Environ Sci Pollut Res (2013) 20:6150–6159
DOI 10.1007/s11356-013-1668-z

RESEARCH ARTICLE

Assessing heavy metal pollution in the surface soils of a region that had undergone three decades of intense industrialization and urbanization

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Received: 18 December 2012 / Accepted: 20 March 2013 / Published online: 2 April 2013

Abstract Heavy metals in the surface soils from lands of six different use types in one of the world's most densely populated regions, which is also a major global manufacturing base, were analyzed to assess the impact of urbanization and industrialization on soil pollution. A total of 227 surface soil samples were collected and analyzed for major heavy metals (As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, and Zn) by using microwave-assisted acid digestion and inductively coupled plasma–mass spectrometry (ICP-MS). Multivariate analysis combined with enrichment factors showed that surface soils from the region ($>7.2\times10^4$ km^2) had mean Cd, Cu, Zn, and As concentrations that were over two times higher than the background values, with Cd, Cu, and Zn clearly contributed by anthropogenic sources. Soil pollution by Pb was more widespread than the other heavy metals, which was contributed mostly by anthropogenic sources. The results also indicate that Mn, Co, Fe, Cr, and Ni in the surface soils were primarily derived from lithogenic sources, while Hg and As contents in the surface soils were controlled by both natural and anthropogenic sources. The pollution level and potential ecological risk of the surface soils both decreased in the order of: urban areas>waste disposal/treatment sites~industrial areas>agricultural lands~forest lands>water source protection areas. These results indicate the significant need for the development of pollution prevention and reduction strategies to reduce heavy metal pollution for regions undergoing fast industrialization and urbanization.

Keywords Heavy metal · Pollution assessment · Land use type · Spatial pattern · Multivariate analysis · Potential ecological risk

Responsible editor: Zhihong Xu

Electronic supplementary material The online version of this article (doi:10.1007/s11356-013-1668-z) contains supplementary material, which is available to authorized users.

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Introduction

Soil pollution by heavy metals is a significant environmental problem worldwide (Alloway 1995). In particular, heavy metal pollution of surface soils due to intense industrialization and urbanization has become a serious concern in many developing countries (Mireles et al. 2012; Wei and Yang 2010; Yaylalı-Abanuz 2011). The accumulation of heavy metals in surface soils is affected by many environmental variables, including parent material and soil properties, as well as by human activities, such as industrial production, traffic, farming, and irrigation. Large areas of land can be contaminated by heavy metals released from smelters, waste incinerators, industrial wastewater, and from the application of sludge or municipal compost, pesticides, and fertilizers. Irrespective of their sources in the soil, accumulation of heavy metals can degrade soil quality, reduce crop yield and the quality of agricultural products, and thus negatively impact the health of human, animals, and the ecosystem (Nagajyoti et al. 2010). It is important to identify the sources of heavy metals, besides quantifying their concentrations and spatial variability in the soils.

The Pearl River Delta (PRD), which has a total population of over 40 million, is one of the most densely urbanized regions in the world. The delta has become one of the leading hubs of China's economic growth and a major manufacturing base of China and the world since the economic reform in the late 1970s. Before the mid-1980s, the PRD was dominated by farms and rural villages, and the fertile alluvial soils were cultivated intensively, growing two to three crops per year. Today, the region hosts a wide range of manufacturing plants, producing textiles, clothing, plastic and electronic products, among other commodities for domestic consumption and exports. The region is also featured with a dense network of large cities, including Guangzhou, Shenzhen, Zhuhai, and Dongguan. The rapid industrialization and urbanization over the past three decades has brought significant environmental problems to the region, including widespread water pollution, photochemical smog, and soil and sediment pollution. Previous studies have observed significant enrichment of heavy metals in the surface sediments of the Pearl River Estuary (Li et al. 2000, 2001; Liu et al. 2003). There is a pressing need to assess the distributions of heavy metals in the surface soils, which serve as an important sink, to understand the overall status of heavy metal pollution and the associated ecological risk in the region. The results are also helpful for the management of environment in areas undergoing fast industrial transformation.

This study investigates, for the first time, the heavy metal pollution of surface soils from all six major types of land uses in the PRD. A total of 227 surface soil samples were collected across the PRD, and their heavy metal contents were analyzed with inductively coupled plasma–mass spectrometry after closed-vessel microwave digestion. The overall pollution status was assessed using the pollution indices of heavy metals, while the possible sources of heavy metals were identified by correlation matrix and multivariate analyses, including principal component analysis (PCA) and cluster analysis (CA). The influence of human activities on heavy metal accumulation in the surface soils was also evaluated by enrichment factors, and the ecological risk posed by the heavy metal pollutants was quantitatively assessed by their potential ecological risk indices.

Materials and methods

Sample collection and chemical analyses

A total of 227 surface soil samples (0–0.1 m depth) were collected on hexagonal sampling grids (12.9 km edge length) from an area (Fig. 1) of more than 7.2×10^4 km^2 in the PRD of Guangdong Province to evaluate the spatial distributions of the heavy metals. Based on the dominant land use patterns, each of the sampling sites was classified as one of six land use types: agricultural land, industrial area, waste disposal/treatment site, urban area, forest land, and water source protection area. The hexagonal sampling plan was not followed exactly in the urban areas where more samples were taken. Four sub-samples were taken within an area of 100 m^2 from each sampling location and combined to obtain a representative sample. The collected soil samples were dried at 60 °C, sieved through a 2.0-mm Nylon sieve to remove sand, gravel, and plant debris, and stored in glass bottles at room temperature.

