

Original Research

Pb, Zn, and Cd Distribution and Migration at a Historical Zinc Smelting Site

Wenjie Lin^{1*}, Tangfu Xiao^{2**}, Wanchun Zhou¹, Zengping Ning²

¹Chemistry College, Hanshan Normal University, Chaozhou 521041, China

²State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China

Received: 25 March 2014

Accepted: 8 July 2014

Abstract

This study targeted a historical zinc smelting site from southwestern China and investigated the distribution, mobility, and dispersion patterns of trace metals in the surrounding environment. A series of soil, smelting slag, stream sediment, stream water, and groundwater samples were collected from the smelting site and analyzed for Pb, Zn, and Cd. The results showed that the smelting site was seriously polluted with Pb, Zn, and Cd from past smelting fume deposition and smelting slags. Metal fractions and ratios were applied to identify metal dispersion and mobility. During smelting, Cd was preferably volatilized and transported into the surrounding environment, Zn was predominantly recuperated, and Pb was predominantly retained in smelting slags. Metals in contaminated soils were more mobile than those in slags, but slags still posed long-term risk to the surrounding environment with elevated metals. The relative amounts of vertical transport of metals appeared to follow the order of Cd > Zn > Pb, similar to the mobility order by BCR sequential extractions. Sediments and suspended particulate matter (SPM) in the local stream were derived from the contaminated soils and slags. Compared to the local groundwater with little metal pollution, the stream water at the smelting site was heavily polluted with Pb, Zn, and Cd. Elevated metals in the stream water occurred predominantly in SPM due to soil and slag erosion.

Keywords: historical zinc smelting, metal pollution, mobility, soils, aqueous environment

Introduction

Metal mining and smelting activities are major sources of introduction of metals into the environment to cause considerable soil and water pollution [1-3]. Since metals are non-biodegradable, their pollution usually poses a long-term risk to the environment and human health. The environmental impacts of metals depend strongly on metal toxicity, mobility, and bioavailability in substrates, which are also of importance for risk assessment and pollution remediation [4-6]. For evaluation of environmental impact at mining and smelting sites, identification of metal properties

and dispersion patterns in the surrounding environment is fundamental.

The total concentration of soil metals is a useful indicator of contamination assessment. However, the mobility of metals, as well as their bioavailability and toxicity, greatly depends on their existing forms, the metal properties, environmental factors, and soil properties [7-9]. Metals exist in various fractions, such as water-soluble, exchangeable, carbonate-associated, Fe-Mn oxide-associated, organic-associated, and residual fractions. Water-soluble and exchangeable fractions are considered to be bioavailable; carbonate-associated, Fe-Mn oxides-associated and organic associated fractions may be potentially bioavailable; while the residual fraction is mainly not bioavailable [7, 9, 10]. Sequential extraction procedures are widely applied for

*e-mail: lwjzwc@hstc.edu.cn

**e-mail: xiaotangfu@vip.gyig.ac.cn

assessing metal speciation in soils [11-13]. In the current study, a modified version of BCR extraction procedure was proposed by Rauret et al. [14]. This method was selected because of good reproducibility and recoveries [15-17].

Historical zinc smelting in southwest China goes back to the 17th century. Local indigenous zinc smelting had low recovery for zinc and no recovery for other metals. In addition, fumes were emitted without any purification during smelting processes, which contained elevated concentrations of Pb, Zn, and Cd [18, 19]. Although indigenous zinc smelting was halted in southwest China in 2004, there remain large quantities of waste slag heaps piled up around the abandoned smelting furnaces, and huge tracts of formerly cultivated land remain barren. Slag heaps and polluted soils, as a reservoir of metals, pose a potential risk to the surrounding environment. Previous studies have shown that the local surface water, air, soil, and crops are contaminated with metals, especially Pb, Zn, and Cd [18, 20-22]. However, source identification of such metals and pathways to the surrounding environment has not been fully discussed.

Metals in mine areas can migrate to the surrounding environment through both horizontal and vertical directions and eventually reach to the local aquatic environment. The dispersion of metals is usually influenced by physicochemical factors of soil [23, 24]. Metals could exhibit various behaviors during migration and leaching, which is closely related to fraction transfer [25]. Elemental ratio is an effective index applied to distinguish metal origin and migration [26, 27]. Therefore, elemental ratio combined with metal fraction is useful for revealing migration of metals.

In this study, the concentrations of Pb, Zn, and Cd and their geochemical fraction compositions were measured in various substrates of smelting slag, soil, water, and sediment at a historical zinc smelting site in southwest China for purpose of assessing the distribution and fraction of Pb, Zn, and Cd, and depicting the origin and migration of Pb, Zn, and Cd in the local environment. The obtained knowledge will be beneficial to better evaluate the environmental impact of Pb, Zn, and Cd, and for proposing an appropriate approach for remediation at historical metal smelting sites.

Materials and Methods

Study Area

The study area is located at Magu, Hezhang County, Guizhou Province, southwest China (Fig. 1). The sub-tropical continental monsoon climate is warm and humid with an annual precipitation of 1000-1500 mm and an annual average temperature of 10-13°C. The study area is part of a karst terrain attaining an elevation of 2000-2200 m above sea level. The outcropped rocks are composed of limestone and clay stone the Permian period. The regional soil is characterized by acidic yellow soil with pH values of 5-6 [28].

The local zinc smelting activity started back in the 17th century. The main ore minerals for Zn smelting are spha-

Table 1. Physicochemical properties of slag and soil samples.

Samples	SL (n = 10) ^A	CS (n = 14)	BS (n = 5)
pH	8.62±1.06a ^B	4.19±0.30b	5.22±0.35b
EC (dS·m ⁻¹)	1.42±0.14a	0.15±0.02b	0.07±0.01c
OM (%)	11.8±1.98a	1.48±0.08b	1.18±0.20b
Clay (%)	13.2 ±1.6a	34.6±4.3b	32.5±5.4b
Silt (%)	29.4 ±2.5a	31.4 ±5.3a	33.7±5.8a
Sand (%)	56.3±8.7b	34.2 ±6.4a	33.8±4.3a

^An – Number of samples.

