Urban Environmental Geochemistry of Trace Metals: A Review

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"Capsule": *Urban environmental geochemistry as a scientific discipline provides valuable information on trace metal contamination of the urban environment and its associated health effects.*

Abstract

As the world's urban population continues to grow, it becomes increasingly imperative to understand the dynamic interactions between human activities and the urban environment. The development of urban environmental geochemistry has yielded a significant volume of scientific information about geochemical phenomena found uniquely in the urban environment, such as the distribution, dispersion, and geochemical characteristics of some toxic and potentially toxic trace metals. The aim of this paper is to provide an overview of the development of urban environmental geochemistry as a field of scientific study and highlight major transitions during the course of its development from its establishment to the major scientific interests in the field today. An extensive literature review is also conducted of trace metal contamination of the urban terrestrial environment, in particular of urban soils, in which the uniqueness of the urban environment and its influences

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on trace metal contamination are elaborated. Last, potential areas of future development in urban environmental geochemistry are identified and discussed.

Keywords: Urban environmental geochemistry; Trace metals; Urban soils; Urban environmental quality; Metal isotopes; GIS; Phytoremediation

1. Introduction

According to the World Urbanization Prospects: 2001 Revision prepared by the United Nations, the world's population is expected to grow from 6.1 billion in 2000 to 8.3 billion in 2030. As of 2000, an estimated 47% of the world's population already lived in urban areas, and the urban population will likely exceed 50% by 2007. The statistics also indicate that nearly all of the expected growth in population in the next three decades (2000-2030) will take place in urban areas, with almost no growth in the rural population (United Nations, 2001). The statistics undeniably suggest that the urban environment will soon become the most dominant human habitat for the first time in history.

From an environmental and health perspective, this profound geographical development will have a critical influence on our immediate environment and its quality for human health. On a daily basis, numerous human activities, including municipal, industrial, commercial, and agricultural operations, release a variety of toxic and potentially toxic pollutants into the environment (Nriagu, 1979; Nriagu and Pacyna, 1988; Nriagu, 1996). Within the urban environment, where these activities are especially intense, emissions of both metal and organic pollutants are often vastly accelerated, inevitably rendering the urban environment particularly susceptible to environmental degradation and contamination (Nriagu, 1988; Kreimer, 1992; Thornton, 1993).

Metals are non-biodegradable and accumulative in nature. Elevated emissions and their deposition over time can lead to anomalous enrichment, causing metal contamination of the surface environment. The prolonged presence of the contaminants in the urban environment, particularly in urban soils, and their close proximity to the human population can significantly amplify the exposure of the urban population to metals via inhalation, ingestion, and dermal contact (Mielke and Reagan, 1998; Boyd et al., 1999; Mielke et al., 1999). A human health concern is usually associated with excessive exposures to metals that cause toxic effects to biological organisms, herein referred as trace metals of environmental concerns. These trace metals may include non-essential ones, such as Cd and Pb that can be toxic even at trace levels, and biologically essential elements, such as Cu and Zn, which might cause toxic effects at elevated concentrations. The direct health impacts of trace metal contamination of the urban environment are usually difficult to assess due to the complexity of the medical factors involved. Nonetheless, it is generally accepted that children represent the most sensitive group (Watt et al., 1993; Nriagu et al., 1996; Shen et al., 1996). The exposure of children to trace metals can increase greatly through their ingestion of metal-laden soil particles and dust via frequent hand-to-mouth activities. The toxicological effects are further aggravated by the unique physiology of children, the sensitivity of their developing vital organs, and different chemical forms of metals involved (Hrudey et al., 1996). Other indirect consequences of trace metal contamination of the urban environment include the subsequent migration of the pollutants to receiving bodies of water via urban runoff, resulting in the trace metal enrichment of sediments (Sutherland and Tolosa, 2000; Ip et al., 2004). This may affect the quality of aquatic ecosystems and increase the body loadings of aquatic organisms through bioaccumulation and biomagnification, potentially causing trace metal contamination of the food chain (Callender and Rice, 2000). Thus, trace metal contamination of the urban environment can have long-term and far-reaching environmental and health implications.

Given the growing dominance of the urban environment and the potentially profound health implications of trace metal contamination, many facets of environmental phenomena uniquely found in urban settings have been investigated. Of particular interest in this review paper is the development of the discipline of *Urban Environmental Geochemistry* and its relevance to trace metal contamination of the urban terrestrial environment, especially of urban soils. The term urban geochemistry was coined by Thornton in 1990 to describe research activities concerning the role of geochemists at the interface of environmental geochemistry and urban pollution (Thornton, 1991). Urban environmental geochemistry can be defined as a field of scientific study that uses the chemistry of the solid earth, its aqueous and gaseous components, and life forms to examine the physical, chemical, and biological conditions of an urbanized environment (Siegel, 2002). The information yielded gives insights into the mobilization, dispersion, deposition, and distribution of potentially toxic metals/metalloids in urban ecosystems. This knowledge plays a vital role in the assessment of trace metal contamination and in the evaluation of its potential environmental and health implications. Furthermore, it is increasingly recognized that the synchronization of such information into urban planning can facilitate the development of healthy and sustainable urban environments. Hence, there is an obvious need for a greater understanding of urban environmental quality (Vlahov and Galea, 2002; Brown, 2003; de Hollander and Staatsen, 2003; Northridge et al., 2003; Pacione, 2003; van Kamp et al., 2003).

Urban environmental geochemistry has become an important scientific discipline today. Since its establishment, a wealth of scientific knowledge in trace metal contamination of the urban environment has accumulated. Nonetheless, literature reviews extensively summarizing past and current relevant studies are rare. Hence, the primary objectives of this review paper are 1) briefly review the historical development of urban environmental geochemistry as a field of scientific study, 2) to convey the increasing significance of urban environmental geochemistry to human health and the environment as a whole, 3) to highlight the uniqueness and applicability of investigative techniques in the study of trace metal contamination of urban environment, 4) to provide an overview of the literature on trace metal contamination of the urban terrestrial environment, particularly of urban soils, by gathering relevant scientific evidence from past and current studies, and 5) to identify potential areas of future development in urban environmental geochemistry.

2. Development of urban environmental geochemistry

Elevated concentrations of trace metals as a result of human activities have been recorded since ancient times (Nriagu, 1996). However, excessive releases of toxic trace metals into the urban environment and the associated health implications only became apparent in the 1960s when anthropogenic Pb contamination of the urban environment was denoted. Patterson (1965) wrote that "the industrial use of lead is so massive today that the amount of lead mined and introduced into our relatively small urban environments each year is more than 100 times greater than the amount of natural lead leached each year from soils by streams and added to the oceans over the entire earth." Scientific studies of environmental geochemical phenomena within urbanized areas began to emerge. In addition to Pb, some of the early studies on the quality of the urban environment (Purves, 1966 & 1968; Purves and Mackenzie, 1969) also examined the contamination of urban soils in Scotland with Cu, B, and Zn. Purves and Mackenzie (1970) also showed evidence of elevated concentrations of trace metals in vegetables grown in the urban environment. A multi-elemental approach was employed by Klein (1972), where he examined the spatial distribution of Hg, Ag, Cd, Co, Cr, Cu, Ni, Pb, and Zn in an urban area of Michigan, U.S.A. Collectively, these studies led to the early revelation of trace metal contamination of the urban environment and paved the way for the development of urban environmental geochemistry as a scientific discipline.

