Acidic leaching of potentially toxic metals cadmium, cobalt, chromium, copper, nickel, lead, and zinc from two Zn smelting slag materials incubated in an acidic soil[☆]

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ABSTRACT

A column leaching study, coupled with acid deposition simulation, was conducted to investigate the leaching of potentially toxic metals (PTM) from zinc smelting slag materials (SSM) after being incubated in an acid Alfisol for 120 days at room temperature. Two SSMs (SSM-A: acidic, 10 yrs exposure with moderate high PTM concentrations versus SSM-B: alkaline, 2 yrs exposure with extremely high PTM concentrations), were used for the incubation at 0.5, 1, 2.5, 5 wt% amendment ratios in triplicate. Five leaching events were conducted at day 1, 3, 7, 14, and 28, and the leaching of PTMs mainly occurred in the first three leaching events, with the highest PTM concentrations in leachate measured from 5 wt% SSM amendments. After leaching, 2.5, 12, 5.5, 14, 11, and 9 wt% of M3 extractable Pb, Zn, Cd, Co, Cr, and Ni could be released from 5 wt% SSM-A amended soils, being respectively 25, 12, 4, 2, 2, and 2 times more than those from 5 wt% SSM-B amended soils. In the leachates, the concentrations of PTMs were mostly affected by leachant pH and were closely correlated to the concentrations of Fe, Al, Ca, Mg and P with Cd, Pb, and Zn showing the most environmental concern. Visual MINTEQ 3.1 modeling suggested metallic ions and sulfate forms as the common chemical species of PTMs in the leachates; whereas, organic bound species showed importance for Cd, Pb, Cu, and Ni, and $CdCl^+$ was observed for Cd. Aluminum hydroxy, phosphate, and sulfate minerals prevailed as the saturated minerals, followed by chloropyromorphite ($Pb_5(PO_4)_3Cl$) and plumbogummite ($PbAl_3(PO_4)_2(OH)_5 \cdot H_2O$) in the leachates. This study suggested that incubation of SSMs in acidic soil for a long term can enhance the release of PTMs as the forms of metallic ions and sulfate when subjected to acid deposition leaching.

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1. Introduction

Metal smelting activities not only induce huge emissions of fumes and dust but also produce tons of smelting wastes such as smelting slags, mine tailings, sewage sludges, and combustion residues. The production of smelting wastes (especially slags) has received great attentions in recent years due to the high content of PTMs in these slags (Ettler et al., 2009; Khorasanipour and Esmaeilzadeh, 2016; Lanteigne et al., 2012; Morrison and Gulson, 2007; Piatak and Seal, 2010; Sueoka and Skakibara, 2013; Yang

et al., 2010). Smelting slags could be re-migrated by wind erosion, natural weathering, rainfall flushing under natural conditions, or by human transportation, re-entering surrounding soils, surface water, or ground water. Many studies have demonstrated that smelting slag-contaminated soils could increase PTMs access by crops and vegetables, induced by alteration of chemical forms or mineral phases of PTMs in contact with soil solutions or soil biota (Basta and Gradwohl, 2000; Farago and O'Connell, 1983; Gzyl, 1995; Ivask et al., 2004; Kierczak et al., 2013; Liang et al., 2013; Little and Martin, 1972; Sobanska et al., 2000; Verner et al., 1996). Morphological alteration of smelting slags in acidic soils could be directly observed under a microscope (Birkefeld et al., 2006; Sobanska et al., 2000). Some laboratory or field simulation experiments, such as metallurgical slags as soil amendments (Dieckmann et al., 2003), copper slags buried in soils (Birkefeld et al., 2006), one year in-situ

alteration experiment (Pareuil et al., 2010), and long term in-situ implantation (Chrastny et al., 2014), were conducted to monitor the release potential of PTMs from slags. Dieckmann's results indicated at pH 5, large increases in the phytoavailable fraction of Cd, Zn, and Pb up to ~10, ~20, and ~20 times as compared to the control soil when 10 wt% of slags were amended (Dieckmann et al., 2003). Birkefeld's study demonstrated that 18 months' exposure to field acidic forest soil resulted in 10 wt% mass loss of copper slags, faster than exposure in laboratory conditions, due to strong field biological activities (Birkefeld et al., 2006). Their study also indicated a more rapid dissolution of PbO particles than copper slag particles in soils (Birkefeld et al., 2006). However, alteration on larger Mn-rich slag particles were not evidenced in one year's bury in an acidic soil, probably due to the shorter contact time with the soil (Pareuil et al., 2010). Dahmani-Muller et al. (2001) reported the highest concentrations of Cd, Pb, and Cu in the shoots and roots of *Arabidopsis halleri* grown in soils amended with waste slags when compared with other metal-bearing solids. In general, the mineralogy of slags (including grain size, mineral phase and mineral composition) and physico-chemical and biological properties of receiving soils are regarded as to co-control the availability of PTMs from slag-affected soils (Bade et al., 2010; Birkefeld et al., 2006; Ettler, 2016; Negim et al., 2010; Parra et al., 2014; Sobanska et al., 2016).

The availability of PTMs in soils can be evaluated by numerous methods, such as single batch leaching/extraction (using acidic solution (inorganic or organic), salt solution, buffer solution, or distilled/deionized water), in vitro test, sequential extraction procedures (BCR or Tessier's procedure), adsorption/desorption experiments, etc. In recent years, a flow-through or dynamic leaching method, i.e. column leaching, was frequently adopted to study the mobilization of PTMs in soils contaminated by mining/smelting activities (Ash et al., 2015, 2016; Balint Nimirciag et al., 2013; Hu et al., 2014; Mouni et al., 2016; Navarro et al., 2008). Previous studies indicated a wide range of solubility of PTMs from the soils contaminated via mining/smelting activities, dependent on pH/composition of leaching solution, mineral phases of mining/smelting materials, and soil properties (Piatak et al., 2015; Potysz et al., 2016; Tiwari et al., 2015; van der Sloot et al., 2011). Acidic solution leaching proved to be effective for potential release of PTMs from smelting slags (Cappuyns et al., 2014; Chrastny et al., 2014; De Andrade Lima and Bernardez, 2011; Ettler et al., 2016; Seignez et al., 2008). Simulation modeling suggested ionic species as the dominant form of metals in leachate, such as Pb^{2+} and Zn^{2+} (Navarro et al., 2008); Pb^{2+}, Zn^{2+}, and Cu^{2+} (Islam et al., 2016), and are mainly controlled by Pb–Zn sulfide mineral phases (Cappuyns et al., 2014).

Zinc smelting activities back in the 80s and 90s in northwestern Guizhou, China produced numerous smelting slag material (SSM) dumps, which contained high contents of Pb, Zn, and Cd (Bi et al., 2009; Yang et al., 2006). The regional karst geological setting is theoretically regarded as a barrier to resist the release of potentially toxic metals; however, it is also sensitive to erosion by acid deposition which is severe in this region due to routine consumption of high sulfur coals (Tanner et al., 1997; Zhao et al., 1988). Therefore, the potential release severity of PTMs from SSM-contaminated soils remains uncertain. We hypothesized that when SSMs settle down in the adjacent soils, in the long term, mobilization of PTMs would be enhanced via a series of physicochemical reactions at the soil-SSM interface, accelerating the transportation of these metals into runoff water when subjected to acid deposition, thus deteriorating the quality of the surrounding surface water and the soils they settled. Accordingly, the objectives of this study were 1) to examine the leachability of PTMs Pb, Zn, Cd, Co, Cr, Cu, Ni from zinc

smelting slag materials-amended acidic soils under the acid deposition condition; 2) to simulate the possible chemical species of PTMs in the leachate.

2. Materials and method

2.1. Smelting slag materials

Two zinc smelting slag materials (SSMs) were sampled from smelting waste dumps in northwestern Guizhou, China. The SSM is a mixture of zinc smelting slags, combustion cokes, clay materials, and even low-grade mine tailings, etc., piling and accumulating after each smelting activity to form smelting waste dumps. The first (SSM-A) was collected from a dump with an environmental exposure of 10 years in the open field while the other one (SSM-B) was from the dump exposed for only 2 years. After collection, the materials were air dried, cracked, and passed through a 1 mm sieve before further analyses. The main mineral compositions of the two SSMs are presented in Supplement 1. SSM-A had low pH (3.86) and a much lower total concentration of PTMs Cd, Co, Cr, Cu, Ni, Pb, and Zn, as compared to SSM-B (Table 1).

