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Pb contamination and isotopic composition of urban soils in Hong Kong

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Abstract

In the urban environment, intense human activities can lead to degradation of environmental quality and have potential long-term effects on human health. In the present study, Pb contamination of urban soil cores in Hong Kong was investigated using a combination of the "total" concentration, chemical partitioning and isotopic composition of Pb in the soils. The analytical results showed that urban soil cores in close vicinity to high traffic volumes (>40,000 vehicles per day) were usually contaminated with Pb, suggesting atmospheric deposition of Pb as a consequence of vehicular emissions arising from the combustion of leaded gasoline in the past. Increasing Pb concentrations were generally associated with decreasing $^{206}Pb/^{207}Pb$ ratios of the contaminated soil cores, offering strong evidence of accumulation of Pb derived from anthropogenic sources. In selected contaminated soil cores, the $^{206}Pb/^{207}Pb$ ratios tended to increase in the order: carbonate < exchangeable < Fe-Mn oxide < organic < residual fractions. The distribution of the $^{206}Pb/^{207}Pb$ ratios in the five operationally defined chemical fractions showed that the $^{206}Pb/^{207}Pb$ ratios generally increased with increasing stability, demonstrating preferential association of anthropogenic Pb with the carbonate, exchangeable, Fe-Mn oxide and organic fractions in the soils.

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Keywords: Pb contamination; Pb isotope; chemical partitioning of Pb; urban soils; Hong Kong

1. Introduction

According to the United Nations, over 45% of the world's total population currently resides in urban areas, and this figure is projected to surpass the majority benchmark, reaching 60% by 2030 (United Nations, 2001). As the urban population continues to grow, understanding of urban environmental quality and its associated implications for the environment and human health is becoming increasingly important. In the urban environment, where population and traffic densities tend to be high, the influences of intense human activities are profound and far-reaching.

Human activities have significantly increased the global emissions of trace metals in the surface environment (Nriagu, 1979; Nriagu and Pacyna, 1988). It is generally believed that anthropogenic releases of Pb in the environment in the modern era are largely attributable to the use of tetraethyl lead in leaded gasoline as an anti-knock agent. Due to the non-biodegradability and cumulative tendency of Pb, the prevalent use of tetraethyl lead has left behind footprints of Pb contamination in the surface environment (Lau and Wong, 1982; Francek, 1992; Othman et al., 1997; Lin et al., 1998; Sutherland et al., 2000). Soils represent a major sink for heavy metals in the terrestrial environment (Adriano, 1986). Excessive accumulation of Pb in urban soils may result not only in heavy metal contamination of the soils but also in increased human exposure to Pb due to

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its close proximity to human activities, causing long-term potential health concerns (Nriagu and Pacyna, 1988; Kelly et al., 1996, Li et al., 2001).

Pb is a biologically non-essential heavy metal. It is teratogenic, carcinogenic, toxic at low concentrations and bioaccumulative in organisms. The toxicological effects of Pb are particularly detrimental to young children, since it tends to damage the nervous system, resulting in retardation of normal brain development. Other physiological effects of over-exposure to Pb include anaemia, coma, and neurological defects. Young children are also more vulnerable to Pb poisoning than adults because of their hand-to-mouth activity and unique physiology (Watt et al., 1993; Hrudey et al., 1996). The natural background blood Pb level is estimated to be 0.016 μg/dl (Flegal and Smith, 1992). The World Health Organization currently defines Pb poisoning as having a blood Pb 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 Pb level, may also result in long-term negative effects on the normal brain development of children (Needleman, 1980).

Pb isotopic analysis has been increasingly applied in environmental studies of Pb contamination of air (Chiaradia et al., 1997; Flament et al., 2002), soils (Hansmann and Koppel, 2000; Wong et al., 2002), sediments (Farmer et al., 1996; Kersten, 1997; Erel et al., 2001), and plants (Gelinas and Schmit, 1997; Marcantonio et al., 1998). Pb in the environment has four isotopic forms, ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb. ^{204}Pb is non-radiogenic and therefore remains stable over time. ^{206}Pb, ^{207}Pb and ^{208}Pb are radiogenic and derived from ^{238}U, ^{235}U and ^{232}Th, respectively. The isotopic characteristics of Pb are dependent upon the original composition and age of the ore bodies. In general, the

^{206}Pb/^{207}Pb ratios of naturally derived Pb are high (>1.20). In comparison, the ^{206}Pb/^{207}Pb ratios of anthropogenic Pb tend to be low, ranging from 0.96 to 1.20 (Sturges and Barrie, 1987). Owing to these inherited differences in Pb isotopic signatures between natural and anthropogenic Pb, the use of Pb isotopic analysis can assist in the identification of Pb sources and, in some cases, may also enable the apportionment of Pb contaminant sources (Gélinas and Schmit, 1997; Kersten, 1997; Marcantonio, et al., 1998; Semlali et al., 2001).

