Copyright Undertaking

A STUDY OF TRACE METAL CONTAMINATION OF URBAN SOILS IN HONG KONG AND AGRICULTURAL SOILS IN THE PEARL RIVER DELTA

By Coby, Sze Chung WONG

A Thesis for the Degree of Master of Philosophy

Department of Civil and Structural Engineering
The Hong Kong Polytechnic University

2002

Abstract of thesis entitled 'A Study of Trace Metal Contamination of Urban Soils in Hong Kong and Agricultural Soils in the Pearl River Delta' submitted by Sze Chung Wong for the degree of Master of Philosophy at The Hong Kong Polytechnic University in September 2001.

ABSTRACT

This Master of Philosophy thesis embodies an in-depth study of trace metal contamination of urban soils in Hong Kong and agricultural soils in the Pearl River Delta in terms of degree of contamination, chemical speciation, sources of contaminants, as well as potential associations among trace and major elements. Furthermore, the study has also attempted to investigate the potential implications of trace metal contamination in the two areas, as well as other cities in the subtropical region.

Urban soil profiles of six study areas, including five urban parks and one roadway divider, were analyzed for trace and major metal concentrations. The chemical partitioning and Pb isotopic composition of selected soil profiles were also determined. The analytical results showed that some urban soil profiles were contaminated with Cu, Pb and Zn, in accordance to the Netherlands Soil Regulatory Standard. Furthermore, the enrichment of these trace metals at the surface layer was generally more significant than that at the subsurface, suggesting atmospheric and/or surface deposition of the trace metals. Although soil concentrations of the other trace metals, including Cd, Co, Cr, Mo, Ni, and V, were below the "T" values, they generally exhibited a decreasing tendency with

increasing soil depth, suggesting surface soil enrichment with these trace metals as well. The chemical partitioning of Cu, Pb, and Zn indicated that the percent distribution of Cu in the mobile and potentially bioavailable fraction varied with soil depth and among sampling sites. Soil Pb in the exchangeable and carbonate fractions accounted for 10-40% of total soil Pb, and the percent distribution of these fractions generally increased with increasing depth. Also, exchangeable and carbonate-bound Zn in the soil profiles, representing 5-40% of total soil Zn, decreased with increasing soil depth. Pb isotopic compositions of the selected urban soil profiles offered strong evidence of binary mixing of anthropogenic Pb at roadside study areas, where gasoline-derived Pb was likely a major source of anthropogenic Pb. Using a binary mixing model, it was roughly estimated that as high as 85% of total anthropogenic Pb at the central divider could have been derived from leaded gasoline.

In the study of trace metal contamination of agricultural soils, it was found that some crop, paddy and natural soils were grossly contaminated with Cd, Cr, Cu, Ni, Pb, and Zn. Mean Pb and Cd concentrations of the crop, paddy and natural soils in the Pearl River Delta exceeded the corresponding Class A values in the Chinese Soil Regulatory Guidelines, possibly indicating a spatially extensive Pb and Cd enrichment of the soils. Moreover, the comparatively elevated trace metal concentrations of the crop soils suggested that the crop soils might have received a higher input of trace metals than the paddy and natural soils. The chemical partitioning patterns of Co, Cr, Cu, Ni, Pb, V, and Zn not only gave insight to solubility and potential mobility of the trace metals but also showed influences of different cultivation methods on soil geochemistry. Based upon Pb isotopic

composition of total soil Pb and Pb in the five chemical fractions, it was evident that some of the selected soils were affected by anthropogenic Pb, possibly automobile and industrial Pb. It also revealed that anthropogenic Pb tended to reside in the exchangeable, Fe-Mn oxide and organic/sulphide fractions in the soils.

ACKNOWLEDGEMENT

First of all, I would like to express my sincere gratitude to my chief supervisor, Dr. X.D. Li, for his support during the course of the study. I also owed many thanks to numerous individuals who offered me their kindness and continuous encouragement in these two years. These individuals included Mr. W.S. Lam, Mr. C.W. Lau, Dr. W.X. Lui, Prof. Z.G., Sheng, Mr. W.F. Tam, Mr. C.C. Wang, Prof. C.X. Wang, Dr. D.C. Wang and all of my friends at PolyU. Special thanks were also devoted to Mr. Eric Yong at Perkin Elmer, Dr. J.W.C. Wong at the Department of Biology and fellow researchers at the Quality Research Laboratory, School of Chinese Medicine both at The Hong Kong Baptist University for their technical support.

TABLE OF CONTENT

LIST OF TABLES

LIST OF FIGURES

CHAPTER ONE INTRODUCTION

Soil is a fundamental component for life. Ecologically, it not only supports primary production in the terrestrial environment but also plays an important role in element and water recycling. From its functional perspective in the human society, this natural resource is also valued for its physical strength as foundations for buildings, its nurturing ability as substrates for plant growth in food and timber production, as well as, for its capacity as source and sink for contaminants (Bullock and Gregory, 1991).

> "Soil is the ultimate and most important sink of trace elements in the terrestrial environment. Most of the trace element inventory in a particular ecosystem is in the soil" (Adriano, 1986).

Human activities have significantly increased the global emission of trace metals in the surface environment (Nrigua, 1979; Nriagu and Pacyna, 1988). Due to non-biodegradability and cumulative tendency of trace metals in soils, the accelerated releases of trace metals may result in gradual accumulation of the contaminants in open/exposed surface soils, potentially resulting in trace metal contamination of the soils. In the urban environment, where intense human activities take place, soils are likely more vulnerable to the contamination (Thornton, 1992; Jim, 1998; Mielke et al., 1999; De Kimpe, 2000).

Soil contamination with trace metals could potentially cause long-term deleterious effects on human health and the environment as a whole (Nriagu, 1988; Thornton, 1993). Elevated concentrations of trace metals could reduce biological activities in soil and, if exceeding the critical values, induce toxic effects to fauna and flora (Adriano, 1986; Kataba-Pendias and Pendias, 1992). Migration of the contaminants may also cause contamination of other ecosystems. Subsequent bioassimilation and bioaccumulation of trace metals in plants and animals could also lead to contamination of the food chains (Jackson et al., 1993; McLaughlin et al., 1999; Sutherland et al., 2000).

1.1 Background

In Hong Kong (HK) and the Pearl River Delta (PRD), there is an increasing concern over potential trace metal contamination of urban soils and agricultural soils in the respective environments. Situated in the subtropical region, HK adjoins the PRD in Guangdong Province of South China, where the two areas share an increasingly synergetic partnership both economically and environmentally.

HK is a highly urbanized city, with some of the highest population and traffic densities in the world (HKSAR, 2000). It is also recognized as one of the most important financial centres in the world and perceived as a major gateway to China. The PRD is one of the most rapidly developing areas in China. Even though it is less economically developed in comparison with HK, its massive industrial development and subsequent expansion of the population in the last few decades have allowed it to gain significant recognition regionally and internationally. The intense human activities in HK and the proliferation of industrialization and urbanization in the PRD have brought about tremendous economic gains to the areas. However, at the same time, they have also accelerated the releases of trace metals into the environment, provoking a concern over possible trace metal contamination of urban and agricultural soils in the urban and increasingly urbanized environments, respectively.

Previous trace metal assessments of the terrestrial environment of HK have found elevated concentrations of trace metals, including Cd, Cu, Pb and Zn, in soils, dusts and plants. Some of these studies have also linked the enrichment of urban surface soils with industrial activities, traffic, and the possible use of agrochemicals (Lau and Wong, 1982; Tam et al., 1987; Wong, 1996; Wong et al., 1996; Chen et al., 1997; Wong and Mak, 1997; Li et al., 2001a). Despite of the large number of scientific studies, limited information regarding the vertical distribution, chemical speciation, and sources of trace metals in urban soil profiles has been gathered.

Trace metal contamination of agricultural soils has not been widely investigated in the PRD. However, existing evidence has shown that the intensifying urban and industrial activities, in conjunction with the lack of pollution controls, have resulted in significant degradation of air and water quality in the area (Hills et al., 1998; Guangdong Environmental Protection Bureau, 1996). Moreover, heavy metal pollution of soils in some industrial areas has been reported (Yan et al., 2000). Given the interconnection among soil and water in an agricultural system, it is plausible that agricultural soils in the PRD might have also been impacted by human activities.

Trace metal enrichment/contamination of the urban soils in HK may enhance human exposures to trace metals via inhalation, ingestion and dermal contact, particularly in young children (Haan, 1991; Watt et al., 1993; Hrudey et al., 1996). Meanwhile, trace metal contamination of the agricultural soils may increase trace metal uptake by food crops and, therefore, jeopardize food quality and safety. Since fresh vegetables and produces in HK are largely imported from the neighbouring PRD, the potential consequence of the contamination of foodstuffs may further increase exposure of the residents of Hong Kong.

As a whole, the potential implications of trace metal contamination of soils may be far-reaching. According to the World Bank statistics, over 45% of the world's population currently resides in urban areas, and this figure is projected to surpass the majority benchmark reaching 60% by 2030 (World Bank, 2000). As the urban population continues to grow, understanding of urban environmental geochemistry and its implications on human health becomes increasingly important (Kreimer, 1992; Walker, 1999). An in-depth study of trace metal contamination of urban soils in HK and agricultural soils in the PRD could promote the understanding of potentially associated environmental and health implications (Appleton and Ridgeway, 1993). Since urban environmental geochemistry is being practiced mainly in western and central Europe, a study of such could also provide valuable and insightful information of the characteristics and geochemical behaviours of trace metal contaminants in the subtropical

Southeast Asian region, where some of the most rapid population growth is anticipated (Xie and Cheng, 2001). In addition, the study would serve a meaningful purpose in the formulation of future strategic soil management by providing useful information on geochemical composition of trace metals in urban and agricultural soils in the developed and rapidly developing areas of the subtropical region (Chen et al., 1999 & 2001; Plant et al., 2001).

1.2 Objectives of the present study

In response to the needs for an investigation of trace metal contamination of urban soils in HK and agricultural soils in the PRD, the objectives of this study are:

1) to assess trace metal concentrations of urban soil profiles in HK and agricultural soils of the PRD,
2) to evaluate trace metal contamination of urban soil profiles of HK and agricultural soils of the PRD,
3) to characterize chemical fractionation and potential bioavailability of trace metal contaminants in the soilss,
4) to attempt to identify sources and, if possible, compute fractional contribution of different trace metal contaminant (Pb) sources in the soils,
5) to identify elemental associations of trace metals and major elements in the soils,
6) to examine potential associations of trace metals between urban soils of HK and agricultural soils of the PRD, and
7) to investigate the potential implications of urban and industrial activities on soils in the two regions and, perhaps, other cities in the subtropical region.

In order to achieve the above objectives, a combination of analytical and statistical approaches is necessary. The analytical approaches include the determination of: 1) concentrations of trace metals and major elements in soil samples using an acid digestion method, 2) chemical speciation of trace metals in soil samples using a sequential chemical extraction method, and 3) isotopic composition of Pb in soil (total and fractionated) samples. Elemental association will be investigated by means of statistical analyses, such as Pearson correlation and principal component analysis, from which input patterns and sources of trace metals may be postulated.

1.3 Outline of the thesis

The body of this thesis is divided into six major chapters. Chapter One contains an introduction, an outline and objectives of the thesis to allow readers to understand the scientific rationales and significance of the present study. A literature review is provided in Chapter Two, which presents scientific information on sources and geochemical characteristics of trace metals in soils. In addition, a general review of current status and potential environmental and health consequences of trace metal contamination of urban and agricultural soils and information on assessment of trace metal contaminated soils are given. Chapter Three embodies a detailed description of methods and materials used during the course of the study. Results and discussion of the study of trace metal contamination of urban soils in HK and agricultural soils in the PRD are then given in Chapters Four and Five, respectively. Raw data from which the results are derived is provided in Appendix A. Lastly, a general conclusion is presented in Chapter Six, in which major findings of the study are recapitulated. Moreover, recommendations, future study areas and constraints encountered during the study are also given in this chapter.

CHAPTER TWO LITERATURE REVIEW

Trace metals, as a group, consist of many inorganic elements. In the present study, the term "trace metals" defines elements that occur in natural and perturbed systems in small amounts and that, when present in sufficient concentrations, are toxic to living organisms. Due to technical and time limitations, the present study focuses primarily on nine trace metals, which include cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), molybdenum (Mo), nickel (Ni), lead (Pb), vanadium (V) and zinc (Zn). In order to investigate possible elemental associations among trace and major elements, some major elements, such as calcium (Ca), iron (Fe), magnesium (Mg) and manganese (Mn), are also included in the study.

2.1 Sources of trace metals in soils

In general, trace metals in the surface environment are derived from a wide range of sources, of both natural and anthropogenic origins.

2.1.1 Natural sources of trace metals

Trace metals that are present naturally in soils are released via natural weathering processes of geological materials and other natural occurrences. As shown in Table 2-1, these natural occurrences include volcanic eruption, forest fires and seasalt sprays. Soil concentrations of trace metals originated from these natural processes are usually low but may vary considerably dependent upon regional characteristics of geological formation (Kim and Thornton, 1993). The natural parent geological sources of some trace metals are listed in Table 2-2. The influences of the parent materials are generally more dominant in temperate areas, such as the United Kingdom than the tropical region and on more mature land surfaces, such as those in Australia, where weathering processes have been vigorous or of much greater duration. This is primarily because of the mobilization and secondary distribution of chemical elements and the formation of secondary minerals in the tropical region and mature land surfaces (Thornton, 1992). The natural soil background concentrations of the nine trace metals of Poland, Canada, UK and China are presented in Table 2-3.

Table 2-1 Worldwide emissions of trace metals from natural sources

Source	Worldwide annual emissions (× 10^6 kg)				
	Cd	Cu	Ni	Pb	Zn
Windblow dusts	0.1 (0.001-0.22)	12 (0.14-26)	20 (0.24-44)	16 (0.19-35)	25 (0.30-55)
Forrest fires	0.012 (0.001-0.07)	0.3 (0.025-1.7)	0.6 (0.05-3.3)	0.5 (0.04-2.8)	2.1 (0.18-12)
Volcanogenic particles	0.52 (0.3-7.8)	3.6 (2.3-54)	3.8 (2.4-56)	6.4 (4.2-96)	7.0 (4.6-105)
Vegetation	0.2 (0.2-2.7)	2.5 (2.5-33)	1.6 (1.6-21)	1.6 (1.6-21)	9.4 (9.4-125)
Seasalt sprays	~0.001	0.08 (0.02-0.2)	0.04 (0.01-0.08)	0.02 (0.01-0.05)	0.01 (0.004-0.02)
Total	0.83	18.5	26.0	24.5	43.5

Source: Nriagu (1979)

Table 2-2 Natural sources of some metals and elements

Element	Natural sources or metals. Metallic minerals
As	Metal arsenides and arsenates, sulfide ores (arsenopyrite), Arsenite ($HasO_2$), volcanic gases, geothermal springs
Cd	Zinc carbonate and sulfide ores, copper carbonate and sulfide ores
Cr	Chromite ($FeCr_2O$), chromic oxide (Cr_2O_3)
Cu	Free metal (Cu^0), copper sulfide (CuS_2), chalcopyrite ($CuFeS_2$), mine drainage
Pb	Galena (PbS)
Hg	Free metal (Hg^0), Cinnabar (HgS)
Ni	Ferromagnesian minerals, ferrous sulfide ores, Pentladite
Zn	Zinc blende (ZnS), Willemite ($ZnSiO_4$), Calamine ($ZnCO_3$), mine drainage

Source: Novotny (1995)

Table 2-3 Background concentrations (mg/kg) of trace metals in soils of various regions.

Elements	Canada[a]	China[b]	Poland[c]	UK[d]
Cd	0.8	0.097 ± 0.079	-	<1 – 2
Co	5	12.7 ± 6.40	3.6	-
Cr	15	61.0 ± 31.07	16.8	15 – 300
Cu	25	22.6 ± 11.41	6.3	2 – 60
Mo	2	2.0 ± 2.54	-	<1 – 5
Ni	16	26.9 ± 14.36	7.4	2 – 100
Pb	15	26.0 ± 12.37	-	10 – 150
V	-	82.4 ± 32.68	-	-
Zn	55	74.2 ± 32.78	-	25 – 200

[a] Ontario Ministry of Agriculture and Food and Ontario Ministry of Environment 1992.
[b] China Environmental Protection Department, 1990.
[c] Dudka, 1993
[d] Thornton, 1992.

2.1.2 Anthropogenic sources of trace metals

In addition to the natural sources, trace metals are also emitted into the surface environment from a variety of anthropogenic sources. It has been widely recognized that elevated trace metal concentrations in the surface environment are largely attributed to human activities. As shown in Table 2-4, anthropogenic emissions of Cd, Cu, Ni, Pb and Zn were substantially higher than natural emissions (Nriagu, 1979). The difference between natural and anthropogenic emission was most significant for Pb, where anthropogenic Pb emission was nearly 20-fold of naturally derived Pb. A substance flow analysis conducted by Guinee et al. (1999) suggested that emissions of Cd, Pb and Zn to air, water and agricultural soil would increase by approximately 30%, while a significant increase (>100%) was predicted for Cu due to a shift from the present accumulation in products and materials to emissions to the environment.

Table 2-4 Worldwide emissions of trace metals (10^6 kg)

Cd	Cu	Pb	Ni	Zn
Worldwide annual emissions from natural sources:				
0.83	18.5	24.5	26.0	43.5
Worldwide anthropogenic emissions during 1975:				
7.3	56	449	47	314
Worldwide total metal emissions before 1980:				
316	2,175	19,578	1,003	13,995

Source: Nriagu (1979)

Owing to the wide application of trace metals, numerous potential anthropogenic sources of trace metals may be present in the urban environment. With respect to trace metal contamination of urban soils in HK and agricultural soils in the PRD, important anthropogenic sources of trace metals typically include traffic-related activities, industrial activities, mining and smelting activities, and the application of agrochemicals and sewage sludges (Wong et al, 1996; Chen *et al.*, 1999; Yan et al., 2000).

2.1.2.1 Traffic-related activities

Traffic-related activities have been associated with the release of a number of trace metals. In particular, it is generally acknowledged that the predominance of Pb in the surface urban environment is originated from vehicle exhaust as a direct consequence of the combustion of tetraethyl lead, an anti-knock additive in leaded gasoline (Lau and Wong, 1982; Ho and Tai, 1988; Ho, 1990; Francek, 1992; Othman et al.,1997; Lin et al., 1998). Additionally, the combustion of fossil fuel, including petroleum, coal, and oil, can also release other trace metals, such as Cd, Zn, Cr, and V (CCME, 1997a). Moreover, traffic-related activities are also accountable for the emission of Cd and Zn since Cd is used as a stabilizer in vehicle tires and rubbers, and Zn is used in the production of alloys and the galvanization of iron to prevent rusting, weathering and corroding of these vehicle parts (CCME, 1997a; Monaci et al., 2000).

Owing to the long-term deleterious health effects of Pb on humans, especially in young children, the use of tetraethyl lead in gasoline has been prohibited in many countries, such as the United States and Canada, where tetraethyl lead is substituted with manganese methylcyclopentadienyl (MMT; Silbergeld, 1999). The phase out of leaded gasoline has since resulted in a steady decline in the rate of aerial Pb deposition in many parts of the world (Chiaradia, 1997; Pichtel *et al.*, 1997; Wang et al., 1997; Maravelias, 1998). Meanwhile, it has been reported that the combustion of MMT in gasoline caused an increase in Mn concentration of some roadside soil and plants through the release of inorganic Mn particulates in the forms of phosphates, oxides, and halides, (Lytle et al., 1995). A number of toxicology studies have since suggested the potential link between a rise in environmental Mn exposure and neurological symptoms similar to those of Alzheimer disease, which has caused some controversy over the long-term use of MMT (Zayed et al., 1994; Davis et al., 1999; Mergler, 1999; Silbergeld, 1999). Nonetheless, owing to its relative abundance in soils, such an increase may represent a minor percentage of total soil Mn, thus presenting a limited immediate health concern.

In HK, a step-wise reduction in Pb content of gasoline was initiated in 1992, and the sale of leaded gasoline was officially banned in April 1999 (Hong Kong Environmental Protection Department, 2000). In the PRD, both leaded and unleaded gasoline are available commercially.

2.1.2.2 Industrial activities

Environmental emissions of trace metals by industrial activities are usually industry-specific. Due to the large variety of past and current industrial activities in HK and the PRD, it is impossible to review all members of this category. Instead, some examples are briefly discussed below.

Industrial emission of Cd has been related to its use in protective plating on steel, making of various alloys, pigments for plastics, enamels and glazes, a stabilizer for plastics, fungicides, nickel/cadmium dry cell batteries, and PVC (Thornton, 1983; Yim & Nau, 1987; Adriano et al., 1997). In Canada, a significant fraction of environmental Cd is believed to have originated from electroplating processes since the electroplating industry accounts for about 60% of cadmium use (CCME, 1997a). In addition to the combustion of leaded gasoline, the emission of Pb has also been associated with the manufacture of batteries, lead pipes, cable covering and paint. Zn may be released through its use in the manufacture of items, such as paints, rubber, cosmetics, plastics, batteries, and soaps. Major industrial applications of Cu are the production of electrical equipment, such as wiring and motors, brass and bronze. Thus, Cu may be emitted from the producers of these metallic products. Industrial use of V in the production of high-strength, low-alloy steel and tool and die steels can also lead to discharge of V. V can also be found in the chemical industry as catalysts in the production of polymeric plastics, sulfuric and nitric acids, as a mordant in dyes and printing fabric inks, and in vanadium-gallium tape for use in superconductors (CCME, 1997a).

2.1.2.3 Mining and smelting activities

The releases of trace metals via mining and smelting activities have been a major environmental concern despite of increasingly stringent environmental regulations and continuous improvement in pollution control and management practices in the industry. Mining and smelting activities involve the excavation and extraction of minerals from metal-rich raw geological materials. In general, high-temperature treatments involved in the mineral production generate metal-rich particulates, which are emitted via atmospheric emission and eventually deposit on the surface environment in the surrounding. Also, waste products, whether in the forms of wastewater and solid wastes, generated in the processes usually contain high concentrations of trace metals (Li and Thornton, 1993 a&b; Allan, 1995; Rybicka, 1995). Depending on the type of ore deposit and minerals to be extracted, these processes may release a variety of different trace metals. For instance, very high concentrations of Cd, Pb and Zn were found in the vicinity of a Pb-Zn smelter in UK (Li and Thornton, 1993 a&b).

Locally in HK, mining and smelting industry represents a minor percentage (less than HK$0.05 billion per year) of the economy (HKSAR, 2000). However, a major Zn-Pb deposit situated at Fankou in the PRD, which supplies Zn and Pb for local industrial consumption, may play an influential role in the regional distribution of trace metals in the surface environment (Zhu et al., 2001).

2.1.2.4 Application of agrochemicals and sewage sludges

Agrochemicals and sewage sludges contain various levels of trace metals (see Table 2-5). Some soil amendments, such as sewage sludges and phosphate fertilizers may contain excessively high concentrations of toxic trace metals, including Cd and Pb. In fact, it was estimated that 346 tonnes of Cd would enter the environment of European Union annually in the form of fertilizers by 2000 (Alloway, 1990). In China, the application of inorganic fertilizers has increased drastically from 3.9 kg/ha in 1949 to 379 kg/ha in 1995, which was more than 2.5 times the world average. The application rates varied regionally from 200 kg/ha in northern regions to 500 kg/ha in Zhejian to over 800 kg/ha in Guangdong and Fujian (Li et al., 1997). Neller and Lam (1994) also reported an increase of 40% in the use of chemical fertilizers in the PRD between 1986 and 1989. Moreover, land application of chicken manure and other animal wastes may also increase Cu levels in soils as the diets of livestock are often enriched with Cu for better feed conversion (Cheung and Wong, 1983). The use of these organic fertilizers in China has declined over the years. It was reported that the ratio of organic fertilizers to total fertilizers used in China has declined from 60% in 1980 to 46% in 1995 (Li et al., 1997). Cu enrichment of soils may also be associated with application of copper sulphate as an agricultural poison (Crounse et al., 1983).

China is the world's second largest producer of pesticides. The use of agricultural poison and other pesticides in China increased by 110 times between 1952 and 1990. Most of its pesticide products are highly toxic and persistent, and approximately 90% of them are used in the cultivation of cotton, rice, oilseeds and horticultural crops (Li et al., 1997). Without proper soil management, continuous and heavy use of them in soils may lead to the gradual accumulation of these trace metals, posing potential environmental and health implications (Kataba-Pendias, 1995). Therefore, these agrochemicals should be applied based on soil loading capacity for trace metals in order to safeguard food production (Chen et al., 2001).

Table 2-5 Agricultural sources of trace metals in soils (mg/kg on dry weight basis)

Elements	Sewage sludges	Phosphate fertilizers	Limestones	Nitrogen fertilizers	Manure	Pesticides (%)
As	2-26	2-1,200	0.1-24.0	2.2-120	3-25	22-60
Cd	2-1500	0.1-170	0.04-0.1	0.05-8.5	0.3-0.8	-
Co	2-260	1-12	0.4-3.0	5.4-12	0.3-24	-
Cr	20-40,600	66-245	10-15	3.2-19	5.2-55	-
Cu	50-3,300	1-300	2-125	<1-15	2-60	12-50
Hg	0.1-55	0.01-1.2	0.05	0.3-2.9	0.09-0.2	0.8-42
Mn	60-3,900	40-2000	40-1,200	-	30-550	-
Mo	1-40	0.1-60	0.1-15	1-7	0.05-3	-
Ni	16-5,300	7-38	10-20	7-34	7.8-30	-
Pb	50-3,000	7-225	20-1,250	2-27	6.6-15	60
V	20-400	2-1,600	20	-	-	45
Zn	700-49,000	50-1,450	10-450	1-42	15-250	1.3-25

Source: Kabata-Pendias and Pendias, 1992.

2.2 Routes of inputs and outputs of trace metals

In general, the releases of trace metals are categorized into point and non-point sources. Point sources include traffic, industries, mining, and smelting, while non-point sources include fly ash, irrigation, and the application of sewage sludge, fertilizers and pesticides (Thornton, 1983 & 1992). Major routes for input into soils include aerial deposition (e.g., aerosols, particulate matter, resuspended and air-borne dusts, etc.) and land application (fertilizers, pesticides, solid wastes, other soil amendments, etc.). Although the majority of anthropogenic trace metals is emitted into the atmosphere in the form of aerosol particulate, it is believed that a substantial quantity of it is eventually deposited on land. For instance, the annual atmospheric emission of Cd is estimated to be 8100 tonnes, of which 7300t is contributed by anthropogenic sources, and 5700 tonnes per year will eventually deposit on land (Alloway, 1990).

Once trace metals deposit in soils, various soil processes, including dissolution, sorption, complexation, migration, precipitation, occlusion, diffusion, binding by organic substances, absorption and sorption by microbiota, and volatilization, may take place (Kataba-Pendias, 1993). The major output pathways can be represented primarily by leaching, erosion and by losses through plant tissue removal for food, feed stuff, and fibre.

2.3 Geochemical characteristics of trace metals in soils

Trace metals are usually relatively stable in soils under normal conditions and relatively insoluble in water with long biological half-lives. Their reactivity, solubility and biological availability at the soil-water-biota interface are governed by a highly complex equilibrium, which is, in turn, controlled by soil pH, organic matter, hydrous oxides of Fe, Mn, and Al, and many other factors. Hence, a change in these factors could potentially alter physical, chemical and biological interactions of trace metals with their surrounding biota and abiota (Adriano, 1986; Kabata-Pendias, 1993).

2.3.1 Soil pH

Among the various factors, soil pH is considered most influential in determining trace metal solubility and potential bioavailability in soils. Generally, trace metals, including Zn, Cu and Co, are relatively insoluble and immobile under neutral and alkaline conditions. In acid environment where soil pH drops below 6.5, they become readily soluble and thus easily leachable (Kataba-Pendias and Pendias, 1992). A reduction in soil pH may also be accompanied by an increase in potential bioavailability of trace metals (Kabata-Pendias, 1993; Murray and Hendershot, 2000). However, the effects of soil pH, on some other metals, such as Cd, may deviate from what is normally expected, since Cd remains bioavailable even under alkaline conditions (Adriano et al., 1997).

2.3.2 Organic matter

Organic matter is partially responsible for the capacity of soils as a sink for trace metals, as some trace metals in soils tend to form weak and strong complexes with organic matter, especially with humic and fulvic acids. Those that fix strongly to organic matter include Cr^{3+}, Fe^{3+}, Pb, Cu and Hg, fix fairly Cd, Ni, and Co, and those that fix slightly are Mn and Zn. Due to the relative abundance of organic matter in surface soils, trace metal complexation with organic matter can lead to a greater absorption and subsequent accumulation of these metals in surface soils, resulting in immobilization of trace metals. However, microbial decomposition of organic matter may release trace metals from stable complexes and consequently increase its mobility. In addition, the presence of high concentrations of dissolved organic matter in soil leachates can also enhance trace metal mobility (Adriano, 1986; Kabata-Pendias, 1993).

2.3.3 Hydrous oxides

Hydrous oxides, including Fe and Mn oxides, are naturally abundant in soils as nodules, concretion, cement between particles, and coating on particles. They play a prominent role in the fixation of trace metals in soils, as they are excellent scavengers for trace metals. Trace metals, such as Co, Pb and Zn, are usually significantly associated with these hydrous oxides. Trace metals fixed by Fe and Mn oxides are relatively stable under oxidative conditions. However, these compounds may become thermodynamically unstable and disintegrated when soil conditions change, e.g. a reduction in soil pH and depletion of oxygen (Adriano, 1986; Kabata-Pendias, 1993).

2.3.4 Chemical forms / Speciation

Geochemically, an element introduced into and naturally present in the soil may possess one or more of the following forms: dissolved in soil solution, held onto exchange sites of organic solids or inorganic constituents, occluded or fixed into soil minerals, precipitated with other compounds in soils, and incorporated into biological material. These chemical forms may be seen as a partial reflection of potential solubility. Furthermore, they may also be used to estimate potential health and environmental effects of trace metals since speciation can greatly influence the expression of biotoxicity (Tessier and Campbell, 1990; Jackson et al., 1993; Chapman et al., 1998). For instance, zinc sulphate is readily soluble in soil solution; whereas, zinc oxide is relatively insoluble. Also, Zn^{2+} seems to be the predominating form in terms of bioavailability, and other biologically active fraction of Zn in soils may also consist of its soluble, exchangeable, and complexed forms (Walsh et al., 1994).

2.3.5 Others

Other important factors governing solubility and potential toxicity of trace metals are initial forms of the metals, redox potential, cation exchange capacity, aeration of the soils, microbial activities, and interactions among trace metals, e.g., antagonistic relationships of Cd with Zn, Ca, and Se (Adriano, 1986; Kabata-Pendias, 1993; CCME, 1997a; Sauve et al., 1997).

2.4 Trace metal contamination of soils

Trace metal contamination of soils has become a global environmental and health issue because of its prevalence in many parts of the world (Adriano, 1986; Nriagu, 1988). Soils in the environment, particularly urban and agricultural soils, are vulnerable to trace metal contamination due to their close proximity to human activities (Kreimer, 1992).

2.4.1 Trace metal contamination of urban soils

Trace metal contamination of urban soils have been extensively studied in many industrialized nations in Europe and North America, such as Britain (Culbard et al., 1988; Thornton, 1991; Li et al., 1993a&b; Wang et al., 1997), Germany (Lux, 1993; Meyer et al., 1999), and the United States (Mielke, 1984; Lin et al., 1998; Wong, 1998; Mielke et al., 1999). Generally, trace metal enrichment of soils progresses with decreasing distance to city centres (Thornton, 1991). A three-year study carried out by Pocock (1984) collected evidence showing that 6% of the urban soils in Borough may contain in excess of 2,200 mg/kg of Pb, 11% with 15 mg/kg or more of Cd, and 70% at risk of exceeding 560 mg/kg of Zn. As shown in Table 2-6, geometric mean concentrations of Cd, Pb and Zn in

London were more elevated than in Britain as a whole, giving strong evidence of the influences of human activities (Culbard et al., 1988).

Table 2-6 Geometric mean of trace metal concentrations (mg/kg) of soils in Britain

	Cd		Pb		Zn	
	All study locations	London boroughs	All study locations	London boroughs	All study locations	London boroughs
Garden soil	1.2	1.3	266	654	278	424
Vegetable plot soil	1.2	1.4	270	571	321	522
Public garden soil	1.2	1.0	185	294	180	183

Source: Culbard et al., 1988.

In recent years, similar studies have been carried out in the Asian-Pacific region, where rapid industrialization and urbanization are anticipated. Indeed, trace metal contamination of urban soils in Japan (Komai, 1981), Australia (Tiller, 1992), as well as HK (Wong et al., 1996) has also been investigated. In South Australia, Victoria and Queensland, at least two-thirds of recorded contaminated urban sites are primarily concerned with trace metals. Some of the major sources of trace metals include defence works, electroplating and heat treatment premises, metal treatment, scrap yards, service stations, tanning and associated trades (Tiller, 1992). Soil contamination has also been reported in other cities in the subtropical region, including Korea (Chon *et al.*, 1995), Vietnam (Thuy *et al.*, 2000), Thailand (Wilcke *et al.*, 1998), and China (Zhang, 1994; Xiong, 1998; Zhang et al.,1999). Table 2-7 contains trace metal concentrations of urban soils in some cities in the Asian region.

