

Fractionation characterizations and environmental implications of heavy metal in soil from coal mine in Huainan, China

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Abstract The toxicity and availability of heavy metals in soil are determined by modes of occurrence of metals. Therefore, the quantification of associations of heavy metals is more significant than the assessment of their total concentrations. Thirty soil samples that were collected from coal mining areas with different mining durations in Huainan Coalfield were employed to determine the modes of occurrence and potential environmental implications of heavy metals. Sequential chemical extraction procedure was carried out to determine the fractionation profiles of heavy metals. The elevated concentrations of heavy metals in the mining activities areas indicated that the mining activities (mining, transportation, utilization and waste disposal) might be one of the sources for the heavy metal pollution in soil. The fractionation characterizations are various among different heavy metals. According to the international sediment quality guidelines (SQGs) calculations, the adverse biological effects caused by Cd, Cr, Pb and Zn are expected to be negligible. For As and Cu, the occasional adverse biological effects are predicted. The risk assessment code reveals that these heavy metals could pose a medium risk to the ecosystem. Consequently, environmental issues involved in heavy metals in the studied coal mining area soil deserve urgent concern.

Keywords Coal mine · Soil · Heavy metal · Fractionation · Environmental impact

Introduction

The rapid development of the coal mining industry in China over the past 20 years has resulted in serious environmental issues (Zhou et al. 2014a). The heavy metals, which are presented in less than 0.1 % in matrix (coal, coal wastes), are of great concern due to their toxicity, persistence and non-degradability (Dai et al. 2008; Finkelman et al. 2002; Ribeiro et al. 2010; Scott et al. 2009; Zhang et al. 2003). Heavy metal in soil may be derived from both natural source and anthropogenic contributions. Among these, the anthropogenic sources, typically coal mining activities, are regarded as the main sources. The heavy metals in coal (coal wastes) were released and accumulated in soil by various processes (leaching, weathering, combustion and biological reaction) (Gidarakos et al. 2009; Shafer et al. 2012; Singh and Paul 2001; Zhang et al. 2008; Zhou et al. 2014b, c). Therefore, the study on the environmental implications of heavy metals in soil around coal mining areas is of significance.

Evaluation of total concentrations of heavy metals in soil provides important information for contamination levels when compared with the background values. Nevertheless, the assessment of the total contents of heavy metals could not be able to provide information about its toxicity and bioavailability (Gadh 1991; Cabarcas-Montalvo et al. 2012). Consequently, it is important to induce chemical fractionation to investigate the potential environmental implications.

Currently, the associations of heavy metals could be investigated by both theoretical calculations and

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experimental determination (Jain et al. 2010). Among them, the sequential chemical extraction procedure is regarded as the sophisticated method for the modes of occurrence of heavy metals. Once the associations of heavy metals in soil were obtained, its bioavailability and toxicity could be ascertained (Jain et al. 2010). The exchangeable and carbonate bound are weakly bound and regarded as more rapidly bioavailable. The Fe–Mn oxides and organic matter bound have a scavenging effect and may provide a deposition for heavy metals; the release ratio of heavy metal from these fractions was determined by the pH and redox potential (Burt et al. 2014). The heavy metal in residual was regarded as inert fraction and retained at soil. Therefore, the improved sequential extraction method reported by Tessier et al. (1979) was employed to determine the fractionations of heavy metal in soil.

Huainan Coalfield is the national identified coal base and coal-electricity base, which contains 17 coal mines and 21 coal-fired power plants. Intensive coal mining and long-scale mining duration inevitably led to high retention capacity for heavy metals in soil and eventually resulted in potential environmental and health risks. In spite of the significant environmental issues of heavy metals in coal mining areas' soil, reports on the heavy metals' fractionation and ecological risk assessment in Huainan are extremely limited (Li et al. 2010; Wang et al. 2012). Therefore, the objectives of this study are: (1) to determine the contamination levels of heavy metals in coal mining areas' soil; (2) to investigate the fractionation characteristics of heavy metals; and (3) to evaluate the potential environmental and ecological risks posed by these contaminated soils. This study provides basic information for local environmental management and use for reference for other coal mining activities areas.