Since the recognition of its potential long-term environmental and health implications, the sale of leaded gasoline has been gradually phased out in many parts of the world, including Hong Kong. A stepwise reduction of tetraethyl lead in leaded gasoline was initiated by the Hong Kong Government in 1992. The sale of leaded gasoline was officially banned in April 1999 (EPD, 2000). Previous assessments of urban soils in Hong Kong have found elevated concentrations of Pb in many locations, including those in playgrounds and parks (Lau and Wong, 1982; Tam et al., 1987; Ho and Tai, 1988; Wong, 1996; Wong et al., 1996; Chen et al., 1997; Wong and Mak, 1997; Li et al., 2001). In addition to traffic emissions, these studies have also indicated that Pb contamination of urban soils in Hong Kong could also be caused by other sources, such as atmospheric Pb emissions from industrial activities, coal burning and land applications of agrochemicals (Wong et al., 1996; Li et al., 2001).

Despite the availability of valuable information from previous studies, the vertical distribution of Pb in the urban soils of Hong Kong is seldom investigated. Furthermore, information on the isotopic composition of Pb in urban soils, as well as other environmental compartments in Hong Kong, is rare. So far, few studies have revealed differences in the chemical distribution of anthropogenic and naturally-derived Pb in urban soils. An understanding of the possible relationship between the distribution of

anthropogenic and natural Pb and chemical partitioning of the contaminant in soils may provide vital information regarding the geochemical properties of natural and anthropogenic Pb. Hence, the primary objectives of the present study were 1) to assess the Pb contamination of urban soil cores in Hong Kong, 2) to study the chemical partitioning of Pb using a 5-step sequential chemical extraction method, 3) to examine the isotopic composition of total Pb and Pb in various chemical forms in the soils, and 4) to identify possible sources of the contaminant in the urban soils.

2. Methods and materials

2.1 Study area

Hong Kong is situated in the subtropical region, adjoining Guangdong Province in southern China (see Fig. 1). It is one of the most densely populated and trafficked cities in the world. Hong Kong has a total area of 1,086 km^2, which is comprised of Hong Kong Island (HK Is.), the Kowloon Peninsular (KL), the New Territories and outlying islands (NT). Its population of 6.8 millions and associated urban and industrial development have generally been concentrated on approximately 18% of the total area, due to the predominance of a mountainous landscape. The population densities on HK Is. and in KL and the NT are 17,200, 44,210 and 3,520 persons/km^2, respectively.

2.2 Study sites

Five study sites including four urban parks and one roadway divider were chosen within the urban environment of KL. The four urban parks included Carpenter Road Park (CRP), Hutchison Park (HC), Sham Shui Po Park (SSP), and a leisure park situated at the intersection between Nathan Road and Gascoigne Road (NG). The study sites are generally situated in commercial and/or residential areas with annual average daily traffic (AADT) ranging from relatively low (~8,500 vehicles per day) to high (>42,600 vehicles per day). Generally, urban soils in these four study sites were vegetated and managed as garden soils. Situated immediately adjacent to both directions of traffic (AADT >44,200 vehicles per day), the roadway divider, namely CSW, stretched from a residential area to an industrial area along Cheung Sha Wan Road. Soils in CSW were also vegetated, but management was kept minimal due to limited access.

2.2 Sample collection and analysis

Multiple urban soil cores were collected from each of the five study sites using a stainless steel hand auger in the spring of 2000. Soil cores up to 40 cm in length were collected at CRP and HC and sliced at 10-cm intervals. However, owing to the presence of rubble at the subsurface layers, soil cores at NG and SSP reached a maximum depth of 30 cm, and soil cores of 20 cm were collected at CSW. To ensure the representativeness of soil samples from each study site, composite soil sampling strategy was used in this study. Each of the composite soil samples, except for those at CSW, was bulked from the corresponding sections (0-10, 10-20, 20-30, 30-40 cm) of 9 individual cores collected over a 2 m $\times$ 2 m grid and then stored in polyethylene bags. Due to the elongated shape

of the CSW site, each of the composite soil samples was made up of six individual cores collected along the middle of the roadway divider. The number of composite soil samples was determined according to the size of the study site. Sampling locations were chosen based on the field conditions to avoid slope, metallic objects and obvious soil disturbance.

The collected soil samples were dried at 50^oC for 3 days in an oven and sieved through a 2 mm-polyethylene sieve to remove stones and other coarse debris. The soil samples (<2.0 mm) were homogenized and then ground in a mortar with a pestle until fine particles were obtained. To determine the Pb concentrations of the soils, the prepared samples were treated using a strong acid digestion method (Wong et al., 2002). Briefly, the soil samples (0.250 g) were digested in concentrated HNO_3 and $HClO_4$ (4:1) by volume. The mixtures were heated progressively in an aluminum block until they were nearly dry. 10.0 ml of 5% (v/v) HNO_3 were then added to the test tubes and heated at 70^oC for 1 hr. Upon cooling, the solutions were decanted into polyethylene tubes and centrifuged at 3500 rpm for 10 minutes. Pb concentrations of the solutions were measured by inductively coupled plasma–atomic emission spectrometry (ICP-AES *Perkin-Elmer Optima 3300DV*). For quality control, blanks, replicates and standard reference materials (NIST SRM 2709 San Joaquin Soil) were inserted into the sample batch, representing 10%, 20% and 10% of the sample population, respectively. The precision and bias in the analysis were generally <10%. The overall Pb recovery rate of the standard reference material (18.9 mg/kg) was ~85%.

