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Probing the distribution and contamination levels of 10 trace metal/metalloids in soils near a Pb/Zn smelter in Middle China

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Abstract The horizontal and vertical distribution patterns and contamination status of ten trace metal/metalloids (Ag, Bi, Co, Cr, Ge, In, Ni, Sb, Sn, Tl) in soils around one of the largest Chinese Pb–Zn smelter in Zhuzhou City, Central China, were revealed. Different soil samples were collected from 11 areas, including ten agricultural areas and one city park area, with a total of 83 surface soil samples and six soil cores obtained. Trace metal/metalloids were determined by inductively coupled plasma–mass spectrometry after digestion by an acid mixture of HF and HNO_3. The results showed that Ag, Bi, In, Sb, Sn, and Tl contents decreased both with the distance to the Pb–Zn smelter as well as the soil depth, hinting that these elements were mainly originated from the Pb–Zn smelting operations and were introduced into soils through atmospheric deposition. Soil Ge was influenced by the smelter at a less extent, while the distributions of Co, Cr, and Ni were roughly even among most sampling sites and soil depths, suggesting that they were primarily derived from natural sources. The contamination status, as revealed by the geo-accumulation index (I_{geo}), indicated that In and Ag were the most enriched elements, followed by Sb, Bi, and Sn. In general, Cr, Tl, Co, Ni, and Ge were of an uncontaminated status.

Keywords Soil · Trace metal/metalloid · Distribution · Source identification · Contamination assessment · Pb–Zn smelting

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Introduction

Soil contamination by trace metal/metalloids is a worldwide concern due to environmental, biological, and human health reasons (Bi et al. 2006; Karadaş and Kara 2011; Dudka et al. 1996; Nahmani and Lavelle 2002). Atmospheric emissions, wastewater discharges, and solid waste disposals have been considered the three main pathways introducing trace metals and metalloids into soils (van Alphen 1999; Khan et al. 2008; Cheng 2003; Hu et al. 2013; Liu et al. 2005). Nriagu and Pacyna (1988) have estimated the amount of trace metals entering into different environmental compartments (e.g., atmosphere, aquatic ecosystems, and soils) as a result of worldwide human activities in the year 1983 and showed that non-ferrous metal production was one of the most significant sources.

Zinc (Zn) and lead (Pb) are two key non-ferrous metals being used in many fields in modern society, such as anti-corrosion, batteries, alloys, radiation shield, etc. During the extraction and smelting processes of Zn and Pb ores, a range of associated trace metal/metalloids will be released into the surrounding environment, and as a consequence, influence the receptors of potential concern (Nriagu and Pacyna 1988; Meadows and Watmough 2012; Zhang et al. 2011). Nowadays, China is the largest producer of Pb and Zn in the world, with an annual production of Pb of 4.16 million tonnes and Zn 5.21 million tonnes in the year 2010 (China Nonferrous Metals Industry Association 2011). Most Pb and

some of Zn are traditionally extracted from sulfide mineral concentrates by roasting, sintering, and then smelting. Smelting is the reduction of oxides to elemental metal and is usually accomplished by pyrometallurgical methods with carbon (coke or coal) and carbon monoxide in a furnace (Zhang et al. 2011). While over 70 % of Zn is produced with the hydrometallurgical process, this method involves steps of roasting the ores and then extracting metals using electricity (electrowinning or electrolysis process; Jiang 2004, 2006). Notably, due to the lack of effective control measures for many smelters in their early development stage, large quantities of trace elements in Zn and Pb ores have been released into the ambient environment; for example, as much as 0.31 million tonnes Pb and 0.88 million tonnes Zn have cumulatively escaped into the environment from the Pb/Zn smelting process in China before 2007 (Zhang et al. 2011).