Samples (~20 g) of dried soils were finely powdered by an agate ball-grinder and sieved to pass 0.15-mm Nylon sieve. The powdered samples (~0.2 g) were then digested by trace metal grade acids (9.0 mL of HNO_3 and 3.0 mL of HF) using a MARS microwave digestion system (CEM, USA) according to EPA method 3052 (USEPA 1996). After evaporating the digestion liquids to near dryness to remove HF, the residuals were re-dissolved with dilute HNO_3 and diluted with triple-distilled water. The concentrations of heavy metals in the final solutions were measured by a 7700X Inductively Coupled Plasma-Mass Spectrometer (Agilent, USA). The instrument was calibrated prior to each set of measurements, and 50 μg/L of Bi, In, Lu, Rh, and Tb was used as the internal standards. With respect to quality control and assurance, procedural blanks, standard reference materials (certified standard reference estuarine sediment NIST 1646a, and Chinese standard reference soils GSS6, GSS7, and GSS16), and 10 % replicates of the sample load were routinely inserted in the

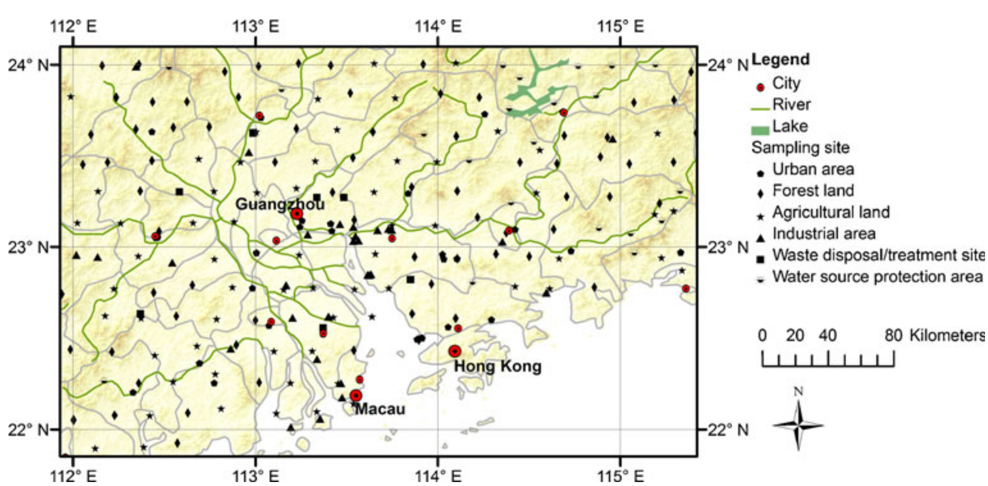

Fig. 1 The study area and sampling site locations in Guangdong Province, China

digestion sequence. The recovery rates for the target heavy metals in the standard reference materials were reasonably good (77–119 %).

Data analyses

The pollution level by a given heavy metal, *i*, was evaluated with the single pollution index (PI_i), calculated as the ratio between the metal concentration (C_i) in a soil sample and its reference value (S_i):

$$PI_i = \frac{C_i}{S_i} \quad (1)$$

The S_i values for As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn were based on the grade II criteria (agricultural soil) specified in the Standards for Soil Environmental Quality of China (SEPA 1995), which are summarized in Table S1. The overall pollution status of the surface soils by the heavy metals was assessed by the Nemerow pollution index (PI_N) (Cheng et al. 2007):

$$PI_N = \sqrt{\frac{PI_{ave}^2 + PI_{i\max}^2}{2}} \quad (2)$$

where PI_{ave} and $PI_{i\max}$ are the mean and maximum of the pollution indices for individual heavy metals, respectively. Pollution of the surface soils by the heavy metals was classified into five levels based on the corresponding PI_N values (Table S2).

The possible sources of heavy metals in the surface soils were identified with correlation matrix and multivariate analyses. The correlation coefficients were calculated to investigate the associations among the measured heavy metals, while PCA and CA were implemented to further identify metals having similar distribution patterns. All statistical analyses of data were conducted using the SAS software package.

The enrichment factors (EFs) of heavy metals were calculated to quantitatively assess the contributions of anthropogenic sources to the concentrations observed in the surface soils of the PRD. The EF of individual heavy metal in the soil was calculated as:

$$EF = \frac{C_i/C_r}{B_i/B_r} \quad (3)$$

where C_i and C_r are the concentrations of the target metal and the reference metal in the soil sample, while B_i and B_r are the background concentrations of the target metal and the reference metal in unpolluted soils from the same region. Heavy metals with EF values close to 1 are considered as mainly of natural origins (Sutherland 2000). The background levels of heavy metals in the natural soils of Guangdong Province (Table S3) were used as the baseline values. EFs for all the heavy metals measured in this study except Co and Fe were calculated using Mn as the reference metal, and five levels of enrichment were classified for the heavy metals in the soils based on their EF values (Table S4).