The chemical partitioning of Pb in selected soil cores at the contaminated study sites (CSW and NG) and one slightly contaminated site (CRP) was determined using a modified Tessier's 5-step sequential chemical extraction method as described in Li et al. (1995). The extracted metals from these five consecutive steps are operationally defined

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into five chemical fractions: 1) readily soluble and exchangeable (exchangeable), 2) carbonate-bound, specifically adsorbed, and weak organic and inorganic complexes (carbonate), 3) bound to iron and manganese oxides (Fe-Mn oxide), 4) bound to stable complexes of organic and/or sulphide (organic), and 5) residual fraction containing primary and secondary minerals held within their crystal structure, respectively (residual). It is generally acknowledged that the reactivity and potential bioavailability of heavy metals increase with increasing solubility (Li and Thornton, 2001). The exchangeable and carbonate fractions are the two most mobile forms of metals in soils and are hence considered potentially bioavailable. Heavy metals in the Fe-Mn oxide and organic fractions are usually relatively immobile and stable, but may sometimes become mobile and bioavailable with time or upon changes of soil conditions, e.g. decrease in soil pH. Heavy metals in the residual fraction are regarded as the most stable and least bioavailable form. Quality control measures similar to those in the total metal analysis were implemented. The Pb concentrations of the extracted solutions were measured by ICP-AES. The Pb concentrations of procedural blanks were generally <5% of those of the analytical samples. The recovery rates calculated based on the sum of the five fractions over the total metal concentrations determined independently ranged between 85% and 110%.

All solutions from the strong acid digestion were diluted using 5% HNO_3 and analyzed for Pb isotopic composition using Inductively Coupled Plasma – Mass Spectrometry (ICP-MS *Perkin Elmer Elan 6100 DRC^{Plus}*). Moreover, one core in each study site was selected for determination of the isotopic composition of Pb in the five chemical fractions by ICP-MS. Instrumental parameters of 200 sweeps/reading, nine readings and a dwell time of 50 ms were set. The relative standard deviation (RSD) of

the nine measurements of each of the solutions was <0.3%. A standard reference material, the Common Lead Isotopic Standard (NIST SRM 981), was used for calibration and quality control. Blank solution (5% HNO_3) and the standard reference material were inserted after every 10 sample solutions, to detect any drift. The average measured $^{206}Pb/^{207}Pb$ ratio of the standard reference material (NIST SRM 981) was 1.0936 ± 0.0027, which was in good agreement with the certified standard value (1.0933).

3. Results and Discussion

3.1 Pb concentrations of urban soil cores

The mean Pb concentrations and ranges of urban soil cores at the five study sites are presented in Table 1. In addition, the annual average daily traffic (AADT) of the study sites and regulatory values of the Netherlands Soil Contamination Guidelines are also included. Since Hong Kong has not established its own soil regulatory guidelines, the Netherlands Soil Contamination Guidelines, commonly referred to as the Dutch Soil Standard, are used to evaluate the Pb contamination of soils (Department of Soil Protection, Netherlands, 1994). According to the Dutch Soil Standard, soil Pb concentrations below the target value, T, indicate that the concentrations are within the maximum background levels. However, soil Pb concentrations exceeding the T value suggest that the soils may be contaminated. Soil Pb concentrations higher than the intervention value, I, indicate that the soils are contaminated and immediate investigation and possible remediation are required.

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The results showed that the mean Pb concentrations of the soil cores at CSW and NG exceeded the T value of 85 mg/kg, which suggests possible Pb contamination of the soils. The soil cores collected at CRP, HC and SSP were generally considered relatively uncontaminated, as the mean Pb concentrations of the soil cores were below the T value. Although the analytical results indicated that the soil Pb concentrations of all of the study sites were below the I value, indicating that no immediate investigative or remedial action was required, the upper ranges of Pb concentrations of the soils at all of the study sites exceeded the T value, strongly suggesting extensive Pb enrichment in urban soils of Hong Kong. The vertical distribution of Pb at CSW exhibited topsoil enrichment patterns substantiated by the elevated Pb concentrations of the surface soils (0-10 cm) relative to those of the subsurface (10-20 cm). Furthermore, Pb contamination was found throughout the soil cores at NG, indicative of the possible downward movement of Pb and/or mixing effects as a consequence of soil tillage and planting.

3.2 Chemical partitioning of Pb

The chemical partitioning of Pb in the selected soil cores at the contaminated sites, CSW and NG, is depicted in Fig. 2, and that at the comparatively uncontaminated site CRP is also included for comparison. Despite the differences in Pb concentrations at the three sites, the distribution of Pb in the five chemical fractions displayed a similar pattern. In general, the results showed that Pb was predominantly associated with the Fe-Mn oxide fraction in the study areas, accounting for ~60% of the total Pb in soils. This was in agreement with previous studies (Harrison et al., 1981; Li et al., 2001; Wong et al., 2002), where Fe-Mn oxides acted as important scavengers of Pb in soils. The second

largest fraction of Pb was found in the carbonate fraction (10-20% of the total Pb). Pb in the organic and residual fractions collectively accounted for about 20% of the total Pb, and the percent distribution of the organic fraction decreased slightly with increasing depth. It appeared that the decreases in the organic fraction were compensated by increases in the percent distribution of the Fe-Mn oxide fraction, which could be explained by the relatively high organic content in the surface soils. Pb in the exchangeable fraction was the lowest among the five fractions. The chemical partitioning of the Pb generally showed that the majority of the Pb in the soils was relatively stable. Nonetheless, the comparatively significant association of Pb with the carbonate fractions indicated that ~20% of the total Pb (~15-35 mg/kg) could be easily soluble and potentially bioavailable in these urban soils.