Over the past three decades, urban environmental geochemistry went through several major transitions, one of which was a strong geographical movement guided by the emergence of urbanized and industrialized centers. This geographical phenomenon was such that studies published in the 1970s and 1980s were primarily conducted in developed and industrialized countries in North America and Europe, where major urban centers were located. These studies included some large-scale geochemical surveys in some countries, such as the U.K. and the U.S. (Thornton and Webb, 1979; Thornton and Plant, 1980; Carey et al., 1980). Understandably, comparatively few studies were performed in other regions at that time. This started to change towards the end of the 1980s, when some developing regions began to experience rapid urbanization and industrialization, and signs of potential trace metal contamination in the urban areas of these regions became increasingly noticeable. In Southeast Asia, in particular, rapid economic and industrial development, coupled with a lack of pollution controls, has prompted massive investigative efforts to quantify anthropogenic trace metal emissions and evaluate the environmental consequences. Today, studies of urban environmental geochemistry have developed into a global phenomenon with few geographical boundaries.

During the infancy of urban environmental geochemistry, a great deal of effort was devoted to investigating the prevalence of Pb contamination in the urban environment, not to mention its long-term adverse toxic effects on children. Many of the early studies on urban environmental geochemistry assessed Pb contamination, whether of roadside soils, dust, and atmospheric particulates within an urban environment. Although Pb continues to be one of the most studied contaminants in the urban environment, other toxic and potentially toxic trace metals, such as Cd, Cu, Ni, and Zn, are also frequently evaluated. Similar to Pb, these trace metals are among those in greatest use commercially and among the most emitted, with toxicological effects on humans who are excessively exposed to them (Nriagu and Pacyna, 1988; Järup, 2003). Furthermore, the inclusion of these trace metals also enhances the revelation of interactions, influences, and/or fingerprints of simultaneous sources of emission (Alloway, 1990; Huang et al., 1994). It should be noted that such a transition from a single- to multi-element approach was readily achievable due to technological advances in analytical equipment, such as the development and increasing availability of Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES). Today, compelled by the growing environmental and health awareness of the public, assessments of an array of trace metals in soils, sediments, water, air, as well as foodstuffs are demanded by regulatory guidelines. Those routinely regulated trace metals include As, Ba, Cd, Co, Cr, Cu, Hg, Pb, Mo, Ni, V, and Zn (Department of Soil Protection, Netherlands, 1994; CCME, 1997; National Environmental Protection Agency, 1995). As our knowledge of the toxicological effects of trace metals widens, and shifts in the commercial and industrial applications of selected trace metals become apparent, trace metals of significant environmental and health interest can expand beyond this array of trace metals to include elements that were previously considered trivial (see Section 5.1).

3. Recognition of the uniqueness of urban environments

An urban environment is unique in the sense that it is an environment that has been highly modified by mankind to accommodate a larger number of human inhabitants than a natural system is normally incapable of. Some distinctive characteristics of a typical urban environment obviously include a dense population and a relatively high level of productivity primarily driven by non-agricultural activities. An urban environment may also include above- and underground infrastructure, buildings, and an extensive network of pavements along with a high density of motorized transportation systems (Fig. 1). These characteristics are only possible under one condition, that is, through considerable physical alterations to the environment. These alternations, in turn, give rise to physical, chemical, and biological characteristics that make the urban environment different from a natural ecosystem. Recognition of these urban characteristics and their influences on the dispersion, distribution, and deposition of trace metals is imperative. These issues must be taken into account when an environmental investigation of such an environment is conducted. This is because investigative principles of environmental geochemistry normally applicable in a natural or relatively undisturbed environment might become deficient or inappropriate when implemented in an urban setting. In some cases, the modification of existing techniques and/or derivation of a new methodology may be necessary if meaningful and scientifically sound conclusions are to be drawn (De Kimpe and Morel, 2000). Using urban soils as an example, the discussion below highlights some physical factors of an urban environment that are worthy of attention during an assessment of trace metal contamination of urban soils.

3.1 Origin of urban soils

Natural and undisturbed soils usually exhibit a vertical stratum of soil formation commonly referred to as Horizons A, B, and C. Each of these horizons represents a zone of specific soil properties, functionality, and microbiological activities. Furthermore, the origin of these natural and undisturbed soils can usually be traced back to the natural and geological processes of their parent materials, whether their formation is associated with geological weathering, volcanic activities, and/or sedimentation. In other words, soils generally display common geological and mineralogical characteristics with their parent materials. Therefore, the geological composition of bedrock enables an approximate estimation of background levels of trace metals in soils and often the leads to the postulation of anthropogenic inputs when excessive trace metals are detected (e.g., Covelli and Fontolan, 1997; Praharaj et al., 2003; Banat et al., 2005). Although this approach has been widely accepted in the evaluation of trace metal contamination of soils, its applicability can be severely limited in an urban setting where it is highly questionable that the soils originate from a single source.

In fact, soils in the urban environment tend to be highly disturbed due to intense human activities in the surroundings and may even be exogenous, i.e. transported from elsewhere (Bullock and Gregory, 1991; Craul, 1999). In development terms, urban soils are frequently referred to as “made ground.” As a result, they do not necessarily exhibit a stratified profile of soil formation nor relate directly to their immediate geological materials. Signs of the enrichment of surface soil with trace metals could become obscured, and soil contamination may also be masked. Uncertainty as to the origin of the soils, the possible frequent mixing of the soils, and other physical disturbances could greatly limit the validity of some conventional geochemical principles, such as the use of the factor of enrichment, in evaluations of trace metal contamination (Reimann and De Caritat, 2000). Equivalently, it would also be difficult to evaluate the relative contributions of the metals from natural and anthropogenic processes based solely on concentrations of the trace metals in the soils and on their geological background. Other techniques may also need to be incorporated.

3.2 Dispersion and deposition of trace metals

In an urban environment, trace metals can be emitted from numerous anthropogenic sources (Fig. 2). Activities with a noticeable impact on the urban environment typically include traffic-related activities (fossil fuel combustion, wear and tear of vehicular parts, and leakages of metal-containing motor oils), industry-specific activities, the disposal of municipal waste (incineration and landfill), and the corrosion of construction/building materials (Barltrop, 1979; Kelly et al., 1996; van der Sloot et al., 1996; Tossavainen and Forssberg, 1999; Councell et al., 2004; Nadal et al., 2004). Sometimes, other metal-emitting facilities, such as coal power generating plants and mining and smelting operations, if located in or near urban areas, can also play an important role in the distribution of anthropogenic trace metals. Regardless, trace metals from these "urban" sources are primarily released via atmospheric emissions (Nriagu and Pacyna, 1988; Kubin and Lippo, 1996; Wong et al., 2003). Upon emission, they tend to adhere to particulate matter to form fine particulates and dust (Vesper and White, 2003). The metal-laden particles remain transient in ambient air until they are deposited on land and in water. The dispersion and distribution of trace metals are highly dependent on the size of the particles and on the surface properties of the substrate on which the metals are deposited. Those deposited on land in an urban setting can be readily relocated and dispersed by wind, rain, and surface runoff (Callender and Rice, 2000).