2.2. Soil amendment

About 50 kg of bulk soil was collected from a citrus grove after the covered vegetation and litter layer was removed. After air-dried and plant debris was removed, the soil was passed through a 1 mm sieve and stored in an air tight container. The soil was Alfisol (sandy, siliceous, hyperthermic, Arenic Glossaqualf), with a pH of 4.62, EC 221 $\mu S\ cm^{-1}$ and total organic carbon of 7.14 g kg^{-1} (Table 1). The two SSMs were amended in the soil in triplicate at ratios of 0.5, 1.0, 2.5, and 5.0 wt%. The soil without any SSM amendments was used as a control. After being thoroughly mixed and adjusting the soil moisture to 70 wt% field holding capacity, the mixtures were incubated for 120 days at room temperature before being subjected to Mehlich 3 (M3) extraction and column leaching. The total contents of PTMs in the soils after incubation are presented in Supplement 2.

2.3. Mehlich 3 extractible and total content of major elements and potentially toxic metals

Availability of major elements Al, Ca, Fe, K, Mg, Mn, Na, and P and PTMs Pb, Zn, Cd, Co, Cr, Cu, and Ni in the above incubated soils was estimated by extracting the soils with M3 solution at a solid to solution ratio of 1:10 (Mehlich, 1984) in triplicate. The extractant was composed of 0.2N acetic acid, 0.25N ammonium nitrate, 0.015N ammonium fluoride, 0.013N nitric acid, and 0.001M EDTA with pH adjusted to 2.5 ± 0.1 using 1M HCl or 1M $NH_3 \cdot H_2O$. The extracts were filtered through a Whatman 42 filter paper and analyzed for the concentrations of the major elements and PTMs with ICP-OES (Vista MPX, Varian, USA). The total contents of major elements and PTMs in the soil, SSMs, and SSM-amended soils were determined with the ICP-OES following the multi-acid (HNO_3, $HClO_4$, and HF) digestion method (Tessier et al., 1979) after the subsamples were air dried and grounded to < 0.125 mm using an agate miller.

2.4. Column leaching

Acidic leaching solution (ALS) was constructed by mixing concentrated H_2SO_4 and HNO_3 at a ratio of 9:1 (w/w) (the typical acid rain composition in southern China, Zhou et al., 1988), then the mixture was diluted with DI water to the final concentrations of

Table 1
Basic properties of the soil and smelting slag materials (SSMs) used in this study.

Years of disposal after smelting		Soil	SSM-A	SSM-B
			10	2
pH		$4.6 \pm 0.038b$	$3.9 \pm 0.015c$	$8.1 \pm 0.025a$
EC	($\mu S\ cm^{-1}$)	$220 \pm 2.3c$	$2800 \pm 15a$	$2300 \pm 15b$
Total organic C	($g\ kg^{-1}$)	$7.2 \pm 0.021c$	$48 \pm 0.42b$	$68 \pm 2.6a$
Total organic N	($g\ kg^{-1}$)	$0.37 \pm 0.03c$	$1.0 \pm 0.04a$	$0.54 \pm 0.06b$
Total Al	($mg\ kg^{-1}$)	$1700 \pm 49c$	$14000 \pm 700b$	$18000 \pm 470a$
Total Fe	($mg\ kg^{-1}$)	$840 \pm 29c$	$77000 \pm 3100a$	$6100 \pm 900b$
Total Ca	($mg\ kg^{-1}$)	$440 \pm 23c$	$3900 \pm 190b$	$22000 \pm 360a$
Total Mg	($mg\ kg^{-1}$)	$120 \pm 5.5c$	$1100 \pm 50b$	$2000 \pm 47a$
Total P	($mg\ kg^{-1}$)	$67 \pm 0.36c$	$210 \pm 7.2b$	$310 \pm 8.4a$
Total Cd	($mg\ kg^{-1}$)	< DL	$9.6 \pm 0.46b$	$24 \pm 1.2a$
Total Co	($mg\ kg^{-1}$)	$0.15 \pm 0.045c$	$23 \pm 0.88b$	$31 \pm 0.48a$
Total Cr	($mg\ kg^{-1}$)	$1.9 \pm 0.18c$	$38 \pm 0.95b$	$83 \pm 3.2a$
Total Cu	($mg\ kg^{-1}$)	$7.2 \pm 0.70c$	$62 \pm 2.6b$	$100 \pm 3.4a$
Total Ni	($mg\ kg^{-1}$)	$1.2 \pm 0.15c$	$64 \pm 2.3b$	$66 \pm 0.58a$
Total Pb	($mg\ kg^{-1}$)	$3.8 \pm 0.054c$	$510 \pm 74b$	$7700 \pm 1200a$
Total Zn	($mg\ kg^{-1}$)	$7.5 \pm 0.25c$	$1100 \pm 20b$	$14000 \pm 150a$

Note: data are present as mean ± standard deviation. DL represents detection limit. Rows with varying letters represent differences at <5% significance levels among the soil, SSM-A, and SSM-B.

~0.02N H_2SO_4 and ~0.002N HNO_3. The ALS was thus prepared by adjusting 10 L of DI water to pH 4.50 (the average pH of acid deposition in the study region, Zhao et al., 1988) using the diluted acid mixture.

One kilogram of the above incubated soil mixture was packed into a Plexiglas column (the design of this column is described in Yang et al., 2008) in triplicate. Prior to the leaching, the packed columns were saturated for 3 days with deionized water to remove air pockets and to maintain an equilibrium of chemical and biological reactions. Five leaching events were conducted at day 1, 3, 7, 14, and 28 with188.4 mL of ALS each supplied with a peristaltic pump at a speed of ~1.57 mL per minute. Therefore, the total amount of ALS applied after the five leaching events was 942 mL, equivalent to the average of one quarter's rainfall in the zinc smelting region (2001–2003). The leachate from each leaching event was then subjected to a series of chemical analyses.

The pH and EC of leachate were determined using a pH/Conductivity Meter (Multi 3420, WTW, Germany) (USEPA method 150.1). After being filtered through a 0.45 μm membrane, one portion of the leachate was acidified with concentrated HNO_3 to pH < 2 and analyzed for PTMs (Pb, Zn, Cd, Co, Cr, Cu, and Ni) and Al, Ca, Fe, K, Mg, Mn, Na, and P using ICP-MS (Platform ICP, GV instruments, UK) (USEPA method 200.8). Another portion of the leachate without acidification was then analyzed for chloride, fluoride, nitrate, phosphate, and sulfate with Ion Chromatography (ICS-90, Dionex, USA) (USEPA method 300.0) and DOC and DON with TOC analyzer (Elementar, High TOC II, Germany) (USEPA method 415.1), respectively.

2.5. Quality assurance and quality control (QA/QC)

QA/QC for instrumental analyses was accomplished by using the standard calibration curve ($R^2 > 0.995$), initial calibration verification (ICV), a QC sample, matrix spike samples, and laboratory blanks. The recoveries of ICV and QC sample were 90–110 wt% and 90–120 wt%, respectively. Matrix spike recoveries were 80–120 wt%, and the laboratory blank (DI H_2O) was less than method detection limits.

2.6. Potentially toxic metal speciation modeling in leachate

Visual MINTEQ software (Version 3.1) was used to model the PTM species in the leachate. The input files included DOC and inorganic compounds with a fixed pH measured from the leachate and ionic strength to be calculated by the software itself. The ICA-Donnan model was used for organic complexation.

2.7. Leaching index

Leaching index (LI, wt%) is calculated using the following equation:

$$LI\ (wt\%) = \frac{\sum \frac{C_i(mg/L)V_i(mL)}{M(kg)}}{C_{m3}(mg/kg)} \times 100$$

where C_i is the concentration of metals Pb, Zn Cd, Co, Cr, Cu, or Ni in leachate at leaching event i (i = 1, …, 5), V_i is the volume of ALS, M is

Table 2
Soil pH, EC, and Mehlich 3 extractable potentially toxic metals ($mg\ kg^{-1}$) after a 120 days' incubation with amendments of varying smelting slag materials.

