Factors influencing the heavy metal bioaccessibility in soils were site dependent from different geographical locations

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Received: 4 February 2015 / Accepted: 26 April 2015 / Published online: 8 May 2015
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Abstract A soil survey was conducted in urban areas from five sites, including Beijing, Baotou, Datong, Fuyang, and Xiantao in China. The objective was to explore the most significant factors that may impact the bioaccessibility of heavy metals (Bio-HMs), including As, Cr, Cu, Pb, and Zn, in soils. Twenty to 30 composite soil samples were collected at each site. The various soil properties, including pH, particle size, Fe/Mn, and organic matter contents, were analyzed. The chemical operated forms of HMs in soils were measured by the Bureau of Reference (BCR) sequential extraction scheme, while the Bio-HMs were determined by the simple bioaccessibility extraction test (SBET) procedure. The concentrations of total heavy metals (T-HMs) in soils from different sites (cities) were in the range as As (5.69–9.86), Cr (77.42–230.20), Cu (15.68–36.54), Pb (14.12–58.93), and Zn (38.66–183.46) mg/kg. Cu and Pb had higher relative bioaccessibilities (48–70 %) than those of As and Cr (6–15 %), indicating higher health risks of the former than the latter two HMs. The Bio-HMs for various HMs were comparable to the first two or three combined BCR extracted fractions, with an exception of Cu, whose Bio-HMs were larger than the combined three BCR fractions, indicating that Cu was highly accessible in soils as compared with other HMs. Factor analysis showed that all variables, including soil property

parameters and BCR extracted fractions, could be represented by three common factors extracted with higher than 0.5 loadings and ~80 % cumulative contribution to the total variance. Among the three common factors, factor 1, containing mainly pH, texture, and Fe/Mn variables, and factor 3, containing mainly organic matter variable, could be attributed to geographical regions, while factor 2, containing mainly BCR extracted fractions, could be ascribed to relative bioaccessibility of HMs (R-Bio-HMs). Interactive mapping of the main factors and cluster analysis were consistent, which supported the “site gathering” of the soil sample pools, suggesting that the Bio-HMs in soils in different geographical localities were site dependent.

Keywords BCR · Factor analysis · Geographical location · SBET · Soil properties

Introduction

Heavy metal (HM) contamination has raised serious concern due to its environmental persistence, biogeochemical recycling, and ecological risks. Urban soils are the sink of large amounts of HMs from a variety of sources, including dumping wastes, waste incineration, vehicle emissions, smelting, smokestack emissions, fertilizer application, and sewage sludge production (Thornton et al. 2008). HMs in urban soils may potentially transfer to humans via ingestion, dermal contact, or breathing, especially to children due to the “hand to mouth” pathway during outdoor activities in playground and recreational areas (Laidlaw and Filippelli 2008; Li et al. 2011; Okorie et al. 2011). It has been noted that toxic metals such as arsenic (As), chromium (Cr), copper (Cu), lead (Pb), and zinc (Zn) have been increasingly entered in the urbanized areas during the past decades (Schmidt 2010;

Responsible editor: Zhihong Xu

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Thornton et al. 2008; Wong et al. 2006), consequently posing serious health risks to humans.

It is well known that the mobility, bioavailability, and ecotoxicity of HMs are dependent strongly on their specific chemical forms, or ways of binding in soils, rather than the total elemental contents (Pueyo et al. 2001). Additional studies documenting the bioaccessibility of HMs (Bio-HMs), defined as the fraction that is soluble in the gastrointestinal environment and potentially available for absorption, is the major part that may render health risks (Luo et al. 2012b; Sauve et al. 2000). On the basis of BCR sequential extraction (Rauret et al. 1999; Van Herreweghe et al. 2003), the forms of HMs are classified into exchangeable (water and acid-soluble, F1), easily reduced (iron/manganese oxyhydroxides, F2), oxidizable (organic matter and sulfides, F3), and residual fraction (F4). The occurrence and relative distribution of an element among these various phases, and the physical relation between the phases in the soils, will control an element's dissolution properties and, hence, its bioavailability. Specific chemical forms of HMs as well as Bio-HMs have been intensively documented on obtaining bioaccessible factors to be incorporated in health risk assessment models in the study areas.