Table 2-7 Mean metal concentrations of urban soils in Asian cities

City (Country)	Cd	Cr	Cu	Pb	Zn	References
Sakai (Japan)	-	-	122	-	410	Komai, 1981
Kishiwada (Japan)	-	-	65	-	177	
Manila (Philippines)	0.57	114	199	214	440	Pfeiffer et al., 1988
Changchun (China)	-	-	-	46.10	-	Zhang, 1994
Lanzhou (China)	-	-	-	36.16	-	
Qingdao (China)	-	-	-	57.84	-	
Wuhan (China)	-	-	-	70.16	-	
Seoul (Korea)	3.1	-	84	240	271	Chon et al., 1995
Bangkok (Thailand)	0.29	26.4	41.7	47.8	118	Wilcke et al., 1998
Danang-Hoian (Vietnam)	0.8	92.2	76.0	3.6	141.8	Thuy et al., 2000

In HK, the majority of previous studies assessed the extent of trace metal enrichment/contamination in urban soils and dusts in various types of microenvironments, including parks, playgrounds, households, and roadside (Lau and Wong, 1982; Chen *et al.*, 1997; Wong and Mak, 1997; Tong and Lam, 1998 & 2000; Wang et al., 1998; Li et al., 2001a). As shown in Table 2-8, trace metal concentrations of dusts and soils were considerably elevated. An extensive trace metal assessment of urban park soils in HK conducted by Li et al. (2001a) found that urban park soils were generally more enriched with Cd, Cu, Pb and Zn than country park soils. A general metal assessment of soils in HK (Sewell, 1999) also found some grossly contaminated soils (see Table 2-9).

Table 2-8 Average trace metal concentrations in dusts and surface soils in Hong Kong

	Cd	Cu	Pb	Zn	References
Roadside dust	n.d.-28	16-271	132-3876	423-8160	Lau and Wong, 1982
Urban dust	7.6	635	1287	2902	Yim and Nau, 1987
Roadside dust	-	248	1080	1373	Ho, 1990
Playground dust	2.6	201	302	1571	Wong and Mak, 1997
Road dust	-	238-391	379-754	1731-2396	Wang et al., 1998
Home dust	17.6	981	220	2005	Tong and Lam, 1998
School dust	8.48	247	200	2293	
House dust	4.3	311	157.4	1408	Tong and Lam, 2000
Urban dust	3.77	173	181	1450	Li et al., 2001a
Roadside soil	12-54	3-205	21-229	29-259	Lau and Wong, 1982
Playground soil	2.30-2.97	2.87-66	111-395	52-546	Wong and Mak, 1997
Urban soil	0.94	16.1	89.9	58.8	Chen et al., 1997
Urban Park Soil	2.18	24.8	93.4	168	Li et al., 2001a

Table 2-9 Trace metal concentrations (mg/kg) in soils of Hong Kong

Elements	Mean	Median	Standard deviation
As	27	14	58
Cd	0.52	0.33	0.62
Co	6	5	4
Cr	49	29	61
Cu	19	10	95
Hg	0.58	0.34	0.64
Mo	3.5	2.2	14.8
Ni	11	10	14
Pb	104	72	133
V	43	37	26
Zn	141	80	445

Source: Sewell, 1999.

2.4.2 Trace metal contamination of agricultural soils

Agricultural soil contamination with trace metals has been extensively investigated over the years due to its direct association with human health (Kataba-Pendias, 1995). In Japan, mean Cd, Cu, Pb and Zn concentrations of paddy soils were 0.45, 32, 29 and 82 mg/kg, respectively (Kitagishi and Yamane, 1981). Crop soils in Hangzhou, China contained 0.30, 26.7, 32.1, and 82.7 mg/kg of Cd, Cu, Pb and Zn, respectively (Weng and Chen, 2000).

2.5 Potential environmental and health implications

Trace metal contamination of urban and agricultural soils can result in long-term potential implications on human health and the environment as a whole. From the perspective of human health, major exposure routes to trace metals for the general population are through inhalation of aerosol, ingestion of food, water and soil, and dermal contact with water and soil (Hrudey *et al.*, 1996). Children are particularly susceptible to trace metal exposure due to hand-to-mouth activities (Watt et al., 1993), and they are also more vulnerable to trace metal toxicity than adults because of their unique physiology (Hrudey *et al.*, 1996).

2.5.1 Trace metal toxicity

With regard to biotoxicity, trace metals may be classified into two groups: essential and non-essential trace metals. Essential trace metals, such as Co, Cr, Cu, Mo, Ni, V and Zn, are needed in trace quantities for normal biological functions in plants and/or animals. Consumption of them beyond the optimal ranges, both deficiency and excess, may lead to harmful health effects (Aylett, 1979; Crounse et al., 1983; Barceloux, 1999). Pb and Cd are non-essential trace metals because they have no known biological roles in animals and plants. Since they are toxic to biota at low concentrations, they are also considered to be important in terms of food-chain contamination (McLaughlin et al., 1999). Hence, further elaboration of their toxicological information is given below.

Pb is teratogenic, carcinogenic and toxic in a cumulative way. Clinically, high levels of Pb concentrations in humans can cause anaemia, coma, neurological defects, and retardation of brain development and functions. It is considered especially detrimental to young children because crucial brain development happens during childhood. Ideally, blood lead levels in human should be nearly non-detectable. The natural background blood Pb level is estimated to be 0.016 μg/dl (Flegal and Smith, 1992). The World Health Organization (WHO) currently defines lead poisoning with lead blood level of 10 μg/dl or above (CDC, 1991). Nonetheless, increasing evidence suggests that extended sub-clinical exposure to Pb, even below the defined blood lead level, may also result in long-term negative effects on normal brain development of children (Needleman, 1980; Shen et al., 1996).

Cd has become a major environmental and health concern because of its high toxicity at low concentrations, high mobility and bioavailability (Aylett, 1979; Alloway, 1990; Mueller, 1994). Over-exposure of Cd is known to be carcinogenic and teratogenic. An estimation of 20 $\mu g/m^3$ Cd concentrations in air could result in kidney damage after sufficient exposure for a long period of time (Crounse et al., 1983). The tolerable maximum intake of Cd ranges between 400 and 500 μg/week recommended by WHO. Because of its bioaccumulative tendency in human organs, long-term subclinical exposures may result in adverse health effects, particularly diseases of the kidneys, such as renal tubular dysfunction and pulmonary emphysema (Aylett, 1979).

2.5.2 Environmental and health implications

Elevated trace metal concentrations of soils could induce toxic effects on soil fauna and phototoxicity on flora, which may also be accompanied by a reduction of soil fertility, interfering plant growth and food production (Das et al., 1997). This may translate into financial loss. Furthermore, trace metal contamination of agricultural soils could potentially increase biological uptakes of trace metals and cause food chain contamination through bioaccumulation and biomagnification (Mueller, 1994; Samecka-Cymerman and Kempers, 1999; Adriano et al., 1997). In the absence of vegetation or other coverings, trace metal contaminated soils, particularly surface soils, may become prone to erosion in the event of heavy rainfall or strong wind. Subsequent re-suspension and re-deposition of the metal-enriched soil particles, whether in the forms of metal-laden airborne dusts or toxic runoffs, may spread the contaminants beyond the urban boundary, causing a potential concern for contamination of other ecosystems (Novotny, 1995; Marsalek, 1986).

In order to further illustrate the potential environmental and health consequences associated with trace metal contamination of soils, a case study conducted by Sutherland et al. (2000) is presented here. Sutherland et al. were appointed to investigate into the cause of significant biological accumulation of Pb and other trace metals in fish in Honolulu, Hawaii. In the National Contaminant Biomonitoring Program in the United States, Pb, Cu, and Zn concentrations in three species of fish captured from Manoa watershed in Honolulu, Hawaii were found to be significantly elevated among the 1,984 fish samples. Since the area was away from intense urban and industrial activities, no obvious contaminant source was initially found. After an in-depth investigation, Sutherland et al. found that the trace metals in fish had originated from automotive emissions and vehicle wear in a roadside system. The metals were emitted from automobile exhausts and wearing of vehicle parts and deposited on roadside soils, which later leached into the marine ecosystem.

2.6 Assessment of trace metal contaminated soils

This section contains an introduction to analytical tools that are used to assess concentrations and chemical speciation of trace metals in soils and to Pb isotopic analysis. Also, in view of the absence of a local soil regulatory guideline in HK, some pros and cons of major overseas regulatory guidelines for trace metal contamination are briefly discussed here.

2.6.1 Acid digestion of soils

In order to determine the inorganic constituents of a solid material, including soil and sediment, the material is usually treated with a concentrated inorganic acid or a combination of concentrated acids at high temperatures. This decomposition technique is generally referred to as a strong acid digestion method. The purpose of this treatment is to dissolve the inorganic elements that are attached to particle surface and/or entrapped in crystal structure of the material and to transform the solid material into solution form, that can be readily analyzed using conventional analytical equipment, such as Atomic Absorption Spectrometry (AAS) and Inductively Coupled Plasma (ICP), which are approved by the US EPA (Hossner, 1996).

Acid digestion methods generally call for the use of hydrofluoric acid (HF), sulfuric acid (H_2SO_4), hydrochloric acid (HCl), nitric acid (HNO_3), perchloric acid ($HClO_4$), and/or aqua-aqui. A complete acid digestion, which includes the breakdown of silica compounds and other crystal lattices, can only be accomplished using HF, while the use of the other acids can achieve partial breakdown of silica structures. Hence, acid digestion methods without using HF are sometimes recognized as pseudo acid digestion methods. Nonetheless, these digestion methods are considered adequate in reflecting metal concentrations of a given environmental sample (Hossner, 1996).

In the present study, a combination of $HClO_4$ and HNO_3 is utilized in the acid digestion method for various reasons. $HClO_4$ is selected because it is one of the strongest mineral acids with powerful oxidizing properties when concentrated and hot, and it produces less interference in spectrometric determination than H_2SO_4. Since all common perchlorates, except potassium perchlorates, are readily soluble, the use of $HClO_4$ can also maximize recovery of metals during the process. The addition of HNO_3 is to facilitate the dissolution of the sample and to prevent explosive reactions of organic materials with $HClO_4$ (Hossner, 1996).

2.6.2 Sequential chemical extraction of trace metals in soils

As mentioned previously, trace metals exist in many chemical forms in soils. Many extraction procedures are available to differentiate the various forms of metals in soils. Some are aimed at evaluating bioavailability (e.g. extraction methods by 0.1 N HNO_3, EDTA, DTPA, and other exchange resins), while others (e.g. sequential chemical extractions) may be used to examine chemical speciation of trace metals, from which solubility and potential bioavailability may be estimated (Tessier et al., 1979; Gibson and Farmer, 1986; Mahan et al., 1987; Rupa and Shukla, 1999; Houba et al., 2000; Sun et al., 2001).

A five-step sequential chemical extraction, commonly referred to as the Tessier's method, is probably one of the most widely used sequential chemical extraction methods (Tessier et. al., 1979) that defines metals into five fractions with increasing stability through the use of progressively reactive extractants. The extracted metals from these five consecutive steps are operationally defined into the five fractions: 1) readily soluble and exchangeable, 2) carbonate-bound, specifically adsorbed, and weak organic and inorganic complexes, 3) bound to iron and manganese oxides, 4) bound to stable complexes of organic and/or sulphide, and 5) residual fraction containing primary and secondary minerals held within their crystal structure, respectively. It is acknowledged that reactivity and potential bioavailability of trace metals generally increases with increasing solubility. Thus, the first two forms are considered the two most mobile forms of metals in soils and are usually considered potentially bioavailable. Metals in the third and fourth fractions (the Fe-Mn oxide and organic-bound fractions) are generally relatively immobile and stable but may sometimes become mobile and bioavailable with time or upon changes of soil conditions. Metals in the residual fraction are considered most stable and, thus, least bioavailable.

2.6.3 Pb isotopic analysis

Lead in the environment has four isotopic forms, ^{204}Pb, ^{206}Pb, ^{207}Pb, and ^{208}Pb. The relative abundance of these natural isotopes are approximately 1.4, 24.1, 22.1, and 52.4%, respectively. Among the four Pb isotopes, only ^{204}Pb is non-radiogenic and, therefore, remains stable over time. The other three radiogenic isotopes, ^{206}Pb, ^{207}Pb, and ^{208}Pb, are derived from ^{238}U, ^{235}U, and ^{232}Th, respectively. Pb isotope composition of a given sample therefore depends on the age and U/Pb and Th/Pb ratios of the parent material(s) from which the Pb is derived. Because of these inherited isotopic characteristics of Pb in the environment, Pb isotopic composition has become a powerful tool in anthropogenic Pb detection, source identification, and distinguishing naturally-derived Pb from anthropogenic Pb (Sturges and Barrie, 1987; Munksgaard *et al.*, 1998; Hansmann and Koppel, 2000). In some cases, Pb isotopic composition may also enable the apportionment of two Pb sources in the specimen of interest given the Pb isotopic signature of each of the known sources (Gélinas and Schmit, 1997; Kersten, 1997; Marcantonio et al., 1998).

In general, the ^{206}Pb/^{207}Pb ratio of a sample is the most frequently used ratio to differentiate Pb-contaminated and uncontaminated soils. The ^{206}Pb/^{207}Pb ratios of naturally-derived Pb, e.g. rock-released Pb, are usually higher than 1.20. The ^{206}Pb/^{207}Pb ratios of anthropogenic Pb derived from ore bodies, ranging from 0.92 to 1.20, are usually low in comparison with those of natural origin. The only known exception is Pb derived from ore bodies in Missouri that has a ratio between 1.28 and 1.33 (Sturges and Barrie, 1987; Munksgaard *et al.*, 1998; Hansmann and Koppel, 2000). Usually, the $^{206}Pb/^{207}Pb$ ratios of anthropogenic Pb derived from lead sulfide ore deposits in the U.S., Canada and Australia are 1.213-1.221, 1.148-1.153 and 1.04, respectively (Sturges and Barrie, 1987).

In HK, publication of Pb isotopic studies of environmental samples is rare. On the other hand, a relatively large volume of Pb isotopic information in South China as well as the PRD has been gathered by Zhu (1995, 1998) and Zhu et al. (1989, 2001). Geochemical mapping of background Pb of various ores and rocks in South China block has shown that both Th-derived (^{208}Pb) and U-derived (^{206}Pb, ^{207}Pb) isotopes are enriched in crust and mantle. The background Pb isotopic composition of South China can be characterized by $^{206}Pb/^{204}Pb>18.4$, $^{207}Pb/^{204}Pb>15.53$ and $^{208}Pb/^{204}Pb>38.4$ (Zhu, 1995). Also, the $^{206/207}Pb$ ratios of various types of environmental samples, including automobile exhaust and ore deposit (1.1604 and 1.1716, respectively) collected in the PRD have been determined (Zhu *et al.*, 2001).

2.6.4 Statistical analyses

The application of multivariate statistical analyses in geochemical studies can assist in the identification of pollution sources and apportionment of natural and anthropogenic contributions. (Facchinelli et al., 2001; Hwang et al., 2001). Some of the most commonly used statistical methods in geochemical studies of soils and sediments include Pearson correlation and Principal Component Analysis (PCA). Hence, a brief introduction of these statistical methods is given.

Pearson correlation is a bivariate statistical analysis that detects the relationship between two variables. Pearson correlation coefficient, as an output, is indicative of one of the three possible relationships (positive, negative and zero correlation) between the two sets of variables. A positive Pearson correlation coefficient indicates that measurements of one variable tend to increase when measurements of the other variable increase. A negative Pearson correlation coefficient shows that increasing measurements of one variable is associated with decreasing measurements of the other. A zero correlation indicates no relationship between the two variables. In other words, Pearson correlation coefficients are used to indicate linearity of the relationship between two elements. Generally, a significantly positive coefficient may indicate that an increase of one element is accompanied by an increase of the other, which may also suggest simultaneous inputs of the two elements. Furthermore, a significant correlation indicated by this bivariate Pearson correlation coefficient is also used to verify the output of the principle component analysis, where multivariate correlation is examined.

In comparison, the calculation of multivariables becomes more complicated. To observe some statistical and physical correlation among multivariables, one may resort to multivariate statistical techniques, such as PCA. PCA is one of the best known techniques that enables the visualization of a series of multivariate samples by effectively reducing the number of variables to a small number of new variables, principle components. A graphical display of samples in a scatter-graph drawn on the newly generated principal components can demonstrate environmental, or other, trends, as similar samples appear close together and dissimilar samples far apart. PCA is usually used on a fairly large samples (>10) and a large number of variables (>10). The variables should be continuous, but discontinuous and ordinal measurements are often used. However, the interpretation of results may become ambiguous (Pentecost, 1999).

2.7 Regulatory standards

A soil regulatory guideline has not been established in HK. In the past, many researchers used overseas regulatory guidelines to assess the extent of trace metal contamination of urban soils in HK. The Netherlands Soil Contamination Guidelines (Department of Soil Protection, Netherlands, 1994), commonly referred to as the Dutch Soil Standard, has been a popular choice for many local researchers, including the local regulatory authority, Environmental Protection Department. In spite of the frequent adoption of the Dutch Soil Standard, the applicability of this standard and the others developed in the temperate region may be limited in HK because of the inherited differences in geochemical and climatic characteristics. Also, a general drawback of this standard and many others is the assessment of trace metal contamination of soils solely based on total metal concentrations of the soils. Although the associated simplicity of this mechanism provides a convenient and time-efficient tool for evaluation, other influential factors governing bioavailability and biotoxicity of trace metals may become neglected, hindering fate prediction in the initial stage of a trace metal assessment of soils.

Three regulatory guidelines, including the Netherlands Soil Contamination Guidelines, the Canadian Environmental Quality Guidelines

(CCME, 1997b), and the Chinese Soil Quality Standards (National Environmental Protection Agency, 1995) are given in Appendix B. Each of these standards shows a unique regulatory approach towards trace metal assessment of soils. In the present study, the Netherlands Soil Contamination Guidelines (the Dutch Soil Standard) will be used in the assessment of trace metal contamination of urban soils in HK for three major reasons. First of all, its comparatively conservative "T" values allow a cautious assessment of trace metal contamination of soils. Secondly, it provides a definitive interpretation of soil contamination by giving maximum background concentrations, "T" values, and of the need for investigative and possible remedial actions by setting the maximum permissible concentrations, "I" values. Thirdly, its use in the present study provides a common ground for comparison with previous studies also conducted in HK.

In the evaluation of trace metal contamination of agricultural soils in the PRD, the use of the Chinese Soil Quality Guideline is deemed most appropriate for an obvious reason that the Guideline is developed based on Chinese geological characteristics and climatic conditions. Furthermore, the formulation of the Guideline is intended for use in agricultural soils.

CHAPTER THREE METHODOLOGY

In this chapter, detailed descriptions of the study areas and methods and materials used during the course of the study are provided.

3.1 Study areas

A description, including topography and historical development, of HK and the PRD is given in this section. The information will help in the interpretation of the analytical results and derivation of associated potential environmental implications presented in later chapters of this thesis.

3.1.1 Hong Kong

HK is located at the southeast of China between latitudes 22°37' and 22°9'N and longitude 113°52' and 114°30'E, adjoining Guangdong Province (see Figures 3-1 and 3-2). It has a population of 6.8 millions and a total area of 1,100 km^2, which comprises of the Kowloon Peninsula, Hong Kong Island, the New Territories and outlying islands. In addition to being one of the most densely populated cities in the world, traffic density in HK is also among some of the highest in the world. In March 1999, there were 499,400 licensed vehicles and only 1,869 km of roads – 425 on Hong Kong Island, 430 in Kowloon, and 1,014 in the New Territories (HKSAR, 2000).

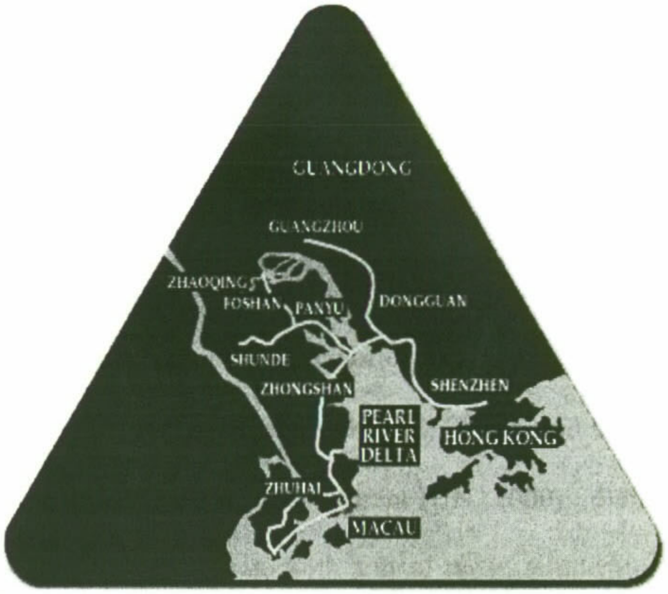


Figure 3-1 Map of the PRD and Hong Kong

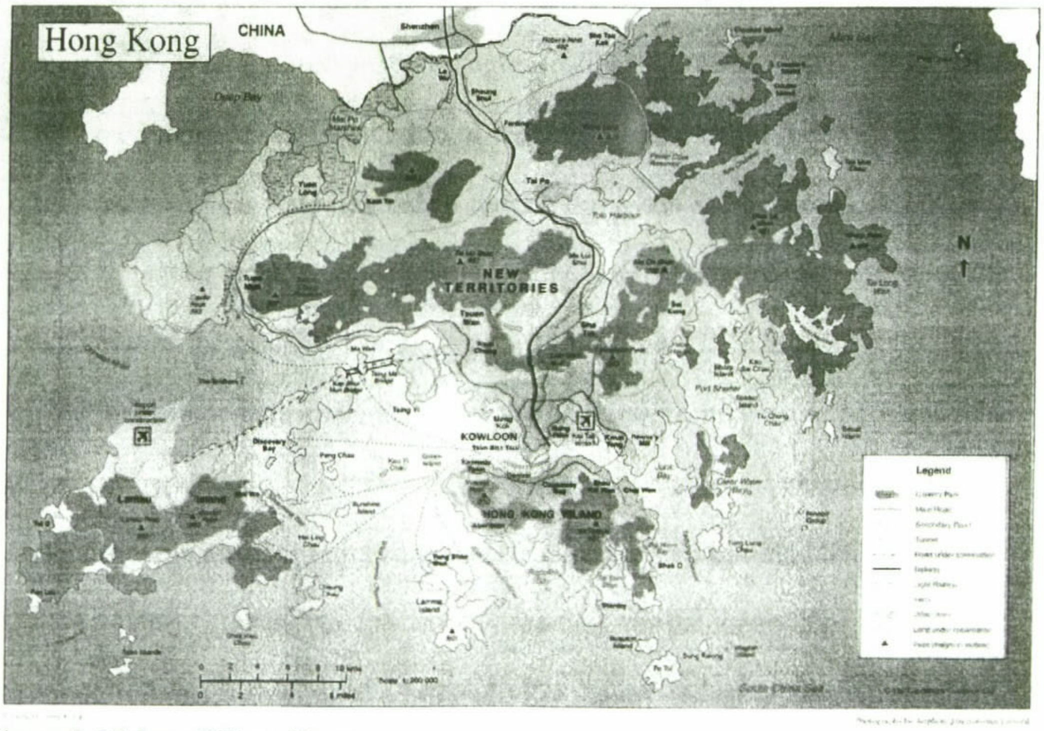


Figure 3-2 Map of Hong Kong

Since over 80% of HK's natural terrain is dominated by mountains and hills with steep slopes, urban and industrial development has generally concentrated on approximately 16% of the total land space, which is largely distributed in the Kowloon Peninsula, along the coastal area of Hong Kong Island, and in selected districts of the New Territories. The population densities in Kowloon, Hong Kong Island, and the New Territories and Islands are 44210, 17200, and 3520 persons/km^2, respectively, (HKSAR, 2000), and the whole population essentially lives in an urbanized environment (UN, 2000). Being in the subtropical region, HK has a mild climate with annual mean temperature, relatively humidity, and total rainfall of 23.0°C, 77% and 2214 mm, respectively (HKSAR, 2000).

Historically, HK underwent a dramatic transformation from a small fishing village a century ago to an internationally recognized financial centre today. It has also become an important shipping centre in the world and a major gateway to China. Today's achievement was initiated in the 1960's when the economy of HK was engaged in textile, light, and manufacturing industries taking an advantage of the large supply of inexpensive labour then. At that time, HK had over 2000 major and 200,000 minor industries, and many of them were metal-related industries, such as can production, enamelware, batteries, basic industrial chemicals, paints, lacquers and integrated circuit boards, electroplating, ship building and boat yards (Morton, 1989). Owing to the implementation of the open-door policy and economic reforms in Mainland China in 1978, many industrial activities in HK were attracted by inexpensive land and labour in the Mainland and subsequently migrated northwards in search of a better industrial and manufacturing environment. Since then, industrial activities in HK have subsided noticeably, and so have the associated environmental issues. Although the economic input of industrial and manufacturing sector remains important, the economic structure of HK is increasingly geared towards other sectors, such as financial, technological, and services and tourism sectors.

3.1.2 The Pearl River Delta

The PRD is situated in the southern part of Guangdong Province, China, linking with HK at its southeastern boundary (Figure 3-2). It has a total area of 41,600 km^2 and a population of over 25 millions. Being one of the first economic zones in China, industrialization and urbanization in the region has been rapid in the last few decades. The proliferation of these industrial activities has subsequently given rise to many cities. Guangzhou, Shenzhen, Dongguan, Zhongshan, Foshan and Zhuhai have become major industrial production bases; of which Guangzhou is the largest light industrial production base in China. Similar to HK, the PRD has a humid subtropical weather with an annual average temperature and rainfall of 22°C and 1,690 mm, respectively.

In the PRD, agriculture has traditionally been a major sector to the local economy. The favourable weather conditions allow an annual agricultural production of ten to fifteen crops of vegetables and three crops of grains. However, in the midst of rapid industrial and urban development, many farmlands in the PRD have been converted to other land uses. Sustainability of the remaining agricultural lands is under increasing threat partly because of degrading environmental qualities and partly because of heavy application of agrochemicals (Siamwalla, 1996; Li et al., 1997; Chen et al., 1999).

3.2 Site selection and soil sampling

3.2.1 Urban soil profiles of Hong Kong

The study of trace metal contamination of urban soil profiles was conducted at six study sites, including one roadway divider and five urban parks. In an alphabetical order, they were Carpenter Road Park (CRP), a roadway divider along Cheung Sha Wan Road (CSW), Hutchison Park (HC), Lam Tin Park (LT), Nathan Road Leisure Park at the intersect between Nathan Road & Gascoigne Road (NG), and Sham Shui Po Park (SSP). All of the six study sites were situated in Kowloon, where the population density was highest.

HK has a large population and a shortage of land space. In order to provide sufficient leisure facilities in the urban environment, some urban parks and amenity facilities are built on marginal lands, where they are inevitably subjected to undesirable impacts of urban and industrial activities from the surrounding roads and industrial buildings. CRP was an urban park in a residential and commercial setting in Kowloon City. It was surrounded by medium-density traffic roadways and adjacent to a shopping centre. The park was either covered with lawn or vegetated with flowering plants, shrubs and trees. The vegetation in this urban park was frequently trimmed and manicured, and flowering plants were planted seasonally. CSW was a roadway divider in an industrial and residential area in Sham Shui Po. Immediately adjacent to both roadways of high traffic densities, it was elongated in shape and densely vegetated with shrubs for aesthetic purpose. Soil and plant management of this study site was minimal. HC was located in a residential area in Hung Hom. This urban park was surrounded by a transformer facility and some newly constructed apartment buildings. Vegetation in this park was also frequently manicured. It should be noted that soils in this park were previously found to be enriched with Cd (Li et al., 2001a). LT was an urban park developed on a hillside that was away from intense urban operations. Soils at this study site mainly originated from its natural surrounding, but some potting soils were used in planting areas. NG was a leisure park located in a commercial area adjacent to heavy traffic. Soils at NG were largely vegetated, but some exposed soils were found. SSP was located adjacent to a roadway with a medium traffic volume in a residential setting. Soils in this park, also imported from elsewhere, were vegetated with flowering plants, shrubs as well as some large trees. In general, these urban parks were used by visitors of all ages. The site characteristics and the corresponding annual average traffic densities (AADTs) of these study areas are presented in Table 3-1.

Table 3-1 Study areas of urban soils in Hong Kong

Site ID	AADT[a]	Site Characteristics
CRP	8690	In a commercial/residential area, surrounded by traffic
CSW	44205	Immediately adjacent to high traffic densities, vegetated, stretching from an industrial area to a residential area
LT	14090	Developed on hillside in a residential area, no obvious contaminant sources present
HC	14870	In a residential area, previous industrial activities nearby
NG	42630	Situated in a commercial and residential area, adjacent to heavy traffics from Nathan Road and Gascoigne Road
SSP	23020	Situated in a residential area, adjacent to Lai Chi Kok Road

a. Annual average daily traffic (in vehicle per day); The Annual Traffic Census, 1997, TSD Publication no. 98CAB3, Traffic and Transport Survey Division, the Government of Hong Kong SAR.

At CRP, LT and HC, urban soil profiles between 0 and 40 cm were collected at 10-cm intervals (0-10, 10-20, 20-30, and 30-40cm) using a stainless steel auger. However, due to the presence of gravel and stony debris below the depth of 20 cm, soil profiles between 0 to 20 cm were obtained at CSW. Also, for fear of obstruction of electrical cables and other utility pipelines, the auger could only penetrate to a maximum depth of 30 cm at SSP and NG. Since there were many potential sampling locations within each study area, a selection process was employed, in which specific site locations were determined based on initial site visits. Also, the following conditions were avoided: 1) known/observable sources of trace metals, i.e. metallic fences and fire hydrants, 2) obstruction of pipes and cables in the subsurface, and 3) narrow or hilly landscape.

In order to ensure representative of the soil samples, excessive soil particles on the surface of each soil core were removed with a brush prior to packaging. Each of the composite soil samples collected in the five urban parks was composed of 9 subsamples obtained at each intersect "X" in a 2m by 2m grid (Figure 3-3). Soil sampling at the roadway divider, CSW, used a sampling grid shown in Figure 3-4 because of its elongated shape. All of the collected soil samples were stored in polyethylene bags and analyzed for trace and major metal concentrations, soil pH, and loss on ignition. Furthermore, selected soil profiles were subjected to additional analyses, including chemical speciation and Pb isotopic composition.

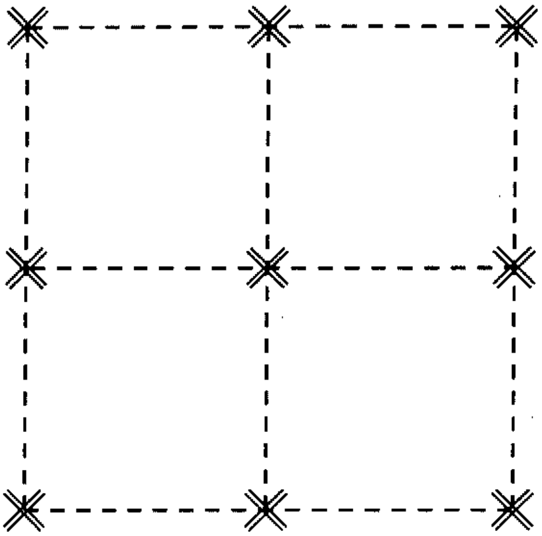


Figure 3-3 Sampling grid of urban soil profiles in urban parks

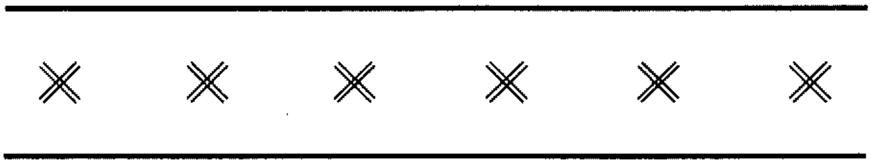


Figure 3-4 Sampling grid of urban soil profiles at CSW

3.2.2 Agricultural soils of the PRD

An extensive soil sampling program was carried out in collaboration with The Guangzhou Institute of Geochemistry, Chinese Academy of Sciences. A total of 78 soil samples, consisting of 39 crop soils, 19 paddy soils and 20 natural soils, were collected in the PRD (see Figure 3-5). The locations of the crop soils were relatively evenly distributed across the study area. On the other hand, the majority of the paddy soils were situated in the relatively less developed areas in the northern and eastern sides of the region. The natural soils were generally collected from uncultivated and/or remote areas, such as forests and mountaintops, in the region. The crop soils were predominantly used for fruit and vegetable production, and the paddy soils were used to cultivate rice – a major staple food in southern China.

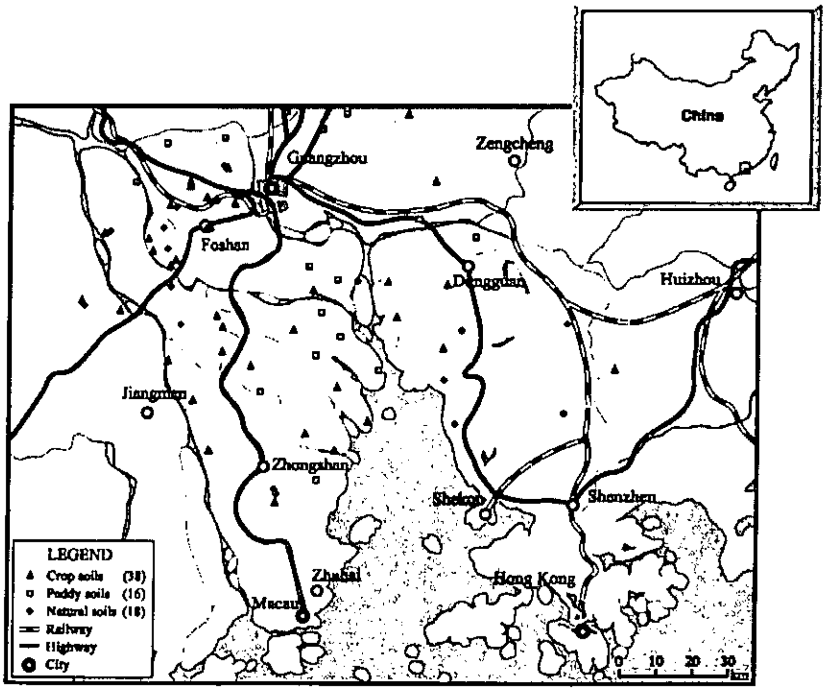


Figure 3-5 Sampling locations of agricultural and natural soils in the PRD

The crop and paddy soils consisting of 3 to 5 subsamples were collected between the depths of 0 and 15cm, which was representative of the plough layer. Each of the natural soils was made of 9 subsamples obtained between 0 and 5cm. All soil samples were collected using a hand auger and then stored in polyethylene bags. All of the soil samples were analyzed for trace and major metal concentrations. However, due to the vast number of the soil samples, selected soil samples were analyzed for soil pH, chemical speciation and Pb isotopic composition.