Materials and methods

Study area and sampling

Huainan Coalfield (N32°32'45"–N33°0'24", E116°21'21"–E117°11'59") is located in central China. The climate of this area is a typical seasonal temperature semi-humid monsoon. The average temperature and annual rainfall are 15 °C and 921 mm, respectively. According to local perennial wind direction (southeast wind and northwest wind), samples were collected from the southeast and northwest directions at distance of 10, 50, 100, 300 and 600 m from the coal mining areas. A total of 30 soil samples for Xinzhuangzi Coal Mine ($n = 10$), Panyi Coal Mine ($n = 10$) and Dingji Coal Mine ($n = 10$) were collected (Fig. 1). The mining histories of the selected coal mines are decreased as Xinzhuangzi Coal Mine (68 years

old) > Panyi Coal Mine (22 years old) > Dingji Coal Mine (8 years old). These samples were collected from the upper 20 cm of soil in farmland that has not been disturbed for several months using a stainless steel spade, and stored in a plastic bag immediately. In order to obtain a representative sample, subsamples were scraped from five separated level areas randomly around each soil site and then pooled to an integrated sample. When taken back to the laboratory, the soil samples were air-dried and crushed to pass through a 2-mm mesh sieve to homogenize for the subsequent chemical analysis.

Chemical analysis

The homogenous soil samples and standard reference material (GBW07406 (GSS-6)) were extracted by an acid mixture solution (HCl/HNO₃/HF) with the ratio of 3:3:2 in a microwave oven. The digested procedure was carried out at 120 °C for 20 min and then heated at 180 °C for 25 min (Zhou et al. 2014b). After extraction, the digested solution was heated at 210 °C to disperse the excess acid mixture solution. Finally, the treated solution was quantified to 25 ml by colorimetric tube for the subsequent analysis. The concentrations of heavy metals (As, Cd, Cr, Cu, Pb and Zn) in the selected soil samples were determined using an inductively coupled plasma mass spectrometry (ICP-MS), with the limit of detection (LOD) and limit of quantity (LOQ) of 0.01 µg/L, 0.001 µg/L, 0.007 µg/L, 0.009 µg/L, 0.001 µg/L and 0.047 µg/L, and 0.03 µg/L, 0.004 µg/L, 0.024 µg/L, 0.03 µg/L, 0.005 µg/L and 0.16 µg/L, respectively. The quality control was subjected to standard references materials GBW07406 (GSS-6). The certified values of As, Cd, Cr, Cu, Pb and Zn in the standard reference materials GBW07406 (GSS-6) are 220 ± 14, 0.13 ± 0.03, 75 ± 6, 390 ± 14, 314 ± 13 and 220 ± 14 mg/kg, respectively. The calibrating solution (contains As, Cd, Cr, Cu, Pb and Zn) with a value of 10 mg/L was employed to calibrate the instrument. Meanwhile, reagent blanks were paralleled in the whole extraction processes to minimize background interference. The acceptable precision is within ±5 wt% for all the heavy metals. In addition, once the difference between the standards and the calibrated values was more than 5 %, the apparatus was required to recalibrate. In order to guarantee the precision and accuracy of the experimental data, all the measurements for each sample were taken in triplicates. The relative standard deviations of the three times analysis were ranged from –1.73 to 2.69 % and below the control level of ±5 wt%.

The sequential chemical extraction method reported by Tessier et al. (1979) was employed to provide information about the modes of occurrence of heavy metals in soil. The selected samples were subjected to specific solvents in five-