The potential ecological risk of heavy metal pollutants in the surface soils of the PRD was evaluated using the ecological risk index (RI) introduced by Hakanson (1980). The RI was calculated as the sum of risk factors of the heavy metals:

$$RI = \sum E_i \quad (4)$$

where E_i is the single risk factor for heavy metal *i*, and is defined as:

$$E_i = T_i f_i = T_i \frac{C_i}{B_i} \quad (5)$$

where T_i is the toxic-response factor for heavy metal *i*. According to Hakanson (1980) and Xu et al. (2008), the T_i values for Hg, Cd, As, Ni, Cu, Pb, Cr, and Zn are 40, 30, 10, 5, 5, 5, 2, and 1, respectively. The ratio f_i is the metal pollution factor calculated from the measured concentration C_i and the background concentration B_i in unpolluted soils. Again, the background concentrations of heavy metals in the natural soils of Guangdong Province (Table S3) were used to represent the corresponding B_i values in this study. The potential ecological risk of heavy metals in the soils was then classified into five categories based on the values of E_i and RI (Table S5).

Results and discussion

Status of soil pollution by heavy metals

The box and whisker plots shown in Fig. 2a summarize the basic statistics for the concentrations of heavy metals investigated in the surface soils of the PRD. The mean concentrations of Co, Cr, Fe, Hg, Mn, Ni, and Pb in the soil samples were 8.6, 67.2, 5,092, 0.07, 371, 26.0, and 51.4 mg/kg, respectively. When compared with the background contents of these heavy metals in the soils of Guangdong Province (Table S3), Cd, Cu, Zn, and As showed mean concentrations more than two times higher than the background values, suggesting the surface soils in the PRD had been polluted by anthropogenic sources. Based on the criteria listed in the Environmental Quality Standard for Soils in China (SEPA 1995), approximately 21.1, 15.4, 8.8, and 12.3 % of the soil samples were moderately or heavily polluted by Cd, Cu, Zn, and As, respectively. The heavy metal contents in the agricultural soils of the PRD are comparable to those in other regions undergoing industrial transformation in China (Table S6). Meanwhile, the concentrations of heavy metals in the urban soils were higher than those in Beijing and Hong Kong, but comparable to those

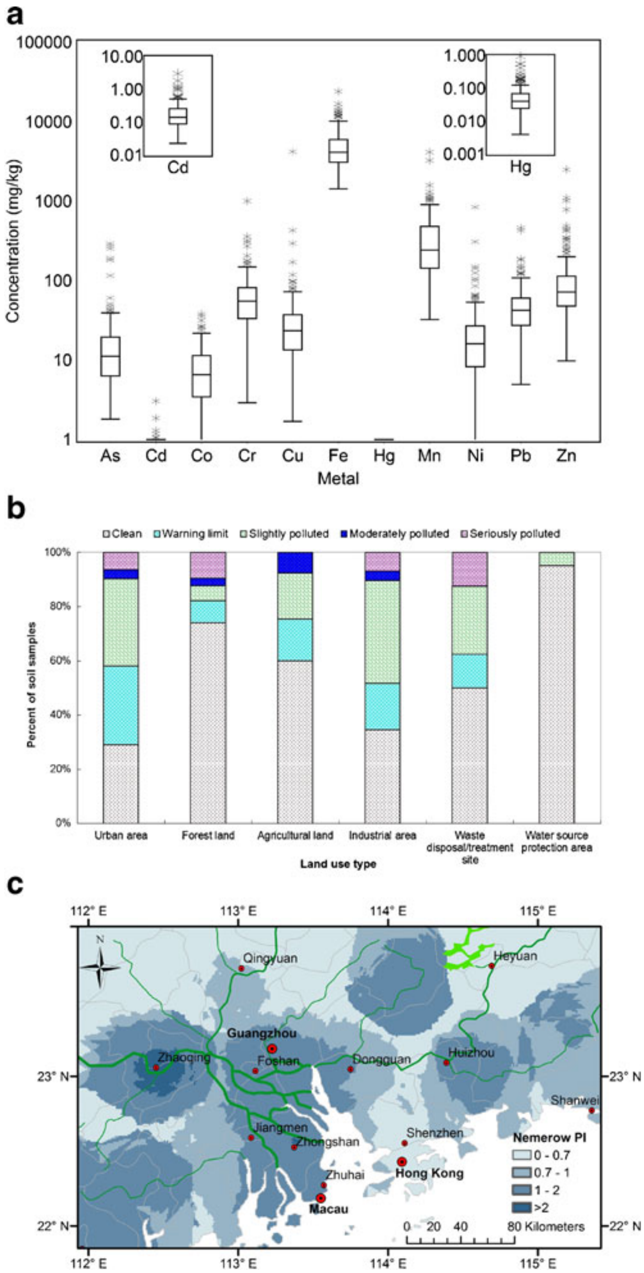

Fig. 2 Heavy metal pollution of the surface soils in the PRD: **a** Box-and-whisker plots of the heavy metal concentrations, where the *band near the middle of the box* is the median and the *bottom and top of the box* are the lower and upper quartiles, respectively. The *vertical lines* (*whiskers*) represent the 1.5 interquartile ranges of the lower and upper quartiles, and data outside the whiskers are outliers and are plotted as *stars*; **b** levels of heavy metal pollution in the surface soils from lands of different use types indicated by the Nemerow pollution indices; and **c** the spatial distribution of the heavy metal pollution level (the Nemerow pollution index) in the PRD

from Shenyang, a heavy industry base in China (Table S6), which indicates that heavy metal pollution is an environmental problem worthy of significant attention in the PRD.