Several studies have attempted to identify which soil properties (pH, soil organic matter content) might have sound effects on Bio-HMs (Kim et al. 2002; Oomen et al. 2002; Ruby et al. 1999). Metal solubility was found to increase at lower while decrease at higher pH values (Ljung et al. 2007; Rieuwerts et al. 1998; Sauve et al. 2000). The effect of pH in affecting the Bio-HMs was observed to be due to its

influence on most of the chemical species of HMs in soils (Basta et al. 1993). Luo et al. (2012a, b) reported that the concentrations of HMs in the particle fractions of urban soils generally increased with the decreased particle size in Hong Kong, and the optimal accumulation had happened in the finest fractions ($<50\ \mu\text{m}$) (Luo et al. 2012b). Iron and manganese (Fe/Mn) oxides as well as organic matter can reduce the mobility of metals in soils via adsorption reactions (Chuan et al. 1996; Zimdahl and Skogerboe 1977). Therefore, many studies often used pH, soil texture, organic matter, and Fe/Mn oxides to predict the availability of HMs in soils (Rodrigues et al. 2013). However, it is still not clear which of these parameters is robust enough to be allowed for an estimation of the bioaccessibility, since those developed predicting models varied in sites (Hund-Rinke and Krdel 2003; Rieuwerts et al. 1998). Besides, the properties of the soils had been dramatically changed because of the increasing anthropogenic activities.

Bioaccessibility data are clearly an additional tool toward furthering our understanding of human health risk at contaminated sites and have the potential to act as a pragmatic decision-support tool (Okorie et al. 2011). Therefore, the impact factors of Bio-HMs had been widely studied. However, the dominant factors which may influence Bio-HMs in the prospect from one region to another have rarely been studied. The present study thus attempted to focus on metal chemical forms and the variability of soil properties that may be contributing to the Bio-HMs of As, Cr, Cu, Pb, and Zn from various types of soils in various geographical locations in

Fig. 1 A diagram showing the location of the study sites with sampling distribution

China. The objectives were (1) to investigate the potential influencing factors (soil properties, heavy metal chemical forms) that may affect the Bio-HMs and (2) to examine whether these influencing factors can be categorized as a combined regional factor. The study was expected to contribute to provide basis on HM risk assessment of urban soils at various sites within various geographical belts in China.

Materials and methods

Sites and sampling

Sample collection was conducted at five sites during November 2013 to January 2014. The sites, including Beijing, Baotou, Datong, Fuyang, and Xiantao, are distributed in different areas of administration and geographical locations in China (Fig. 1). Site descriptions are summarized in Table 1.

The sampling in Beijing was performed at the former Capital Steel Iron Company, which had been notorious as a heavy contamination source in Beijing, the capital of China, and was closed and moved to Hebei province after 2007 (Cheng et al. 2013; Guo et al. 2013). In Baotou, soil samples were collected in adjacent to the steel plants in southwest of Baotou city. Sampling in Datong and Fuyang were conducted at parks in the central area of the cities, while in Xiantao, samples were collected in the central residential areas.

At each site, five subsamples within a sampling plot of 5 m×5 m were collected down to a depth of 20 cm to form a composite sample. Soil samples were air-dried, picked out stone and plant debris, then crashed and passed through a 2 mm nylon sieve. The pH was measured in a 1 to 2.5 soil-water suspension using a pH meter. The content of organic matter was analyzed using the Walkley-Black method. The particle size of the soil was determined using laser diffraction analysis method.

Determination of total concentration and bioaccessibility of multi-elements

Subsample less than 150 μm in particle size was obtained by using an ultracentrifuge mill (Luo et al. 2012a). To determine the HM concentrations, a portion of the subsample was accurately weighted and digested with a concentrated acid mixture (HNO₃, HF, and HClO₄) (Fu and Wei 2012). The total concentration of As, Cr, Cu, Pb, and Zn in the samples were measured in the digested solution using inductively coupled plasma optical emission spectrometer (ICP-OES, PE, USA). Certified soil reference (GBW-07453) was used to check the accuracies of the analysis. The recoveries of HMs were within the ranges of 84–110 %.