3.3 Laboratory preparation and analyses

Detailed descriptions of soil preparation and laboratory analyses are given in this section. It should be noted that treatments of urban soil profiles of HK and agricultural soils of the PRD were identical unless stated otherwise.

3.3.1 Soil sample preparation

Soil preparation of the urban soil samples of HK was slightly different from that of the agricultural and natural soil samples of the PRD. The urban soil samples were dried at 50°C for at least 3 days in an oven. They were passed through a pre-washed 2mm-polyethylene sieve to remove coarse debris and stony materials. The sieved soil particles (<2.0 mm) were ground in a porcelain mortar with a pestle until fine particles (~200 μm) were obtained. The prepared samples were then stored in polyethylene bags.

The collected agricultural soils were air-dried at 20°C (in order to preserve its organic constitutes for a future study of organic contamination). They were then sieved through a 2-mm polyethylene sieve. The soil samples (<2.0 mm) were ground in a motorized agate grinder. The prepared samples were stored in polyethylene bags. Prior to all laboratory analyses, the soil samples, including urban and agricultural soils, were placed in a dessicator overnight to minimize the potential effects of residual moisture content.

3.3.2 Soil pH

For the determination of soil pH, 4.0 g of soil (<2mm, air-dried) were weighed into a polystyrene centrifuge tube. 10.0 ml of deionized water (DIW) were added. The tubes were capped and shaken for 30 minutes to produce a suspension on a mechanical shaker (Model *Stuart Scientific*). After the tubes were centrifuged at 3000rpm for 5 minutes, and the pH of the solutions was measured using an *Orion Research* 701A digital ionalyzer, that had been previously calibrated at pH 4.0, 7.0 and 9.0 using standard buffer solutions. The pH reading of each sample was taken by swirling the electrode in the solution until a constant value was obtained. The glass electrode was rinsed with DIW between readings, and the calibration was carried out at every 15 samples (Allen et al., 1974).

3.3.3 Loss on ignition

The organic carbon content of the urban soil samples was determined based on the loss of carbon on ignition (LOI). About 15.0 g of soil samples were weighed and placed in a pre-weighed evaporating dish. [Note: all evaporating dishes were previously heated at 550°C in an oven for 24 hours and stored in a dessicator before use.] The soil and the evaporating dish were heated in an oven at 105°C for 24 hours to evaporate moisture. After cooling in a dessicator, the mass of the dried soil and the dish was measured and recorded. The dried soil and the dish were heated in the oven at 450°C for 24 hours to remove combustible carbon sources. The soil residual and the dish were cooled and then placed in a dessicator. The mass of the soil residual and the dish was recorded once again. Three replicates of each sample were analyzed. The loss of carbon on ignition (on a dry weight basis) was calculated using Equation 3-1:

W_{dish} = weight of an empty dish (in g)

$W_{dish+dried\ soil}$ = weight of an empty dish + dried soil (after 105°C; in g)

$W_{dish+residual\ soil}$ = weight of an empty dish + residual soil (after 450°C; in g)

LOI = loss of carbon on ignition on a dry basis (in %)

Equation 3-1 - Calculation for loss on ignition (LOI):

$$LOI = [W_{dish+residual\ soil} - W_{dish+dried\ soil}] / [W_{dish+dried\ soil} - W_{dish}] \times 100\ \%$$

3.3.4 Trace metal concentrations of soils

The prepared soil samples were analyzed for their trace metal concentrations using an acid digestion method, as followed. About 0.250 g of the soil samples were weighed into pre-washed Pyrex test tubes, in which 4.0 ml of concentrated nitric acid (HNO_3) and 1.0 ml of concentrated perchloric acid ($HClO_4$) were added. The test tubes containing the mixtures were placed in an aluminium block, in which they were heated at 50°C for 3 hours, 150°C for 3 hours, 190°C for 18 hours and 195°C for 5 minutes until complete dryness. After the test tubes were cool, 10.0 ml of 5% HNO_3 was added and thoroughly mixed using a vortex. The test tubes were then heated at 70°C for 1 hour. Upon cooling, the mixtures were poured into polyethylene tubes. Prior to trace metal analysis, the mixtures were centrifuged at 3500 rpm for 10 minutes. Trace metal concentrations of the solutions were measured using Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP-AES; *Perkin Elmer 3300 DV*).

All glass- and plastic-ware was soaked in 10% nitric acid overnight and rinsed thoroughly with DIW before use. For quality assurance, blanks, duplicates, and standard reference materials from the National Institute of Standards and Technology and Imperial College (NIST SRM 2709 for San Joaquin Soil and HRM2, respectively), representing 10%, 20%, and 10% of the sample population, respectively, were inserted in each set of the acid digestion. The recovery rates for the trace metals and some major elements in the internal standard reference materials (HRM2) for soil metal analyses were around 85 to 110 %. However, same acid digestion for NIST SRM 2709 yielded low recovery rates ranging from 50% to 90% for the very low concentrations of some trace metals.

The calibration standard solutions were prepared from Perkin Elmer Atomic Spectroscopy Standard - Quality Control Standard 21, which contained a total of 21 elements, including Cd, Co, Cr, Cu, Mo, Ni. Pb, V, and Zn. The calibration of the ICP-AES was performed for every batch of samples with a sample population of no more than 40. Trace elements were calibrated at 0.05, 0.1, 0.5, 1.0, 2.0, and 5.0 mg/l, while major elements, such as Ca, Mg, Mn and Fe, were calibrated at 5.0, 10.0, 50.0 mg/l. The ICP-AES was set to perform 3 replicate measurements for each sample automatically. Upon the completion of the measurement, the spectrum of each of the elements was inspected, and wavelength adjustment was made when necessary.

3.3.5 Chemical fractionation of trace metals in soils

A modified version of Tessier's method was used in determining the chemical fractionation of trace metals in soils (Tessier et al., 1979; Li et al., 1995). 1.000 g of the soil samples was weighed and placed into Nalgene® polysulfone centrifuge tubes. 8.0 ml of 0.5 M $MgCl_2$ (adjusted to pH 7.0 with diluted NH_4OH) were added. The tubes were then capped and shaken on a mechanical shaken (180° horizontal movement or back and forth movement) for 20 minutes. After the tubes were centrifuged at 3000 rpm for 10 minutes, 5 ml of the supernatant were extracted and placed in pre-washed Pyrex test tubes. The residual supernatants in the centrifuge tubes were carefully discarded to avoid loss of solids. 8.0 ml of DIW was then added into the centrifuge tubes and hand-shaken for 2 minutes to rinse off the extraction solution. The rinsing solution was then decanted after centrifugation at 3000 rpm for 10 minutes.

Preferably, solutions for ICP-AES analysis should be formed of the same matrix to reduce interference. Therefore, a standard procedure was used to treat all supernatants from each of the extraction steps. 1.0 ml of conc. nitric acid was mixed with the extracted supernatants in the test tubes and heated at 120°C for 4 hours and then 150°C until dry unless stated otherwise. After cooling, 10.0 ml of 5% nitric acid were added into the test tubes and heated at 65°C for 1 hour. The solution was then decanted into polyethylene tubes for subsequent ICP analysis.

After the completion of the first step, the second step could be initiated by adding 8.0 ml of NaOAc to the solid residues in the centrifuge tubes. The tubes were mechanically shaken for 5 hours and then centrifuged. 2.0 ml of the supernatants were then extracted and placed into clean test tubes. The supernatants were treated with 1.0 ml conc. HNO_3, centrifuged, and stored in polyethylene tubes, as described in step 1. Similarly, the excess supernatants were discarded after the solid residues were rinsed with 8.0 ml DIW as described previously.

In the third step, 20.0 ml of 0.04 M $NH_2OH{\cdot}HCl$ in 25 % (v/v) HOAc were added to the solid residues and thoroughly mixed in the capped centrifuge tubes. The solutions were heated at 96°C for 6 hours uncapped during which the tubes were agitated on an hour basis. After cooling, DIW was added to the centrifuge tubes to compensate water loss so that a total volume of 20 ml remained unchanged. The centrifuge tubes were capped, shaken for 5 minutes, and then centrifuged at 3000 rpm for 10 minutes. 15.0 ml of the supernatant were emptied into test tubes and treated with 1.0 ml of conc. nitric acid. It was made to a final volume of 10.0 ml using 5% nitric acid as described in Step 1.

In step 4, 3.0 ml 0.02M HNO_3 and 5.0 ml 30% H_2O_2 (adjusted to pH 2.0 using weak acetic acid) were added to the solid residues. Uncapped, the centrifuge tubes were heated progressively until the temperature reached 85°C and remained at 85°C for 2 hours with occasional agitation. The tubes were then removed from the heating block and cool. Additional 3.0 ml of 30 % H_2O_2 (pH 2.0) were added, and the tubes were heated at 85°C for 3 additional hours. During the heating process, agitation was applied hourly. Using 5.0 ml 3.2 M NH_4OAc and DIW, the solution was brought back to a volume of 20.0 ml. The tubes were then shaken for 30 minutes and centrifuged. 15.0 ml of the supernatant were removed and placed in test tubes for treatment with HNO_3.

Lastly, the solid residue remaining in the centrifuge tubes was transferred to Pyrex test tubes by thorough suspension in DIW. The test tubes were then heated at 120°C to evaporate excess DIW. To completely dissolve metals in the solid residue, 4.0 ml conc. HNO_3 and 1.0 ml $HClO_4$ were added and heated at 50°C for 3 hours, 75°C for 30 minutes, 100°C for 30 minutes, 150°C for 3 hours, 175°C for 30 minutes, and 190°C for 3 hours until dry. After cooling, 10.0 ml of 5% HNO_3 were added to the test tubes and heated at 65°C for 1 hour. The solutions were then poured into polyethylene tubes and centrifuged. Trace and major metals concentrations of the solutions were measured by ICP-AES. Quality control measures similar to those in the determination of total metal concentrations were implemented. The recovery rates calculated based on the sum of the five fractions over the total metal concentrations determined independently ranged between 85% to 110%.

3.3.6 Lead isotopic composition

The Pb isotopic composition of the digested solutions and extraction solutions were determined using Inductively Coupled Plasma – Mass Spectrometer (ICP-

MS ELAN 6100) at the School of Chinese Medicine of The Hong Kong Baptist University. Due to the high sensitivity of the ICP-MS, dilution of all of the sample solutions using 5% HNO_3 was required. Also, prior to isotope analysis, tubings and other essential internal components of the ICP-MS was flashed with 5% HNO_3 followed by Milli-Q water until the intensity count of Pb^{208} was sufficiently low (<150 counts per second), to avoid potential contamination from residual Pb. Instrumental parameters, including 200 sweeps/reading, 7 replicates, and dwell time of 50 ms, were set. A standard reference material Common Lead Isotopic Standard (NIST SRM 981) was used for quality control. Furthermore, blank (5% HNO_3) and standard reference material samples were inserted in every 10 sample solutions to detect drift.

3.4 Statistical analyses

All computational and statistical analyses were performed using computer software Excel 97 and SPSS 8.0. These analyses consisted of descriptive statistics, Pearson correlation and Principal component analysis (PCA).

An attempt was made to statistically analyze the results of the urban soil study. In the data treatment for PCA, both trace and major metal concentrations of urban soil profiles were treated as one group due to the limited number of samples at some study sites. However, the results were not helpful in terms of understanding the association among the trace and major metals, which was probably due to the limited number of samples and variations in terms of soil types, soil depth, and metal concentrations.

Among the 78 agricultural and natural soil samples collected in the PRD, one crop soil sample (C21) was grossly contaminated with Zn. The measured Zn concentration (993mg/kg) was over 10 times higher than the mean value of the crop soils, thus considered as an outliner. Instead of removing this measurement from the statistical analyses, it was decided that it would be replaced by an average value of Zn concentrations of the two geographically closest crop soils, namely C19 and C20. Also, since soil Mo concentrations were largely undetected, this variable was excluded from the statistical analyses. For other elements, instead of eliminating the undetectable trace metal concentrations of some soil samples, they were assigned a value equivalent to half of the corresponding detection limits (Cd: 0.02mg/kg) to maintain continuity and large sample population sizes. In the computation of Pearson correlation coefficients and PCA, trace metal concentrations of the soils of the PRD were treated independently by soil types, namely crop, paddy and natural soils. Principal component factors were obtained for the three soil types using a rotation method Varimax with Kaiser normalization.

CHAPTER FOUR TRACE METAL CONTAMINATION OF URBAN SOILS OF HONG KONG

4.1 Soil pH and loss on ignition

Average (and range) soil pH and loss on ignition of urban soil profiles in HK are presented in Table 4-1. The soil pH of the soil profiles varied from slightly acidic (5.05) to slightly alkaline (8.40). The soil profiles at LT, HC, NG and SSP were slightly acidic, while slightly alkaline soils were usually found at CRP and CSW.

The average LOI of the soil profiles ranged from 4.99% to 6.31% at the upper surface (0-10cm) and from 2.17% to 5.66% at the subsurface (Table 4-1). The LOI of the soil profiles was the lowest at CSW, and the highest was found at HC. In general, the LOI of the soil profiles, except for SSP, tended to decrease with increasing depth, which was anticipated since organic matter tended to accumulate at soil surface. Measurements of LOI of the present study were generally lower than those reported by Jim (1998). This could be attributed to soil management practices, where fallen leaves and other organic debris were usually removed in urban parks for hygiene and aesthetic purposes.

Table 4-1 Average (range) soil pH and organic content of urban soil profiles

Location	N	Soil depth (cm)	Soil pH	Organic content (%)
CRP	7	0-10	7.71 (7.01-8.38)	5.56 (4.12-7.12)
		10-20	8.16 (7.31-8.64)	4.79 (1.83-6.62)
		20-30	8.32 (7.14-8.69)	5.10 (4.38-6.39)
		30-40	8.40 (7.50-8.68)	4.91 (3.53-7.00)
CSW	2	0-10	8.11 (8.03-8.19)	4.99 (4.60-5.37)
		10-20	7.36 (7.16-7.55)	2.17 (1.69-2.64)
LT	5	0-10	6.43 (5.12-7.91)	4.78 (4.27-5.59)
		10-20	6.32 (5.35-8.07)	4.79 (3.94-5.64)
		20-30	6.33 (5.47-7.94)	4.48 (3.66-5.94)
		30-40	6.12 (5.05-7.93)	4.37 (2.90-6.55)
HC	6	0-10	6.65 (6.25-7.03)	6.31 (4.66-8.82)
		10-20	6.54 (5.43-7.35)	5.90 (4.35-8.45)
		20-30	6.95 (5.68-8.04)	5.97 (4.88-8.60)
		30-40	7.23 (5.21-8.39)	5.66 (3.97-8.60)
NG	4	0-10	6.41 (5.97-6.87)	5.91 (4.98-6.49)
		10-20	6.61 (6.20-7.04)	4.82 (3.63-5.80)
		20-30	7.11 (6.71-7.92)	4.51 (3.35-5.66)
SSP	2	0-10	5.82 (5.74-5.90)	4.90 (4.12-5.68)
		10-20	6.82 (6.65-6.99)	5.47 (4.42-6.51)
		20-30	6.78 (6.03-7.53)	5.84 (5.81-5.87)

4.2 Trace metal concentrations of urban soil profiles

Mean and range concentrations of Cd, Co, Cr, Cu, Mo, Ni, Pb, V and Zn of urban soil profiles of HK are presented in Tables 4-2 & 4-3. Within the urban environment of HK, it is nearly impossible to find pristine soils that have never been impacted by human activities. Nonetheless, to adequately compare trace metal concentrations of impacted and "non-impacted" soils, trace metal concentrations of country park soils may be representative of the background levels. Trace metal concentrations of country park soils collected in the Kowloon District (Cd: 0.10-0.17mg/kg; Cu: 3.84-7.46mg/kg; Pb: 6.04-12.73mg/kg; Zn: 55.75-90.97mg/kg) were reported by Poon et al. (1999). In comparison with these background values, concentrations of these trace metals reported in the present study were considerably elevated. In accordance to the Dutch Soil Standard, mean Pb, Zn and Cu concentrations of urban soil profiles at CRP, CSW, LT and NG (values shown in bold in Tables 4-2 & 4-3) exceeded the corresponding "T" values, suggesting Pb, Zn and Cu contamination of these soils.

Table 4-2 Mean and range concentrations of Cd, Co, Cr & Cu in urban soil profiles of Hong Kong

Site ID	N	Depth (cm)	mg/kg	Cd	Co	Cr	Cu
CRP	7	0-10	Mean	0.73	2.63	20.1	25.4
			Range	0.47-0.87	1.63-3.28	14.0-28.8	8.65-52.4
		10-20	Mean	0.72	2.49	19.9	**68.1**
			Range	0.39-1.12	1.90-3.06	13.0-25.0	6.98-390
		20-30	Mean	0.69	2.49	19.5	**44.1**
			Range	0.39-0.92	2.03-3.14	13.4-25.6	6.06-226
		30-40	Mean	0.65	2.39	18.5	31.1
			Range	0.43-0.80	1.15-3.12	12.4-24.4	3.35-144
CSW	2	0-10	Mean	0.45	2.84	53.5	**105**
			Range	0.37-0.52	2.51-3.16	46.8-60.2	102-108
		10-20	Mean	n.d.[a]	1.28	16.4	**39.9**
			Range	-	0.61-1.95	11.3-21.5	35.4-44.4
LT	5	0-10	Mean	0.07	1.64	11.5	4.94
			Range	0.02-0.16	0.74-2.17	9.21-13.3	2.60-6.63
		10-20	Mean	0.04	1.63	11.8	4.38
			Range	0.09-0.16	0.77-2.53	9.03-14.5	2.15-6.26
		20-30	Mean	0.01	1.40	10.4	3.70
			Range	0.02-0.12	0.74-2.03	8.23-15.7	1.78-5.36
		30-40	Mean	0.05	1.30	11.7	3.45
			Range	0.03-0.17	0.46-2.29	8.11-21.4	1.41-5.90
HC	6	0-10	Mean	0.19	2.10	14.2	2.24
			Range	0.06-0.43	1.00-4.88	10.8-18.6	0.96-3.87
		10-20	Mean	0.14	1.72	12.8	1.76
			Range	0.03-0.29	0.91-2.89	9.85-16.1	0.32-5.23
		20-30	Mean	0.32	2.01	14.2	2.72
			Range	0.20-0.47	0.59-2.90	10.4-17.8	0.75-8.38
		30-40	Mean	0.30	2.64	16.5	5.11
			Range	0.08-0.80	1.44-3.91	13.0-27.1	1.67-8.40
NG	4	0-10	Mean	0.38	5.71	34.6	**74.1**
			Range	0.17-0.59	3.18-8.22	20.4-59.0	55.8-99.3
		10-20	Mean	0.36	4.34	22.8	**55.3**
			Range	0.36-0.36	2.73-8.43	11.9-38.1	25.2-94.6
		20-30	Mean	n.d.	4.90	17.0	32.0
			Range	-	2.40-9.51	7.30-27.6	7.03-47.0
SSP	2	0-10	Mean	n.d.	3.08	20.5	8.74
			Range	-	2.80-3.36	19.9-21.1	5.05-12.4
		10-20	Mean	n.d.	3.09	20.0	9.85
			Range	-	3.04-3.14	19.9-20.1	6.37-13.3
		20-30	Mean	n.d.	2.49	17.2	5.42
			Range	-	1.51-3.48	14.7-19.7	2.97-7.86
Dutch Soil Standard		T values		0.8	20	100	36
		I values		12	240	380	390

[a] below detection limit

Table 4-3 Mean and range concentrations of Mo, Ni, Pb, V & Zn in urban soil profiles of Hong Kong

Site ID	Depth (cm)	mg/kg	Mo	Ni	Pb	V	Zn
CRP	0-10	Mean	0.73	7.18	65.5	9.13	96.4
		Range	0.21-1.60	4.89-9.30	40.0-103	4.89-15.9	58.8-127
	10-20	Mean	0.52	6.94	60.7	8.71	111
		Range	0.10-1.21	5.66-8.44	32.8-84.6	4.74-13.6	42.7-358
	20-30	Mean	0.47	6.70	58.1	7.96	94.3
		Range	0.17-1.31	5.52-8.71	41.9-74.3	4.52-11.3	36.8-230
	30-40	Mean	0.46	6.72	60.7	7.09	77.4
		Range	0.11-0.82	3.79-9.88	30.0-96.5	3.54-11.8	33.4-206
CSW	0-10	Mean	2.28	22.2	**185**	10.3	**645**
		Range	1.74-2.82	16.0-28.3	170-199	8.45-12.1	554-735
	10-20	Mean	0.86	6.28	**85.3**	4.85	**173**
		Range	0.46-1.27	5.06-7.50	72.3-98.3	4.74-4.96	139-207
LT	0-10	Mean	1.61	6.08	**139**	2.75	55.3
		Range	0.74-2.79	3.90-7.66	113-153	1.39-4.02	30.5-81.7
	10-20	Mean	1.56	6.27	**146**	2.59	55.4
		Range	0.60-3.08	4.34-8.21	138-155	1.00-4.17	37.7-77.5
	20-30	Mean	1.58	5.87	**148**	2.46	48.8
		Range	0.51-2.32	4.12-8.06	124-163	0.82-6.61	35.4-62.0
	30-40	Mean	1.24	5.87	**154**	3.28	47.5
		Range	0.48-2.42	4.16-7.68	128-175	0.60-11.3	34.2-54.6
HC	0-10	Mean	n.d[a]	4.27	54.4	3.55	49.9
		Range	-	2.48-5.93	24.9-77.7	2.02-5.13	28.4-135
	10-20	Mean	0.05	3.83	55.9	3.90	29.1
		Range	n.d.-0.05	4.87-6.58	22.6-82.5	1.53-8.27	18.6-46.6
	20-30	Mean	0.09	4.42	62.5	5.44	36.6
		Range	n.d.-0.09	2.47-7.03	31.3-110	1.65-9.35	25.5-70.3
	30-40	Mean	0.13	4.82	63.3	7.73	36.9
		Range	n.d.-0.13	3.18-6.14	33.6-112	3.22-20.8	19.7-49.2
NG	0-10	Mean	0.66	14.1	**249**	8.80	**318**
		Range	0.06-1.33	10.6-21.2	196-393	4.14-13.2	206-495
	10-20	Mean	0.47	10.1	**235**	7.71	**203**
		Range	0.05-1.10	7.02-14.9	149-377	1.88-14.9	84.6-360
	20-30	Mean	0.52	6.61	**221**	6.05	126
		Range	0.29-0.75	4.37-8.86	138-428	0.56-14.5	32.6-205
SSP	0-10	Mean	n.d	5.57	78.8	11.1	63.5
		Range	-	5.04-6.09	70.6-87.0	9.57-12.7	44.7-82.2
	10-20	Mean	n.d.	5.64	82.4	11.3	66.6
		Range	-	5.42-5.87	68.9-95.8	10.3-12.2	49.0-84.2
	20-30	Mean	n.d.	5.65	74.5	8.39	42.7
		Range	-	5.09-6.20	58.3-90.6	7.51-9.28	28.5-56.9
Dutch Soil Standard	T values		10	35	85	N/A[b]	140
	I values		200	210	530	N/A	720

[a] below the detection limit [b] not available

4.2.1 Pb

Pb contamination of urban soil profiles was most severe at NG, followed by CSW and LT. Soil Pb concentrations at NG and CSW decreased with increasing depth, and the difference in soil Pb concentrations between the surface and subsurface layers was significant at CSW and NG. Since CSW and NG were in close vicinity to major roadways with high traffic densities, it was highly likely that some of the soil Pb was released as a consequence of the combustion of leaded gasoline via atmospheric emission. Since CSW was located in an industrial area, some soil Pb at CSW could have also come from nearby industrial activities. In contrast with soil Pb distribution at CSW and NG, Pb concentrations of the soil profiles at LT remained elevated throughout the depth and showed a slight increase with increasing depth. The relatively even distribution of Pb in soils and that LT was situated in a residential area away from heavy traffic eliminated the possible contribution of gasoline Pb. According to the park manager, soils at LT were largely obtained from the same area. Hence, it was unlikely that Pb contaminant at the study site came from imported soils. Application of fertilizers and herbicides may be related to Pb contamination. Nonetheless, further study is needed.

4.2.2 Zn

Excessive Zn concentrations were found at CSW and NG, where the concentrations declined with increasing depth. The Zn concentrations of surface soils at CSW and NG were approximately 3 times higher than those of the subsurface, suggesting significant surface enrichment of the contaminant. Soil Zn contamination at these study areas was likely attributed to traffic-related activities, as Zn could be released from the combustion of fossil fuels and corrosion of galvanized vehicle parts. Since industrial activities have been associated with industrial activities, anthropogenic Zn in urban soils of CSW might have been contributed from industrial activities (Yim and Nau, 1987).

4.2.3 Cu

The Cu enrichment of urban soil profiles was found at CSW, NG and CRP, in a decreasing order of severity. Soil Cu concentrations at CSW and NG generally decreased with increasing depth. In the subsurface soil (20-30cm) at NG, soil Cu concentration declined to a level below the "T" value. Interestingly, Cu concentration of the surface soils (0-10cm) at CRP was below the "T" value, and it increased dramatically at the intermediate layer (10-20cm), from which soil Cu concentrations gradually declined again. This sudden increase in trace metal concentrations in the subsurface layers (10-40cm) at CRP may be an indication of recent incorporation of new surface soils at the study site. During the course of planting, surface soils may sometimes be removed and replaced with new planting soils. A similar phenomenon was also discovered at HC, where all analyzed trace metal concentrations of the profiles showed an alternating pattern. The incoherent vertical distribution of trace metals at CRP and HC could also be attributed to soil tillage, which may result in mixing of surface and subsurface soils.

4.2.4 Other trace metals

In general, mean concentrations of the other trace metals, Co, Cr, Mo, Ni, and V, of urban soil profiles were below the corresponding "T" values recommended in the Dutch Soil Standard, and they were low in comparison with those reported by Sewell (1999). Nonetheless, these trace metal concentrations at the surface layers were generally higher than those at the subsurface, indicating possible surface and/or atmospheric deposition of Co, Cr, Mo, Ni and V on soils in the urban environment of HK.

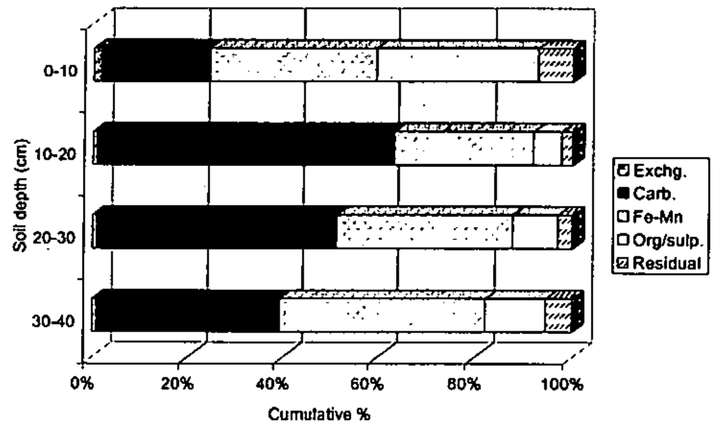
4.3 Chemical fractionation of trace metals of selected urban soil profiles

Chemical fractionation of Cu, Pb and Zn of selected urban soil profiles was analyzed. The results are graphically presented in Figures 4-1 to 4-3.

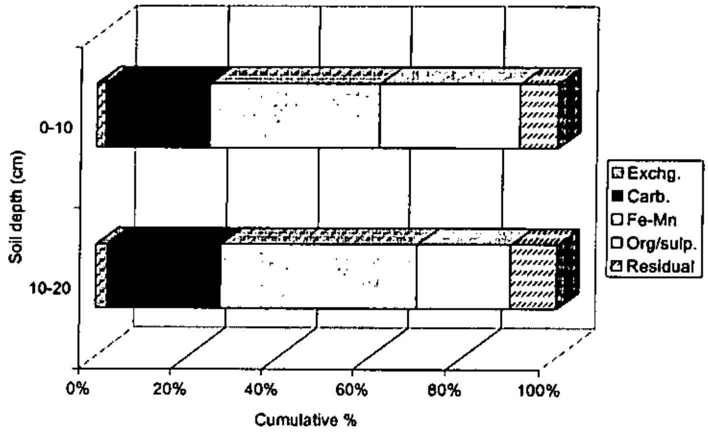
4.3.1 Cu

The chemical partitioning of Cu varied with soil depth and significantly among the study sites (Figure 4-1). Soil Cu in surface soils at CRP (0-10cm) was strongly associated with the carbonate, Fe-Mn oxide, and organic fractions (Figure 4-1a). Soil Cu at the subsurface (10-40cm) was predominantly associated with the carbonate and Fe-Mn oxide fractions. The exchangeable Cu was generally low, accounting for <3% of total soil Cu. However, the exchangeable and carbonate Cu ranged between 20-60% of total soil Cu, representing the readily soluble and potentially bioavailable fraction. At CSW, soil Cu was mainly bound in the Fe-Mn oxide fraction, followed by the carbonate and organic fractions (Figure 4-1b). The percent distribution of Cu in the organic fraction was slightly reduced at the subsurface. Readily soluble Cu, that is, Cu in the exchangeable and carbonate fractions, accounted for ~20% of total soil Cu. Soil Cu at HC was relatively evenly distributed among the four non-residual fractions, and the percent distribution of Cu in the residual fraction at HC was low (<10%). Soil Cu in the exchangeable and carbonate fractions represented 10-30% and 20-30% of total soil Cu at HC, respectively, indicating a significant fraction of readily soluble and bioavailable Cu in the soils. The chemical fractionation of soil Cu at HC also showed an alternating pattern with increasing soil depth. At LT, soil Cu was mainly found in the residual fraction (20-40%). The percent distribution of Cu in the exchangeable and carbonate fractions, accounting for 20-30%, increased with increasing depth at LT. Soil Cu at NG was strongly associated with the Fe-Mn oxide and organic fractions (Figure 4-1e). The percent distribution of Cu in the exchangeable and carbonate fractions remained relatively constant along the profiles. Cu in the Fe-Mn oxides increased with increasing depth, whereas Cu in the organic fraction decreased with increasing depth. At SSP (Figure 4-1f), the predominance of soil Cu in the organic and residual fractions was found at the surface layers (0-10 and 10-20cm). At the subsurface (20-30cm), the percent distribution of Cu in the organic fraction was greatly reduced, and the association of soil Cu with the Fe-Mn oxide and residual fractions was strong. The association of soil Cu with the exchangeable and carbonate fractions increased with increasing depth.

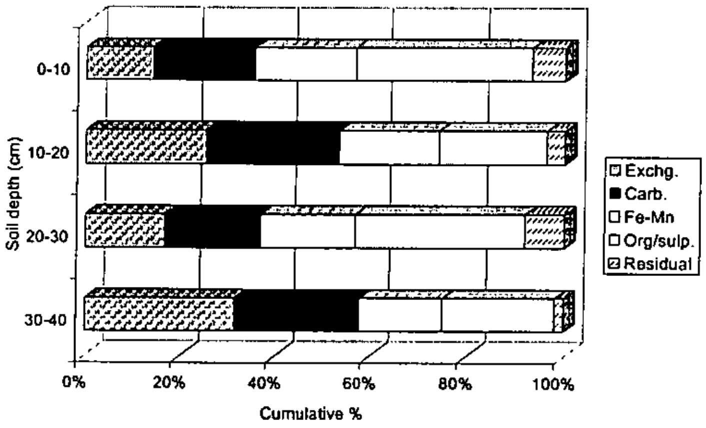
a) CRP



b) CSW



c) HC



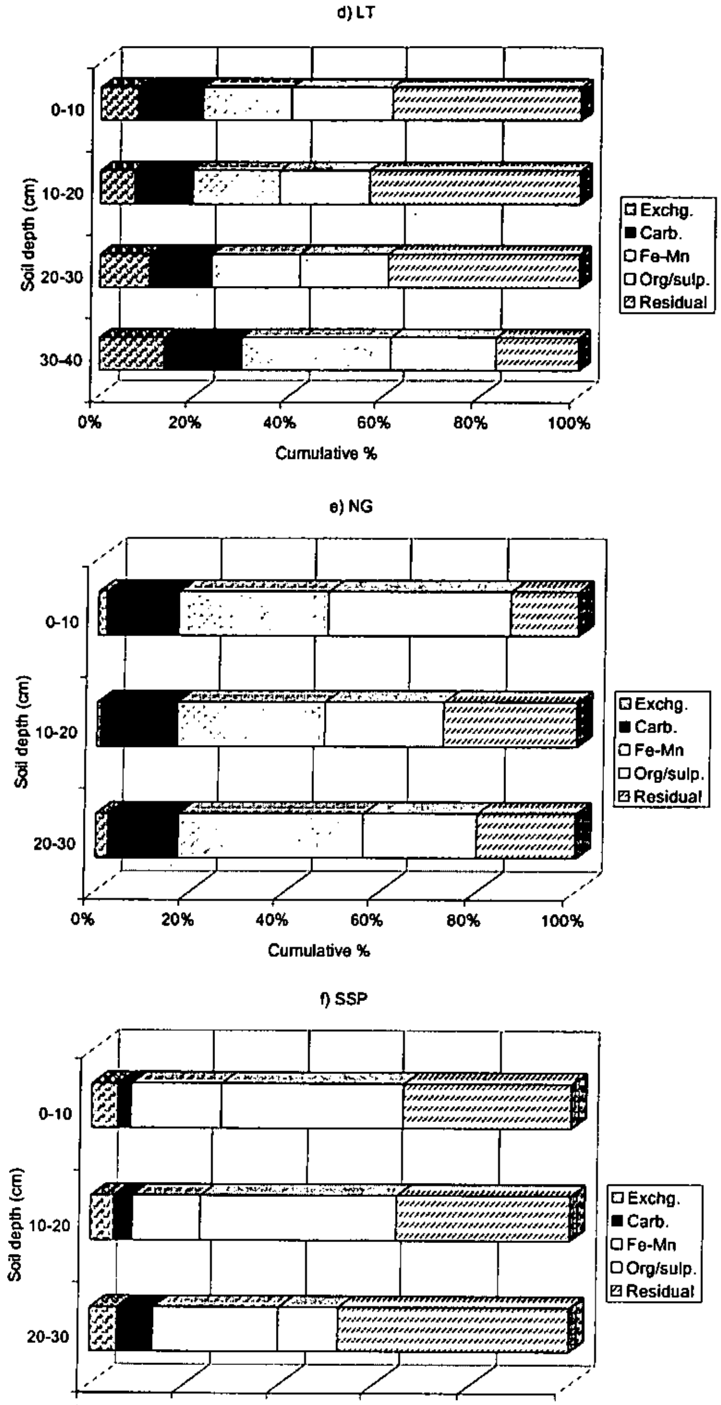


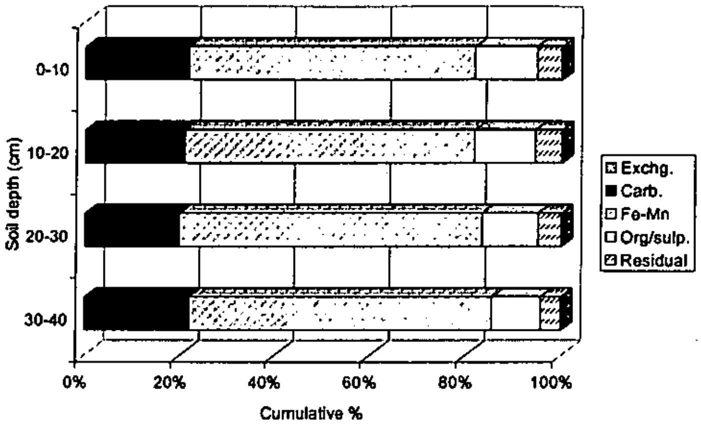
Figure 4-1 The chemical partitioning of Cu in urban soil profiles of Hong Kong

In general, the chemical partitioning of soil Cu showed a large variation among the five chemical fractions and study sites. Soil Cu in the exchangeable and carbonate fractions represented >20% of total soil Cu. At the Cu-contaminated sites (CSW and NG), soil Cu in these fractions may present potential environmental and health concern in the urban environment.