Table 1 shows the mean values of pollution indices for heavy metals in the surface soils from lands of different use types in the PRD. Overall, the pollution levels of heavy metals decreased in the order of Cd∼Zn∼Cu>As∼Cr∼Ni>Pb∼Hg. The soils from the water source protection areas had the lowest mean values of pollution indices of heavy metals in general. High pollution indices for Cd, Zn, and Cu were observed in the soils from the urban areas, waste disposal/treatment sites, and industrial areas, where the surface soils had been subjected to stronger influence of human activities compared to the other areas. Meanwhile, the soils from the forest lands showed relatively high levels of As and Ni.

The Nemerow pollution indices (PI_N) also varied significantly for the surface soils of different land use types (Table 1). The soils from the water source protection areas had PI_N values ranging from 0.28 to 1.05 (mean, 0.45), which is indicative of minimum pollution by heavy metals. With the PI_N values in the range of 0.30 to 2.90 (mean, 0.82), the soils from the agricultural lands were also in good quality in general. The PI_N values of the soils from the forest lands varied from 0.23 to 15.24 (mean, 1.23), indicating that overall slight pollution by heavy metals occurred in the forest lands while some sites were severely polluted. The soils from the industrial areas had the highest mean PI_N value (3.05), followed by those from the urban areas (1.33) and waste disposal/treatment sites (1.27).

Figure 2b shows the levels of heavy metal pollution in the surface soils from lands of different use types in the PRD based on the Nemerow pollution indices. Only less than approximately 35 % of the surface soils from the urban areas and industrial areas could be classified as "clean" with respect to heavy metal pollution, while over 90 % of the soils from the water source protection areas were "clean." Overall, the Nemerow pollution indices show that for different land use types, the overall heavy metal pollution of the surface soils in the PRD decreased in the order of: urban areas>waste disposal/treatment sites∼industrial areas>agricultural lands∼forest lands>water source protection areas.

Figure 2c depicts the spatial distribution pattern of soil heavy metal pollution in the PRD based on the Nemerow pollution indices. Heavy metal pollution ranging from warning to moderate levels was observed in most parts of the PRD, indicating the wide occurrence of heavy metal pollution in the surface soils. The highest pollution level was found in the area surrounding Zhaoqing, which is concentrated with metalliferous mining and smelting industries. Another major area with heavy pollution was located between Guangzhou and Zhuhai, covering Foshan, Zhongshan, and Jiangmen. This area covers a cluster of major urban centers in the PRD and hosts a wide range of industries producing acid batteries, electronics, textiles, and clothes, among other consumer products, which could release a range of heavy metals. In addition, vehicular emissions were also a major source of heavy metals in this highly urbanized area with heavy traffic.

Table 1 Mean pollution indices of As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn in the surface soils from lands of six different use types in the PRD and the corresponding Nemerow pollution indices

Land use type	Single pollution index								Nemerow pollution index			
	As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	Mean	Min	Median	Max
Urban area	0.61	1.48	0.45	0.87	0.37	0.57	0.34	1.02	1.33	0.32	0.90	7.33
Forest land	0.94	0.35	0.51	0.52	0.16	0.81	0.15	0.29	1.23	0.23	0.47	15.24
Agricultural land	0.49	0.79	0.41	0.64	0.23	0.59	0.19	0.51	0.82	0.30	0.58	2.90
Industry area	0.55	0.97	0.41	3.65	0.22	0.66	0.23	1.08	3.05	0.31	0.85	60.29
Waste disposal/treatment site	0.52	1.11	0.81	1.23	0.23	1.12	0.38	1.08	1.27	0.28	0.83	4.72
Water source protection area	0.35	0.39	0.26	0.21	0.19	0.18	0.14	0.24	0.45	0.28	0.42	1.05

Identification of the sources of heavy metals

Table 2 shows the correlation matrix of the heavy metals in the surface soils of the PRD. The correlation coefficient between Cr and Ni was 0.93, which indicates a strong linear correlation at the 0.01 significance level and a common origin of these metals. Cu and Zn formed another highly correlated pair with a correlation coefficient of 0.82, suggesting they probably originated from some common sources. Mn exhibited strong positive correlations with both Fe (0.50) and Co (0.53). Fe and Mn occur naturally at abundant levels and are thus barely affected by human activities, which explains their apparent correlation in the surface soils. Co is also widely scattered in the Earth's crust, and its correlations with Fe (0.49) and Mn (0.53) indicate that its occurrence in the surface soils was mainly due to natural sources. The lack of significant linear correlation between As and the other heavy metals suggests that its sources were quite different from those of the others.

