Heavy Metals in Agricultural Soils of the Pearl River Delta, South China

S.C. Wong[1], X.D. Li[1*], G. Zhang[2], S.H. Qi[2] and Y.S. Min[2]

[1]*Environmental Engineering Unit, Department of Civil and Structural Engineering, The Hong Kong Polytechnic University, Hung Hom, Hong Kong*

[2]*State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, 510640, China*

[*] corresponding author, E-mail address: cexdli@polyu.edu.hk; Fax: (852) 2334-6389; Tel: (852) 2766-6041

Abstract

There is a growing public concern over the potential accumulation of heavy metals in agricultural soils in China owing to rapid urban and industrial development and increasing reliance on agrochemicals in the last several decades. Excessive accumulation of heavy metals in agricultural soils may not only result in environmental contamination, but elevated heavy metal uptake by crops may also affect food quality and safety. The present study is aimed at studying heavy metal concentrations of crop, paddy and natural soils in the Pearl River Delta, one of the most developed regions in China. In addition, some selected soil samples were analyzed for chemical partitioning of Co, Cu, Pb and Zn. The Pb isotopic composition of the extracted solutions was also determined. The analytical results indicated that the crop, paddy and natural soils in many sampling sites were enriched with Cd and Pb. Furthermore, heavy metal enrichment was most significant in the crop soils, which might be attributed to the use of agrochemicals. Flooding of the paddy soils and subsequent dissolution of Mn oxides may cause the loss of Cd and Co through leaching and percolation, resulting in low Cd and Co concentrations of the paddy soils. The chemical partitioning patterns of Pb, Zn and Cu indicated that Pb was largely associated with the Fe-Mn oxide and residual fractions, while Zn was predominantly found in the residual phase. A significant percent fraction of Cu was bound in the organic/sulphide and residual phases. Based on the $^{206}Pb/^{207}Pb$ ratios of the five fractions, it was evident that some of the soils were enriched with anthropogenic Pb, such as industrial and automobile Pb. The strong associations between anthropogenic Pb and the Fe-Mn oxide and organic/sulphide phases suggested that anthropogenic Pb was relatively stable after deposition in soils.

1. Introduction

Soil serves many vital functions in our society, particularly for food production. It is thus of extreme importance to protect this resource and ensure its sustainability. Deteriorating environmental conditions and increasing reliance on agrochemicals have led to a growing public concern over the potential accumulation of heavy metals and other contaminants in agricultural soils (Nriagu, 1988; Alloway, 1990; Kabata-Pendias and Pendias, 1995). Owing to rapid economic development, heavy metal contamination of agricultural soils has also become increasingly serious in China (Siamwalla, 1996; Li et al., 1997; Chen et al., 1999).

The Pearl River Delta (PRD) is situated in the southern part of Guangdong Province, China (see Fig. 1). It has a total area of 41,600 square kilometers with a population of over 25 millions. The study area (see Fig. 1) is situated within the PRD, which includes several major cities. Among them, Guangzhou, Shenzhen, Dongguan, Zhongshan, Foshan and Zhuhai are major industrial production bases in the region, of which Guangzhou is the largest light industrial production base in China. The area has a humid subtropical weather with an annual average temperature and rainfall of 22°C and

1,690 mm, respectively. The mild climate favours agriculture allowing an annual production of ten to fifteen crops of vegetables and three crops of grains.

In the last two decades, the region has undergone a rapid transition from a traditionally agricultural-based economy to an increasingly industrial- and technological-based economy. The establishment of industrial operations and subsequent expansion of the population have considerably increased industrial and municipal wastewater discharge and other pollutant emissions in the region (Guangdong Environmental Protection Bureau, 1996; Hills et al., 1998). Coupled with the lack of pollution controls, human activities associated with these developments have caused significant impacts on the local environment (Chen, 1992; Florig, 1997; Hill et al., 1998; Ji et al., 2000; Li et al., 2000). An increase in contaminant emissions may pose substantial implications on the local agriculture, as heavy metals may enter and accumulate in agricultural soils through irrigation and atmospheric deposition, which could enhance the risk of metal contamination of the food chains in the region (Haygarth and Jones, 1992; Chen et al., 1999).