^Ba, b, and c refer to significant differences at p<0.05 according to the LSD test in the same row.

lerite (ZnS) and calamine (ZnCO₃) [28]. The local coals, applied to burn zinc ores in column furnaces, contain sulfur at 3.5% [19]. Devoid of purification, fumes emitted during smelting contained elevated concentrations of Pb, Zn, and Cd, and contaminated the ambient soil and water through wet and dry deposition [20, 29]. The smelting fume deposition has seriously damaged the local vegetation, and the consequent soil and water erosion has resulted in a large amount of alluvial deposits into the local streams [19].

Sampling Procedure

The sampling sites for zinc smelting slag, soil, water, and stream sediment are shown in Fig. 1. Five zinc ore (ZO) samples were collected from the mining sites, 5 km northwest of the study area. Ten slag (SL) samples were collected from the top 15 cm of the slag piles. Fourteen contaminated soil (CS) samples were collected from the top 15 cm soils surrounding the slag piles. Five background soil (BS) samples were also collected from the area with similar stratigraphy to the study area, 10 km northeast of the smelting area, for estimation of natural geochemical baselines. Each sample consisted of 5-10 sub-samples from a 1 m² area. Six soil profiles were chosen at the location of BS1, BS2, CS2, CS12, SL2, and SL8, respectively. Each soil profile was sampled at 0.5 m intervals to a depth of 2.1 m. The 0.9 m and 1.5 m layers of slag above the two soil profiles were also sampled at the location of SL2 and SL8. Six stream water (SW) samples were collected from the local streams in rainy season and dry reason, respectively, where six stream sediment (SE) samples were also collected. Three groundwater (GW) samples were collected from the local wells surrounding the smelting sites in rainy and dry seasons.

Sample Preparation and Analytical Methods

The CS, BS, and SL samples were air-dried at ambient temperature, ground (<2 mm), and sieved to an adequate size (<63 μm) for further analysis. Due to the strong association and affinity of metals with fine-grained soil components [30] and that the <63 μm size fraction of soil or sedi-

Table 2. Concentrations of heavy metals in ore, slag, sediment, and soil.

Samples	Pb (mg·kg ⁻¹)		Zn (mg·kg ⁻¹)		Cd (mg·kg ⁻¹)	
	M±SD	Range	M±SD	Range	M±SD	Range
CS (n=14)	227±113	109-586	400±160	182-887	10.6±5.4	4.02-20.2
BS (n=5)	63±17	43-85	88±19	67-116	0.45±0.14	0.32-0.65
SL (n=10)	4232±1473	1626-6502	8770±2819	5563-14012	56.9±19.4	32.2-87.2
SE (n=6)	1252±240	935-1537	1881±299	1490-2278	21.8±4.1	15.9-27.6
ZO (n=5)	7689±1523	5815-13732	225003±66496	155124-334432	425±95	330-565

n – number of analyzed samples. M±SD indicate mean±standard deviation

ment likely reflects the hydromorphical dispersion of metals in mining or smelting sites, we used the <63 μm fraction for the sequential extraction and total acid digestion methods. The <2 mm soil fraction was used for physicochemical properties.

Water samples (stream water and groundwater) were collected in an acid pre-cleaned bottle. Water samples were filtered through a dry pre-weighed 0.45 μm cellulose acetate membrane using a vacuum filter. Filtrates were collected in an acid-washed bottle and stored in the dark at 4°C for the dissolved metals analysis. The membranes with suspended particulate matter (SPM) were then dried to constant weight at 105°C and re-weighed. SPM content was calculated using membrane weight change before and after filtering. SE samples were air-dried at ambient temperature, and then ground and sieved (< 63 μm) for metals analysis.

Measurement of physicochemical properties of the slag and soil samples was based in the methods of Lu [31].

The texture was determined using the hydrometer method. The pH value was measured by a pH meter (solid:deionized water = 1:2.5). For electrical conductivity (EC) we used an EC meter (DDS-307, Shanghai, China) (solid:deionized water = 1:5). Organic matter (OM) was measured by dichromate oxidation.

All the sample powders of ZO, BS, SL, SE, and SPM from waters were digested by wet-ashing in HNO₃-HClO₄-HF (5:1:1 by volume) mixtures to determine the total metal concentrations. Sequential extraction was performed using the BCR three-step procedure recommended by the Community Bureau of Reference, in which metals are divided into weak acid extracted fraction (F1), reducible fraction (F2), oxidizable fraction (F3), and residual fraction (F4). The specific procedures were based on the method of Wang et al. [32].

The concentrations of Pb, Zn, and Cd were measured using inductively coupled plasma mass spectrometry (ICP-

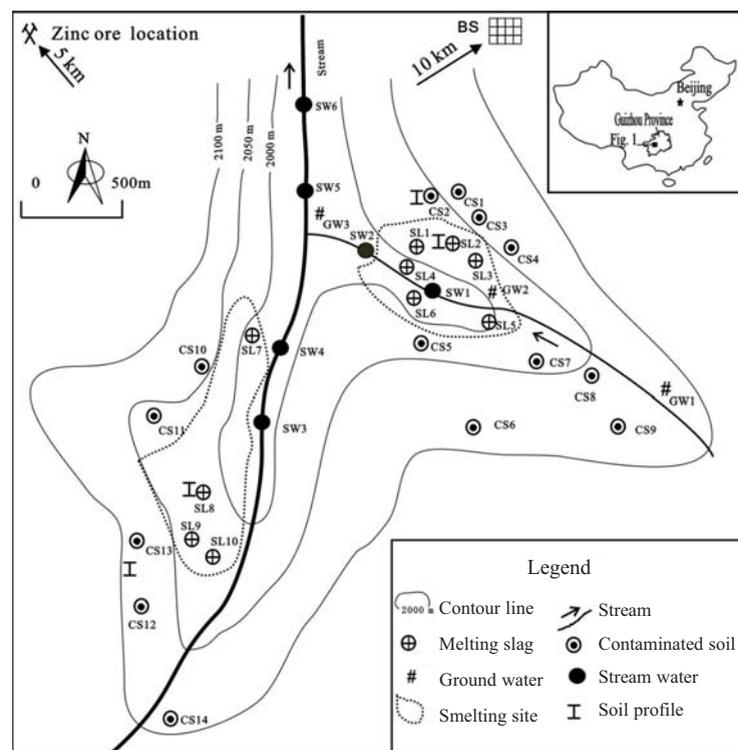


Fig. 1. Map showing the study area and the sampling sites.

