

# Contamination and potential mobility assessment of heavy metals in urban soils of Hangzhou, China: relationship with different land uses

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**Abstract** Concentration and distribution of heavy metals (Cd, Cu, Pb and Zn) in urban soils of Hangzhou, China, were measured based on different land uses. The contamination degree of heavy metals was assessed on the basis of pollution index (PI), integrated pollution index (IPI) and geoaccumulation index ( $I_{geo}$ ). The 0.1 mol l<sup>-1</sup> HCl extraction procedure and gastric juice simulation test (GJST) were used to evaluate the potential mobility and environmental risk of heavy metals in urban soils. The average concentration of Cd, Cu, Pb and Zn in urban soils was measured at 1.2 (with a range of 0.7–4.6), 52.0 (7.4–177.3), 88.2 (15.0–492.1) and 206.9 (19.3–1,249.2) mg kg<sup>-1</sup>, respectively. The degree of contamination increased in the order of industrial area (IA) > roadside (RS) > residential and commercial areas (RC) > public park and green areas (PG). The PIs for heavy metals indicated that there is a considerable Cd, Cu, Pb and Zn pollution, which originate from traffic and industrial activities. The IPI of these four metals ranged from 1.6 to 11.8 with a mean of 3.5, with the highest IPI in the industrial area. The assessment results of  $I_{geo}$  also supported that urban soil were moderately contaminated with Cd and to a lesser extent also with Cu, Pb and Zn. The IP and  $I_{geo}$  values reveal the pollution degree of heavy metal was the order of Cd > Pb > Zn ≈ Cu. It was shown that mobility and bioavailability of the heavy metals in urban soils increased in the order of Cd > Cu > Zn ≈ Pb. Owing to high mobility of Cd and Cu in the urban soils, further investigations are needed to

understand their effect on the urban environment and human health. It is concluded that industrial activities and emissions from vehicles may be the major source of heavy metals in urban contamination. Results of this study present a rough guide about the distribution and potential environmental and health risk of heavy metals in the urban soils.

**Keywords** Heavy metal · Urban soil · Land use · Mobility · Pollution index · Gastric juice simulation test (GJST)

## Introduction

Urban soils can be considered as a sink of pollutants and a source of pollution with the capacity to transfer pollutants to groundwater, into the food chain and into the human body (De Kimpe and Morel 2000; Paterson et al. 1996; Wong et al. 2006). Many authors have reported the contamination of heavy metals in urban soils (Biasioli et al. 2006, 2007; Chen et al. 1997, 2005; Chirenje et al. 2004; Chon et al. 1995; Chung and Li 2002; Imperato et al. 2003; Kelly et al. 1996; Lee et al. 2006; Li et al. 2001; Linde et al. 2001; Lu et al. 2003; Madrid et al. 2002; Manta et al. 2002; Möller et al. 2005; Morton-Bermea et al. 2008; Odewande and Abimbola 2008; Paterson et al. 1996; Pichtel et al. 1997; Sanchez Martin et al. 2000; Thuy et al. 2000; Wilcke et al. 1998). These studies have provided valuable information about possible contamination of heavy metals in urban soils, including chemistry, mobility and bioavailability of the heavy metals in the urban environment. Studies on urban soils in many cities around the world showed that urban soils had significantly higher levels of Cd, Cr, Cu, Pb and Zn (Biasioli et al. 2007; Li

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et al. 2001; Lu et al. 2003; Morton-Bermea et al. 2008; Wong et al. 2006). These heavy metals came from a variety of sources, including industrial discharge, vehicle emission, waste disposal, the weathering of building structures and other urban activities. Thus, topsoils and dusts in the urban areas have been used as an indicator to evaluate contamination of heavy metals by atmospheric deposition and industrial activities (Chon et al. 1995; Davies et al. 1987; Han et al. 2006; Harrison et al. 1981; Li et al. 2001; Shi et al. 2008). In particular, soil pollution in urban and industrial areas influences both the quality of life and people's health. There is substantial evidence that children and senior adults exposed to an environment with high heavy metal contamination were affected by inhaling or ingesting dusts (Mielke et al. 1999; Poggio et al. 2008). This is especially true in the case of soils in urban areas that are used for residential or recreational activities. In such areas, soils easily come into direct contact with humans, especially children, so that soil metals can be directly transferred to them. The impact of heavy metals in soils on human health has attracted a great deal of attention from governmental and regulatory bodies who are concerned in reducing the human health risk associated to the environmental pollution. Therefore, surveys on the distribution and concentration of heavy metals in the urban soils are important for planning management strategies to achieve better urban environmental quality and to control the risk associated with the excessive increase of heavy metals in the environment.

Although the total heavy metal concentration in soils is reported as an indicator of urban environmental quality, the severity of pollution depends not only on total heavy metal concentration of the soil, but also on the proportion of their mobile and bioavailable forms (Chang et al. 2001; Ge et al. 2000; Kim et al. 2005; Li 2008; Lu et al. 2003; Poggio et al. 2008). Heavy metals in urban soils exist in variable forms, such as exchangeable or adsorbed forms, and this influences their mobility and bioavailability for uptake by organisms and transfer into the food chain. In order to evaluate the long-term impact of heavy metals on urban environments and risks to residents, it is necessary to examine the chemical forms and mobility of heavy metals in urban soils. These so-called mobile or soluble bioavailable forms are often estimated through various extraction solutions (Adriano 1986; Chang et al. 2001; Ge et al. 2000; Mercier et al. 2002; Poggio et al. 2008). A series of testing procedures (i.e., toxicity characteristics leaching procedure (TLCP), extraction procedure (EP), American Society for Testing and Materials methods (ASTM) and gastric juice simulation test (GJST), etc., were developed to estimate the potential mobility and bioavailability of the soil-bound heavy metals (Chang et al. 2001; Kim et al. 2005; Madrid et al. 2007; Mercier et al. 2002).

