on plant, animal and human health.

As a result of demographic changes in population distribution and family framework the UK is currently facing a serious shortage of housing stock. The UK Government policy to meet current and future requirements aims to build 3 million new houses by 2016 (Barker, 2003), some 60% to be built on previously developed “brownfield” land in urban and peri-urban areas rather than on protected “greenfield” land in rural areas. (ODPM, 2001).

The term “brownfield” has been defined as “any land or premises which has previously been used or developed and is not currently fully in use, although it may be partially occupied or utilised. It may also be vacant, derelict or contaminated. Therefore a brownfield site is not necessarily available for immediate use without intervention” (Alker et al, 2000). Intervention would usually include some form of remediation.

In the industrial cities and towns of Britain, most of the brownfield land is contaminated to some extent by trace metals and/or organics derived from present day and past industry, domestic use and transport systems. The present research addresses, in particular, the metals cadmium, copper, lead, nickel and zinc which if present in large concentrations, may be toxic to plants, animals and man. Human exposure to metals in contaminated land may arise through inhalation, direct ingestion of soil and dust, and consumption of food plants.

The production of urban geochemical maps based on systematic sampling of soils and multi-element analytical procedures has been a natural development from earlier multi-purpose geochemical mapping in the UK where the focus has been on applications to mineral exploration, agriculture, water quality and human health (Webb et al 1978; BGS 1978-2007). Previously, large urban conurbations were not sampled to avoid the influence of metal contamination from housing, commerce and industry. However, the majority of the population live in towns and cities and are potentially exposed to a wide range of contaminants. Sampling, analytical and mapping techniques were modified and applied for the production of maps showing the distribution of a large number of chemical elements in surface and subsurface soils in urban areas (Kelly et al, 1996; Fordyce et al, 2005). In the British Geological Survey (BGS) the increased interest in urban geochemistry led to the GSUE project (Geochemical Survey of the Urban Environment) as an offshoot of the regional G-BASE (Geochemical Baseline Survey of the Environment) programme, which has now generated data and maps for some 25 urban areas. These maps are based on the total concentration of metals in soils and focus attention on “hotspots” where human exposure is potentially high.

The multi-faceted research described in this paper fell within the Urban Regeneration and Environment Programme (URGENT) of the UK Natural Environment Research Council under the title of “Studies into metal speciation and bioavailability to assist risk assessment and remediation of brownfield sites in urban areas”. It was undertaken by a consortium of four UK institutions over the period 1999 to 2002 with the primary aims of providing assistance to local government and other stakeholders into the interpretation of urban geochemical maps and of providing a decision support system for risk assessment related to metal contaminated soils in urban areas.

The research development and approaches undertaken may be of relevance to the post Katrina situation in New Orleans. Pre Katrina geochemical mapping of New Orleans (Mielke et al, 1999; Mielke et al, 2007) will have been overridden by possible changes in the distribution of metal contaminants in surface soils resulting from flooding and sediment deposition resulting from the hurricane in 2005.

The strategies applied in the UK research, mainly to assess the distribution, speciation, bioavailability and potential human exposure to metals, and in particular Pb, comprised:

- a) the compilation of urban geochemical maps
- b) the application of chemical and mineralogical speciation techniques
- c) high precision measurements of lead isotopic ratios
- d) the use of micro-porous polymer devices to sample soil pore water for measurement of metal concentration
- e) the development of pragmatic models to estimate the free ion activity of metals and their uptake into vegetable crops
- f) the compilation of maps to denote areas in which metals may present a hazard to local population groups
- g) the development of an integrated geographical information system to present data in a user friendly fashion for local government and other stakeholders

Urban Geochemical Mapping

The research was centred on two English midland cities, Wolverhampton and Nottingham, both with strong industrial backgrounds and with varying degrees of redevelopment. Under the “Urban Geochemistry” division of the British Geological Survey (BGS) G – BASE programme (Johnson and Breward , 2004), comprehensive collections of soil samples (0 – 15cm) were taken on an approximate grid pattern at a sampling density of four samples per square kilometre (Wolverhampton N = 293; Nottingham N = 642). Analyses by XRF and ICP – AES for 35 metallic elements were processed into the digital BGS G-BASE GIS database and colour maps showing metal distribution presented by percentile-classified inverse-distance weighted gridding. An example is shown by the lead map for Wolverhampton (figure 1) which focuses attention on several areas in which concentrations in soils are elevated, commonly referred to as “hotspots” (Kelly et al, 1996; Ferguson et al, 1999).