3.3 Isotopic composition of total Pb and Pb in the five chemical fractions

The means and ranges of $^{206}Pb/^{207}Pb$ ratios in the soil cores are provided in Table 2. In Hong Kong, information on the Pb isotopic composition of environmental samples is rare. In order to effectively evaluate the analytical results and identify the potential sources of anthropogenic Pb in the soils, the Pb isotopic signatures of some geological materials, including granite, volcanic rocks and uncontaminated soils, in the neighboring Pearl River Delta region are used (see Table 3). According to Zhu (1995), the isotopic composition of the background geological materials in Southern China can be characterized as $^{206}Pb/^{204}Pb > 18.4$, $^{207}Pb/^{204}Pb > 15.53$ and $^{208}Pb/^{204}Pb > 38.4$ ($^{206}Pb/^{207}Pb > 1.185$). Table 3 also contains the $^{206}Pb/^{207}Pb$ ratios of Pb derived from major Pb ore bodies in various parts of the world. A comparison of the $^{206}Pb/^{207}Pb$

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isotopic ratios between the geological materials in the region and anthropogenic Pb derived from the various Pb ores showed that the $^{206}Pb/^{207}Pb$ ratios of anthropogenic Pb are usually lower than those of the background geogenic sources.

The mean $^{206}Pb/^{207}Pb$ ratios of the soil cores varied from 1.131 ± 0.008 at CSW to 1.212 ± 0.006 at HC. The mean $^{206}Pb/^{207}Pb$ ratios of total Pb at CRP, HC and SSP were relatively high and generally comparable with those of the natural Pb. At HC and SSP, Pb in the various soil cores at the two sites had similar $^{206}Pb/^{207}Pb$ ratios. Furthermore, the $^{206}Pb/^{207}Pb$ ratios at HC and SSP remained relatively stable with depth, giving evidence of relatively little contamination with Pb of low $^{206}Pb/^{207}Pb$ ratios in these two sites. In contrast, the $^{206}Pb/^{207}Pb$ ratios of total Pb at CSW and NG tended to increase with increasing soil depth. Such a vertical distribution strongly indicated topsoil enrichment of Pb with low $^{206}Pb/^{207}Pb$ ratios at these study sites. The $^{206}Pb/^{207}Pb$ ratios of total Pb at CSW and NG, particularly of the surface soils, were noticeably lower than the natural background values, giving a strong indication of the presence of anthropogenic Pb in the soils. Since these two sites were in close proximity to high traffic volumes, Pb contamination of the soils was partially attributed to Pb input from vehicular emissions. As shown in Table 2, the standard deviation for the four soil cores at NG was relatively large. For example, four composite soil cores (namely SP1, SP2, SP3 and SP4) were collected at NG. The $^{206}Pb/^{207}Pb$ ratios of the four composite soil samples at the top layer (0-10 cm) were 1.143, 1.183, 1.150 and 1.201, corresponding to Pb concentrations of 207, 196, 202 and 393 mg/kg, respectively. The standard deviation was calculated using these $^{206}Pb/^{207}Pb$ ratios, resulting in a mean ratio of 1.169 ± 0.027 as shown in Table 2. The wide range of $^{206}Pb/^{207}Pb$ ratios at this site could indicate the influence of the wide range

of the Pb concentrations in these soils and/or that the soil samples could be contaminated with Pb derived from different sources.

The $^{206}Pb/^{207}Pb$ ratios in the five chemical fractions from three selected individual samples, one each from CRP, CSW and NG are depicted in Fig. 3. Pb concentrations of the soil core at CRP were 49.4, 62.8, 73.9 and 96.5 mg/kg at 0-10, 10-20, 20-30 and 30-40 cm, respectively. This soil core was selected for comparison purposes because of the "inverted" vertical distribution of Pb (Pb enrichment in subsoil) and comparatively low Pb concentrations as compared to CSW and NG. As shown in Fig. 3a, the $^{206}Pb/^{207}Pb$ ratios of the surface soils (0-10 and 10-20 cm) were generally higher than those of the subsurface layers (20-30 and 30-40 cm), which were consistent with the distribution of soil Pb concentrations. The $^{206}Pb/^{207}Pb$ ratios of Pb in the residual fraction were always higher than those in the non-residual fractions. The $^{206}Pb/^{207}Pb$ ratios of Pb in the residual fraction throughout the core were generally above 1.19, which was representative of the $^{206}Pb/^{207}Pb$ ratios of natural geological materials. The high $^{206}Pb/^{207}Pb$ ratios of residual Pb were also consistent with the general understanding that heavy metals in the residual fraction usually originate from natural geological materials in less contaminated soils (Li and Thornton, 2001). Even though the $^{206}Pb/^{207}Pb$ ratios of total Pb were close to those of the background values, differences of the $^{206}Pb/^{207}Pb$ ratios of Pb in the five chemical fractions suggested that Pb in the soil core was probably derived from more than one source. In the Pb-enriched subsurface layers (20-30 and 30-40 cm), the $^{206}Pb/^{207}Pb$ ratios were the lowest in the carbonate fraction, from which they gradually increased in the exchangeable, Fe-Mn oxide and organic fractions. The variation of the $^{206}Pb/^{207}Pb$ ratios indicated that anthropogenic Pb tended to be associated with the potentially readily soluble and mobile fractions. In comparison, Pb in the relatively uncontaminated surface