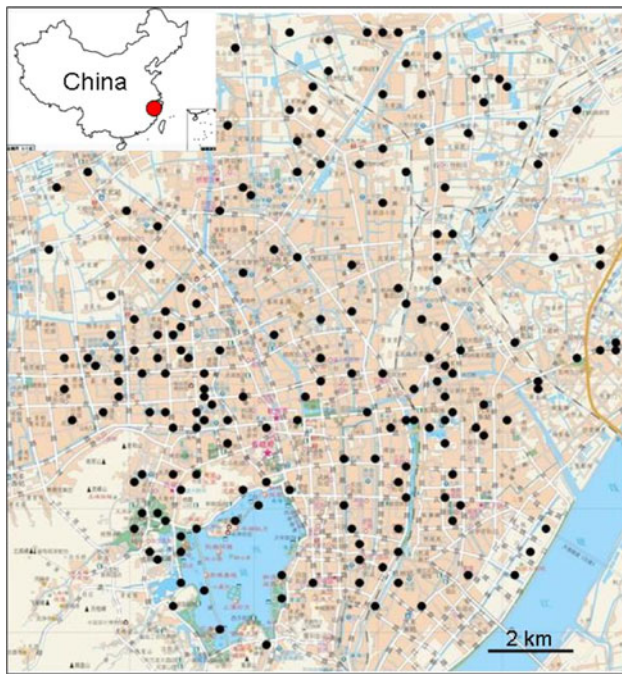
Dilute HCl has been widely used to distinguish mobile or available metals from more resistant forms in soils and to offer a useful, low cost alternative suitable for routine survey of the metal status of soils in an urban environment (Chang et al. 2001; Poggio et al. 2008; Yang et al. 2003). Moreover, the human bioaccessibility of metals that have entered the gastro-intestinal tract by direct ingestion of soils is often estimated through gastric juice simulation extraction (Mercier et al. 2002). The use of the human bioaccessibility test is desirable in order to define the amount of an element that is actually readily available for uptake and especially human bioaccessible metal fractions. However, the limited information on human bioaccessible fractions of pollutants in urban soils mainly refers to As and Pb (Mercier et al. 2002; Yang et al. 2003). There is a lack of information on the human bioaccessibility for other typical urban pollutant metals such as Cd, Cu and Zn.

China has experienced a rapid urbanization and industrialization in the last decades. The rapid growth of industry, population and number of vehicles exerts heavy pressure on the urban environment. Heavy metal pollution of urban soils has become a major environmental issue in China as it seriously affects the quality of the urban environment and represents a risk to human health. Although concentration of heavy metals in urban soils has been well documented in some developed industrial countries, such information still is very insufficient in China. The aim of this study was (1) to determine the concentrations of Cd, Cu, Pb and Zn in urban soils resulting from different land use patterns, (2) to assess the degree of heavy metals contamination in urban topsoils and (3) to examine potential mobility and accessibility of heavy metals to the human body.

## Materials and methods

### Study area and sampling

Hangzhou city is an important tourist city and capital of Zhejiang province. It is situated in eastern China (Fig. 1). Geographically, the city is located latitude 30°16' north and longitude 120°12' east. The city has a history of more than 2,200 years and an estimated population of 5 million. The rapid increase in population and the high urbanization growth rate have made it one of the most densely populated areas in the country. The studied area typically has a subtropical climate with an average temperature of 16.5°C and an average annual rainfall of 1,455 mm. The area has a flat topography with an altitude of 3–6 m, and soils are developed from the marine sediments with low concentrations of heavy metals (Soil Survey Office of Zhejiang Province 1994).



**Fig. 1** Sketch map showing the studied area and sampled locations

The sampling sites were selected in order to cover the main municipality and a good geographical spread (Fig. 1). Four land-use areas exposed to different pollution sources (industrial area, roadside, residential and commercial areas, and park and green areas) were demarcated for sampling. Soils in the industrial area were sampled from bare and green lands within and around a coal-burning power plant, steel and iron plant, chemical and manufacturing factories. Roadside soils were sampled from the edge of roads with high traffic density. Soils in residential and commercial areas were sampled in small scattered green areas of residential and commercial sites. The soil samples in park and green areas were collected from larger parks and green land where the land use has not changed for at least 20 years. The soil samples were taken from the uppermost layer of the soil profile (0–10 cm), where industrial dusts and emissions from vehicles have been deposited. At each sampling site, a composite sample was collected from the topsoil using a stainless-steel trowel and stored in a plastic bag. The composite sample was obtained by mixing five to six subsamples collected from the same site. A total of 182 urban topsoil samples were collected. The soil samples were air-dried, ground and passed through a 2-mm sieve and stored in self-locking polythene bags for use.