Simple bioaccessibility extraction test (SBET) (Luo et al. 2011; Madrid et al. 2008) was used to assess the bioaccessibility of As, Cr, Cu, Pb, and Zn. Briefly, 50 ml of the 0.4 M

Table 1 The geographic characters of the sampling sites

Sites in area	Beijing	Baotou	Datong	Fuyang	Xiantao
Sample numbers	20	30	20	20	20
Site land use	Closed steel plant	Adjacent to steel plants	City park	City park	Residential
Province located	Beijing	Inner Mongolia	Shanxi	Anhui	Hubei
GPS coordination	39° 54' N 116° 10' E	40° 38' N 109° 45' E	40° 5' N 113° 16' E	32° 53' N 115° 48' E	30° 22' N 113° 27' E
Annual average temperature (°C)	12.9	7.18	6.97	15.3	16.5
Annual precipitation (mm)	532.0	297.6	371.6	910.0	1199.6
Climate zone	Semi-humid monsoon	Arid continental monsoon	Semi-arid continental monsoon	Semi-humid monsoon	Subtropical monsoon
Soil type	Cinnamon soil, moisture soil	Chestnut soil	Brown soil, cinnamon soil	Yellow brown soil	Yellow soil, yellow brown soil
Geographic/geological position	North China Plain	Inner Mongolia Plateau	Datong Basin	Central middle Yangtze Plain	Central China Plain

Annual precipitation are obtained from China Meteorological Administration
The data of soil type is come from China Soil Scientific Database (<http://www.soil.csdb.cn/>)

glycine extraction solution was added to 0.5 g of sieved (<150 μm fraction), air-dried soil material in a 100 ml polythene centrifuge tube. The tubes were shaken end over end at 37 °C for 1 h at 30 rpm. To ensure that all pH values were within in 0.5 U of the starting pH (1.5), the pH was measured in part of the unfiltered extraction fluid. The mixtures were centrifuged at 3000 rpm for 10 min after shaking; the extracted suspension was filtered with 0.45 μm cellulose acetate disk filter. The test for each sample was duplicated. Blanks and reference soil materials (GW07412a) were used in each batch of the tests to check the accuracies of the analysis. The recoveries of the tests were within the ranges of 82–119 %. The determination of Bio-HMs was the same as described above for T-HM concentrations.

BCR sequential extraction

Sequential extraction techniques were vastly used in determining the specific chemical forms of HMs associated with the T-HMs in different environmental media and to estimate the bioaccessibility of HMs. The principle of this method is based on the selective extraction of heavy metals in different physicochemical fractions of a material using specific solvents (Bruder-Hubscher et al. 2002).

In order to harmonize the various sequential extraction procedures used for HM phase analysis, a BCR three-step sequential extraction scheme was proposed by the European Community Bureau of Reference in 1992 (the Standards Measurement and Testing Program) (BCR). Subsequently, this scheme was improved as a result of further collaborative studies (Rauret et al. 1999). In this study, a revised version of the BCR sequential extraction procedure was used to test the HM phases (Baig et al. 2009; Rauret et al. 1999; Van Herreweghe et al. 2003). In brief, the forms of HMs were classified into exchangeable (water and acid-soluble, F1),

easily reduced (Fe/Mn oxyhydroxides, F2), oxidizable (organic matter and sulfides, F3), and residual fraction (F4). The solution that used in this process is presented in Table 2.

Statistical analysis

Statistical analysis was carried out using SPSS 20.0 software. Correlation analysis was performed by Pearson test to reveal the relationship among various factors, including total Bio-HM concentrations and soil property parameters. Cluster and factor analysis were performed to identify the weight of influencing factors. Moreover, stepwise regression analysis was applied to determine the dominate factors that might influence the Bio-HMs. All data except pH were log transformed to reduce the variation of variables before statistical analysis (Rodrigues et al. 2013).