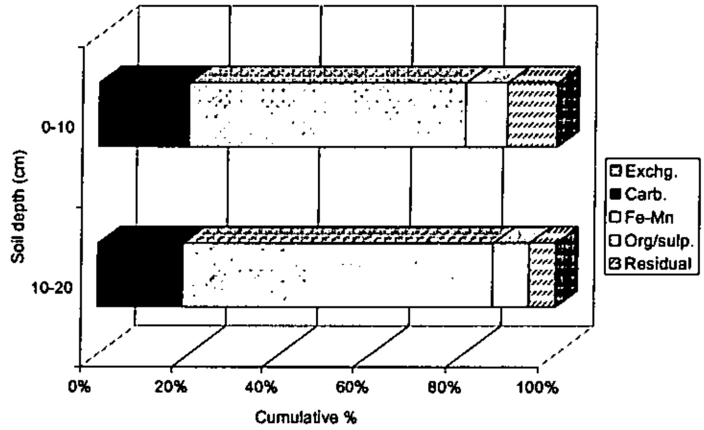
4.3.2 Pb

Soil Pb at CRP and CSW was predominantly associated with the Fe-Mn oxides, accounting for ~60% of total soil Pb (Figures 4-2a & b). Pb in the exchangeable fraction was generally undetected, and Pb in the carbonate fraction represented <20% of total soil Pb at both CRP and CSW. Soil Pb in the organic and residual fractions were relatively low. Similarly, over 40% of total soil Pb was found in the Fe-Mn oxide fraction at HC and LT (Figures 4-2c & d). Also, the percent distribution of soil Pb in the organic and residual fractions was low. However, exchangeable and carbonate-bound Pb were relatively high (2-15% and 20-40%, respectively). Figures 4-1e and 4-1f showed that soil Pb at NG and SSP were also strongly associated with the Fe-Mn oxides (>60%). The exchangeable Pb at these sites was generally low. Collectively, the exchangeable and carbonate Pb represented 10-20% of total soil Pb. The organic and residual Pb fractions were also low.

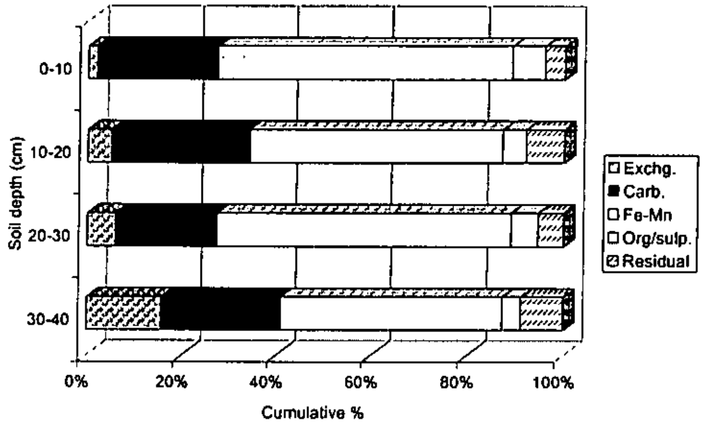
a) CRP



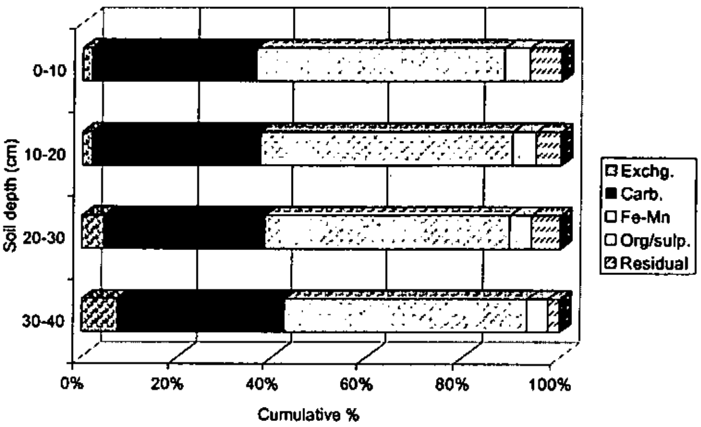
b) CSW



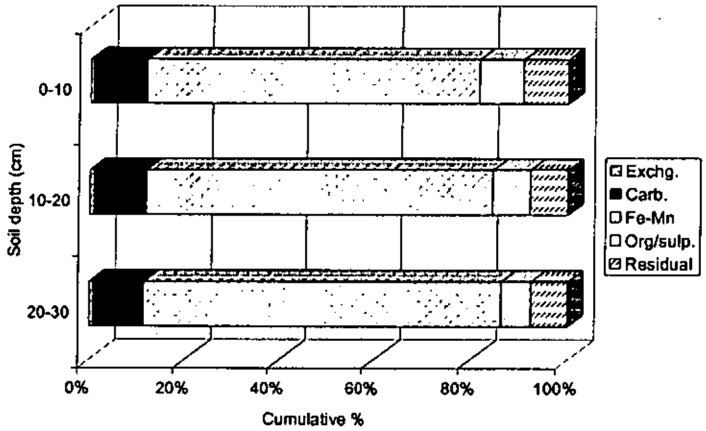
c) HC



d) LT



e) NG



f) SSP

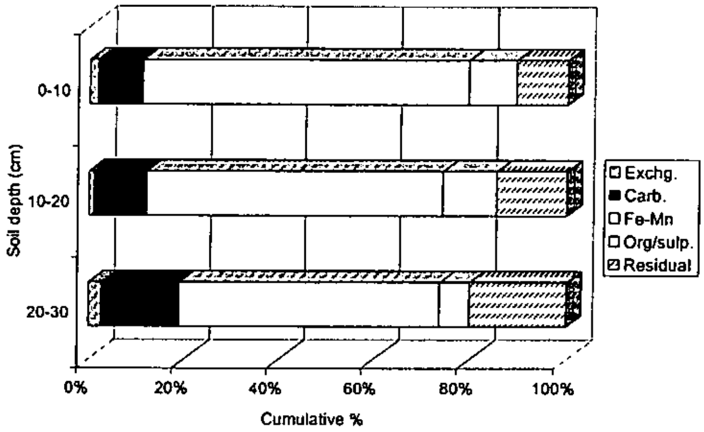


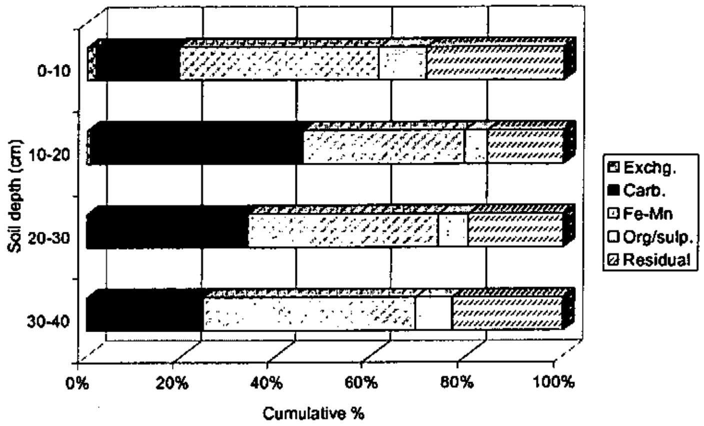
Figure 4-2 The chemical partitioning of Pb in urban soil profiles of Hong Kong

The distribution of soil Pb in the exchangeable and carbonate fractions at HC, LT and SSP showed a slight increase with increasing soil depth, while a similar trend was not observed at CRP, CSW, and HG. Also, the increasing percent distribution of exchangeable and carbonate-bound Pb with increasing depth at these locations may suggest leaching of the readily mobile Pb in soils. Despite of the differences in soil properties, the chemical partitioning of Pb in urban soil profiles showed that soil Pb was predominantly associated with the Fe-M oxide fraction regardless of soil depth and study sites. This is in agreement with previous studies (Harrison et al., 1981; Li et al., 2001a) that Fe-Mn oxides are important scavengers of trace metals in soils. Also, the percent distribution of soil Pb in the organic and residual fractions was relatively insignificant, generally representing for less than 20% of the total soil Pb. The exchangeable and carbonate Pb in the soil profiles was generally high (>20%), representing the readily soluble and potential bioavailable fraction. Although the percent distribution of exchangeable and carbonate Pb of the present study was high in comparison with that of urban soils (Li et al., 2001a), it was comparable to that of roadside soils (Harrison et al., 1981). At the contaminated areas, CSW, LT and NG, where the exchangeable and carbonate Pb accounted for 10-40% of the total soil Pb, as high as 60 mg/kg of Pb may be readily soluble and potentially bioavailable. Hence, further investigation on its environmental implications is strongly recommended.

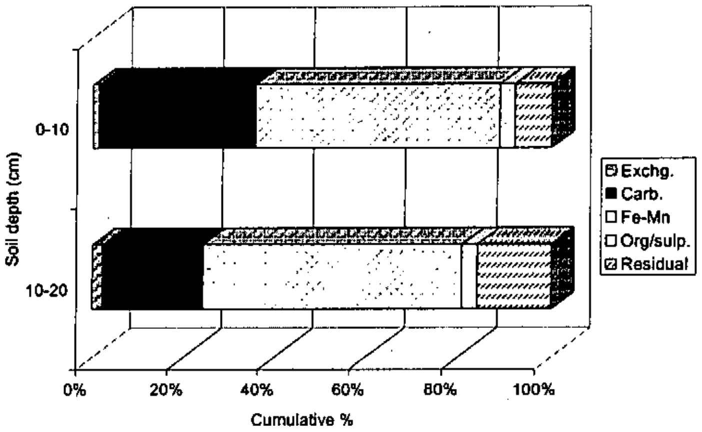
4.3.3 Zn

In general, the chemical partitioning of soil Zn showed that the exchangeable and organic-bound Zn of urban soil profiles generally accounted for relatively small fractions of total soil Zn, <5% and <10%, respectively (see Figure 4-3). At CRP (Figure 4-3a), soil Zn was strongly associated with the Fe-Mn oxide, carbonate and residual fractions. Similar to the distribution pattern of soil Cu, soil Zn in the carbonate fraction was least significant at the uppermost surface (0-10cm) and most significant at the layer immediately below (10-20cm) and gradually decreased with increasing soil depth. At CSW, soil Zn was dominantly bound in the Fe-Mn oxide, followed by the carbonate and residual fractions (Figure 4-3b). Compared to the upper soil surface (0-10cm), the percent distribution of Zn in the carbonate fraction at the subsurface (10-20cm) was reduced, and those in the Fe-Mn oxide and residual fractions increased. As shown in Figures 4-3c and 4-3d, the predominance of soil Zn at HC and LT was associated with the residual fraction, accounting for >60% of the total soil Zn, followed by the Fe-Mn oxide fraction. Alike the chemical fractionation of soil Cu, the percent distribution of soil Zn in the five fractions at HC alternated with increasing soil depth. In comparison, the association of Zn with the carbonate and Fe-Mn oxide fractions decreased with increasing depth. Soil Zn at NG (Figure 4-3e) was strongly associated with the Fe-Mn oxide fraction, followed by the residual and carbonate fractions. The chemical partitioning pattern also showed a gradual reduction in the distribution of soil Zn in the carbonate and Fe-Mn oxide fractions, accompanied by an increase in the residual Zn fraction, with increasing depth.

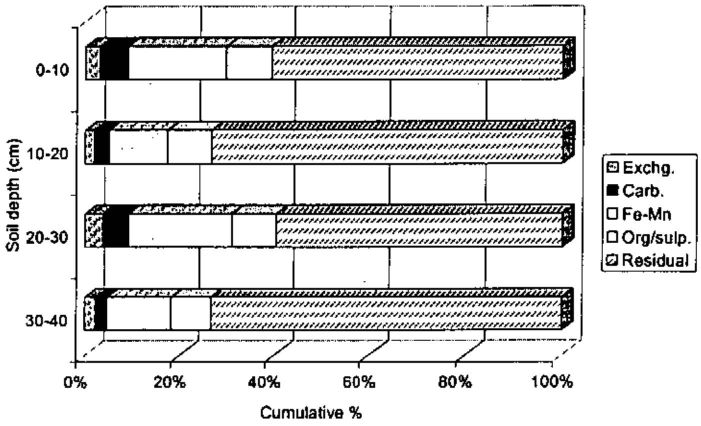
a) CRP



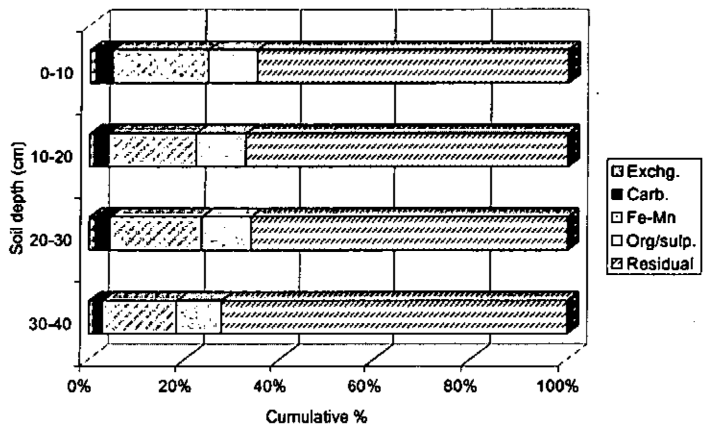
b) CSW



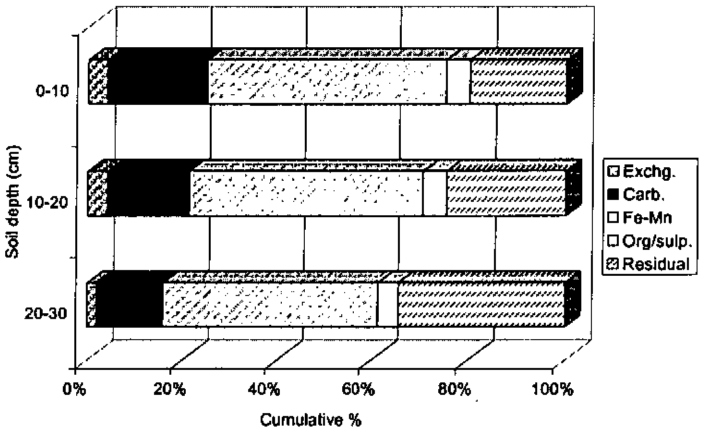
c) HC



d) LT



e) NG



f) SSP

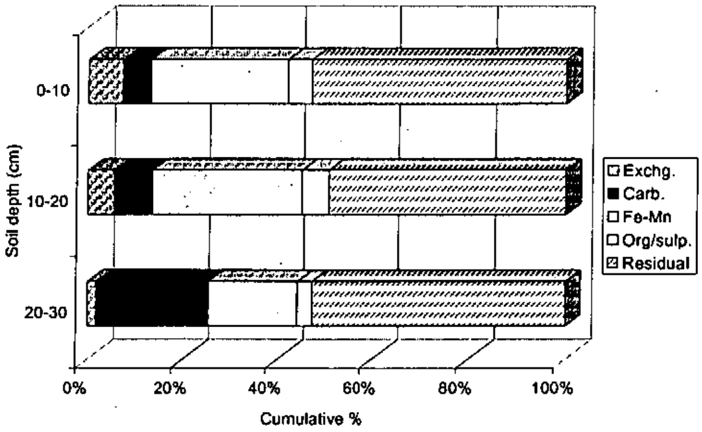


Figure 4-3 The chemical partitioning of Zn in urban soil profiles of Hong Kong

Soil Zn of urban soil profiles at SSP was strongly associated with the residual and Fe-Mn oxide fractions between 0-20cm and with the residual and carbonate fractions at the subsurface (20-30cm). The exchangeable Zn decreased with increasing depth, while soil Zn in the carbonate fraction increased significantly with increasing depth. This significant increase in the percent distribution of the carbonate fraction at the subsurface was also observed for soil Cu and Pb at SSP.

The chemical partitioning of soil Zn generally showed that soil Zn in the exchangeable and carbonate fractions decreased with increasing depth at the Zn-contaminated areas, e.g. CSW and NG, where soil Zn in the exchangeable and carbonate fractions accounted for ~20% of total soil Zn. In terms of absolute concentration, as much as 130 mg Zn/kg soil may become mobile and bioavailable. The uptake by plant and environmental health issues require some further detailed investigations.

4.4 Pb isotopic composition of urban soils

Lead isotopic composition of total soil Pb of the selected urban soil profiles was determined. The mean ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb ratios ranged from 17.556 - 19.115, 15.516 - 15.837, and 36.796 - 39.421, respectively (see Table 4-4). The ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb ratios showed limited variation throughout the depth of the soil profiles at LT, and SSP. The ratios at HC decreased slightly with increasing depth, while those at CRP, CSW, and NG showed an obvious increasing tendency with increasing depth. The ^{206}Pb/^{207}Pb ratios of the soil profiles ranged from 1.131 at the surface soil (0-10cm) of CSW to 1.212 at the surface layers (0-10 and 10-20cm) of HC. At the subsurface, the $^{206}Pb/^{207}Pb$ ratios varied between 1.160 at CSW and 1.209 at HC. The $^{206}Pb/^{207}Pb$ ratios of soil Pb remained relatively high ($^{206}Pb/^{207}Pb > 1.950$) at LT, HC and SSP. The $^{206}Pb/^{207}Pb$ ratios were constant throughout the profiles at LT and SSP, and the ratios declined slightly with increasing depth at HC. The $^{206}Pb/^{207}Pb$ ratios at CSW, NG, and CRP were comparatively low and showed an increasing tendency with increasing depth.

The measured $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ ratios of soil Pb at CRP, LT, HC and SSP were consistent with the general isotopic composition of the background values ($^{206}Pb/^{204}Pb>18.4$, $^{207}Pb/^{204}Pb>15.53$ and $^{208}Pb/^{204}Pb>38.4$) in southern China (Zhu, 1995). However, the $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ ratios detected at CSW and NG were lower than the background values, potentially suggesting the presence of non-natural Pb in the soils at these study sites.

Table 4-4 Mean (± standard deviation) Pb isotopic composition of urban soil profiles

Location	Depth (cm)	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	$^{206}Pb/^{207}Pb$
CRP	0-10	18.698±0.228	15.816±0.076	39.152±0.490	1.182±0.012
	10-20	18.790± 0.250	15.809±0.038	39.224±0.270	1.189±0.015
	20-30	18.864±0.227	15.837±0.048	39.381±0.294	1.191±0.013
	30-40	18.889±0.401	15.816±0.097	39.421±0.712	1.194±0.019
CSW	0-10	17.556±0.177	15.516±0.051	36.796±0.390	1.131±0.008
	10-20	18.175±0.261	15.662±0.052	37.832±0.395	1.160±0.013
LT	0-10	19.064±0.126	15.773±0.073	39.072±0.411	1.209±0.004
	10-20	19.081±0.110	15.798±0.053	39.158±0.352	1.208±0.004
	20-30	19.074±0.205	15.773±0.107	39.056±0.562	1.209±0.005
	30-40	19.115±0.080	15.813±0.034	39.306±0.210	1.209±0.005
HC	0-10	19.001±0.153	15.678±0.057	39.253±0.350	1.212±0.006
	10-20	18.999±0.154	15.674±0.058	39.188±0.409	1.212±0.006
	20-30	18.954±0.174	15.662±0.077	39.039±0.388	1.210±0.006
	30-40	18.872±0.065	15.641±0.059	38.864±0.320	1.207±0.001
NG	0-10	18.226±0.574	15.589±0.135	37.564±0.932	1.169±0.027
	10-20	18.446±0.652	15.656±0.086	38.056±0.823	1.178±0.036
	20-30	18.598±0.636	15.674±0.087	38.206±0.826	1.186±0.035
SSP	0-10	18.908±0.229	15.810±0.053	39.334±0.301	1.196±0.010
	10-20	18.883±0.132	15.798±0.035	39.271±0.277	1.195±0.006
	20-30	18.940±0.231	15.798±0.071	39.314±0.493	1.199±0.009

The $^{206}Pb/^{207}Pb$ ratio of soil Pb is probably the most frequently used ratio in detecting the influence of anthropogenic Pb. Usually, naturally derived Pb has a high $^{206}Pb/^{207}Pb$ ratio (>1.20). Whereas, the $^{206}Pb/^{207}Pb$ ratios of anthropogenic Pb are low, ranging from 0.90 to 1.20. Based on the high soil Pb concentrations and the low $^{206}Pb/^{207}Pb$ ratios at CSW and NG, it was evident that urban soil profiles at these study sites were enriched with anthropogenic Pb. Furthermore, the decreasing tendency of soil Pb concentrations and the increasing tendency of ^{206}Pb/^{207}Pb ratios with increasing depth at CSW and NG gave strong indication of anthropogenic Pb enrichment of the surface soils. Pb contamination of these study sites was likely attributed to the combustion of leaded gasoline via atmospheric deposition.

Interestingly, elevated soil Pb concentrations measured at LT did not appear to correlate with the measured Pb isotopic ratios. The ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb ratios of soil Pb were high and in agreement with those of naturally derived Pb given by Zhu (1995). Despite of the elevated soil Pb concentrations, the ^{206}Pb/^{207}Pb ratios also remained relatively high and constant throughout the soil profiles. The ratios were incomparable with the values at CSW and NG that was impacted by anthropogenic Pb (e.g. gasoline). These results may suggest that the soils could be naturally enriched with Pb or that the excessive anthropogenic Pb had come from some high ^{206}Pb/^{207}Pb ratio sources. It appeared that the former reason was more appropriate because of the relatively even distribution of soil Pb along the profiles and the absence of major Pb sources at LT.

In addition to the detection of anthropogenic Pb, Pb isotopic composition may also allow the identification and apportionment of anthropogenic Pb sources as well. The distribution of ^{206}Pb/^{207}Pb and ^{206}Pb/^{208}Pb ratios of the urban soil profiles is depicted in Figure 4-4. Significantly and positively linear correlation between the ^{206}Pb/^{207}Pb and ^{206}Pb/^{208}Pb ratios was found at CSW and NG (R^2 =

0.90 and 0.82, respectively). The $^{206}Pb/^{207}Pb$ and $^{206}Pb/^{208}Pb$ ratios at CRP and SSP were also positively correlated to a less extent (R^2 = 0.56 and 0.43, respectively), but zero correlation was found at HC and LT ($R^2 = 0.015$ and 0.005, respectively). The significantly linear relationships between $^{206}Pb/^{207}Pb$ and $^{206}Pb/^{208}Pb$ ratios of the soil profiles at CSW and NG gave strong evidence of binary mixing of anthropogenic Pb in the soil profiles. Furthermore, since these two study areas were immediately adjacent to major roadways in high-traffic zones, the Pb-contaminated soils at CSW and NG were likely enriched with gasoline-derived Pb. However, linearity of the correlation between $^{206}Pb/^{207}Pb$ and $^{206}Pb/^{208}Pb$ of soil Pb at the other study areas showed moderate and little significance. Therefore, the determination of the number of anthropogenic Pb sources at these study areas was not possible. Further study is recommended.

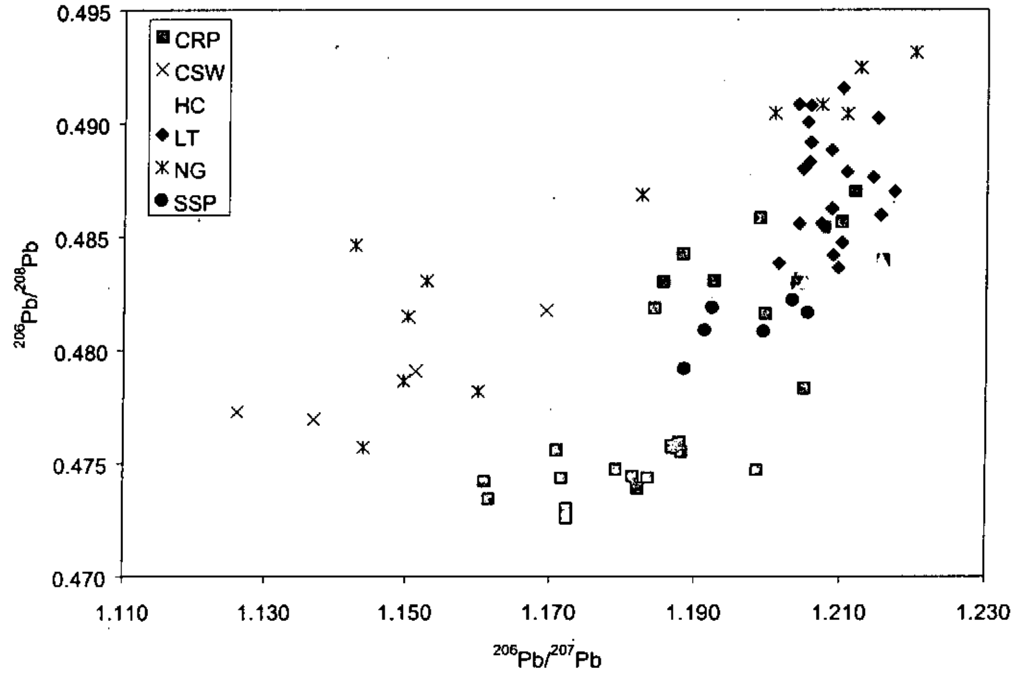


Figure 4-4 The $^{206}Pb/^{207}Pb$ and $^{206}Pb/^{208}Pb$ ratios of selected urban soil profiles of Hong Kong

In theory of geochemistry, it would be possible to compute the apportionment of each of the two Pb sources in the cases of binary mixing using Equations 4-1 and 4-2. Therefore, an attempt was made to roughly estimate the proportional contribution of Pb from leaded gasoline and industrial activities using the scenario at the roadway divider, CSW. Since information on Pb isotopic compositions of environmental samples and contaminant sources in HK is extremely rare, several assumptions must be made. To calculate the $^{206}Pb/^{207}Pb$ ratio of the excess lead, $^{206}Pb/^{207}Pb_{excess}$, it was conservatively assumed that the $^{206}Pb/^{207}Pb$ ratios of leaded gasoline and natural Pb in HK ($^{206}Pb/^{207}Pb_{gas}$ and $^{206}Pb/^{207}Pb_{base}$, respectively) were 1.12 and 1.20, respectively. The $^{206}Pb/^{207}Pb_{gas}$ ratio of 1.12 was assumed based on that the $^{206}Pb/^{207}Pb$ one of the anthropogenic Pb had to be lower than the measured $^{206}Pb/^{207}Pb$ (1.13) at CSW. The $^{206}Pb/^{207}Pb_{base}$ ratio of 1.20 was assumed that the isotopic composition of Pb in Hong Kong was similar to those in the Pearl River Delta. However, it should be noted that Pb isotopic signatures of leaded gasoline sold in HK might have changed from time to time depending on demand and supply of the market, as in Southwest Germany (Puchelt and Kramar, 1998). Baseline Pb concentration of uncontaminated soil, C_{Pbbase}, was assumed to be 9.09 mg/kg, based on the trace metal assessment of country park soils within the Kowloon District (Poon et al., 2000). Also, it was assumed that the $^{206}Pb/^{207}Pb$ of industrial Pb, $^{206}Pb/^{207}Pb_{indus}$, was 1.169. This value was extracted from Farmer and Eades (1998). Using these inputs (see Table 4-5), it was calculated that as much as 85% of excessive anthropogenic Pb of surface soils at CSW (0-10cm) could have originated from leaded gasoline. At the subsurface (10-20cm), Pb derived from leaded gasoline accounted for approximately 28% of excessive anthropogenic Pb in the soils. These estimates were able to support the idea that, even though the sale of leaded gasoline had gradually been phased out in HK since 1992, gasoline-derived Pb remained persistent in soils for relatively long time. From another point of view, the results also indicated that solubility and mobility of Pb in soils were limited under the current soil conditions.

Equation 4-1 - determination of the $^{206}Pb/^{207}Pb$ of excess Pb

$$^{206}Pb/^{207}Pb_{excess}=[(C_{Pbmeas}\times{}^{206}Pb/^{207}Pb_{meas})-(C_{Pbbase}\times{}^{206}Pb/^{207}Pb_{base})]/(C_{Pbmeas}-C_{Pbbase})$$

Equation 4-2- apportionment of anthropogenic sources of excess Pb using the two-source model

$$Pb_{gas}(\%) = [(^{206}Pb/^{207}Pb_{indus} - {}^{206}Pb/^{207}Pb_{excess})\times 100] / (^{206}Pb/^{207}Pb_{indus} - {}^{206}Pb/^{207}Pb_{gas})$$

Table 4-5 Inputs for the calculation of apportionment of Pb sources

		$^{206}Pb/^{207}Pb$	Pb conc. (mg/kg)
Pb_{gas}	Gasoline Pb	1.12	-
Pb_{base}	Baseline/background Pb	1.20	9.09
Pb_{indus}	Industrial Pb	1.169	-
Pb_{meas}	Road divider; 0-10cm	1.131	185
	Road divider; 10-20cm	1.160	85.3

4.5 Potential environmental implications

Trace metal contamination of urban soils represents a long-term environmental and health concern to the general population of HK, particularly young children.

In the urban environment of HK, urban parks and other leisure facilities are often built on marginal lands due to scarcity and prohibitive cost of land space. Since mixed land use is common in HK, soils in these urban parks may be subjected to various forms of degradation (Jim, 1998), including trace metal contamination as demonstrated in the present study. Although numerous trace metal assessments of urban soils have been conducted in HK, both understanding of the associated potential environmental and health implications and recognition of the need for sustainable soil management are limited.

By focusing on urban soils in the Kowloon district, where the population is densest in HK, the study could relate the findings to the majority of the general population. In the present study, it was found that surface soils in some urban parks were contaminated with trace metals, including Cu, Pb and Zn. Potential implications of heavy metal contaminated soils could be all-year-around. In the spring, rain acidity could enhance mobility and potential bioavailability of trace metals by lowering soil pH. Summer torrential rainfall may induce erosion of soils and thus urban runoff enriched with trace metal laden particles, which would eventually be discharged into the marine ecosystem. In the fall and winter, when events of rainfall is infrequent, resuspension of soil particles and dusts by strong wind may increase human exposure to trace metals via inhalation of metal-laden particles. Furthermore, children playing in these parks might also ingest the metal-laden soil particles via hand-to-mouth activity. Over time, an increase in trace metal intake through either of the pathways could potentially enhance susceptibility of individuals, especially the young and elderly, to various diseases.

Based on the chemical partitioning of trace metals in urban soil profiles, it was clearly shown that high Zn and Pb concentrations were in the readily soluble and mobile forms at the soil surface. The moderate solubility and potential leachability of the metals may eventually pose a long-term environmental concern over the possible contamination of the marine ecosystem. Like in many other cities, urban runoffs in HK do not receive any treatment prior to discharge into the marine water body (Marsalek, 1986). The discharge of the urban runoffs into the marine water body may lead to contamination of marine sediments and potential enhancement of bioassimilation of trace metals by benthic organisms and other marine life forms. In fact, trace metal contamination of marine biota and marine ecosystem was most serious in the Victoria Harbour (Morton, 1989; Blackmore, 1998). These metals, if consumed by benthic organisms and others higher in the trophic levels, could potentially enter the food chains via bioaccumulation and biomagnification, as in the case at Manoa, U.S.A. (Sutherland et al., 2000).

CHAPTER FIVE RESULTS AND DISCUSSION - AGRICULTURAL SOILS OF THE PEARL RIVER DELTA

5.1 Soil pH

The average soil pH of the selected crop, paddy and natural soils were 5.88 (4.06-7.22), 5.76 (5.69-5.90), and 4.56 (4.07-5.18), respectively. The results indicated that both of the agricultural and natural soils in the PRD were usually slightly acidic in nature, which was in agreement with the common characteristics of soils in South China.

