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Distribution patterns and sources of heavy metals in soils from an industry undeveloped city in Southern China

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A R T I C L E I N F O

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A B S T R A C T

The accumulations of heavy metals in urban soils are derived from natural parent materials and complex anthropogenic emission sources. This paper investigated metal contamination in urban soils at an industry undeveloped city (Haikou) in southern China, an ideal place to quantitatively assess the contribution of metals from different sources. The concentrations of most heavy metals in the urban soils of Haikou were much lower than their guideline values and that of those from other big cities in China. In contrast, the chemical speciation of metals in this study was similar to those from other cities. The spatial distributions of heavy metals and principal component analysis (PCA) revealed that basaltic parent materials, traffic emissions, and coal combustion were the main factors controlling the distribution of metals in the soils. The Pb isotope signatures of the Haikou soils were greatly different from those of the Beijing and Shanghai soils, but similar to those of the Guangzhou soils, suggesting the common sources of Pb in southern China cities. The results of ternary mixing model of Pb isotopes showed that the contributions of Pb from natural background, coal combustion and traffic emission sources were 5.3–82.4% (mean: 39.7 ± 21.1%), 0–85.7% (mean: 25.5 ± 24.6%), and 1.9–64% (mean: 34.8 ± 22.9%), respectively. This suggests that traffic emission is still the most important anthropogenic source of Pb in Haikou.

1. Introduction

Heavy metal contamination in urban environments becomes a worldwide issue due to their persistence and high toxicity to humans (Wei and Yang, 2010; Men et al., 2020; Jia et al., 2020; Liu et al., 2020a, Liu et al., 2020b). Soil, an essential urban ecosystem component, serves as not only a sink but also a source of urban metal pollutants. Metals retained by urban soils can be agitated and re-suspended into the atmosphere and may impair human health by inhalation, direct ingestion, and dermal contact (Ljung et al., 2006; Yamamoto et al., 2006; Amato et al., 2009; Bi et al., 2013; Han et al., 2020). Extensive studies have reported a strong correlation between blood lead levels (BLLs) of kids and Pb concentrations in urban soils (Laidlaw et al., 2005; Ren et al., 2006; Laidlaw and Taylor, 2011; Li et al., 2020). Thus, heavy metals caused soil contamination is an important assessment aspect of the urban environmental quality.

Urbanization in China has unfold at an unprecedented rate in the past three decades, resulting in substantial deterioration of urban environments, including water, atmosphere, and soils (Kelly et al., 1996; Li et al., 2001; Manta et al., 2002; Chen et al., 2005; Duzgoren-Aydin et al., 2006; Liu et al., 2019a, Liu et al., 2019b, Liu et al., 2020a,Liu et al., 2020b; Liu et al., 2021). Wei and Yang (2010) and Luo et al. (2012) summarized the accumulation of heavy metals in soils from several typical China's cities and found many of them were polluted by more than one type of heavy metals. The occurrences and distribution patterns of heavy metals in urban soils are mainly controlled by the sources of metals, and thus the source discrimination of metals is becoming a real necessity. In metropolises, metals in soils are originated from natural parent materials and anthropogenic sources, including traffic emissions, coal combustion, and various industrial activities (Bi et al., 2007, 2009,

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2017; Wang et al., 2020a). Heavy metals emitted from complex industrial processing generally have similar characteristics (e.g., similar concentrations, compositions, isotope ratios) to those from traffic emissions and coal combustion, making them difficult to be distinguished from each other by source apportionment models or isotope fingerprints (Huang et al., 2014; Bi et al., 2017; Wang et al., 2019b). In order to assess the contamination by sole industrial activities, many researchers conducted field studies restricted to urban industrial areas, but this is still unable to totally exclude the impacts from traffic emissions and coal combustion (Zhu et al., 2013a, b; Wang et al., 2020b). Therefore, quantifying the contribution from traffic emissions and coal combustion is essential to source discrimination of heavy metals in urban environment.

Haikou, the capital of Hainan province in South China, is the industry least developed capital city in China after Lhasa. In 2019, the whole industry output of Haikou is about 50 billion yuan, only 2.5% of those of Beijing (HMBS, 2019). Atmospheric emission inventories indicated that heavy metal pollutants in the whole Hainan province are predominantly from traffic emissions and coal combustion, while the contribution from industrial emissions (excluding coal emissions from industrial boilers) is quite limited (Li et al., 2012; Tian et al., 2012a, b, 2015). Thus, it is believed that heavy metals settled in urban soils of Haikou are mainly derived from parent materials, traffic emissions, and coal combustion. This makes Haikou an ideal place for quantitative assessment of the contribution of metals from different sources. In this research, soil samples were collected from different urban regions of Haikou, and the total concentrations and chemical speciation of heavy metals, as well as Pb isotope compositions were detected. The main objectives of the study are 1) to address the occurrences and distribution patterns of heavy metals in urban soils with a less industry impact and 2) to trace and quantify the specific sources (parent materials, traffic emissions, and coal combustion) of heavy metals in the urban soils using principal component analysis (PCA) and lead isotope compositions. The results of this study may provide a useful reference for tracing the sources and assessing the contamination degrees of heavy metals in other cities.