Results

Soil properties

The soil properties, including pH, particle size, organic matter, and Fe/Mn content are presented in Table 3. The pH values varied from 7.69 in Fuyang to 7.99 in Baotou, revealing the alkaline properties of soils at the sampling sites. The particle sizes of the soils appeared to be distinctly variable among the five sites, with soils in Fuyang and Xiantao being mainly composed of silt (69 and 64 %, respectively), while in Baotou, the dominant proportion was sand (70 %), and the percentages of silt in Beijing and Datong (44–46 %) were comparable to that of sand (46–47 %), indicating that soils from Fuyang and Xiantao were less coarse in texture than soils from Beijing and Datong, while soils from Baotou appeared the coarsest. Among the five sites, organic matter of the soils

Table 2 Sequential extraction procedure of BCR

BCR forms	Fractions in representation	Extraction reagents	Extraction pH	Extraction processes
F1 (step 1)	Exchangeable, water and acid-soluble (carbonates)	Solution A: acetic acid, 0.11 mol/l ¹	4.5–6	1 g soil sample+40 ml solution A shaking for 16 h at 22±5 °C (overnight); agitation: 3000 rpm, 20 min
F2 (step 2)	Easily reduced (iron/manganese oxyhydroxides)	Solution B: hydroxyl ammonium chloride, 0.1 mol/l ¹	2	Residual fraction of step 1+40 ml solution B shaking for 16 h at 22±5 °C (overnight); agitation: 3000 rpm, 20 min
F3 (step 3)	Oxidizable (organic matter and sulfides)	Solution C: hydrogen peroxide, 8.8 mol/l	2	Residual fraction of step 2+20 ml solution C for 2 h at 85±2 °C (repeat one time)
		Solution D: ammonium acetate, 1.0 mol/l		Residual fraction of above+50 ml solution D shaking for 16 h at 22±5 °C (overnight); agitation: 3000 rpm, 20 min

Table 3 Basic statistics of soil property parameters

	Beijing	Baotou	Datong	Fuyang	Xiantao
pH	7.71±0.13	7.99±0.17	7.79±0.10	7.69±0.10	7.79±0.15
Clay (%)	7.90±1.92	3.31±1.16	9.31±2.44	15.73±6.26	7.87±2.75
Silt (%)	45.69±5.93	26.27±6.04	44.01±5.38	69.05±4.54	63.9±6.93
Sand (%)	46.41±7.41	70.43±7.07	46.68±7.40	15.22±4.16	28.22±8.80
Organic matter (%)	6.68±2.23	4.13±1.72	5.78±1.88	3.46±1.38	2.63±1.03
Mn (mg/kg)	813±328	1192±986	453±29.0	509±48.0	575±87.0
Fe ₂ O ₃ (%)	6.24±1.79	8.83±3.56	4.17±0.31	4.29±0.21	4.61±0.67

Data are means±SD

Table 4 The total, bioaccessible (Bio-HMs), relative bioaccessible (R-Bio-HMs), and BCR extracted forms of heavy metals in the soils at five sites