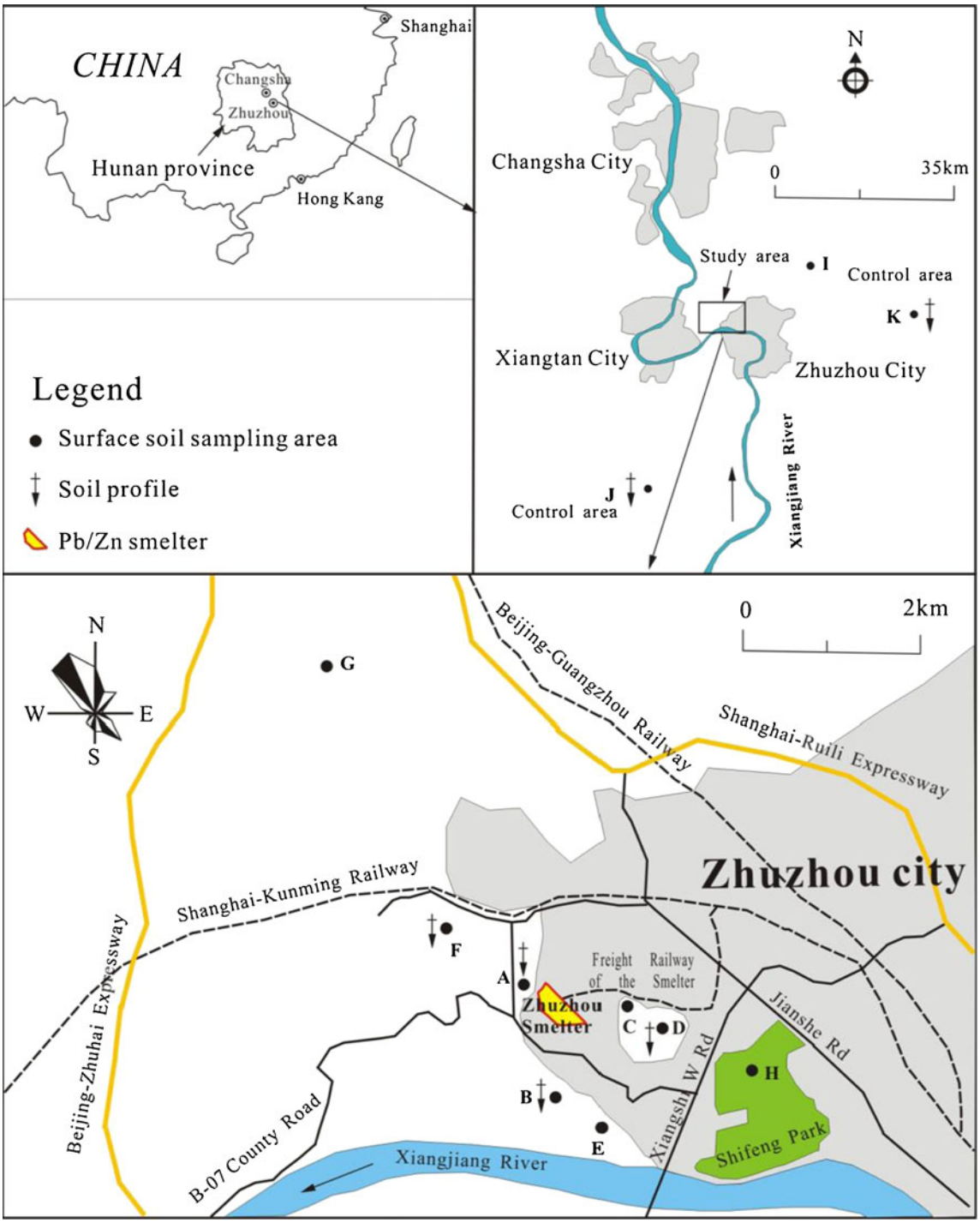

Fig. 1 Sketch map showing the soil sampling locations around the Pb–Zn smelter

The environmental impacts of Pb/Zn smelting in China were manifested by several aspects: atmospheric emissions (Wu et al. 2012; Zhang et al. 2011), soil and ground dust pollutions (Du et al. 2008; Zheng et al. 2010), crop and vegetable contaminations (Bi et al. 2006; Wang et al. 2008; Li et al. 2006), water and sediment pollutions (Cui and Liu 1988; Peng et al. 2011; Zheng et al. 2008), biological alterations (Yang et al. 2004), and human health problems (Zheng et al. 2007, 2010). Some of these have been summarized by Zhang et al. (2012).

As one of the most important environmental media, soil supports human beings by providing a living space and food. Therefore, soil is essential for humans, but once it is contaminated with metal/metalloids, it becomes hard to clean up. Meanwhile, heavy metals in soil could imperil human's health through the food chain and the direct soil ingestion pathway (Zheng et al. 2007; Poggio et al. 2009); at the same time, they could deteriorate the surrounding environment through leaching out into the water system and reemitted into the atmosphere (Chen et al. 2010; Wang et al. 2007). Although various studies carried out earlier have revealed heavy metal contamination in soils at different Pb–Zn smelting complexes in China (Bi et al. 2006; Li et al. 2006; Shang et al. 1996; Wei et al. 2009), attention was mainly focused on some highly toxic elements, such as Pb, Zn, Cd, Hg, Cu, and As. However, information about other trace elements that may be associated with Pb–Zn ores was grossly lacking. Therefore, comprehensive understanding of the environmental impacts by Pb–Zn smelting is largely hindered.

Zn and Pb concentrates are found enriched up to 20 metal/metalloids (Ye et al. 2011; Factory Records of Zhuzhou Smelter 1983, 1995). Some smelters in China have taken measures to recover part of the valuable elements through the leaching residues, the dust, the flue gas, etc. As one of the largest Chinese Pb–Zn smelters that produced around 10 % Zn ingot in China, Zhuzhou smelter recovered Cu, Au, Ag, Bi, Te, Cd, In, Tl, Ge, Ga, Hg, Co, Se, and sulfuric acid as by-products (Factory Records of Zhuzhou Smelter 1983, 1995). Although soil contamination with six metal/metalloids (Pb, Zn, Cu, As, Hg, Cd) around this smelter has been reported (Li et al. 2011), we are eager to further know whether other elements had also been contaminated in soils.

In this study, we report ten trace metal/metalloids—sliver (Ag), bismuth (Bi), cobalt (Co), chromium (Cr), germanium (Ge), indium (In), nickel (Ni), antimony (Sb), tin (Sn), and thallium (Tl)—in soils around Zhuzhou smelter in east Hunan Province, China, with the aim of exploring and examining the spatial distributions, contamination status, and sources of these metal/metalloids. The concentrations of the studied elements in Zn and Pb concentrates used by the smelter are shown in Electronic supplementary material (ESM) Table S1. It is shown that Ag, Bi, In, Sb, and Sn are at relatively high levels in Zn/Pb concentrates compared to the provincial background soils (ESM Table S1). For this study, these elements were chosen mainly because of the possibility of their emissions from the Pb–Zn smelting process or the adverse impact on the organism. Most of the elements were reported for the first time in soils at the Pb/Zn smelting sites in China, and the results will provide much insight into the biogeochemistry of these elements in soils and facilitate the understanding of the environmental impacts of Pb/Zn smelting on these elements.

Materials and methods

Study area and the smelter

Zhuzhou City is the second largest city of Hunan Province, located in the middle of Xiangjiang (a tributary of Yangtze River) watershed, southeast of the provincial capital Changsha (about 50 km) and bordering Jiangxi Province to the east (Fig. 1). Zhuzhou, along with Changsha and Xiangtan, is part of the Chang–Zhu–Tan Golden Triangle. The city has developed rapidly from being a small town in the early 1950s to an industrialized hub with the establishment of a wide range of industries (such as metallurgy, machine manufacture, chemicals, and building materials). At the end of 2009, the population of Zhuzhou City was around 1 million. The city has a typical north subtropical monsoon type of climate, with wind direction predominantly from the northwest, and the

Table 1 Information regarding the locations and soil types of each sampling area

Sampling area	Locations and soil sample types
A	150–300 m west of the smelter, vegetable plots, surface and profile soils
B	1.3 km south of the smelter, vegetable plots, surface and profile soils
C	1.1 km east of the smelter, vegetable plots, surface soils
D	1.6 km east of the smelter, vegetable plots, surface and profile soils
E	1.7 km SE of the smelter, vegetable plots, surface soils
F	1.6 km NW of the smelter, vegetable plots and paddy fields, surface and profile soils
G	3.9 km NW of the smelter, vegetable plots and paddy fields, surface soils
H	2.9 km east of the smelter, forest in Shifeng Park, surface soils
I	15.5 km NE of the smelter, vegetable plots and paddy fields, surface soils
J	38 km SW of the smelter, vegetable plots and paddy fields, surface and profile soils
K	35 km east of the smelter, vegetable plots, surface and profile soils

annual average temperature, precipitation, and weed speed are 17.6 °C, 1409 mm, and 2.1 m s^{-1}, respectively. The topography of the city is dominated by alluvial plain and gentle hills reaching an elevation of 50–200 m above sea level. Soils in this region mainly consist of acid krasnozem (red earth), which is typical for southern China.

Zhuzhou smelter, located on the northwestern outskirts of Zhuzhou City (as shown in Fig. 1) and occupies an area of 0.74 km^2, is the largest Zn producer and also the fourth largest Pb producer in China which started operating from the late 1950s. In recent years, the smelter's output of Zn and Pb ingots has reached up to around 0.45 and 0.10 million tonnes per year, respectively. The production techniques were hydrometallurgy for Zn and pyrometallurgy for Pb. An overview of the environmental quality of nine mining and smelting areas in Hunan Province indicated that this smelter annually discharged over 30 tonnes of trace metals during the early 2000s, which constitutes over 90 % of the total emissions of trace metals in Zhuzhou City (Lei et al. 2008). Some metals (such as Cd and Zn) in soils around this smelter were the most contaminated among the different mining and smelting areas in Hunan Province (Zhou et al. 2013). Furthermore, the dry deposition flux of Pb, Zn, Cd, and Cu was higher near the smelter stack, with Cu, Pb, Zn, and Cd deposition rates of 35, 90, 200, and 6 kg km^{-2} $month^{-1}$, respectively (Wang and Arne 2003). Our previous research revealed that the surface soil (0–20 cm) around this smelter (<4 km) has accumulated 6.5 tonnes Hg, 2,750 tonnes Pb, 3,920 tonnes Zn, 64 tonnes Cd, 296 tonnes Cu, and 114 tonnes As, respectively (Li et al. 2011); the street dust adjacent to the smelter was contaminated by at least 12 trace metal/metalloids (Li et al. 2013).