2. Materials and methods

2.1. Sample collection and preparation

Hainan Province is situated in the southern of China (18°10′-20°10′N, 108°37′-111°03′E) and the domain area is 33,920 km^2. Climate in this region is tropical monsoon with a mean yearly rainfall of 1600–2500 mm and a mean yearly temperature of 23–25 °C. Haikou city, the capital of Hainan province, is a world-famous resort, with an area of 2304 km^2 and a population of 2.33 million by the end of 2019. Geologically, the surface outcrops are Cenozoic mafic volcanic rocks and Quaternary unconsolidated sediments, and the major type of soil is latosol.

Soil samples were collected from different urban areas of the Haikou city, including industrial area, commercial area, residential area, resort area, street and suburban district (Fig. 1a). A sum of 70 surface soils (0–20 cm) were collected. Each sample comprised of 3–7 sub-samples from a 2 m × 2 m zone. The samples were air-dried at 25 °C and disaggregated and sieved by a 1 mm polyethylene sieve to get rid of stones, coarse substances, and other debris. Subsequently, the dried soil was ground to fine powder for geochemical analysis.

2.2. Analytical methods

For the analysis of major elements and heavy metal concentrations of the soils, the collected samples were digested using the following procedures: the samples (about 50 mg) were accurately weighed into a Teflon tube with 3 mL of Nitric acid and 0.5 mL of Hydrofluoric acid added. The tubes were digested for 48 h at 150 °C. Each digest solution was then evaporated to near dryness at 90 °C. Then, 3 mL of HNO_3 and 2 mL of ultrapure water (2 ml, Milli-Q) were added to each residue, and the closed Teflon tubes were kept at 150 °C again for 6 h. After cooling down, the solution was diluted to 50 mL using ultrapure water (Bi et al., 2017). The speciation of heavy metals in urban soils was evaluated using a sequential extraction procedure that was modified from Tessier et al. (1979). This method divided the metals into six phases: F1, exchangeable fraction (2.5 g soil extracted by 25 ml of 1 M $MgCl_2$, $pH = 7.0$, for 20 min); F2, carbonate bound fraction (1 M NaOAc adjusted to $pH = 5.0$ with acetic acid, for 6 h); F3, humic acids (HA) bound fraction (0.1 M $Na_4P_2O_7$, $pH = 10.0$, for 3 h); F4, Fe–Mn oxides bound fraction (0.04 M $NH_2OH{\cdot}HCl$ in 25% (v/v) HOAc at 96 °C, for 6 h); F5, organic matter and sulfides bound fraction (5 ml of 30% H_2O_2 and 3 ml of 0.02 M HNO_3 for 2 h, a second 3 ml of 30% H_2O_2 for 3 h, at 85 °C); F6, residual fraction (total digestion with a concentrated mixture of $HCl/HNO_3/HF/HClO_4$) (Fu et al., 2011).

Major elements (Al, Fe, Mn, Ti and V) and heavy metals (As, Cd, Cr, Cu, Ni, Pb, Sb and Zn) of the digested solutions were determined by ICP-AES (Agilent 5100, Australia) and ICP-MS (Agilent 7500a, Australia), respectively. The measurements were validated by method blanks, duplicates, and certified reference materials (Chinese National Standard Soils GBW07423). The average recovery for the metals ranged from 85 to 110% (Wang et al., 2019b).

The Pb isotopic composition of source-related samples and atmospheric deposition particulate samples was measured by thermal ionization mass spectrometry (TIMS, Finnigan MAT 261). A standard reference material (NIST SRM 981) was used for calibration. Pb blanks during the study's course are small than 1‰ of the total Pb that was analyzed in each sample. A mass fractionation correction was conducted based on the standard (NIST SRM 981). Analytic uncertainties (±2 standard deviation) are as follows: $^{206}Pb/^{204}Pb < 0.0017$, $^{207}Pb/^{204}Pb < 0.0014$, $^{208}Pb/^{204}Pb < 0.0038$.

2.3. Statistical analysis

The data were statistically processed by the statistical package SPSS v25.0 (SPSS Inc.). One-Way ANOVA analysis was performed to evaluate the difference of metal concentrations between different urban areas. The heavy metal concentrations were mapped based on the inverse distance method using ArcGIS 10.2 software (ESRI, Redlands, CA, USA) to allow the spatial patterns to be assessed. Principal component analysis (PCA) was conducted using factor extraction with eigenvalues >1 after varimax rotation.

The pollution status of heavy metals in the soils was quantified using the Nemerow pollution index (Lee et al., 2006), which is the most widely used method for soil metal pollution assessment in China (CEPA, 2004). It includes single factor pollution index (P_i) and integrated pollution index (P_N), which are defined as follows:

$$P_i = C_i / T_i \tag{1}$$

$$\mathrm{P_N} = \sqrt{\frac{1}{2}\left(\mathrm{Pi}^2_{\mathrm{Max}} + \mathrm{Pi}^2_{\mathrm{Ave}}\right)} \tag{2}$$

$$P_{iAve} \sum_{i=1}^{n} w_i P_i \Big/ \sum_{i=1}^{n} w_i \tag{3}$$

where C_i is the concentration of a given metal in soil samples, and T_i is the corresponding target concentration. Here we chose the Dutch soil guidelines (VROM, 2000) as the target values due to their universality and rigor (Luo et al., 2012). $P_{i\ Max}$ and $P_{i\ Ave}$ are the maximum and weighted average values of P_i of the considered metals, respectively. w_i is the weighting factor of the metals, which is 3 for As, Cd, and Pb, and 2 for Cu, Cr, and Ni, respectively. According to P_N, the soil quality is classified as five degrees: clean ($P_N \leq 0.7$), precautionary ($0.7 < P_N \leq 1.0$), slightly polluted ($1.0 < P_N \leq 2.0$), moderately polluted ($2.0 < P_N \leq$