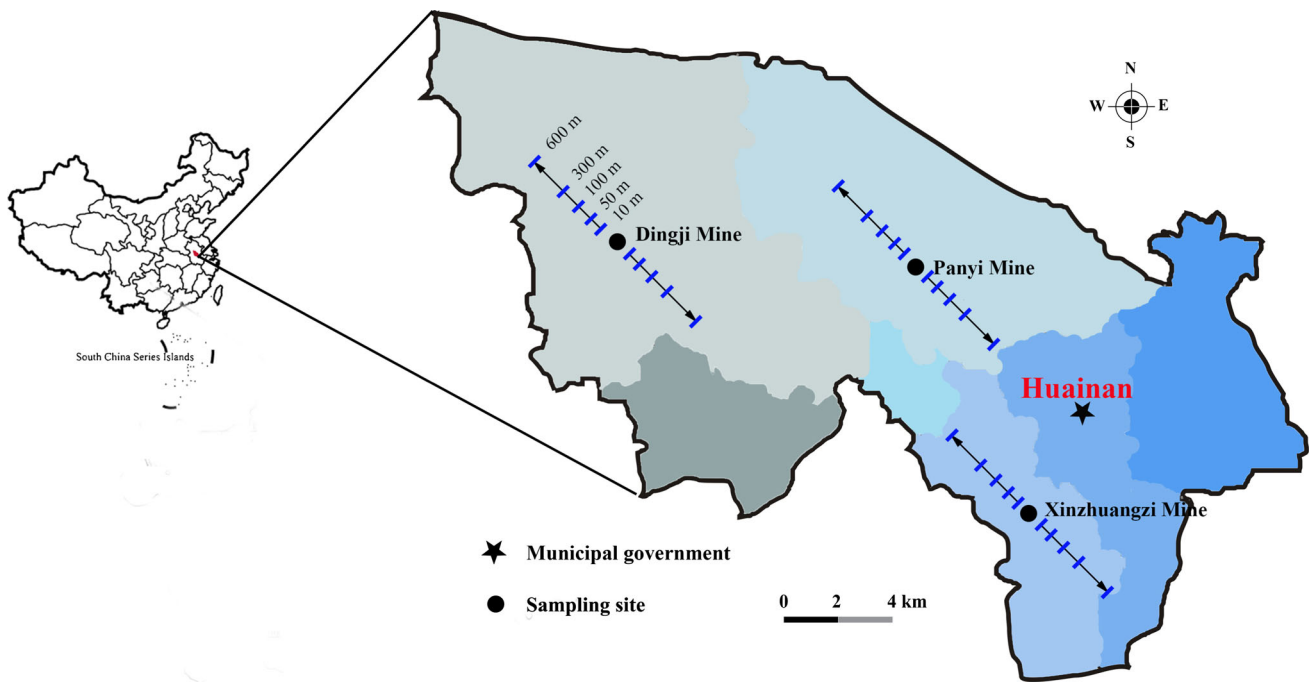


Fig. 1 Location of the selected coal mine in Huainan Coalfield

step sequential chemical extraction procedure in the following order:

1. Exchangeable: 1.5 g powdered sample was digested with 15 ml 1.0 M $MgCl_2$ (pH 7.0) for 1 h under room temperature, and supernatant was obtained by centrifugation at 3800 rpm for 15 min.
2. Carbonate bound: The residues from step (1) were extracted by 15 ml 1 M CH_3COONa (pH 5.0) and agitated continuously for 5 h, and suspension was obtained by centrifugation at 3800 rpm for 15 min.
3. Fe–Mn oxides bound: The residues from step (2) were extracted by 30 ml 0.04 M $NH_2OH \cdot HCl$ in 25 % (v/v) and agitated continuously for 6 h, and suspension was obtained by centrifugation at 3800 rpm for 15 min.
4. Organic matter bound: The residues from step (3) were extracted by 4.5 ml 0.02 M HNO_3 and 7.5 ml 30 % H_2O_2 (pH 2.0) for 2 h under 85 °C. A 4.5 ml 30 % H_2O_2 (pH 2.0 with HNO_3) was added under 85 °C and agitated for 3 h again. Then, 7.5 ml 3.2 M NH_4OAc in 20 % (v/v) HNO_3 was added and diluted to 100 ml.
5. Residual: The residues from step (4) were treated by an acid mixture of (3:3:2) $HCl/HNO_3/HF$ mixture in a microwave oven.

The modes of occurrence of heavy metals could be clustered into five parts as: exchangeable, carbonate bound, Fe–Mn oxides bound, organic matter bound and residual. After extracted, the fractions obtained by each extraction step were measured for As, Cd, Cr, Cu, Pb and Zn by ICP-

MS. In order to assess the potential mobility of heavy metals, the compliance leaching test RN 12457 Part 2 procedure was implemented (EN 12457-2 2002) in this study. Briefly, the selected soil samples were treated by deionized water at a solid-to-liquid ratio of 1:10 kg/L and agitated for 24 h. Each sample was analyzed in triplicate. The concentrations of heavy metals in leachates are measured by ICP-MS, and the anion concentrations (F^- , SO_4^{2-} and Cl^-) in leachates were determined by high-performance ion chromatography (HPIC). The quality control and reagent blanks were consistent with the procedure used for the aforementioned powered samples.