Soil sample collection

In this study, soil samples were collected during two field campaigns, which were done in January 2008 and November 2011, respectively. A total of 83 surface soil samples (0–20 cm) and six soil cores (0–50 cm) were collected from 11 areas around the smelter, which included ten agricultural areas (vegetable plots and paddy fields) and a city park area, coded as A to K as shown in Fig. 1. In the first campaign, soils were taken from areas of A to I, whereas in the second one, areas J and K were evaluated. Sites were selected such that soils were not contaminated by the slag pile and wastewater from the

Table 2 Statistical summary of trace metal/metalloids content (in milligrams per kilogram) in the surface soils of this study (N=83)

Sampling area	Elements	Ag	Bi	Co	Cr	Ge	In	Ni	Sb	Sn	Tl
A (N=9)	Min–Max	1.57–3.71	8.39–16.90	18–21	85–96	1.77–2.09	2.15–4.22	34–37	13.2–19.4	14.8–26.3	0.91–1.35
	Mean±SD	2.92±0.73	13.82±2.93	20±1	89±3	1.91±0.10	3.43±0.72	35±1	16.6±2.0	21.2±3.6	1.19±0.13
B (N=8)	Min–Max	0.91–1.88	5.59–21.40	14–17	72–107	1.79–2.11	1.00–1.98	32–41	13.1–19.6	13.4–21.0	1.24–1.58
	Mean±SD	1.31±0.29	9.01±5.22	16±1	82±11	1.90±0.11	1.49±0.36	36±3	15.5±2.3	17.5±3.0	1.41±0.11
C (N=5)	Min–Max	1.28–2.11	5.47–10.38	17–19	90–96	1.74–1.88	1.19–2.77	40–43	8.8–13.9	10.3–20.5	0.76–0.90
	Mean±SD	1.59±0.32	8.01±2.33	18±1	93±3	1.80±0.05	1.87±0.58	41±1	10.5±2.1	14.2±4.1	0.84±0.07
D (N=7)	Min–Max	0.66–1.00	2.31–3.95	12–20	72–104	1.60–1.78	0.44–1.06	23–41	5.1–8.8	3.9–10.0	0.55–0.70
	Mean±SD	0.78±0.18	3.20±0.57	15±3	89±13	1.70±0.06	0.70±0.28	30±7	6.5±1.4	6.1±2.3	0.62±0.05
E (N=7)	Min–Max	1.17–1.63	5.37–8.66	12–15	60–122	1.58–1.81	1.14–1.45	27–32	10.0–12.7	14.0–21.6	0.97–1.37
	Mean±SD	1.42±0.17	6.91±1.32	14±1	77±22	1.71±0.08	1.32±0.10	30±2	11.5±0.9	16.8±2.8	1.22±0.16
F (N=14)	Min–Max	1.07–2.69	3.11–8.04	23–30	138–199	1.68–2.27	1.02–2.37	41–58	8.4–15.9	6.8–18.8	0.57–0.76
	Mean±SD	1.67±0.51	4.80±1.23	27±2	167±19	1.88±0.17	1.44±0.37	47±6	11.8±2.3	11.4±3.4	0.66±0.05
G (N=10)	Min–Max	0.64–1.02	1.94–2.83	11–18	79–97	1.28–1.92	0.47–0.77	22–27	5.9–9.2	3.7–6.7	0.54–0.71
	Mean±SD	0.85±0.12	2.45±0.31	14±2	87±6	1.66±0.18	0.63±0.10	24±2	7.6±1.2	5.0±0.9	0.62±0.06
H (N=3)	Min–Max	0.66–0.82	3.65–5.01	3–16	47–78	1.67–1.75	0.74–0.97	7–29	5.9–8.9	8.1–10.2	0.48–1.09
	Mean±SD	0.75±0.08	4.12±0.77	9±7	59±17	1.70±0.04	0.84±0.12	16±11	7.7±1.6	9.1±1.1	0.76±0.31
I (N=11)	Min–Max	0.28–0.34	0.71–1.84	12–28	76–106	1.42–1.67	0.07–0.16	31–42	2.5–3.7	0.5–3.5	0.47–0.69
	Mean±SD	0.31±0.02	1.09±0.40	15±4	91±9	1.54±0.07	0.10±0.02	34±3	3.2±0.4	1.4±0.9	0.62±0.06
J (N=5)	Min–Max	0.50–0.64	0.44–1.02	11–19	76–115	1.41–1.63	0.07–0.15	20–29	2.2–3.9	4.3–15.1	0.49–0.56
	Mean±SD	0.59±0.06	0.78±0.24	14±4	88±16	1.55±0.09	0.12±0.04	24±3	2.7±0.7	6.8±4.7	0.53±0.03
K (N=4)	Min–Max	0.33–0.66	0.41–1.47	13–17	70–108	1.38–1.67	0.04–0.08	24–43	1.0–2.4	4.4–5.4	0.54–0.76
	Mean±SD	0.48±0.14	1.05±0.51	15±2	88±17	1.55±0.14	0.06±0.02	33±8	1.5±0.6	4.9±0.5	0.63±0.10
Background[a]		0.11	1.05	15	71	2.0	0.03	32	1.9	4.3	0.61

Min minimum, *Max* maximum

[a] Background values of Hunan soils (SEPA 1990)