Today's agriculture in China has become increasingly reliant upon agrochemical usage (Li et al., 1997a&b). According to the Food and Agriculture Organization, the use of inorganic fertilizer in China increased by about 100 times from 3.9 kg/ha in 1949 to 379 kg/ha in 1995, which was more than 2.5 times of the world's average. The application rate was even higher in Guangdong Province, approximating 800 kg/ha (Li et al., 1997a). Neller and Lam (1994) also reported an increase of 40% in the use of chemical fertilizers in the PRD between 1986 and 1989. China is the world's second largest producer of pesticides. Pesticide production of 260,000 tonnes was recorded in 1994. About 90% of the pesticides is used on cotton, rice, oilseeds and horticultural crops (Li et al., 1997a). Some fertilizers and pesticides are known to contain various levels of heavy metals,

4

including Cd and Cu (Kabata-Pendias and Pendias, 1992). Therefore, continuous and heavy application of these agrochemicals and other soil amendments can potentially exacerbate the accumulation of heavy metals in agricultural soils over time (Siamwalla, 1996; Chen et al. 1999).

The contamination of agricultural soils can pose long-term environmental and health implications (Needleman, 1980; Mueller, 1994; McLaughlin, et al., 1999). Hence, there is an increasing need to study heavy metal distribution and accumulation in agricultural soils (Li et al., 1997a&b). Chemical speciation plays an influential role in solubility and potential bioavailability of heavy metals in soils. A sequential chemical extraction method, for example, Tessier's method (Tessier et al., 1979), partitions metals into five sequential fractions of an increasing order of solubility. In order to distinguish between natural and anthropogenic Pb sources, Pb isotopic composition has been used in many studies (e.g., Farmer and Eades, 1996; Gelinas and Schmit, 1997; Marcantonio et al., 1999), where it serves as a tracer when contrasted with natural ores and known anthropogenic Pb sources, such as automobile Pb.

The PRD is one of the first regions to experience massive industrialization and urbanization in China in recent years. A study of the PRD could provide valuable and insightful information for other regions in China. Moreover, the findings may also be useful in the formulation of strategic sustainable agriculture in China and other regions in the future. Thus, the primary objectives of the present study are: (1) to examine heavy metal concentrations of agricultural and natural soils in the PRD, (2) to study the chemical partitioning and elemental associations of heavy metals in the soils, and (3) to investigate the potential sources of heavy metal contaminants in the region.

2. Materials and methods

2.1. Soil sampling

72 soil samples, consisting of 38 crop soils, 16 paddy soils and 18 natural soils, were collected in the study area (see Fig. 1). The locations of the crop soils were relatively evenly distributed across the region. 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 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. The natural soils were generally collected from uncultivated and/or remote areas, such as forests and mountaintops, in the region. These soils were generally thin and sandy. The crop and paddy soils consisting of 3 to 5 subsamples were collected between the depths of 0 and 15cm, which were 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.

2.2. Analytical methods

The collected soil samples were air-dried at 20°C for 3 days and sieved through a 2mm-polyethylene sieve to remove large debris, stones and pebbles. They were then ground in a mechanical agate grinder until fine particles (<200 µm) were obtained. The prepared soil samples were analyzed for their heavy metal concentrations using an acid digestion method (Li and Thornton, 1993). About 0.250 g of the soil samples were

weighed and placed into Pyrex test tubes. 4.0 ml conc. nitric acid and 1.0 ml conc. perchloric acid were added. The mixtures were heated in an aluminum block at 50^oC for 3 hours, 150^oC for 3 hours, 190^oC for 18 hours until complete dryness. After the test tubes were cool, 5% (0.8M) nitric acid was added and heated at 60^oC for 1 hour with occasional mixing. Upon cooling, the mixtures were decanted into polyethylene tubes and centrifuged at 3500 rpm for 10 minutes. Heavy metal concentrations of the solutions were measured using Inductively Coupled Plasma -Atomic Emission Spectrometry (ICP-AES; *Perkin Elmer 3300DV*).