3.2.1 Limited metal fixation ability

Distribution of the metals in soil profiles is primarily governed by factors, including the solubility of metals, properties of soil, and other environmental conditions, in undistributed soils (Hernandez et al., 2003). Natural and undisturbed soils permit the percolation of water, which serves as a vertical refuge for trace metal contaminants, as metal-adsorbed particulates (and dissolved metals) carried by water travel along the soil profile and are trapped in different layers. In the urban environment, however, the percolation of rainwater through urban soils is usually significantly reduced due to the absence of large, soil-covered areas. Sometimes, the presence of underground infrastructure and utilities can also restrict soil depth and disrupt the percolation of water, causing soil saturation and ponding. One would expect that the ability of the urban terrestrial environment to fixate or immobilize metal pollutants is therefore severely limited in comparison with that of the natural environment. Furthermore, the urban environment is predominantly occupied by infrastructure, pavements, and buildings, and covered with artificial materials such as asphalt, concrete, metals, tiles, glass panels, and wood (with or without paint). Surfaces composed of these materials exhibit remarkably different metal sorption properties as compared to natural substrates commonly encountered in the natural environment, e.g. soils and plants. Even though artificial materials with a porous surface may display the capacity to retain metals, where their micro-structure can potentially serve as a reservoir for metal pollutants, these materials may be inferior to soils in terms of their metal adsorption capacity and could even become a source of pollutants (van der Sloot et al., 1996; Tossavainen and Forssberg, 1999; Andersson et al., 2004). As a result, metal-enriched particulates and dust deposited in the urban environment often remain relatively mobile and tend to disperse, due to the lack of means of physical entrapment and adhesion to substrates. However, in some urban soils, metal mobility may be limited due to the effect of a rise in soil pH resulting from spillages of cement and other materials containing lime.

3.2.2 "Preferential" relocation and transport of trace metals

The dispersion and deposition of metal-enriched particulates and dust in the urban environment are governed by physical and micro-environmental factors, including topography, wind direction, and urban runoff. Wind direction in the urban environment is highly influenced by the positioning and topography of buildings. In the presence of buildings, air movements may become channeled (e.g., between two rows of buildings), obstructed (e.g., at a T junction) and/or confined (e.g., at a confined street corner). All of this can cause changes in wind speed and direction that could subsequently affect the dispersion and deposition of dust and particulates, resulting in the preferential deposition of heavy metals, where stagnant metal-laden particulates concentrate. Moreover, dust and particulates on paved surfaces can be readily re-suspended by wind and/or easily swept by urban runoff. Undoubtedly, this phenomenon serves as a sorting mechanism that separates coarse particles from fine particulates (Hoydysh et al., 1987; Dempsey et al., 1993; Laracazenave et al., 1994; Al-Chalabi and Hawker, 1997). The re-suspension of the fine particulates represents a major health concern, since the fine particulates can be readily inhaled and become embedded in human lungs. More importantly, fine particulates, such as $PM_{2.5}$, can readily penetrate the alveolar membrane to enter the blood stream.

Urban runoff travels down gradients in accordance with the urban landscape, specifically topography and slope gradients. Dust and other fine materials are swept and flushed along its path, whereby the runoff initially becomes highly enriched with metal contaminants. This process of relocation by urban runoff not only physically transports the contaminants to open soil surfaces and surrounding aquatic ecosystems via gully and drainage systems, but also chemically alters the contaminants, by dissolving soluble metals (Fig.1 and 2). Since urban runoff is usually discharged with little or no treatment, this process can greatly affect the quality of the surrounding water bodies and biota (Check, 1997; Mason et al., 1999; Turer et al., 2001; Duzgoren-Aydin et al., 2004).

4. Trace metal contamination of the urban terrestrial environment

Soils serves as the most important sink for trace metal contaminants in the terrestrial ecosystem. Their presence in the terrestrial environment represents a stationary source of trace metals, which may have a long half life of perhaps several hundred years (*e.g.*, Pb). Urban soils are therefore an important indicator of human exposure to trace metals in the urban terrestrial environment (Nriagu, 1988, Watt et al., 1993; Mielke and Reagan, 1998; Boyd et al., 1999; Mielke et al., 1999). Regardless of their functionality, they are highly susceptible to physical disturbance and chemical contamination due to their proximity to intense human activities. Unlike soils in rural and suburban areas, in the urban environment open/exposed soils, with or without vegetation, are usually fragmented and small in size. Because of urban planning, they are commonly found in greenbelts along roadsides and in leisure and recreational facilities, such as playgrounds and parks, where they are used as a substrate to grow plants for buffering and aesthetic purposes. They can sometimes also be found in private backyards, in small plots used to grow food (Bullock and Gregory, 1991; Craul, 1999; Chiesura, 2004; Hough et al., 2004). These leisure facilities are an integral component of healthy urban living. Since they are frequently visited by children and the elderly, an understanding of the environmental quality of these urban facilities is crucial.

Table 1 contains a list of published works and elements of interest in studies of trace metal contamination of urban soils in a) Europe, b) America, and c) Asia-Pacific. The list is by no means comprehensive. Instead, the purpose is to provide a general summary of cities and elements that have been studied in the past. As shown in Table 1, studies on urban soil contaminated with trace metals have been conducted in many parts of the world in both developed and developing countries, and a wide range of trace metals has been examined. The U.K. and Hong Kong are probably two of the most extensively studied urban environments. The former represents a European country with a long history of industrial and mining activities, while the latter represents an Asian metropolitan area with very high population and traffic densities, and light industries in the recent past. Since urban soil contamination in the U.K. has been reviewed by other researchers (e.g., Davies, 1990; Thornton, 1991), Hong Kong is used as an example in the discussion below.

4.1 Hong Kong as an example in the Asia-Pacific region

Hong Kong is located along the southeast coast of China, adjoining Guangdong province. It is a densely populated city with a population of nearly 7 million and a total land area of 1,100 km^2. It has approximately 520,000 vehicles on 1,928 km of roads. Trace metal contamination of urban soils in Hong Kong has been studied since the 1970s. An early studies conducted by Wong and Tam (1978) showed Pb contamination in roadside soils and vegetables in Hong Kong. Today, trace metal enrichment/contamination of soils in the urban environment of Hong Kong in various environmental settings has been documented in a number of publications (see Table 1).