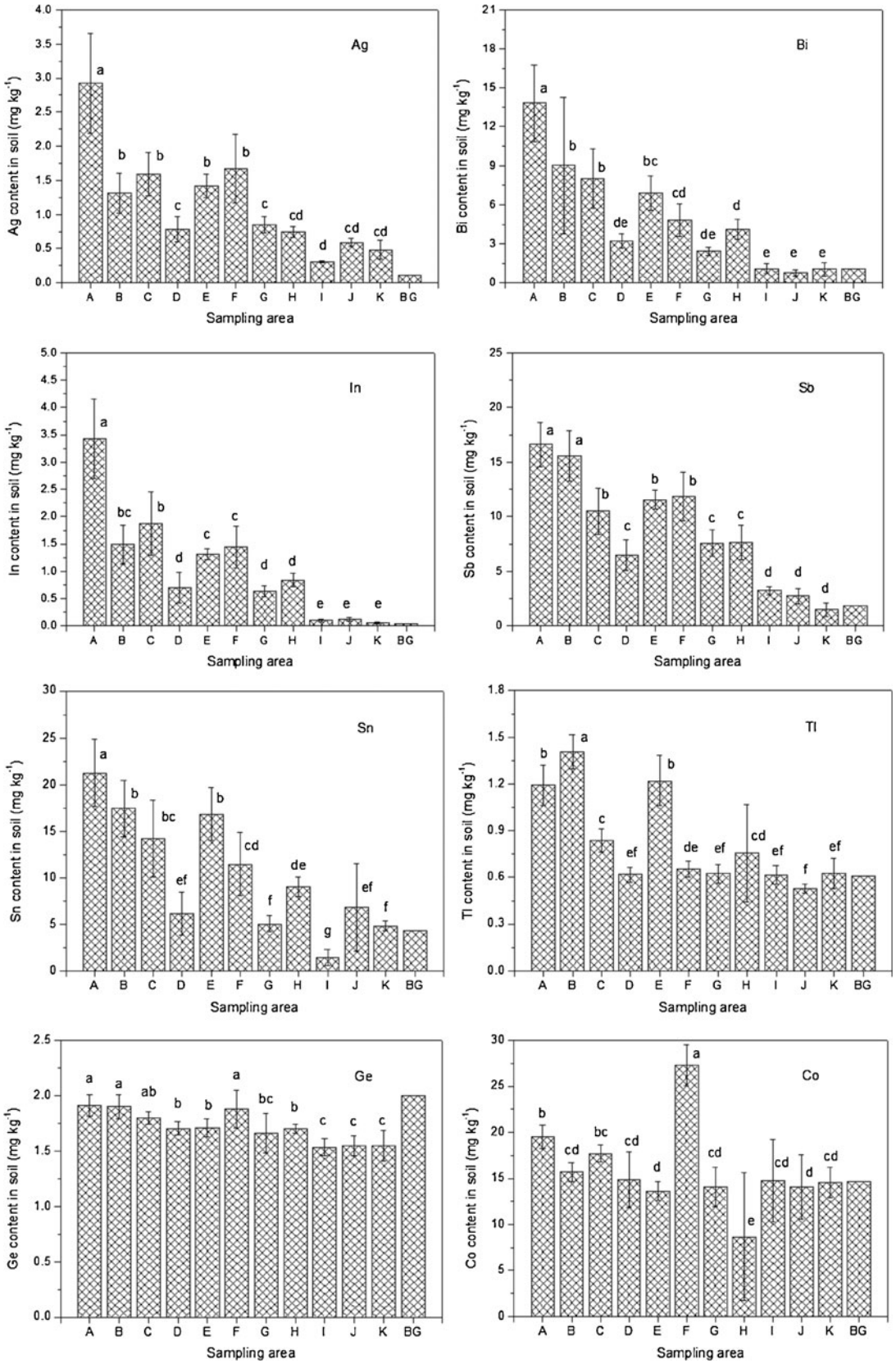

Fig. 2 Comparison of the arithmetical means of the ten studied elements in different sampling areas (*error bar* represent one standard deviation and *BG* stands for the background value of Hunan soils; SEPA 1990). *Different letters on the bars* indicate significant difference ($p<0.05$) in the trace metal/metalloids concentrations between the different sampling areas; on the contrary, the *same letter* implies no significant difference ($p>0.05$))

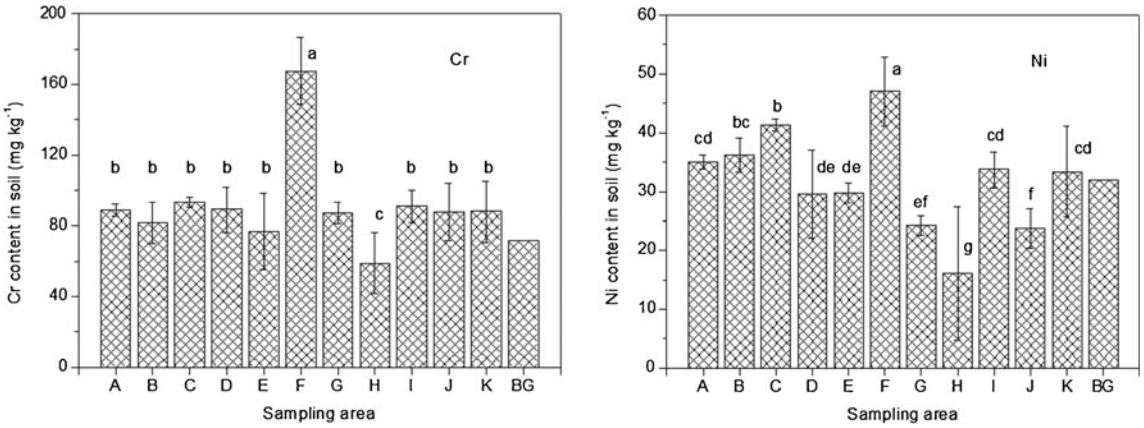

Fig. 2 (continued)

smelter. Most agriculture fields within 4 km of the smelter (areas A–G) were in the dominant wind direction, while soils from another three agriculture fields (I, J, and K) with distances ranging from 15 to 38 km in the east and south served as the control sites. Forest soils from the nearby city park (H in Fig. 1) were gathered to further assess the ecological impact from the smelter. The description of each area is listed in Table 1. Surface samples were collected from different plots at a 20- to 30-m interval in each area, and every sample consisted of a composite of four to five subsamples. During the sampling, paddy fields were fallow with no standing water and the vegetable plots were planted with common winter vegetables (such as Chinese cabbage, turnip, lettuce, celery, etc.). Soil profiles were taken from six areas (A, B, D, F, J, and K) and were divided into six depths, i.e., 0–5, 5–10, 10–20, 20–30, 30–40, and 40–50 cm. Samples were kept in airtight polyethylene bags for storage, and later in the laboratory, these soils were air-dried and ground to pass through a 100-mesh nylon sieve (0.149 mm) for proper analysis. Great caution was paid to avoid cross-contamination during the entire process.

Analytical methods

For the determination of ten metal/metalloids, a wet digestion procedure coupled with inductively coupled plasma–mass spectrometry (ELAN DRC-e, PerkinElmer Inc., Canada) measurement was adopted from Qi and Grégoire (2000). Briefly, 50 mg of the sample was digested using 1 ml of HF and 1 ml of HNO_3 in PTFE-lined stainless steel bombs heated to 190 °C for 24 h. After cooling down, the solutions in polytetrafluoroethylene (PTFE)-lined containers were evaporated to dry on an electric hot plate at a temperature of 140 °C, added 0.5 ml HNO_3, and dried again. After, 2 ml of HNO_3, 2 ml of Milli-Q water (18.2 MΩ cm, Millipore Inc.), and 500 ng rhodium (Rh) in liquid solution were successively added into the containers for a 5-h additional heating at 140 °C. Finally, about 0.4 ml of the digest was transferred into a centrifuge tube and diluted with Milli-Q water to make up a volume of approximately 10 ml. Rhodium was used as an internal standard to correct for matrix effects and instrumental drift. All the reagents used were trace metal grade.

Quality assurance and quality control were implemented by method blanks, duplicate samples, and standard reference materials (SRM). The concentration in the samples was determined in duplicates for every ten regularly processed samples and indicated that the bias is lower than 5 %. Four SRMs—GBW07305, GBW07405, GBW(E) 070009, and NIST 2710—representing a wide range of metal content from background to extreme enrichment were analyzed. The average recovery ($C_{(\text{element, measured})}/C_{(\text{element, certified})} \times 100$) of the analyzed elements in four SRMs ranged between 85 and 113 %. The detection limit and detailed recovery of each element were shown in ESM Table S2.