5.2 Trace metal concentrations of agricultural soils

Mean, median and range of trace metal concentrations of the crop, paddy and natural soils are presented in Table 5-1. The results showed that some agricultural and natural soils were grossly contaminated with trace metals, including Cd, Cr, Pb and Zn. In accordance with the Environmental Quality Standard for Soils (National Environmental Protection Agency of China, 1995), these soils were deemed unsuitable for agricultural purposes. Furthermore, mean Cd and Pb concentrations of the crop, paddy and natural soils were elevated compared to the corresponding Class A background values, implying Cd and Pb enrichment of these soils. The mean Co, Cr, Cu, Ni and Zn concentrations of the crop, paddy and natural soils were generally below the threshold values, and soil Mo concentrations were generally undetected.

Table 5-1 Mean, median, and range of trace metal concentrations in crop, paddy and natural soils of the PRD

Soil Type	(mg/kg)	Cd	Co	Cr	Cu	Mo	Ni	Pb	V	Zn
All soils	Mean	0.48	7.73	61.4	24.8	n.d.	18.4	37.8	36.3	68.7
(n=78)	Median	0.48	7.31	54.3	17.6	-	16.2	32.8	33.7	66.0
	Range	n.d.[a] -1.76	n.d.-39.9	5.66-317	1.41-189	-	1.45-78.6	7.74-180	3.26-114	11.1-284
Crop soils	Mean	0.56	8.87	69.8	32.2	n.d.	20.6	39.3	38.9	83.0
(n=39)	Median	0.62	10.0	67.6	25.0	-	18.9	32.8	38.6	82.1
	Range	n.d.-1.47	n.d.-16.9	5.66-317	4.10-189	-	1.45-62.5	10.1-180	3.26-76.0	11.1-284
Paddy soils	Mean	0.33	6.68	56.3	21.1	n.d.	16.9	36.9	36.2	61.5
(n=19)	Median	0.19	4.34	52.5	13.9	-	11.6	36.4	30.3	51.7
	Range	n.d.-0.90	0.74-16.9	19.1-99.5	3.02-50.5	-	4.54-36.1	15.9-81.3	12.5-71.8	18.5-107
Natural soils	Mean	0.47	6.50	49.8	14.0	n.d.	15.4	35.8	31.4	47.7
(n=20)	Median	0.34	1.64	42.1	7.27	-	7.53	31.5	22.6	28.7
	Range	n.d.-1.76	0.22-39.9	13.3-144	1.41-44.0	-	3.55-78.6	7.74-135	4.91-114	14.8-110
Chinese Soil Standard[b]	Class A	≤ 0.20	N/A[c]	≤90	≤ 35	N/A	≤40	≤ 35	N/A	≤ 100

a. Not detected.

b. National Environmental Protection Agency of China, 1995

c. Not available.

As depicted in Figure 5-1, mean concentrations of all of the trace metals, except Cd, descended in the order: crop soils > paddy soils > natural soils. Mean Cd concentrations showed the order: crop soils > natural soils > paddy soils. The results possibly suggested that trace metal inputs to the crop soils were higher than those of the paddy and natural soils, which could be associated with soil sample distribution and/or a high usage rate of agrochemicals. In recent years, rapid industrial and urban development in China has imposed paramount pressure on the environment. In the PRD, being one of the most rapidly developing regions in South China, these human activities have caused significant water and air pollution. The paddy and natural soils were located farther away from major city centres. On the other hand, the crop soils were situated close to major cities and industrial sites. Therefore, the potential influences of urban and industrial activities on the crop soils would likely be more noticeable than those on the paddy and natural soils. Also, in order to meet the high production rate, soils are intensively cultivated, resulting in depletion of soil fertility. To compensate nutrient loss, chemical fertilizers and other soil amendments are commonly used. Indeed, trace metal contamination of agricultural soils in China has been associated with the continuous and heavy applications of agrochemicals (Chen et al., 1999).

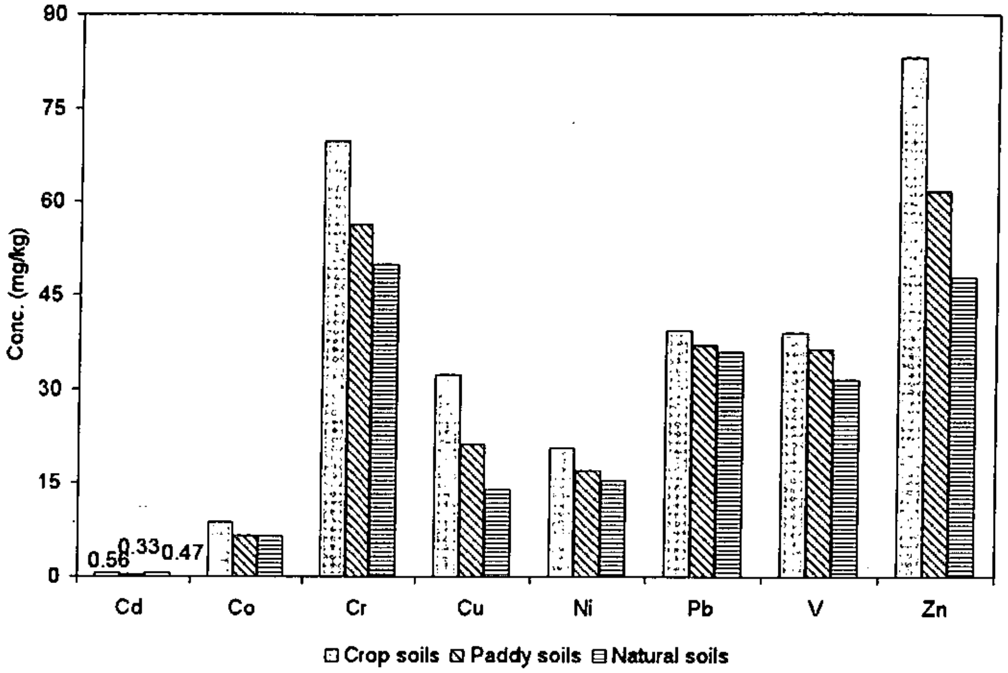


Figure 5-1 Mean trace metal concentrations of crop, paddy and natural soils of the PRD

5.3 Chemical fractionation of trace metals of selected agricultural and natural soils

Figures 5-2 to 5-8 display the chemical partitioning of trace metals, including Co, Cr, Cu, Ni, Pb, V, and Zn, of the selected soils. Although some variability was observed among the individual samples, the averaged partitioning distribution of each of the soil groups was used to identify possible distinctions among them.

Figure 5-2 showed that Co in the crop and natural soils was strongly associated with Fe-Mn oxide and residual fractions. In the paddy soils, Co was associated dominantly with the residual fraction and weakly with the Fe-Mn oxide fraction. Soil Cr in the crop, paddy and natural soils was predominantly associated with the residual fraction, followed by the organic and Fe-Mn oxide fractions (Figure 5-3). It appeared that the percent distribution of Cr in the four non-residual fractions was greatest in the crop soils and smallest in the natural soils. A significant fraction of Cu in the crop and paddy soils was bound in the organic/sulphide phase, followed by the residual phase (Figure 5-4). Cu in the natural soils was mainly associated with the residual fraction and secondarily with the organic/sulphide fraction. In general, the exchangeable and carbonate-bound Cu generally accounted <10% of the total Cu, and the percent of Cu in the residual fraction decreased in the order: natural soils > paddy soils > crop soils. The chemical partitioning of Ni showed that a significant fraction of Ni (>60%) was in the residual form, followed by the organic and Fe-Mn oxide fractions (Figure 5-5). Similar to some of the trace metals, the percent distribution of the four non-residual fractions increased in the order: natural, paddy and crop soils. Pb in the crop soils was largely associated with Fe-Mn oxides, followed by the organic/sulphide and residual fractions (Figure 5-6). In the paddy soils, a large fraction of Pb was also bound in the Fe-Mn oxide phase, and the second most important fraction was the residual phase. The two most abundant fractions for Pb in the natural soils were the residual and Fe-Mn oxide fractions. Pb in the carbonate fraction accounted for ~20% of the total soil Pb. In general, the percent of exchangeable Pb in the soils was very low. As shown in Figure 5-7, the chemical partitioning of V in the crop, paddy and natural soils was relatively similar. Soil V was predominantly associated with the residual fraction (>70%) and secondarily with the Fe-Mn oxide fraction (~20%). In all of the three different soil groups, Zn was predominantly associated with the residual fraction and secondarily with the Fe and Mn oxides (Figure 5-8). The percent distribution of Zn in the exchangeable, carbonate and Fe-Mn oxide fractions in the paddy soils was less significant than those of the crop and natural soils.

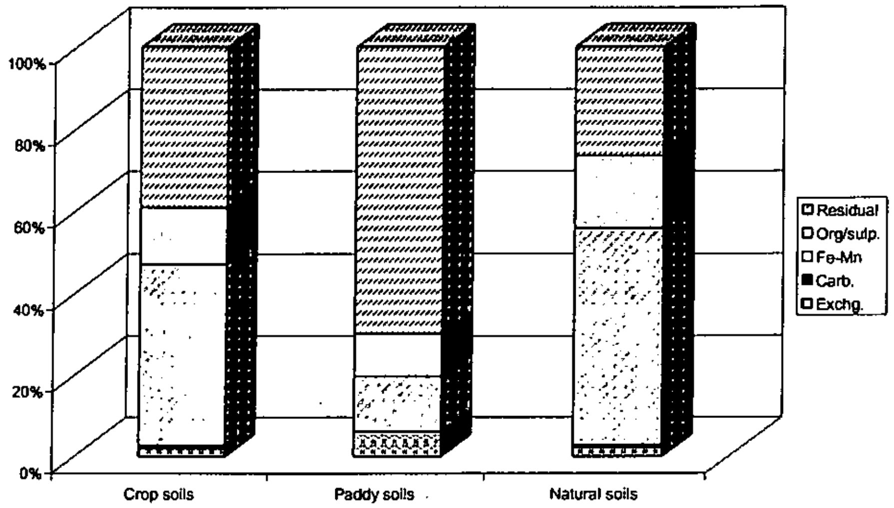


Figure 5-2 Chemical partitioning of Co in selected soils

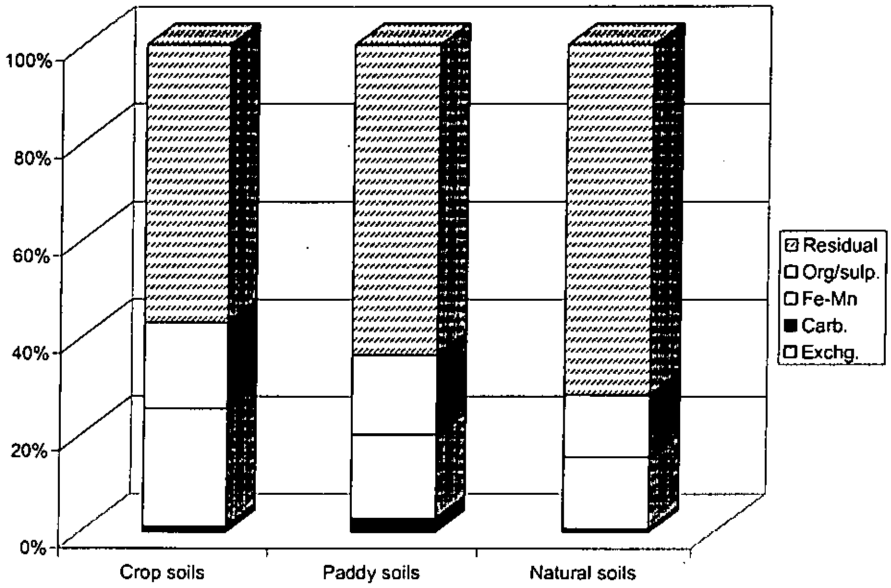


Figure 5-3 Chemical partitioning of Cr in selected soils

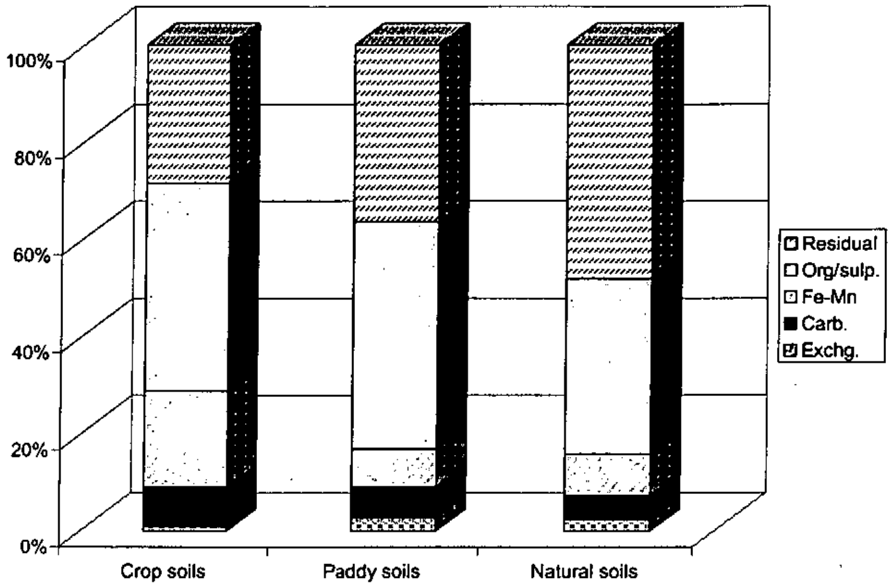


Figure 5-4 Chemical partitioning of Cu in selected soils

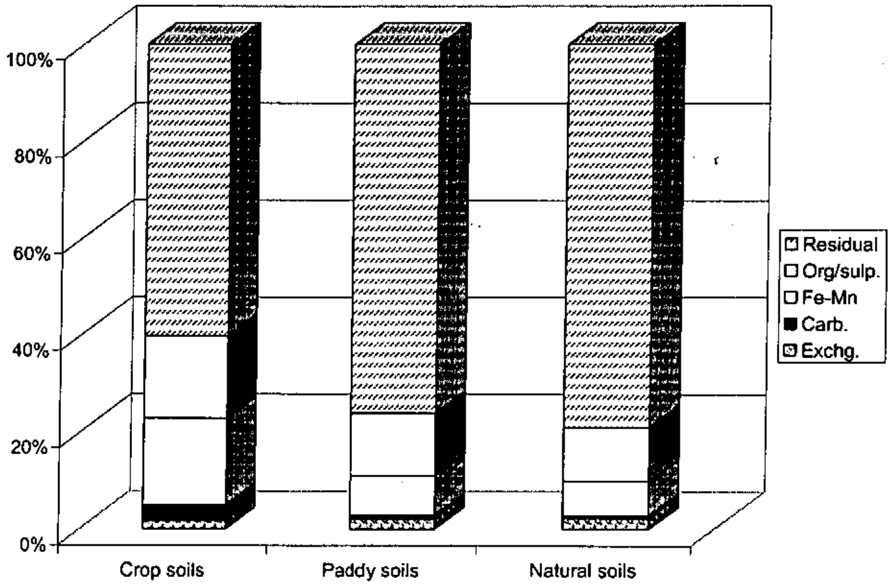


Figure 5-5 Chemical partitioning of Ni in selected soils

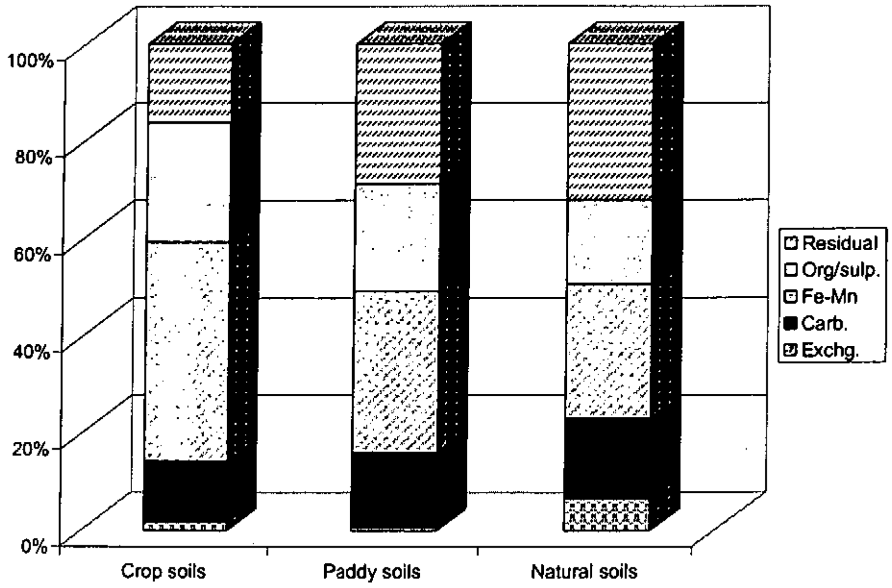


Figure 5-6 Chemical partitioning of Pb in selected soils

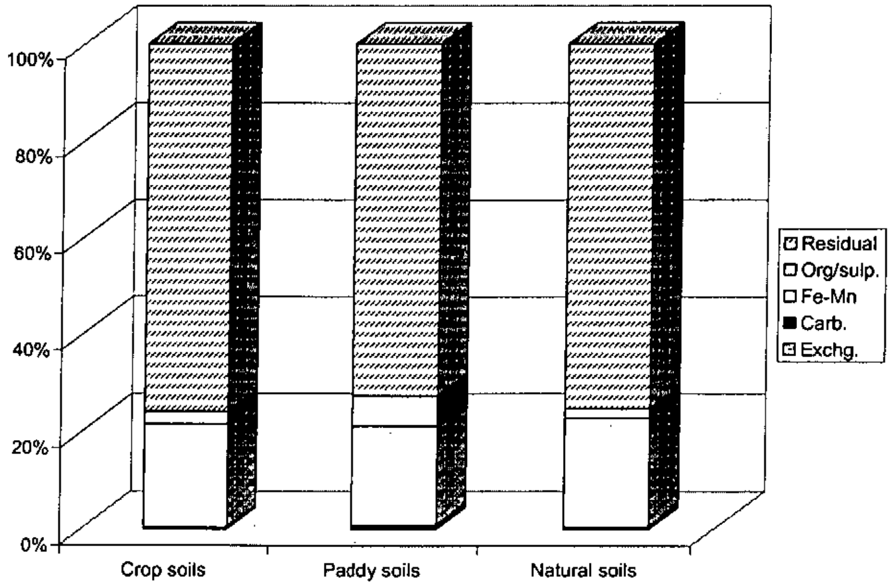


Figure 5-7 Chemical partitioning of V in selected soils

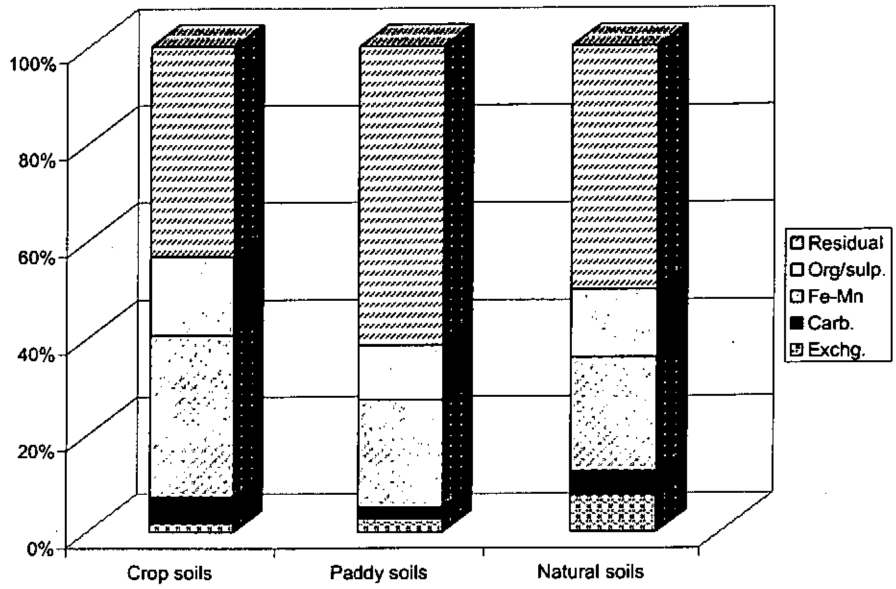


Figure 5-8 Chemical partitioning of Zn in selected soils

To sufficiently understand the possible influences and associations of trace elements in these soils, the chemical partitioning of some major elements of the crop, paddy and natural soils are provided. Figures 5-9 to 5-11 display the chemical partitioning patterns of the major elements, Ca, Fe and Mn. The chemical partitioning of Ca in the crop, paddy and natural soils show that Ca was largely distributed in the exchangeable fraction (>60%). The association of Ca with the carbonate and Fe-Mn oxide fractions was more significant in the crop soils than in the paddy and natural soils (see Figure 5-9). The chemical partitioning of Fe in the crop, paddy, and natural soils showed that Fe in the soils was mainly in the residual fraction (see Figure 5-10). The association of Fe with the Fe-Mn oxide fraction was more significant in the crop and paddy soils than in the natural soils. Mn in the crop and natural soils was dominantly associated with the Fe-Mn oxide fraction (see Figure 5- 11). On the other hand, Mn in the paddy soils was strongly dominated in the residual fraction, and the association of Mn with the Fe-Mn oxides was evidently weaker than that in the crop and natural soils.

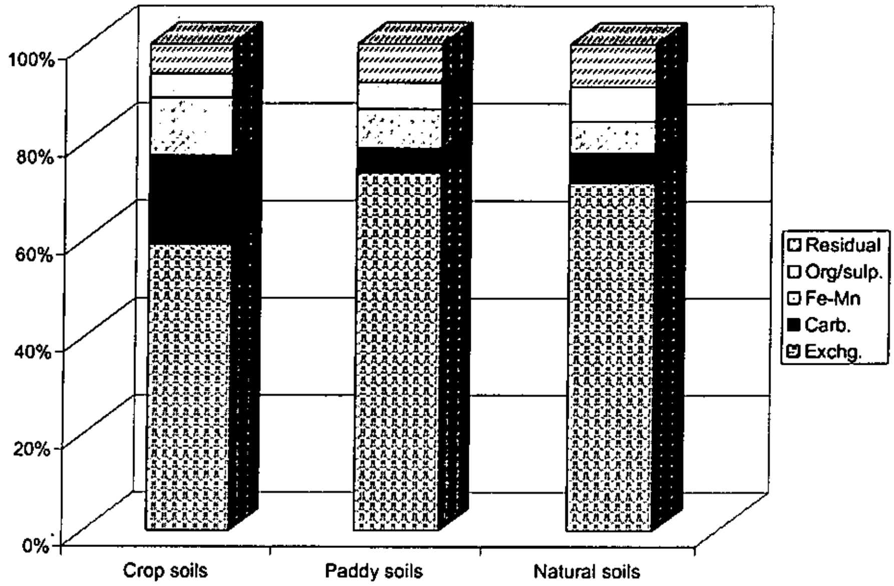


Figure 5-9 Chemical partitioning of Ca in selected soils

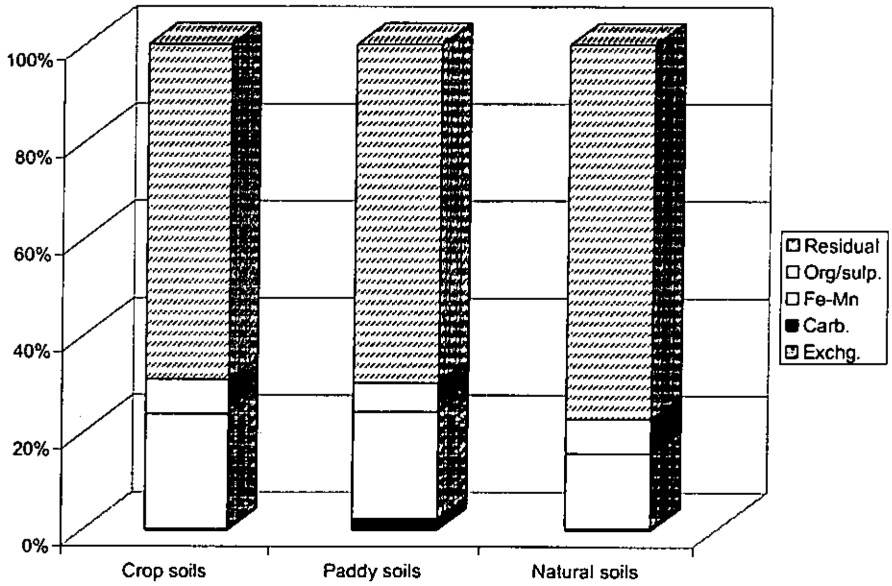


Figure 5-10 Chemical partitioning of Fe in selected soils

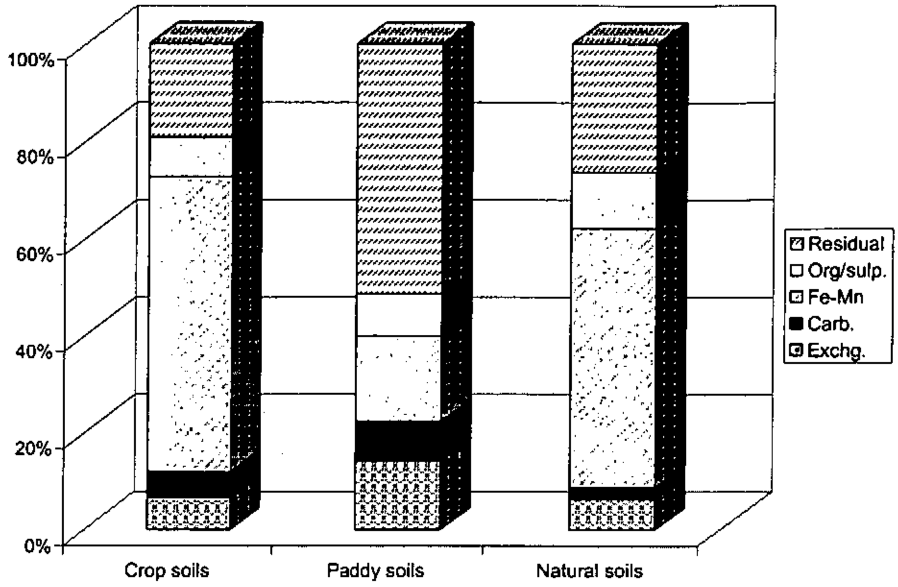


Figure 5-11 Chemical partitioning of Mn in selected soils

The chemical partitioning of trace and major metals gave some insight to the potential mobility and bioavailability of trace metals and influences of different cultivation methods. The differences in the chemical distribution of Co between the paddy soils and the crop and natural soils were likely attributed to differences in cultivation methods. In general, soil Co in the crop and natural soils was predominantly associated with the Fe-Mn oxides. However, flooding of the paddy soils caused dissolution of Mn oxides and soil Co and subsequently leaching of Co. This was reflected from a significant percent reduction of soil Co in the Fe-Mn oxide fraction and an increase in the percent distribution of Co in exchangeable and residual fractions in the paddy soils as compared to that in the crop and natural soils. The dissolution of Mn oxides was also evident in the chemical partitioning of soil Mn, where soil Mn in the Fe-Mn oxide fraction was greatly reduced. Soil Cr in the exchangeable and carbonate fractions presented <3% of the total soil Cr. Therefore, mobility and potential bioavailability of soil Cr were limited. The relatively high percent distribution of soil Cr in the four non-residual fractions in the crop soils may reflect a high input of anthropogenic Cr in the crop soils. The strong association between soil Cu and the organic fraction was in agreement with the general finding that Cu forms the most stable complexes with organic matters (Adriano, 1986). The readily soluble and potentially bioavailable fractions generally accounted for <10% of total soil Cu. These results indicated that a significant fraction of soil Cu was relatively stable in the soils. Similar to that of soil Cr, the chemical partitioning of soil Ni showed that mobility and potential bioavailability of Ni were limited. Furthermore, the comparatively high percent of soil Ni in the four non-residual fractions may be associated with a high input of Ni in the crop soils. The exchangeable Pb in the soils were generally low, accounting for <3 % of total soil Pb. Collectively, Pb in the exchangeable and carbonate fractions accounted for ~20% of total soil Pb, representing the readily soluble and potentially bioavailable Pb fraction. The relatively large fraction of soil Pb in the exchangeable and carbonate fractions in the paddy soils could be partially attributed to the acidic property of the soils. In comparison, the proportion of Pb in the Fe-Mn oxide fraction of the crop soils was noticeably larger than that of the paddy and natural soils. Furthermore, the residual Pb in the crop soils was less significant than those in the paddy and natural soils. These differences indicated that a greater fraction of Pb in the crop soils might be attributed to anthropogenic Pb sources. The chemical partitioning of soil V was very similar among the crop, paddy and natural soils. Soil V in the exchangeable and carbonate fraction represented a very minor percent fraction of total soil V, thus a limited concern for potential bioavailability. Soil Zn in the exchangeable and carbonate/specifically adsorbed fractions accounted for <10% of total soil Zn. The less important association of Zn with the exchangeable, carbonate, and Mn-Fe oxide fractions in the paddy soils may indicate the influence of flooding in the paddy soils, as Zn migrates downward readily in soil profiles (Kabata-Pendias and Pendias, 1992).

In general, trace metals were strongly associated with the Fe-Mn oxide, organic and residual fractions. The high proportion of trace metals in non-residual fractions of the crop soils may suggest greater contribution of anthropogenic metals. Mobility and potential bioavailability of some trace metals were also generally high in the crop soils. The relatively large exchangeable and carbonate fractions of Pb and Zn in the natural soils could be attributed to low soil pH. The percent distribution of trace metals in the Fe-Mn oxide fraction was generally less significant in the paddy soils than in the crop soils. As discussed previously, this was likely attributed to the reduction of Mn oxides induced by flooding of the paddy soils.

5.4 Identification of contaminant sources

Isotopic composition of both total Pb and Pb in the five chemical fractions of the selected crop, paddy and natural soils were determined. The isotopic ratios of the total soil Pb and fractionated Pb are presented in Tables 5-2 and 5-3, respectively. (In Table 5-3, Exchg: exchangeable fraction; Carb: carbonate/specifically adsorbed fraction; Fe-Mn: Fe-Mn oxide fraction; Org/sulp: organic/sulphide fraction; residual: residual fraction.) The average $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$ ratios of total soil Pb were 18.275±0.014, 15.328±0.086, and 37.753±0.522, respectively.

Table 5-2 Isotopic composition of total soil Pb of the selected soils in the PRD

Soil ID	$^{206}Pb/^{207}Pb$	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$
C4[a]	1.202	18.494	15.385	38.134
C12	1.182	18.021	15.244	37.238
C19	1.196	18.433	15.408	37.948
C21	1.178	17.900	15.198	36.918
C62	1.200	18.347	15.291	37.737
C64	1.173	17.928	15.291	37.502
P72	1.204	18.522	15.385	38.491
P76	1.214	18.764	15.456	38.380
N22	1.173	17.887	15.244	37.233
N23	1.199	18.451	15.385	37.949

[a] Prefixes "C", "P", and "N" of the soil ID correspond to the crop, paddy, and natural soils, respectively.

Table 5-3 Pb isotopic composition of the five chemical fractions of selected soils

Soil ID	Fraction	^{206}Pb/^{207}Pb	^{206}Pb/^{204}Pb	^{207}Pb/^{204}Pb	^{208}Pb/^{204}Pb
C4	Exchg	1.192	18.537	15.552	38.527
	Carb	1.194	18.828	15.773	39.640
	Fe-Mn	1.190	18.678	15.699	38.779
	Org/sulp	1.192	18.828	15.798	39.371
	Residual	1.196	18.740	15.674	38.806
C12	Exchg	1.155	17.747	15.361	37.358
	Carb	1.175	18.499	15.748	39.080
	Fe-Mn	1.169	18.353	15.699	38.383
	Org/sulp	1.170	18.361	15.699	38.410
	Residual	1.185	18.629	15.723	38.813
C19	Exchg	1.163	18.907	16.260	39.514
	Carb	1.195	18.419	15.408	38.754
	Fe-Mn	1.180	18.727	15.873	39.408
	Org/sulp	1.183	18.714	15.823	39.332
	Residual	1.198	18.923	15.798	39.763
C21	Exchg	1.168	18.051	15.456	37.779
	Carb	1.169	18.350	15.699	38.765
	Fe-Mn	1.164	17.742	15.244	37.685
	Org/sulp	1.168	18.228	15.601	37.995
	Residual	1.182	18.642	15.773	38.937
C62	Exchg	1.191	18.329	15.385	37.925
	Carb	1.192	18.719	15.699	39.355
	Fe-Mn	1.185	18.756	15.823	39.279
	Org/sulp	1.188	18.791	15.823	39.358
	Residual	1.198	18.888	15.773	39.336
C64	Exchg	1.160	20.753	17.889	43.907
	Carb	1.164	18.449	15.848	39.325
	Fe-Mn	1.162	18.362	15.798	38.967
	Org/sulp	1.162	18.380	15.823	39.242
	Residual	1.193	18.997	15.924	41.132
P72	Exchg	1.192	18.659	15.650	38.751
	Carb	1.191	18.723	15.723	39.758
	Fe-Mn	1.187	18.716	15.773	39.636
	Org/sulp	1.188	18.824	15.848	39.965
	Residual	1.191	18.815	15.798	39.877
P76	Exchg	1.169	18.270	15.625	38.231
	Carb	1.165	18.202	15.625	38.703
	Fe-Mn	1.160	18.209	15.699	38.818
	Org/sulp	1.163	18.313	15.748	39.006
	Residual	1.201	19.086	15.898	40.496
N22	Exchg	1.166	17.940	15.385	37.483
	Carb	1.171	18.504	15.798	39.545
	Fe-Mn	1.165	18.484	15.873	39.410
	Org/sulp	1.166	18.534	15.898	39.423
	Residual	1.168	18.423	15.773	39.054
N23	Exchg	1.196	18.400	15.385	38.008
	Carb	1.198	18.898	15.773	39.544
	Fe-Mn	1.189	18.718	15.748	39.310
	Org/sulp	1.191	18.812	15.798	39.406
	Residual	1.203	19.098	15.873	40.132

The PRD is situated on the Cathaysian tectonic block, and its outcropping basement rocks are mainly Mesozoic granites and some Mesozoic-Cenozoic volcanics. The Pb isotopic composition of these geological materials can be used to represent the natural background (Table 5-4; Zhu, 1995). In the study area, industrial Pb from the Fankou Pb-Zn deposit and automobile exhaust were considered as the two main sources of anthropogenic Pb (Zhu et al, 2001). The Pb isotopic composition of these anthropogenic Pb sources has been analyzed by Zhu (1995 & 1998) and Zhu et al. (1989& 2001). In comparison with the Pb isotopic composition of the natural Pb sources, the average ratios of the present study were generally low.