In general, Cd, Cu, Pb, and Zn in urban soils are the most frequently investigated trace metals in Hong Kong. The vast majority of the studies examined the distribution of trace metals in surface soils (<20 cm). This surface soil sampling method has often been used primarily because the impact of trace metal contamination is usually most obvious in surface soils. The assessment of surface soils also allows for a greater understanding of the potential health risks to the urban population. A large-scale survey of urban soil quality with respect to trace metal concentrations was conducted in Hong Kong, in which nearly 600 soil samples

(0-15 cm) were collected from urban and country parks of Hong Kong (Li et al., 2001). A comparison of the concentrations of Cu, Pb, and Zn in soils in the urban and country parks indicated that soils within the urban environment were generally more enriched than those outside of the urban perimeter. The mean concentrations of Cu and Zn in urban soils (24.8 and 168 mg/kg, respectively) were at least four and two times higher than those of rural soils (5.17 and 76.6 mg/kg, respectively), while the mean Pb concentration of urban soils (89.9 mg/kg) was one magnitude higher than that of rural soils (8.66 mg/kg). A study carried out recently by Li et al. (2004) employed a systematic sampling method (4-5 samples per km^2) to collect 152 urban soil samples in the highly urbanized and most densely populated area of Kowloon with a population density of 17,200 persons/km^2 (Fig. 3). For the first time in the study of urban soil, this study incorporated geographical information system (GIS) technology to examine the distribution of trace metals and elucidate their relationship with urban geographical features, such as traffic densities and land uses. The GIS-based geochemical maps graphically illustrated the distribution of trace metals in urban soils in Kowloon (see Fig. 4). More importantly, they revealed a strong association between trace metal enrichment and the locations of road junctions, major roads, and industrial buildings.

In addition to trace metal concentrations, some studies have attempted to elucidate the origin(s), potential bioavailability, and reactivity of the contaminants using various chemical extraction methods and Pb isotope compositions. For example, Wong and Li (2004) attempted to compare trace metal concentrations of urban soils at increasing depths. In the process, they clearly demonstrated that there are some field limitations to collecting samples in an urban environment. Nonetheless, the study showed that Pb concentrations in the subsurface (>20cm) tended to decline rapidly with increasing soil depth. Furthermore, this distribution pattern reflected the historical influence of nearby activities as the metals accumulated. This is generally valid for trace metals (e.g., Pb) that are relatively insoluble and highly affinitive to soil surfaces and organic matter. However, for trace metals that are relatively soluble and loosely bound to soil surfaces (e.g., Cd), a distribution pattern may reflect the possible downward migration of the metals through the infiltration of rainwater.

Lead isotopic signatures have been used to substantiate and quantify the influence of anthropogenic Pb in various environmental samples, e.g. sediments, air, and soils. Lead isotopes in urban soils in Hong Kong were probably first reported by Wong and Li (2004) and further examined by Duzgoren-Aydin et al. (2004). In general, the results of Pb isotopic ratios (Pb^{206}/Pb^{207} and Pb^{208}/Pb^{207}) in these studies provided supporting evidence of the contribution of non-geogenic Pb in the urban environment. It also indicated that the distribution of Pb in urban soils, as well as in the corresponding gully sediments, decreased with increasing distance from traffic, and sometimes correlated positively with increasing traffic volume in Hong Kong. Based on the previous studies, it can be concluded that trace metal contamination of urban soils in Hong Kong has largely been caused by traffic-related activities and, sometimes in the past, by light industrial activities. Solid evidence has indicated that Pb contamination is associated with the use of leaded gasoline. Furthermore, the contamination of urban soil with other trace metals has, to varying degrees, been attributed to other traffic-related activities, including the combustion of fossil fuels and the wear and tear of tires and galvanized metal parts.

5. Possible future research directions

Environmental geochemical studies of the urban environment are becoming increasingly sophisticated, and the complexity of the issues being investigated and the depth of understanding being sought have led to the accumulation of a considerable amount of scientific knowledge. Nevertheless, trace metal contamination of the urban environment remains a major environmental and health concern, under which one could identify many issues that can offer opportunities for further progress or that have yet to be explored. In the following, an attempt is made to elucidate several areas of urban environmental geochemistry in which further advancements can be of significant scientific value. These areas are: 1) the inclusion of non-traditional but environmentally important metals, 2) further explorations into the environmental applications of other metal isotopes (e.g. Cu and Zn), 3) the incorporation of computerized aids to visualization and GIS, and 4) the potential use of phytoremediation in urban areas.

5.1 Inclusion of other trace metals

In the past, trace metal assessments of urban soils frequently examined trace metals that were traditionally significant for the environment and health, particularly Cd, Cu, Pb, and Zn. On the other hand, the distribution of other trace metals in the urban environment has received comparatively limited attention. Historically, Pb was the most important trace metal in the urban environment. Lead pollution was considered a serious health problem in the urban environment. Its prevalence provoked extensive scientific investigations leading to the withdrawal of tetraethyl lead from leaded gasoline. With the diminishing prevalence of Pb, the question to ask is what is next? Trace metals emitted from traffic-related activities and their influences have changed drastically, which has led to more complex input and distribution patterns of trace metals in the urban environment. Furthermore, growing applications of other trace metals may also magnify the complexity of urban soil contamination. Although not the only source of trace metal contaminants, traffic-related activities continue to exert a widespread influence on the urban environment. Hence, rare earth elements (REEs), platinum group elements (PGEs), and manganese (Mn) have been recommended as environmental indicators of traffic and other “urban” activities, especially where leaded gasoline is no longer in use (Kitto et al., 1992; Huang et al., 1994; Zayed et al., 1999a&b; Cinti et al., 2002; Sutherland, 2003; Zereini et al., 2004). These elements have been chosen for their usefulness in the identification of sources of contaminants and their potential health implications. Literature concerning the occurrence of PGEs in the environment, their transformations and possible human health effects have been reviewed Pyrzyńska (2000) and more recently by Ravindra et al. (2004).

It has been documented that atmospheric emissions of REEs and PGEs can be attributed to abrasion and corrosion of catalytic converters coupled with fuel combustion, as fossil fuels contain trace quantities of REEs (0.5 – 2.0 % in the oxide forms), and catalytic converters in vehicles are now dominantly made with PGEs (Kitto et al., 1992; Huang et al., 1994; Zereini et al., 2004). Work conducted in U.K. towns over the period 1982-1998 has clearly demonstrated that there has been an increase in PGEs in road dust (Farago et al., 2000; Hutchinson et al., 2000). Further indications that traffic is the source of Pt were obtained by comparing Pt with Au in soils and dust sampled in the London borough of Richmond, U.K., in 1994 (Farago et al., 1995 & 1996). Concentrations of Pt, like those of Pb, which originate from traffic, are higher in road dust than they are in soil samples. For Au, which does not originate from traffic, concentrations are higher in soils than in road dust. In addition, within an increasingly technologically advanced environment, surface enrichment with REEs may also become increasingly apparent, as REEs are also used in the production of magnetic materials, high temperature superconductors, Pb-free solders in electronic assemblies, and in ceramics and glasses (Yu and Chen, 1995; Hirano and Suzuki, 1996; Wu et al., 2004). The inclusion of REEs in studies on the urban environment can be valuable and constructive, as they may shed light on interactions, influences and/or fingerprints of simultaneous emission sources (Hirano and Suzuki, 1996; Angelone et al., 2002).