Treatments	pH	EC	Cd	Co	Cr	Cu	Ni	Pb	Zn
Control	$4.7 \pm 0.01f$	$220 \pm 10e$	$0.035 \pm 0.007\,h$	$0.080 \pm 0.001f$	$0.020 \pm 0.002f$	$4.2 \pm 1.6a$	$0.21 \pm 0.005g$	$1.23 \pm 0.071f$	$1.8 \pm 0.11h$
A 0.5	$5.0 \pm 0.01d$	$410 \pm 16d$	$0.063 \pm 0.006g$	$0.12 \pm 0.002e$	$0.073 \pm 0.023cde$	$6.0 \pm 1.5a$	$0.29 \pm 0.026f$	$1.62 \pm 0.15f$	$4.6 \pm 0.23g$
A l.0	$4.9 \pm 0.12e$	$410 \pm 23d$	$0.093 \pm 0.006g$	$0.13 \pm 0.010e$	$0.060 \pm 0.010de$	$5.8 \pm 4.6a$	$0.32 \pm 0.015f$	$2.2 \pm 0.86f$	$7.0 \pm 0.35f$
A 2.5	$4.8 \pm 0.06f$	$520 \pm 39c$	$0.16 \pm 0.012e$	$0.16 \pm 0.006d$	$0.057 \pm 0.006de$	$4.7 \pm 1.3a$	$0.37 \pm 0.026e$	$2.5 \pm 0.26f$	$14 \pm 0.35e$
A 5.0	$4.4 \pm 0.08g$	$690 \pm 38b$	$0.27 \pm 0.006c$	$0.19 \pm 0.002c$	$0.047 \pm 0.006ef$	$5.0 \pm 2.2a$	$0.43 \pm 0.026d$	$3.3 \pm 0.01e$	$25 \pm 0.49d$
B 0.5	$5.4 \pm 0.08c$	$400 \pm 130d$	$0.13 \pm 0.017f$	$0.16 \pm 0.006d$	$0.080 \pm 0.010cd$	$3.4 \pm 2.1a$	$0.38 \pm 0.012de$	$16 \pm 4.3d$	$28 \pm 0.58d$
B l.0	$5.4 \pm 0.01c$	$390 \pm 38d$	$0.21 \pm 0.020d$	$0.21 \pm 0.021c$	$0.10 \pm 0.026c$	$2.0 \pm 0.16a$	$0.49 \pm 0.006c$	$27 \pm 3.2c$	$64 \pm 13c$
B 2.5	$5.7 \pm 0.06b$	$610 \pm 52bc$	$0.40 \pm 0.010\,b$	$0.32 \pm 0.015b$	$0.16 \pm 0.012b$	$4.8 \pm 0.82a$	$0.63 \pm 0.032b$	$69 \pm 11b$	$120 \pm 6.6\,b$
B 5.0	$6.2 \pm 0.04a$	$910 \pm 55a$	$0.71 \pm 0.044a$	$0.53 \pm 0.026a$	$0.25 \pm 0.020a$	$4.7 \pm 1.1a$	$0.94 \pm 0.062a$	$99 \pm 8.4a$	$300 \pm 36a$

Note: A: SSM-A, B: SSM-B. 0.5, 1.0, 2.5, 5.0 mean the amendment ratios of SSMs in the soil at levels of 0.5, 1.0, 2.5, and 5.0 wt%, respectively. Columns with varying letters represent differences at <5% significance levels among treatments.
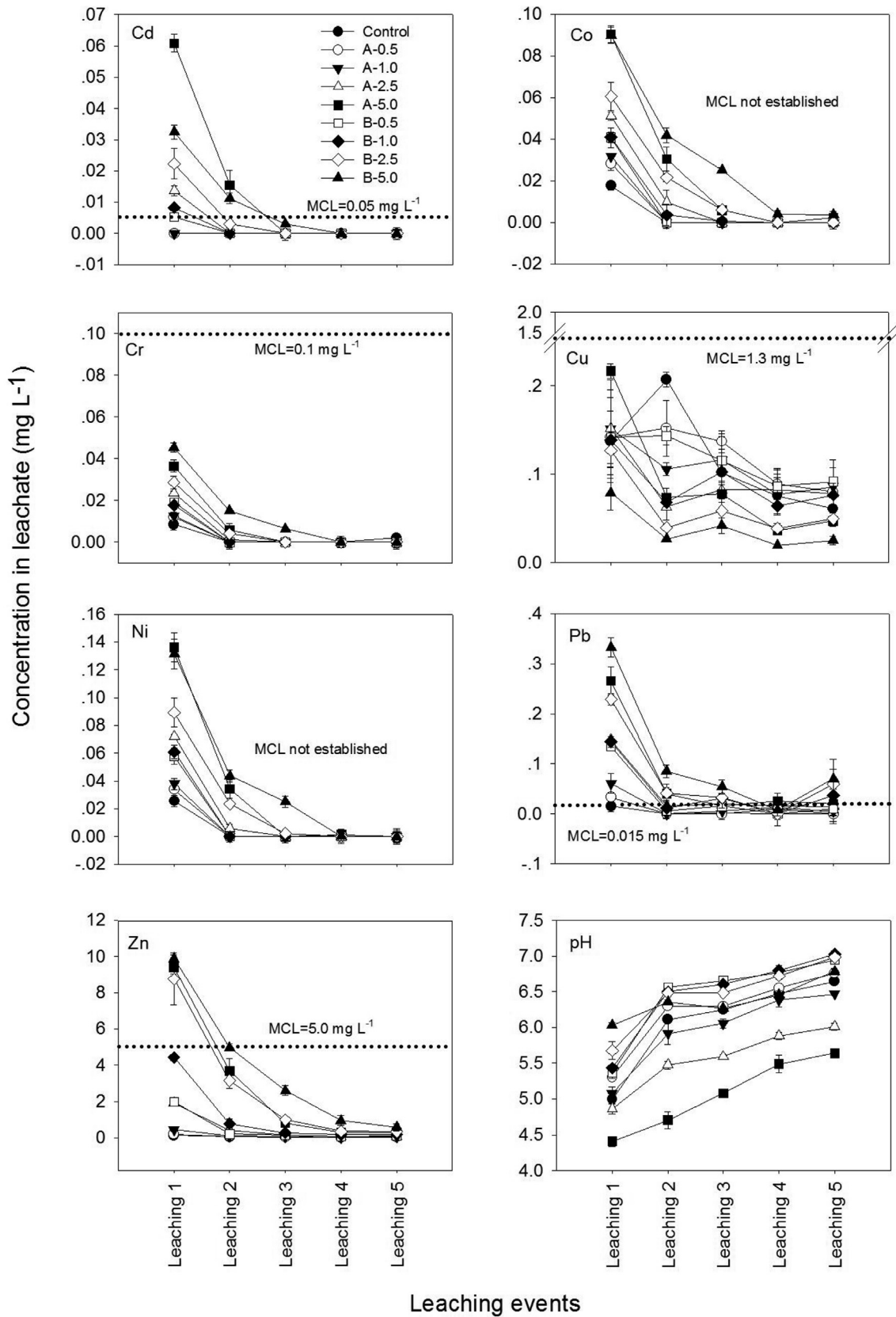
Fig. 1. Behavior of potentially toxic metals and leachate pH during varying leaching events (A and B: zinc smelting slag materials A and B. Numbers after A and B represent amending ratios of zinc smelting slag materials A and B in the soil; MCL = maximum contaminant level by US Environmental Protection Agency).

the quantity of incubated soils used for leaching (1 kg), and $\sum$ means the sum of the five leaching events; whereas, C_{m3} represents the M3 extractable concentrations of Pb, Zn Cd, Co, Cr, Cu, or Ni in the incubated soils.

2.8. Data processing

All the statistic calculations were performed using SPSS 16.0 software (SPSS Inc., Richmond, California) after the datasets were normalized. Analysis of variance (ANOVA) and the post-hoc multiple comparison procedure were used to compare the difference of PTM concentrations in leachate from varying amendment ratios of SSMs at a significance level of $P < 0.05$. A hierarchical cluster

dendrogram was adopted to correlate the cations and PTMs in the leachate; thereafter, graphing was completed using SigmaPlot 10.0 software (SPSS Inc., Richmond, California).