To make the results more easily interpretable, PCA with VARIMAX normalized rotation was applied. According to the Kaiser criterion (Kaiser 1960), five principal components extracted from the variables with eigenvalues >1 were retained for further analysis (Table S7). Table 3 shows the factor loadings of the heavy metals and their communalities from the PCA. The communalities shown by the variables, considering the five major factors only, varied from 65 % for Cd to 99 % for As, indicating that all the heavy metals were well represented by these five principal components. In the interpretation of PCA patterns, factor loadings greater than 0.71 are typically considered excellent, while those less than 0.32 are regarded as very poor (Nowak 1998). With the exception of Pb and Cd, each heavy metal had one and only one factor loading greater than 0.71 on the five rotated factors. Factor 1 was dominated by Mn, Fe, Co, and Cd, and accounted for 22.9 % of the total variance. The factor loading of Cd (0.53) was not as high as those of the other metals within the same group (0.82 for Mn, 0.79 for Fe, and 0.78 for Co), and was also partially represented in Factor 4 with a comparable factor loading of 0.56, suggesting a quasi-independent behavior within this group. Cu and Zn were highly associated, displaying high factor loading values (0.95 and 0.91, respectively) in Factor 2. Factor 3, which accounts for 17.8 % of the total variance, was dominated by Cr and Ni. Factor 4 was dominated by Hg, Pb, and Cd, with Hg having the highest loading (0.83). The attribution of Pb was ambiguous, given the loading values of 0.46 and 0.64 in Factor 2 and Factor 4, respectively. The heavy metal As was isolated in Factor 5 with

Table 2 Pearson's correlation matrix of heavy metals in the surface soils of the PRD

Metal	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Cd	Hg	Pb
Cr	1.00										
Mn	0.04	1.00									
Fe	0.21**	0.50**	1.00								
Co	0.22**	0.53**	0.49**	1.00							
Ni	0.93**	0.08	0.17**	0.25**	1.00						
Cu	0.08	0.03	0.08	0.05	0.11	1.00					
Zn	0.14*	0.15*	0.27**	0.23**	0.15*	0.82**	1.00				
As	0.08	0.14*	0.10	0.05	0.01	0.03	−0.01	1.00			
Cd	0.10	0.28**	0.46**	0.42**	0.08	0.08	0.46**	0.04	1.00		
Hg	−0.02	0.06	0.06	0.12	−0.03	0.00	0.19**	0.00	0.23**	1.00	
Pb	0.11	0.16*	0.28**	0.31**	0.09	0.25**	0.63**	0.12	0.56**	0.32**	1.00

* $p<0.05$; ** $p<0.01$

Table 3 The rotated component matrix of heavy metals in the surface soils of the PRD (PCA factor loadings greater than 0.32 are shown in bold)

Metal	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Communality
Cr	0.09	0.04	**0.98**	0.02	0.05	0.97
Mn	**0.82**	0.01	−0.05	−0.06	0.12	0.70
Fe	**0.79**	0.10	0.12	0.09	0.04	0.66
Co	**0.78**	0.03	0.18	0.17	−0.04	0.67
Ni	0.11	0.06	**0.97**	−0.02	−0.02	0.96
Cu	−0.02	**0.95**	0.04	−0.08	0.02	0.91
Zn	0.19	**0.91**	0.08	0.31	−0.04	0.97
As	0.08	0.00	0.03	0.02	**0.99**	0.99
Cd	**0.53**	0.21	0.02	**0.56**	−0.05	0.65
Hg	−0.05	−0.07	−0.03	**0.83**	−0.01	0.70
Pb	0.25	**0.44**	0.05	**0.67**	0.11	0.72

a dominant loading of 0.99. The PCA loadings for the first three rotated components are plotted in Fig. 3a, which visually illustrates the associations among these heavy metals in the surface soils of the PRD.

Hierarchical cluster analysis was also used in this study to identify the relatively homogeneous groups of heavy metals. Figure 3b shows that Cr and Ni were significantly correlated with each other and formed a cluster. Strong association was also observed between Cu and Zn, which were associated with Pb and Cd at later stages. Mn, Co, and Fe formed the third group in the cluster analysis, indicating similar distribution patterns. As expected, As was isolated from the other heavy metals, which is indicative of lack of association with the others in the soils.

The enrichment levels of the heavy metals were calculated to help further identify their sources in the surface soils of the PRD. Table 4 summarizes the descriptive statistics of the EF values of the heavy metals. All the heavy metals evaluated showed maximum EFs much greater than 10, which indicates that some areas had been strongly impacted by anthropogenic sources of heavy metals (Liu et al. 2003). The mean EF values of Cd, Cu, Zn, and As were greater than or close to 3, suggesting that they had been polluted by anthropogenic sources. The degree of heavy metal enrichment in the surface soils of the PRD decreased in the order of Cd>Cu>As>Zn. The mean EF values of Pb, Hg, Cr, and Ni were comparable, ranging from 1.07 for Hg to 2.16 for Ni. Meanwhile, the median EF values of Cr, Ni, and Hg were less than or close to 1, indicating that these metals in over half of the surface soils were originated predominantly from natural sources. The median EF value of Pb (1.38) was close to that of As (1.40), suggesting that they have been impacted widely by anthropogenic sources.