soil (0-10 cm) showed low $^{206}Pb/^{207}Pb$ ratios in the exchangeable fraction, possibly indicating the relatively fresh deposition of anthropogenic Pb. The $^{206}Pb/^{207}Pb$ ratios in other fractions also exhibited a unique pattern, where the $^{206}Pb/^{207}Pb$ ratios in the carbonate and residual fractions were high, while the $^{206}Pb/^{207}Pb$ ratios of the Fe-Mn oxide and organic fractions were comparatively low. At the 10-20 cm soil layer, the isotopic distribution of Pb appeared to contain mixing of features from both the surface and subsurface soils. The noticeable reduction in the $^{206}Pb/^{207}Pb$ ratios from 0-10 cm to 30-40 cm (except the exchangeable fraction) strongly indicated the anthropogenic origin of Pb in the subsurface soil layer (30-40 cm) at this study site. This may be due to the use of relatively uncontaminated soil materials for recent cultivation at this urban park.

At the contaminated site CSW, Pb concentrations of the selected soil core were 170 and 72.3 mg/kg at 0-10 and 10-20 cm, respectively. The $^{206}Pb/^{207}Pb$ ratios (~1.12-1.18) of Pb in the five chemical fractions were usually lower than those of the natural geological materials and those at the less contaminated CRP site (see Fig. 3b). The distribution of Pb isotope composition indicated that the lowest $^{206}Pb/^{207}Pb$ ratios were associated with the carbonate fraction (~1.12). The $^{206}Pb/^{207}Pb$ ratios then increased in the following order: exchangeable, Fe-Mn oxide, organic and residual fractions. It was also found that the $^{206}Pb/^{207}Pb$ ratios were generally lower in the surface soil (0-10 cm) than in the subsurface soil (10-20 cm), suggesting more anthropogenic input to the surface soils of elevated Pb concentration at this study site.

Soil Pb concentrations at 0-10, 10-20 and 20-30 cm of the selected NG soil core were 207, 181 and 144 mg/kg, respectively. The distribution of the $^{206}Pb/^{207}Pb$ ratios in the five chemical fractions at NG ranged between ~1.13 and ~1.16, which were comparable to those at CSW (see Fig. 3c). The low $^{206}Pb/^{207}Pb$ ratios in the residual

fraction measured at both CSW and NG could be attributed to the possible presence of Pb from anthropogenic sources. Similar to those of CSW, the $^{206}Pb/^{207}Pb$ ratios of the selected soil samples at NG also exhibited an increasing tendency in the following order: carbonate, exchangeable, Fe-Mn oxide, organic and residual fractions. Furthermore, the $^{206}Pb/^{207}Pb$ ratios of Pb in the five chemical fractions in the surface soils (0-10 and 10-20 cm) were lower than those of the subsurface (20-30 cm), indicating that there was surface enrichment of anthropogenic Pb at NG. The distribution of the $^{206}Pb/^{207}Pb$ ratios in the five chemical fractions of the soils suggested that anthropogenic Pb tended to be associated with the non-residual fractions. Furthermore, the comparatively low $^{206}Pb/^{207}Pb$ ratios of Pb in the carbonate fraction of contaminated soils offered solid evidence that the contribution of anthropogenic Pb in the carbonate fraction was proportionately higher than in the Fe-Mn oxide fraction of these soils.

3.4 Possible Pb sources

In addition to the detection of anthropogenic origin, Pb isotopic composition may also allow the apportionment of anthropogenic Pb sources. The linearity of the relationship between the $^{206}Pb/^{207}Pb$ and $^{206}Pb/^{208}Pb$ ratios could provide insight into the mixing patterns of Pb in soils. Significant and positive 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 (R^2 = 0.56 and 0.43, respectively), while no significant correlation was found at HC (R^2 = 0.015). The significantly linear relationships between the $^{206}Pb/^{207}Pb$ and $^{206}Pb/^{208}Pb$ ratios at CSW and NG gave a strong indication of the binary mixing of two

major Pb sources. Since these two study sites were close to major roadways with high traffic volumes, Pb contamination of the soil cores was likely attributable to the atmospheric deposition of Pb as a consequence of vehicle emissions arising from the combustion of leaded gasoline in the past.

In order to make estimate of the contribution of Pb from leaded gasoline, several assumptions had to be made. The first was that the ^{206}Pb/^{207}Pb ratio of geochemical background Pb in Hong Kong (^{206}Pb/^{207}Pb$_{base}$) was about 1.20. The second was that the Pb concentration in uncontaminated soil in Hong Kong (C_{Pbbase}) was approximately 30 mg/kg. Using a binary mixing model, it was possible to calculate the ^{206}Pb/^{207}Pb ratios of excess Pb (^{206}Pb/^{207}Pb$_{excess}$) using the measured Pb concentrations and isotopic composition at CSW (C_{Pbmeas} and ^{206}Pb/^{207}Pb$_{meas}$). Using the Equation,

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

^{206}Pb/^{207}Pb$_{excess}$ was calculated to be 1.118. Therefore, the lead used in gasoline in Hong Kong before 1999 was probably derived from the ores with low ^{206}Pb/^{207}Pb ratios, such as at Broken Hill in Australia.