To effectively identify influence of anthropogenic Pb in the soils, the $^{206}Pb/^{207}Pb$ ratios of the total soil Pb were examined. The $^{206}Pb/^{207}Pb$ ratios of the agricultural and natural soils ranged between 1.173 and 1.214 (Table 5-2). As shown in Table 5-4, the $^{206}Pb/^{207}Pb$ ratios of galena samples (PbS) from the Fankou Pb-Zn deposit (1.1716) and of automobile exhausts (1.1604) are evidently lower than those of the local background values, while the Pb isotopic composition of some background environmental samples of South China is relatively high. The $^{206}Pb/^{207}Pb$ ratios of some soil samples (C4, C19, P72, P76, and N23) were comparable with the background values. However, some other soil samples, such as C21, C64, and N22, showed low $^{206}Pb/^{207}Pb$ ratios, suggesting that the soils contained Pb from anthropogenic sources. Furthermore, the $^{206}Pb/^{207}Pb$ ratios of the paddy soils were generally higher than those of the crop and natural soils, which may suggest relatively significant anthropogenic Pb enrichment of the crop and natural soils.

Table 5-4 Pb isotopic composition of natural background and pollution sources in the PRD

	$^{206}Pb/^{207}Pb$	$^{208}Pb/^{207}Pb$	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$
Granite in the eastern Cathaysia[a]	1.1834	2.4680	18.546	15.672	38.679
Granite in Pearl River Delta[a]	1.1842	2.4824	18.574	15.685	38.937
Volcanic rocks in Foshan[b]	1.1993	2.4965	18.611	15.518	38.741
Uncontaminated soils[c]	1.1952	2.4815	18.620	15.579	38.660
Fankou Pb-Zn deposit[a]	1.1716	2.4725	18.382	15.690	38.793
Automobile exhausts in Pearl River Delta[c]	1.1604	2.4228	18.097	15.577	37.740

a. Zhu, 1998
b. Zhu et al., 1989
c. Zhu et al., 2001

Figure 5-12 depicts the distribution of the $^{206}Pb/^{207}Pb$ and $^{206}Pb/^{208}Pb$ ratios of the soil samples of the present study and some environmental samples of the PRD previously determined by Zhu et al. (2001). The correlation between the $^{206}Pb/^{207}Pb$ and $^{206}Pb/^{208}Pb$ ratios of the soil samples ($R^2 = 0.49$) was positively linear. If the $^{206}Pb/^{207}Pb$ and $^{206}Pb/^{208}Pb$ ratios of P72 (circled in Figure 5-12) were removed, linearity of the correlation ($R^2 = 0.75$) was enhanced. In both cases, the distribution of the $^{206}Pb/^{207}Pb$ and $^{206}Pb/^{208}Pb$ ratios of the soil samples appeared to be significantly correlated with those of the car exhaust.

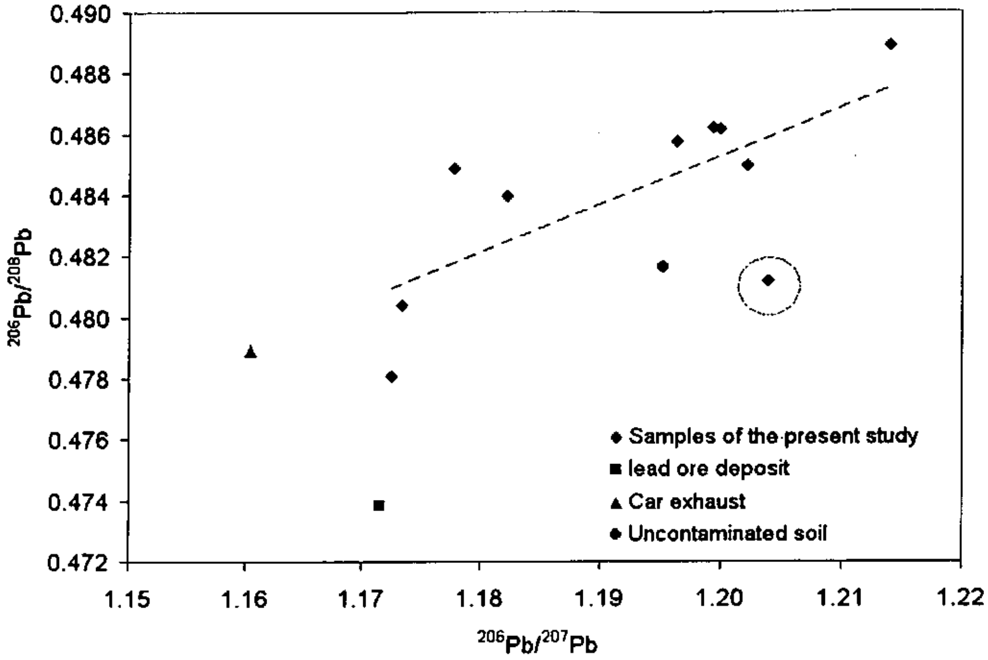


Figure 5-12 $^{206}Pb/^{207}Pb$ vs. $^{206}Pb/^{208}Pb$ of total soil Pb of agricultural and natural soils of the PRD (Zhu et al., 2001)

The distribution of the $^{206}Pb/^{207}Pb$ ratios of the five chemical fractions of the selected agricultural and natural soils is depicted in Figure 5-13. The distribution of $^{206}Pb/^{207}Pb$ ratios showed that, of the majority of the soil samples, the $^{206}Pb/^{207}Pb$ ratios in the residual fraction ranged between 1.18 and 1.20, consistent with the natural background values. Moreover, the $^{206}Pb/^{207}Pb$ ratios of the four non-residual fractions were generally lower than those of the residual fraction. This phenomenon indicated that these soils were enriched by anthropogenic Pb, and confirmed that anthropogenic Pb, having lower $^{206}Pb/^{207}Pb$ ratios compared to natural Pb, often disguised itself in the readily and moderately mobile forms. Although the $^{206}Pb/^{207}Pb$ ratios of the five chemical fractions varied among the soil samples, it was obvious that the $^{206}Pb/^{207}Pb$ ratios of the exchangeable, Fe-Mn oxide and organic fractions were generally lower than those of the carbonate and residual fractions. The noticeably low $^{206}Pb/^{207}Pb$ ratios of the exchangeable, Fe-Mn oxide and organic/sulphide fractions gave strong evidence that the soils were enriched with anthropogenic Pb to some degree, and that anthropogenic Pb tended to reside in the exchangeable, Fe-Mn oxides and organic forms in the soils. The high $^{206}Pb/^{207}Pb$ ratios of the carbonate/specifically adsorbed fraction indicated that the carbonate fraction played a less significant role in the fixation of anthropogenic Pb in the soils.

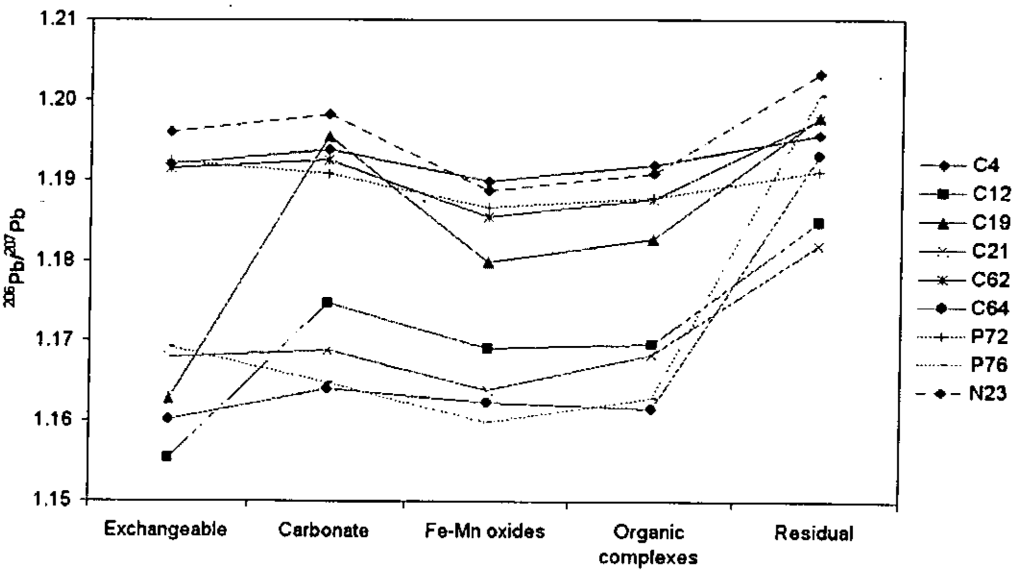


Figure 5-13 $^{206}Pb/^{207}Pb$ of the five fractions of the selected agricultural and natural soils in the PRD

In the study of Pb accumulation in sediment profiles of the Pearl River Estuary, the $^{206}Pb/^{207}Pb$ ratios in the five fractions showed an increasing order: exchangeable < Fe-Mn oxides < organic/sulphide < carbonate < residual fractions (Li et al., 2001b). This result is consistent with the present study that accumulation of anthropogenic Pb in soils was also found in the Fe-Mn oxides and organic fractions. The results are also consistent with the chemical partitioning of Pb in soils, where strong associations of soil Pb with Fe-Mn oxides and organic/sulphide were observed.

In Figure 5-13, two groups of soils could be distinguished based on the $^{206}Pb/^{207}Pb$ distribution patterns. One group of the soils (C4, C19, C62, P72 & N23) tended to have higher $^{206}Pb/^{207}Pb$ ratios of the four non-residual fractions (>1.18), while the other group (C12, C21, C64 & P76) generally showed lower $^{206}Pb/^{207}Pb$ ratios (<1.18). This phenomenon may suggest that these soils were affected by different Pb sources. Based on the field investigation, the soils at C12 and C21 were irrigated with wastewater and close to nearby industrial activities. A common Pb source was reflected by the similar distribution of $^{206}Pb/^{207}Pb$ ratios in the five chemical fractions between these two soils. For C64 and P76, the uniformed distribution pattern of $^{206}Pb/^{207}Pb$ ratios of the five fractions may also indicate a common origin of anthropogenic Pb. Both C64 and P76 were situated close to major roads. The ratios of the four non-residual fractions (~1.16) of the soils were comparable to that of the $^{206}Pb/^{207}Pb$ ratio of automobile Pb (1.1604) in the region and the acid extracted Pb in surface soils beside an expressway (Zhu et al., 2001). Therefore, anthropogenic Pb at these two sites likely came from vehicular exhaust.

5.5 Elemental association of trace and major metals

The Pearson correlation coefficient matrixes between some major elements and trace metals of the crop, paddy and natural soils are presented in Tables 5-

5 to 5-7, respectively. In the crop soils, Pb was strongly and moderately associated with Cd, Co and Cr. However, in the paddy and natural soils, Pb showed no correlation with the other elements. In general, all major elements and trace metals, except for Pb, were significantly correlated with each other in all three types of soils. The weak relationships of Pb with the other elements suggested its unique geochemical properties and/or sources in the soil environment of the PRD.

Table 5-5 Pearson correlation coefficient matrix for all crop soils (n=39) in the PRD

	Ca	Cd	Co	Cr	Cu	Fe	Mg	Mn	Ni	Pb	V
Cd	0.668**	1.000									
Co	0.671**	0.866**	1.000								
Cr	0.725**	0.635**	0.646**	1.000							
Cu	0.787**	0.590**	0.635**	0.942**	1.000						
Fe	0.514**	0.783**	0.826**	0.600**	0.485**	1.000					
Mg	0.711**	0.852**	0.947**	0.685**	0.647**	0.855**	1.000				
Mn	0.695**	0.781**	0.877**	0.583**	0.580**	0.776**	0.924**	1.000			
Ni	0.793**	0.806**	0.873**	0.860**	0.856**	0.797**	0.915**	0.844**	1.000		
Pb	0.304	0.432**	0.359*	0.319*	0.293	0.247	0.252	0.097	0.255	1.000	
V	0.550**	0.744**	0.832**	0.576**	0.494**	0.914**	0.891**	0.834**	0.803**	0.166	1.000
Zn	0.756**	0.670**	0.701**	0.827**	0.883**	0.654**	0.695**	0.656**	0.886**	0.277	0.578**

**. Correlation is significant at the 0.01 level (2-tailed)

*. Correlation is significant at the 0.05 level (2-tailed)

Table 5-6 Pearson correlation coefficient matrix for all paddy soils (n=19) in the PRD

	Ca	Cd	Co	Cr	Cu	Fe	Mg	Mn	Ni	Pb	V
Cd	0.747**	1.000									
Co	0.760**	0.899**	1.000								
Cr	0.712**	0.902**	0.917**	1.000							
Cu	0.763**	0.856**	0.937**	0.924**	1.000						
Fe	0.661**	0.855**	0.886**	0.933**	0.853**	1.000					
Mg	0.812**	0.864**	0.976**	0.937**	0.961**	0.882**	1.000				
Mn	0.853**	0.803**	0.917**	0.772**	0.845**	0.746**	0.896**	1.000			
Ni	0.763**	0.910**	0.970**	0.967**	0.970**	0.893**	0.981**	0.850**	1.000		
Pb	0.010	0.048	0.071	0.032	0.007	0.274	0.021	-0.014	0.038	1.000	
V	0.733**	0.878**	0.952**	0.976**	0.968**	0.904**	0.976**	0.824**	0.986**	0.008	1.000
Zn	0.746**	0.887**	0.942**	0.913**	0.923**	0.922**	0.934**	0.811**	0.950**	0.276	0.932**

**. Correlation is significant at the 0.01 level (2-tailed)

*. Correlation is significant at the 0.05 level (2-tailed)

Table 5-7 Pearson correlation coefficient matrix for all natural soils (n=20) in the PRD

	Ca	Cd	Co	Cr	Cu	Fe	Mg	Mn	Ni	Pb	V
Cd	0.626**	1.000									
Co	0.892**	0.617**	1.000								
Cr	0.699**	0.669**	0.812**	1.000							
Cu	0.785**	0.572**	0.766**	0.721**	1.000						
Fe	0.654**	0.567**	0.776**	0.966**	0.756**	1.000					
Mg	0.873**	0.511**	0.930**	0.709**	0.631**	0.651**	1.000				
Mn	0.852**	0.582**	0.845**	0.701**	0.793**	0.711**	0.651**	1.000			
Ni	0.908**	0.621**	0.982**	0.849**	0.760**	0.800**	0.928**	0.842**	1.000		
Pb	-0.147	-0.204	-0.090	0.062	0.135	0.160	-0.155	0.003	-0.077	1.000	
V	0.682**	0.668**	0.787**	0.977**	0.703**	0.930**	0.665**	0.716**	0.837**	0.056	1.000
Zn	0.813**	0.573**	0.822**	0.772**	0.962**	0.785**	0.705**	0.808**	0.818**	-0.014	0.763**

**. Correlation is significant at the 0.01 level (2-tailed)

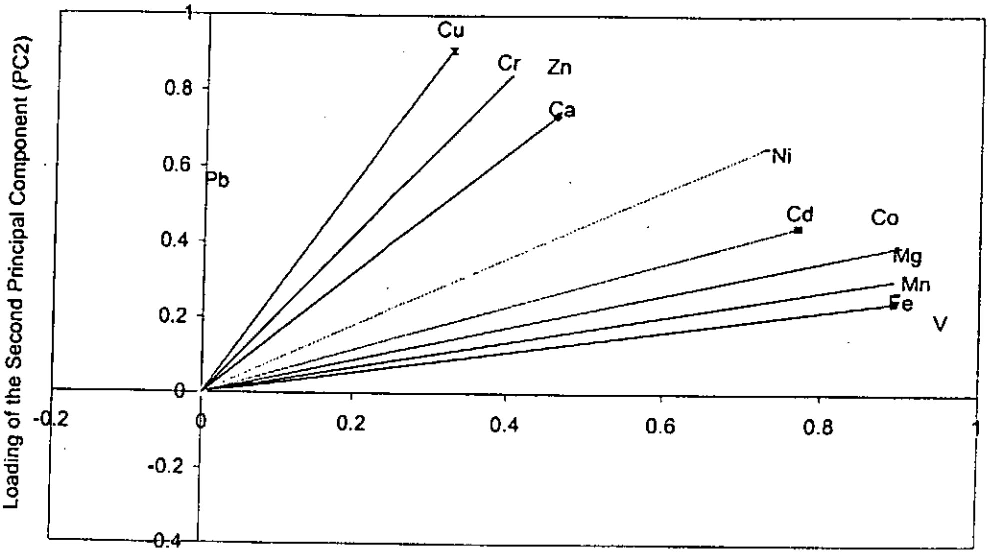
*. Correlation is significant at the 0.05 level (2-tailed)

In the PCA, the first two principal components accounted for 82.2, 91.1, and 82.4% of the total variance for the crop, paddy and natural soils, respectively. The principal component loadings of the soils are shown in Table 5-8 and depicted in Figure 5-14. In the crop soils, Pb was strongly dominated by the second component (PC2). Cu, Cr, Zn and Ca formed a closely associated group, while the other elements were significantly dominated by the first component (PC1). In the paddy soils, Pb was predominantly associated with PC2, and the other elements were significantly governed by PC1 (Figure 5-14b). Furthermore, Fe and Zn in the paddy soils were strongly associated with each other, while the other elements clustered together. Again, PC2 showed predominance over Pb in the natural soils (Figure 5-14c). Virtually no association was found between soil Pb and PC1. Other trace and major metals in the natural soils tended to be dominated by PC1 and clustered together.

Table 5-8 The rotated component matrixes of the crop, paddy and natural soils of the PRD

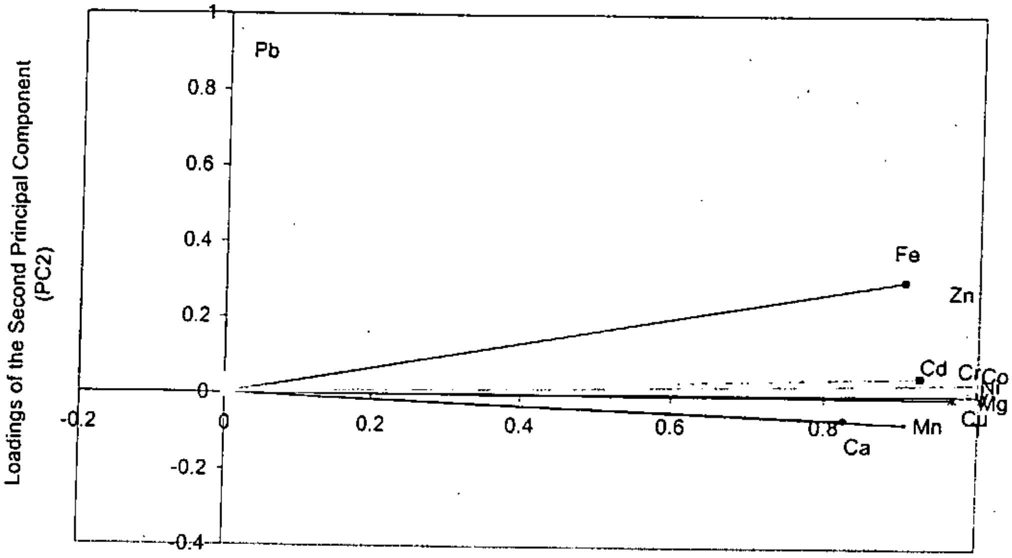
	Crop soils		Paddy soils		Natural soils	
	PC1	PC2	PC1	PC2	PC1	PC2
Ca	0.459	0.734	0.825	-0.062	0.897	-0.245
Cd	0.769	0.442	0.924	0.049	0.704	-0.226
Co	0.855	0.411	0.978	0.057	0.947	-0.152
Cr	0.401	0.842	0.959	0.050	0.917	0.153
Cu	0.324	0.907	0.967	-0.005	0.873	0.157
Fe	0.892	0.243	0.903	0.301	0.892	0.274
Mg	0.896	0.391	0.987	0.003	0.845	-0.268
Mn	0.886	0.300	0.902	-0.072	0.874	-0.024
Ni	0.727	0.653	0.988	0.033	0.960	-0.129
Pb	0.052	0.495	0.013	0.989	-0.002	0.935
V	0.928	0.195	0.979	0.012	0.902	0.153
Zn	0.473	0.788	0.945	0.274	0.909	0.033

(a) the crop soils



Loadings of the First Principal Component (PC1)

(b) the paddy soils



Loadings of the First Principal Component (PC1)

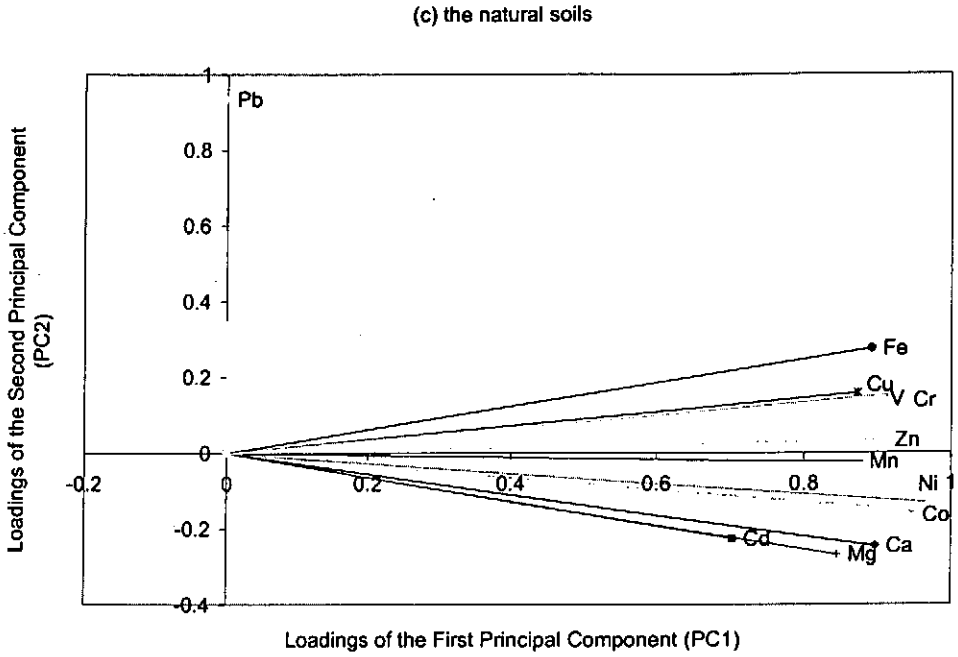


Figure 5-14 The principal component analysis loading plots of trace metals and major elements in a) crop soils, b) paddy soils, and c) natural soils of the PRD

The results of Pearson correlation and PCA collectively showed that elemental association of Pb with other elements was weak in the crop, paddy and natural soils. In contrast, the other trace metals and major elements were generally highly correlated with each other. The results may indicate that Pb in the soils had unique geochemical behaviours and, possibly, originated from sources that were different from the other elements. Given the extensiveness of the spatial coverage of the soil samples in the PRD and the analytical results of Pb isotopic ratios, it was noted that anthropogenic Pb in the agricultural and natural soils had originated from automobile exhaust and industrial activites. In the PCA, the distinctive association among Ca Cu, Cr, and Zn in the crop soils and relatively strong dominance by PC2 may suggest that these elements shared similar geochemical properties and/or originated from common sources. Given the comparatively high soil pH of the crop soils and the significant Pearson correlation between Cd, Cr, Co and Pb, these trace metals might have entered the crop soils through the applications of agrochemicals, such as lime, fertilizers and pesticides. The close association between Fe and Zn in the paddy soils may reflect the influences of flooding in rice cultivation. In the crop and natural soils, Fe and Mn were closely associated with each other. The weak association between Fe and Mn in the paddy soils was likely attributed to prolong flooding of the soils, which had resulted in the dissolution of Mn oxides and Co in the soils.

5.6 Potential environmental implications

The agricultural and natural soils in the PRD have shown signs of impacts of human activities. Despite of the relatively short history of industrialization and urbanization, excessive trace metals and footprints of anthropogenic Pb, such as leaded gasoline and industrial wastewater, were found in the crop, paddy and natural soils in the PRD. Even though mean trace metal concentrations of the agricultural soils did not signal severe contamination, the discovery of some grossly contaminated crop, paddy and natural soils warranted the need for environmental protection and sustainable agricultural soil management. Owing to the acidic nature of soils in the PRD and the prevalence of acid rain in the coastal area of China (Whelpdale et al., 1997; Ji et al., 2000), trace metals might become more soluble and mobile over time. This would cause a potential concern over groundwater contamination and other environmental and health consequences.

China is expected to achieve steady and positive economic growth in the foreseeable years. As a major economic zone, the PRD will likely continue to develop economically and industrially, and its population will likely expand as well. To avoid repetition of some serious environmental problems that have been experienced in some developed countries, e.g. Japan, implementation and enforcement of pollution control measures and sustainable soil management must be prompt. Given the current development trend in Asia, there is also a need for the formulation and implementation of sustainable soil management in other Asian countries. Even though, at the moment, trace metal contamination of urban and agricultural soils in these Asian countries is not serious, a proactive soil management and long-term vision are particularly important since many of these countries are heavily involved in agriculture and reliant on its economic output.

CHAPTER SIX CONCLUSIONS, RECOMMENDATIONS AND FUTURE STUDIES

Trace metal contamination of both urban and agricultural soils in HK and the PRD has also provoked long-term associated environmental and health concerns. In the present study, an in-depth investigation of trace metal contamination of urban soil profiles in HK and agricultural soils in the PRD was conducted. Some major findings of the study of urban soils in HK are:

1. Some urban soil profiles of HK were slightly and moderately contaminated with Cu, Pb and Zn, and the most severe cases of trace metal contamination were generally found at roadside areas.
2. Soil concentrations of trace metals, including Cd, Co, Cr, Mo, Ni, and V, generally showed a decreasing tendency with increasing depth, suggesting surface application and/or atmospheric deposition.
3. Pb and Zn concentrations in the exchangeable and carbonate fractions represented relatively significant percents of the total soil Pb and Zn. This may pose potential environmental and health implications.
4. Binary mixing of anthropogenic Pb in urban soil profiles was found at some roadside sites. Based on the Pb isotopic composition of the soil samples, it was estimated that as much as 85% of total anthropogenic Pb in the soils had originated from gasoline-derived Pb.

The trace metal study of agricultural soils in the PRD revealed that:

1. The crop, paddy and natural soils in the PRD were enriched with Cd and Pb.
2. Trace metal concentrations of the crop soils were generally more elevated than

those of the paddy and natural soils, suggesting a higher input of trace metals in the crop soils.

3. The chemical partitioning of trace metals and major elements gave insight to the influences of differences in cultivation methods, particularly on the leaching of Co and Mn in the paddy soils.
4. Results of the Pb isotopic and statistic analyses gave some evidence of the input of anthropogenic Pb in the soils, including gasoline and industrial Pb.
5. The Pb isotopic composition of the five chemical fractions of the soils showed that anthropogenic Pb in the soils generally tended to reside in the exchangeable, Fe-Mn oxide and organic fractions.

Collectively, the present study demonstrated that urban and agricultural soils within the urban perimeters of HK and the PRD were affected by urban and industrial activities. In comparison, trace metal contamination of soils was more severe in the urban environment of HK than in that of the PRD. Despite of the differences in the duration of urban and industrial development, soil enrichment of Pb was a partial consequence of the combustion of leaded gasoline in both areas.

6.1 Recommendations

With respect to trace metal contamination of urban soils, several recommendations are made:

1. Urban soils should be vegetated or covered to minimize soil loss either via resuspension of soil particles and/or urban runoff, thus reducing potential exposure to trace metals through inhalation and ingestion of trace metals disguised in aerosols and dusts.

2. Regular trace metal assessments of urban soils, especially those in playgrounds, parks, and other amenity facilities, ought to be conducted to ensure compliance of regulatory guidelines.
3. In case of excess of soil metal concentrations, the contaminated soils should be removed and properly handled in accordance with existing relevant regulations for contaminated materials.
4. Urban soil management strategy, including remedial measures, should be formulated and implemented.

With respect to trace metal contamination of agricultural soils of the PRD, several recommendations are as follow:

1. Proactive pollution prevention and pollution control measures must be implemented to minimize the releases of contaminants from the intensifying urban and industrial activities.
2. Use of agrochemicals containing high concentrations of trace metals should be prohibited whenever an alternative is available.
3. A practical and effective soil management strategy should be implemented and enforced to ensure long-term sustainability of the non-renewable resource.
4. Awareness of potential consequences of trace metal contamination of agricultural soils should be promoted among farmers, regulators, enforcement officers, as well as the general public.
5. Trace metal concentrations of agricultural soils should be monitored regularly to safeguard ample and safe supply of food crops.

6.2 Future study area

In order to further understand the potential ecological and health implications of trace metal contaminants in soils, the inclusion of biological components, such as fauna and flora specimens in toxicity evaluation and environmental risk assessment is recommended. With respect to trace metal contamination of urban soils, future scientific studies may emphasize on the promotion of efficiency and applicability of soil remedial treatments. In particular, effort may be devoted to phytoremediation because of its low cost and non-invasiveness. In terms of the prevention of trace metal contamination of agricultural soils in the PRD and other rapidly developing regions, future studies may involve the practical application of scientific information on sustainable management of agricultural soils.

6.3 Constraints of the study

The completion of this undertaking was indeed a challenge primarily because of the inherited complexity of the study topic itself. Dynamic interactions between human activities and the urban environment greatly expanded the potential number of unknown conditions that could affect the outcome of the study. Due to the presence of debris and other underground utility components, it was impossible to collect urban soils that were deep enough to reach the relatively undisturbed layer. Also, it was virtually impossible to find undisturbed soils in the urban environment at the same location at consecutive times over a period of some years. For these reasons, fluxes of trace metals and accurate historical Pb record in urban soil profiles could not be determined. Furthermore, the lack of isotopic information, for example, on the gasoline Pb isotope pattern over time in HK, has limited the potential usefulness of the Pb isotopic results.

REFERENCES

Adriano, D.C. *Trace Elements in the Terrestrial Environment,* Springer-Verlag, New York (1986)

Adriano, D.C., Albright, J., Whicker, F.W., and Iskandar, I.K. "Remediation of metal- and radionuclide-contaminated soils". In Iskandar, I.K. and Adriano, D.C., eds., *Remediation of Soils Contaminated with Metals*, Science Reviews, Northwood (1997)

Allan, R.J. "Impact of Mining Activities on the Terrestrial and Aquatic Environment with Emphasis on Mitigation and Remedial Measures". In Salomons, W., Forstner, U., and Mader, P., eds., *Heavy Metals: Problems and Solutions*, pp.119-140 (1995)

Allen, S.E., Grimshaw, H.M., Parkinson, J.A. and Quarmby, C. *Chemical Analysis of Ecological Materials*, Blackwell, Oxford (1974)

Alloway, B.J. "Cadmium". In Alloway, B.J., ed., *Heavy Metals in Soils*, Blackie & Son, New Jersey, pp.100-124 (1990)

Appleton, J.D. and Ridgway, J. "Regional geochemical mapping in developing countries and its application to environmental studies". *Applied Geochemistry*, Suppl. Issue, no. 2, pp.103-110 (1993)

Aylett, B.J. *The Chemistry, Biochemistry and Biology of Cadmium*, Webb, M, ed., Elsevier, Amsterdam (1979)

Barceloux, D.G. "Zinc". *Journal of Toxicology – Clinical Toxicology*, Vol. 37, pp.279-292 (1999)

Blackmore, G. "An overview of trace metal pollution in the coastal waters of Hong Kong". *The Science of the Total Environment*, Vol. 214, pp.21-48

(1998)

Bullock, P. and Gregory, P.J. *Soils in the Urban Environment*, British Society of Soil Science, Blackwell Scientific Publications, Oxford (1991)

CCME (Canadian Council of Ministers of the Environment) *Canadian Soil Quality Guidelines for 20 Substances* (1997a)

CCME (Canadian Council of Ministers of the Environment) *Recommended Canadian Soil Quality Guidelines*, ISBN: 1-895-925-92-4 (1997b)

CDC (Center for Diseases Control) *Preventing Lead Poisoning in Young Children: A Statement from the CDC*, CDC, Atlanta (1991)

Chapman, P.M., Wang, F.Y., Janseen, C., Persoone, G., and Allen, H.E. "Ecotoxicology of metals in aquatic sediments: binding and release, bioavailability, risk assessment, and remediation". *Canadian Journal of Fishery and Aquatic Science*, Vol. 55, pp.2221-2243 (1998)

Chen, T.B., Wong, J.W.C., Zhou, H.Y., and Wong, M.H. "Assessment of trace metal distribution and contamination in surface soils of Hong Kong". *Environmental Pollution*, Vol. 96, pp.61-68 (1997)

Chen, H.M., Zheng, C.R., Tu, C., and Zhou, D.M. "Studies on loading capacity of agricultural soils for heavy metals and its applications in China". *Applied Geochemistry*, Vol. 16, pp.1397-1403 (2001)

Chen, H.M., Zheng, C.R., Tu, C., and Zhu, Y.G. "Heavy metal pollution in soils in China: status and countermeasures". *Ambio*, Vol. 28, pp.130-134 (1999)

Cheung, Y.H., and Wong, M.H. "Utilization of animal manures and sewage sludges for growing vegetables". *Agricultural Wastes*, Vol. 5, pp.63-81 (1983)

Chiaradia, M., Gulson, B.L., James, M., Jameson, C.W., and Johnson, D. "Identification of secondary lead sources in the air of an urban environment". *Atmospheric Environment*, Vol. 31, pp.3511-3521 (1997)

Chon, H.T., Kim, K.W., and Kim, J.Y. "Metal contamination of soils and dusts in Seoul metropolitan city, Korea". *Environmental Geochemistry and Health*, Vol. 17, pp.139-146 (1995)

Crounse, R.G., Pories, W.J., Bray, J.T., and Mauger, R.L. "Geochemistry and Man: Health and Disease". In Thornton, I., ed., *Applied Environmental Geochemistry*, Academic Press, London, pp.267-330 (1983)

Culbard, E.B., Thornton, I., Watt, J., Wheatley, M., Moorcroft, S., and Thompson, M. "Metal contamination in British urban dusts and soils". *Journal of Environmental Quality*, Vol. 17, pp. 226-234 (1988)

Das, P., Samantaray, S., and Rout, G.R. "Studies on cadmium toxicity in plants: a review". *Environmental Pollution*, Vol. 98, pp.29-36 (1997)

Davis, J.M., Jarabek, A.M., Mage, D.T., and Graham, J.A. "Inhalation health risk assessment of MMT". *Environmental Research*, Vol. 80, pp.103-104 (1999)

De Kimpe, M. "Urban soil management: a growing concern". *Soil Science*, Vol. 165, pp.31-40 (2000)

Department of Soil Protection, Netherlands *The Netherlands Soil Contamination Guidelines, Netherlands Intervention Values for Soil Remediation*, Reference # DBO/07494013 (1994)

Dudka, S. "Baselisne concentrations of As, Co, Cr, Cu, Ga, Mn, Ni and Se in surface soils, Poland". *Applied Geochemistry*, Suppl. Issue, no. 2, pp.23-28 (1993)

Facchinelli, A., Sacchi, E., and Mallen, L. "Multivariate statistical and GIS-based approach to identify heavy metal sources in soils". *Environmental* Pollution, Vol. 114, pp.313-324 (2001)

Farmer, J.G., and Eades, L.J. "Stable lead isotope record of lead pollution in Loch Lomond sediments since 1630 A.D.". *Environmental Science and Technology*, Vol. 30, pp.3080-3083 (1998)

Flegal, A.R. and Smith, D.R. "Lead levels in Preindustrial Human". *New England Journal of Medicine*, Vol. 326, pp.1293-1294 (1992)

Francek, M.A. "Soil lead levels in a small town environment: a case study from Mt Pleasant, Michigan". *Environmental Pollution*, Vol. 76, pp.251-257 (1992)

Gelinas, Y., and Schmit, J.P. "Extending the use of the stable lead isotope ratios as a tracer in bioavailability study". *Environmental Science and Technology*, Vol. 31, pp.1968-1972 (1997)

Gibson, M.J., and Farmer, J.G. "Multi-step sequential chemical extraction of heavy metals from urban soils". *Environmental Pollution (Series B)*, Vol. 11, pp.117-135 (1986)

Guangdong Environmental Protection Bureau. Guangdong province environmental quality report, 1991-1995, Guangdong EPB, Guangzhou, China (1996).