Table 3. Concentrations of heavy metals in aqueous environments.

Water samples	Dissolved metals			Total metals			SPM		
	$(\mu\text{g}\cdot\text{L}^{-1})$			$(\mu\text{g}\cdot\text{L}^{-1})$			$(\text{mg}\cdot\text{kg}^{-1})$		
	Pb	Zn	Cd	Pb	Zn	Cd	Pb	Zn	Cd
Rainy season Stream water (n=6) ^{a)}									
Mean	3.66	69.7	2.23	210	490	6.54	896	1892	18.4
Min	2.85	56.2	1.23	115	314	3.30	811	1598	12.8
Max	4.42	102	3.23	339	726	9.00	1005	2209	21.9
Groundwater (n=3)									
Mean	0.70	5.48	1.56	3.11	9.22	1.58	30.4	80.8	0.60
Min	0.62	4.96	1.42	2.84	8.50	1.45	27.5	70.6	0.50
Max	0.83	5.25	1.82	3.46	10.6	1.84	35.4	101	0.70
Dry season Stream water (n=6)									
Mean	2.72	57.3	1.27	156	284	5.04	965	1549	22.3
Min	0.72	12.1	0.34	27.6	65.7	1.12	763	1126	18.3
Max	4.56	118	0.06	357	643	10.7	1316	1782	25.7
Groundwater (n=3)									
Mean	0.43	5.65	0.12	0.43	5.65	0.12	nd ^{b)}	nd	nd
Min	0.32	4.52	0.08	0.32	4.52	0.08	nd	nd	nd
Max	0.52	6.84	0.16	0.45	6.84	0.16	nd	nd	nd

^{a)}n – Number of samples. ^{b)}nd – Non-detectable.

MS, ELAN DRC-e, Perkin Elmer, USA) at the Institute of Geochemistry, Chinese Academy of Sciences. The analytical precision, determined based on the standard quality control procedures of the laboratory using the standard reference materials of rock (OU-6, AMH-1, GBPG-1), soil (TILL-1), internal standards (Rh at 500 $\mu\text{g}/\text{L}$), duplicates, and reagent blanks to ensure the reliability of the data. The analytical precision of trace metals is better than $\pm 10\%$.

Statistical Analysis

Statistical analyses were performed using SPSS (Version 17.0). Data with replicates are expressed as the means \pm standard deviation. Fisher's least significant difference (LSD) was used at $p < 0.05$ for mean separations [28].

Results and Discussion

General Properties of Solid Substrates

The general properties of CS, BS, and SL are presented in Table 1. Mean pH values were 4.19, 5.22, and 8.62 for CS, BS, and SL, respectively. The SO_2 -derived acid deposition from the smelting fumes could be responsible for the relatively high acidity in CS. The local zinc ore of spha-

lerite as well as the sulfur-bearing coal applied for smelting produced SO_2 during the smelting process and consequently resulted in dry/wet acid deposition into the ambient soil. On the contrary, SL was alkaline (pH = 8.62), which was attributed to large amounts of carbonate (host rock) in ZO decomposed into soda lime during smelting [28]. The EC values in SL averaged at 1.42 dS/m, presenting high salinity levels [33]. Compared to BS (0.07 dS/m), EC values in CS significantly increased, which could be due to the elevated solubility of metals resulting from low pH values. Average values of OM were 11.8% for SL, 1.48% for CS, and 1.18% for BS. OM in SL was significantly higher than those in CS and BS, which could be due to insufficient combustion of coal during the smelting process. According to the international system of soil texture classification standard, the soil texture of CS is the same as that of BS, and classified as loamy clay; however, SL is classified as sand loam.

Pb, Zn, and Cd in Solid Substrates

The concentrations of Pb, Zn, and Cd in the solid substrates are listed in Table 2. ZO for processing Zn averaged at 225,003 $\text{mg}\cdot\text{kg}^{-1}$ Zn, 8,690 $\text{mg}\cdot\text{kg}^{-1}$ Pb and 425 $\text{mg}\cdot\text{kg}^{-1}$ Cd, respectively. Due to the poor technology for historical zinc smelting, elevated Pb, Zn, and Cd in SL were 4,232 $\text{mg}\cdot\text{kg}^{-1}$ Pb, 8,770 $\text{mg}\cdot\text{kg}^{-1}$ Zn, and 56.9 $\text{mg}\cdot\text{kg}^{-1}$ Cd. The concentra-

tions of Pb, Zn, and Cd in CS averaged at 208 mg·kg⁻¹, 400 mg·kg⁻¹, and 10.6 mg·kg⁻¹, respectively - significantly higher than those in BS. The concentrations of Pb, Zn, and Cd in SE at the smelting sites averaged 1,252, 1,881 and, 21.8 mg·kg⁻¹, respectively. Pb, Zn, and Cd concentrations appeared to be in the order ZO > SL > SE > CS > BS. The results suggest that large amounts of Pb, Zn, and Cd had accumulated in SL, CS, and SE surrounding the smelting sites.