	Total (mg/kg)	Bio-HMs (mg/kg)	R-Bio-HMs (%)	BCR extracted forms (mg/kg)				
				F1	F2	F3	Sum (F1-2) (F1+F2)	Sum (F1-3) (F1+F2+F3)
Beijing (<i>n</i> =20)								
As	9.86±9.75	0.59±0.18	5.98	0.09±0.07	0.41±0.15	0.07±0.04	0.50±0.20	0.56±0.21
Cr	116.0±35.70	14.44±2.23	13.19	0.26±0.19	6.35±3.10	8.48±2.05	6.61±3.20	15.09±5.08
Cu	32.76±35.72	15.31±11.13	63.05	0.98±0.83	7.02±8.03	5.71±6.62	8.00±8.84	13.71±15.16
Pb	35.78±18.31	25.20±13.83	70.13	1.81±0.97	26.68±13.71	3.83±2.11	28.50±14.58	32.33±16.33
Zn	183.5±163.5	116.3±146.9	54.61	47.84±76.29	73.34±73.69	7.62±9.32	121.2±146.2	128.8±152.0
Baotou (<i>n</i> =30)								
As	8.61±5.11	0.85±0.63	9.87	0.23±0.17	0.50±0.31	0.07±0.14	0.73±0.31	0.80±0.44
Cr	230.2±84.61	23.75±9.36	10.54	0.82±0.42	9.17±5.02	13.81±14.05	9.99±5.03	23.81±17.92
Cu	25.11±9.31	7.92±1.76	34.64	0.70±0.30	3.65±1.05	3.96±3.98	4.35±1.07	8.31±4.00
Pb	58.93±65.81	22.54±22.22	41.19	2.97±4.84	20.15±20.09	3.50±3.57	23.12±19.92	26.62±22.73
Zn	78.44±74.97	35.34±38.56	42.81	12.67±26.48	20.44±16.44	6.47±9.27	33.11±30.00	39.58±32.88
Datong (<i>n</i> =20)								
As	7.62±7.17	1.02±0.32	13.39	0.18±0.22	0.63±0.24	0.13±0.09	0.81±0.31	0.94±0.34
Cr	83.46±8.01	12.43±0.61	15.02	0.93±0.42	3.62±0.62	7.45±1.71	4.55±0.78	12.00±2.07
Cu	36.54±48.29	9.35±2.09	45.25	0.66±0.26	3.31±0.92	3.69±1.98	3.97±0.88	7.66±2.09
Pb	21.28±6.74	14.20±5.40	66.20	1.47±0.67	15.30±6.58	3.72±2.68	16.76±6.78	20.48±9.03
Zn	40.71±24.70	10.89±9.06	25.69	13.80±15.21	13.34±8.60	2.49±5.50	27.14±18.19	29.64±21.24
Fuyang (<i>n</i> =20)								
As	5.69±3.36	0.65±0.09	16.83	0.13±0.04	0.34±0.09	0.02±0.03	0.47±0.10	0.49±0.11
Cr	77.42±14.7	11.44±0.48	15.14	0.54±0.18	4.15±0.86	8.57±0.85	4.70±0.94	13.27±1.49
Cu	15.68±3.29	7.46±1.12	48.61	0.49±0.05	3.42±0.75	1.27±0.38	3.92±0.77	5.19±0.79
Pb	15.96±3.36	8.78±1.70	55.78	0.98±0.09	10.98±1.86	2.66±0.52	11.96±1.90	14.62±2.20
Zn	38.66±11.58	3.98±4.20	10.05	0.52±1.75 ^a	10.38±3.45	0.84±0.89	10.90±4.29	11.74±4.68
Xiantao (<i>n</i> =20)								
As	8.25±4.31	0.70±0.33	11.71	0.11±0.15	0.43±0.21	0.03±0.04	0.54±0.33	0.57±0.34
Cr	87.3±10.36	12.41±1.01	14.36	0.58±0.18	6.64±1.61	8.67±1.02	7.22±1.72	15.89±2.08
Cu	23.49±11.36	11.11±2.25	53.55	1.08±0.34	5.87±1.64	2.71±1.06	6.95±1.88	9.66±2.07
Pb	14.12±4.32	9.45±2.87	67.88	0.97±0.18	11.02±3.32	1.86±0.60	12.00±3.45	13.86±3.87
Zn	58.58±26.91	10.94±19.79	13.75	7.05±14.76	13.94±9.48	2.75±1.52	20.99±24.00	23.74±25.13

Data are means±SD except the column of R-Bio-HMs (%)

^a Only five samples were detected with this form

in Beijing was the highest, followed by Datong, Baotou, Fuyang, and Xiantao. Concentrations of Mn were 813 and 1192 mg/kg in Beijing and Baotou, while the corresponding contents of Fe_2O_3 were 6.24 and 8.83 %, respectively, much higher than those in the other three sites ($P < 0.01$).

Heavy metal concentrations

T-HMs and Bio-HMs

The average concentrations of the total and bioaccessible As, Cr, Cu, Pb, and Zn from all five sampling sites are presented in Table 4. The concentrations of T-HMs in soils from different sites (cities) were in the range as As (5.69–9.86), Cr (77.42–230.20), Cu (15.68–36.54), Pb (14.12–58.93), and Zn (38.66–183.46) mg/kg, while concentrations of Bio-HMs were in the range as As (0.59–1.02), Cr (11.44–23.75), Cu (7.46–15.31), Pb (8.78–25.20), and Zn (3.98–116.33) mg/kg. Fuyang had the lowest T-HMs as well as Bio-HMs, while Beijing and Baotou had significantly higher concentrations on both the total and bioaccessible fractions than those from the other sites. Both of the total and bioaccessible Zn in Beijing were remarkably higher than those of the other four sites, being 183.46 and 116.33 mg/kg, respectively.

The relative bioaccessibility of HMs (R-Bio-HMs), defined as the percentage of Bio-HMs to T-HMs, varied in HM elements, as ranged in 10–70 %. Among those, Cu and Pb showed higher R-Bio-HMs ranges as of 48–70 %, while As and Cr showed lower R-Bio-HMs as 6–15 %; the variations of R-Bio-Zn (10–55 %) were greater than those of other HMs (Table 4).