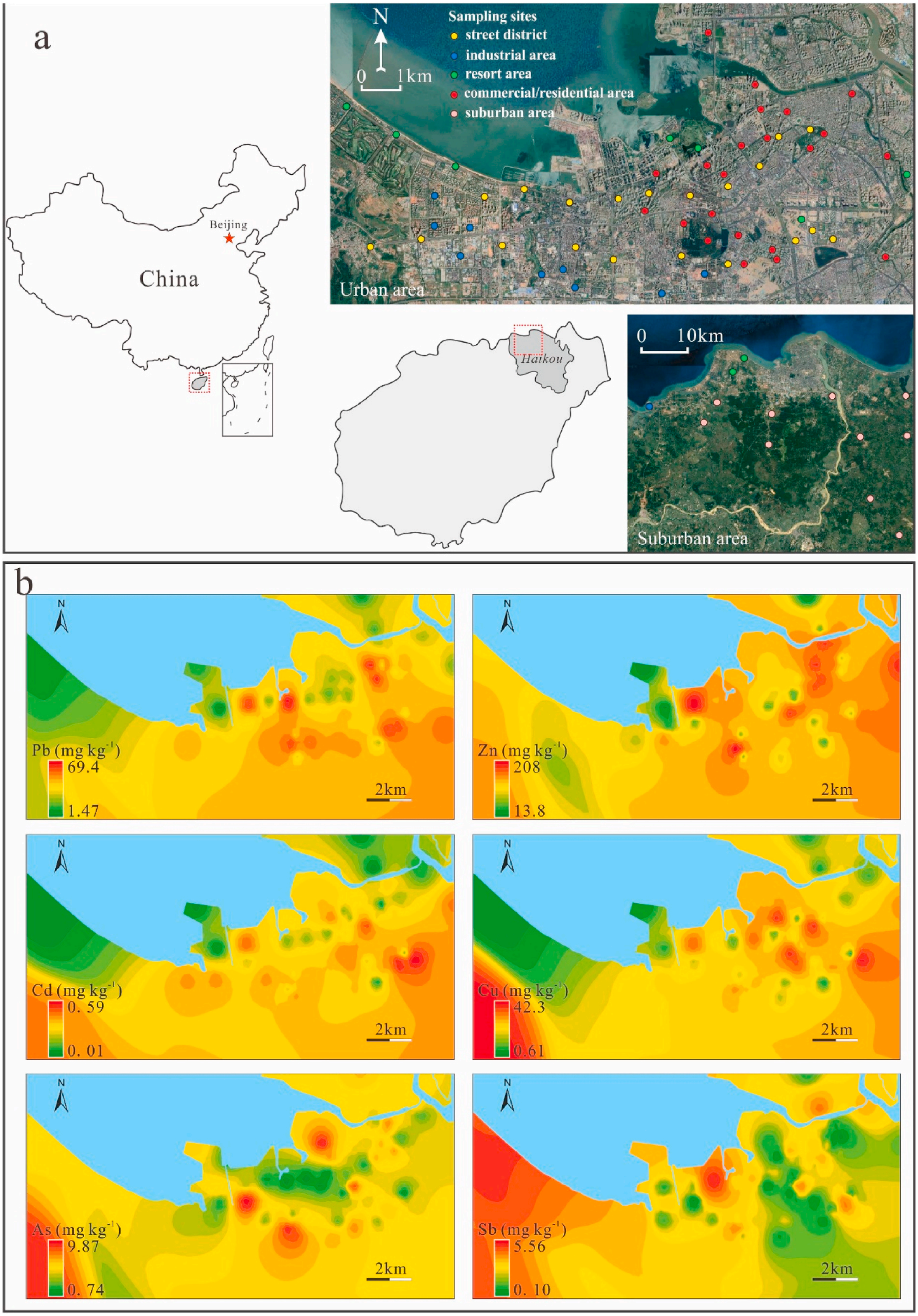

Fig. 1. The map of study area. a: sampling location, b: geochemical maps of Pb, Zn, Cd, Cu, As, and Sb in soils from urban areas of Haikou city.

3.0), and heavily polluted ($P_N > 3.0$).

3. Results

3.1. Major elements and heavy metal concentrations

The concentrations of major elements and heavy metals in the soils are listed in Table 1. The major element concentrations varied widely, ranging from 0.01 to 15.4 g/kg for Al, 2.94 to 148 for Fe, 0.05–1.19 g/kg for Mn, 0.31–30.2 g/kg for Ti, and 0.18 to 13.2 for V, respectively. The ranges of As, Cd, Cr, Cu, Ni, Pb, Sb and Zn concentrations in the soils were 0.74–9.87 mg/kg, 0.01–1.34 mg/kg, 8.1–376 mg/kg, 0.61–98.7 mg/kg, 1.46–190 mg/kg, 1.47–69.4 mg/kg, 0.11–1.68 mg/kg and 13.8–208 mg/kg, respectively (Table 1). The mean concentrations of heavy metals were generally higher than their corresponding median values, indicating that the dispersion of the data depended on the high values. In comparison with the background values of China's soils, the Cd, Cr and Ni concentrations were higher, while other metal concentrations were lower or comparable in the collected soils. In addition, the concentrations of most the metals in this study were lower than their guideline values (Table 1), indicating a limited anthropogenic impact in this city.