Guinee, J.B., van den Bergh, J.C.J.M., Boelens, J., Fraanje, P.J., Huppes, G., Kandelaars, P.P.A.A.H., Lexmond, Th.M., Moolenaar, S.W., Olsthoorn, A.A., Udo de Haes, H.A., Verkuijlen, E., and van der Voet, E. "Evaluation of risks of metal flows and accumulation in economy and environment". *Ecological Economics*, Vol. 30, pp. 47-65 (1999)

Haan, M. "Childhood lead exposure: an influence of soil and paint lead levels". *Archive of Environmental Health*, Vol. 46, pp.185 (1991)

Hansmann, W., and Koppel, V. "Lead-isotopes as tracers of pollutants in soils". *Chemical Geology*, Vol. 171, pp.123-144 (2000)

Harrison, R.M., Laxen, D.P.H., and Wilson, S.J. "Chemical associations of lead, cadmium, copper, and zinc in street dusts and roadside soils". *Environmental Science and Technology*, Vol. 15, pp. 1378-1383 (1981)

Hills, P., Zhang, L., Liu, J.H. "Transboundary pollution between Guangdong Province and Hong Kong: threats to water quality in the Pearl River Estuary and their implications for environmental policy and planning". *Journal of Environmental Planning and Management*, Vol. 41, pp.375-396 (1998)

Hong Kong Environmental Protection Department *Personal contact* (2000)

Ho, Y.B. "The effect of Pb reduction in petrol on the Pb content of kerbside dust in Hong Kong". *The Science of the Total Environment*, Vol. 93, pp.411-418 (1990)

Ho, Y.B., and Tai, K.M. "Elevated levels of lead and other metals in roadside soil and grass and their use to monitor aerial metal depositions in Hong Kong". *Environmental Pollution*, Vol. 49, pp.37-51 (1988)

HKSAR (Hong Kong Special Administrative Region) *Hong Kong in Figures* Government of the Hong Kong Special Administrative Region, Hong Kong (2000)

Hossner, L.R. "Dissolution for total elemental analysis". In Sparks, D.L., Page, A.L., Helmke, P.A., Loeppert, R.H., Soltanpour, P.N., Tabatabai, M.A., Johnson, C.T., and Summer, M.E., eds., *SSSA Book Series: 5*

Methods of Soil Analysis Part 3 – Chemical Methods, Soil Science Society of America, Wisconsin, pp.49-64 (1996)

Houba, V.J.G., Temminghoff, E.J.M., Gaikhorst, G.A., and van Vark, W. "Soil analysis procedures using 0.01 M calcium chloride as extraction reagent". *Communications in Soil Science and Plant Analysis*, Vol. 31, pp.1299-1396 (2000)

Hrudey, S.E., Chen, W. and Rousseaux, C.G. *Bioavailability in Environmental Risk Assessment*, CRC Press, Boca Raton (1996)

Hwang, C.K., Cha, J.M., Kim, K.W., and Lee, H.K. "Application of multivariate statistical analysis and a geographic information system to trace element contamination in the Chungnam Coal Mine area, Korea". *Applied Geochemistry*, Vol. 16, pp.1455-1464 (2001)

Jackson, T.A., Klaverkamp, J.F., and Dutton, M.D. "Heavy metal speciation and its biological consequences in a group of lakes polluted by a smelter, Flin Flon, Manitoba, Canada". *Applied Geochemistry*, Suppl. Issue no. 2, pp.285-289 (1993)

Ji, G.L., Wang, J.H., and Zhang, X.N. "Environmental problems in soil and groundwater induced by acid rain and management strategies in China". In Huang, P.M., and Iskandar, I.K., eds., *Soils and Groundwater Pollution and Remediation: Asia, Africa and Oceania*, CRC Press, London, pp. 201-224 (2000).

Jim, C.Y. "Soil characteristics and management in an urban park in Hong Kong". *Environmental Management*, Vol. 22, pp.683-695 (1998)

Kataba-Pendias, A. "Behavioural properties of trace metals in soils". *Applied Geochemistry*, Suppl. issue no. 2, pp.3-9 (1993)

Kataba-Pendias, A. "Agricultural problems related to excessive trace metal contents in soils". In Salomons, W., Forstner, U., and Mader, P., eds., *Heavy Metals: Problems and Solutions*, Springer-Verlag, Berlin Heidelberg, pp. 3-18 (1995)

Kataba-Pendias, A. and Pendias, H. *Trace Elements in Soils and Plants*, 2nd ed. CRC Press, Boca Raton, FL (1992)

Kersten, M. "Source appointment of Pb pollution in the coastal waters of Elefsis Bay, Greece". *Environmental Science and Technology*, Vol. 31, pp.1295-1301 (1997)

Kim, K.W. and Thornton, I. "Influence of Ordovician uraniferous black shales on the trace element composition of soils and food crops, Korea". *Applied Geochemistry*, Suppl. Issue No. 2, pp.249-255 (1993)

Kitagishi, K., and Yamane, I. *Heavy Metal Pollution in Soils of Japan*, Japan Scientific Societies Press, Tokyo (1981)

Komai, Y. "Heavy metal pollution in urban soils". In Kitagishi, K., and Yamane, I., eds., *Heavy Metal Pollution in Soils of Japan*, Japan Scientific Societies Press, Tokyo, pp.193-217 (1981)

Kreimer, A. "Environmental management and urban vulnerability". *World Bank Discussion Paper*, Vol. 168, World Bank, Washington, DC (1992)

Lau, W.M., and Wong, H.M. "An ecological survey of lead contents in roadside dusts and soils in Hong Kong". *Environmental Research*, Vol. 28, pp.39-54 (1982)

Li, X.D., Coles, B.J., Ramsey, M.H. and Thornton, I. "Chemical partitioning of the new National Institute of Standards and Technology Standard Reference Materials (SRM 2709-2711) by sequential extraction using inductively coupled plasma atomic emission spectroscopy". *Analyst*, Vol. 120, pp.1415-1419 (1995)

Li, X.D., Poon, C.S., and Liu, P.S. "Heavy metal contamination of urban soils and street dusts in Hong Kong". *Applied Geochemistry*, Vol. 16, pp.1361-1368 (2001a).

Li, X.D., Shen, Z.G., Wai, O.W.H., and Li, Y.S. "Chemical forms of Pb, Zn and Cu in the sediment profiles of the Pearl River Delta". *Marine Pollution Bulletin*, Vol. 42, pp.215-223 (2001b)

Li, X.D. and Thornton, I. "Multi-element contamination of soils and plants in old mining areas". *Applied Geochemistry*, Suppl. Issue No. 2, pp.51-56 (1993a)

Li, X.D. and Thornton, I. "Arsenic, antimony and bismuth in soil and pasture herbage in some old metalliferous mining areas in England". *Environmental Geochemistry and Health*, Vol. 15, pp.135-144 (1993b)

Li, X.Y., Zhu, C.S., Tschirley, J.B., Webb, S.E., and Morton, A. "Sustainable agriculture and rural development in China, Part I: the agro-ecosystem and China's rural economy". In *Promotion of sustainable agriculture and rural development in China: elements for a policy framework and a National Agenda 21 Action programme*, FAO/Un.d.P/Ministry of Agriculture, China (1997)

Lin, Z.X., Harsbo, K., Ahlgren, M., and Qvarfort, U. "The source and fate of Pb in contaminated soils at the urban area of Falun in central Sweden". *The Science of the Total Environment*, Vol. 209, pp.47-58 (1998)

Lux, W. "Long-term heavy metal and As pollution of soils, Hamburg, Germany". *Applied Geochemistry*, Suppl. Issue No. 2, pp.135-143 (1993)

Lytle, C.M, Smith, B.N., and McKinnon, C.Z. "Manganese accumulation along Utah roadways: a possible indication of motor vehicle exhaust pollution". *The Science of the Total Environment*, Vol. 162, pp.105-109 (1995)

Mahan, K.I., Foderato, T.A., Garza, T.L., Martinez, R.M., Maroney, G.A., and Trivisonno, M.R. "Microwave digestion techniques in the sequential extraction of calcium, iron, chromium, manganese, lead, and zinc in sediments". *Analytical Chemistry*, Vol. 59, pp.938-945 (1987)

Maravelias, C., Athansalelis, S, and Dona, A. "Reduction in lead pollution in Greece during the past two decades". Archives of Environmental Health, Vol. 53, pp.424-426 (1998)

Marcantonio, F., Flowers, G.C., and Templin, N. "Lead contamination in a wetland watershed: isotopes as fingerprints of pollution". *Environmental Geology*, Vol. 39, pp.1070-1076 (1998)

Marsalek, J. "Toxic Contaminants in Urban Runoff. In Torno, H., Marsalek, J., and Desbordes, M., eds., *Urban Runoff Pollution*, Springer Verlag, Berlin, pp.39-57 (1986)

McLaughlin, M.J., Parker, D.R., and Clarke, J.M. "Metals and micronutrients – food safety issues". *Field Crop Research*, Vol. 60, pp.143-163 (1999)

Mergler, D. "Neurotoxic effects of low level exposure to manganese in human populations". *Environmental Research*, Vol. 80, pp.99-102 (1999)

Meyer, I., Heinrich, J., and Lippold, U. "Factors affecting lead, cadmium, and arsenic levels in house dust in a smelter town in Eastern Germany". *Environmental Research*, Vol. 81, pp.32-44 (1999)

Mielke, H.W. "Urban lead levels in Minneapolis: the case of the Hmong children". *Environmental Research*, Vol. 34, pp.64-76 (1984)

Mielke, H.W., Gonzales, C.R., Smith, M.K., and Mielke, P.W. "The urban environment and children's health: soils as an integrator of lead, zinc, and cadmium in New Orleans, Louisiana, U.S.A.". *Environmental Research*, Section A, Vol. 81, pp.117-129 (1999)

Monaci, F., Moni, F., Lanciotti, E., Grechi, D., and Bargagli, R. "Biomonitoring of airborne metals in urban environments: new tracers of vehicle emission, in place of lead". *Environmental Pollution*, Vol. 107, pp.321-327 (2000)

Morton, B. "Pollution of the coastal waters of Hong Kong". *Pollution Bulletin*, Vol. 20, pp.310-318 (1989)

Mueller, M. "Distribution of cadmium in the food chain (soil-plant-human) of a cadmium exposed area and the health risks of the general population". *The Science of the Total Environment*, Vol. 156, pp.151-158 (1994)

Munksgaard, N.C., Batterham, G.J., and Parry, D.L. "Lead isotope ratios determined by ICP-MS: investigation of anthropogenic lead in seawater and sediment from the Gulf of Carpentaria, Australia". *Marine Pollution Bulletin*, Vol. 36, pp.527-534 (1998)

Murray, Y.Ge P. and Hendershot, W.H. "Trace metal speciation and bioavailability in urban soils". *Environmental Pollution*, Vol. 107, pp.137-144 (2000)

National Environmental Protection Agency *Environmental Quality Standard for Soils*, GB 15618-1995, Beijing, China (1995).

Needleman, H.L. "Low Level Lead Exposure – the Clinical Implications of Current Research". Raven Press, New York (1980)

Neller, R.J., and Lam, K.C. "The environment". In Yeung, Y.M. and Chu, D.K.Y., eds., *Guangdong: Survey of a Province Undergoing*

Rapid Change, Chinese University Press, Hong Kong (1994)

Novotny, V. "Diffuse Sources of Pollution by Toxic Metals and Impact on Receiving Water". In Salomons, W., Forstner, U., and Mader, P., eds., *Heavy Metals: Problems and Solutions*, Springer-Verlag, Berlin, pp.33-52 (1995)

Nriagu, J.O. "Global inventory of natural and anthropogenic emissions of trace metals to the atmosphere". *Nature*, Vol. 279, pp.409-411 (1979)

Nriagu, J.O. "A silent epidemic of environmental metal poisoning?" *Environmental Pollution*, Vol. 50, pp.139-161 (1988)

Nriagu, J.O. and Pacyna, J.M. "Quantitative assessment of worldwide contamination of air, water and soils by trace metals". *Nature*, Vol. 333, pp.134-139 (1988)

Ontario Ministry of Agriculture and Food and Ontario Ministry of Environment *Trace metal distribution in soils*, Ontario (1992)

Othman, I., Al-Oudat, M., and Al-Masri, M.S. "Lead levels in roadside soils and vegetation of Damascus city". *The Science of the Total Environment*, Vol. 207, pp.43-48 (1997)

Pentecost, A. *Analyzing Environmental Data*, Pearson Education Limited, England (1999)

Pichtel, J., Sawyerr, H.T., and Czarnowska, K. "Spatial and temporal distribution of metals in soils in Warsaw, Poland". *Environmental Pollution*, Vol. 98, pp.169-174 (1997)

Plant, J., Smith, D., Smith, B., and Williams, L. "Environmental geochemistry at the global scale". *Applied Geochemistry*, Vol. 16, pp.1291-1308 (2001)

Pocock, R.L. "Airborne deposition of heavy metals to land". In *4th*

International Environment and Safety Conference Proceeding, London, U.K., pp. 27-29 (1984)

Poon, C.S., Liu, P.S., and Li, X.D. *Heavy metal levels in country and urban park soils in Hong Kong*, the Hong Kong Polytechnic University, Construction Industry Development Studies & Research Centre, Hong Kong (1999)

Puchelt, H., and Kramar, U. "Anthropogenic Pb contamination of soils, southwest Germany". *Applied Geochemistry*, Suppl. Issue no. 2, pp.71-73 (1998).

Rupa, T.R., and Shukla, L.M. "Comparison of four extractants and chemical fractions for assessing available zinc and copper in soils of India". *Communications of Soil Science and Plant Analysis*, Vol. 30, pp.2579-2591 (1999)

Rybicka, E.H. Environmental Impact of the Mining Industry in Poland. In Salomons, W., Forstner, U., and Mader, P., eds., *Heavy Metals: Problems and Solutions*, Springer-Verlag, New York, pp.271-286 (1995)

Samecka-Cymerman, A., and Kempers, A.J. "Bioindication of heavy metals in the town Wroclaw (Poland) with evergreen plants". *Atmospheric Environment*, Vol. 33, pp.419-430 (1999)

Sauve, S., McBride, M.B., and Hendershot, W.H. "Speciation of lead in contaminated soils". *Environmental Pollution*, Vol. 98, pp.149-155 (1997)

Sewell, R.J. *Geochemical Atlas of Hong Kong*. Geotechnical Engineering Office, Civil Engineering Department, the Government of Hong Kong Special Administrative Region, HK (1999)

Shen, A.M., Rosen, J.F., and Wu, S.M. "Childhood Lead Poisoning in China". *The Science of the Total Environment*, Vol. 181, pp.101-109 (1996)

Siamwalla, A. "Agricultural sustainability in rapidly industrializing

Asian economies". In *Integration of Sustainable Agriculture and Rural Development in Agricultural Policy*, FAO, Winrock International (1996)

Silbergeld, E.K. "Introduction MMT: science and policy". *Environmental Research*, Vol. 80, pp.93-95 (1999)

Sturges, W.T. and Barrie, L.A. "^{206}Pb/^{207}Pb isotope ratios in the atmosphere of North America as traces of United States and Canadian emissions". *Nature*, Vol. 329, pp.144-146 (1987)

Sun, B., Zhao, F.J., Lombi, E., and McGrath, S.P. "Leaching of heavy metals from contaminated soils using EDTA". *Environmental Pollution*, Vol. 113, pp.111-120 (2001)

Sutherland, R.A., Tolosa, C.A., Tack, F.M.G., and Verloo, M.G. "Characterization of selected element concentrations and enrichment ratios in background and anthropogenically impacted roadside areas". *Archives of Environmental Contamination and Toxicology*, Vol. 38, pp.428-438 (2000)

Tam, N.F.Y., Liu, W.K., Wong, M.H., and Wong, Y.S. "Heavy Metal Pollution in Roadside Urban Parks and Gardens in Hong Kong". *The Science of the Total Environment*, Vol. 59, pp.325-328 (1987)

Tessier, A. and Campbell, P.G.C. Partitioning of Trace Metals in Sediments and its Relationship to Their Accumulation in Benthic Organisms. In Broekaert, J.A.C., Gucer, S., and Adams, F. eds., "*Metal Speciation in the Environment*", Springer-Verlag, New York, pp.545-569 (1990).

Tessier, A., Campbell, P.G.C., and Bisson, M. "Sequential extraction procedure for the speciation of particulate trace metals". *Analytical Chemistry*, Vol. 51, pp.844-851 (1979)

Thornton, I. *Applied Environmental Geochemistry*, Academic Press, London (1983)

Thornton, I. "Metal contamination of soils in urban areas". In Bullock, P. and Gregory, P.J., eds., *Soils in the Urban Environment*, British Society of Soil Science, Blackwell Scientific Publications, Oxford (1991)

Thornton, I. "Environmental geochemistry and health in the 1990s: a global perspective". *Applied Geochemistry*, Suppl. Issue, no.2, pp.203-210 (1993)

Thuy, H.T.T., Tobschall, H.J., and An, P.V. "Distribution of heavy metals in urban soils – a case study of Danang-Hoian Area (Vietnam)". *Environmental Geology*, Vol. 39, pp.603-610 (2000)

Tiller, K.G. "Urban soil contamination in Australia". *Australian Journal of Soil Research"*, Vol. 30, pp.937-957 (1992)

Tong, S.T.Y., and Lam, K.C. "Are nursery schools and kindergartens safe for our kids? The Hong Kong study". *The Science of the Total Environment*, Vol. 216, pp.217-225 (1998)

Tong, S.T.Y., and Lam, K.C. "Home sweet home? A case study of household dust contamination in Hong Kong". *The Science of the Total Environment*, Vol. 256, pp.115-123 (2000)

UN (United Nations) *World Development Indicators*, United Nations, Washington, D.C. (2000)

Walker, L.R. *Ecosystem of the World, Vol. 16, Ecosystems of Disturbed Ground*, Elsevier Science, Amsterdam (1999)

Walsh C.T., Sandstead, H.H., Prasad, A.S., Newberne, P.M., and Fraker, P.J. "Zinc: health effects and research priorities for the 1990s".

Environmental Health Perspectives, Vol. 102, pp.5-46 (1994)

Wang, Y., Thornton, I., and Farago, M. "Changes in Lead Concentrations in the Home Environment in Birmingham, England over the Period 1984-1996". *The Science of the Total Environment*, Vol. 207, pp.149-156 (1997)

Wang, W.H., Wong, M.H., Leharne, S., and Fisher, B. "Fractionation and biotoxicity of heavy metals in urban dusts collected from Hong Kong and London". *Environmental Geochemistry and Health*, Vol. 20, pp.185-198 (1998)

Watt, J., Thornton, I., and Cotter-Howells, J. "Physical evidence suggesting the transfer of soil Pb into young children via hand-to-mouth activity". *Applied Geochemistry*, Suppl. Issue no. 2, pp.269-272 (1993)

Weng, H.X., and Chen, X.H. "Impact of polluted canal water on adjacent soil and groundwater systems". *Environmental Geology*, Vol. 39, pp. 945-950 (2000)

Whelpdale, D.M., Summers, P.W., and Sanhueza, E. "A global overview of atmospheric acid deposition". *Environmental Monitoring and Assessment*, Vol. 48, pp.217-247 (1997)

Wilcke, W., Muller, S., Kanchanakool, N., and Zech, W. "Urban soil contamination in Bangkok: heavy metal and aluminium partitioning in topsoils". *Geoderma*, Vol. 86, pp.211-228 (1998)

Wong, D.M.W. "Characterization of Ambient Levels of Metals and Polycyclic Aromatic Hydrocarbons for Surficial Soil in the Urban Piedmont Region of New Jersey". *ASTM Spec. Tech. Publ.*, Vol. 1333, pp.120-139 (1998)

Wong, J.W.C. "Heavy Metal Contents in Vegetables and Market Garden Soils in

Hong Kong". *Environmental Technology*, Vol. 17, pp.407-414 (1996)

Wong, J.W.C., and Mak, N.K. "Heavy metal pollution in children playgrounds in Hong Kong and its health implications". *Environmental Technology*, Vol. 18, pp.109-115 (1997)

Wong, M.H., Wong, J.W.C., and Chen, T.B. "Trace metal contamination of the Hong Kong soil environment: a review". In Naidu, R., Kookana, R.S., Oliver, D.P., Rogers, S., McLaughlin, M.J., Klumer Acad. Publ., Dordrecht, eds., *Contaminants and the soil environment in the Australasia-Pacific Region*, pp.501-511 (1996)

World Bank http://www.worldbank.org/data/countrydata/countrydata.html (2000)

Xie, X.J., and Cheng, H.X. "Global geochemical mapping and its implementation in the Asia-Pacific region". *Applied Geochemistry*, Vol. 16, pp.1309-1321 (2001)

Xiong, Z. "Heavy Metal Contamination of Urban Soils and Plants in Relation to Traffic in Wuhan City, China". *Toxicological and Environmental Chemistry*, Vol. 65, pp.31-39 (1998)

Yan, W, Chi, J.S., Gu, S.C., Tang, X.Z., and Chen, Z. "Characteristics and Prevention Countermeasures of Heavy Metal Pollution of Soils (Sediments) in Industrial Areas of the Pearl River Delta". *Soil and Environmental Science*, Vol. 9, pp.177-182 (2000)

Yim, W.W.S. and Nau, P.S. "Distribution of lead, zinc, copper and cadmium in dust from selected urban areas of Hong Kong". *Hong Kong Engineer*, January 1987, pp.7-14 (1987)

Zayed, J., Gerin, M., Loranger, P., Begin, D., and Kennedy, G. "Occupational and environmental exposure of garage workers and taxi drivers to airborne manganese arising from the use of methylcyclopentadienyl manganese tricarbonyl in unleaded gasoline". *American Industrial Hygiene Association*, Vol. 55, pp.53-58 (1994)

Zhang, X. "Lead Content of Urban Soils in China". *Journal of Environmental Science*, Vol. 6, pp.355-360 (1994)

Zhang, H., Ma, D., Xie, Q., and Chen, X. "An approach to studying heavy metal pollution caused by modern city development in Nanjing, China". *Environmental Geology*, Vol. 38, pp.223-228 (1999)

Zhu, B.Q. "The mapping of geochemical provinces in China based on Pb isotopes". *Journal of Geochemical Exploration*, Vol. 55, pp.171-181 (1995)

Zhu, B.Q. *Theory and Application of Isotopic Systematic in Earth Science.* Science Press, Beijing (in Chinese) (1998)

Zhu, B.Q., Chen, Y.W., and Peng, J.H. "Lead isotope geochemistry of the urban environment in the Pearl River Delta". *Applied Geochemistry*, Vol. 16, pp.409-417 (2001)

Zhu, B.Q., Wang, H.F., Mao, C.X., Zhu, N.J., Huang, R.S., and Peng, J.H. "Geochronology of and Nd-Sr-Pb isotopic evidences for mantle source in the ancient subduction zone beneath Sanshui Basin, Guangdong Province, China". *Chinese Journal of Geochemistry*, Vol. 8, pp.65-71 (1989)

APPENDIX A ANALYTICAL RESULTS

Table A-1 Trace metal concentrations (mg/kg) of soil profiles at CRP

Soil ID	Cd	Co	Cr	Cu	Mo	Ni	Pb	V	Zn
S1 0	0.85	2.15	18.6	25.0	0.32	7.60	60.4	6.47	127
S1 1	0.82	2.08	19.0	19.3	0.10	6.25	54.6	7.53	94.5
S1 2	0.71	2.34	17.3	17.9	0.27	5.55	54.9	6.54	89.9
S1 3	0.69	2.46	21.1	15.0	0.37	6.02	66.1	6.43	79.2
S2 0	0.87	1.63	17.9	40.5	0.22	4.89	48.9	4.89	126
S2 1	1.12	1.90	23.3	390	0.33	7.07	62.8	5.78	358
S2 2	0.89	2.11	22.2	226	0.17	6.63	73.9	6.57	230
S2 3	0.80	2.59	24.1	144	0.31	9.49	96.5	9.33	206
S3 0	0.77	2.98	20.0	19.4	0.28	7.18	61.5	8.60	99.9
S3 1	0.93	2.99	22.0	17.1	0.31	7.25	54.0	7.59	80.9
S3 2	0.92	2.76	18.8	14.6	0.33	6.95	47.8	7.61	77.2
S3 3	0.80	2.27	15.1	11.1	0.46	5.52	40.2	6.23	59.8
S4 0	0.82	3.24	28.8	52.4	0.74	9.30	103	15.9	110
S4 1	0.68	2.49	25.0	21.9	0.25	8.44	80.3	13.6	90.3
S4 2	0.72	2.57	25.6	16.6	0.32	8.71	74.3	11.3	70.7
S4 3	0.66	2.54	24.4	7.95	0.61	9.88	61.1	11.8	44.3
S5 0	0.47	2.64	14.0	8.65	0.92	5.50	70.0	4.96	58.8
S5 1	0.39	2.88	13.0	7.05	1.21	5.66	55.9	4.74	42.8
S5 2	0.39	2.49	13.4	6.06	1.31	5.52	56.6	4.52	36.8
S5 3	0.43	2.57	13.3	4.64	0.82	5.19	56.1	4.08	33.5
S6 0	0.75	3.28	23.3	22.1	1.60	8.63	74.4	11.49	88.0
S6 1	0.57	3.06	18.7	14.4	0.76	7.40	84.6	9.65	65.6
S6 2	0.57	3.14	20.7	20.3	0.55	7.43	57.4	9.51	96.3
S6 3	0.60	3.12	18.7	31.3	0.55	7.13	74.9	8.25	83.2
S7 0	0.58	2.46	18.2	9.94	1.03	7.15	40.0	11.56	65.2
S7 1	0.56	2.03	18.1	6.98	0.64	6.55	32.8	12.1	48.1
S7 2	0.61	2.03	18.5	8.04	0.33	6.10	41.9	9.70	58.8
S7 3	0.54	1.15	12.4	3.35	0.11	3.79	30.0	3.54	35.7

Table A-2 pH, organic content (%), and major element concentrations (mg/kg) of soil profiles at CRP

Soil ID	pH	OC	Al	Ca	Fe	Mg	Mn
S1 0	7.44	5.89	27318	2083	12231	557	601
S1 1	7.73	5.26	24001	1641	13257	548	551
S1 2	8.40	4.38	32498	2394	12778	631	613
S1 3	8.50	3.86	33397	3181	13107	607	682
S2 0	7.25	4.12	20957	1537	14294	597	771
S2 1	8.08	4.15	28413	2206	17705	585	697
S2 2	8.53	4.52	35986	5042	15964	617	642
S2 3	8.42	5.52	48670	8000	16498	599	578
S3 0	7.91	5.08	30493	3418	12479	516	436
S3 1	8.37	4.55	29839	4849	13405	521	521
S3 2	8.50	4.44	32638	5555	12250	499	422
S3 3	8.65	3.53	28509	6536	11713	505	487
S4 0	7.87	7.12	46109	3363	16249	719	346
S4 1	8.34	6.62	48941	6042	15936	664	329
S4 2	8.41	6.39	41737	6154	16712	604	348
S4 3	8.36	7.00	56823	3709	17126	419	326
S5 0	8.38	4.88	34833	4905	11551	452	465
S5 1	8.62	5.16	39148	5799	11032	436	365
S5 2	8.69	5.17	41197	5572	11393	421	372
S5 3	8.68	4.95	33971	4252	10792	371	379
S6 0	8.13	6.29	39785	3887	15955	595	463
S6 1	8.64	5.95	48625	5473	13749	506	498
S6 2	8.54	5.37	41369	6332	13596	608	430
S6 3	8.67	5.22	38245	6983	13211	630	495
S7 0	7.01	5.54	30274	1673	12567	795	375
S7 1	7.31	1.83	30156	1443	12402	613	271
S7 2	7.14	5.40	27228	1562	13345	609	431
S7 3	7.50	4.30	21082	850	10892	263	580

Table A-3 Trace metal concentrations (mg/kg) of soil profiles at CSW

Soil ID	Cd	Co	Cr	Cu	Mo	Ni	Pb	V	Zn
S1 0	0.37	2.51	46.8	102	1.74	16.0	170	12.1	735
S1 1	n.d.	0.61	11.3	35.4	1.27	5.06	72.3	4.74	139
S2 0	0.52	3.16	60.2	108	2.82	28.3	199	8.45	554
S2 1	n.d.	1.95	21.5	44.4	0.46	7.50	98.3	4.96	207

Table A-4 pH, organic content (%), and major element concentrations (mg/kg) of soil profiles at CSW

Soil ID	pH	OC	Al	Ca	Fe	Mg	Mn
S1 0	8.03	5.37	15120	4603	16160	588	441
S1 1	7.55	1.69	16011	1684	8774	218	839
S2 0	8.19	4.60	24136	3735	17895	628	714
S2 1	7.16	2.64	21255	1818	12902	480	693

Table A-5 Trace metal concentrations (mg/kg) of soil profiles at LT

Soil ID	Cd	Co	Cr	Cu	Mo	Ni	Pb	V	Zn
S1 0	n.d.	1.97	12.6	6.63	2.79	7.66	139	4.02	30.5
S1 1	n.d.	2.01	14.5	6.26	3.08	8.21	147	4.17	37.7
S1 2	0.02	2.03	15.7	5.36	2.23	8.06	152	6.61	35.4
S1 3	0.17	2.29	21.4	4.04	0.75	7.68	174	11.3	34.2
S2 0	0.15	2.17	13.3	5.50	1.78	6.84	113	3.66	81.7
S2 1	0.09	1.46	12.4	4.89	1.57	7.01	138	2.91	77.5
S2 2	0.05	1.19	9.90	3.67	1.94	5.67	163	1.77	62.0
S2 3	0.04	0.99	9.27	2.81	2.42	5.58	175	1.24	53.1
S3 0	0.02	1.80	12.8	5.40	0.83	6.95	140	2.76	59.4
S3 1	n.d.	2.53	12.4	5.26	0.84	7.23	143	2.63	53.5
S3 2	n.d.	1.60	9.86	4.73	0.91	6.78	124	2.22	53.5
S3 3	n.d.	1.51	11.7	5.90	0.79	7.67	128	2.66	54.6
S4 0	0.10	0.74	9.21	4.60	1.91	3.90	153	1.95	46.5
S4 1	0.09	0.77	10.8	3.35	1.71	4.34	155	2.26	49.6
S4 2	n.d.	0.74	8.23	2.95	2.32	4.72	156	0.87	38.6
S4 3	0.03	0.46	8.21	3.09	1.76	4.25	132	0.61	42.8
S5 0	0.16	1.54	9.53	2.60	0.74	5.05	152	1.39	58.6
S5 1	0.16	1.39	9.03	2.15	0.60	4.55	147	1.00	58.8
S5 2	0.12	1.45	8.43	1.78	0.51	4.12	145	0.82	54.8
S5 3	0.14	1.23	8.11	1.41	0.48	4.16	162	0.60	52.5