4. Conclusion

The present study provided strong evidence of the anthropogenic sources of Pb contamination of urban soils in Hong Kong. The Pb isotope composition showed that Pb contamination of urban soils could be partially attributed to the use of leaded gasoline in the past. Despite the discontinued use of leaded gasoline, Pb from the past emissions still remained a major contaminant of soils in the urban terrestrial environment of Hong Kong.

While the chemical distribution of Pb indicated that a large percentage of Pb was associated with the Fe-Mn oxide fraction, the isotopic composition of Pb in the five chemical fractions demonstrated that anthropogenic Pb in contaminated soils tended to reside in all four of the non-residual fractions, especially in the carbonate fraction, suggesting the potential solubility and mobility of anthropogenic Pb in soils.

Acknowledgements

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Table 1

Pb concentrations (mg/kg) of urban soils at the five study sites

	Depth (cm)		CRP	CSW	HC	NG	SSP
Number of composite soil samples			7	2	6	4	2
AADT*			Low	High	Medium	High	Medium
Pb conc.	0-10	Mean	65.5	185**	54.4	249**	78.8
		Range	40.0-103	170-199	24.9-77.7	196-393	70.6-87.0
	10-20	Mean	60.7	85.3**	55.9	235**	82.4
		Range	32.8-84.6	72.3-98.3	22.6-82.5	149-377	68.9-95.8
	20-30	Mean	58.1	-	62.5	221**	74.5
		Range	41.9-74.3	-	31.3-110	138-428	58.3-90.6
	30-40	Mean	60.7	-	63.3	-	-
		Range	30.0-96.5	-	33.6-112	-	-
Dutch Soil Standard***		T value	85				
		I value	530				

* Annual average daily traffic (Low ≤ 10000, 10000 < Medium < 40000, High ≥ 40000 vehicles per day)

** Mean soil Pb concentration exceeded the T value recommended by the Dutch Soil Standard.

*** The Netherlands Soil Contamination Guidelines, Netherlands (1994).

Table 2

Mean ($\pm$ standard deviation) and range of $^{206}Pb/^{207}Pb$ ratios in urban soil cores at each study site

Study sites	Soil depth (cm)	$^{206}Pb/^{207}Pb$ Mean	$^{206}Pb/^{207}Pb$ Range
CRP (n=7)	0-10	1.182 $\pm$ 0.012	1.162 – 1.200
	10-20	1.189 $\pm$ 0.015	1.171- 1.208
	20-30	1.191 $\pm$ 0.013	1.172 – 1.212
	30-40	1.194 $\pm$ 0.019	1.161 – 1.216
CSW (n=2)	0-10	1.131 $\pm$ 0.008	1.126 – 1.137
	10-20	1.160 $\pm$ 0.013	1.151 – 1.170
HC (n=6)	0-10	1.212 $\pm$ 0.006	1.204 – 1.218
	10-20	1.212 $\pm$ 0.006	1.205 – 1.219
	20-30	1.210 $\pm$ 0.006	1.202 – 1.218
	30-40	1.207 $\pm$ 0.001	1.205 – 1.208
NG (n=4)	0-10	1.169 $\pm$ 0.027	1.143 – 1.201
	10-20	1.178 $\pm$ 0.036	1.144 – 1.211
	20-30	1.186 $\pm$ 0.035	1.153 – 1.213
SSP (n=2)	0-10	1.196 $\pm$ 0.010	1.189 – 1.203
	10-20	1.195 $\pm$ 0.006	1.191 – 1.199
	20-30	1.199 $\pm$ 0.009	1.192 – 1.205

Table 3

^{206}Pb/^{207}Pb ratios of geological materials in the Pearl River Delta and of major Pb ore bodies in various parts of the world

		^{206}Pb/^{207}Pb
Geological materials in the Pearl River Delta:	Granite in the eastern Cathaysia[a]	1.183
	Granite in Pearl River Delta[a]	1.184
	Volcanic Rocks in Foshan[b]	1.199
	Uncontaminated soils[c]	1.195
Major Pb ore bodies:	Missouri, USA[d]	1.385
	Idaho, USA[d]	1.052
	Altay, Kazakhstan, Russia[d]	1.131
	Broken Hill, Australia[d]	1.037
	British Columbia, Canada[d]	1.064
	New Brunswick, Canada[d]	1.160
	Ontario, Canada[d]	0.920
	Cerro de Pasco, Peru[d]	1.200
	Trepca, Yugoslavia[d]	1.195
	Durango, Mexico[d]	1.192

a. Zhu, 1998
b. Zhu et al., 1989
c. Zhu et al., 2001
d. Vanhaecke et al., 1999

List of Figure Captions

Fig. 1. Sampling locations of urban soils in Hong Kong.

Fig. 2. Chemical partitioning of Pb in selected urban soil cores at a) CRP, b) CSW and c) NG.