The trace metal concentrations in soils from different functional areas are showed in Fig. 2. The significantly high ($p < 0.05$) concentrations of Pb (mean 41.8 ± 19.2 mg/kg) and As (mean 5.6 ± 2.7 mg/kg) were found in samples from the street district and industrial areas, respectively. However, the significantly high ($p < 0.01$) concentrations of Cd, Cr, Cu, and Ni were unexpectedly found in those samples from the suburban district. In addition, the soils of the suburban district had significantly low ($p < 0.05$) concentrations of Sb.

3.2. The speciation of heavy metals

The sequential chemical fractions of trace metals in the selected soil samples are shown in Fig. 3. Cd in the soils was mainly associated with exchangeable (7.6–34.7%), Fe–Mn oxides (5.6–47.2%) and residual (8.4–55.9%) fractions, while the carbonate (8.9–22.3%), HA (2.8–19.6%), and OM and sulfides (6.2–21.8%) bound fractions were less important. Pb was mainly controlled by the Fe–Mn oxides bound fraction (25.8–81.0%), and the residual fraction (3.1–58.9%) was the second dominant. For Cu and Zn, the residual form was the most important chemical fraction (Cu, 34.1–88.6%; Zn, 28.8–74.2%), followed by the Fe–Mn oxides bound (Cu, 4.5–31.5%; Zn, 6.7–37.8%) and HA bound (Cu, 4.6–30.5%; Zn, 3.3–19.5%) fractions. Cr and Ni in the soils were present predominantly in the residual fraction (Cr, 84.2–96.8%; Ni, 71.7–95.6%), while the portions of the other fractions were generally less than 5%.

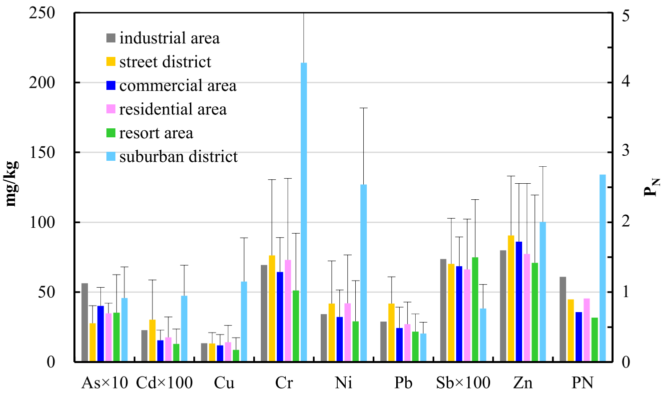

Fig. 2. Concentrations and pollution index (PN) of heavy metals in soils among different functional areas of Haikou.

3.3. Pb isotopic compositions

The Pb isotopic compositions of the soil samples, as well as the potential Pb sources, are presented in a three-isotope graph ($^{206}Pb/^{207}Pb$ vs. $^{208}Pb/^{207}Pb$) (Fig. 4). Generally, the natural sources, including marine sand, bedrock, and natural soils, had more radiogenic Pb compositions with $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ ratios of 1.19–1.22 and 2.039–2.085, respectively. In contrast, Pb from the anthropogenic sources exhibited a less radiogenic signature. Pb from the coal combustion dust in Haikou had $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ ratios of 1.162–1.171 and 2.103–2.113, respectively; and Pb from the vehicle exhaust had $^{206}Pb/^{207}Pb$ and $^{208}Pb/^{206}Pb$ ratios of 1.149–1.171 and 2.099–2.126, respectively. The soils from Haikou had intermediate Pb isotopic compositions ($^{206}Pb/^{207}Pb$, 1.172–1.195; $^{208}Pb/^{206}Pb$, 2.076–2.104) and fell between the natural and anthropogenic sources on the plot of $^{206}Pb/^{207}Pb$ vs. $^{208}Pb/^{206}Pb$.

4. Discussion

4.1. Distribution patterns of heavy metals in urban soils

Compared with other big cities in China, Haikou had obvious lower As, Cu, Pb, and Zn concentrations in the soils, which were attributed to the undeveloped industry (Fig. 5). However, the concentrations of Cr and Ni were much higher than that of those from most cities, revealing a high geological background of these metals in Haikou. The distribution patterns of heavy metals among different functional areas of Haikou further supported this statement. Significantly high ($p < 0.01$) concentrations of Cd, Cr, Cu, and Ni were simultaneously observed in suburban

Table 1
The concentrations of major elements and heavy metals in urban soils of Haikou.