The chemical forms of HMs

The sequential extraction results for each HMs are presented in Fig. 2. As expected, the distribution patterns of the three

forms of the same element as revealed by BCR procedure changed largely within the same site (Fig. 2). Among all the five sites, As and Cr contained the highest residual fractions as around 90 %, followed by Cu (60 %) and Zn (30 %), while Pb occupied the lowest residual fraction as only 10 %; the same order was seen for R-Bio-HMs (Table 4). These indicate that As and Cr could hardly be released under natural conditions in the sites in this study. The percentages of exchangeable F1 and oxidizable fraction F3 seemed to have little variation (0–10 %) for all five HMs studied, except exchangeable Zn, which were 10–30 %. Arsenic and Cr contained a relatively lower easily reduced fraction F2, while the rest three HMs displayed greater percentages, with Cu (20 %), Pb (40–70 %), and Zn (30 %), indicating that the HMs varied largely in this fraction.

For comparison, the percentages of each chemical form of the elements as well as the Bio-HMs are presented in Fig. 2. Bio-HMs are generally comparable to the combined three BCR fractions Sum (F1–3) (F1+F2+F3), except Bio-Pb and Bio-Zn, which are equitable to the combined two BCR fractions Sum (F1–2), while Bio-Zn in Datong, Fuyang, and Xiantao are more close to only one fraction of BCR F1. These indicate that Bio-HMs had a fixed pattern for each HMs in this study, reflecting the differences in contribution from both area factors and the HM species itself.

Factor analysis and regression analysis

To estimate the factors that might influence the Bio-HMs, factor analysis was performed. The rotation of principal component was carried out by the varimax method. All the factors including soil properties and most HM BCR forms were included as variables, except the BCR F1 of Zn, which was excluded because only 5 of 20 samples could be detected with this form at Fuyang (Tables 4 and 5).

Fig. 2 The percentages of relative bioaccessible heavy metals (R-Bio-HMs) and BCR extracted forms to total heavy metal concentrations at various sampling sites. F1, exchangeable; F2, water and acid-soluble (carbonates), F3, easily reduced (iron/manganese oxyhydroxides) oxidizable (organic matter and sulfides); Sum (F1–2) and Sum (F1–3) represent F1+F2 and F1+F2+F3, respectively

Table 5 The factor loadings of various variables of soil property parameters and BCR extracted forms

Variables	As			Cr			Cu			Pb			Zn		
	Fac_1	Fac_2	Fac_3	Fac_1	Fac_2	Fac_3	Fac_1	Fac_2	Fac_3	Fac_1	Fac_2	Fac_3	Fac_1	Fac_2	Fac_3
pH	0.768			0.600			0.763			−0.601			0.807		
Clay	−0.908			−0.741			−0.911			0.894			−0.921		
Silt	−0.888			−0.648	0.632		−0.890			0.918			−0.842		
Sand	0.816			0.617	−0.573		0.838			−0.906			0.801		
Organic matter			0.907			0.833						0.934		0.625	0.603
Mn	0.752			0.902			0.719				−0.780		0.526		0.713
Fe ₂ O ₃	0.834			0.882			0.813				−0.695		0.631		0.690
F1		0.842		−0.626		−0.513					0.900		NA	NA	NA
F2		0.943			0.951			0.946			0.597		0.844		
F3		0.592	0.595	−0.566	0.653			0.537	0.728	0.780	0.307		0.529	0.013	
Sum (F1-2) (F1+F2)		0.990			0.919			0.966			0.809		0.931		
Sum(F1-3) (F1+F2+F3)		0.986			0.866			0.932			0.768		0.906		
Eigenvalues	4.147	3.974	1.574	4.184	4.033	1.411	4.169	3.929	1.673	4.637	3.890	1.341	3.930	3.142	1.516
Percent contribution (%)	34.56	33.12	13.12	34.86	33.61	11.76	34.75	32.74	13.94	38.65	32.42	11.17	35.73	28.56	13.78
Cumulative percent contribution (%)	34.56	67.68	80.80	34.86	68.47	80.23	34.75	67.48	81.42	38.65	71.06	82.23	35.73	64.23	78.07