Data processing and contamination assessment methods

To identify the correlation among different trace metal/metalloids in soils and their possible sources, Pearson's correlation coefficient analysis and hierarchical cluster analysis were carried out using SPSS v.11.5 (SPSS Inc., Chicago, IL). This software was also used to compare the means of each element among different sampling areas with one-way analysis variance.

The contamination status for a single element was assessed with the geo-accumulation index (I_{geo}) approach (Müller 1969). This method assigns the metal/metalloid pollution to seven (0–6 grade) enrichment classes, ranging from background concentration to very heavily contaminated, as follows:

Table 3 Comparison of soil trace metal/metalloid contents (in milligrams per kilogram) in different non-ferrous smelting complexes in the world

Industrial type	Locations	Ag	Bi	Co	Cr	Ge	In	Ni	Sb	Sn	Tl	Reference
Pb–Zn smelting	Zhuzhou, China	0.63–3.71 (1.50)[a]	1.9–21.4 (6.5)	3–30 (18)	47–199 (103)	1.28–2.27 (1.80)	0.44–4.22 (1.51)	7–58 (35)	5.1–19.6 (11.4)	3.7–26.3 (12.7)	0.48–1.58 (0.90)	This study[b]
Zn smelting	Auby, France	0.25–0.83 (0.45)	0.1–0.8 (0.2)	7–11 (8)	41–70 (51)	–[c]	0.09–0.28 (0.15)	13–40 (19)	1.7–9.2 (3.0)	2.0–7.3 (3.2)	0.32–0.56 (0.45)	Sterckeman et al. (2002)
Pb–Zn smelting	Noyelles-Gdt, France	0.12–2.38 (0.83)	0.2–1.0 (0.5)	6–13 (10)	35–60 (47)	–	0.06–0.55 (0.24)	10–35 (20)	1.5–14.5 (6.8)	2.1–5.8 (3.4)	0.29–0.89 (0.48)	Sterckeman et al. (2002)
Pb–Zn smelting	Veles, Macedonia	–	–	3–38 (13)	17–1800 (160)	–	0.01–9.2 (0.24)	7–600 (54)	0.2–110 (2.0)	–	–	Stafilov et al. (2010)
Pb–Zn minging and smelting	Kosovska Mitrovica, Kosovo	0.1–58 (1.9)	0.1–110 (4.5)	2.7–160 (28)	7–1100 (110)	–	–	7.6–2600 (230)	0.10–1400 (17)	–	0.10–7.7 (0.59)	Šajn et al. (2013)
Pb–Zn minging and smelting	Suszec, Poland	–	–	–	14–82 (34)	–	–	2.3–16 (6.4)	0.34–2.26 (0.81)	–	–	Loska et al. (2004)
Cu–Ni smeltingr	Kola Peninsula, Russia	–	–	15–120	4–31	–	–	115–9288	–	–	–	Barcan and Kovnatsky (1998)
Cu mining and smelting	Daye, China	–	–	8–69 (17)	17–187 (46)	–	–	8–102 (29)	–	–	–	Yin et al. (2012a)
Sb mining and smelting	Lengshuijiang, China	–	–	–	81–316	–	–	29–86	10–2159	–	–	Wang et al. (2010)
Sn–W Mining	SFA, Portugal	1.0–3.0 (1.0)	–	5–169 (19)	131–326 (206)	–	–	7–472 (41)	6.0–19.0 (8.6)	6–167 (30)	–	da Silva et al. (2013)

[a] Range and arithmetic mean (shown in parenthese)

[b] Results within 4 km to the smelter

[c] Not available

$$I_{\text{geo}} = \log_2\left[\frac{C_{Sample}}{(1.5 \times C_{\text{Background}})}\right] \quad (1)$$

where C_{Sample} is the concentration of the element in the samples and $C_{\text{Background}}$ is the geochemical background value of a given element. The description of I_{geo} classes is supplied in ESM Table S3 according to Müller (1969).

Results and discussion

Trace metal/metalloids in surface soils

The descriptive statistics of the ten observed elements in surface soils from 11 areas are presented in Table 2 in relation to the provincial background value of each element. The ranges of each element (in milligrams per kilogram) in polluted (<4 km, A–H) and control areas (I–K, shown in parentheses) were as follows: Ag, 0.63–3.71 (0.28–0.66); Bi, 1.94–21.40 (0.41–1.84); Co, 3–30 (11–28); Cr, 47–199 (70–115); Ge, 1.28–2.27 (1.38–1.67); In, 0.440–4.220 (0.037–0.155); Ni, 7–58 (20–43); Sb, 5.12–19.60 (0.98–3.92); Sn, 3.7–26.3 (0.5–15.1); Tl, 0.48–1.58 (0.47–0.76), respectively. A comparison of each metal/metalloid at different sampling areas is shown in Fig. 2. From Fig. 2 and Table 2, it can be seen that six metal/metalloids (Ag, Bi, In, Sb, Sn, and Tl) exhibited a profound variability over several to tens of magnitude in concentrations between different areas, i.e., the concentrations of the metal/metalloids decrease as the distance from the smelter increases. The difference between the polluted (<4 km to the smelter) and control areas is significant ($p < 0.05$, Fig. 2). Compared with the control areas, the most affected area A has increased concentrations of In by 51 times; Bi, 13 times; Ag and Sb, 5 times; Sn, 4 times; Tl, 1 time. The Ge content dropped slightly with distance to the smelter, with only 20 % increase in area A versus the control areas. Other elements such as Co, Cr, and Ni showed roughly identical contents between different areas (variations within 1 magnitude), but with the exception of areas F and H, where they displayed higher and lower values, respectively (Fig. 2).

Wind directions also showed a clear effect on the accumulation of elements in soils, for example, sampling areas D and F, located at an identical distance to the smelter (1.6 km); elements related to Pb/Zn smelting activities (such as Ag, Tl, Sn, Sb, Bi, and In) in area D are much lower than that in area F since area D is east of the smelter (a non-dominant wind direction) while area F is in the northwest (dominant wind direction; Fig. 1). Therefore, contamination along the wind direction (northwest–southeast) is much heavier than the wind transection (northeast–southwest), and this has been confirmed by the distribution patterns of 12 trace metal/metalloids in the street dust that is impacted by the smelting process (Li et al. 2013). Although sampling area C is also located at the non-predominant wind direction (east), and not far from area D (distance around 0.5 km), this area suffered more serious contamination than area D; this may be a result of the influence of a nearby freight railway that carries the raw materials to the smelter (Fig. 1).