	Mean	SD	Min	Median	Max	National soil background of China[a]	Chinese soil quality standard (II)[b]	Target value of Dutch soil guidelines[c]
Al (g/kg)	27.5	13.7	3.86	27.4	63.4			
Fe (g/kg)	46.5	34.4	2.94	37.8	148			
Mn (g/kg)	0.28	0.24	0.05	0.19	1.19			
Ti (g/kg)	6.28	5.40	0.31	4.79	30.2			
V (g/kg)	3.56	2.81	0.18	2.77	13.2			
As (mg/kg)	3.83	2.08	0.74	3.42	9.87	11.2	30	29
Cd (mg/kg)	0.25	0.22	0.01	0.19	1.34	0.097	0.3	0.8
Cr (mg/kg)	89.5	75.9	8.10	65.7	376	61	200	100
Cu (mg/kg)	19.1	21.6	0.61	11.1	98.7	23	100	36
Ni (mg/kg)	50.0	45.9	1.46	31.9	190	27	50	35
Pb (mg/kg)	29.2	16.8	1.47	25.7	69.4	27	300	85
Sb (mg/kg)	0.66	0.35	0.11	0.60	1.68	1.21		
Zn (mg/kg)	84.7	46.6	13.8	73.7	208	74	250	140

[a] The national background soil values (NBSVs) (Chen et al., 1991).

[b] The guideline value for the Environmental Quality Standard for Soils (II) in China (CEPA, 1995).

[c] Values for soil remediation proposed by Dutch Ministry of Housing, Spatial Planning and Environment (VROM, 2000).

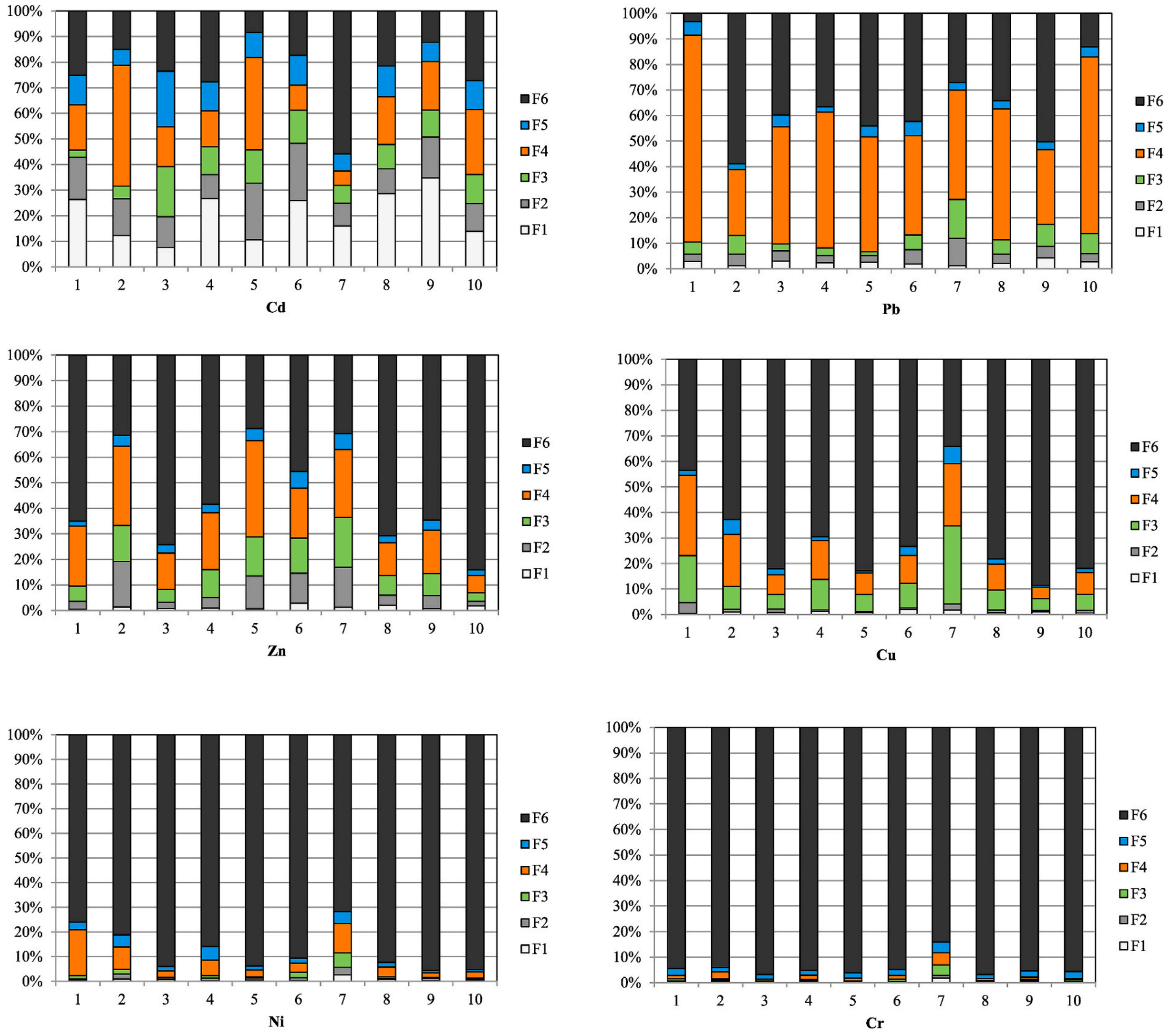

Fig. 3. Chemical speciation (%) of heavy metals in soils of Haikou. Sample 1 and 2 from industrial area, 3 from commercial area, 4 and 5 from residential area, 6 and 7 from resort area, 8 and 9 from street and 10 from suburban district.