The smelting fume depositions and the smelting slag were the two main metal pollution sources to the local environment. The smelting sites were located along the local stream banks, downhill from the sampling sites of CS (Fig. 1). Therefore, Pb, Zn, and Cd in CS were only from the smelting fume deposition [20], whereas their occurrences in SL were not only from the slag themselves but also from the fume deposition. Pb, Zn, and Cd concentrations in SL were significantly higher than those in CS, suggesting that smelting residues were a major source contribution to Pb, Zn, and Cd in SL.

Elemental ratio is an effective index applied to distinguish metal origin [26, 27]. The ratios of Pb/Cd and Zn/Cd in ZO, SL, SE, CS, and BS are plotted in Fig. 2. The mean Pb/Cd ratio in SL (75) was substantially higher than that in ZO (24). This suggested that Cd was predominantly volatilized during smelting due to the low boiling point of Cd at 767°C, but Pb in ZO was predominantly retained in SL due to the high boiling point of Pb at 1,740°C. On the contrary, compared to ZO the mean Zn/Cd ratio in SL comparably decreased, suggesting that most of the Zn (boiling point at 907°C) in ZO was recuperated in liquid form dur-

ing smelting. The mean Pb/Cd and Zn/Cd ratios in CS were significantly lower than those in SL and BS, and suggested that large amounts of Cd were transported from the smelting fume deposition onto CS during smelting than Zn and Pb. The mean Pb/Cd and Zn/Cd ratios in SE were 58 and 88, respectively, and both were between the counterparts of CS and SL. It is also observed that Pb, Zn, and Cd in SE were between those in SL and CS (Fig. 2). It is suggested that SE in the stream could be derived from SL and CS.

BCR extraction procedures are commonly used because they could provide information about origin, bioavailability, and mobilization of metals in solid materials, though the used reagents are not very selective toward one particular species and cannot completely solubilize species [34]. BCR extraction fractions include weak acid fraction (weakly absorbed metals retained on the soil surface), reducible fraction (associated with Fe and Mn hydrous oxides), oxidizable fraction (associated with organic and sulfide matter), and residual fraction (hold within the crystal structure of primary and secondary minerals) in sequence [30]. The mobility and bioavailability of metals decrease approximately in the order of the extraction sequence [34]. The distribution of Pb, Zn, and Cd in various geochemical fractions in SL, SE, CS, and BS are shown in Fig. 3. Pb in SL was predominantly located in the oxidizable fraction (49%) and the residual fraction (27%), with smaller portions in the reducible fraction (17.8%) and the weak acid extracted fraction (6.2%). Compared to SL, elevated Pb existed in the weak acid extracted fraction in CS and BS, while Pb in the weak acid extracted fraction in SE was between CS and SL. Zn in SL was associated predominantly with the reducible

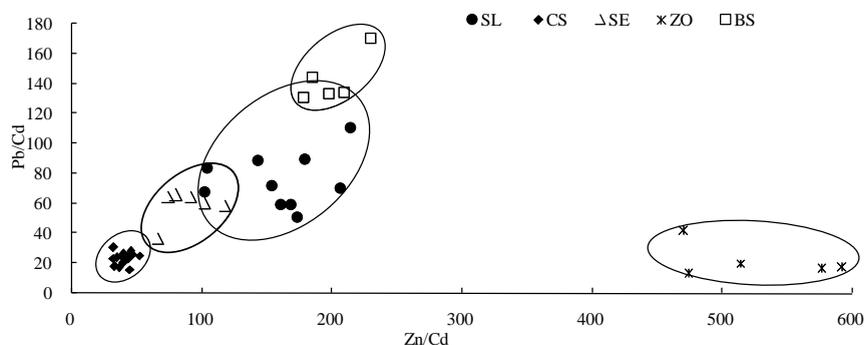


Fig. 2. Plot of Pb/Cd and Zn/Cd in solid substrates.

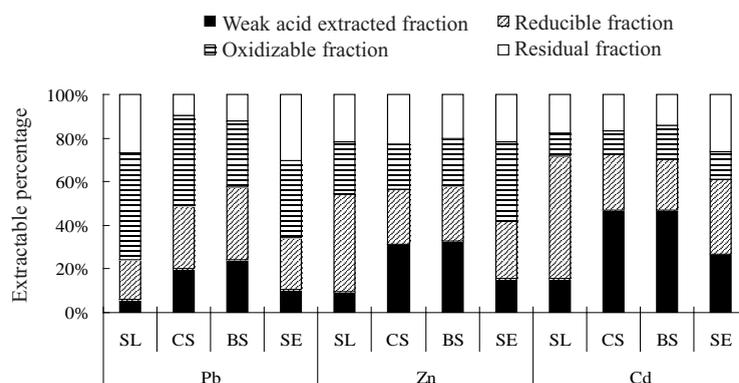


Fig. 3. Percentage distribution of Pb, Zn, and Cd in various geochemical fractions of slag, soil, and stream sediment.

fraction (44.9%), followed by the oxidizable fraction (23.7%), the residual fraction (21.8%), and the weak acid extracted fractions (9.7%). Cd in SL exhibited a similar fraction to Zn, with the highest portion in the reducible fraction. However, Cd in the weak acid extracted fraction (15.6%) increased substantially. The weak acid extracted Cd in CS, BS and SE also increased substantially, up to 47.0%, 46.9%, and 26.7% of the total Cd, respectively.