In comparison with the provincial background value of each element, six metal and metalloids (Ag, Bi, In, Sb, Sn, and Tl) were obviously enhanced in soils, even in the city park (H) and control areas (especially for In, Ag, and Sb; cf. Table 2 and Fig. 2), showing the clear impacts of Pb/Zn smelting operations on the horizontal distributions of these elements. However, Ge in soils is somewhat lower than the provincial background, which may be a result of the fluctuation of Ge content in the bed rocks of local and provincial regions. The increase of Cr, Ni, and Co in soils is less than a fold, hinting that the influence of Pb/Zn smelting is limited, although the concentrations of Cr, Ni, and Co in surface soils are comparable to the background values at most sampling sites; they are significantly elevated at site F, which suggested that there should be a local source responsible for this enrichment, but we have not identified it yet. In addition, as the standards for the soil environmental quality of China (SEPA 1995) have specified the contents of eight metal/metalloids (As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn) in soils, in this study, we compared Cr and Ni contents with the grade II criteria (suitable for

Table 4 Comparison of the studied elements (in milligrams per kilogram) in the upper layer (0–20 cm) agricultural soils with that in street dusts (Li et al. 2013), both collected within 4 km from the Pb/Zn smelter

Environmental media		Ag	Bi	Co	Cr	Ge	In	Ni	Sb	Sn	Tl
Agricultural soil (N=60)	Min–Max	0.62–3.71	1.94–21.40	11–30	60–199	1.28–2.27	0.44–4.22	22–58	5.1–19.6	3.7–26.3	0.54–1.58
	AM	1.53	6.65	19	105	1.80	1.55	35	11.6	12.9	0.91
	Median	1.35	5.44	17	90	1.79	1.29	35	11.5	13.5	0.73
Street dust (N=13)	Min–Max	0.95–28.7	2.50–295	11–33	62–258	1.44–7.02	1.44–86.6	25–88	5.5–115.4	6.7–312.1	0.64–13.6
	AM	6.91	41.26	17	123	2.70	13.79	44	37.0	57.7	2.55
	Median	4.62	13.30	14	115	2.03	4.54	41	19.6	27.9	1.25

Min minimum, *Max* maximium, *AM* arithmetical mean

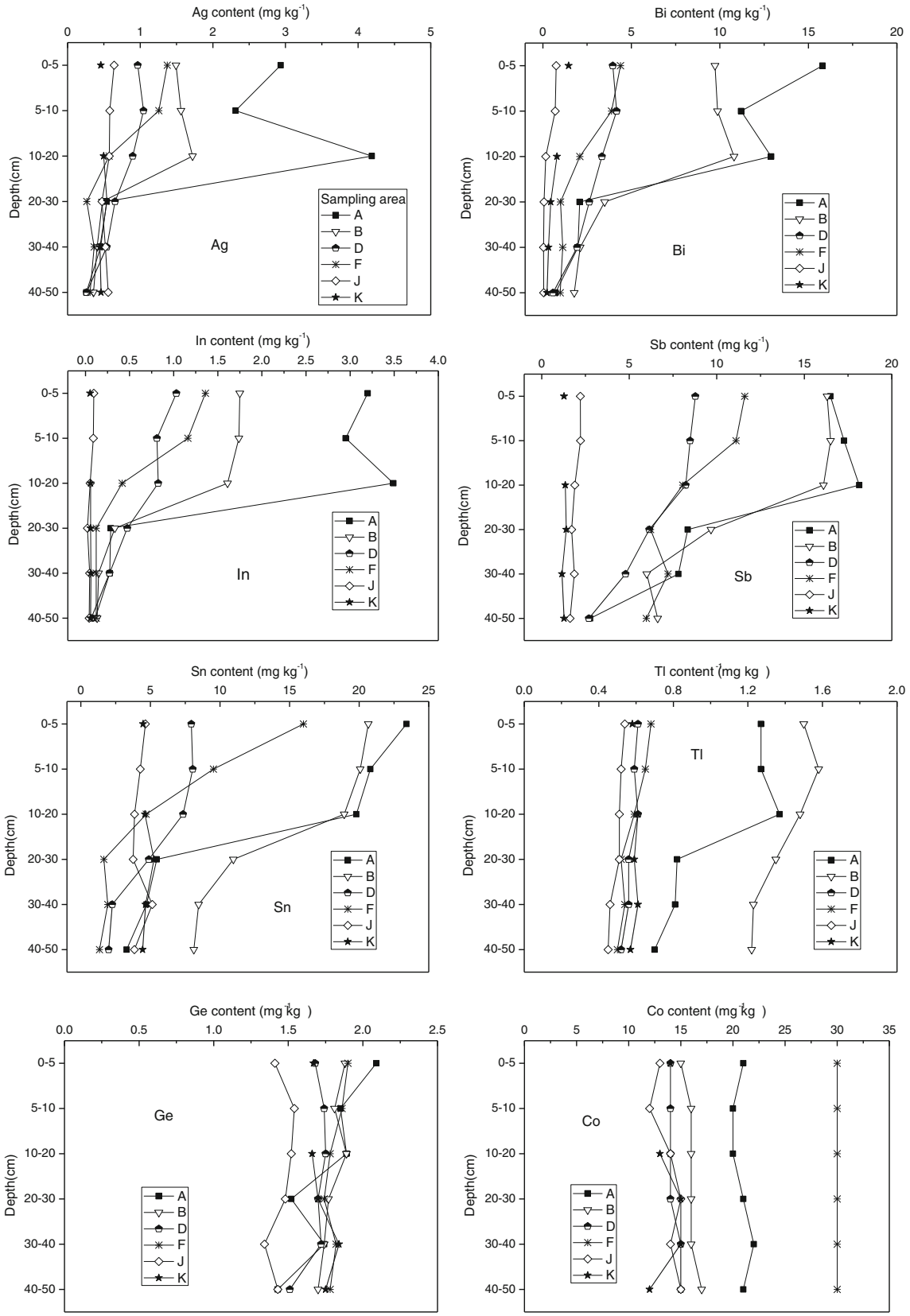

Fig. 3 Vertical profiles of the measured metal/metalloids in six soil cores (soil layer 5–10 cm in area K was not collected)

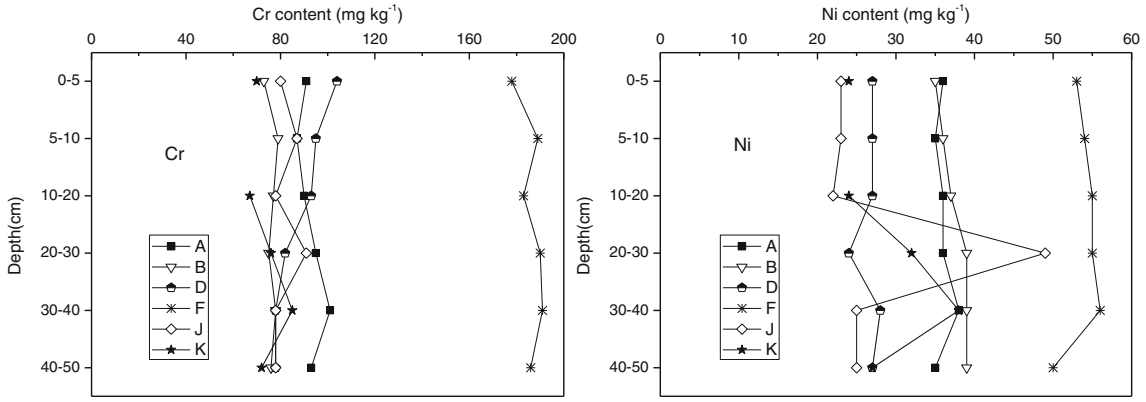

Fig. 3 (continued)

agricultural soil with pH<6.5) of this standard, as shown in ESM Table S4. Our previous study showed that the soil pH in most of the study areas is acidic (<6.5; Li et al. 2011). It was disclosed that the majority of the samples contained Ni below the criterion of 40 mg kg^{-1}, with areas C (41±1 mg kg^{-1}) and F (47±6 mg kg^{-1}) slightly exceeding it (Table 2 and Fig. 2). For Cr, only five individual samples of vegetable plots from area F (153–171 mg kg^{-1}) surpassed the criterion for dry land soil (150 mg kg^{-1}); all other samples are far below this criterion.