districts where no industrial factories were distributed. These high levels of metals in soils had also been reported by Wang et al. (2019a), which were most likely to be derived from the basaltic parent materials, since basalts in Hainan province had similar high concentrations of Cr (254 mg/kg), Cu (53 mg/kg), and Ni (130 mg/kg) (Li et al., 2014). On the contrary, the significantly high concentrations of Pb observed in the street district should be associated with traffic emissions. The pillar industries in Haikou are food processing and pharmaceutical industries (HMBS, 2019), none of which belongs to metal pollution sources. Therefore, the relative high levels of As in soils from the industrial area might be associated with coal combustion emission from coal fired power plant (CFPP) and industrial boilers (Zhu et al., 2013). In addition, the soils from different urban functional areas of Haikou had similar concentrations of Sb, which were about twice of those in the suburban district (Fig. 2). This suggests that Sb accumulated in the urban environment of Haikou is derived from similar anthropogenic area pollution. A previous study demonstrated that the main emission sources of Sb in Hainan province were coal combustion (67%), municipal solid waste incineration (16.5%) and brake wear (16.5%) (Tian et al., 2012b).

The spatial distributions of heavy metals in soils from urban areas further confirmed the constraints of anthropogenic activities (Fig. 1b). The highest concentrations of Pb were found in samples from the street district, and the second high concentrations were found in those from the industrial area. On the other hand, As showed an inverse pattern with the highest concentrations in the industrial area and second high concentrations in the street district. For Cu, Cd and Zn, high concentrations could be found in both the street district and the industrial area. For Sb, however, high concentrations were mainly distributed in the industrial area, revealing their coal combustion origin, which was comparable to the emission inventory of Sb in this region (Tian et al., 2012b).

The single factor pollution indexes (P_i) of Ni (mean 1.5) and Cr (0.92) were either higher than or approximately 1, which were again attributed to their high background concentrations. While the other metals had a Pi (As: 0.13, Cd: 0.31, Cu: 0.61, Pb: 0.34, Zn: 0.60) of far lower than 1. The integrated pollution indexes (P_N) indicated that the suburban area was moderately polluted ($P_N = 2.68$) and the industrial area was slightly polluted ($P_N = 1.22$) by the heavy metals, while the other urban areas belonged to the degree of clean to precautionary situation ($P_N = 0.63–0.91$) (Fig. 2). The pollution delineated for the suburban area was mainly dependent on their high Ni and Cr concentrations as mentioned above.

4.2. Heavy metal mobility in urban soils

The chemical speciation of metals was usually used to evaluate their

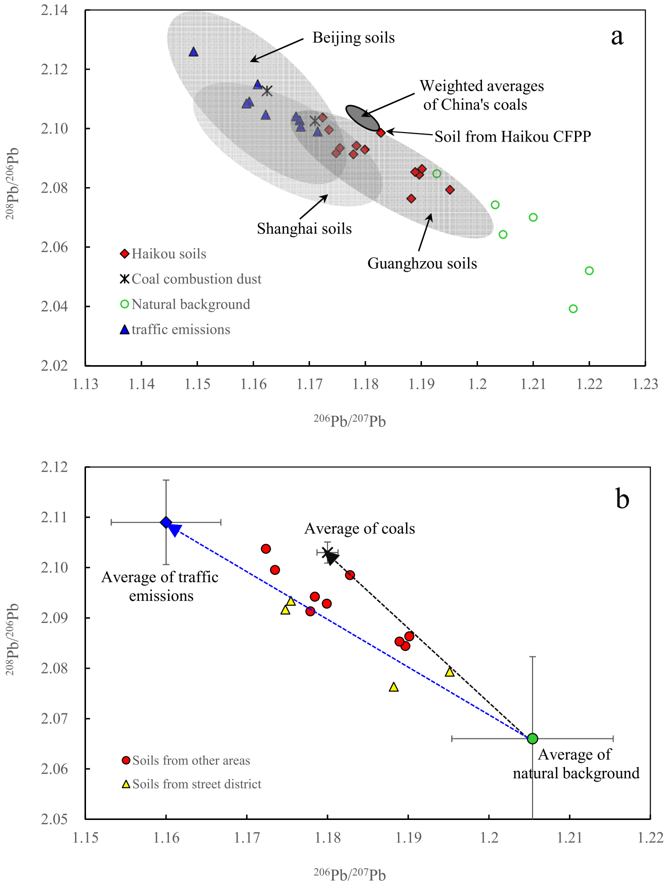

Fig. 4. Diagram of 206Pb/207 Pb vs 208Pb/206 Pb in soils of Haikou and comparison with other sources. The data of Beijing, Shanghai, and Guangzhou soils are from Yu et al. (2016), Li et al. (2011), and Liang et al. (2019), respectively. Other data are from Bi et al. (2017).