**Soil analyses**

All soil samples were analyzed for pH, organic carbon contents, total iron content and particle size distribution using standard procedures. Soil pH was measured in a 1:5

(w/v) suspension of soil and water using a glass electrode. The organic carbon content was measured by the  $K_2Cr_2O_7$  oxidation method. Distribution of particle sizes was made using the pipette method. Total iron was extracted with *aqua regia* and measured by atomic absorption spectrometry (AAS). Heavy metals were extracted by using a combination of concentrated acids of  $HF-HNO_3-HClO_4$  in a microwave digestion oven. Concentrations of Cd, Cu, Pb and Zn were determined by AAS. The accuracy of determination was controlled by means of duplicates, reagent blanks and reference materials. Analysis errors were below 5–10%.

A subset of 20 selected soil samples was extracted with  $0.1\text{ mol l}^{-1}$  HCl solution and GJST, and analyzed by AAS (Mercier et al. 2002; Yang et al. 2003). The metal fractions obtained by these extractions are defined as mobilizable and human bioavailable, respectively. The amount of HCl-extractable metals was measured by AAS after shaking with  $0.1\text{ mol l}^{-1}$  HCl for 1 h at a soil:solution ratio of 1:5. The GJST extract was according to the method described by Mercier et al. (2002). In brief, 6 ml of glacial acetic acid was added to 8 l of distilled water heated to  $37^\circ\text{C}$  in a water bath. The soils were placed in the bottle with the extraction liquid in a liquid/soil ratio of 22.2. Concentrated HCl was added over a 20-min period to obtain a pH of approximately 6, and then agitated for 20 min on an agitator. The samples were returned to the water bath and were acidified with HCl to a pH of 4 over another 20-min period. These operations were repeated for a pH value of 2.5 and 2. At the end of extraction, the samples were left to settle for 5 min and then filtered. The samples were acidified to a pH of less than 1 with concentrated  $HNO_3$ . The temperature was maintained between 35 and  $39^\circ\text{C}$ .

**Contamination assessment methods**

The pollution index (PI), integrated pollution index (IPI) and geoaccumulation index ( $I_{geo}$ ) were calculated to assess the contamination level of heavy metals in soils. The PI was defined as the ratio of heavy metal concentration in the studied soils to the background content of the corresponding metal in soil. The PI of each metal was classified as either low ( $PI \leq 1$ ), moderate ( $1 < PI \leq 3$ ) or high ( $PI > 3$ ). The IPI of four metals for each sample was defined as the mean values of the metal PI and then classified as low ( $IPI \leq 1$ ), moderate ( $1 < IPI < 2$ ) or high ( $IPI > 2$ ) (Chen et al. 2005; Morton-Bermea et al. 2008).

$I_{geo}$  is calculated by the following equation:

$$I_{geo} = \log_2[C_n/1.5B_n]$$

where  $C_n$  represents the measured concentration of the metal  $n$  and  $B_n$  is the background value of the metal in soils. The constant 1.5 is introduced to minimize the effect

of possible variations in the background values that may be attribute to lithological variations in the soils. The  $I_{geo}$  was classified into six categories:  $<0$  = practically unpolluted,  $0-1$  = unpolluted to moderately polluted,  $1-2$  = moderately polluted,  $2-3$  = moderately to strongly polluted,  $3-4$  = strongly polluted,  $4-5$  = strongly to extremely polluted and  $>5$  = extremely polluted (Müller 1969).

#### Data analysis

The range, mean and other statistical analyses were performed using Excel and SPSS for Windows statistics software.

## Results and discussion

### Soil characteristics

The statistical summary of the physical and chemical properties of the urban soils are presented in Table 1. The data show that wide ranges are found in the values of measured variables. This wide range of soil properties is likely to be related to differences in land uses and/or pollution degree among the various sampling sites. Table 1

showed that the urban soil pH varied between 4.3 and 8.4. Industrial soils were slightly alkaline with a mean pH of 7.9, and soils of park and green areas were slightly acidic with a mean pH of 6.7. Compared to the pH value of natural soils from subtropical regions (Soil Survey Office of Zhejiang Province 1994), the pH value of the studied urban soils is much higher. The pH variation in the soils can be attributed to the high content of carbonate, ash and cinders of anthropogenic origin. Soil organic carbon shows a wide variation, ranging from 9.1 to 78.3 mg kg<sup>-1</sup>. Data on sand, silt and clay contents also indicate that urban soils have a wide textural variation. The concentration of iron varies in the range of 4.19–71.92 g kg<sup>-1</sup>. Industrial soils have the highest content of iron, with a mean value of 39.1 g kg<sup>-1</sup>.