The results of PCA, CA, and EF analyses are consistent on the basic distribution patterns of the heavy metals evaluated. Together, they suggest that the heavy metals in the surface soils of the PRD could be classified into the following five groups:

The first group consists of Mn, Co, and Fe, which comprise the first factor of PCA that is the most important component and of lithogenic origin rather than the result of human activities. The variability in the concentrations of these metals in the surface soils of the PRD was mainly controlled by the parent materials of the soils.

The second group includes Cu, Zn, Pb, and Cd, which are controlled primarily by human activities. The second factor of PCA contains mainly Cu and Zn, and can be considered as an

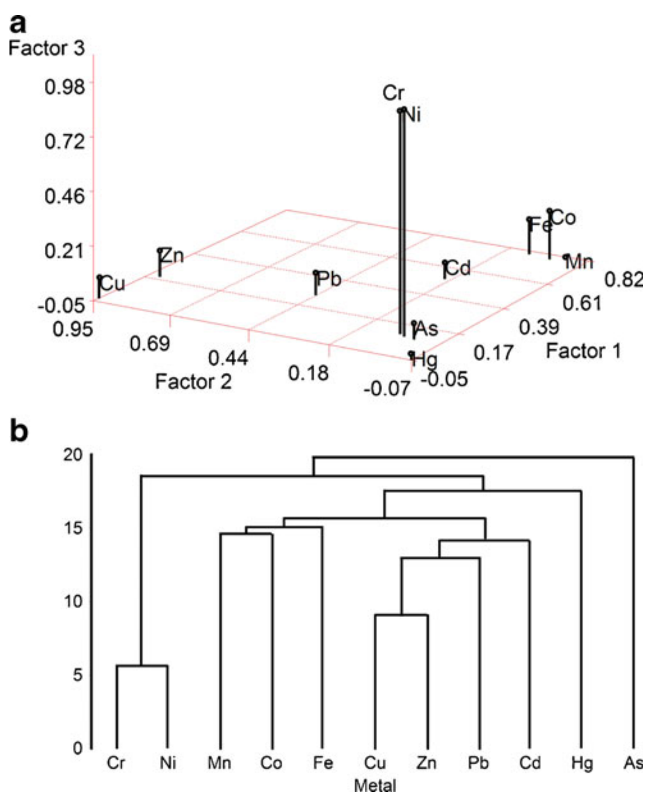

Fig. 3 Multivariate analyses of heavy metals in the surface soils of the PRD: **a** 3-D plot for PCA loadings of the heavy metals. **b** Hierarchical dendogram of the heavy metals obtained by the single-linkage clustering method

Table 4 The basic statistics of the enrichment levels of heavy metals in the surface soils of the PRD

Metal	Enrichment factor								
	Mean	Standard deviation	Minimum	5 %	25 %	50 %	75 %	95 %	Maximum
As	3.00	7.92	0.13	0.25	0.74	1.40	2.74	7.91	106.0
Cd	3.97	2.95	0.17	0.71	1.73	3.38	5.29	10.0	20.9
Cr	2.03	3.10	0.04	0.18	0.51	1.07	2.21	6.15	33.1
Cu	3.03	14.06	0.05	0.31	0.80	1.53	2.78	5.79	212
Hg	1.07	1.66	0.00	0.09	0.31	0.66	1.29	3.03	20.2
Ni	2.16	4.70	0.00	0.00	0.53	1.12	2.41	5.57	54.9
Pb	1.73	1.66	0.04	0.37	0.73	1.38	2.23	4.45	17.8
Zn	2.48	3.41	0.13	0.55	1.11	1.71	2.92	6.60	45.5

anthropogenic component. Meanwhile, Pb and Cd are loaded on both Factor 2 and Factor 4 of the PCA. The EF values of Cd in the surface soils varied from 0.12 to 20, with about 46.3 % of the soil samples classified as moderate enrichment and 25.6 % as significant enrichment. Zn and Cu were also present at moderate to significant enrichment levels in the surface soils of the PRD, with Zn in 56.8 % of the soil samples and Cu in 47.6 % of the soil samples fallen in these two categories. Extremely high EF values were also found for the heavy metals in this group, with Zn showing a maximum EF value of 59.5 and Cu having an even higher maximum EF of 261.7. These results consistently suggest that the elevated levels of Cd, Zn, and Cu in the surface soils of the PRD resulted largely from anthropogenic sources. More detailed assessment finds that samples enriched with Cd, Cu, and Zn were mainly located in the urban areas, industrial areas, and agricultural lands, confirming that human activities contributed greatly to the accumulation of these metals in the surface soils. Soil pollution by these metals probably resulted from industrial and vehicular emissions, wastewater irrigation, and the application of pesticides and fertilizers on agricultural lands. Compared to Cd, Cu, and Zn, Pb had lower EF values (0.04 to 15.9), while Pb pollution was more widespread than the other heavy metals. Pb in the surface soils was probably contributed by deposition of the atmospheric Pb emitted from vehicles and industrial point sources, which could be carried over very long distances, as well as the application of lead-containing pesticides on agricultural lands (Cheng and Hu 2010a; Kober et al. 1999).