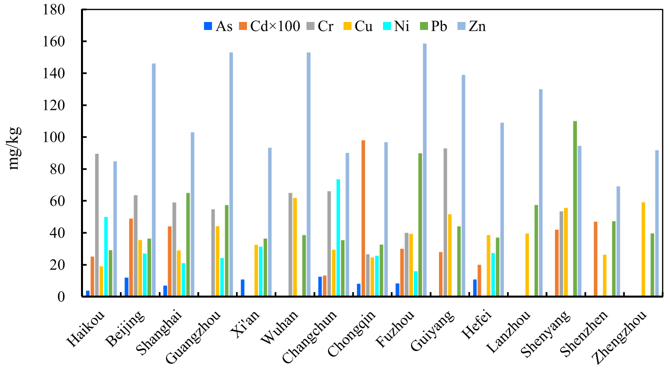

Fig. 5. The comparison of heavy metal concentrations in urban soils between Haikou and other capital cities in China (data of Wuhan from Yang et al., 2007; data of Changchun from Yang et al., 2011; data of Shanghai from Li et al., 2011 and Wang et al., 2018; data of Xi'an from Chen and Lu, 2018; data of Guangzhou from Liang et al., 2019; data of Beijing from Liu et al., 2020a,Liu et al., 2020b; data of the other cities from Luo et al., 2012).

mobility and availability in soils. Exchangeable and carbonate adsorbed fractions are regarded as weakly bonded metals which may equilibrate with aqueous phase and thus turn into more quickly bioavailable (Pardo et al., 1990; Wang et al., 2019b), whereas the residual fraction of metals was strongly bonded in mineral lattices and thus difficult to be moved.

The results of chemical sequential extraction revealed that more than 30% of Cd was associated with exchangeable and carbonate fractions, which showed a high mobility in the urban soils. Based on the portions of exchangeable and carbonate fractions, the mobility of trace metals in the urban soils of Haikou was in the decreasing order: Cd > Zn > Pb > Cu > Ni > Cr, which was in good agreement with previously studies conducted in big cities (Lu et al., 2007; Luo et al., 2012), suggesting the common characteristics of metal speciation in urban soils. Besides, it is noteworthy that substantial portions (about 10%) of Cd, Cu, and Zn remained in the HA fraction, which might be available to soil organisms. The high portion of Fe–Mn oxides bound Pb in the soils suggested that Pb in the urban environment should be emitted as oxides through high temperature combustions, such as coal combustions and traffic emissions. Compared with other metals, Cr and Ni showed a higher stability in the soils and thus were not easily leachable and bioavailable.

4.3. *Source attributions of trace metals in urban soils*

4.3.1. *Deducing from PCA analysis*

The distribution of heavy metals, together with major elements, in the urban soils of Haikou was determined by three principal components (PCs) that explained 75.3% of the total variances (Fig. 6). PC1 explained 53.7% of the total variances with higher loadings of Cd, Cu, Cr, Ni, Fe, Mn, Ti and V. PC2 was related to Pb, Zn and Al, accounting for 12.6% of the variances. Arsenic and Sb were associated in PC3, accounting for 9.0% of the variances. The accumulations of Cd and Cu in the urban environment are usually derived from anthropogenic emissions (Duzgoren-Aydin et al., 2006; Gong et al., 2010). However, Cd and Cu in this study showed close relationships with the basaltic parent materials related elements (Cr, Ni, Fe, Mn, Ti and V) (Wang et al., 2019a). This suggested that a substantial amount of Cd and Cu in the soils might be derived from natural sources. The spatial distribution patterns of Pb, As, and Sb within urban areas indicated that PC2 should be related to traffic emissions, and PC3 might be associated with coal combustion emissions.

4.3.2. *Deducing from Pb isotopic composition*

The Pb isotopic compositions of urban soils depended largely on the sources of Pb. The signatures of Pb isotopes of the Haikou urban soils differed greatly from those of the Beijing and Shanghai soils, indicating a clear difference of Pb sources between Haikou and these two big cities (Fig. 4a). However, the Pb isotope ratios of Haikou soils distributed within the range of those of Guangzhou (Fig. 4a), which suggested that Pb in urban soils from southern China cities may have common sources. Coal combustion, traffic emissions and nonferrous metal mining and smelting are the most common anthropogenic sources of Pb in the urban

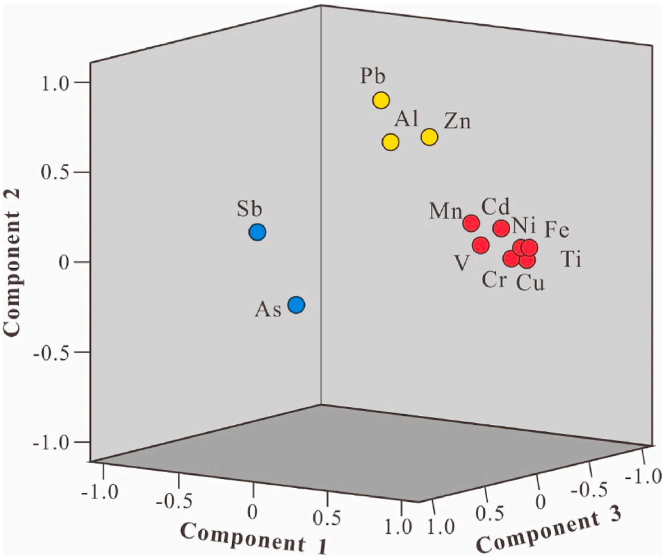

Fig. 6. PCA result of the soils in the three-dimensional space.