All glass- and plastic-wares were soaked in 10% nitric acid overnight and rinsed thoroughly with deionized water before use. For quality control, reagent blanks, replicates and standard reference materials (NIST SRM 2709), representing 10, 20, and 10% of the total sample population, respectively, were incorporated in the analysis to detect contamination and assess precision and bias. The analytical results showed no signs of contamination and that the precision and bias of the analysis were generally <10%. The recovery rates for the heavy metals and some major elements in the international standard reference material (NIST SRM 2709) were around 85 to 105%.

Selected soil samples were analyzed for the chemical partitioning of Co, Cu, Fe, Mn, Pb and Zn using a sequential chemical extraction method (Tessier et al., 1979; Li et al., 1995). The extraction method operationally defines the metals in five chemical forms: 1) exchangeable fraction (0.5 M $MgCl_2$), 2) carbonate-bound and specifically adsorbed fraction (1 M NaOAc), 3) the Fe-Mn oxide fraction (0.04 M $NH_2OH^.HCl$), 4) organic/sulphide fraction (30% H_2O_2/ 3.2 M NH_4OAc in 20% HNO_3), and 5) residual fraction ($HClO_4/HNO_3$). Generally, heavy metals in the exchangeable and carbonate-bound fractions are considered readily and potentially bioavailable, while the Fe-Mn oxide and

organic/sulphide fractions are relatively stable under normal soil conditions. Heavy metals in the residual fraction are entrapped within the crystal structure of the minerals and, thus, represent the least liable fraction. Quality controls similar to that of the acid digestion method were carried out in the experiment. The overall recovery rates of Co, Cu, Fe, Mn, Pb and Zn (the sum of the five fractions compared to the total metal concentrations) were 94, 107, 114, 93, 88 and 94%, respectively.

Solutions from the sequential chemical extraction of 9 selected soil samples were analyzed for Pb isotopic composition using Inductively Coupled Plasma - Mass Spectrometer (ICP-MS; *Perkin Elmer ELAN 6100*). Prior to the isotope analysis, Pb concentrations of the solutions were adjusted to 400 μg/l or below. The solutions were diluted by factors of 5 and 20 using 5% (0.8M) HNO_3 for the exchangeable fraction and other phases, respectively. In the analysis, dwell time of 50 ms and 200 sweeps were used. 7 replicates of each sample were measured, and the RSD was generally <1.0%. An international standard reference material (NIST 981 Common Lead Isotope) was used for analytical quality control. The measured average ratios of $^{204}Pb/^{207}Pb$, $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{207}Pb$, (0.0646±0.0003, 1.0934±0.0016, and 2.3681±0.0069, respectively) of the standard reference material were in good agreement with the certified standard values (0.0646, 1.0933, and 2.3704, respectively).

The pH values of the selected soil samples were also determined using the method described by Allen et al. (1974). About 4.0 g of the soils (<2 mm) were mixed with 10.0 ml of deionized water in centrifuge tubes. The mixtures were shaken for 30 minutes on a mechanical shaker and then centrifuged at 3000 rpm for 10 minutes. pH of the supernatants were measured using a pre-calibrated pH meter (Oakton Acron Series).

2.3 Statistical analysis

In order to investigate elemental associations among the heavy metals and major elements in the soils, Pearson correlation and principle component analysis (PCA) were performed for each of the soil groups using SPSS 8.0. In the PCA, Varimax with Kaiser normalization was used as the rotation method in the analysis. Instead of eliminating heavy metal concentrations below detection limits of some soil samples, a value corresponding to half of the detection limit (for example, 0.02 mg Cd/kg) of the element was assigned. A visual check of the analytical results found that Zn concentration of a crop soil (namely C21; 992 mg Zn/kg soil) was exceedingly high and, therefore, was considered as an outliner. In all data treatment, Zn concentration of this crop soil was replaced by an average of Zn concentrations of two geographically closest crop soils (namely C19 & C23).