3. Result and discussion

3.1. Potentially toxic metal extractability in soils after smelting slag material amendments

After 120 days' incubation, SSM-B amendments in the soil resulted in twice M3 extractable metals Cd, Co, Cr, Cu, Ni, 10–30 times Pb, and 10 times Zn as much as SSM-A amendments at the same amendment ratios (Table 2). The M3 extractable metals in the
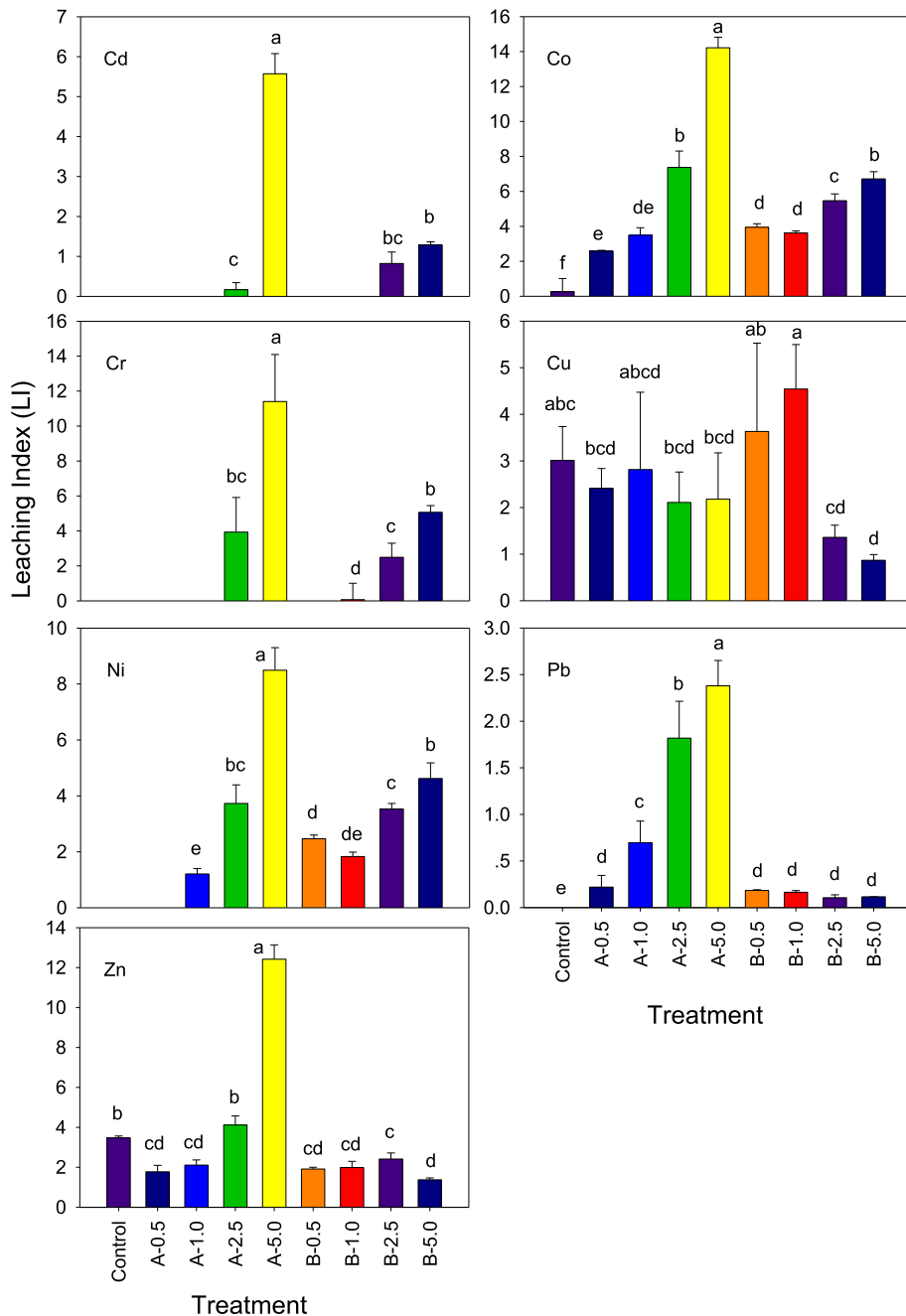
Fig. 2. Leaching index (LI) of different potentially toxic metals in the soils amended with varying ratios of smelting slag materials (A and B: zinc smelting slag materials A and B. Numbers after A and B represent their amending ratios in the soil. Varying letters on the bars represent differences at <5% significance levels among treatments).

soil was positively corresponded with the SSM amendment ratios (Table 2); especially, when the soil was amended at 5 wt% SSM, M3 extractable Pb, Zn, Cd, and Ni approximately accounted for 11, 42, 57, and 9.8 wt% and 25, 43, 60, and 20 wt% of the total metals with amendments of SSM-A and SSM-B, respectively (refer to Supplement 2). Both SSM-A and SSM-B amendments in the soil surged the total metal contents and M3 extractable metals (except for Cu) as compared with the control soil (Table 2 and Supplement 2).

Under the incubation condition in the soil, the extractability of PTMs from the SSMs could be affected by: soil factor (physical, chemical, and biological properties), SSM factor (difference in PTM contents, mineral associations, and amendment ratios), and their interaction (Douay et al., 2009; Lanteigne et al., 2012). Among these, soil pH plays a key role: acidic soil could enhance the mobilization of metals from slag particles incubated in the soils (Birkefeld et al., 2006; Dieckmann et al., 2003). Therefore, the acidic property of the studied soil (pH 4.62) could attribute more profoundly to the extractability of PTMs from the SSM-B amendments (Table 2). There existed remarkable differences in the mineral phases and total PTMs between the two SSMs (Supplement 1, Table 1), which could affect the M3 extractability of PTMs (Ettler, 2016; Kierczak et al., 2013; Sobanska et al., 2016). Carbonate minerals are sensitive to acid attack, their decomposition can result in the release of Ca and Mg, accompanied by the elevation in EC and pH. Fe/Al sesqui-oxides/hydrous oxides are stable at surface environment however, they could become unstable under reduction conditions. Mineralization/assimilation of organic matter in acidic soil or at a saturation condition could promote the production of dissolved organic carbon/nitrogen. The close associations of carbonate minerals, Fe/Al sesqui-oxides/hydrous oxides and organic matters with PTMs would therefore, affect the extractability of the PTMs from the SSM-amended soils (Table 2). The increase in pH of the SSM-B amended soils versus that of SSM-A amendments (Table 2) corresponded with the interaction of soil components and SSM mineral assemblages (Chrastny et al., 2014). The substantially extractable PTMs in 5 wt% SSM-B amended soils responded with the abundant PTM contents in the SSM-B (Table 2, with Cu the exception), agreeing with the previous reports (Dieckmann et al., 2003; Ettler et al., 2012; Negim et al., 2010). This suggested that PTMs from the SSMs amendment in the acidic soil could be largely mobilized during 120 days' incubation.

3.2. Leaching behaviors of potentially toxic metals

Under the simulated acid leaching condition, PTMs Pb, Zn, Cd, Co, Cr, and Ni showed a much similar tendency: large leaching of these metals mainly occurred in the first three leaching events, after which the leaching became stable (Fig. 1). However, leaching

of Cu was different, its concentration in leachate fluctuated during the five leaching events (Fig. 1). Concentrations of Cd, Co, Cr, and Ni in leachate were in the same magnitude, which were 10 times lower than Cu and Pb, and 100 times lower than Zn. The highest concentrations of Cd, Pb, and Zn in leachate were 10, 20, and 2 times higher than USEPA primary (0.005 mg/L for Cd and 0.015 mg/L for Pb) and secondary (5 mg/L for Zn) maximum contaminant levels (MCLs) for drinking water/groundwater. This phenomenon was more evident for soils with 5 wt% SSMs amendments. The Cr and Cu in leachate were below their primary USEPA MCLs (0.1 and 1.3 mg/L) for drinking water/ground water. Massive quantities of DOC, DON, Ca and Mg in leachates from SSM amended soils were also observed in the initial leaching events while reverse trends were true for Al and Fe in leaching (Supplement 3). In contrast, leachate pH increased along with leaching events (Fig. 1).