Using these urban databases as guidelines, 50 composite surface soils (0 – 15cm) were collected for detailed investigation within the Wolverhampton and Nottingham urban and periurban areas. These sites were chosen to represent a range of urban land uses including: past and current industrial locations, transport sidings, waste disposal sites, recreational areas, household gardens and allotments, urban nature reserves and woodland, and to cover a range of metal concentrations. These soils were analysed for 35 metallic elements and other soil chemistry parameters including pH and organic matter content. The data identified considerable variations in metal contents and acidity and allowed a strategic selection of soils from various brownfield sites for more detailed study.

Close spaced sampling on a 5 metre grid at one of the heavily contaminated sites in Wolverhampton, the Cosely Nature Reserve, a reclaimed landfill previously used for the disposal of canal dredgings and industrial waste, illustrates the difficulty of selecting an appropriate sampling technique to obtain a representative soil sample. As seen in Figure 2, concentrations of copper varied widely within an area of 4,000 m², ranging from < 100 to > 5,000 mg/kg. The arithmetic mean for the site as a whole is 2,300 mg/kg Cu.

Chemical Speciation, Metal Solubility and Bioavailability

A single 0.12 M hydrochloric acid extraction was performed on each soil to provide a first approximation to the amount of Pb, Cu and Zn in an available form to the human receptor. This *in vitro* method, which is used to predict the solubility of a metal under the acid conditions of the GI tract has been shown to model the uptake of Pb into the body when compared with an *in vivo* animal model (Davis et al, 1992; Ruby et al, 1993).

Soils were then analysed by a sequential chemical extraction scheme using the established 5-step Tessier method modified for the analysis of soil samples by ICP-AES (Li et al, 1995). This operationally defined 5-step scheme assesses the association of metals with different soil phases and the implications this has for trace metal mobility and subsequent availability to sensitive environmental receptors. Correlation analysis between the results of these extractions, total metal concentrations in the soil, soil pH and organic matter (determined by loss-on-ignition) was used to assist in the interpretation of trace metal partitioning across the phases.

The details of the methods used for chemical speciation and the results obtained for selected sites in Wolverhampton are presented in the paper by Thums et al in this volume. An important finding was that the majority of the Pb was found in the residual fraction with sometimes as much as 80% or more in this relatively insoluble phase (Thums et al, this volume). This fraction, desolved by an attack of nitric, perchloric and hydrofluoric acids, comprises the clay fraction, phosphates, residual organic materials, slag material, alloys and other chemically resistant compounds. It follows that, in many cases, the Pb present in “hotspots” identified on the urban geochemical maps may be of very low solubility and biologically inert, thus not presenting an obvious risk to health in local population groups. This is seen to be the case at the heavily contaminated Cosely Nature

Reserve (Figure 3). On the other hand, a significant proportion of Cu is associated with organic phases and the Fe-Mn oxide fraction, suggesting a greater solubility and potential availability to receptors. However, the apparent high Cu content of the Fe-Mn oxides may be due to a weakness in the standard Tessier system, whereby some Cu-bearing organic material may be extracted by the nominal Fe-Mn oxide stage (Breward et al., 1996).

Other indices of trace metal availability included determination of isotopically exchangeable Cd and Zn, (Young et al. 2006) and solution metal concentration following extraction of soil pore water using microporous polymer (“Rhizon”) samplers. These data were then used to validate and re-parameterise a model of metal solubility which predicts the activity of a range of metals in soil pore water from soil geochemical characteristics. Isotopically exchangeable Zn (Zn_E) was compared with the 5-step sequential chemical extraction data. There was reasonable agreement between values of Zn_E and the cumulative Zn extracted by the first three steps of the extraction scheme across two orders of magnitude of soil Zn concentration (Young et al., 2006). However, there was considerable scatter in the data which underlines the difference inherent in these two approaches. Ideally sequential extraction procedures address the question of chemical form or fraction whereas isotopically exchangeable metal is a measure of chemical reactivity.