From a global perspective (Table 3), traces of metal/metalloids like Ag, Bi, In, Sb, Sn, and Tl in soils around Zhuzhou smelter are much elevated than other Zn and Pb smelters located in northern France (Sterckeman et al. 2002) and Macedonia (Stafilov et al. 2010), but it is very similar to a Pb–Zn mining and smelting area in Kosovo (Šajn et al. 2013). The difference in the degree of contamination of these elements was considered to be a result of the smelting history, production capacity, technology of operations, and environmental protection measures that were implemented. For other elements, such as Co, Cr, and Ni, the discrepancy was not distinct and was assumed to reflect the geological backgrounds. Compared with other types of nonferrous smelting activities, such as Cu, Ni, Sb, Sn smelting, etc., as shown in Table 3, Ni was at an astonishingly high level at a Cu–Ni smelting area in Russia (Barcan and Kovnatsky 1998), Sb at a Sb mining and smelting area in China (Wang et al. 2010), and Sn at a Sn–W mining area in Portugal (da Silva et al. 2013). This showed that different ore types were responsible for this difference.

For a specific comparison with street dust collected around Zhuzhou smelter (Li et al. 2013), the results obtained showed that agricultural soils contained relatively lower levels (p <0.05) of Ag, Bi, In, Sb, Sn, and Tl than that of street dust (Table 4). This could be a result of a dilution effect by the plowed layer of bulk soil since the dust from the Zn and Pb smelting processes hosts much higher levels of Ag (82–2,150 mg kg^{-1}), Bi (390–480 mg kg^{-1}), In (58–590 mg kg^{-1}), Sb (880–1,440 mg kg^{-1}), Sn (89–2,100 mg kg^{-1}), and Tl (119–120 mg kg^{-1}), as revealed in ESM Table S5 (Factory Records of Zhuzhou Smelter 1983). However, no significant differences were found for Co, Cr, Ge, and Ni between these two types of environmental media (agricultural soils and street dust) since the dust from the smelter contains low levels of these elements (ESM Table S5). Therefore, a dilution effect would be a leading cause for the difference between the street dust and soil for Ag, Bi, In, Sb, Sn, and Tl.

Trace metal/metalloids in soil cores

The vertical profiles of the ten observed elements in six soil cores were illustrated in Fig. 3. It is shown that elevated concentrations of Ag, Bi, In, Sb, Sn, and Tl in surface soils (0–20 cm) sharply decrease between 20 and 30 cm and are relatively low at 30- to 50-cm depth. Furthermore, Sb, Sn, and Tl in the lower layers (30–50 cm) at areas A and B were still evidently higher than in other areas, suggesting the mobilization of these elements. Nevertheless, more research is needed to explore the maximum depth that could be impacted by the smelter since Sterckeman et al. (2000) and Verner et al. (1996) have found that some trace metals could be mobilized for up to 2 m down around Pb/Zn smelters in France and Poland. However, the profiles of other elements (Co, Cr, Ge, Ni) were relatively stable throughout the soil cores. Similar to the surface soils, the soil core in area F has much higher Co, Cr, and Ni contents than in other areas; this may be induced by an unidentified local source in area F.

The above findings regarding the soil profile patterns were supported by the trace elemental contents in dusts emitted from this smelter (as seen in ESM Table S5) and a Pb–Zn smelter in France (Sterckeman et al. 2002); in the latter case, the dust also contained extremely high levels of Ag (145–2,120 mg kg^{-1}), Bi (160–193 mg kg^{-1}), In (33–153 mg kg^{-1}), Sb (666–705 mg kg^{-1}), Sn (277–884 mg kg^{-1}), and Tl (49.3–73.4 mg kg^{-1}) and lower contents of Co (2–23 mg kg^{-1}), Cr (50–105 mg kg^{-1}), and Ni (9–68 mg kg^{-1}). Street dust within 4 km to the Zhuzhou smelter also showed somewhat high

levels of Ag (0.95–29 mg kg^{-1}), Bi (2.5–295 mg kg^{-1}), In (1.44–87 mg kg^{-1}), Sb (5.5–115 mg kg^{-1}), Sn (6.7–312 mg kg^{-1}), and Tl (0.64–14 mg kg^{-1}; Li et al. 2013).

Source identification

In our previous study, six metal/metalloids (Pb, Zn, Cu, Hg, Cd, As) in soils around Zhuzhou smelter were investigated. As much as 2.89 mg kg^{-1} Hg, 1,200 mg kg^{-1} Pb, 3,350 mg kg^{-1} Zn, 41.1 mg kg^{-1} Cd, 157 mg kg^{-1} Cu, and 93 mg kg^{-1} As were found, and these elements were considered to be introduced by the same source, namely, the smelter (Li et al. 2011). Combined with these data, we conducted cluster and the correlation coefficient analysis (Fig. 4 and ESM Table S6) to differentiate the sources of the different elements of this study. It showed that two distinct sources could be responsible for the origins of the ten observed elements in this study, i.e., source 1 for seven elements (Ag, In, Sb, Sn, Bi, Ge, Tl) and source 2 for the other three elements (Co, Cr, Ni). Based on the relationship of distance to the smelter and the wind directions, along with the horizontal and vertical distribution patterns discussed in "Trace metal/metalloids in surface soils" and "Trace metal/metalloids in soil cores," it could be deduced that source 1 is the Zn/Pb smelter and source 2 is the natural source. Atmospheric deposition is thought as the primary pathway introducing the former group of elements into soils, as revealed by the horizontal and vertical distribution patterns. Trace metal composition and abundance of emission from Pb/Zn smelters were largely dependent on the ore types as different genesis of Zn and Pb ores usually hold different levels of trace elements (Ye et al. 2011; Yin et al. 2012b). Notably, Zhuzhou smelter lacks its own ore resource and purchases Zn/Pb concentrates from over 80 mines throughout the country, even importing some from other countries such as Peru, Australia, Turkey, etc. (Factory Records of Zhuzhou Smelter 1983, 1995). Therefore, the trace metal/metalloid levels in soils nearby the smelter could reflect the integrated composition of the trace metals and metalloids in the Chinese Zn/Pb ores. In this study, the elements emitted from the smelter were much similar to a Pb and a Zn smelter in northern France (Sterckeman et al. 2002; Douay et al. 2008), except for Ni which was emitted in significantly larger quantities from the French smelters. In the present study, the results