Methylcyclopentadienyl manganese tricarbonyl (MMT), an organometal, was introduced to unleaded gasoline as an anti-knock agent to substitute for tetraethyl lead in leaded gasoline. Levels of Mn in the urban environment were therefore anticipated to rise (Lytle et al., 1995). Manganese has received increasing attention in recent years, as toxicological evidence of the negative health effects of excessive exposure to Mn emerges. Mn is an essential element for the proper functioning of plants, animals, and humans. A deficiency of Mn can lead to serious health effects, such as the impairment of neurological functions, seizures, osteoporosis, and mental retardation. However, Mn is a neurotoxin and can cause irreversible neurological disease at high levels of inhalation, for example, in the case of industrial exposure. Prolonged and subclinical exposure to Mn is also suspected to cause cancer, and neurologic and psychiatric disorders, including Parkinson's- and schizophrenia-like symptoms (Davis et al., 1999; Mergler, 1999; Silbergeld, 1999; Zayed et al., 1999a & b). There have been indications that MMT could become a successor to Pb in the urban environment in terms of its pervasiveness and long-term health effects. In the U.S., the approved level of MMT used as a gasoline additive is $^{1}/_{32}$ gram per gallon Mn (~0.008 g Mn/L) but MMT is currently used in only a very small amount of U.S. gasoline (about 0.3 percent of the total U.S. gasoline pool). Until recently, the U.S. Clean Air Act banned the use of MMT in reformulated gasoline (about 30 percent of U.S. gasoline) and the state of California does not allow the use of MMT in gasoline. MMT has been withdrawn from some countries, such as Canada, ironically for its mechanical impact on vehicle emission control systems (US EPA, 2005).

Some of these "non-traditional" but environmentally important metals include mercury (Hg) and tin (Sn). Mercury, Sn and their organic compounds are chosen for their toxicity, increasing prevalence in the urban environment and a general paucity of information in terms of their distribution, behaviours and ecotoxicity in the urban environment. Future studies of urban environmental geochemistry may emphasize on organic Hg and organic Sn, for it is well recognized that the toxicity of these compounds is significantly more severe than that of their inorganic counterparts (Dopp et al., 2004). Many previous studies have investigated their distribution, biogeochemical behaviours and toxicity of organic Hg and organic Sn (Schroeder and Munthe, 1998; Hoch, 2001; Pacyna et al., 2003; Seigneur et al., 2004). Nonetheless, very few have been carried out in an urban environment. Recently, organic Hg and organic Sn were identified as two of the twelve persistent toxic pollutants in the Regionally Based Assessment of Persistent Toxic Substances in Central and North East Asia of the Regional Report of United Nations Environment Programme (UNEP, 2002), in which more information on the pollutants in the region was urged.

5.2 Use of other metal isotopes

The identification and differentiation of trace metals between anthropogenic and natural sources using an isotopic technique have largely been limited to Pb (Ault et al., 1970; Gulson et al., 1981; Farmer et al., 1996; Callender and Rice, 2000; Hansmann and Koppel, 2000; McGill et al., 2000; Semlali et al., 2001 & 2004). Innovative uses of other isotopes in environmental studies remain limited. In recent years, considerable advancements have been made in Cu and Zn isotopic analytical techniques using plasma source mass spectrometry (Marechal et al., 1999; Archer and Vance, 2004; Ingle et al., 2004; Mason et al., 2004a & b). It is believed that the achievement has improved the applicability, precision, and reliability of Cu and Zn isotope analyses. Copper and Zn are two of the most common contaminants in the urban environment. It would be beneficial to further explore the potential environmental applications of Cu and Zn isotopes. Future scientific research may emphasize the collection of background information on Cu and Zn isotopes and an understanding of basic relationships between the environment (natural sources) and anthropogenic activities (anthropogenic sources). An effort should also be made to compile the Cu and Zn isotopic signatures of various environmental compartments and, eventually, to construct a database so as to substantiate the validity and applicability of Cu and Zn isotopic signatures in the identification/quantification of sources, and environmental health studies in a manner similar to that for Pb isotopes.

5.3 Computerized tools for visualization and GIS analysis

It is becoming increasingly popular to incorporate digitized and computerized technologies in studies of urban environmental geochemistry. These technologies may include geographical information systems (GIS) and global positioning system (GPS) in the interpretation and presentation of data and in geochemical modeling. Thus far, there have been few studies (e.g., Facchinelli et al., 2001; Thums and Farago, 2001; Li et al., 2004; Lee et al., 2005) that have made use of GIS to graphically and digitally present the distribution of trace metals in urban environments. Visualization can be enhanced significantly by computer-aided modeling using GIS. On the regional and national scales, the geochemical mapping of trace and major elements can be used as a tool for visualization, to make it easier to identify the possible location(s) of contaminated areas. Furthermore, existing GIS databases may incorporate population density, the locations of utilities and structural features, and topography. This allows the analytical data to be manipulated with this additional information, offering several advantages in trace metal assessments of urban soils. First, GPS allows precise positioning of soil sampling locations. Digital records of the positions can easily be transferred to and stored in a computer, where geochemical maps of trace metals can be made and easily digitalized. Furthermore, given the ease of manipulating and transferring the data, the data can readily be incorporated with other existing GIS information. For example, a better understanding of the interactions between trace metals and the urban environment can also be obtained by overlaying the trace metal distribution with key urban features, e.g. topography, traffic networks, and locations of buildings and industrial facilities (Li et al., 2004; Lee et al., 2005). Furthermore, a scale of potential health impacts may be extrapolated by comparing the data with demographic information and health records.

5.4 Urban phytoremediation

Soil remediation is required when the risk of human exposure to contaminants exceeds an acceptable level and/or when the soil needs to be restored to its original functionality. The fundamental factors governing the selection of an appropriate soil remediation treatment include the level of cleanup desired, length of time allowed, chemical forms and amounts of contaminants, site characteristics, and the cost involved (Iskandar and Adrian, 1997). Considering these factors, phytoremediation can be a preferable soil remedial technique for the removal of trace metals, especially in an urban environment. A simple definition of phytoremediation is the use of plants, sometimes in conjunction with microorganisms and chemical reagents, to clean up contaminated sites, mostly in water and soil, through either the bio-absorption of the contaminants or the transformation of the contaminants to less toxic compounds. Phytoremediation is an innovative remedial technique developed for cleaning up the environment. It has been an area of active research in the past twenty years, and the commercialization of this technology has been initiated (Cunningham and Ow, 1996; Boyajian and Carreira, 1997; Baker et al., 2000; McGrath and Zhao, 2003).

In the urban environment, trace metal emissions from anthropogenic sources can probably be described as continuous because human activities within it take place on a daily basis. Even though the rate of deposition fluctuates with time, urban soils can become enriched with multiple elements given a considerable duration of exposure. The excessive deposition of trace metals in urban soils itself is therefore a long-term natural phenomenon accelerated by human activities. Furthermore, it is also realistic to expect simultaneous inputs of multiple contaminants. The contamination of urban soil resulting from this long-term and multi-element deposition makes phytoremediation an attractive remedial method. Plants exhibit a gradual uptake of metals over a period of time and can be repeated seasonally. In the view of Iskandar and Adriano (1997), phytoremediation should also be considered in sites where the concentration of metals is not too high to be considered toxic even to the hyperaccumulators and other plants, but high enough to warrant soil remediation action. In fact, this has been a common characteristic of contaminated urban soils in many countries. In addition, urban soils generally tend to be most enriched in the upper layer. Hyperaccumulators and high biomass plants with an active root zone of less than 2 m can therefore easily cater to contaminated urban soils. Furthermore, phytoremediation can be readily applied to restore contaminated soils of any size. It is especially advantageous for contaminated urban soils that are fragmented and small in size where applications of traditional remedial methods can be impractical and cost-prohibitive. Compared to other kinds of in-situ remediations of contaminated sites, which may cost between \$10 and \$100 per cubic meter, techniques such as phytoremediation, in which plants are cultivated the same way a farmer plants a field or orchard, may cost as little as \$0.05 per cubic meter (Watanabe, 1997).