F1, F2, and F3 represent the first, second, and third steps of BCR extracted fractions, respectively; for details, refer to Table 2

NA not available

Three factors, with loadings greater than 0.5 and ~80 % cumulative contributions to all variables, were extracted (Table 5). For all the five HMs, Fac_1 explained 34–38 % of the total variance and had the eigenvalue of 3.9–4.7, containing high positive loadings of pH, clay, silt, sand, Mn, and Fe_2O_3 , which can be ascribed as the soil properties factor; Fac_2 explains 28–34 % of the total variance and had the eigenvalue of 3.1–4.0, containing high positive loadings of the BCR fractions of F1, F2, F3, Sum (F1-2), and Sum (F1-3), which can be attributed to BCR extraction form factors; Fac_3 occupied 11–14 % of the total variance with the eigenvalue of 1.3–1.7, with high positive loadings of organic matter, which can be determined as the soil organic matter factor.

The interactive factor loadings of Fac_1 and Fac_2 showed that the main factors influencing R-Bio-HMs generally led the samples to be “site gathering” for each HMs (Fig. 3). On the scatter diagrams, among the five sites, Baotou and Fuyang left

the largest space with each other as distributed on the opposite right or left, while Beijing, Datong, and Xiantao were between them with some extent of overlapping. All HMs except Pb had similar gathering patterns. The site gathering effect was most pronounced for Cr, while the least was seen for As (Fig. 3a, b).

Cluster analysis was also performed for the five sites using the three common factors (Fac_1, Fac_2, and Fac_3) and R-Bio-HMs as the variables, respectively (Fig. 4). The results were quite similar, with only a change position was seen between Beijing and Datong.

The common factors were further regressed with R-Bio-HMs to see the direction and extent of influence of each factor on bioaccessibility of HMs. It seems that Fac_2, representing the chemical forms of HMs in soils, had the largest and positive influence on R-Bio-HMs, while the impact of Fac_1 and Fac_3 might be comparable. The impacts of the two factors, representing soil physical-chemical properties for Fac_1 and

Fig. 3 The scatter diagrams of Fac_1 and Fac_2 of the five heavy metal elements

Fig. 4 The cluster dendrogram of the five sites based on **a** Fac_1 and Fac_2; **b** the relative bioaccessibilities (R-Bio-HMs)

soil biological property for Fac_2, on the R-Bio-HMs, differed between HMs and factors themselves. For instance, for Pb and Zn, the impacts were positive, whereas for Cr, they were negative; for Cu, Fac_1 was negative while Fac_2 was positive; for As, Fac_1 was negative while Fac_2 did not show impact (Table 6).

Discussion

The present study was conducted to explore the potential impacts of factors on the bioaccessibility of HMs in soils coming from different regions with varying climate conditions from south to north China. The relative bioaccessibility of Cu and Pb were generally higher than those of As and Cr (Table 4), suggesting higher human accessibility of the former than the latter two HMs. The R-Bio-HMs were generally comparable to the combined two- or three-step BCR extracted fractions (Fig. 2), suggesting that Bio-HMs were contributed by various forms of HMs in soils except the residue, which was bound to the inner crystal lattice in the minerals in soils, thus could hardly be mobilized (Ko et al. 2005; Luo et al. 2012a; Tessier et al. 1979). However, for Cu, the R-Bio-HMs were evidently greater than the three combined BCR fractions, suggesting that Cu in soils could be easily mobilized and become

accessible to biota in soils and human who ingest the soils (Van Herreweghe et al. 2003; Wu et al. 2015). For Pb and Zn, the R-Bio-HMs were generally less than the combined first two steps of BCR extracted forms, indicating that the organic complexation and residue forms of HMs contributed little to the bioaccessibility of HMs in soils.