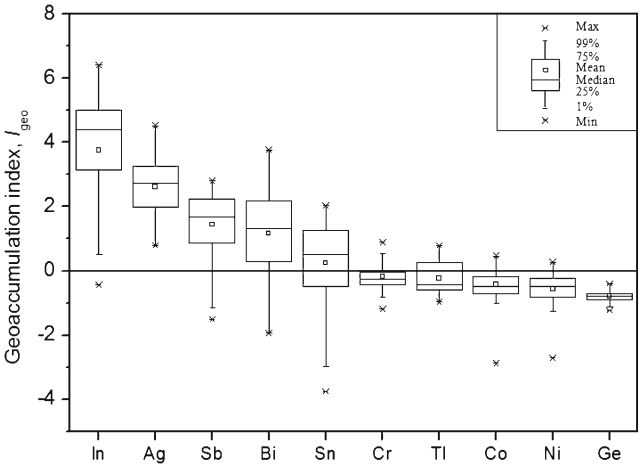

Fig. 5 Box plot of the geo-accumulation index (I_{geo}) of the studied elements in all surface soils

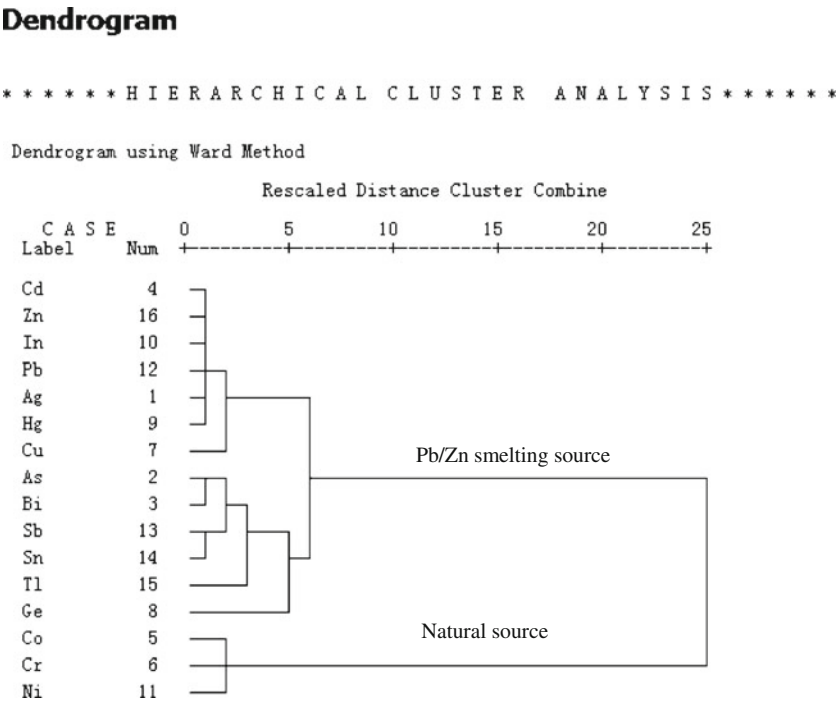

Fig. 4 Hierarchical clustering of 16 elements in the surface soils of this and a previous study (Li et al. 2011)

indicate that the smelter as a source of Ni, together with Co and Cr, is less significant.

Contamination assessment

The contamination status of the ten analyzed trace metal/metalloids in surface soils was approached by using the concept of geo-accumulation index. Figure 5 indicates the overall severity of contamination gauged by the median of the geo-accumulation index and decreased in the following order (with the medians of I_{geo} shown in parentheses): In(4.41)>Ag(2.73)>Sb(1.68)>Bi(1.31)>Sn(0.51)>Cr(−0.26)>Tl(−0.42)>Co(−0.48)>Ni(−0.50)>Ge(−0.79). The contamination status of In and Ag was most predominantly severe, with medians of geo-accumulation index>2, belonging to classes of moderate to extreme contamination (cf. ESM Table S3). The maximum geo-accumulation index as high as 6.41 was attained for In from area A, which is closest to the smelter. The median geo-accumulation indices of Sb, Bi, and Sn ranged from 0 to 2, indicating that the soil is of uncontaminated to moderately contaminated status. However, Cr, Tl, Co, Ni, and Ge exhibit a median of $I_{geo}<0$, suggesting a largely uncontaminated status (Fig. 5 and ESM Table S3). The results of I_{geo} at the different areas are shown in ESM Fig. S1. The distribution patterns of I_{geo} at the different areas were similar to those shown in Fig. 2, with the I_{geo} of Ag, Bi, In, Sb, Sn, and Tl clearly higher in areas A–H (<4 km to the smelter) than I–J (controls).

Since the soil quality standard of China has regulated only eight metal/metalloids, as stated before, it is hard to separate geochemical anomalies from the geochemical background for other metals or metalloids. In this study, we adopted the concept of [mean±2 standard deviation] to estimate the threshold values dividing background data from anomalies (Reimann and Garrett. 2005). The mean and the standard deviation were calculated based on the underneath part of the soil cores (40–50 cm) at areas D, F, J, and K that were recognized as less impacted by the smelter, as aforementioned. The calculated threshold values (in milligrams per kilogram) were Ag, 0.671; Bi, 1.58; Co, 34; Ge, 3.00; In, 0.141; Sb, 7.18; Sn, 6.45; and Tl, 0.915, respectively. Along with these values, one could easily scrutinize whether the soils are contaminated or not and use these data to assess the clean effect of soil remediation endeavors in the future.

Similar to the work we conducted earlier (Li et al. 2011), we preliminarily estimated the accumulation of six metal/metalloids, which were obviously introduced by the smelting activities, in agricultural soils through combining the soil density (1.26 g cm^{-3}; Guo and Zhu 2004) and soil metal/metalloid content at different areas. It is shown that surface soils (0–20 cm) within 4 km to the smelter have accumulated 0.7 tonne Tl, 9.1 tonnes In, 10.6 tonnes Ag, 24 tonnes Sn, 25 tonnes Bi, and 80 tonnes Sb.

Conclusions

The extensive Pb/Zn smelting operations on the northwest part of Zhuzhou City have resulted in the enrichment of Ag, Bi, In, Sb, Sn, and Tl in nearby soils, and the concentrations decreased with distance to the smelter and the soil depth and enriched along the wind direction. While Ge was slightly influenced by the smelting operation, Co, Cr, and Ni were originated by the natural sources in most sampling areas, except for area F where an unidentified source caused the moderate enrichment of these three elements. It is shown that In and Ag were the major pollutants, followed in lesser quantities by Sb, Bi, and Sn. In addition, Cr, Tl, Co, Ni, and Ge were at uncontaminated levels on the whole. The observations also highlighted the existence of contaminants such as Sb, Sn, and Tl below the surface soils in areas close to the smelter, which could be the result of the transfer of metals from the topsoil to the deeper layers. Threshold values were put forward to differentiate contaminated levels and background levels, and the accumulations of six metal/metalloids in the surface soil were also estimated.

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