Although all fractions except for residuals are generally bio-available [35], metals bounded to the weak acid extracted fraction are most readily available to plants and living organisms, and can be applied to the prediction of qualitative mobility of metals in different soil systems [36-38]. Therefore, metals present in the weak acid extracted fraction in the present study were interpreted to be relatively more mobile. The results indicated that the proportion of

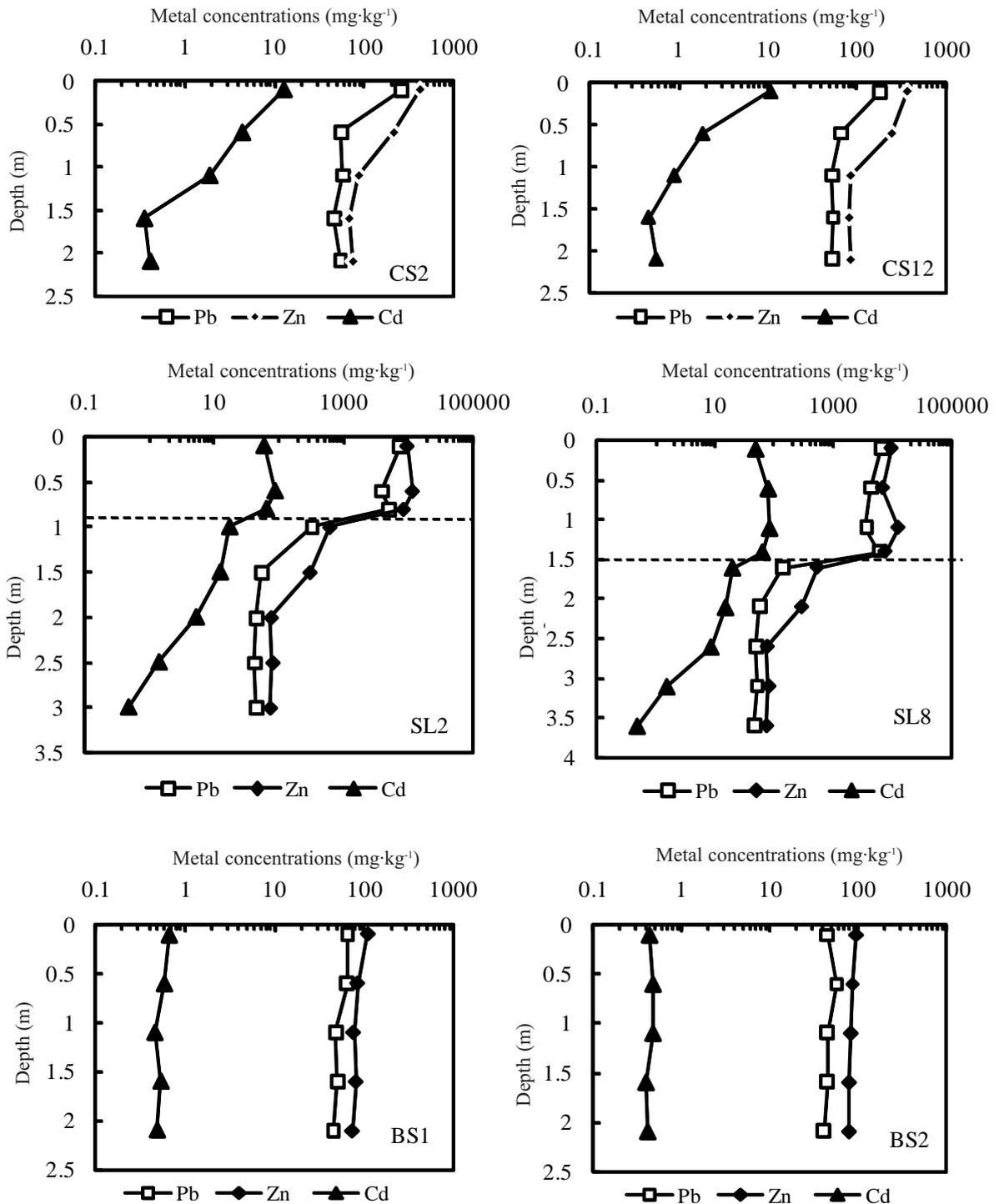


Fig. 4. Pb, Zn, and Cd distribution patterns in soil profiles at CS2, CS12, SL2, SL8, BS1, and BS2. The dotted lines at SL2 and SL8 represents the boundary between slag pile (above) and initial soil (below).

metals associated with the weak acid extracted fraction in CS, SE, and SL followed the sequence of $Cd > Zn > Pb$ (Fig. 3), suggesting for similar metal mobility and bioavailability in the solid substrates at the smelting site. Soil physical and chemical properties were closely related to mobility of metals. Higher pH values may restrain mobility of Pb, Zn, and Cd in SL by precipitation and adsorption, therefore the percentage of the weak acid extracted fraction of these metals was observed in SL higher than in CS and BS [39]. Fe/Mn oxides and soil OM were reported to be efficient scavengers for trace metals and reduce their mobility and risk of leaching [9, 40, 41]. There was a higher percentage of oxidizable fraction for Pb than for Zn and Cd, while there was higher percentage of reducible fraction for Zn and Cd than for Pb. Pb was liable to be bond to soil OM, while Zn and Cd was liable to be bond to Fe and Mn oxides. However, SL has higher concentrations of weak acid-extracted metals than BS, due to higher total concentrations of metals accumulated in SL. As such, SL may pose a long-term environmental risk to the environment, particularly when impacted by acid rain erosion [39, 42, 43].

Pb, Zn, and Cd Distribution in Soil Profiles

Concentrations of Pb, Zn, and Cd in the six selected soil profiles are plotted in Fig. 4. Metals in the soil profiles at BS1 and BS2 present soil background levels. Pb, Zn, and Cd concentrations were similarly distributed in the two profiles at BS1 and BS2. A similar trend of vertical metal distribution was observed in the two soil profiles at CS2 and CS12. Pb, Zn, and Cd concentrations showed an obvious vertical downtrend. Pb, Zn, and Cd decreased to the regional background levels at a depth of about 0.6 m, 1.1 m, and 1.6 m, respectively. This distribution pattern suggested an origin by atmospheric deposition [44].

There are a top 0.9 m slag layer and a top 1.5 m slag layer at the location of SL2 and SL8, respectively, under which is an initial soil layer (Fig. 4). Elevated Pb, Zn, and Cd concentrations in slag layer were observed at SL2 and SL8. Pb, Zn, and Cd concentrations abruptly decreased from slag layer to initial soil layer. The total concentrations of Pb, Zn, and Cd in top initial soil were higher in SL profiles than in CS profiles, indicating more metals into soil profiles from SL release than from fume deposition. Similarly, the total concentrations of Pb, Zn, and Cd in initial soil profiles under SL also showed an obvious vertical downtrend, and reached the regional background levels at a depth of 0.6 m, 1.1 m, and 2.1 m, respectively. Unlike CS profiles, Cd in SL profiles migrated to a deeper layer.