From a practical point of view, it is unnecessary in most case to excavate and relocate contaminated soils when phytoremediation can be implemented. Not having to use large machinery and excavation equipment not only enables means greater flexibility and room to maneuver in an urban setting where space is limited, but also enhances the aesthetic quality of the remedial process. Furthermore, the use of plants in phytoremediation is benign and non-destructive to soil fertility and physical integrity, preserving the microbiological productivity and normal functionality of the soils after treatment. Hyperaccumulators, as well as other high biomass plants, may also possess another advantage. Since bare soils without cover are prone to erosion induced by wind and runoff resulting in an increase in the likelihood of human exposure via wind-blown dust (Iskandar and Adriano, 1997), a vegetative cover can act as a physical barrier to protect soil (Beard, 1994). Lastly, phytoremediation can be readily incorporated in the existing greening program of an urban area, as in the city of Toronto where brownfields were converted into green spaces (De Sousa, 2003). In a healthy and sustainable city, the role of green spaces serves as a leisure facility and facilitates other environmental functions, such as the purifying the air and water, filtering wind and noise, and stabilizing the microclimate (Chiesura, 2004). If managed properly, the treatment can be implemented in a cost-effective manner. Regardless, the success of a remediation scheme relies on careful planning and on a full understanding of the contaminated area and its surroundings.

Although phytoremediation appears to be an attractive alternative, several aspects of this treatment method await further improvement. Furthermore, cases of field trials in urban environments are rare. Lead is one of the most commonly encountered pollutants in the urban environment. Since the plant uptake of metals strongly depends upon the solubility and bioavailability of the metal, Pb, usually stable and inert in soil, is a typical "problematic" heavy metal in phytoremediation. Few known plants can accumulate Pb under normal soil conditions. To increase the efficiency of phytoremediation, chelators such as EDTA (ethylenediaminetetraacetic acid) are used as soil amendments to render Pb more available to the plants (Huang et al., 1997; Watanabe, 1997; Shen et al., 2002). Some fear that this could result in groundwater pollution and that elevated concentrations of metals in plants could have ecological implications (Boyajian and Carreira, 1997). In recent years, some easily biodegradable chelates, such as EDDS (S,S-ethylenediaminedisuccinic acid), have been proposed to enhance the phytoextraction of heavy metals from contaminated soils (Grčman et al., 2003; Kos and Leštan, 2003; Tandy et al., 2004; Luo et al., 2005). At this point, the application of phytoremediation is limited, primarily due to the lengthy time requirement and the lack of an effective and safe means to dispose of the plants. Nevertheless, given the advantages of phytoremediation, further explorations into its efficiency and applicability within urban areas are necessary.

6. Conclusion

The urban environment will soon become the most dominant human habitat in history. The pressure from the activities of the urban population is intense, as anthropogenic emissions of potentially toxic trace metals have accelerated considerably. Balancing the delicate geochemical cycle in the urban environment while sustaining the activities of a dense population can be very challenging. Recognition of the susceptibility of the urban environment to environmental degradation and the potential adverse effects on human health is motivating the continuous pursuit of knowledge in urban environmental geochemistry. Urban environmental geochemistry as a scientific discipline has provided valuable knowledge on the mobilization, dispersion, deposition, and distribution of potentially toxic metals/metalloids in urban ecosystems. This knowledge is crucial to the sustainable development of urban environments. Future research efforts may be directed to the study of non-traditional trace metal pollutants, the development of metal isotopes, the exploration of computerized tools for visualization and analysis, and the application of phytoremediation in the urban environment.

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List of Tables

List of Figures

Table 1
Trace metals of interest in selected studies of trace metal contamination of urban soils in (a) Europe, (b) the America and Africa, and (c) Asia-Pacific region.
(a) Europe

Study area	Metals of interest	References
Scotland	B, Cu	Purves, 1966
Scotland	B, Cu, Pb, Zn	Purves, 1968
Scotland	B, Cu, Pb, Zn	Purves and Mackenzie, 1969
Scotland	B, Cu, Ni, Pb, Zn	Purves and Mackenzie, 1970
U.K.	Cd, Cu, Pb, Zn	Harrison et al., 1981
U.K.	Cd, Cu, Pb, Zn	Culbard et al., 1988
Poland	As, Co, Cr, Cu, Ga, Mn, Ni, Se	Dudka, 1993
Falun, Sweden	Pb	Lin et al., 1998
Berlin, Germany	Ag, As, B, Ba, Be, Bi, Br, Cd, Ce, Co, Cr, Cs, Cu, F, Ga, Ge, Hg, I, In, La, Mn, Mo, Nb, Ni, Pb, Rb, Sb, Se, Sn, Sr, Ta, Te, Th, Ti, Tl, U, V, W, Y, Zn, Zr	Birke and Rauch, 2000
Poznan, Poland	Cd, Cu, Pb, Zn	Grzebisz et al., 2002
Naples, Italy	Cd, Cu, Hg, Pb, Zn, Pt	Angelone et al., 2002
Rome & Latium, Italy	Pt	Cinti et al., 2002
Seville, Spain	Cu, Pb, Zn	Madrid et al., 2002
Gibraltar	Li, Na, K, Be, Mg, Ca, Sr, Ba, Al, La, Ti, V, Cr, Mo, Mn, Fe, Co, Ni, Cu, Ag, Zn, Cd, Pb, P, S, As	Mesilio et al., 2003
Jakobstad, Finland	Ag, As, Au, Ba, Bi, Cd, Co, Cr, Cu, Ga, Hg, La, Mn, Mo, Ni, Pb, Sb, Sc, Te, Th, Ti, Tl, U, V, W, Zn	Peltola and Åström, 2003
Tarragona, Spain	As, Cd, Cr, Hg, Mn, Pb, V	Nadal et al., 2004
Jordan	Cd, Cr, Hg, Pb, Zn	Banat et al., 2005

(b) America and Africa

Study area	Metals of interest	References
Michigan, U.S.A.	Hg, Ag, Cd, Co, Cr, Cu, Ni, Pb, Zn	Klein, 1972
Champaign-Urbana, IL, U.S.A.	Cd, Pb	Solomon and Hartford, 1976
USA	As, Cd, Hg, Pb	Carey et al., 1980
Pampean region, Argentina	Cd, Co, Cu, Cr, Ni, Pb, Zn	Lavado et al., 1998
St. Louis, U.S.A.	As, Cd, Cu, Cr, Hg, Ni, Yb, Sb, Sn, Zn	Kaminski and Landsberger, 2000
Montreal, Canada	Cd, Cu. Ni. Pb, Zn	Ge et al., 2000
Cincinnati, Ohio, U.S.A.	Cd, Cu, Cr, Ni, Pb, Zn	Turer et al., 2001
Hawaii, USA	Pt	Sutherland, 2003
Botswana, Gaborone	Sc, Cr, Co, Ni, Cu, Zn, Nb, Cd, Pb	Zhai et al., 2003