The five sites studied are distributed in different areas with varying geographical conditions (Fig. 1, Table 1), consequently demonstrating variety in soil properties (Table 3). The varied soil properties in sites can be attributed to, in large extent, the soil parent materials and hydrothermal conditions (Li et al. 2014, 2015). However, the elevation of heavy metals in Beijing and Baotou were relatively greater than those in other sites, as the two cities might have received more intensive anthropogenic inputs (Madrid et al. 2008). In this study, factor analysis had extracted three main factors, including Fac_1, containing mainly pH and soil texture parameters; Fac_2, representing BCR extracted forms of HMs, and Fac_3, containing mainly organic matter (Tables 5 and 6). The interactive diagram of the loadings of Fac_1 and Fac_2 clearly supports the gathering of the samples in sites, and in the diagrams, sites in greater geographic distance are located in larger space, while sites in nearer geographic distance tend to locate in smaller space. These results may suggest that the R-Bio-HMs in soils, contributed mainly by the first two or three

Table 6 Factors with high loadings (absolute value>0.5) and their standardized coefficients in stepwise regression with R-Bio-HMs

HMs	Fac_1 Variables involved	Fac_2	Fac_3	Fac_1 Standardized coefficient	Fac_2 Standardized coefficient	Fac_3 Standardized coefficient	R-squared
As	pH, clay, silt, sand, Mn, Fe ₂ O ₃	F1, F2, F3, FSum(F1-2), Sum(F1-3)	Organic matter, F3	−0.104	0.941	—	0.897
Cr	pH, clay, silt, sand, Mn, Fe ₂ O ₃ , F1	Silt, clay, F2, F3, Sum(F1-2), Sum(F1-3)	Organic matter, F1	−0.502	0.459	−0.155	0.487
Cu	pH, clay, silt, sand, Mn, Fe ₂ O ₃	F1, F2, F3, Sum(F1-2), Sum(F1-3)	Organic matter, F3	−0.21	0.906	0.239	0.922
Pb	pH, clay, silt, sand, F2, F3, F123	Mn, Fe ₂ O ₃ , F1, F2, Sum(F1-2), Sum(F1-3)	Organic matter	0.431	0.595	0.435	0.730
Zn	pH, clay, silt, sand, Mn, Fe ₂ O ₃ , F3	Organic matter, F2, Sum(F1-2), Sum(F1-3)	Organic matter, Mn, Fe ₂ O ₃	0.405	0.563	0.342	0.581

BCR extracted forms, can be largely impacted by geographical regional factors. Among the five HMs, the site gathering was most pronounced for Cr; this is reasonable since Cr mainly come from natural sources (Manta et al. 2002; Wei and Yang 2010), having no or little “noise” effect except in some localities with Cr-containing industries, as compared to the other four HMs, which have been usually contaminated by anthropogenic activities within and around the cities (Li et al. 2001; Luo et al. 2011; Wong et al. 2006). The cluster analysis results were consistent with those of interactive factor loading diagram, indicating that sites from the north China, including Beijing, Datong, and Baotou, and sites from the south China, including Xiantao and Fuyang (Fig. 1, Table 1), were more closer in soil properties and HM bioaccessibilities, respectively. Although the gathering effects for As, Cu, Pb, and Zn in the interactive diagram were weaker than that for Cr, they were still clearly reflective on the geographical impacts on the HM bioaccessibilities. The results suggest that even with minor to moderate contamination of these HMs in soils, the impacts of the geographical factors on HM bioaccessibilities can still be predicted using general universe models incorporating the soil properties to obtain reasonable values in R-Bio-HMs, providing the data bank for soil HMs and properties that is large enough (Caboche et al. 2010). Hopefully, this can be expected to be realized in China since relevant data are actually available through several large scale surveys in the country during the past decades.

Conclusion

This study demonstrated that bioaccessibility of HMs in soils collected in five sites was largely impacted by soil properties, and such impacts could be differentiated with geographical localities. The main influencing factors in soils on bioaccessibility of HMs were soil pH, texture, Fe/Mn oxides, and organic matter. Future studies can be focused on building universe models incorporating these factors to predict the bioaccessibility of HMs in the soils based on geographical locations with large-scale difference. As such, more reliable health risk assessments can be obtained with reduced costs.

Acknowledgments We thank Dr. Nan Zhang and Mr. Kai Fan for their assistance in field sampling. This study was supported by the National Science and Technology Support Program in the 12th Five-Year Plan of China “Integration and Demonstration of Environmental Monitoring Techniques for Villages and Towns” (No. 2012BAJ24B03) and the Key Project of the Knowledge Innovation Program of IGSNRR (2012ZD002).

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest. This research do not involve human participants and/or animals.

All other authors have read the manuscript and have agreed to submit it in its current form for consideration for publication in the Journal;

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