Fig. 3. ^{206}Pb/^{207}Pb ratios of Pb in the five chemical fractions of one selected urban soil core at a) CRP, b) CSW and c) NG. Note: The error bars represent the relative standard deviation (RSD 0.3%) of the nine analytical readings.
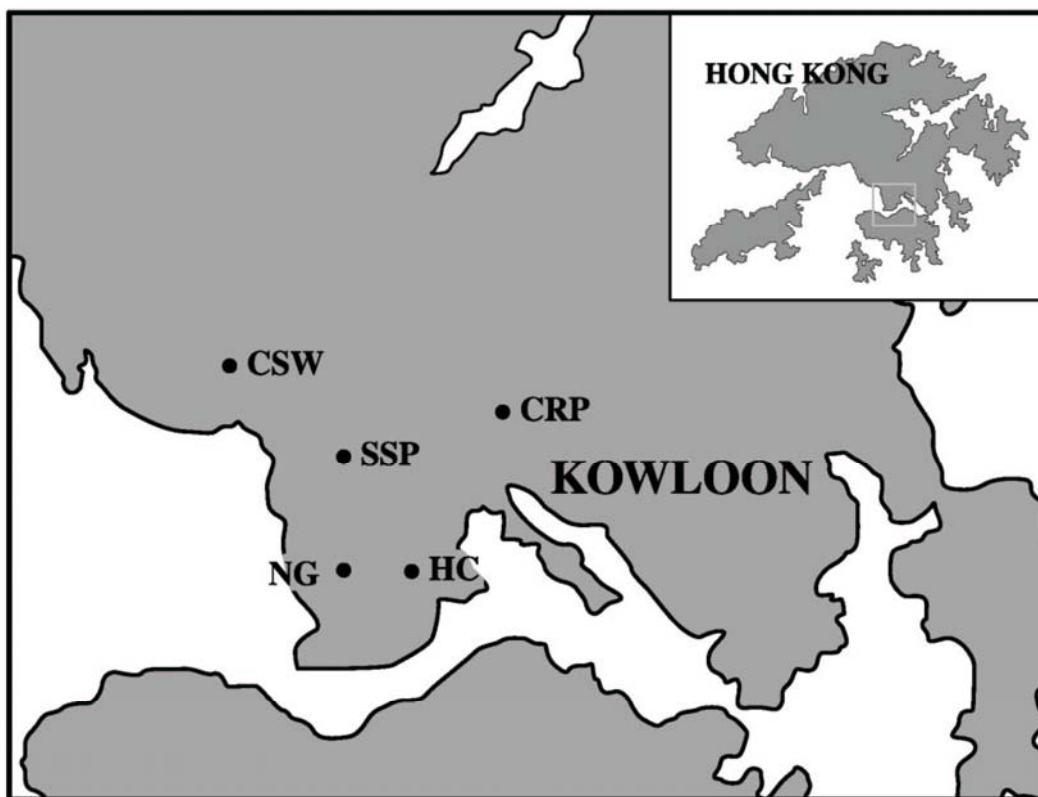
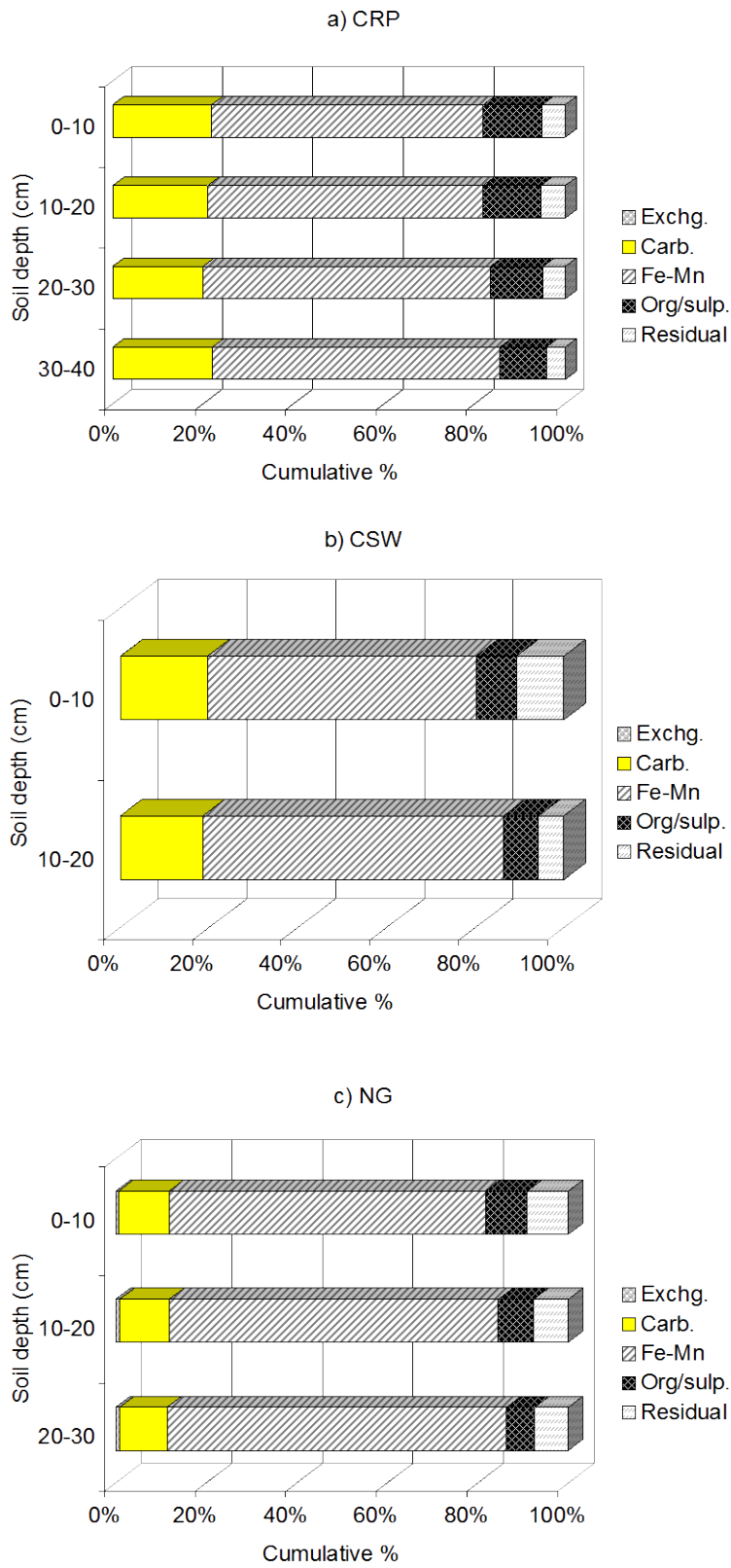Fig. 1 Sampling locations of urban soils in Hong Kong