(c) Asia-Pacific region

Study area	Metals of interest	References
Hong Kong	Pb	Wong and Tam, 1978
Japan	Cu, Zn	Komai, 1981
Hong Kong	Cd, Cu, Pb, Zn	Lau and Wong, 1982
Hong Kong	Cd, Cu, Mn, Pb, Ni, Zn	Tam et al., 1987
Hong Kong	Cd, Cu, Fe, Mn, Pb, Zn	Ho and Tai, 1988
Australia	As, Cd, Cr, Co, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Sn, Tl, Zn	Tiller, 1992
China	Pb	Zhang, 1994
Seoul, Korea	Cd, Cu, Pb, Zn	Chon et al., 1995
Hong Kong	As, Cd, Cu, Pb, Zn	Chen et al., 1997
Hong Kong	Cd, Cu, Pb, Zn	Wong and Mak, 1997
Bangkok, Thailand	Cd, Cr, Cu, Mn, Ni, Pb, Zn; SCE	Wilcke et al., 1998
Wuhan, China	Cd, Cu, Pb, Zn	Xiong, 1998
Hong Kong	Cd, Cu, Pb, Zn	Poon et al., 1999
Nanjing, China	As, Cd, Cu, Co, Cr, Ni, Pb, Mn, Sb, V	Zhang et al., 1999
Danang City and Hoian, Vietnam	Cd, Co, Cr, Cu, Ni, V, Pb, Zn, Zr	Thuy et al., 2000

Hong Kong	Cd, Cu, Pb, Zn	Li et al., 2001
China	Cu, Zn, Pb and Cr	Lu, et al., 2003
Hong Kong	Pb	Wong and Li, 2004
Australia	Cu, Pb, Zn	Snowdon and Birch, 2004
Hong Kong	Cd, Cu, Pb, Zn	Li et al., 2004
China	Cu, Ni, Pb, Zn	Chen et al., 2005
Hong Kong	Cd, Co, Cr, Cu, Ni, Pb, Zn	Lee et al., 2005

Fig. 1.

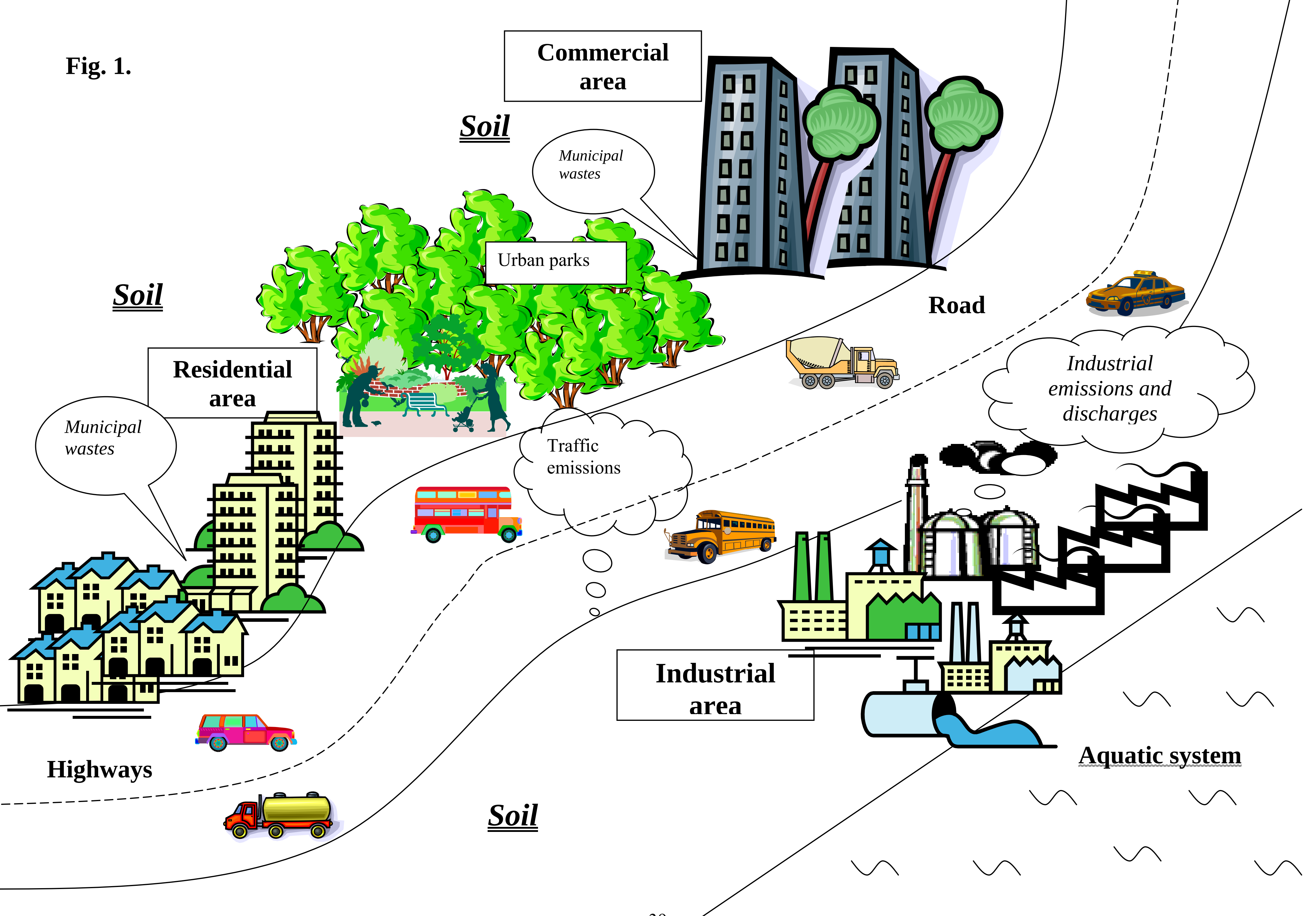
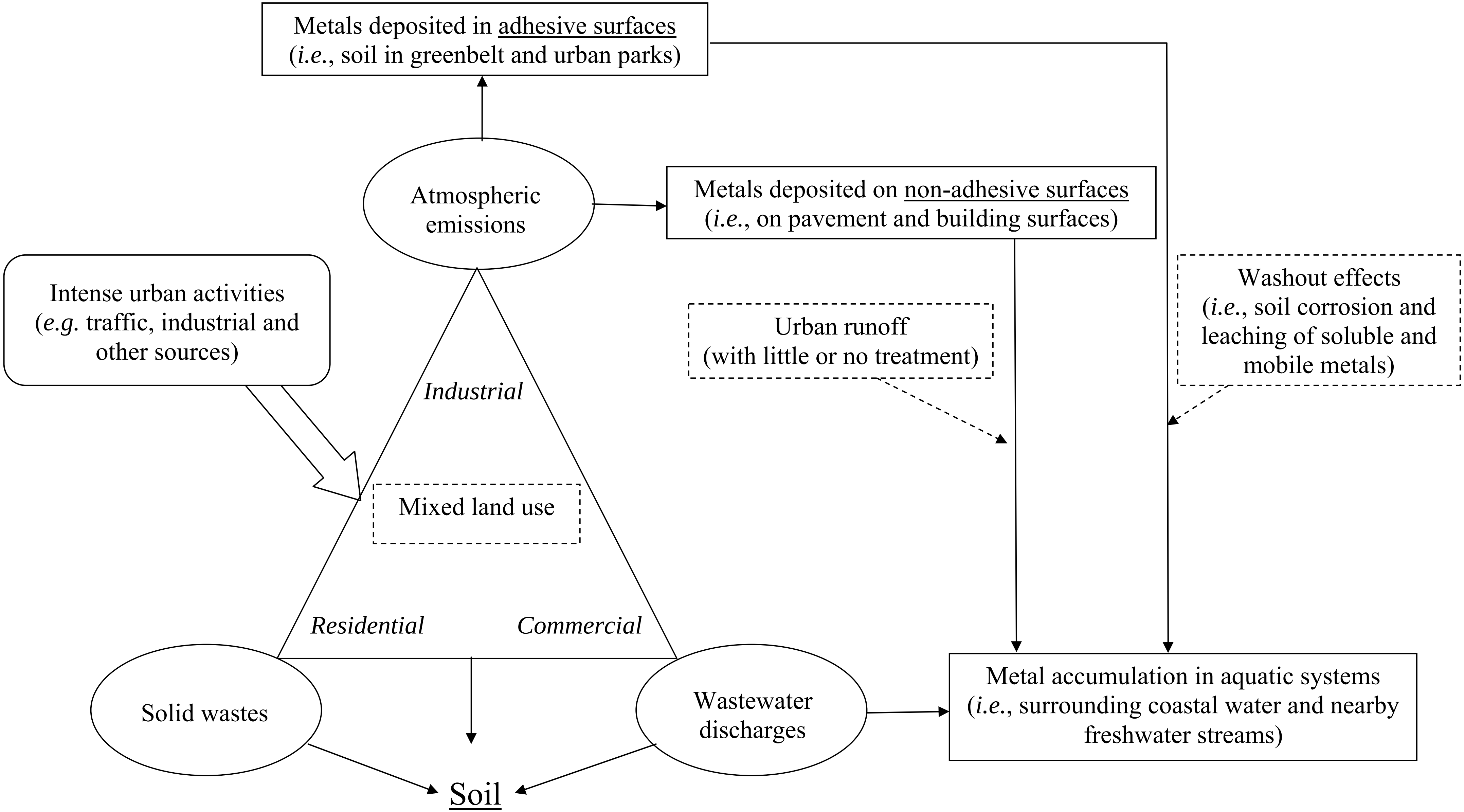