Results and discussion

The concentration of heavy metal

The contents of heavy metals in the selected soil samples were consistent with the results presented by other previous studies (Table 1) (Komnitsas and Modis 2006; Qiao et al. 2011). When compared with the background values of the Huainan historical data (Yang et al. 1997), the concentrations of As, Cd, Cu (except Panyi Mine) and Pb (except Panyi Mine and Dingji Mine) were higher in the selected soil samples. Typically for As and Cd, the concentrations of As and Cd in Xinzhuangzi Mine, Panyi Mine and Dingji Mine are about 3.4-, 2.2-, 1.4- and 2.9-, 2.1-, 1.7-fold higher than that of Huainan soil, respectively. In

Table 1 Concentration of heavy metals in the selected soils (mg/kg)

	Xinzhuangzi Mine (<i>n</i> = 10)		Panyi Mine (<i>n</i> = 10)		Dingji Mine (<i>n</i> = 10)		Background value		ERL-ERM
	Range	Average	Range	Average	Range	Average	Huainan Soil	Chinese Soil	
As	10.6–58.3	35.6 ± 12.6	11.6–33.6	23.7 ± 5.9	8.5–26.8	16.3 ± 5.4	10.5	11.2	8.2–70
Cd	0.07–0.28	0.17 ± 0.10	0.04–0.18	0.13 ± 0.06	0.06–0.20	0.10 ± 0.06	0.06	0.09	1.2–9.6
Cr	32.3–58.6	46.5 ± 8.5	26.4–58.6	43.3 ± 10.8	28.5–48.6	36.2 ± 7.6	91.5	61	81–370
Cu	24.3–50.3	34.7 ± 8.4	14.6–43.5	26.7 ± 9.4	13.5–46.2	31.6 ± 12.5	30.7	22.6	34–370
Pb	11.3.0–36.2	25.8 ± 7.5	10.8–35.7	22.4 ± 7.3	12.6–34.5	20.6 ± 7.8	23.5	26	46.7–218
Zn	28.3–57.6	42.6 ± 12.1	31.4–43.5	37.4 ± 5.9	37.4–60.8	47.3 ± 10.7	58.4	74.2	150–410

comparison with the Chinese soil (Wei et al. 1991), As, Cd and Cu are higher in the Xinzhuangzi Mine, Panyi Mine and Dingji Mine. The elevated concentrations of heavy metals in the mining activities areas indicated that the mining activities (mining, transportation, utilization and waste disposal) may be one of the sources for the heavy metal pollution in soil (Gidaracos et al. 2009; Ribeiro et al. 2010; Zhang et al. 2003). The concentrations of heavy metals increase gradually with increasing mining duration, which indicated that the coal mining activities might lead to potential environmental implications.

The concentrations of heavy metals in soil are attributed to the host mineral composition, soil physicochemical properties, soil formation mechanism and the pollution sources (Al-Khashman 2012; Candeias et al. 2014; Chen et al. 2014). Arsenic, Cd, Cu, Pb and Zn are known as chalcophile elements. There have been many investigations into the modes of occurrence of these elements in coal and reported that these elements are mainly associated with sulfide minerals (pyrite, siderite) and clay minerals (Finkelman et al. 2002; Dai et al. 2008). Under natural weathering processes, the chemical bonds of the sulfide minerals could be broken and decomposed easily through oxidation. As a consequence, these elements (As, Cd, Cu, Pb and Zn) that existed in the sulfide minerals would release from coal/coal gangue under natural weathering and dispose into the soil. Heavy metal in soil may be derived from both natural source and anthropogenic contributions. The correlation coefficients among the selected heavy metals in soils are analyzed and summarized in Table 2. The positive correlation coefficients of As with Zn ($r = 0.664$), Cd with Cu ($r = 0.675$), Cd with Zn ($r = 0.647$), Cu with Pb (0.623) and Cu with Zn ($r = 0.583$) indicate that these heavy metals may be derived from similar pollution sources (coal mining activities) and associated with sulfide minerals. For Cr, various studies demonstrated that Cr mainly existed in association with clays and organic matter (Querol et al. 1996; Finkelman et al. 2002), while Cr in the selected samples is mainly associated with residual and existed in clay minerals.

Table 2 Correlation coefficients between heavy metal in the selected soils (*n* = 30)

	As	Cd	Cr	Cu	Pb	Zn
As	1	0.397	0.047	0.478	0.432	0.664*
Cd		1	0.083	0.675*	0.395	0.647*
Cr			1	−0.136	−0.087	−0.096
Cu				1	0.623*	0.583*
Pb					1	0.458
Zn						1

* Significant at 0.05 level (two-tailed)

Therefore, the correlations were not observed between Cr and other heavy metals.