Based on distribution of metals in the soil profiles, the mobility of these three metals were in the following order: $Cd > Zn > Pb$. This was consistent with the order of mobility of metals obtained metal fraction.

Pb, Zn, and Cd Concentrations in Aqueous Environments

Pb, Zn, and Cd concentrations in stream water and groundwater in different seasons are plotted in Table 3.

Total concentrations of Pb, Zn, and Cd in stream water were significantly higher than those in groundwater in rainy or dry seasons. It was also observed that total concentrations of Pb, Zn, and Cd in rainy season were higher than those in dry season. The permissible values of Pb, Zn, and Cd in the Surface Water Source Standards for Centralized Drinking Water (GB3838-2002, China) were $50 \mu\text{g}\cdot\text{L}^{-1}$, $1000 \mu\text{g}\cdot\text{L}^{-1}$, and $5 \mu\text{g}\cdot\text{L}^{-1}$, respectively. As shown in Table 3, mean total concentrations of Pb, Zn, and Cd in stream water exceeded the standardized limits in both dry and rainy seasons, while total concentrations of Pb, Zn, and Cd in groundwater all were below the limits.

Dissolved metals in stream water were predominantly higher than those in groundwater. It was also observed that the dissolved metal concentrations in stream water were higher in the rainy season than in the dry season, whereas groundwater showed similar distributions of dissolved metals in different seasons.

The concentrations of Pb, Zn, and Cd in SPM of stream water averaged $896 \text{ mg}\cdot\text{kg}^{-1}$, $1,892 \text{ mg}\cdot\text{kg}^{-1}$, and $18.4 \text{ mg}\cdot\text{kg}^{-1}$, respectively, in the rainy season, similar to those in the dry season, but the loads of SPM in stream water were higher in the rainy season than in the dry season. The total metal contents in stream water were higher in the rainy season than in the dry season, and this was likely attributed to more severe soil erosion from CS or SL in the rainy season than in the dry season.

SPM and SE of stream water exhibited similar distribution of metals, and their concentrations of Pb, Zn, and Cd were between counterparts in CS and SL (Tables 2 and 3). It is suggested that SPM and SE had the same origins from SL and CS.

The loads of SPM of groundwater were quite low, even undetectable in the dry seasons. The mean concentrations of Pb, Zn, and Cd in SPM were 30.4 , 80.8 and $0.6 \text{ mg}\cdot\text{kg}^{-1}$, respectively, much lower than those in stream water (Table 3), but similar to those in BS (Table 2). The results suggested that SPM of groundwater were derived from BS. It is also indicated that groundwater was hardly polluted with Pb, Zn, and Cd. The downward migration of Pb, Zn, and Cd in the profiles reach a depth of 0-2.1 m (Fig. 4), further supporting this statement.

There existed two pathways through which metals may transfer to the stream water. One was through runoff in dissolved form, and the other was through soil erosion in the form of SPM. Dissolved Pb, Zn, and Cd in stream waters were only 1.6%, 14.7%, and 26.5% of the total metals, respectively, suggesting that the adsorption capacity of metals was $Pb > Zn > Cd$, which was similar to the results reported by some researchers [45, 46]. In addition, the data showed that Pb, Zn, and Cd in stream water were derived predominantly from soil erosion and transferred to lower reaches predominantly through SPM (Table 3). The results suggested that the reduction of SPM into stream water may help metal reduction in the streams. Therefore, the eco-stabilization for soil erosion by means of revegetation and/or terraced dam-blocking is a vital approach to retard metal dispersion to the aqueous environment at historical zinc smelting sites [47].

Conclusions

The investigated historical zinc smelting sites were severely polluted with Pb, Zn, and Cd through past smelting fume deposition and smelting slag erosion. During smelting, more Cd was volatilized and transported onto the surrounding environment than Pb and Zn, Zn was predominantly recuperated, and Pb was predominantly retained in smelting slag. There existed higher percentages of weak acid extracted Pb, Zn, and Cd in contaminated soil than in smelting slag, but the concentrations of the weak acid extracted Pb, Zn, and Cd in smelting slag were higher than those in contaminated soil, posing long-term risk to the surrounding environment. The relative amounts of vertical transport of metals appeared to follow the order of Cd > Zn > Pb, similar to the mobility order by BCR sequential extractions. Metals in the soil profiles predominantly distributed at a depth of 0–0.6 m, and only transferred to the maximum depth of 1.5 m, such that the groundwater was less impacted. Compared to groundwater, the stream water was heavily polluted with Pb, Zn, and Cd mainly through SPM. SE and SPM collected from the stream exhibited similar Pb/Cd and Zn/Cd ratios, concentrations of Pb, Zn, and Cd (between contaminated soil and smelting slag) probably indicating their origins from erosion of contaminated soil and smelting slag.

Acknowledgements

This research was supported by the Guangdong Provincial Science and Technology Foundation (2011B030900010), the State Key Laboratory of Environmental Geochemistry (SKLEG8006), and the Guizhou Provincial Science and Technology Foundation. The authors acknowledge particularly Ziqiang Ao for lab analysis. Thanks also go to Prof. Jayanta Guha at the University of Quebec at Chicoutimi for reading the initial version of the manuscript.