After the five leaching events, greater leaching indexes (LI) of PTMs were observed in soils amended with SSM-A than with SSM-B, with the greatest LI in 5 wt% SSM-A amended soils (Fig. 2). Approximately, 2.5, 12, 5.5, 14, 11, and 9 wt% of M3 extractable Pb, Zn, Cd, Co, Cr, and Ni were leached from the soils amended with 5 wt% SSM-A, which is about 25,12, 4, 2, 2, and 2 times higher than
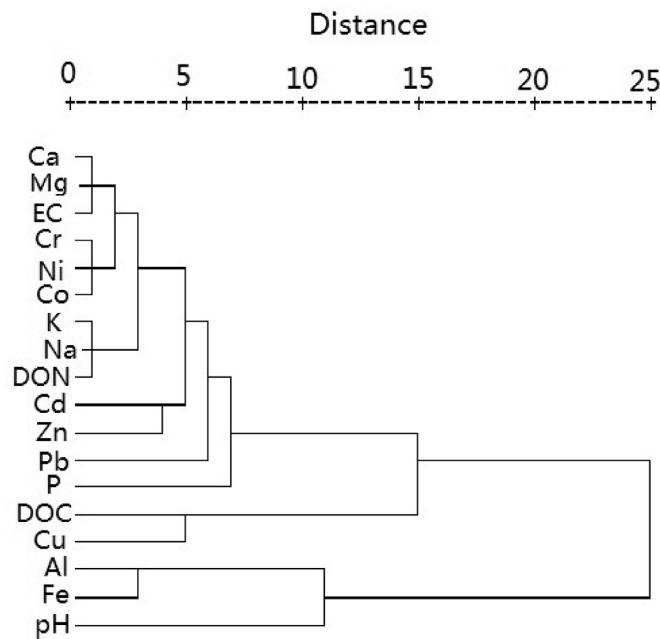

Fig. 3. A hierarchical cluster dendrogram showing the relationship of varying parameters in the leachate.

Table 3

Correlations among Al, Fe, Ca, Mg, Mn, P, pH, EC, DOC, or DON and potentially toxic metals Cd, Co, Cr, Cu, Ni, Pb, and Zn in the leachate from the five leaching events.

	Cd	Co	Cr	Cu	Ni	Pb	Zn	Cd	Co	Cr	Cu	Ni	Pb	Zn
	Leachate from the soils amended with smelting slag material A							Leachate from the soils amended with smelting slag material B						
Al	0.046	−0.142	−0.104	0.059	−0.087	−0.034	−0.015	−0.348**	−0.463**	−0.378**	0.130	−0.406**	−0.280*	−0.460**
Fe	−0.381**	−0.557**	−0.498**	−0.162	−0.503**	−0.444**	−0.444**	−0.478**	−0.597**	−0.509**	0.097	−0.537**	−0.389**	−0.592**
Ca	0.577**	0.859**	0.813**	0.516**	0.800**	0.690**	0.618**	0.695**	0.856**	0.763**	0.088	0.801**	0.692**	0.813**
Mg	0.716**	0.948**	0.950**	0.663**	0.924**	0.854**	0.712**	0.889**	0.971**	0.943**	0.276*	0.956**	0.880**	0.914**
Mn	0.986**	0.891**	0.835**	0.513**	0.900**	0.878**	0.994**	0.952**	0.931**	0.953**	0.302*	0.951**	0.948**	0.950**
P	0.677**	0.821**	0.850**	0.755**	0.828**	0.756**	0.637**	0.856**	0.916**	0.903**	0.278*	0.909**	0.882**	0.857**
pH	−0.619**	−0.776**	−0.705**	−0.317*	−0.724**	−0.682**	−0.683**	−0.593**	−0.744**	−0.711**	−0.479**	−0.743**	−0.656**	−0.681**
EC	0.611**	0.878**	0.872**	0.665**	0.843**	0.758**	0.620**	0.815**	0.932**	0.899**	0.329*	0.920**	0.839**	0.861**
DOC	−0.133	0.113	0.183	0.527**	0.104	−0.011	−0.183	−0.093	−0.015	0.035	0.762**	0.035	−0.004	−0.147
DON	0.312*	0.676**	0.715**	0.565**	0.637**	0.543**	0.297*	0.725**	0.822**	0.840**	0.543**	0.855**	0.811**	0.732**

N = 60; * and ** represent significance levels of $P < 0.05$ and < 0.01, respectively.

the percentages from soils with 5 wt% SSM-B amendments (Fig. 2). This shows that when amended in an acidic soil, PTMs from the acidic SSM were more vulnerable to acidic leaching than those from the alkaline SSM. However, Cu demonstrated a different LI pattern from other PTMs during leaching, showing a less dependence on SSM amendment ratios (Fig. 2).

In the leachates, varying correlations among PTMs (Cd, Co, Cr, Cu, Ni, Pb, and Zn) and Al, Fe, Ca, Mg, Mn, P, pH, EC, DOC, and DON can be observed from both SSM amendments (Table 3). It is interesting to notice that DOC merely demonstrated a positive relationship with Cu whereas, DON positively correlated with all the PTMs (Table 3). Al had negative correlations with Cd, Co, Cr, Ni, Pb, and Zn only within the leachates from SSM-B amended soils (Table 3). A hierarchical cluster dendrogram more clearly suggested pH governing the entire leaching process whereas, pH variation could be regulated by the concentrations of Fe and Al in leachate (Fig. 3). Furthermore, EC corresponded with Ca and Mg, DOC bound with Cu whereas, DON was associated with K and Na, and P grouped with Cd, Pb, and Zn. Metals Cr, Ni, and Co were associated together (Fig. 3).

Many factors could affect the leaching potential of PTMs from the SSM amended soils. The significantly negative correlations among pH and PTMs in leachate (Table 3, Fig. 3) supported the leachate pH as an influential factor contributing PTMs release in leaching (Piatak et al., 2015; Yilmaz et al., 2003). The fact that the highest Pb, Zn, and Cd in the leachates from the 5% SSM-amended soils were 4–8, 10–20, 1–2 times more than their respective maximum amounts leached from bulk SSMs (Supplement 4), favored the pre-mobilization of PTMs from the SSMs being incubated in the acidic soil for 120 days. Under the same leaching condition, significant differences of PTMs in the leachates from the soils with the two SSMs amendments (Figs. 1 and 2) are indicative of the impact of SSM mineralogical phases (Ettler et al., 2009; Piatak and Seal, 2010; Birkefeld et al., 2006). The occurrence of carbonate minerals in the SSMs (Supplement 1) could be supportive of carbonate bound PTMs (Verner et al., 1996; Yang et al., 2010; Ash et al., 2015) and the possible decomposition during acidic leaching (Lee et al., 2012). This might be responsible for the significantly positive correlations among Ca, Mg, EC and the PTMs in the leachates (Table 3, Fig. 3). The strong adsorption capacity of clay materials for the PTMs (Maskall et al., 1996; Uddin, 2017) could be resistant to acid leaching from the soils amended with SSM-B
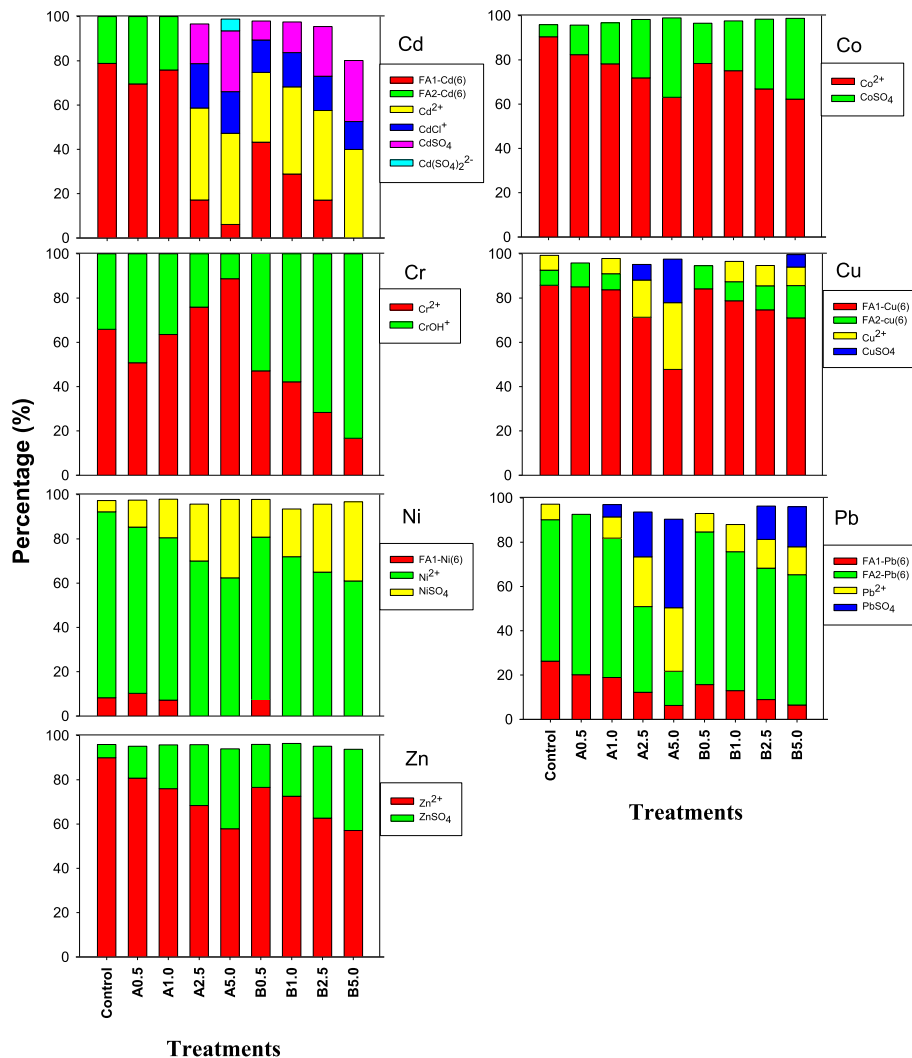