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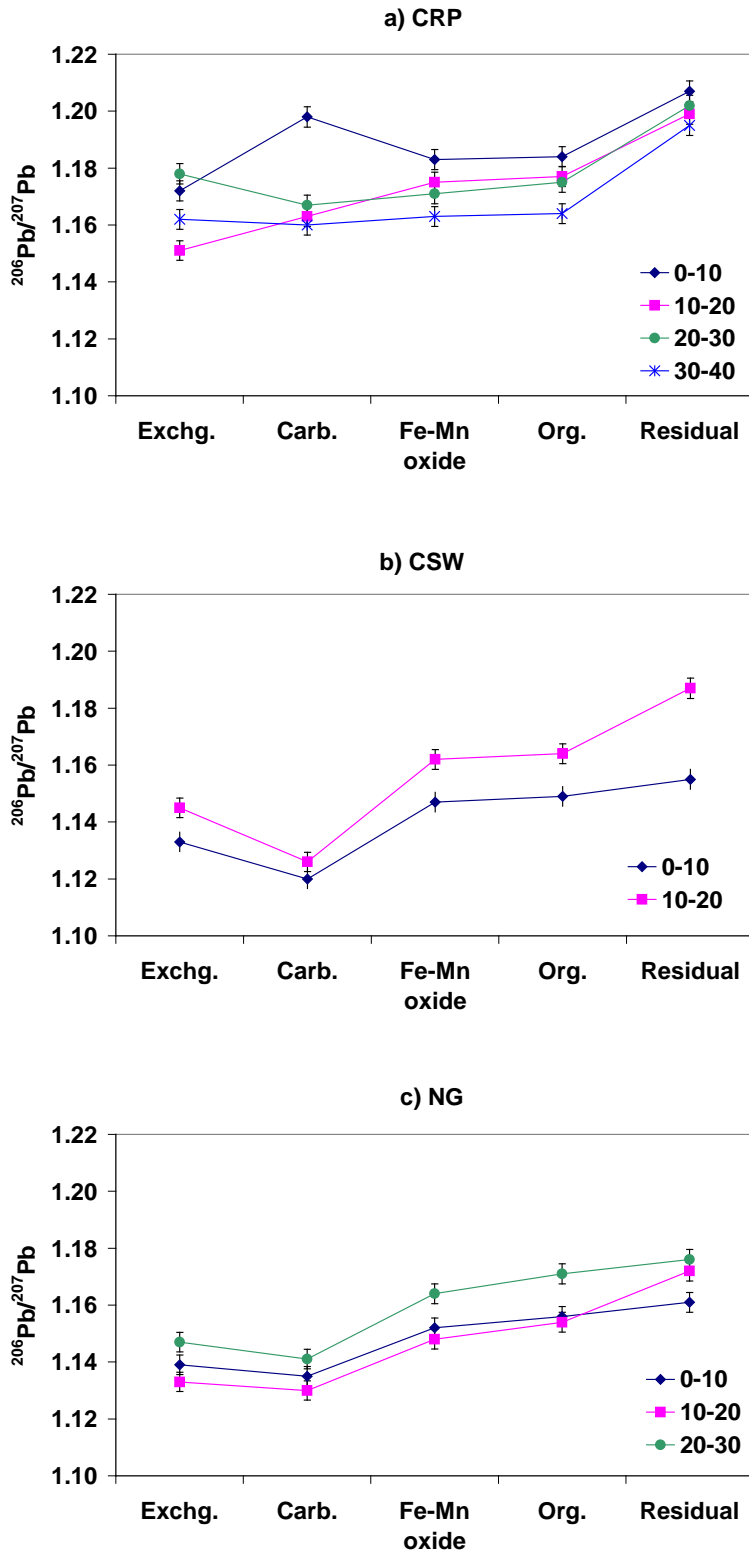
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