### Heavy metals concentrations in urban soils

The means, medians, ranges, standard deviations (SD) and skewness of heavy metals in urban topsoils from Hangzhou city are given in Table 2. Compared to the background value of natural soils in the studied area, the urban soils show significant enrichment in heavy metals. Concentration of Cd in the urban soils was in a range from 0.65 to 4.57 mg kg<sup>-1</sup> with an average of 1.20 mg kg<sup>-1</sup>. Total

**Table 1** Physical and chemical properties of urban soils from Hangzhou

	pH	Organic C (g kg <sup>-1</sup> )	Particle composition (mm, g kg <sup>-1</sup> )			Fe (g kg <sup>-1</sup> )
			2–0.02	0.02–0.002	<0.002	
<b>Industrial area (IA)</b>						
Mean	7.94	26.25	448.38	270.79	280.83	39.05
SD	0.32	9.80	99.16	35.06	102.02	14.33
Minimum	6.98	11.65	306.89	207.07	108.35	23.40
Maximum	8.42	43.95	631.07	316.38	465.42	71.92
<b>Roadside area (RA)</b>						
Mean	7.70	31.60	477.29	312.26	210.45	30.51
SD	0.61	11.70	105.83	80.63	93.53	6.89
Minimum	5.51	12.95	146.88	237.37	44.47	19.85
Maximum	8.65	73.7	634.47	734.42	487.58	59.12
<b>Residential and commercial areas (RC)</b>						
Mean	7.59	27.25	514.73	290.87	194.40	28.92
SD	0.52	8.10	92.77	47.60	89.62	6.27
Minimum	5.73	14.20	197.12	217.46	48.11	19.89
Maximum	8.48	46.55	694.50	511.83	517.07	49.59
<b>Parks and green areas (PG)</b>						
Mean	6.65	30.35	433.08	309.48	257.44	27.98
SD	1.05	13.45	82.03	62.17	77.51	6.83
Minimum	4.25	9.05	254.55	246.50	118.46	4.19
Maximum	8.04	78.25	576.13	548.26	383.24	51.66

SD Standard deviation

**Table 2** Minimum and maximum values, mean, standard deviation (SD), median and skewness for heavy metal concentration (mg kg<sup>-1</sup>) in urban soils

Metal	Minimum	Maximum	Mean	SD	Median	Skewness	BC
<b>Industrial area (IA)</b>							
Cd	1.49	4.57	1.99	0.65	1.86	3.64	
Cu	43.48	177.33	72.26	32.74	53.39	0.81	
Pb	36.39	466.75	138.98	106.93	105.82	2.05	
Zn	100.75	1249.23	345.83	314.16	248.64	2.11	
<b>Roadside area (RA)</b>							
Cd	0.65	2.30	1.31	0.29	1.27	1.12	
Cu	13.98	160.60	58.43	35.14	49.41	1.25	
Pb	32.04	492.09	95.49	81.44	73.15	2.61	
Zn	63.83	692.22	214.83	121.49	181.85	2.53	
<b>Residential and commercial areas (RC)</b>							
Cd	0.70	1.71	1.08	0.21	1.07	1.20	
Cu	14.83	133.96	50.24	26.93	44.33	1.31	
Pb	20.26	344.48	90.60	70.82	63.91	2.42	
Zn	76.68	368.60	210.96	74.13	205.84	0.09	
<b>Park and green areas (PG)</b>							
Cd	0.68	1.27	0.94	0.13	0.92	0.57	
Cu	7.43	149.90	37.52	20.15	36.65	1.50	
Pb	15.04	308.51	55.78	39.04	50.74	2.35	
Zn	19.33	285.88	93.64	61.39	125.94	0.48	
<b>All urban soils</b>							
Cd	0.65	4.57	1.20	0.43	1.12	2.85	0.167
Cu	7.43	177.33	51.95	30.71	44.77	1.50	17.76
Pb	15.04	492.09	88.17	79.25	65.80	2.86	25.61
Zn	19.33	1249.23	206.87	152.19	179.82	3.74	69.00

BC Background concentration (Soil Survey Office of Zhejiang Province 1994)

concentration of Cu was in a range from 7.4 to 177.3 mg kg<sup>-1</sup> with an average of 52.0 mg kg<sup>-1</sup>, being three-fold higher than the background value of the studied area. The total concentration of Pb varied from 15.4 to 492.1 mg kg<sup>-1</sup> with an average value of 88.2 mg kg<sup>-1</sup>, which exceeded the natural background value by three-fold. Concentration of Zn ranged from 19.3 to 1,249.2 mg kg<sup>-1</sup> with an average of 206.9 mg kg<sup>-1</sup>, which was nearly three-fold higher than the background value. Due to their low concentration in the parent materials (Soil Survey Office of Zhejiang Province 1994), elevated concentrations of Cd, Cu, Pb and Zn in the urban soils could be due to long-term accumulation from various polluting sources in the urban environments. In all metals, marked differences between means and medians, large values for SD and large skewness suggest that the data come from non-normal distributions, with some tailings towards lower values. Table 2 also shows that the skewness values of heavy metals for all urban soils are larger than one, which means that all the metals are positively skewed towards the lower concentrations, as can also be confirmed by the fact

that the median concentrations of these metals are lower than their mean concentrations. The concentration of Zn shows a high standard deviation and positive skewness indicating a strong skewness factor for Zn. The strong skewness of Zn is explained by two samples containing especially high Zn content (1,110 and 1,249 mg kg<sup>-1</sup>). Results indicated a strong anthropogenic influence on concentrations of heavy metals.