Fig. 4. Species of potentially toxic metals in the leachate from the soils amended with varying ratios of smelting slag materials (A and B represent zinc smelting slag materials A and B. Numbers after A and B represent amending ratios of zinc smelting slag materials A and B in the soil. All the chemical species modeling was obtained from the Visual MINTEQ software; only the species with percentages larger than 5 wt% are plotted, and all the species are in the aqueous phase. FA1 and FA2 represent weak and strong fulvic acid affinity, respectively).

(rich in clay materials, Supplement 1). This might explain the much lower LIs of PTMs from the soils amended with SSM-B other than SSM-A (Fig. 2), and the negative correlations of Al with PTMs in the leachate from the soils with SSM-B amendments (Table 3). Iron oxides/hydroxides are supposed to retain PTMs in soils with several mechanisms (Bradl, 2004) however, this function can be altered under the transformation of reduction/oxidation conditions. This might explain the negative correlations among Fe and PTMs in the leachate (Table 3, with Cu the exception) and their different behaviors during the leaching events (Supplement 3). The fluctuation of Cu in the leachate might be jointly controlled by source, chemical fractions of Cu and the pH of ALS. Highest amendment ratio of 5% SSM-B merely contributed 42% of the Cu into the soil-SSM mixture (Table 1), due to the higher Cu in the soil. Initial acidic leaching of Cu might be from the soil in a large portion, then Fe/Al sesqui-oxide/hydrous oxide bound, and organic bound Cu could be released at late leaching events. Increase in the pH, Al and Fe in the leachates at late leaching events (Fig. 1, Supplement 3) might suggest a reductive environment occurring at the saturated bottom of the SSM-amended soil columns, which could result in more labile metals (especially Cu) subjected to leaching, associated with the reduction of iron sesqui-oxides/hydrous oxides and dissolved organic matter (Balint et al., 2015).

Organic matter plays a key role as well in controlling the metal availability in soils via adsorption or complexation (Rieuwerts et al., 1998; Pareuil et al., 2010). The close correlation between DOC and Cu in the leachate suggested the formation of Cu complexes with fulvic/humic acids in the SSM amended soils (Table 3). Previous studies implied that metal salts of fulvic acid are readily soluble in soils (Bloomfield, 1981), and the stability constant of Pb(II)-soil fulvic acid complexes could decrease from 6.3 at pH 6 to 4 at pH 4 (Saar and Weber (1980), therefore, under acidic leaching conditions, the solubilization of Cd, Cu, Pb, and Zn could be enhanced by organic matter (Temminghoff et al., 1997; Birkefeld et al., 2006). The positive correlations of DON with the PTMs in leachate (Table 3) might suggest the binding of the metals with organic nitrogen compounds, such as amino acids (Callahan et al., 2006), which free and combined amino acids comprised of 59–78 wt% of the DON in forest soils (Yu et al., 2002). Moreover, at reducing condition, decomposition of organo-metallic complexes (especially Cu) could be enhanced (Balint et al., 2015), which could be linked to the fluctuation of Cu in leachate (Figs. 1 and 2), highlighting the difference from other metals (Fig. 1).

3.3. Species of potentially toxic metals in leachate

All the chemical species modeling was obtained from the Visual MINTEQ software. As simulated, dominant species of Cr in leachate were Cr^{2+} and $CrOH^+$; the percentage of Cr^{2+} increased and $CrOH^+$ decreased in the soils with the elevation of SSM-A amendments; however, the reverse situation was the case in SSM-B amended soils (Fig. 4). Zn and Co were dominated by species Me^{2+} and $MeSO_4$ (Me stands for any of the seven metals), and $MeSO_4$ was proportional with SSM amendment ratios (Fig. 4). Pb and Cu showed the dominance of three species: Me^{2+}, FA1-Me (FA1 represents weak fulvic acid affinity), and FA2-Me (FA2 stands for strong fulvic acid affinity) however, species Me^{2+} and $MeSO_4$ were also proportional with the SSM amendment ratios (Fig. 4). Except for Cd^{2+}, $CdSO_4$, FA1-Cd, and FA2-Cd, species of $CdCl^+$ were also observed for Cd, especially when SSM-B was amended (Fig. 4).

Saturated mineral phases in leachate were dominated by aluminum hydroxy, phosphate, and sulfate minerals, such as alunite $(KAl_3(SO_4)_2(OH)_6)$, diaspore $(AlO(OH))$, gibbsite $(Al(OH)_3)$, plumbogummite $(PbAl_3(PO_4)_2(OH)_5 \cdot H_2O)$, and variscite $(AlPO_4 \cdot 2H_2O)$. Lead minerals chloropyromorphite $(Pb_5(PO_4)_3Cl)$
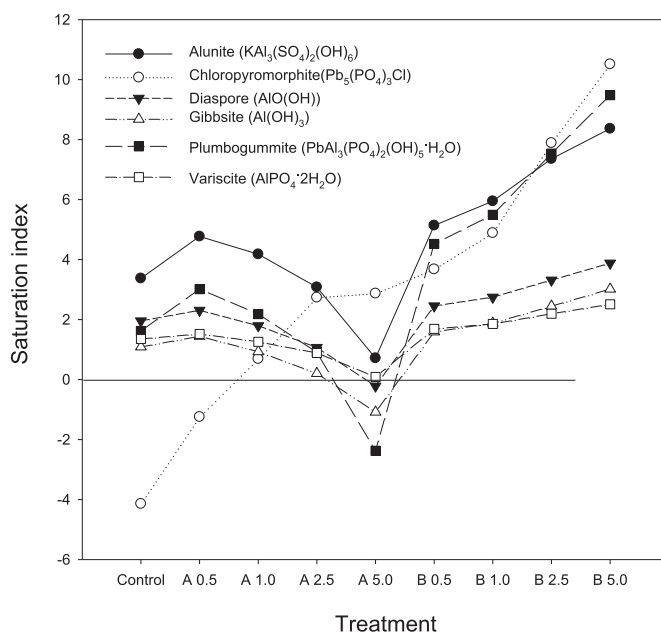

Fig. 5. Saturation index of minerals in leachate as simulated with Visual MINTEQ (A and B represent zinc smelting slag materials A and B. Numbers after A and B represent amending ratios of zinc smelting slag materials A and B in the soil).

and plumbogummite $(PbAl_3(PO_4)_2(OH)_5 \cdot H_2O)$ were also observed (Fig. 5). Except for chloropyromorphite $(Pb_5(PO_4)_3Cl)$, the saturation index (SI) of these minerals showed identical variations: a decrease with SSM-A amendment ratios but an increase with SSM-B amendment ratios (Fig. 5). For chloropyromorphite $(Pb_5(PO_4)_3Cl)$, it had a rising tendency with elevated amendments of SSM-A and SSM-B (Fig. 5).