Detailed Mineralogical Analyses of Individual Soil Particles by Scanning Electron Microscopy

Eight soils were selected to represent contrasting soil types at the “brownfield” sites while displaying both high and variable metal contents peaking at > 1000 mg/kg Pb, in order to understand the controls on bioavailability. These soils were separated into size and density fractions and their constituent portions were analysed for metal contents in order to understand the heavy metal mass balance. The data, illustrated in figure 4, indicate that the bulk of the metals is contained primarily in the fine and lower density fractions, suggesting that adherence and coatings of metals on to fine soil particles is ubiquitous, controlling the heavy metal content.

Further study of higher density fractions ($> 2.8\text{g. cm}^{-3}$) using a scanning electron microscope (SEM) allowed identification of complex metal-rich particles that can be assigned to a specific origin (paint, solder, slag etc) on the basis of morphology, internal structure and composition. These data have shown that anthropogenic contributions are widespread in the soils and contribute to the high metal contents.

A combination of backscattered electron imaging, energy dispersive X-ray analysis and digital image analysis was used to map the occurrence of the highest density particles and assign them to classes of natural and anthropogenic provenance. Populations varied by three orders of magnitude and included sulphides of Pb, Cu, Zn and Fe, Fe-metals (Cu, Cr, Ni, Pb), oxides, steel, brass, slag, solder, paint and alteration products (figure 5). The results indicate a complex natural-anthropogenic metallogeny in contaminated soils with

multiple sources related to the industrial history of individual sites. The use of computer controlled scanning electron microscopy (CCSEM) for particle source apportionment was evaluated for these soils by Langmi and Watt (2003), who concluded significant chemical alteration had occurred in the soil environment, which might alter the apportionment when compared to unaltered source samples for unsectioned grains.

Examination of polished grains also allowed identification of surface reactions probably occurring within the soil environment. Figure 6 shows a particle with a core of silica, calcite, graphite and Pb, with a margin of lead oxide that has weathered on the surface into insoluble lead phosphate – similar to pyromorphite (Cotter-Howells and Thornton, 1991). These weathering crusts have been demonstrated at a number of sites and have important implications for availability of lead in the soil (Davis et al, 1992; Ruby et al 1992; Cotter-Howells and Thornton, 1991). Indeed some studies have demonstrated formation of insoluble lead in the laboratory by addition of phosphorus sources such as bonemeal (Hodson et al, 2001).

Source Apportionment by Lead Isotope Studies

The bulk Pb isotope composition of 25 soils of the joint Wolverhampton-Nottingham urban areas was accomplished by laser ablation of XRF pellets of homogenised soil using a multi-collector ICP-MS instrument to determine the lead isotope signature for the whole soil (McGill et al, 2003). Figure 7 shows a plot of the isotopic ratios $^{206}\text{Pb}/^{207}\text{Pb}$ versus $^{206}\text{Pb}/^{208}\text{Pb}$. The analyses fall on an apparent mixing line that is consistent with having British ore as the radiogenic end member and the other being geologically older petrol-additive Pb (derived from Australian and Canadian ores). This however, does not prove that such end members actually exist within the soils, but they are likely components of mixed and re-mixed lead sources, reflecting the complex industrial history and integration of metals sources in this area.

Isotope analysis was also completed for a range of aqueous sequential extracts, for size and density fractions, soil moisture, vegetable matter grown on four allotments, and individual particle analysis by laser ablation. These document considerable isotopic variation within soils, in a manner that is difficult to predict. Size and density fractions for selected soils show that many of the fractions give an isotope signature very similar to the bulk isotope composition obtained by LA-PIMMS of the corresponding XRF pellet. However the denser 'sink' and coarse-grained fractions often show evidence of particles relatively enriched in one or other Pb isotope end member from the apparent mixing line.