Cr and Ni make up the third group, and they come mainly from natural sources. Only less than 5 % of the soil samples had EF values of Cr or Ni greater than 5 (i.e., significant pollution), indicating that soil pollution by these two metals was relatively limited in the PRD. More detailed analysis shows that Cr and Ni were present at lower enrichment levels in the urban areas and industrial areas compared to the farm lands and forest lands. Therefore, vehicular or industrial emissions could not be primarily responsible for the elevated Cr and Ni levels observed in the surface soils. In general, anthropogenic inputs of Cr and Ni, such as fertilizers and manure, have lower concentrations of these metals than the contents already present in the soils (Alloway 1995). Meanwhile, wastewater had been used to irrigate some agricultural lands in the PRD, but not the forest lands. Consequently, pollution related to agronomic practices could also be ruled out as the main sources of Cr and Ni. Overall, the variability of Cr and Ni in the surface soils appeared to be controlled mainly by the soil parent materials. This conclusion is also consistent with the results of earlier research, which showed a lithogenic control over the distributions of Cr and Ni in the soils of Guangdong Province (Xia and Wu 2011; Yang et al. 2007).

The fourth group contains Hg, which has both natural and anthropogenic sources. The EF values of Hg in the surface soils varied from 0.01 to 30.4, with about 24 % of the samples classified as moderate to very high enrichment levels. Hg exhibited less enrichment in the surface soils of the PRD compared to the heavy metals bearing distinct signatures of anthropogenic impact, such as Cd, Cu, and Zn. Similar to Pb, higher EF values of Hg were also observed in the soils from the urban areas compared to those from the other types of land uses. Combustion of fossil fuels, particular coal, and waste incineration released relatively large amounts of mercury into the atmosphere, while improper disposal of a wide variety of commercial products, including thermometers, blood pressure gauges, and some electrical switches and relays, could also result in soil pollution by Hg (Cheng and Hu 2010b, 2012; Hu and Cheng 2012). Overall, the distribution pattern of Hg in the surface soils indicates that Hg pollution was limited in the PRD, and was contributed by both natural background and anthropogenic inputs.

The final group is made of As, which behaves remarkably different from the other heavy metals in both PCA and CA analyses, implying significantly different sources. About 66.5 % of the soil samples showed deficiency to minimal enrichment of As, while As was present at significant to extremely high enrichment levels in 10.1 % of the soil samples. It was also observed that the soils with EF values greater than 5 were collected from the agricultural lands and forest lands in general, while there was no evidence showing that the emissions and discharges from the industrial and urban areas contributed significantly to the soil As pollution. Besides the natural sources in the parent materials, non-point sources, such as the application of manure, fertilizers, and pesticides, probably also contributed to the elevated levels of As in the agricultural soils.

It should be noted that although the simple multivariate analyses (e.g., PCA and CA) and correlation matrix used in this study provide important information on the potential sources of heavy metals, better statistical and geochemical tools are necessary for apportioning the contributions of natural and anthropogenic sources to the soil heavy metal