Partition behavior of heavy metal

The partition behaviors of heavy metal in soil from different coal mining activities areas are presented in Fig. 2. The speciation characterization of arsenic shows that it was mostly associated with residual, and moderate contributions were composed by Fe–Mn oxides bound, carbonate bound and organic matter/sulfides bound. The above results are in accordance with previous studies reported by Jain (2004) and Rath et al. (2009). Ward (2002) and Zhou et al. (2014b) study the association of As in coal/coal gangue and reported that As in coal/coal gangue mainly existed in residual, organic matter/sulfides bound and Fe–Mn oxides bound (Ward 2002; Zhou et al. 2014b). The proportions of residual, organic matter/sulfides bound and exchangeable As increase with the increase in mining duration. The variation of associations of As among different coal mines may be attributed to the mining activities. It is well known that there are large amounts of sulfide minerals associated in coal/coal waste; these sulfide minerals may be decomposed under various reactions (physical, chemical and biological) (Finkelman et al. 2002; Gidaracos et al. 2009). The obvious negative correlations of exchangeable, organic matter bound and sulfide with carbonate and Fe–Mn oxides bound are given in Table 3. With the decomposition of

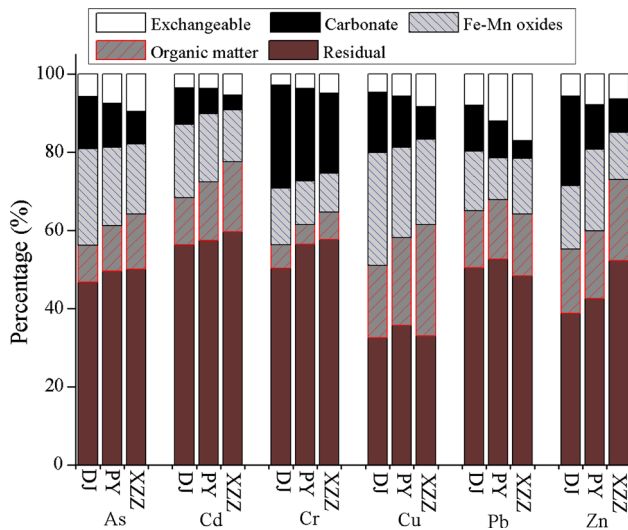


Fig. 2 Mode of occurrence of heavy metal in soil from different coal mining activities areas. *DJ* Dingji Mine, *PY* Panyi Mine, *XZZ* Xinzhuangzi Mine

sulfide minerals, the pH and redox potential are changed and result in the increase in exchangeable and organic matter/sulfide bound and the decrease in carbonate and Fe–Mn oxides bound.

Cadmium mainly existed in residual, organic matter/sulfides bound and Fe–Mn oxides, the rest being associated with carbonate bound and exchangeable (Fig. 2). Tessier et al. (1979) reported that large amounts of Cd could be presented in carbonate bound in Yamaska and St. Francois area. The low rate of carbonate bound in this study may be due to the low pH in the mining activities areas. The negative correlations of exchangeable, organic matter bound and sulfide with carbonate and Fe–Mn oxides bound are given in Table 4. The rates of residual, organic matter bound and exchangeable Cd increase with increasing mining duration, which is consistent with the partition behavior of arsenic.

The fractionation behavior of chromium in Huainan coal mines is predominantly presented in residual and carbonate bound (Fig. 2). There are also appropriate concentrations associated with organic matter bound, Fe–Mn oxides bound and exchangeable. The results are consistent with

the previous studies reported by Pardo et al. (1990) and Rath et al. (2009). The negative correlations of exchangeable and sulfide with carbonate and Fe–Mn oxides bound are given in Table 5. The residual and exchangeable fractions increase gradually with increasing mining duration.

Speciation behavior of copper shows that it is distributed among residual, organic matter/sulfide bound and Fe–Mn oxides bound (Fig. 2). Gibbs (1977) reported that Cu mainly existed in residual, while the concentration bound to Fe–Mn oxides and organic/sulfide is much lower. The different tendency of Cu in this study area may be attributed to the effect of mining activities. The negative correlations of exchangeable and organic matter bound with carbonate and Fe–Mn oxides bound are given in Table 6. The organic matter/sulfide bound and exchangeable increase, while the carbonate bound decreases with increasing mining duration.