Comparison of the isotope compositions of soil moisture and the exchangeable sequential extraction step do appear in general to sample the same labile pool of lead in the soil. This is not the case for every soil however and the divergence between the two methods may be related to sample heterogeneity or the potential for a dynamic equilibrium of exchange to occur which allows the carry-over of metals from one step to another, complicating the interpretation of sequential extraction data. The residual step in undisturbed Nottingham soils (sourced from a domestic garden, racecourse, graveyard and two allotments) is always more influenced by UK ore lead, with each extraction step before it appearing to progressively leach out more of the petrol end member (figure 8). Wolverhampton results show no pattern at all which probably reflects the disturbance and mixing of soil materials and lead sources in fillings for these true brownfield soils. It is also suspected that soil acidity plays a role in making Pb more readily available when low pH soils equilibrate with water, even when the Pb content of the soil is not particularly high. Intra-soil variation for sequential extracts, soil moisture and size and density fractions document arrays of wide isotopic variability, and hence prove that various metal sources are implicated. It was however, difficult to clearly identify a petrol additive (imported or new world lead) component, in the exchangeable fractions, which could indicate fixation of such Pb in poorly understood ways and the time elapsed between the phasing out of Pb petrol additives and this sampling program, potentially allowing the most mobile petrol Pb component to be leached away].

The isotope data have proved vital to distinguishing sources of lead in the soils, and suggesting what might have been the original source materials for industrial by-products now present in the brownfield soils. They have also raised further cautionary issues (soil/reagent metal exchange during extractions) which should be considered when interpreting sequential extraction data. The Pb isotope data form an important, but complex component in the analysis of behaviour of soils with respect to metal mobility.

Predicting Metal Uptake by Vegetables Grown on Urban Soils

Models were developed to predict solubility in the soil and uptake into commonly grown vegetable crops. Metal solubility, depicted as the “free metal ion activity” in the soil pore water was predicted from a pH-dependent Freundlich equation from the total soil metal content, organic carbon content and soil pH (Hough et al, 2004). Published literature (73 studies including Moir, 1992), encompassing 4,500 data points, was then interrogated to derive values for metal concentrations in soils and in vegetable dry matter, together with soil organic matter content and soil pH. The resulting data was used to parameterise a combined solubility-uptake model in which metal concentration in the edible portion of nine commonly grown vegetables was predicted from soil metal content, expressed as mg g⁻¹ of humus carbon, and soil pH. Predictions for uptake of Cd, Cu, Ni and Zn by all vegetables were good as shown for Cd in cabbage and Zn in lettuce (Figure 9). The models for Pb uptake were less satisfactory, possibly reflecting the greater importance of aerial deposition to plants for this element.

Risk Assessment for Urban Population Groups

The potential hazard to the population from the consumption of home grown vegetables has been assessed using the concept of the Hazard Quotient (HQ) (Hough et al, 2004) – the ratio of the average daily dose of the metal (the sum of the total dietary and inhalation exposure and metal in soil and dust ingested) to a reference dose based on the maximum tolerable daily intake that will not result in any deleterious health effects (WHO, 2001). Where the HQ is greater than 1.0, there is a potential risk. Dietary information values for metal exposure from commercial foodstuffs and water, inhalation and dust/soil ingestion have been taken from national and international data sets. The sum of the HQ's for each of the 5 metals has been termed the Hazard Index (HI). This is a somewhat controversial methodology but nonetheless a method of providing an aggregated estimate of risk from a range of contaminants (Hampshire Research Institute, 1995):

$$HI = HQ_{Cd} + HQ_{Cu} + HQ_{Ni} + HQ_{Pb} + HQ_{Zn}$$

Values of HI were then used to produce maps of the urban area of Wolverhampton showing the location of greatest potential risk from combined metal exposure. Gridded data for HI were merged with the BGS Geochemistry Database for Wolverhampton to

produce percentile based colour classified images, which were then imported into a geographical information system (GIS).

For the average person some 90% of the urban conurbation has an HI < 1.0 (suggesting that most of the population are not at risk from metal exposure (Figure 10). However, for the highly exposed infant where ingestion of soil and dust plays an important role, over 50% of the urban area provides an HI between 2 and 3 and over 30% exceeds 3 (Figure 11) (Hough et al, 2004). However, though caution is required when applying this form of risk assessment, an HI of over 1 is still considered undesirable. It may be concluded that these maps indicate that not all sites within this study area may be suitable for housing or allotments without remediation.