3. Results

3.1. Heavy metal concentrations

Descriptive statistics of heavy metal concentrations of the crop, paddy and natural soils are presented in Table 1. The mean concentrations of Cr, Cu, Ni, Pb and Zn descended in the order: crop soils > paddy soils > natural soils, while the mean Cd and Co concentrations showed the order: crop soils > natural soils > paddy soils. In accordance with the Environmental Quality Standard for Soils (National Environmental Protection Agency of China, 1995), mean Cd concentrations of the crop, paddy and natural soils and mean Pb concentrations of the crop and paddy soils were elevated compared to the

corresponding threshold values of natural background (see Table 1). The mean Co, Cr, Cu, Ni and Zn concentrations of the crop, paddy and natural soils were generally below the threshold levels of nationwide natural background.

3.2. Chemical partitioning of Co, Cu, Fe, Mn, Pb and Zn

Fig. 2 displays the chemical partitioning of Co, Cu, Pb, Zn, Fe and Mn of the different soil types. 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. Fig. 2a 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. A significant fraction of Cu in the crop and paddy soils was bound in the organic/sulphide phase, followed by the residual phase (see Fig. 2b). 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. Pb in the crop soils was largely associated with the Fe-Mn oxide phase, followed by the organic/sulphide and residual fractions (see Fig. 2c). 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. In all of the three different soil groups, Zn was predominantly

10

associated with the residual fraction and secondarily with the Fe and Mn oxides (see Fig. 2d).

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 Fig. 2e). 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 predominantly associated with the Fe-Mn oxide fraction (see Fig. 2f). On the other hand, Mn in the paddy soils was predominantly associated with the residual fraction, and the association of Mn with the Fe-Mn oxides was evidently weaker than that in the crop and natural soils.

3.3. Pb isotopic composition

The Pb isotopic composition of the five sequential fractions of the selected soil samples is presented in Table 2. $^{206}Pb/^{207}Pb$ ratios of soil Pb in the five fractions are also depicted in Fig. 3. The $^{206}Pb/^{207}Pb$ ratios exhibited considerable variation among different soil types and within each group. However, the $^{206}Pb/^{207}Pb$ ratios of the different soils showed a general pattern. The $^{206}Pb/^{207}Pb$ ratios were generally the lowest for soil Pb associated with the exchangeable, Fe-Mn oxide and organic/sulphide phases. The $^{206}Pb/^{207}Pb$ ratios of soil Pb in the carbonate/specifically-adsorbed and residual phases were relatively high.

3.4. Soil pH

The average soil pH of the 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.

3.5. Elemental associations

The Pearson correlation coefficient matrixes between some major elements and heavy metals are presented in Table 3. In general, major and trace elements, except for Pb, were significantly correlated with each other in all of the soil groups. In the natural soils, the relatively weak correlation of Cd with the other elements may be attributed to the relatively large number of samples assigned with the value of half of the detection limit as the Cd concentrations (0.02 mg/kg). In the PCA, the first two principle components accounted for 81.4, 90.3, and 84.1% of the total variance for the crop, paddy and natural soils, respectively. The results of the PCA (see Fig. 4) indicated that Pb in the crop soils was dominated by the second component, and the association of Pb with other elements was weak. Pb in the paddy and natural soils also exhibited strong dominance by the second component and a unique feature different from the other elements.

4. Discussion

4.1. Heavy metal concentrations of soils

Elevated concentrations of Cd in the crop, paddy and natural soils and elevated Pb concentrations in the crop and paddy soils (Table 1) were found in the PRD, suggesting potential Cd and Pb contamination of the soils. Although the mean concentrations of Co,

Cr, Cu, Ni and Zn were below the nationwide threshold values, some soils were found moderately contaminated with one or more of these heavy metals. Collectively, these findings suggest that heavy metals have accumulated in soils due to the rapid development of the PRD in recent years.

All heavy metal concentrations were most enriched in the crop soils and the residual Cu, Pb, and Zn in the crop soils were the lowest (Fig. 2) strongly suggested that the crop soils received a comparatively high input of anthropogenic heavy metals, possibly related to the use of agrochemicals and other soil amendments for the high annual crop production. The soil pH of the crop, paddy and natural soils were generally below 7.0, indicating that the soils were acidic. The lower pH of the natural soils (4.56) compared to that of the agricultural soils may partially be due to the coarser texture of the leached soils on hillsides. The higher pH of the crop and paddy soils (5.88 and 5.76, respectively) also suggested that the soils were treated with lime and/or other agrochemicals to increase soil pH and, thus, reduce leaching of nutrients in soils.