Compared to average concentrations in urban soils from other cities, especially old industrialized and larger cities in the world (Table 3), average concentrations of heavy metals in Hangzhou urban soils were lower. Concentrations of Cd, Cu, Pb and Zn were also much lower than those in the industrial cities in China such as Shenyang (Li 2008) and Luoyang (Bai 2007). Li (2008) reported that the average levels of Cd, Cu, Pb and Zn were 8.59, 209.06, 470.19 and 599.92 mg kg<sup>-1</sup> in the urban soils of Shenyang, Northeast China. Chen et al. (1997) studied Hong Kong soil and found the average concentration of Cd, Cu, Pb and Zn was 2.2, 24.8, 93.4 and 168 mg kg<sup>-1</sup>, respectively. Urban soils of Hangzhou were more severely

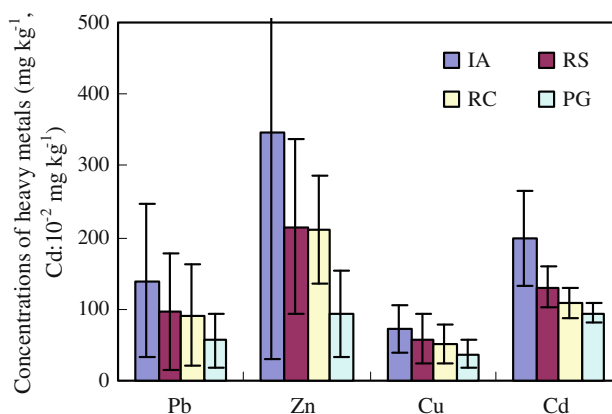
**Table 3** Comparison of mean concentration ( $\text{mg kg}^{-1}$ ) of heavy metals in urban soils from different cities

City	Cd	Cu	Pb	Zn	Reference
Hangzhou, China	1.2	52	88	207	This study
Shanghai, China	0.5	59	71	301	Shi et al. (2008)
Nanjing, China	–	66	107	162	Lu et al. (2003)
Shenyang, China	8.6	209	470	600	Li (2008)
Luoyang, China	1.5	91	90	228	Bai (2007)
Hong Kong	2.2	25	93	168	Li et al. (2001)
London, UK	1.0	73	294	183	Thornton (1991)
Hamburg, Germany	2.0	147	168	516	Imperato et al. (2003)
Stockholm, Sweden	0.4	71	101	171	Linde et al. (2001)
Palermo, Italy	0.7	63	202	138	Manta et al. (2002)
Naples, Italy	–	74	262	251	Imperato et al. (2003)
Madrid, Spain	–	72	161	210	De Miguel et al. (1998)
Sevilla, Spain	–	26	87	148	Biasioli et al. (2007)
Ljubljana, Slovenia	–	26	87	148	Biasioli et al. (2007)
Bangkok, Thailand	0.3	42	48	118	Wilcke et al. (1998)
Hoian, Vietnam	0.8	76	4	142	Thuy et al. (2000)
Seoul, Korea	3.1	84	240	271	Chon et al. (1995)
Damascus, Syria	–	30	10	84	Möller et al. (2005)
Ibadan, Nigeria	8.4	47	95	229	Odeyemi and Abimbola (2008)

contaminated by Cu and Zn when compared to those in Hong Kong soil. The metal concentration found in the urban soils of Hangzhou is generally similar to those found in other urban soil studies of Eastern China (Table 3).

In terms of land-use pattern, industrial and roadside soils showed significantly enhanced concentrations of heavy metals (Fig. 2, Table 2). Concentration of the heavy metals in the urban soils increased in the order of industrial area (IA) > roadside (RS) > residential and commercial areas (RC) > park and green areas (PG). This trend reflects the strong influence of industrial activities and vehicle emission on heavy metal concentration of soils, suggesting that deposition of dusts and wastes from various industrial activities and vehicle emissions may be the main source for contamination of heavy metals in the urban soils. The findings displayed a clear relationship between the land use and soil heavy metal levels. This is consistent with the results reported elsewhere, for example, by Hoian (Thuy et al. 2000), Hong Kong (Chen et al. 1997), Seville (Ruiz-Cortes et al. 2005), Stockholm (Linde et al. 2001) and Warsaw (Pichtel et al. 1997).

The above analyses indicated that topsoils in Hangzhou urban areas had been polluted by the heavy metals Cd, Cu, Pb and Zn. Since China has not established its own soil

**Fig. 2** Distribution of heavy metals in different land-use areas of Hangzhou city. Error bar represents the standard error as a measure for spatial variability. IA industrial area, RS roadside, RC residential and commercial area, PG parks and green areas

regulatory guidelines, Italian legal tolerance limits for residential and green area land use were used to evaluate the heavy metal contamination (Imperato et al. 2003; Poggio et al. 2008). It was found that about 23% of the studied soils were polluted by Pb with its concentration exceeding the  $100 \text{ mg kg}^{-1}$  limit, a standard set for the soils of public, residential and private areas (Imperato et al. 2003). Up to of 60% of the studied samples exceeded the Italian legal tolerance limits for residential and green area land use for at least one metal. In industrial areas, tolerance limits were exceeded in 50% of all soil samples for Pb, 90% for Zn but none for Cu. In roadside soils, 20% of the sampled sites for Pb, 64% for Zn and none for Cu exceeded the limits for residential land use.