Commercial area
Soil
Municipal wastes
Urban parks
Soil
Road
Residential area
Municipal wastes
Industrial emissions and discharges
Traffic emissions
Industrial area
Highways
Aquatic system
Soil

Fig. 2



Metals deposited in adhesive surfaces
(i.e., soil in greenbelt and urban parks)
Atmospheric
emissions
Metals deposited on non-adhesive surfaces
(i.e., on pavement and building surfaces)
Intense urban activities
(e.g. traffic, industrial and
other sources)
Washout effects
(i.e., soil corrosion and
leaching of soluble and
mobile metals)
Urban runoff
(with little or no treatment)
Industrial
Mixed land use
Residential
Commercial
Solid wastes
Wastewater
discharges
Metal accumulation in aquatic systems
(i.e., surrounding coastal water and nearby
freshwater streams)
Soil

Fig. 3. Urban soil sampling locations in Kowloon, Hong Kong (from Li et al., 2004)

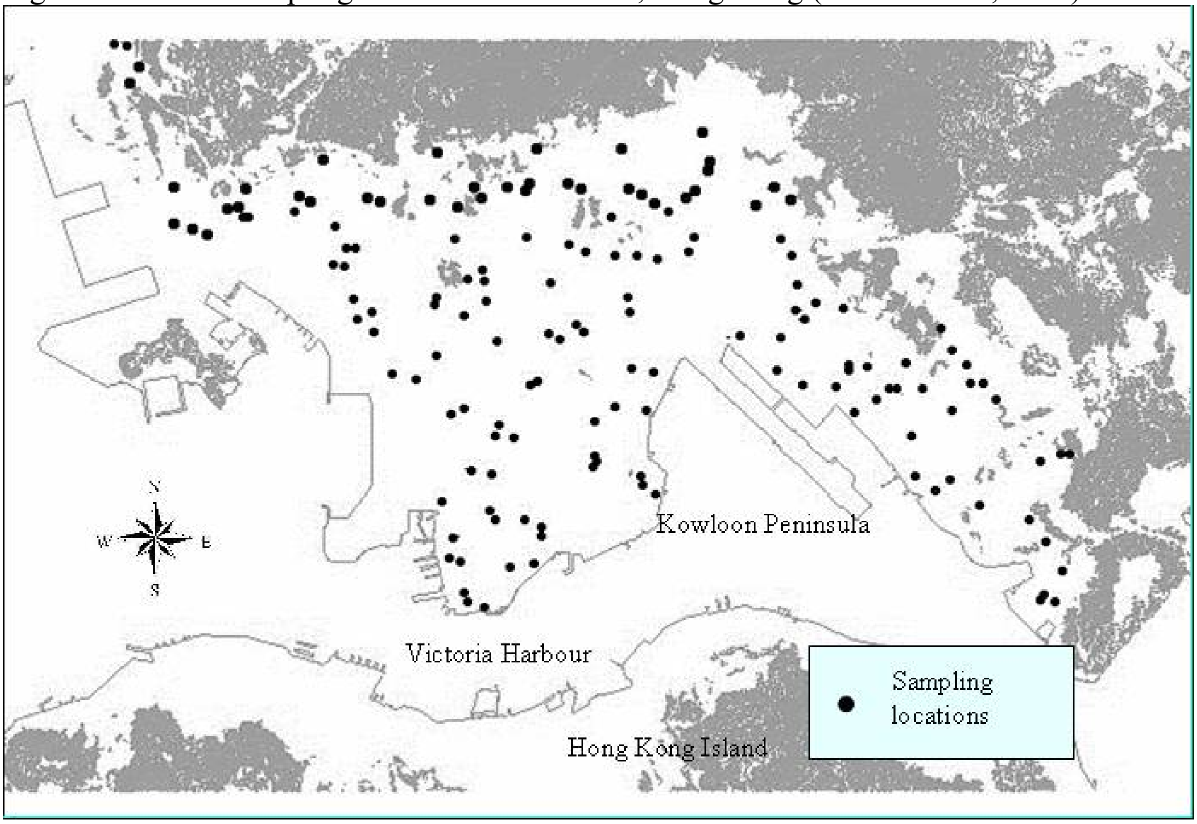


Fig. 4. Distribution of Pb and Zn in the urban soils of Kowloon, Hong Kong (from Li et al., 2004)