Meanwhile, differences in cultivation methods may have also caused a higher output of some heavy metals, such as Cd and Co, in the paddy soils through leaching and percolation. Rice cultivation in paddy fields generally requires moderate flooding. Excessive soil water may enhance leaching and migration of some readily soluble elements, such as Cd, and, possibly, those in exchangeable and weakly bound forms through percolating water (Adriano, 1986; Teruo, 1997; Blum et al., 1997). Therefore, the low Cd concentration of the paddy soils was likely resulted from the loss of the readily soluble Cd through leaching and percolation processes.

Mn oxides play a significant role in the fixation for Co in soils owing to the strong affinity of Co for Mn oxides (Kabata-Pendias and Pendias, 1992). Taylor and McKenzie

(1966) reported that a significant fraction of Co (>70% of total soil Co) was associated with Mn oxide minerals. The low Co concentration of the paddy soils was likely attributed to the dissolution of and subsequent reduction in the Mn oxides induced by flooding. Extended submergence of the paddy soils in water can alter soil chemistry under a reducing environment, which, in turn, increases the reduction and dissolution of compounds, e.g. Mn and Fe oxides. The reduction of Mn was evident in the paddy soils. In contrast to the crop and natural soils, mean soil Mn concentration of the paddy soils (186 mg/kg) was lower than those of the crop and natural soils (320 and 241 mg/kg, respectively), suggesting the loss of Mn in the paddy soils. Moreover, both Mn and Co in the paddy soils (see Fig. 2) were predominately associated with the residual fraction, and their associations with the Fe-Mn oxide fraction were significantly weaker than that of the crop soils, giving additional evidence of dissolution and leaching of Mn and Co. Because of the strong association between Mn and Co, the loss of Mn oxides in the paddy soils could indirectly enhance the solubility and leaching of Co, resulting in the low Co concentration of the paddy soils. Mobilization and leaching of Mn as a consequence of the chemical transformation of the insoluble Mn oxide forms to readily soluble forms were also reflected from the weak associations of Cu, Pb, and Zn with the Fe-Mn oxide phases in the paddy soils compared to that in the crop soils (see Fig. 2). The effect of flooding on Fe oxides was less significant (see Fig. 2e), which is probably due to that the dissolution of Mn oxides usually precedes that of Fe oxides (Adriano, 1986).

4.3. Chemical partitioning of Pb, Cu, Zn and Co

14

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. 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 strong association between soil Cu and the organic fraction is 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. 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 Fe-Mn 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). As discussed previously, the strong association of soil Co with the Fe-Mn oxide phase in the crop and natural soils was anticipated since Co is usually strongly associated with Mn oxides, and flooding likely caused the weak association of soil Co with the Fe-Mn oxide fraction in the paddy soils.

In general, the high proportion of heavy metals in non-residual fractions of the crop soils may suggest greater contribution of anthropogenic metals. The relatively large exchangeable and carbonate fractions of Pb and Zn in the natural soils could be attributed to lower soil pH. Also, the relatively strong association of heavy metals with the

15

organic/sulphide fraction in the crop and paddy soils compared to the natural soils was probably attributed to high organic content in agricultural soils. The percent distribution of heavy 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.

4.4. Elemental associations of heavy metals and major elements

The results of Pearson correlation and PCA showed that elemental association of Pb with other elements was generally weak in the crop, paddy and natural soils, indicating that the relationship between Pb and other elements in these soils was insignificant. In contrast, other heavy metals were generally highly correlated with each other. The statistical results may indicate that Pb in the crop, paddy and natural soils had distinct geochemical behaviours and, possibly, originated from sources that were different from the other elements. In the PCA, the strong associations among Cu, Cr, and Zn in the crop, paddy and natural soils may suggest their common geochemical characteristics. Their associations with Fe and Mn in the natural soils as compared with Ca in the crop soils may indicate the influence of agricultural activities on soils, maybe owing to lime application. Moreover, the weak influence of Mn by the second component in the PCA and the weak association between Fe and Mn in the paddy soils may suggest the leaching of Mn in the paddy soils due to the influence of flooding.