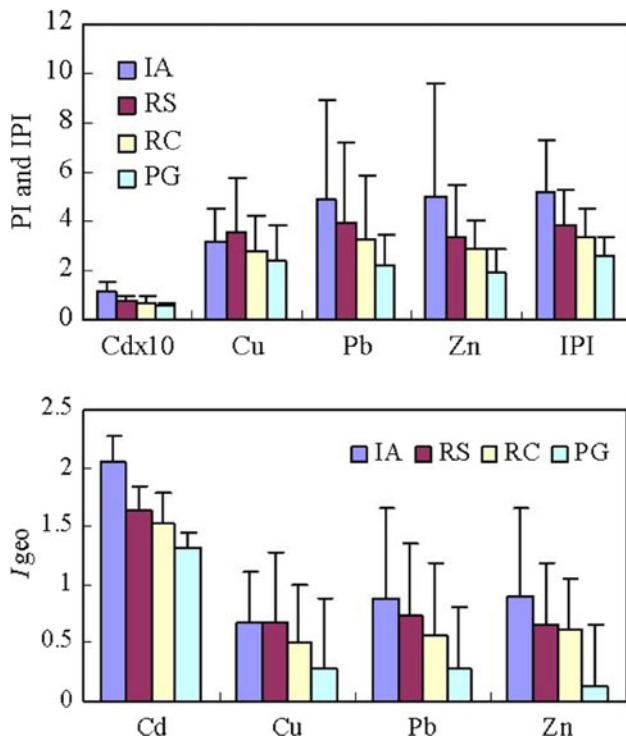
#### Correlation between heavy metals

Inter-element relationships can provide interesting information on heavy metal sources and pathways (Manta et al. 2002). To analyze the relationships among heavy metal concentrations, a Pearson's correlation analysis was applied, and the results are presented in Table 4. Results showed that close correlations existed among Cd, Cu, Pb and Zn. Pb is best correlated with Cu ( $r = 0.652$ ) and well with Zn and Cd ( $r = 0.574$  and  $0.313$ ), which could indicate common contamination source for these metals. Cu shows good correlation with Zn and Cd ( $r = 0.479$  and  $0.301$ ) at a significant level of 0.01. The highly positive correlations among soil heavy metals suggest that these heavy metals had similar pollution levels and similar pollution sources. Therefore, the close relationships among Cd, Cu, Pb and Zn in urban soils might indicate the combined soil pollution by multi-heavy metals as a result of long-term industrial and human activities in urban environments. Other studies also reported the combined soil

**Table 4** Correlation coefficient between heavy metals ( $n = 182$ )

Metals	Cd	Cu	Pb	Zn
Cd	1	0.301**	0.313**	0.349**
Cu		1	0.652**	0.479**
Pb			1	0.574**
Zn				1

\*\*Correlation is significant at the 0.01 level

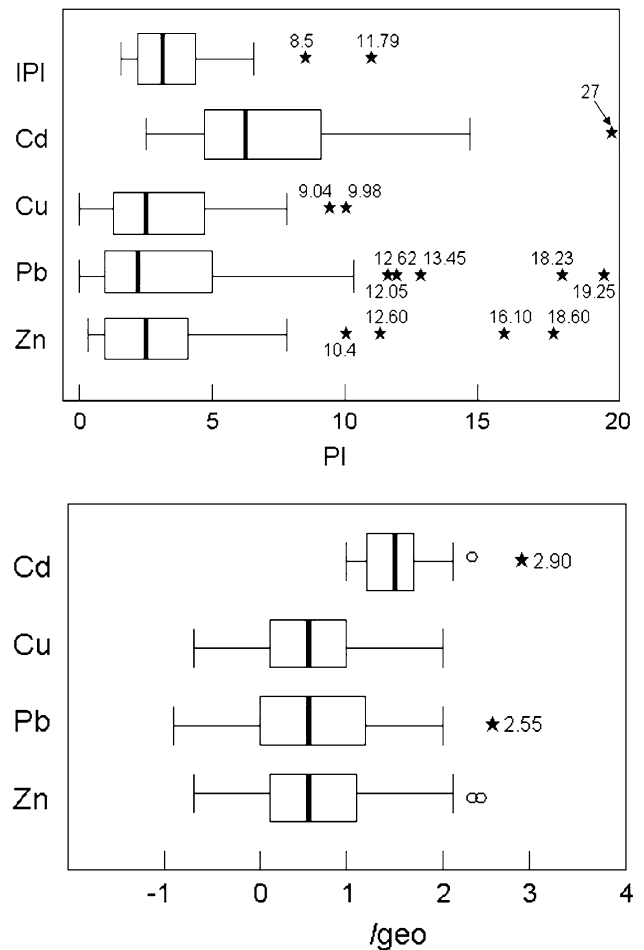


**Fig. 3** Distribution of PI, IPI and  $I_{geo}$  of heavy metals in different land use areas of Hangzhou city. Error bar represents the standard error as a measure for spatial variability. IA industrial area, RS roadside, RC residential and commercial area, PG park and green areas

pollution by multi-heavy metals in urban soils of China (Li 2008; Lu et al. 2003; Shi et al. 2008).