Speciation of PTMs in leachate could be greatly affected by the composition of leachant. The extensive sulfate species from this study (in Fig. 4) can be a good indication of leachant composition influence. This can also be supported by the study of Sobanska et al. (2016) who observed the formation of Pb sulfate species affected by the sulfate-containing fluid under natural weathering. A large portion of PTM in the leachates from the SSM-amended soils was observed as the specie of metallic ions as well (Fig. 4), similar to previous studies (Islam et al., 2016; Navarro et al., 2008), suggesting a cation exchange mechanism in the acid leaching (Butler, 2009). However, the high affinity of PTMs to Fe/Al sesqui-oxide/hydrous oxide minerals and dissolved organic matter could favor the surface adsorption or complexion in leachate (Fisher-Power et al., 2016; Sobanska et al., 2000). These phenomena could be supported by the rising saturation index (SI) of Al minerals with increasing SSM-B amendment ratios (Fig. 5), the close correlations of cations and DOC/DON with PTMs (Table 3, Fig. 3), and the organic complexed species (especially for Cu, Cd, Pb, and Ni, Fig. 4). The existence of chloropyromorphite $(Pb_5(PO_4)_3Cl)$ and plumbogummite $(PbAl_3(PO_4)_2(OH)_5 \cdot H_2O)$ in leachate suggests excess Pb might tend to form further Al and PO_4 complexes. The declining SI index with increasing SSM-A amendments might be explained by the acidic feature of the soils with SSM-A amendments (Table 2) that could prohibit the formation of secondary minerals in the leachates.

4. Conclusion

Availability of PTMs in the two SSMs was enhanced by being amended and incubated in the acidic soil for 120 days. When

subjected to acid deposition simulation leaching, soils with amendments of the acidic SSM demonstrated higher leaching indexes but lower concentrations of PTMs in the leachates than the soils amended with the alkaline SSM. The leaching process was affected by the leachant composition and the geochemical properties of PTM-associated minerals as well. Free metallic ions contributed as the main PTM speciation in leachate, but metallic sulfate complex weighed in when the amendment ratios of SSMs increased in soils. For Cu, Cd and Pb, organic bound speciation showed importance. In the leachates, aluminum hydroxy, phosphate and sulfate minerals were supposed to be the important saturated mineral phases.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.envpol.2018.03.022.

References

Ash, C., Tejnecky, V., Sebek, O., Houska, J., Chala, A.T., Drahota, P., Drabek, O., 2015. Redistribution of cadmium and lead fractions in contaminated soil samples due to experimental leaching. Geoderma 241–242, 126–135.

Ash, C., Tejnecky, V., Boruvka, L., Drabek, O., 2016. Different low-molecular-mass organic acids specifically control leaching of arsenic and lead from contaminated soil. J. Contam. Hydrol 187, 18–30.

Bade, R., Oh, S., Shin, W.S., 2010. Assessment of metal bioavailability in smelter-contaminated soil before and after lime amendment. Ecotoxi. Environ. Safe 80, 299–307.

Balint Nimirciag, R., Buratto, E., Ajmone-Marsan, F., 2013. Leaching of trace metals from soil under alternating oxic-anoxic conditions: a column study. https://doi.org/10.1051/e3sconf/20130119005. (Accessed 8 December 2016).

Balint, R., Said-Pullicino, D., Ajmone-Marsan, F., 2015. Copper dynamics under alternating redox conditions is influenced by soil properties and contamination source. J. Contam. Hydrol. 173, 83–91.

Basta, N.T., Gradwohl, R., 2000. Estimation of Cd, Pb, and Zn bioavailability in smelting-contaminated soils by a sequential extraction procedure. J. Soil Contam. 9, 149–164.

Bi, X.Y., Feng, X.B., Yang, Y.G., Li, X.D., Shin, G.P.Y., Li, F.L., Qiu, G.L., Li, G.H., Liu, T.Z., Fu, Z.Y., 2009. Allocation and source attribution of lead and cadmium in maize (Zea mays L.) impacted by smelting emissions. Environ. Pollut. 157, 834–839.

Birkefeld, A., Schulin, R., Nowack, B., 2006. In situ investigation of dissolution of heavy metal containing mineral particles in an acidic forest soil. Geochim. Cosmochim. Acta 70, 2726–2736.

Bloomfield, C., 1981. The translocation of metals in soils. In: Greenland, D.J., Hayes, M.H.B. (Eds.), The Chemistry of Soil Processes. John Wiley & Sons Ltd, Chichester, p. 470.

Bradl, H.B., 2004. Adsorption of heavy metal ions on soils and soils constituents. J. Coll. Inter. Sci. 277, 1–18.

Butler, B.A., 2009. Effect of pH, ionic strength, dissolved organic carbon, time, and particle size on metals release from mine drainage impacted streamed sediments. Water Res. 43, 1392–1402.

Callahan, D.L., Baker, A.J.M., Kolev, S.D., Wedd, A.G., 2006. Metal ion ligands in hyperaccumulating plants. J. Biol. Inorg. Chem. 11, 2–12.

Cappuyns, V., Alian, V., Vassilieva, E., Swennen, R., 2014. pH dependent leaching behavior of Zn, Cd, Pb, Cu, and As from mining wastes and slags: kinetics and mineralogical control. Waste Biomass Valori 5 (3), 355–368.

Chrastny, V., Vanek, A., Cadkova, E., Ruzickova, A., Galuskova, I., Faturikova, D., Komarek, M., 2014. Lead migration in smelter-impacted deciduous and coniferous organic soil horizons based on a long-term in-situ implantation and laboratory column experiments. Appl. Geochem 48, 168–175.

Dahmani-Muller, H., van Oort, F., Balabane, M., 2001. Metal extraction by Arabidopsis halleri grown on an unpolluted soil amended with various metal-bearing solids: a pot experiment. Environ. Pollut. 114, 77–84.

De Andrade Lima, L.R.P., Bernardez, L.A., 2011. Characterization of the lead smelter slag in Santo Amaro, Bahia, Brazil. J. Hazard. Mater 189, 692–699.

Dieckmann, S., Melzer, O., Bender, L., 2003. Availability of Heavy Metals in Soils and Their Uptake by Vegetable Species. University of Applied Sciences Department of Agricultural Sciences, Osnabrueck, Germany. http://geb.uni-giessen.de/geb/volltexte/2003/1236/.

Douay, F., Pruvot, C., Waterlot, C., Fritsch, C., Fourrier, H., Loriette, A., Bidar, G., Grand, C., de Vaufleury, A., Scheifler, R., 2009. Contamination of woody habitat soils around a former lead smelter in the North of France. Sci. Total Environ. 407, 5564–5577.

Ettler, V., Johan, Z., Kribek, B., Sebek, O., Mihaljevic, M., 2009. Mineralogy and environmental stability of slags from the Tsumeb smelter, Namibia. Appl. Geochem 24 (1), 1–15.

Ettler, V., Kribek, B., Majer, V., Knesl, I., Mihaljevic, M., 2012. Differences in the bioaccessibility of metals/metalloids in soils from mining and smelting areas (Copperbelt, Zambia). J. Geochem. Explor 113, 68–75.

Ettler, V., 2016. Soil contamination near non-ferrous metal smelters: a review. Appl. Geochem 64, 56–74.

Ettler, V., Kvapil, J., Sebek, O., Johan, Z., Mihaljevic, M., Ratie, G., Garnier, J., Quantin, C., 2016. Leaching behavior of slag and fly ash from laterite nickel ore smelting (Niquelandia, Brazil). Appl. Geochem 64, 118–127.

Farago, M.E., O'Connell, J.T., 1983. Soil and plant concentrations of cadmium and zinc in the vicinity of a smelter. Min. Environ. 5, 71–78.

Fisher-Power, L.M., Cheng, T., Rastghalam, Z.S., 2016. Cu and Zn adsorption to a heterogeneous natural sediment: influence of leached cations and natural organic matter. Chemosphere 144, 1973–1979.

Gzyl, J., 1995. Ecological impact and remediation of contaminated sites around lead smelters in Poland. J. Geochem. Explor 53, 251–258.

Hu, P., Yang, B., Dong, C., Chen, L., Cao, X., Zhao, J., Wu, L., Luo, Y., Christie, P., 2014. Assessment of EDTA heap leaching of an agricultural soil highly contaminated with heavy metals. Chemosphere 117, 532–537.

Islam, M.N., Jo, Y.T., Park, J.H., 2016. Leaching and redistribution of Cu and Pb due to simulated road runoff assessed by column leaching test, chemical analysis, and PHREEQC modeling. Environ. Earth Sci. 75, 1041.

Ivask, A., Francois, M., Kahru, A., Dubourguier, H.C., Virta, M., Douay, F., 2004. Recombinant luminescent bacterial sensors for the measurements of bioavailability of cadmium and lead in soils polluted by metal smelters. Chemosphere 55 (2), 147–156.