environments (Bi et al., 2017). The contribution of Pb from nonferrous metal mining and smelting activities in Haikou may be neglected since no such industries were present in this city. The vehicle exhausts and street dusts collected from Haikou had similar ranges of Pb isotope ratios (Fig. 4a), which were comparable to the data from other cities in China (Bi et al., 2017). We thus took their average value ($^{206}Pb/^{207}Pb$: 1.160 ± 0.007, $^{208}Pb/^{206}Pb$: 2.109 ± 0.008) as the end member of the traffic emission source in Haikou. The two fall dust samples collected near the Haikou CFPP had isotope ratios ($^{206}Pb/^{207}Pb$: 1.162–1.171, $^{208}Pb/^{206}Pb$: 2.103–2.113) similar to those of the traffic emissions, but different from those of coals in China (Fig. 4a). Furthermore, their Pb isotope compositions were also different from that of the soil ($^{206}Pb/^{207}Pb$: 1.183, $^{208}Pb/^{206}Pb$: 2.099) collected near this CFPP. Therefore, we speculate that these two fall dust samples may have been contaminated by traffic emissions. Coals used in Haikou were imported from various coal mines within China. In addition, the environment of Haikou might be impacted by coal emissions from surrounding cities. Thus, we used the average ratio of Pb isotopes of China's coals ($^{206}Pb/^{207}Pb$: 1.180 ± 0.001, $^{208}Pb/^{206}Pb$: 2.103 ± 0.002) to represent the end member of coal emission source in this study. The average value of Pb isotopes of the natural background was calculated from uncontaminated natural soils, marine sands, and bedrocks, which was 1.205 ± 0.01 for $^{206}Pb/^{207}Pb$ and 2.066 ± 0.016 for $^{208}Pb/^{206}Pb$, respectively. In the graph of $^{206}Pb/^{207}Pb$ vs. $^{208}Pb/^{206}Pb$, the data of the Haikou soils were distributed approximately within a triangular area with natural background, coal combustion and traffic emission as the three vertices (Fig. 4b). This implied that Pb in the soils was derived mainly from these three sources. The soils from the street district (except one sample) had Pb isotope ratios closer to the side of traffic emissions and natural background, compared with the other soil samples (Fig. 4b). This confirms the reliability of the Pb isotope tracing results.

According to the above discussion, the relative contribution (%) of natural background (a), coal combustion (b) and traffic emission (c) to the soil Pb can be calculated by a ternary mixing model as shown below:

$$\left({}^{206}\mathrm{Pb}/{}^{207}\mathrm{Pb}\right)_{\mathrm{sample}} = a\left({}^{206}\mathrm{Pb}/{}^{207}\mathrm{Pb}\right)_{\mathrm{background}} + b\left({}^{206}\mathrm{Pb}/{}^{207}\mathrm{Pb}\right)_{\mathrm{coal}} + c\left({}^{206}\mathrm{Pb}/{}^{207}\mathrm{Pb}\right)_{\mathrm{traffic}} \tag{4}$$

$$\left({}^{208}\mathrm{Pb}/{}^{206}\mathrm{Pb}\right)_{\mathrm{sample}} = a\left({}^{208}\mathrm{Pb}/{}^{206}\mathrm{Pb}\right)_{\mathrm{background}} + b\left({}^{208}\mathrm{Pb}/{}^{206}\mathrm{Pb}\right)_{\mathrm{coal}} + c\left({}^{208}\mathrm{Pb}/{}^{206}\mathrm{Pb}\right)_{\mathrm{traffic}} \tag{5}$$

$$a + b + c = 1 \tag{6}$$

The calculated results showed that the contributions of Pb from natural background, coal combustion and traffic emission sources were 5.3–82.4% (mean: 39.7 ± 21.1%), 0–85.7% (mean: 25.5 ± 24.6%), and 1.9–64% (mean: 34.8 ± 22.9%), respectively. This suggests that traffic emissions are still the most important anthropogenic source of Pb in Haikou. In contrast, in other cities of China, the contribution of traffic emission related Pb was reduced significantly due to the removed leaded gasoline as well as the increased emissions of Pb from coal combustions (Li et al., 2012; Bi et al., 2017). Overall, the relatively low contribution of coal Pb in Haikou highlights the underdevelopment of industries in this city.

5. Conclusions

The concentrations of heavy metals in urban soils of Haikou were much lower than those of other big cities in China. In contrast, their chemical speciation showed similar characteristics. The significantly high concentrations of Pb and As were found in the samples from the street district and industrial areas, respectively. But significantly high concentrations of Cd, Cr, Cu, and Ni simultaneously occurred in those samples from the suburban district. The results of PCA and Pb isotope composition suggested that heavy metals in the urban soils were mainly derived from natural parent materials, coal combustion and traffic emissions, the contributions of which were 5.3–82.4% (mean: 39.7 ± 21.1%), 0–85.7% (mean: 25.5 ± 24.6%), and 1.9–64% (mean: 34.8 ± 22.9%), respectively, according to the analysis of the ternary isotope mixing models. This result suggested that traffic emission is still the most important anthropogenic source of Pb in Haikou.

Credit author statement

Xiangyang Bi: Data curation, Writing - original draft, Supervision, Writing- Reviewing and Editing. Mohai Zhang: Visualization, Investigation, Validation. Yunjie Wu: Visualization, Investigation. Guangyi Sun: Conceptualization, Methodology, Software, Data curation, Writing - original draft, Supervision, Writing- Reviewing and Editing. Lihai Shang: Visualization, Investigation. Zhonggen Li: Software, Validation. Pengcong Wang: Visualization, Investigation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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