**Assessment of heavy metal pollution**

Pollution index of each metal and an IPI of the four metals were calculated and are presented in Figs. 3 and 4. The PIs of heavy metals varied greatly across the different metals and land-use types. The PI values for Cd in all urban topsoils exhibited the highest values, ranging from 3.9 to 27.4 with an average of 7.4. The mean PI for Cu was 2.9, but 64 samples (35%) had values more than 3, indicating a Cu pollution of soils. The PIs of Pb ranged from 0.6 to 19.3 with a mean of 3.4, and 69 samples had high PI values. The PIs of Zn showed a wide variation, from 0.9 to 18.0, with a



**Fig. 4** Box plots of pollution index (PI), integrated pollution index (IPI) and geoaccumulation ( $I_{geo}$ ) of heavy metals in all urban soils, giving medians (black line), interquartile ranges (boxes), outliers (black star) and ranges excluding outliers

mean value of 3.0. These data indicate that the Cd, Cu, Pb and Zn pollution is widespread in the urban soils. The IP values of these four metals showed the pollution level of the four metals was in the order of Cd > Pb > Zn > Cu. Cd had the highest IP value and was classified as high pollution. The IP of Cu and Pb was 2.9 and 3.4, respectively, indicating moderate pollution. Zn had a relatively lower IP value. The IP values of Cd, Pb and Zn from industrial and roadside areas differed significantly ( $p < 0.01$ ), whereas the IP value of Cu did not differ significantly.

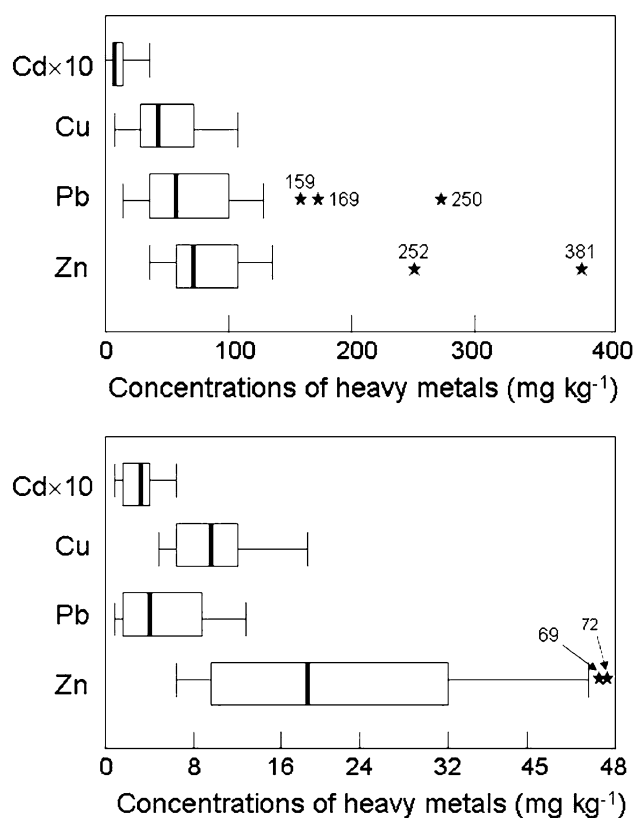
The IPIs of all urban soils varied from 1.6 to 11.8 with an average of 3.5 (Fig. 4). There were 9 samples with IPI values between 1 and 2, and 173 samples with IPI > 2. The industrial and roadside soils had an average IPI of 5.2 and 3.9, respectively, indicating high heavy metal pollution. Thus, the quality of urban soils has been impacted by heavy metals, especially the industrial and roadside soils.

Figures 3 and 4 also show the calculated results of  $I_{\text{geo}}$  of heavy metals in urban topsoils. The  $I_{\text{geo}}$  ranges from 0.2 to 2.9 with a mean value of 1.6 for Cd,  $-0.9$  to 1.9 for Cu with a mean value of 0.5,  $-0.9$  to 2.6 with a mean value of 0.6 for Pb and  $-0.8$  to 2.5 with a mean value of 0.5 for Zn. The mean values of  $I_{\text{geo}}$  increase in the order of  $\text{Cd} > \text{Pb} > \text{Zn} \approx \text{Cu}$ . The mean  $I_{\text{geo}}$  and 91%  $I_{\text{geo}}$  of Cd fall into class 2, indicating moderate pollution, while 9%  $I_{\text{geo}}$  falls between 2 and 3, showing moderately to strongly polluted soils. The mean  $I_{\text{geo}}$  of Pb, Cu and Zn reveal unpolluted to moderately polluted soils. The soil samples from industrial and roadside areas on one hand and park and green areas on the other differed significantly ( $p < 0.01$ ) in the  $I_{\text{geo}}$  values of Cd, Cu, Pb and Zn (Fig. 3).

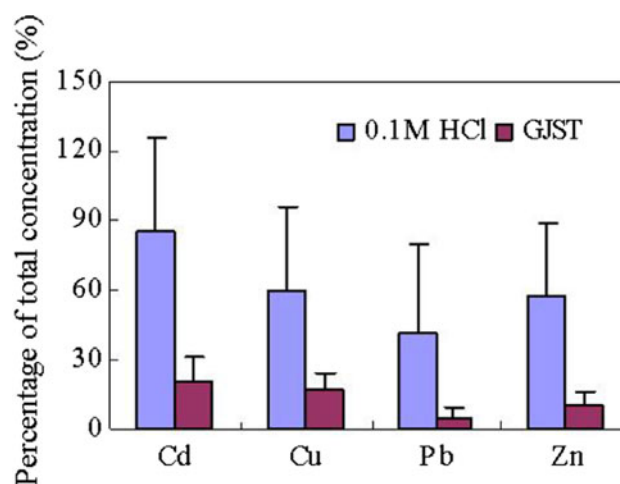
#### Potential mobility and bioaccessibility of heavy metals