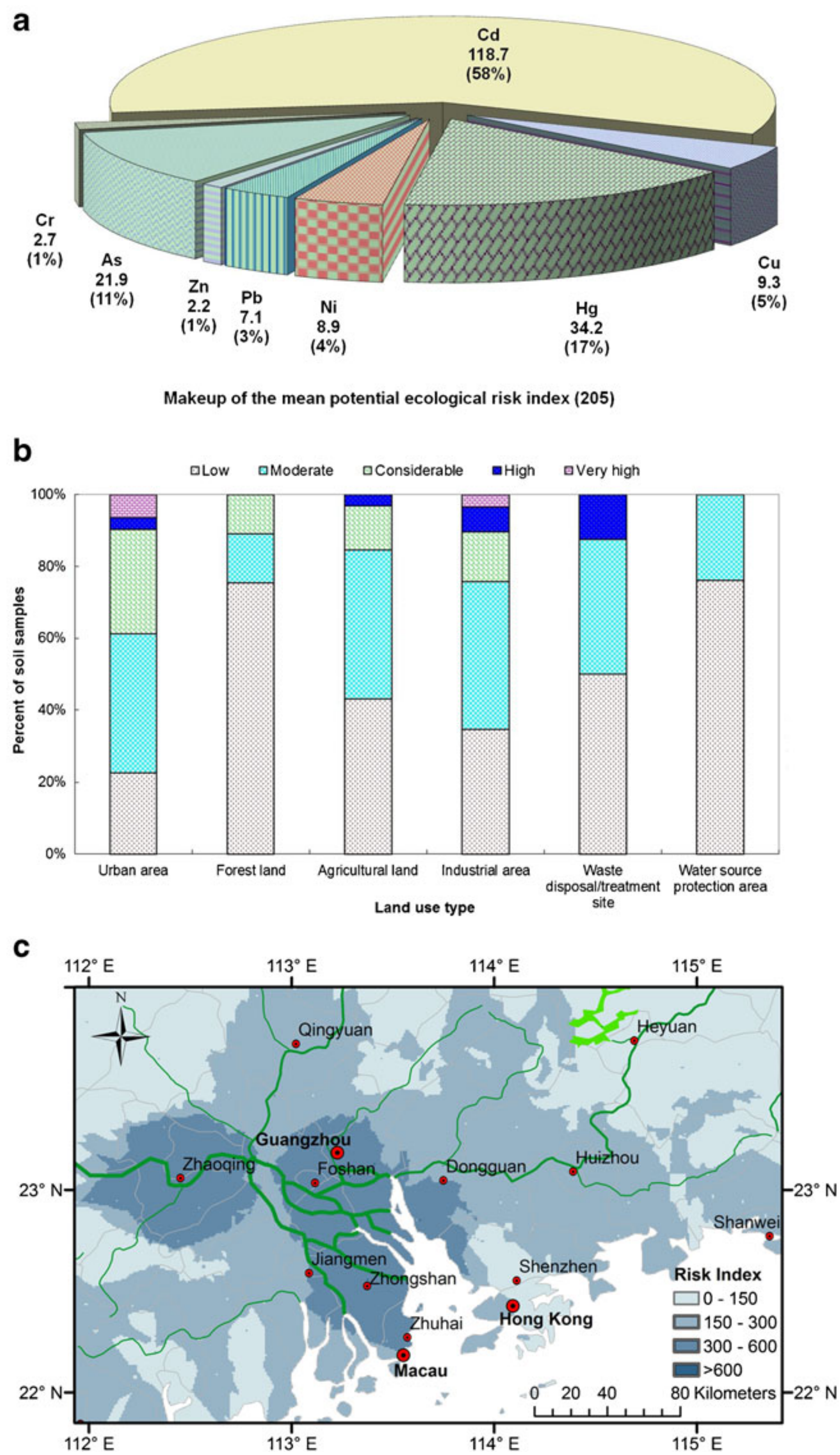

Fig. 4 The potential ecological risk of soil heavy metal pollution in the PRD: **a** Contributions of individual heavy metals to the mean potential ecological risk of the surface soils; **b** Potential ecological risk levels of heavy metals in the surface soils from lands of different use types; and **c** The spatial distribution of the potential ecological risk level

pollution (Cheng and Hu 2010a; Cloquet et al. 2006; Hu and Cheng 2013; Kubosova et al. 2009; Vega et al. 2009; Zhang et al. 2008). Additional characterization of the soil properties (such as soil total organic carbon and available phosphorus) could further help discriminate the natural and anthropogenic contributions on soil heavy metal pollution.

Potential ecological risk of soil heavy metal pollution

Figure 4a shows the mean ecological risk factors of different heavy metals and their contributions to the total potential ecological risk of the surface soils. With a mean risk factor of 118.7, Cd posed the highest level of potential ecological risk, while the other heavy metals had much lower levels of risk with mean risk factor values of less than 40. The average value of the potential ecological risk indices for the surface soils in the PRD, calculated as the sum of the mean risk factors of the heavy metals, is 205, indicating an overall moderate ecological risk posed by the heavy metals. The risk levels for soils from lands of different use types are summarized in Fig. 4b. Similar to the distribution pattern of the Nemerow pollution indices, the potential ecological risk of the surface soils with different land use types in the PRD decreased in the order of: urban areas>waste disposal/treatment sites~industrial areas>farming lands~forest lands>water source protection areas.

Figure 4c shows the spatial distribution pattern of the potential ecological risk indices of heavy metal pollution in the PRD. As expected, the potential ecological risk of the surface soils from the areas with relatively high levels of heavy metal pollution, including the area surrounding Zhaoqing and the area between Guangzhou and Zhuhai, was also high. Overall, the areas with concentrated industrial activities and dense population were typically characterized by higher potential ecological risk compared to the areas with less developed local economy. Therefore, care must be taken to reduce and prevent soil pollution by heavy metals in the course of economic development in the PRD and the rest part of China. It is also worth noting that pollution of surface soils in the PRD is not limited to heavy metals. Pollution of the surface soils by persistent organic pollutants is to be reported later.

Conclusions

Clear accumulations of Cd, Cu, Zn, and As were observed through the investigation of 227 soil samples from lands with six different use types in the PRD, and approximately 21.1, 15.4, 8.8, and 12.3 % of the soil samples were moderately to heavily polluted by Cd, Cu, Zn, and As, respectively. Correlation matrix and multivariate analyses show that Mn, Co, Fe, Cr, and Ni originated predominantly from lithogenic sources, while the contents of Cu, Zn, Pb, and Cd in the surface soils of the PRD were contributed mainly by anthropogenic sources. Hg and As did not bear distinct signatures of anthropogenic impact, and were probably controlled by both natural and anthropogenic sources. The potential ecological risk indices indicated an overall moderate ecological risk from the heavy metal pollutants, with Cd posing the highest level of risk. The heavy metal pollution level (indicated by the Nemerow pollution index) and the potential ecological risk of the surface soils from lands of different use types both decreased in the order of: urban areas>waste disposal/treatment sites~industrial areas>agricultural lands~forest lands>water source protection areas. These findings have important implications for the development of pollution prevention and reduction strategies to reduce heavy metal pollution for regions undergoing fast industrialization and urbanization.

Acknowledgments The authors thank Zaicheng He, Yanli Wei, Liangying Liu, Haiyan Hu, and Baozhong Zhang for help with field sampling. This work was supported in parts by the Natural Science Foundation of China (grant nos. 41202251, 41121063, and 41073079) and the Chinese Academy of Sciences (Y234081001 and "Interdisciplinary Collaboration Team" program). This is contribution No. IS-1648 from GIGCAS.

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