4.5. Possible Pb contaminant sources

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 (Zhu, 1995), and the values are provided in Table 4. In the study area, industrial Pb from the Fankou Pb-Zn deposit and automobile exhaust are the two main sources of anthropogenic Pb. The Pb isotopic composition of these sources have been analyzed by Zhu and his colleagues (Zhu et al., 1989; Zhu, 1998; Zhu, 2001). As shown in Table 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 that of the local background values. A comparison of the $^{206}Pb/^{207}Pb$ ratios in the five fractions with these known sources and natural background may therefore indicate the possible origins of soil Pb in the agricultural and natural soils.

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. However, the $^{206}Pb/^{207}Pb$ ratios in the four non-residual fractions of the soils were generally lower than those of the residual fraction and the natural background sources, which gave evidence that these soils were enriched by anthropogenic Pb. The comparatively low $^{206}Pb/^{207}Pb$ ratios in the exchangeable, Fe-Mn oxide and organic/sulphide fractions indicated that anthropogenic Pb tended to reside in these chemical forms of the soils (see Fig. 3). The low $^{206}Pb/^{207}Pb$ ratios of exchangeable Pb may reflect the presence of recently deposited anthropogenic Pb in the soils. The tendency of anthropogenic Pb associated with the Fe-Mn oxide and organic fractions is consistent with the fact that Pb has a strong affinity for Mn oxides, Fe

17

and Al hydroxides and organic matter (Adriano, 1986; Kataba-Pendias and Pendias, 1992). The high $^{206}Pb/^{207}Pb$ ratios of the carbonate/specifically adsorbed fraction indicated that the carbonate fraction played a less important role in the fixation of anthropogenic Pb in the soils. In a study of Pb accumulation in sediment 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., 2001). This result is similar to the present study of soils of the same study area.

In Fig. 3, 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 and N23) tended to have high $^{206}Pb/^{207}Pb$ ratios of the four liable fractions (>1.18), while the other group (C12, C21, C64 and 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. The metal 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 indicate a common origin of anthropogenic Pb. Both C64 and P76 were situated very close to major roads. The ratios of the four liable 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 come from the vehicular exhaust of major roads.

5. Conclusions

18

The present study examined the distribution of heavy metals in the crop, paddy and natural soils of the Pearl River Delta, South China. Chemical partitioning of Co, Cu, Pb and Zn and Pb isotopic composition of selected soils were also analyzed. In the PRD, Cd enrichment in both the crop, paddy and natural soils and elevation of Pb concentrations in the crop and paddy soils may indicate the influence of environmental release of these heavy metals in the region. Higher concentrations of heavy metals in the crop soils compared to those of the paddy and natural soils were possibly attributed to high usage of agrochemicals and differences in cultivation method. Flooding in rice cultivation has caused the reduction and dissolution of Mn oxides leading to the leaching of Cd and Co in the paddy soils. The chemical partitioning of soil Pb was strongly dominated by the Fe-Mn oxide and residual fractions. Soil Cu and Zn were predominately associated with the organic/sulphide fraction and the residual fraction, respectively. It was found that anthropogenic Pb was strongly associated with the exchangeable, Fe-Mn oxide and organic/sulphide fractions in the soils. The ^{206}Pb/^{207}Pb ratios of these fractions strongly suggested the anthropogenic Pb inputs to the soils, such as Pb from automobile exhaust and industrial sources.

Acknowledgements

References

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

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

Alloway, B.J., 1990. Heavy Metals in Soils. Blackie & Son, New Jersey.

Blum, W.E.H., Brandstetter, A., and Wenzel, W.W., 1997. Trace element distribution in soils as affected by land use. In: Adriano, D.C., Chen, Z.S., Yang, S.S., and Iskandar, I.K. (Eds.), Biogeochemistry of Trace Metals. Science Reviews, Middlesex, pp. 1-42.