Kierczak, J., Potysz, A., Pietranik, A., Tyszka, R., Modelska, M., Neel, C., Ettler, V., Mihaljevic, M., 2013. Environmental impact of the historical Cu smelting in the Rudawy Janowickie Mountains (south-western Poland). J. Geochem. Explor 124, 183–194.

Khorasanipour, M., Esmaeilzadeh, E., 2016. Environmental characterization of Sarcheshmeh Cu-smelting slag, Kerman, Iran: Application of geochemistry, mineralogy and single extraction methods. J. Geochem. Explor 166, 1–17.

Lanteigne, S., Schindler, M., McDonald, A.M., Skeries, K., Abdu, Y., Mantha, N.M., Murayama, M., Hawthorne, F.C., Hochella Jr., M.F., 2012. Mineralogy and weathering of smelter-derived spherical particles in soils: implications for the mobility of Ni and Cu in the surficial environment. Water Air Soil Pollut. 223, 3619–3641.

Lee, P., Kang, M., Jo, H.Y., Choi, S., 2012. Sequential extraction and leaching characteristics of heavy metals in abandoned tungsten mine tailings sediments. Environ. Earth Sci. 66, 1909–1923.

Liang, S., Li, X., Xu, H., Wang, X., Gao, N., 2013. Spatial-based assessment of heavy metal contamination in agricultural soils surrounding a non-ferrous metal smelting zone. Bull. Environ. Contam. Toxicol. 91, 526–532.

Little, P., Martin, M.H., 1972. A survey of zinc, lead and cadmium in soil and natural vegetation around a smelting complex. Environ. Pollut. 3, 241–254.

Maskall, J., Whitehead, K., Gee, C., Thornton, I., 1996. Long-term migration of metals at historical smelting sites. Appl. Geochem 11, 43–51.

Mehlich, A., 1984. Mehlich-3 soil test extractant: a modification of Mehlich-2 extractant. Commun. Soil Sci. Plant Anal. 15, 1409–1416.

Mouni, L., Belkhiri, L., Bouzaza, A., Bollinger, J.L., 2016. Chemical associations and sorption capacity of Pb and Zn: column experiments on a polluted soil from the Amizour mining district (Algeria). Environ. Earth Sci. 75, 96. https://doi.org/10.1007/s12665-015-4854-0.

Morrison, A.L., Gulson, B.L., 2007. Preliminary findings of chemistry and bioaccessibility in base metal smelter slags. Sci. Total Environ. 382 (1), 30–42.

Navarro, A., Cardellach, E., Mendoza, J.L., Corbella, M., Domenech, L.M., 2008. Metal mobilization form base-metal smelting slag dumps in Sierra Almagrera (Almeria, Spain). Appl. Geochem 23, 895–913.

Negim, O., Eloi, B., Bes, C., Gaste, H., Motelica-Heino, M., 2010. Effect of basic slag addition on soil properties, growth and leaf mineral composition of beans in a Cu-contaminated soil. J. Soil Sediment. Contam. 19 (2), 174–187.

Parra, S., Bravo, M.A., Quiroz, W., Moreno, T., Karanasiou, A., Font, O., Vidal, V., Cereceda, F., 2014. Distribution of trace elements in particle size fractions for contaminated soils by a copper smelting from different zones of the Puchuncavi Valley (Chile). Chemosphere 111, 513–521.

Pareuil, P., Bordas, F., Joussein, E., Bollinger, J.C., 2010. Alteration of a Mn-rich slag in contact with soil: in-situ experiment during one year. Environ. Pollut. 158, 1311–1318.

Piatak, N.M., Seal II, R.R., 2010. Mineralogy and the release of trace elements from slag from the Hegeler Zinc smelter, Illinois (USA). Appl. Geochem 25, 302–320.

Piatak, N.M., Parsons, M.B., Seal II, R.R., 2015. Characteristics and environmental aspects of slag: a review. Appl. Geochem 57, 236–266.

Potysz, A., Kierczak, J., Fuchs, Y., Grybos, M., Guibaud, G., Lens, P.N.L., van Hullebusch, E.D., 2016. Charaterization and pH-dependent leaching behavior of historical and modern copper slags. J. Geochem. Explor 160, 1–15.

Rieuwerts, J.S., Thornton, I., Farago, M.E., Ashmore, M.R., 1998. Factors influencing metal bioavailability in soils: preliminary investigations for the development of

a critical loads approach for metals. Chem. Spec. Bioavailab. 10 (2), 61—75.

Saar, R.A., Weber, J.H., 1980. Lead (II)-fulvic acid complexes. Conditional stability constants, solubility and implications for lead (II) mobility. Environ. Sci. Tech. 14, 877—880.

Seignez, N., Gauthier, A., Bulteel, D., Damidot, D., Potdevin, J.L., 2008. Leaching of lead metallurgical slags and pollutant mobility far from equilibrium conditions. Appl. Geochem 23, 3699—3711.

Sobanska, S., Ledesert, B., Deneele, D., Laboudigue, A., 2000. Alteration in soils of slag particles resulting from lead smelting. Earth Planet. Sci. 331, 271—278.

Sobanska, S., Deneele, D., Barbillat, J., Ledesert, B., 2016. Natural weathering of slags from primary Pb-Zn smelting as evidenced by Raman microspectroscopy. Appl. Geochem 64, 107—117.

Sueoka, Y., Skakibara, M., 2013. Primary phases and natural weathering of smelting slag at an abandoned mine site in Southwest Japan. Minerals 3, 412—426.

Tanner, P.A., Lei, H., Huang, M., Shen, Z., 1997. Acid rain and below-cloud scavenging in south-western China. J. Atmos. Chem. 27, 71—78.

Temminghoff, E.J.M., Van der Zee, S.E.A.T.M., deHaan, F.A.M., 1997. Copper mobility in a copper-contaminated sandy soil as affected by pH and solid and dissolved organic matter. Environ. Sci.Tech 31, 1109—1115.

Tessier, A., Campbell, P.G.C., Bisson, M., 1979. Sequential extraction procedure for the speciation of particulate trace metals. Anal. Chem. 51 (7), 844—851.

Tiwari, M.K., Bajpai, S., Dewangan, U.K., Tamrakar, R.K., 2015. Suitability of leaching test methods for fly ash and slag: a review. J. Radiat. Res. Appl. Sci. 8, 523—537.

Uddin, M.K., 2017. A review on the adsorption of heavy metals by clay minerals, with special focus on the past decade. Chem. Eng. J. 308, 438—462.

van der Sloot, H., van Zomeren, A., Comans, R., Hjelmar, O., 2011. Harmonization of leaching test methods in support of EU regulations controlling the beneficial use of industrial slag in construction. In: 2nd International Slag Valorization Symposium. Leuven. 18—20/04/2011.

Verner, J.F., Ramsey, M.H., Helios-Rybicka, E., Jedrzejczyk, B., 1996. Heavy metal contamination of soils around a Pb-Zn smelter in Bukowno. Pol. Appl. Geochem 11 (1—2), 11—16.

Yang, Y., He, Z., Stoffella, P.J., Yang, X., Graetz, D.A., Morris, D., 2008. Leaching behavior of phosphorus in sandy soils amended with organic material. Soil Sci. 173, 257—266.

Yang, Y., Sun, L., Bi, X., Wu, P., Liu, T., Li, F., Liu, C., 2010. Lead, Zn, and Cd in slags, stream sediments, and soils in an abandoned Zn smelting region, southwest of China, and Pb and S isotopes as source tracers. J. Soils Sediments 10, 1527—1539.

Yilmaz, O., Cokca, O.E., Unlu, K., 2003. Comparison of two leaching tests to assess the effectiveness of cement-based hazardous waste solidification/stabilization. Turk. J. Eng. Environ. Sci. 27 (3), 201—212.

Yu, Z., Zhang, Q., Kraus, T.E.C., Dahlgren, R.A., Anastasio, C., Zasoski, R.J., 2002. Contribution of amino compounds to dissolved organic nitrogen in forest soils. Biogeochem 61, 173—198.

Zhou, X.P., Jiang, J.R., Liang, W., Qin, W.J., 1988. Simulated acid rain affecting physico-chemical properties of five soils from south China (In Chinese). Environ. Sci. 3, 6—12.

Zhao, D., Xiong, J., Xu, Y., Chan, W.H., 1988. Acid rain in southwest China. Atmos. Environ. 22, 349—358.