References

- OLAWOYIN R., OYEWOLE S.A., GRAYSON R.L. Potential risk effect from elevated levels of soil heavy metals on human health in the Niger delta. *Ecotoxicol. Environ. Saf.* **85**, 120, **2012**.
- KAPUSTA P., SZAREK-ŁUKASZEWSKA G., STEFANOWICZ A.M. Direct and indirect effects of metal contamination on soil Biota in a Zn-Pb post-mining and smelting area (S Poland). *Environ. Pollut.* **159**, 1516, **2011**.
- LI P., FENG X.B., QIU G.L., SHANG L.H., WANG S.F. Mercury pollution in Wuchuan mercury mining area, Guizhou, Southwestern China: The impacts from large scale and artisanal mercury mining. *Environ. Int.* **42**, 59, **2012**.
- VOEGELIN A., BARMETTLER K., KRETZSCHMAR R. Heavy metal release from contaminated soils: Comparison of column leaching and batch extraction results. *J. Environ. Qual.* **32**, 865, **2003**.
- DIPL., FERRANTELLI P., MEDICI F. Heavy metals extraction from contaminated soil: Recovery of the flushing solution. *J. Environ. Manage.* **77**, 205, **2005**.
- NEMATI K.N., BAKER N.K.A., ABAS M.R.R., SOB-HANZADEH E. Speciation of heavy metals by modified BCR sequential extraction procedure in different depths of sediments from Sungai Buloh, Selangor, Malaysia. *J. Hazard. Mater.* **192**, 402, **2011**.
- RODRÍGUEZ L., RUIZ E., ALONSO-AZCÁRATE J., RINCÓN J. Heavy metal distribution and chemical speciation in tailings and soils around a Pb–Zn mine in Spain. *J. Environ. Manage.* **90**, (2), 1106, **2009**.
- UDOVIC M., LESTAN D. Pb, Zn and Cd mobility, availability and fractionation in aged soil remediated by EDTA leaching. *Chemosphere* **74**, (10), 1367, **2009**.
- ZHONG X.L., ZHOU S.L., ZHU Q., ZHAO Q.G. Fraction distribution and bioavailability of soil heavy metals in the Yangtze River Delta—a case study of Kunshan City in Jiangsu Province, China. *J. Hazard. Mater.* **198**, 13, **2011**.
- HE Z.L., YANGA X.E., STOFFELLAB P.J. Trace elements in agroecosystems and impacts on the environment. *J. Trace Elem. Med. Biol.* **19**, 125, **2005**.
- TESSIER A., CAMPBELL P.G.C., BISSON M. Sequential extraction procedure for the speciation of particulate trace metals. *Anal. Chem.* **51**, 844, **1979**.
- CAMPANELLA L., DORAZIO D., PETRONIO B.M., PIETRANTONIO E. Proposal for a metal speciation study in sediments. *Anal. Chim. Acta.* **309**, 387, **1995**.
- GOMEZ-ARIZA J.L., GIRALDEZ I., SANCHEZ-RODAS D., MORALES E. Metal sequential extraction procedure optimized for heavily polluted and iron oxide rich sediments. *Anal. Chim. Acta.* **414**, 151, **2000**.
- RAURET G., LÓPEZ-SÁNDUZ J.F., SAHUQUILLO A., RUBIO R., DAVIDSON C., URE A., QUEVAUVILLER Ph. Improvement of the BCR three-step sequential extraction procedure prior the certification of new sediment and soil reference materials. *J. Environ. Monit.* **1**, 57, **1999**.
- ŽEMBERYOVÁ M., BARTEKOVÁ J., HAGAROVÁI. The utilization of modified BCR three-step sequential extraction procedure for the fractionation of Cd, Cr, Cu, Ni, Pb and Zn in soil reference materials of different origins. *Talanta* **70**, 973, **2006**.
- PUEYO M., MATEU J., RIGOL A., VIDAL M., LOPEZ-SANCHEZ J.F. RAURET G. Use of modified BCR three-step sequential extraction procedure for the study of trace elements dynamics in contaminated soils. *Environ. Pollut.* **152**, 330, **2008**.
- DAVUTLUOGLU O.I., SECKIN G., ERSU C.B., YILMAZ T., SARI B. Heavy metal content and distribution in surface sediments of the Seyhan River, Turkey. *J. Environ. Manage.* **92**, (9), 2250, **2011**.
- SHEN X., WANG X., ZHU G. Lead and cadmium contaminations to atmospheric environment conducted by zinc smelting. *Environ. Monit. China.* **7**, (6), 8, **1991**.
- LIN W.J., XIAO T.F., AO Z.Q., XING J., MA H.C., HU T.X. Limiting factors of waste land revegetation in indigenous zinc smelting areas of western Guizhou. *Chinese. J. Appl. Ecol.* **18**, 631, **2007**.
- BI X., FENG X., YANG Y., QIU G., LI G., LI F., LIU T. Environmental contamination of heavy metals from zinc smelting areas in Hezhang County, Western Guizhou, China. *Environ. Int.* **32**, (7), 883, **2006**.
- YANG Y.G., LIU C.Q., PAN W., ZHANG G.P., ZHU W.H. Heavy metal accumulation from zinc smelters in a carbon-