Chen, Z.S., 1992. Metal contamination of flooded soils, rice plants, and surface waters in Asia. In: Adriano, D.C., Chen, Z.S., Yang, S.S., and Iskandar, I.K. (Eds.), Biogeochemistry of Trace Metals. Science Reviews, Middlesex, pp. 85-108.

Chen, H.M., Zheng, C.R., Tu, C., and Zhu, Y.G., 1999. Heavy metal pollution in soils in China: Status and countermeasures. Ambio, 28, 130-134.

Farmer, J.G., and Eades, L.J., 1996. Stable lead isotope record of lead pollution in Loch Lomond sediments since 1630 A.D. Environmental Science and Technology, 30, 3080-3083.

Florig, H.K., 1997. China's air pollution risks. Environmental Science and Technology, 31, 274-279.

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

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

Haygarth, P.M., and Jones, K.C., 1992. Atmospheric deposition of metals to agricultural surfaces. In: Adriano, D.C. (Eds.), Biogeochemistry. Lewis Publishers, Boca Raton, pp. 249-276.

Hills, P., Zhang, L., Liu, J.H., 1998. 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, 41, 375-396.

Ji, G.L., Wang, J.H., and Zhang, X.N., 2000. 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.

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

Kabata-Pendias, A., 1995. 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.

Li, X.D., Coles, B.J., Ramsey, M.H., and Thornton, I., 1995. Sequential extraction of soils for multielement analysis by ICP-AES. Chemical Geology, 124, 109-123.

Li, X.D., Shen, Z.G., Wai, O.W.H., and Li, Y.S., 2001. Chemical forms of Pb, Zn and Cu in the sediment profiles of the Pearl River Estuary. Marine Pollution Bulletin, 42, 215-223.

Li, X.D., and Thornton, I., 1993. Multi-element contamination in soil and plant in the old mining area. U.K. Applied Geochemistry, S2, 51-56.

Li, X.D., Wai, O.W.H., Li, Y.S., Coles, B.J., Ramsey, H., and Thornton, I., 2000. Heavy metal distribution in sediment profiles of the Pearl River estuary, South China. Applied Geochemistry, 15, 567-581.

Li, X.Y., Zuo, C.S., Tschirley, J.B., Webb, S.E., and Morton, A., 1997a. Sustainable agriculture and rural development in China, Part 1: 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/UNDP/Ministry of Agriculture, China.

Li, X.Y., Zuo, C.S., Tschirley, J.B., Webb, S.E., and Morton, A., 1997b. Sustainable Agriculture and Rural Development in China, Part 2: China's Transition to SARD. In: Promotion of sustainable agriculture and rural development in China: elements for a policy framework and a National Agenda 21 Action Programme. FAO/UNDP/Ministry of Agriculture, China.

Marcantonio, F., Flowers, G.C., and Templin, N., 1999. Lead contamination in a wetland watershed: isotopes as fingerprints of pollution. Environmental Geology, 39, 1070-1076.

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

Mueller, M., 1994. 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, 156, 151-158.

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

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

Neller, R.J., and Lam, K.C., 1994. The environment. In: Y.M.Yeung & D.K.Y. Chu (Eds.), Guangdong: Survey of a Province Undergoing Rapid Change. Hong Kong, Chinese University Press.

Nriagu, J.O., 1988. A silent epidemic of environmental metal poisoning? Environmental Pollution, 50, 139-161.

Siamwalla, A., 1996. Agricultural sustainability in rapidly industrializing Asian economies. In: Integration of Sustainable Agriculture and Rural Development in Agricultural Policy, FAO/Winrock International.

Taylor, R.M., and McKenzie, R.M., 1966. The association of trace elements with manganese minerals in Australian soils. Australian Journal of Soil Research, 4, 29-39.

Teruo, A., 1997. Cadmium pollution of paddy fields and human health in Japan. In: Adriano, D.C., Chen, Z.S., Yang, S.S., and Iskandar, I.K. (Eds.), Biogeochemistry of Trace Metals. Science Reviews, Middlesex, pp. 217-264.

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

Zhu, B.Q., Wang, H.F., Mao, C.X., Zhu, N.J., Huang, R.S., Peng, J.H., 1989. 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, 8, 65-71.

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

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

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