Table A-6 pH, organic content (%), and major element concentrations (mg/kg) of soil profiles at LT

Soil ID	pH	OC	Al	Ca	Fe	Mg	Mn
S1 0	5.74	5.31	50480	269	8595	166	271
S1 1	5.70	5.64	55228	381	9525	186	369
S1 2	5.56	5.94	50842	328	10415	349	260
S1 3	5.05	8.58	56201	218	14393	499	268
S2 0	7.91	4.27	34293	2531	8626	276	901
S2 1	8.07	3.94	35081	2200	8066	241	942
S2 2	7.94	3.84	33720	1107	7100	138	975
S2 3	7.93	3.52	35540	1006	7354	111	1187
S3 0	6.53	5.59	41401	746	8319	128	697
S3 1	5.75	4.66	48915	419	8304	102	474
S3 2	6.12	4.93	46461	432	7252	95.9	319
S3 3	5.44	5.13	50502	363	7793	107	273
S4 0	5.12	4.36	22009	347	6877	121	1053
S4 1	5.35	5.59	25366	364	7581	136	1122
S4 2	5.47	3.66	28832	234	6436	56.8	1070
S4 3	5.57	2.90	30406	195	6692	47.2	1102
S5 0	6.84	4.38	25159	718	7300	90.9	1085
S5 1	6.73	4.13	27610	521	7233	65.6	1200
S5 2	6.56	4.04	26803	514	6884	53.1	1195
S5 3	6.63	3.77	21278	391	6453	35.8	1139

Table A-7 Trace metal concentrations (mg/kg) of soil profiles at HC

Soil ID	Cd	Co	Cr	Cu	Mo	Ni	Pb	V	Zn
S1 0	0.43	4.88	18.6	3.87	n.d.	5.33	74.8	5.02	135
S1 1	0.18	2.89	14.3	5.23	0.06	6.58	59.9	4.46	46.6
S1 2	0.20	2.42	13.7	8.38	0.09	6.62	54.7	4.91	70.3
S1 3	0.20	2.12	13.1	8.40	0.14	6.14	45.1	4.18	42.5
S2 0	0.17	2.55	14.7	1.62	n.d.	4.47	73.2	3.76	29.9
S2 1	0.05	2.15	11.9	0.32	n.d.	5.22	82.5	3.11	23.7
S2 2	n.d.	2.66	10.8	1.06	n.d.	7.03	73.0	3.43	25.5
S2 3	0.08	2.61	13.4	n.d.	n.d.	4.92	111.6	3.22	20.7
S3 0	0.06	1.00	10.8	0.96	n.d.	3.55	24.9	2.27	35.8
S3 1	0.06	0.91	9.8	n.d.	n.d.	1.87	22.6	1.71	26.8
S3 2	0.35	1.56	16.2	0.75	n.d.	3.14	31.3	8.43	31.7
S3 3	0.80	3.39	27.1	3.06	n.d.	5.75	33.6	20.8	44.7
S4 0	0.13	1.22	12.2	2.27	n.d.	3.86	30.5	3.08	41.7
S4 1	0.29	1.79	14.0	0.89	n.d.	2.18	32.4	8.27	31.0
S4 2	0.47	2.90	17.8	1.18	n.d.	2.47	43.2	9.35	34.3
S4 3	0.41	3.91	16.4	4.10	n.d.	4.18	45.2	10.2	49.2
S5 0	0.11	1.21	11.3	1.51	n.d.	2.48	45.2	2.02	28.4
S5 1	0.03	1.24	10.4	1.51	n.d.	3.81	57.3	1.53	28.1
S5 2	n.d.	0.59	10.4	2.74	n.d.	3.21	62.6	1.65	30.1
S5 3	0.17	2.39	13.0	8.33	n.d.	3.18	59.0	3.64	44.5
S6 0	0.22	1.76	17.9	3.21	n.d.	5.93	77.7	5.13	29.0
S6 1	0.25	1.37	16.1	0.87	n.d.	3.33	80.7	4.32	18.6
S6 2	0.26	1.93	16.3	2.22	n.d.	4.05	110	4.88	27.6
S6 3	0.16	1.44	16.1	1.67	n.d.	4.74	85.2	4.36	19.7

Table A-8 pH, organic content (%), and major element concentrations (mg/kg) of soil profiles at HC

Soil ID	pH	OC	Al	Ca	Fe	Mg	Mn
S1 0	6.77	7.48	48692	626	18042	235	583
S1 1	7.35	5.88	50106	790	14278	244	432
S1 2	8.04	5.10	44300	1458	13659	354	448
S1 3	8.38	3.97	34750	2686	12375	370	442
S2 0	6.25	6.82	38127	503	13052	278	509
S2 1	5.98	6.92	55249	365	12269	188	403
S2 2	5.68	7.03	55699	321	11342	232	374
S2 3	5.49	6.91	53276	236	13575	171	355
S3 0	6.81	5.09	38025	687	11069	264	822
S3 1	6.75	4.35	29721	466	10552	222	814
S3 2	6.86	5.25	37820	685	15875	335	612
S3 3	7.72	6.36	53413	2494	24416	640	336
S4 0	7.03	4.66	34094	800	11984	371	788
S4 1	6.98	4.83	27322	693	13892	340	739
S4 2	7.63	4.96	40193	1026	17744	423	702
S4 3	8.39	4.11	41016	2599	16160	641	599
S5 0	6.68	4.97	28774	661	11146	270	745
S5 1	6.74	4.94	44112	511	11301	227	1050
S5 2	7.47	4.88	29899	791	10368	283	774
S5 3	8.17	4.03	29758	2106	11665	344	722
S6 0	6.33	8.82	62239	637	16465	266	411
S6 1	5.43	8.45	48361	360	16057	169	342
S6 2	6.04	8.60	50979	602	15390	235	606
S6 3	5.21	8.60	56853	310	16177	157	374

Table A-9 Trace metal concentrations (mg/kg) of soil profiles at NG

Soil ID	Cd	Co	Cr	Cu	Mo	Ni	Pb	V	Zn
S1 0	0.17	7.89	34.0	76.6	0.92	12.5	207	13.2	361
S1 1	n.d.	2.73	28.3	71.2	0.44	11.3	181	14.9	261
S1 2	n.d.	3.62	20.0	45.6	0.29	7.32	144	14.5	177
S2 0	n.d.	3.08	25.0	55.8	0.31	12.0	196	4.67	210
S2 1	n.d.	3.06	12.0	25.2	0.26	7.31	149	1.88	84.6
S2 2	n.d.	4.09	7.30	7.03	n.d.	4.37	175	0.56	32.6
S3 0	0.59	3.65	59.0	99.3	1.33	21.2	202	13.2	496
S3 1	0.36	3.12	38.1	94.6	1.10	14.9	231	12.0	361
S3 2	n.d.	2.40	27.6	47.1	0.75	8.86	138	7.38	205
S4 0	n.d.	8.22	20.4	64.8	0.06	10.6	393	4.14	206
S4 1	n.d.	8.43	12.8	30.3	0.05	7.02	377	2.07	106
S4 2	n.d.	9.51	13.1	28.2	n.d.	5.88	429	1.78	88.7

Table A-10 pH, organic content (%), and major element concentrations (mg/kg) of soil profiles at NG

Soil ID	pH	OC	Al	Ca	Fe	Mg	Mn
S1 0	5.97	5.56	25209	2799	16456	597	463
S1 1	6.70	3.63	18076	2072	12752	448	268
S1 2	6.71	3.35	18450	1647	12571	454	265
S2 0	6.87	4.98	41200	1588	14051	271	723
S2 1	6.50	4.61	41589	808	10526	164	653
S2 2	6.80	4.76	36062	531	7996	123	788
S3 0	6.53	6.59	30154	3866	22219	690	523
S3 1	7.04	5.23	35173	2875	19833	642	633
S3 2	7.92	4.25	25669	4182	15434	630	593
S4 0	6.25	6.49	44317	1552	11420	265	1008
S4 1	6.20	5.80	41851	882	9636	179	1041
S4 2	7.00	5.66	35735	1017	9799	149	1082

Table A-11 Trace metal concentrations (mg/kg) of soil profiles at SSP

Soil ID	Cd	Co	Cr	Cu	Mo	Ni	Pb	V	Zn
S2 0	n.d.	2.80	21.1	12.4	n.d.	6.09	70.6	12.7	82.2
S2 1	n.d.	3.14	19.9	6.37	n.d.	5.87	68.9	12.2	49.0
S2 2	n.d.	1.51	14.7	2.97	n.d.	5.09	58.3	7.51	28.5
S3 0	n.d.	3.36	19.9	5.05	n.d.	5.04	87.0	9.57	44.7
S3 1	n.d.	3.04	20.1	13.3	n.d.	5.42	95.8	10.3	84.2
S3 2	n.d.	3.48	19.7	7.86	n.d.	6.20	90.6	9.28	56.9

Table A-12 pH, organic content (%), and major element concentrations (mg/kg) of soil profiles at SSP

Soil ID	pH	OC	Al	Ca	Fe	Mg	Mn
S2 0	5.90	5.68	33701	966	16637	571	392
S2 1	6.99	4.42	41478	863	18198	564	413
S2 2	7.53	5.81	42924	797	14026	364	231
S3 0	5.74	4.12	36920	554	17468	628	413
S3 1	6.65	6.51	42753	1365	15908	638	406
S3 2	6.03	5.87	40186	540	17068	556	390

Table A-13 Pb isotopic composition of urban soil profiles of Hong Kong

Location	Soil ID	^{206}Pb/^{207}Pb	^{206}Pb/^{204}Pb	^{207}Pb/^{204}Pb	^{208}Pb/^{204}Pb
CRP	S1 0	1.172	18.578	15.848	39.315
	S1 1	1.179	18.658	15.823	39.304
	S1 2	1.182	18.724	15.848	39.468
	S1 3	1.184	18.728	15.823	39.481
	S2 0	1.182	18.765	15.873	39.598
	S2 1	1.171	18.499	15.798	38.900
	S2 2	1.172	18.538	15.823	39.082
	S2 3	1.161	18.169	15.649	38.316
	S3 0	1.187	18.871	15.898	39.672
	S3 1	1.187	18.778	15.823	39.470
	S3 2	1.188	18.830	15.848	39.602
	S3 3	1.199	19.084	15.924	40.202
	S4 0	1.162	18.322	15.773	38.702
	S4 1	1.172	18.520	15.798	39.156
	S4 2	1.188	18.856	15.873	39.621
	S4 3	1.205	19.097	15.848	39.926
	S5 0	1.184	18.652	15.748	38.710
	S5 1	1.208	19.079	15.798	39.305
	S5 2	1.212	19.176	15.823	39.377
	S5 3	1.210	19.177	15.848	39.488
	S6 0	1.188	18.655	15.699	38.524
	S6 1	1.199	18.879	15.748	38.860
	S6 2	1.193	18.781	15.748	38.880
	S6 3	1.186	18.642	15.723	38.596
	S7 0	1.200	19.041	15.873	39.538
	S7 1	1.205	19.119	15.873	39.573
	S7 2	1.204	19.141	15.898	39.636
	S7 3	1.216	19.329	15.898	39.941
CSW	S1 0	1.137	17.681	15.552	37.072
	S1 1	1.170	18.359	15.699	38.111
	S2 0	1.126	17.430	15.480	36.520
	S2 1	1.151	17.991	15.625	37.553

Table A-13 (con't) Pb isotopic composition of urban soil profiles of Hong Kong

Location	Soil ID	$^{206}Pb/^{207}Pb$	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$
HC	S1 0	1.204	18.811	15.625	38.978
	S1 1	1.205	18.884	15.674	39.050
	S1 2	1.202	18.804	15.649	38.878
	S1 3	1.205	18.947	15.723	39.228
	S2 0	1.211	19.011	15.699	39.218
	S2 1	1.209	18.915	15.649	38.781
	S2 2	1.208	18.908	15.649	38.870
	S2 3	1.207	18.799	15.576	38.430
	S3 0	1.217	19.172	15.748	39.739
	S3 1	1.219	19.233	15.773	39.864
	S3 2	1.218	19.149	15.723	39.505
	S3 3	1.206	18.900	15.674	39.130
	S4 0	1.215	19.108	15.723	39.509
	S4 1	1.216	19.082	15.699	39.429
	S4 2	1.214	18.964	15.625	39.191
	S4 3	1.208	18.933	15.674	39.056
	S5 0	1.218	19.085	15.674	39.299
	S5 1	1.218	19.061	15.649	39.185
	S5 2	1.215	19.159	15.773	39.350
	S5 3	1.207	18.798	15.576	38.603
	S6 0	1.206	18.821	15.601	38.772
	S6 1	1.206	18.819	15.601	38.821
	S6 2	1.205	18.740	15.552	38.439
	S6 3	1.207	18.859	15.625	38.739
LT	S1 0	1.206	18.897	15.674	38.701
	S1 1	1.205	18.972	15.748	38.879
	S1 2	1.204	18.813	15.625	38.328
	S1 3	1.201	18.979	15.798	39.227
	S2 0	1.209	19.063	15.773	38.998
	S2 1	1.206	18.987	15.748	38.817
	S2 2	1.209	19.125	15.823	39.334
	S2 3	1.210	19.177	15.848	39.563
	S3 0	1.206	18.987	15.748	38.688
	S3 1	1.204	19.054	15.823	39.241
	S3 2	1.205	18.922	15.699	38.612
	S3 3	1.207	19.133	15.848	39.403
	S4 0	1.209	19.189	15.873	39.632
	S4 1	1.210	19.200	15.873	39.700
	S4 2	1.211	19.187	15.848	39.330
	S4 3	1.210	19.170	15.798	39.000
	S6 0	1.214	19.183	15.798	39.341
	S6 1	1.215	19.193	15.798	39.152
	S6 2	1.217	19.322	15.873	39.678
	S6 3	1.215	19.117	15.773	39.340

Table A-13 (con't) Pb isotopic composition of urban soil profiles of Hong Kong

Location	Soil ID	$^{206}Pb/^{207}Pb$	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$
NG	S1 0	1.143	17.609	15.408	36.333
	S1 1	1.144	17.875	15.625	37.575
	S1 2	1.153	17.930	15.552	37.118
	S2 0	1.183	18.507	15.649	38.014
	S2 1	1.207	18.951	15.699	38.614
	S2 2	1.220	19.214	15.748	38.964
	S3 0	1.150	17.908	15.576	37.414
	S3 1	1.150	17.890	15.552	37.156
	S3 2	1.160	18.183	15.674	38.027
	S4 0	1.201	18.879	15.723	38.494
	S4 1	1.211	19.066	15.748	38.879
	S4 2	1.213	19.064	15.723	38.714
SSP	S1 0	1.189	18.746	15.773	39.121
	S1 1	1.199	18.976	15.823	39.467
	S1 2	1.205	19.103	15.848	39.662
	S2 0	1.203	19.070	15.848	39.547
	S2 1	1.191	18.790	15.773	39.076
	S2 2	1.192	18.776	15.748	38.965

Table A-14 Soil pH and trace metal concentrations (mg/kg) of crop soils of the Pearl River Delta

Soil ID[a]	pH	Cd	Co	Cr	Cu	Ni	Pb	V	Zn
C2	4.63	0.14	0.93	35.1	5.83	5.07	16.7	22.4	21.3
C4	5.52	0.77	5.99	62.1	25.0	15.7	82.5	32.5	123
C5	-	0.82	13.9	72.9	34.7	29.3	29.0	43.2	95.2
C7	-	n.d.	0.61	16.3	4.10	4.08	12.5	13.2	21.9
C9	-	0.26	1.67	51.6	10.9	8.73	26.4	43.2	39.6
C10	-	0.01	1.09	27.3	7.61	5.92	18.7	24.6	43.9
C11	-	0.75	10.0	68.2	31.0	23.1	67.6	36.6	119
C12	6.03	0.74	10.2	67.6	59.7	33.7	69.8	40.2	181
C14	-	0.06	2.75	14.8	8.08	5.66	18.7	12.4	36.8
C15	6.24	0.31	6.03	52.2	17.0	18.2	36.2	35.7	63.5
C17	-	0.83	11.8	68.1	35.0	24.9	41.2	44.8	99.1
C19	7.22	0.57	8.09	52.4	23.8	18.9	32.4	33.4	73.4
C20	-	0.76	12.0	62.9	29.6	24.5	39.0	42.7	96.8
C21	7.09	1.36	16.7	150	83.9	29.3	180	40.1	85.1
C25	-	0.85	12.6	69.2	30.6	26.9	23.9	45.3	82.1
C26	-	0.95	14.4	317	189	62.5	29.8	48.1	284
C27	-	1.11	16.9	94.0	47.5	34.0	28.0	68.0	94.5
C28	-	n.d.	0.00	5.66	4.57	1.45	14.8	3.26	17.5
C34	-	n.d.	1.70	29.9	9.83	6.42	25.7	20.9	24.9
C36	-	n.d.	10.3	39.7	12.8	12.0	52.0	23.7	65.6
C38	-	0.82	15.8	103	51.8	36.8	30.4	76.0	101
C42	-	0.48	11.3	83.6	36.1	25.1	90.5	46.5	118
C43	-	n.d.	1.88	39.9	17.4	5.98	32.5	38.4	44.0
C46	-	n.d.	1.50	22.5	17.1	8.97	28.2	13.5	43.2
C50	-	0.57	12.9	88.8	37.6	30.9	38.0	58.8	94.3
C52	-	0.64	14.4	97.7	43.7	32.6	29.2	65.4	92.5
C53	-	1.00	16.3	102	51.1	36.3	34.2	65.1	115
C54	-	0.62	14.1	96.4	51.3	33.5	35.3	66.0	117
C55	5.78	1.47	16.6	96.7	55.5	35.8	32.8	61.5	155
C56	5.60	1.45	16.9	97.0	48.3	35.5	38.1	60.7	124
C57	-	0.95	13.0	80.7	35.2	29.8	35.5	42.1	93.5
C58	-	0.68	7.84	69.6	19.1	17.7	47.7	36.4	74.0
C59	-	0.81	9.36	76.1	24.9	19.5	48.0	44.8	77.1
C62	4.06	0.59	7.89	109	18.0	16.4	45.1	38.6	68.9
C63	-	0.68	7.61	65.0	16.4	17.3	36.6	36.6	65.7
C64	6.66	0.33	11.1	37.7	38.0	9.66	18.3	26.2	93.2
C70	-	0.48	5.69	56.5	10.9	13.7	36.0	38.1	41.8
C73	-	0.07	3.96	24.6	9.11	6.65	22.9	19.2	38.6
C75	-	0.05	0.38	17.8	4.88	3.08	10.1	10.6	11.1

a. Prefixes "C", "P", and "N" symbolize crop, paddy and natural soils, respectively.

Table A-15 Soil pH and trace metal concentrations (mg/kg) of paddy and natural soils of the Pearl River Delta

Soil ID[a]	pH	Cd	Co	Cr	Cu	Ni	Pb	V	Zn
P29	-	0.77	16.9	99.5	50.5	36.1	29.6	71.8	98.4
P31	-	n.d.	2.06	24.5	11.4	6.57	28.9	19.6	35.7
P35	-	n.d.	2.06	26.9	13.6	8.30	38.4	20.9	49.2
P37	-	n.d.	3.46	32.7	8.95	7.21	81.3	18.0	56.9
P40	-	0.72	15.7	89.1	43.9	32.7	31.7	61.2	102
P41	-	0.08	2.39	50.7	14.6	8.90	32.5	25.8	40.9
P44	5.69	n.d.	0.74	19.1	10.1	4.54	21.7	12.5	18.5
P47	-	0.45	11.8	85.5	32.2	28.3	43.4	54.9	93.6
P48	-	0.60	11.2	90.6	36.7	29.1	44.6	58.8	102
P49	-	0.50	12.4	90.5	38.6	29.5	36.6	64.1	92.1
P51	-	0.90	14.5	90.4	42.4	32.3	36.4	60.5	107
P61	-	0.65	9.41	56.1	13.9	16.2	37.2	31.4	70.0
P72	5.90	0.10	2.77	27.1	3.02	6.13	45.3	19.7	38.5
P74	-	0.19	4.34	45.8	14.3	11.6	31.3	31.5	44.5
P76	5.69	0.17	1.86	56.4	7.49	9.60	15.9	27.7	26.3
P77	-	n.d.	1.67	22.8	4.59	6.56	32.4	12.9	19.8
P78	-	0.01	1.78	30.1	11.7	8.80	26.4	21.1	39.5
P79	-	0.29	4.95	52.5	13.1	16.2	38.2	30.3	51.7
P80	-	0.78	7.01	79.2	30.9	23.3	49.9	45.9	81.9
N1	4.30	0.33	1.09	52.6	5.97	6.31	26.3	33.9	24.9
N3	-	0.35	0.83	64.0	1.41	6.68	21.0	27.1	26.2
N6	-	0.17	3.08	35.7	9.06	12.8	46.9	23.5	42.1
N8	-	0.43	1.69	50.5	22.4	9.22	32.9	28.4	66.2
N13	-	0.62	8.43	41.3	23.6	19.4	38.7	30.1	69.2
N15	4.61	1.36	12.2	136	27.5	31.0	54.7	114	84.9
N16	-	0.09	0.92	21.8	4.63	4.28	25.0	15.5	19.3
N22	5.18	1.49	39.9	144	35.9	78.6	17.8	106	110
N23	4.68	0.61	12.6	66.0	30.7	26.9	30.2	47.6	99.2
N24	-	0.82	13.5	69.3	44.0	26.5	53.7	40.0	103
N30	-	n.d.	0.32	42.9	8.57	4.37	134.8	20.9	14.9
N32	-	n.d.	0.22	13.3	1.64	4.41	18.7	4.9	22.5
N33	-	n.d.	2.71	22.5	3.63	7.28	39.5	14.0	30.3
N45	-	n.d.	0.66	29.1	3.35	3.68	15.1	16.0	27.2
N65	-	0.51	12.1	48.2	17.9	16.9	40.4	21.6	52.4
N66	4.50	n.d.	1.26	18.6	5.54	7.17	38.7	9.4	23.0
N68	4.58	0.76	16.1	73.3	21.7	25.2	22.4	47.8	80.9
N69	4.07	0.12	0.38	24.5	2.49	6.31	7.74	6.67	14.8
N71	-	1.76	0.53	22.4	3.85	3.55	8.33	10.2	15.8
N81	-	n.d.	1.59	20.0	5.59	7.78	43.5	10.1	26.6

a. Prefixes “C”, “P”, and “N” symbolize crop, paddy and natural soils, respectively.

Table A-16 Major metal concentrations (mg/kg) of crop soils of the Pearl River Delta

Soil ID	Ca	Fe	Mg	Mn
C2	537	11835	525	29.2
C4	1478	16323	1594	119
C5	1462	17748	3619	359
C7	507	5083	320	43.4
C9	1463	13692	819	36.8
C10	959	8378	622	17.0
C11	2298	17867	2587	294
C12	4931	16512	2574	277
C14	1156	6386	789	161
C15	1871	13941	1610	181
C17	2792	18257	3196	649
C19	2640	14813	2050	239
C20	2767	16657	3155	422
C21	4881	13719	3826	271
C25	6440	17775	4062	565
C26	7676	19037	4576	619
C27	5288	20736	4908	693
C28	363	3491	114	36.0
C34	126	10804	483	41.6
C36	619	12799	1391	189
C38	2501	20199	4655	712
C42	2808	19408	3141	533
C43	791	15468	612	67.5
C46	847	7826	727	50.3
C50	1401	20203	3972	411
C52	1549	20764	4489	475
C53	4850	21247	5814	816
C54	2675	19897	4211	488
C55	3256	20909	4464	707
C56	3398	20666	4247	774
C57	964	18642	3664	384
C58	1118	18001	2329	148
C59	853	18845	2715	339
C62	1307	17057	2105	167
C63	644	17671	2370	191
C64	1449	12211	1330	139
C70	878	15169	1089	162
C73	342	9446	954	197
C75	146	7754	276	27.6

Table A-17 Major metal concentrations (mg/kg) of paddy and natural soils of the Pearl River Delta

Soil ID[a]	Ca	Fe	Mg	Mn
P29	3020	20975	5043	839
P31	780	7817	588	48.1
P35	928	9613	720	79.0
P37	1072	13799	742	100
P40	2450	19458	4308	514
P41	1313	15939	974	80.1
P44	618	7888	403	17.2
P47	1415	19982	3677	359
P48	2366	20750	3802	296
P49	1783	20167	4327	289
P51	5228	19943	4870	752
P61	1130	16200	1812	347
P72	904	12276	746	87.9
P74	594	11785	1067	53.9
P76	1038	11083	872	31.5
P77	684	6388	478	51.7
P78	1137	6533	724	36.6
P79	1667	12703	1586	80.4
P80	1283	17932	1984	77.1
N1	144	15687	744	24.9
N3	141	15522	881	18.3
N6	191	13240	2143	64.7
N8	777	14876	1350	68.9
N13	1524	14483	478	809
N15	603	24397	801	522
N16	156	9842	501	25.6
N22	3232	24671	13154	914
N23	1188	15442	3677	307
N24	1417	17594	3442	497
N30	83.2	13868	328	30.2
N32	91.0	6828	284	51.3
N33	56.0	10766	486	180
N45	427	10904	343	77.7
N65	145	15638	1171	354
N66	153	9681	407	64.9
N68	983	17458	5177	299
N69	117	10968	252	27.2
N71	475	7783	324	34.0
N81	78	9848	459	65.6

a. Prefixes "P" and "N" symbolize paddy and natural soils, respectively.

Table A-18 Lead isotopic composition of soil Pb of the Pearl River Delta

Soil ID[a]	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	$^{206}Pb/^{207}Pb$	$^{206}Pb/^{208}Pb$
C4	18.4938	15.3846	38.1338	1.2021	0.4850
C12	18.0213	15.2439	37.2378	1.1822	0.4840
C19	18.4330	15.4083	37.9476	1.1963	0.4857
C21	17.8997	15.1976	36.9179	1.1778	0.4849
C62	18.3471	15.2905	37.7370	1.1999	0.4862
C64	17.9281	15.2905	37.5015	1.1725	0.4781
P72	18.5215	15.3846	38.4908	1.2039	0.4812
P76	18.7635	15.4560	38.3802	1.2140	0.4889
N22	17.8872	15.2439	37.2332	1.1734	0.4804
N23	18.4508	15.3846	37.9492	1.1993	0.4862

a. Prefixes "C", "P", and "N" symbolize crop, paddy and natural soils, respectively.

Table A-19 Lead isotopic composition of Pb in the five chemical fractions of soils from the Pearl River Delta

Soil ID[a]		$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	$^{206}Pb/^{207}Pb$	$^{206}Pb/^{208}Pb$
C4	F1[b]	18.5365	15.5521	38.5272	1.1919	0.4811
	F2	18.8281	15.7729	39.6404	1.1937	0.4750
	F3	18.6782	15.6986	38.7786	1.1898	0.4817
	F4	18.8278	15.7978	39.3712	1.1918	0.4782
	F5	18.7398	15.6740	38.8056	1.1956	0.4829
C12	F1	17.7465	15.3610	37.3579	1.1553	0.4750
	F2	18.4992	15.7480	39.0803	1.1747	0.4734
	F3	18.3532	15.6986	38.3830	1.1691	0.4782
	F4	18.3611	15.6986	38.4097	1.1696	0.4780
	F5	18.6289	15.7233	38.8129	1.1848	0.4800
C19	F1	18.9073	16.2602	39.5138	1.1628	0.4785
	F2	18.4191	15.4083	38.7535	1.1954	0.4753
	F3	18.7270	15.8730	39.4079	1.1798	0.4752
	F4	18.7136	15.8228	39.3323	1.1827	0.4758
	F5	18.9226	15.7978	39.7630	1.1978	0.4759
C21	F1	18.0510	15.4560	37.7790	1.1679	0.4778
	F2	18.3501	15.6986	38.7645	1.1689	0.4734
	F3	17.7424	15.2439	37.6845	1.1639	0.4708
	F4	18.2278	15.6006	37.9953	1.1684	0.4797
	F5	18.6420	15.7729	38.9369	1.1819	0.4788

a. Prefixes "C", "P", and "N" symbolize crop, paddy and natural soils, respectively.

b. F1: exchangeable fraction; F2: carbonate fraction; F3: Fe-Mn oxide fraction; F4: organic fraction; F5: residual fraction.

Table A-19 (con't) Lead isotopic composition of Pb in the five chemical fractions of soils from the Pearl River Delta

Soil ID[a]		^{206}Pb/^{204}Pb	^{207}Pb/^{204}Pb	^{208}Pb/^{204}Pb	^{206}Pb/^{207}Pb	^{206}Pb/^{208}Pb
C62	F1[b]	18.3292	15.3846	37.9246	1.1914	0.4833
	F2	18.7190	15.6986	39.3548	1.1924	0.4756
	F3	18.7563	15.8228	39.2785	1.1854	0.4775
	F4	18.7911	15.8228	39.3576	1.1876	0.4774
	F5	18.8880	15.7729	39.3360	1.1975	0.4802
C64	F1	20.7531	17.8891	43.9070	1.1601	0.4727
	F2	18.4485	15.8479	39.3249	1.1641	0.4691
	F3	18.3618	15.7978	38.9668	1.1623	0.4712
	F4	18.3797	15.8228	39.2421	1.1616	0.4684
	F5	18.9968	15.9236	41.1322	1.1930	0.4618
P72	F1	18.6588	15.6495	38.7512	1.1923	0.4815
	F2	18.7233	15.7233	39.7579	1.1908	0.4709
	F3	18.7161	15.7729	39.6356	1.1866	0.4722
	F4	18.8241	15.8479	39.9651	1.1878	0.4710
	F5	18.8152	15.7978	39.8768	1.1910	0.4718
P76	F1	18.2703	15.6250	38.2313	1.1693	0.4779
	F2	18.2016	15.6250	38.7031	1.1649	0.4703
	F3	18.2088	15.6986	38.8179	1.1599	0.4691
	F4	18.3134	15.7480	39.0063	1.1629	0.4695
	F5	19.0859	15.8983	40.4960	1.2005	0.4713
N22	F1	17.9400	15.3846	37.4831	1.1661	0.4786
	F2	18.5039	15.7978	39.5450	1.1713	0.4679
	F3	18.4841	15.8730	39.4095	1.1645	0.4690
	F4	18.5342	15.8983	39.4229	1.1658	0.4701
	F5	18.4227	15.7729	39.0536	1.1680	0.4717
N23	F1	18.4000	15.3846	38.0077	1.1960	0.4841
	F2	18.8975	15.7729	39.5442	1.1981	0.4779
	F3	18.7181	15.7480	39.3102	1.1886	0.4762
	F4	18.8120	15.7978	39.4060	1.1908	0.4774
	F5	19.0984	15.8730	40.1317	1.2032	0.4759

a. Prefixes "C", "P", and "N" symbolize crop, paddy and natural soils, respectively.

b. F1: exchangeable fraction; F2: carbonate fraction; F3: Fe-Mn oxide fraction; F4: organic fraction; F5: residual fraction.

APPENDIX B REGULATORY GUIDELINES

The Netherlands Soil Contamination Guidelines (Department of Soil Protection, Netherlands, 1994), as known as, the Dutch Soil Standard, contains a set of target values, "T" values, and a set of investigative values, "I" values. Soil trace metal concentrations below the "T" values indicate that the concentrations are within the maximum background levels. On the other hand, exceeding the "T" values would signify possible soil contamination. If the "I" values were exceeded, undertaking of an immediate investigation and possible remediation would be demanded.

Table B-1 The Netherlands Soil Regulatory Guidelines

Elements	Target Value	Intervention Value
As	29	55
Ba	200	625
Cd	0.8	12
Cr	100	380
Co	20	240
Cu	36	190
Hg	0.3	10
Pb	85	530
Mo	10	200
Ni	35	210
Zn	140	720

In comparison with the Dutch Soil Standard, the Canadian Environmental Quality Guidelines (CCME, 1997) simply provides the maximum allowable concentrations of trace metals in soils of different land uses. Trace metal concentrations of soils of sensitive usage, e.g. residential and agricultural purposes, are strictly regulated, while those for industrial purposes are comparatively relaxed. Recognition of the important relationship between soil usage and potential implications of trace metal contamination on human health could greatly improve potential practicality and effective implementation of the guidelines, wherein compromises between limited resources and human health protection are often required.

Table B-2 Canadian Environmental Quality Guidelines for Soils for various types of land use (mg/kg)

Metals	Land use			
	Agricultural	Residential/Park	Commercial	Industrial
As	12	12	12	12
Ba	750	500	2000	2000
Cd	1.4	10	22	22
Co	N/A[a]	N/A	N/A	N/A
Cr	64	64	87	87
Cr (VI)	0.4	0.4	1.4	1.4
Cu	63	63	91	91
Hg	6.6	6.6	24	50
Mo	N/A	N/A	N/A	N/A
Mn	N/A	N/A	N/A	N/A
Ni	50	50	50	50
Pb	70	140	260	600
V	130	130	130	130
Zn	200	200	360	360

[a] not available

The Chinese National Soil Quality Standards (National Environmental Protection Agency, 1995) has a hierarchical system that classifies soils into three classes based on trace metal concentrations and agricultural purposes. In general, soils containing trace metal concentrations below the Class A values are considered uncontaminated and representative of the natural background levels. If trace metal concentrations of soils are higher than those in Class A but below those in Class B, agricultural uses of these soils may continue. However, soils must not contain trace metals at levels higher than Class C, and soil pH must remain above 6.5 to allow agricultural production.

Table B-3 Chinese National Soil Quality Standards

Elements		Grade A	Grade B (pH<6.5)	Grade C (pH>6.5)
Cd		≤ 0.2	0.30	1.0
Cr	Paddy soil	≤ 90	250	400
	Dryland	≤ 90	150	300
Co		N/A[a]	N/A	N/A
Cu	Farmland	≤ 35	50	400
	Orchard	≤ -	150	400
Pb		≤ 35	250	500
Mo		N/A	N/A	N/A
Ni		≤ 40	40	200
V		N/A	N/A	N/A
Zn		≤ 100	200	500

a. not available