Although metal pollution in soils is traditionally assessed in terms of total element concentrations, it is well known that the hazard that potentially toxic metals represent to living organisms is determined by their chemical forms to a much greater extent than by their total concentrations. The potential mobility and bioaccessibility of heavy metals were estimated by  $0.1 \text{ mol l}^{-1}$  HCl extraction. Many studies on human health risks suggest that extracts with strong acids provide a good prediction for metal uptake by the human body, as they simulate the acid conditions in the stomach. Concentrations of  $0.1 \text{ mol l}^{-1}$  HCl extractable metals are shown in Fig. 5. The amounts of Cd, Cu, Pb and Zn extracted by  $0.1 \text{ mol l}^{-1}$  HCl solutions were, on average, 1.67, 46.92, 108.17 and 148.21  $\text{mg kg}^{-1}$ , respectively. The  $0.1 \text{ mol l}^{-1}$  HCl can extract water soluble, exchangeable and a part of oxide fractions in the soils (Adriano 1986). Therefore, this method may be related to long-term mobility of heavy metals. When the percentage distribution of HCl-extractable heavy metal in the total amount was compared, a much higher percentage of HCl–Cd (86%) and Cu (60%) revealed the relatively higher mobility of Cd and Cu. Pb was the least mobile metal. Only 42% of the total metal concentration was obtained by the  $0.1 \text{ mol l}^{-1}$  HCl extraction.

The GJST-extractable metal concentrations are shown in Fig. 5. The amounts of GJST-extractable Cd, Cu, Pb and Zn, on average, were 0.31, 10.66, 25.06 and 4.72  $\text{mg kg}^{-1}$ , respectively. In order to obtain a comparative measure of human bioaccessibility of metals, the GJST extraction percentage was calculated by dividing the GJST-extractable metal value by the total metal concentration (Fig. 6). The GJST-extractable percentage differs greatly among the different metals. Cd and Cu had higher GJST-extractable percentages, indicating that the heavy metals Cd and Cu have higher human bioaccessibility. The highest GJST-extractable percentage (21%) was observed in Cd, followed



**Fig. 5** Boxplots of  $0.1 \text{ mol l}^{-1}$  HCl (upper diagram) and GJST (lower diagram) extractable heavy metals concentrations in urban soils, giving medians (black line), interquartile ranges (boxes), outliers (black star) and ranges excluding outliers



**Fig. 6** Potential mobility and human bioaccessibility of heavy metals ( $0.1 \text{ mol l}^{-1}$  HCl extractable and GJST extractable metals as a percentage of total concentrations in urban soils)

by Cu (18%), Zn (10%) and Pb (4%). Cd and Cu showed a much higher proportion of  $0.1 \text{ mol l}^{-1}$  HCl and GJST-extractable form. These results indicate that it can be difficult to quantitatively predict the mobility and bioaccessibility of metals in urban soils. However, information



**Table 5** Correlation coefficient between the different metals fractions and total concentrations of heavy metals in urban soils ( $n = 20$ )

	Cd	Cu	Pb	Zn
0.1 mol L <sup>-1</sup> HCl-extractable metal	0.510*	0.740**	0.657**	0.563**
GJST-extractable metals	0.520*	0.671**	0.642**	0.654**

\*Correlation is significant at the 0.05 level

\*\*Correlation is significant at the 0.01 level

about the fractions to which the metals are bound can be valuable in risk assessments of heavy metals.

Significant correlations were found between total concentration of heavy metals and 0.1 mol l<sup>-1</sup> HCl and GJST-extractable metals (Table 5). The 0.1 mol l<sup>-1</sup> HCl and GJST-extractable fractions of Cd, Cu, Pb and Zn showed a strong correlation with the respective total concentration. These results indicate that 0.1 mol l<sup>-1</sup> HCl and GJST-extractable metals in urban soils can be used as indicators of heavy metal pollution. The mobility and bioavailability of metals can provide important information in assessing the potential health risk for the population due to the pollution of heavy metals in the urban environments.

## Conclusions

Chemical analyses showed that urban topsoils in Hangzhou had elevated concentrations of heavy metals Cd, Cu, Pb and Zn, and its concentrations varied among different land-use categories. The highest concentration of heavy metals was observed on topsoils of industrial area and roadside. This suggests that the industrial activities and vehicle emissions may be the main source of heavy metal contamination in urban soils. The assessment of pollution degree of heavy metals was made in terms of PI, IPI and  $I_{geo}$ . The calculated results of PI and  $I_{geo}$  reveal the order of IP and  $I_{geo}$  are Cd > Pb > Zn ≈ Cu. Higher PI and  $I_{geo}$  for heavy metals in urban soils indicate that there is considerable Cd, Pb, Cu and Zn pollution, which mainly originates from traffic and industry activities. According to the assessment of IPI, the urban topsoils were heavily polluted by heavy metals. The pollution levels caused by multi-heavy metals were high, resulting in a high potential risk to environmental quality and human health. The 0.1 mol l<sup>-1</sup> HCl and GJST test showed that Cd and Cu can be easily released. It was shown that the relative mobility and bioavailability of these four metals increased in the order of Cd > Cu > Zn ≈ Pb. The extractable data may provide critical information about binding forms of heavy metal, which can help us to estimate the potential environmental risk. These findings indicate that more attention should be paid to heavy metal contamination of urban soils,

especially Cd and Pb. The assessment of the soil environmental quality of this work can be used as the basis for a regular monitoring program for implementing suitable pollution control measures and therefore possible methods of remediation.

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