Geographical Information System

An integrated geographical information system was developed to help with the interpretation of the urban geochemical maps and to examine spatial relationships between geochemical and geographic features (Thums and Farago, 2001). Geographical layers including geology, transport and infrastructure, past and present industry have been captured from a number of sources including Bridges et al (1997). Point source geochemical data for Wolverhampton surface soils (Kelly, 1996) have also been categorised according to soil guidelines for the evaluation of contaminated land (eg DEFRA – EA, 2002). An example is shown for Pb in surface soils of Wolverhampton, showing the majority of hotspots around junctions of major roads, canals, and industrial areas (Figure 12). These maps and those developed from the risk assessment model have been made accessible to local authorities and other stakeholders. In particular they will be useful to assist with future land use planning and the assessment of inner city and brownfield sites for the provision of housing and public amenities.

Conclusions

This multi-faceted research programme was aimed at developing and applying techniques to assist in the interpretation of urban geochemical maps based on the total urban metal concentration in soils, particularly in relation to potential risk to human health.

Studies were undertaken in the cities of Wolverhampton and Nottingham on selected soils chosen on the basis of geochemical maps compiled as part of the BGS G-Base programme.

Sequential chemical extraction indicated that significant proportions of Pb in brownfield contaminated soils were relatively insoluble and did not necessarily present a risk to local exposed population groups. However, bioaccessability of lead directly ingested from soil and dust by young children was not determined.

Mineralogical analysis by SEM showed a wide range of metal contaminants in brownfield soils and demonstrated that weathering of lead-rich soil particles could lead to transformation of relatively soluble to more insoluble species.

Lead isotope studies further illustrated the complexity of the lead sources in brownfield soils, reflecting the complex industrial history of the two cities. Isotope variations in sequential chemical extracts established a gradient in isotope ratios in some soils indicating probable differences in solubility and availability of different lead sources in the soil.

A combined model developed to predict metal solubility in the soil and uptake into vegetables was successfully validated for Cd, Cu, Ni and Zn but not for Pb. Output from this model was integrated with other exposure variables to calculate an aggregated estimate of risk – the Hazard Index. These exposure data were then merged with point source geochemical data for Wolverhampton to produce maps of potential risk to the average and the highly exposed adult and infant sectors of the population. It was concluded that most of the population were not at risk from metal exposure. More caution should be applied to infants who may directly consume metal contaminated soil and dust.

Geochemical and geographical data have been combined and categorised according to soil guideline values for contaminated land into an integrated GIS and together with maps developed for risk assessment are accessible for future land use planning.

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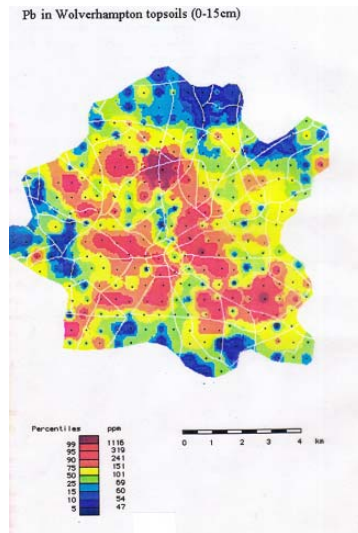
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Fig 1:

Urban Geochemical Maps Wolverhampton



Source: Kelly et al. 1996

Fig 2: Concentrations of Cu in Surface Soils at Cosely Nature Reserve

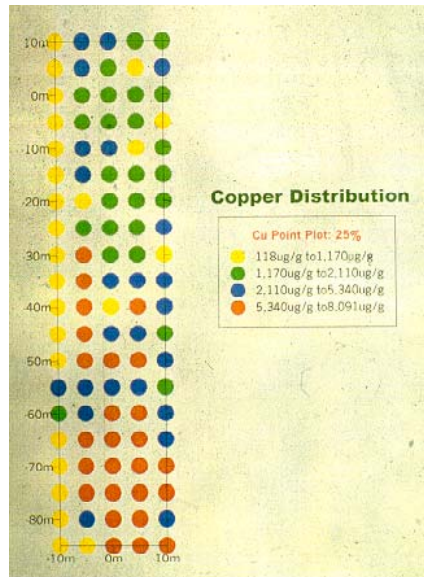


Fig 3:

Partitioning of metals in a sequential chemical extraction

Soil collected from Coseley Nature Reserve, now owned by British Waterways, previous land use was landfill

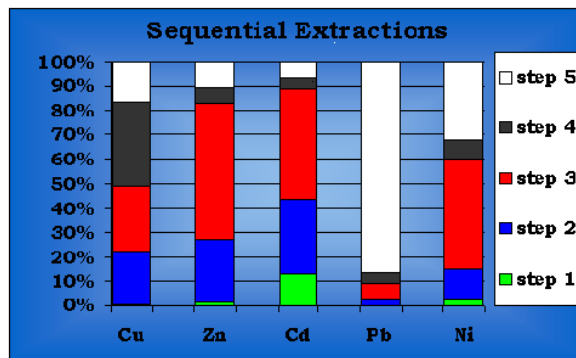


Fig 4:

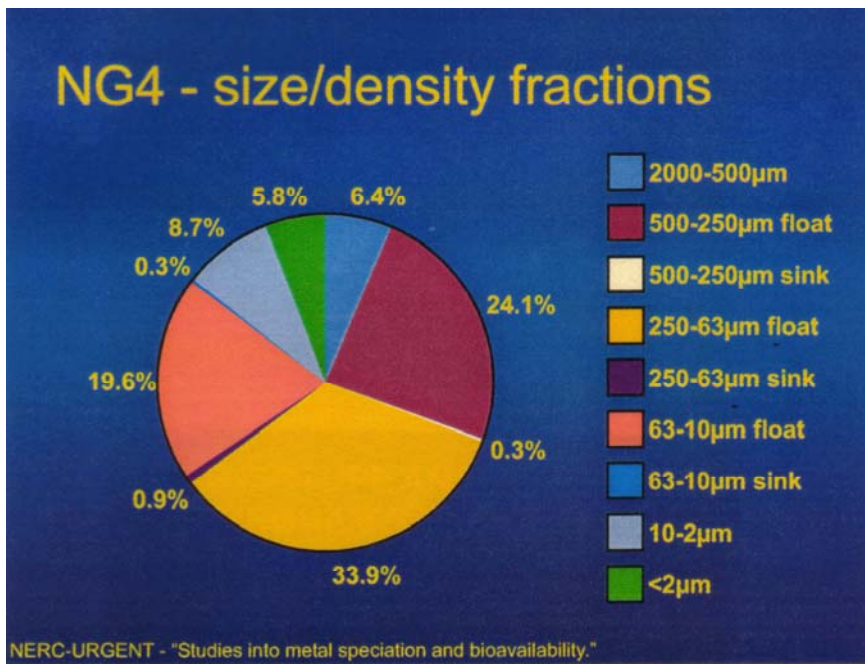
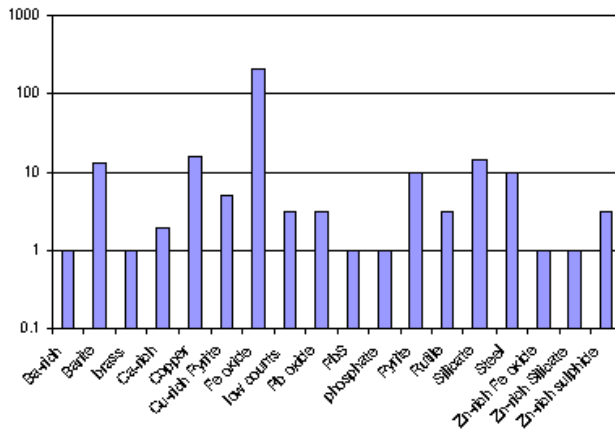


Fig 5:

Populations of natural and anthropogenic heavy metal grains from SEM analysis



Location: Coseley

Source: BGS & University of Middlesex

Fig 6:

Pb Isotope ratios in soil collected from
Wolverhampton and Nottingham from a range
of land uses

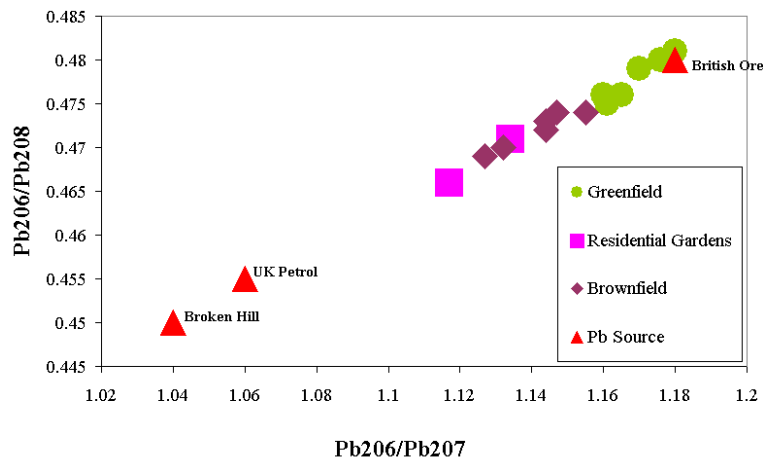


Fig 7:

Nottingham Soils - Sequential Extraction Data

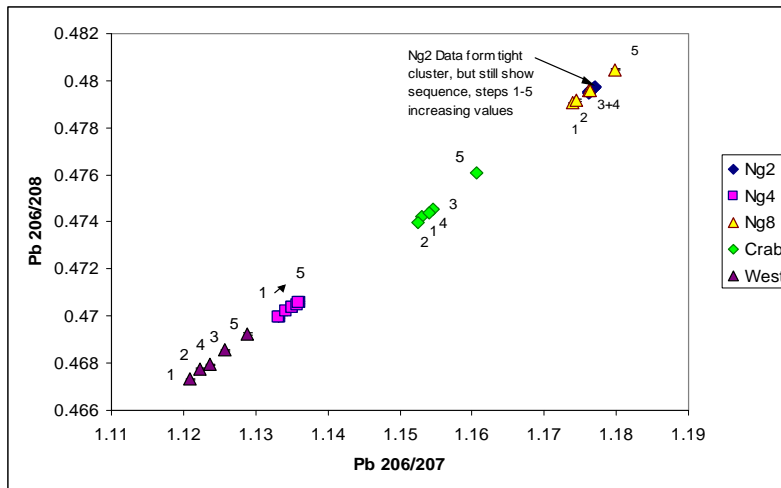


Fig 8:

Cd and Zn Uptake by Vegetables

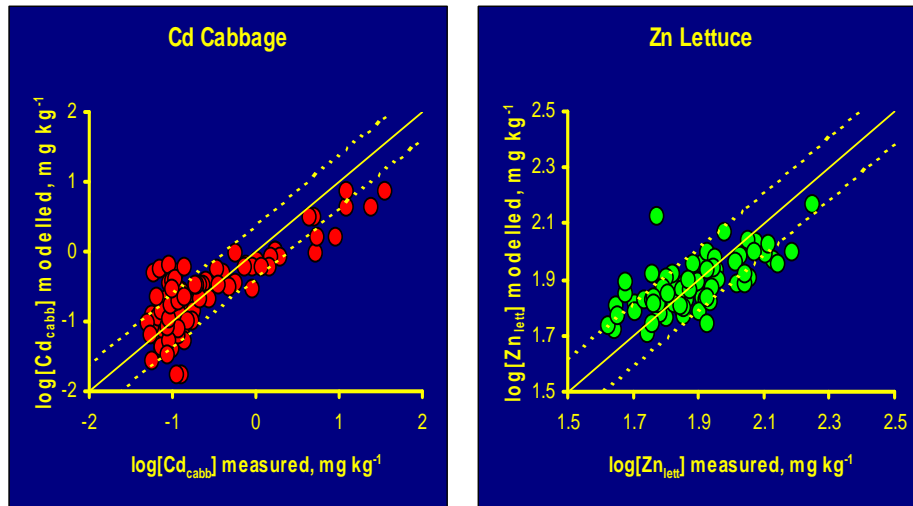


Fig 9:

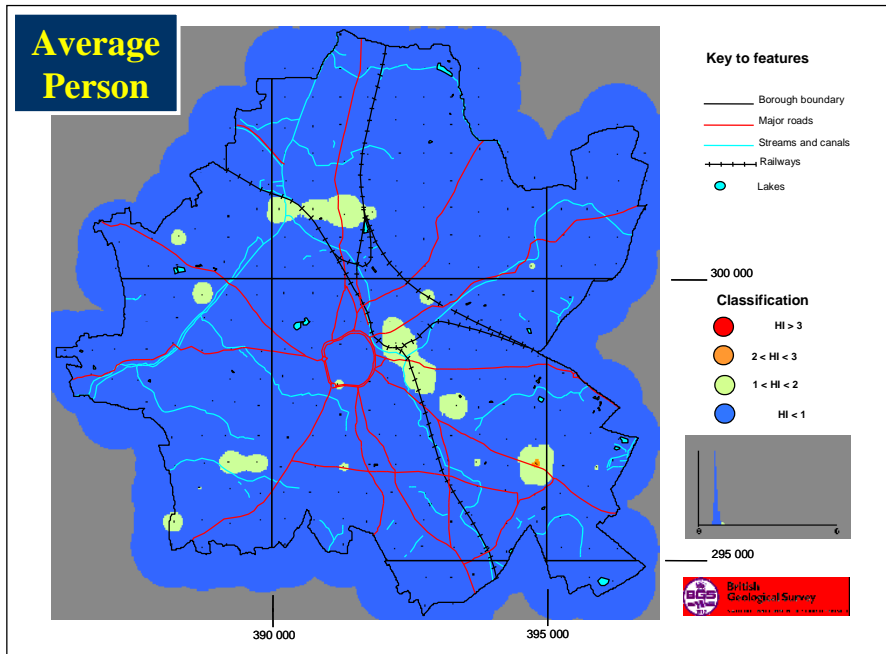


Fig 10:

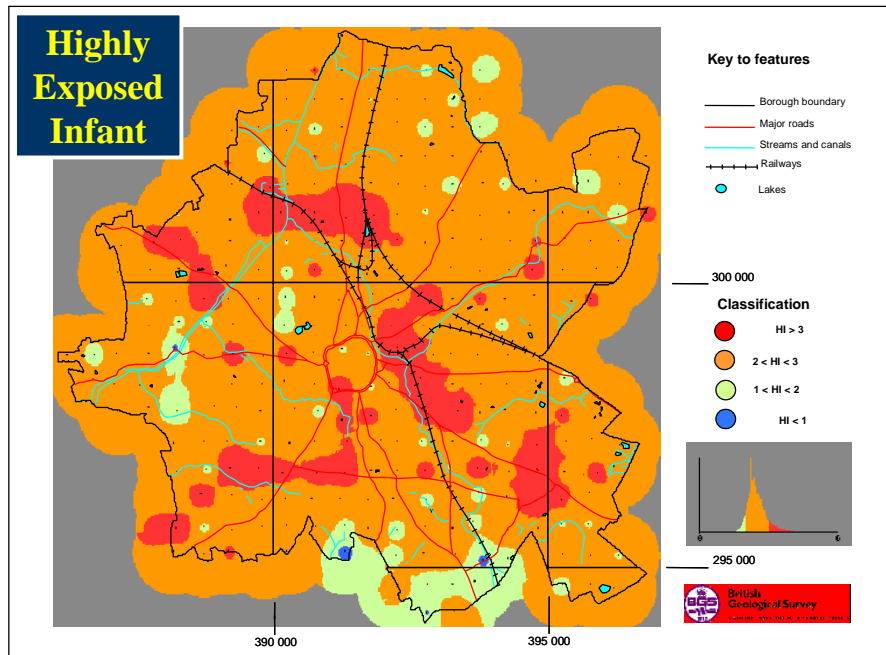


Fig 11:

GIS: Pb categorised by CLEA SGV shown with contemporary industrial areas