- ate rock region in Hezhang County, Guizhou Province, China. *Water Air Soil Poll.* **174**, (1-4), 321, **2006**.
22. YANG Y.G., JIN Z.S., BI X.Y., LI F.L., SUN L., LIU J., FU Z.Y. Atmospheric deposition-carried Pb, Zn and Cd from a zinc smelter and their effect on soil microorganisms. *Pedosphere* **19**, (4), 422, **2009**.
 23. VAZQUEZ S., HEVIA A., MORENO E., ESTEBAN E., PENALOSA J.M., CARPENA R.O. Natural attenuation of residual heavy metal contamination in soils affected by the Aznalcollar mine spill, SW Spain. *J. Environ. Manage.* **92**, (8), 2069, **2011**.
 24. MORENO-JIMENEZ E., PENALOSA J.M., MANZANO R., CARPENA-RUIZ R.O., GAMARRA R., ESTEBAN E. Heavy metals distribution in soils surrounding an abandoned mine in NW Madrid (Spain) and their transference to wild flora. *J. Hazard. Mater.* **162**, 854, **2009**.
 25. HO H.H., SWENNEN R., CAPPUYNS V., VASSILIEVA E., VAN GERVEN T., TRAN T.V. Potential release of selected trace elements (As, Cd, Cu, Mn, Pb and Zn) from sediments in Cam River-mouth (Vietnam) under influence of pH and oxidation. *Sci. Total Environ.* **435**, 487, **2012**.
 26. CASSELMAN C.N., FOX T.R., BURGER J.A., JONES A.T., GALBRAITH J.M. Effects of silvicultural treatments on survival and growth of trees planted on reclaimed mine lands in the Appalachians. *Forest Ecol. Manag.* **223**, 403, **2006**.
 27. ECKEL W.P., RABINOWITZ M.B., FOSTER G.D. Investigation of unrecognized former secondary lead smelting sites: confirmation by historical sources and elemental ratios in soil. *Environ. Pollut.* **117**, 273, **2002**.
 28. LIN W.J., XIAO T.F., WU Y.Y., AO Z.Q., NING Z.P. Hyperaccumulation of zinc by *Corydalis davidii* in Zn-polluted soils. *Chemosphere* **86**, 837, **2012**.
 29. LIN W.J. Ecological degeneration and heavy metals pollution in zinc smelting areas. *Ecol. Environ. Sci.* **8**, 149, **2009**.
 30. RODRIGUEZ L., RUIZ E., ALONSO-AZCARATE J., RINCON J. Heavy metal distribution and chemical speciation in tailings and soils around a Pb-Zn mine in Spain. *J. Environ. Manage.* **90**, 1106, **2009**.
 31. LU R.K. *Methods for soil agricultural chemistry analysis*, Beijing: Chinese agricultural science and technology Press, **1999**.
 32. WANG C., HU X., CHEN M.L., WU Y.H. Total concentrations and fractions of Cd, Cr, Pb, Cu, Ni and Zn in sewage sludge from municipal and industrial wastewater treatment plants. *J. Hazard. Mater.* **119**, 245, **2005**.
 33. HSU S.C., LIU S.C., JENG W.L., LIN F.J., HUANG Y.T., CANDICE LUNG S.C., LIU T.H., TU J.Y. Variations of Cd/Pb and Zn/Pb ratios in Taipei aerosols reflecting long-range transport or local pollution. *Sci. Total Environ.* **347**, 111, **2005**.
 34. ZHANG J., LIU J., LI C., JIN Y., NIE Y., LI J. Comparison of the fixation effects of heavy metals by cement rotary kiln co-processing and cement based solidification/stabilization. *J. Hazard. Mater.* **165**, 1179, **2009**.
 35. TOKALIOGLU S., YILMAZ V., KARTAL S. An assessment on metal sources by multivariate analysis and speciation of metals in soil samples using the BCR sequential extraction procedure. *Clean Soil Air Water* **38**, (8), 713, **2010**.
 36. MANNO E., VARRICA D., DONGARRA G. Metal distribution in road dust samples collected in an urban area close to a petrochemical plant at Gela, Sicily. *Atmos. Environ.* **40**, 5929, **2006**.
 37. KUBOVÁ J., MATUŠ P., BUJDOŠ M., HAGAROVÁ I., MEDVED J. Utilization of optimized BCR three-step sequential and dilute HCl single extraction procedures for soil-plant metal transfer predictions in contaminated lands. *Talanta* **75**, 1110, **2008**.
 38. AKKAJIT P., TONGCUMPOU C. Fractionation of metals in cadmium contaminated soil: Relation and effect on bioavailable cadmium. *Geoderma* **15**, 126, **2010**.
 39. HALE B., EVANS L., LAMBERT R. Effects of cement or lime on Cd, Co, Cu, Ni, Pb, Sb and Zn mobility in field-contaminated and aged Soils. *J. Hazard. Mater.* **199**, 119, **2012**.
 40. GWENZI W., MUNONDO R. Long-term impacts of pasture irrigation with treated sewage effluent on nutrient status of a sandy soil in Zimbabwe. *Nutr. Cycl. Agroecosyst.* **82**, 197, **2008**.
 41. VANĚK A., ETTLER V., GRYGAR T., BORŮVKA L., ŠEBEK O., DRÁBEK O. Combined chemical and mineralogical evidence for heavy metal binding in mining- and smelting-affected alluvial soils. *Pedosphere* **18**, (4), 464, **2008**.
 42. SHU W.S., YE Z.H., LAN C.Y., ZHANG Z.Q., WONG M.H. Acidification of lead/zinc mine tailings and its effect on heavy metal mobility. *Environ. Int.* **26**, 389, **2001**.
 43. ZHAO H.R., XIA B.C., FAN C., ZHAO P., SHEN S.L. Human health risk from soil heavy metal contamination under different land uses near Dabaoshan Mine, Southern China. *Sci. Total Environ.* **417**, 45, **2012**.
 44. BACON J.R., HEWITT I.J. Heavy metals deposited from the atmosphere on upland Scottish soils: Chemical and lead isotope studies of the association of metals with soil components. *Geochim. Cosmochim. Ac.* **69**, 19, **2005**.
 45. ZHENG S., WANG P., WANG C., HOU J., QIAN J. Distribution of metals in water and suspended particulate matter during the resuspension processes in Taihulake sediment, China. *Quatern.Int.* **286**, 94, **2013**.
 46. CHATURVEDI P.K., SETH C.S., MISRA V. Sorption kinetics and leach ability of heavy metal from the contaminated soil amended with immobilizing agent (humus soil and hydroxyapatite). *Chemosphere* **64**, (7), 1109, **2006**.
 47. MORENO-JIMENEZ E., ESTEBAN E., CARPENA-RUIZ R.O., LOBO M.C., PENALOSA J.M. Phytostabilisation with mediterranean shrubs and liming improved soil quality in a pot experiment with a pyrite mine soil. *J. Hazard. Mater.* **201**, 52, **2012**.