The fractionation characterization of lead suggests that the major portion of Pb is existed in residual and moderate contributions are consisted by organic matter/sulfide bound and Fe–Mn oxides bound. Jha et al. (1990) studied Pb association in Delhi soil and reported that Pb is mainly focused on Fe–Mn oxides bound and the different modes of occurrence of Pb may be due to the different soil physicochemical properties, depositional environmental and contamination sources. The obvious negative correlations of exchangeable and organic matter bound with carbonate bound are given in Table 7. The exchangeable increases rapidly with increasing mining duration.

For zinc, the major portion is associated with residual. There are also appropriate ratios of the existence of organic matter/sulfide bound, Fe–Mn oxides bound, carbonate bound and exchangeable, which is consistent with the previous studies reported by Tessier et al. (1979), Jain (2004) and Pardo et al. (1990). The negative correlations of exchangeable, organic matter bound and sulfide with carbonate and Fe–Mn oxides bound are given in Table 8.

Potential leaching behavior and ecological risk assessment

The concentrations of heavy metals and ion in soil leachates were employed to evaluate the heavy metal mobility

Table 3 Correlation coefficients of As among different fractions

	Residual	Organic matter	Fe–Mn oxides	Carbonate	Exchangeable
Residual	1	0.912*	–0.987*	–0.876*	0.895*
Organic matter		1	–0.966*	–0.996*	0.999*
Fe–Mn oxides			1	0.942*	–0.955*
Carbonate				1	–0.999*
Exchangeable					1

* Significant at 0.05 level (two-tailed)

Table 4 Correlation coefficients of Cd among different fractions

	Residual	Organic matter	Fe–Mn oxides	Carbonate	Exchangeable
Residual	1	0.981*	−0.993*	−0.975*	0.959*
Organic matter		1	−0.955*	−0.999*	0.889*
Fe–Mn oxides			1	0.945*	−0.984*
Carbonate				1	−0.874*
Exchangeable					1

* Significant at 0.05 level (two-tailed)

Table 5 Correlation coefficients of Cr among different fractions

	Residual	Organic matter	Fe–Mn oxides	Carbonate	Exchangeable
Residual	1	0.153	−0.994	−0.913*	0.899*
Organic matter		1	−0.257	−0.541	0.569
Fe–Mn oxides			1	0.951*	−0.940*
Carbonate				1	−0.999*
Exchangeable					1

* Significant at 0.05 level (two-tailed)

Table 6 Correlation coefficients of Cu among different fractions

	Residual	Organic matter	Fe–Mn oxides	Carbonate	Exchangeable
Residual	1	0.012	−0.474	0.065	−0.134
Organic matter		1	−0.886*	−0.996*	0.989*
Fe–Mn oxides			1	0.847*	−0.808*
Carbonate				1	−0.997*
Exchangeable					1

* Significant at 0.05 level (two-tailed)

Table 7 Correlation coefficients of Pb among different fractions

	Residual	Organic matter	Fe–Mn oxides	Carbonate	Exchangeable
Residual	1	−0.402	−0.756*	0.664*	−0.543
Organic matter		1	−0.294	−0.951*	0.987*
Fe–Mn oxides			1	−0.012	−0.138
Carbonate				1	−0.988*
Exchangeable					1

* Significant at 0.05 level (two-tailed)

Table 8 Correlation coefficients of Zn among different fractions

	Residual	Organic matter	Fe–Mn oxides	Carbonate	Exchangeable
Residual	1	0.994*	−0.673*	−0.840*	0.091
Organic matter		1	−0.745*	−0.781*	−0.009
Fe–Mn oxides			1	0.166	0.674*
Carbonate				1	−0.616*
Exchangeable					1

* Significant at 0.05 level (two-tailed)

under natural conditions. The contents of heavy metals and waste acceptance criteria for landfilling according to Annex 2 of the 2003/33/CE Council Decision are given in

Table 9. The leaching rate (Lr) of heavy metal is also applied to assess the degree of the heavy metal mobility in the soil during leaching, which is defined as:

Table 9 Concentration of heavy metals of the selected soil leachates and waste acceptance criteria for landfilling according to the Annex 2 of the 2003/33/EC Council Decision

	Coal waste leachates (mg/kg)			Waste acceptance criteria (mg/kg)			Leaching rate (%)
	XZZ (<i>n</i> = 10)	PY (<i>n</i> = 10)	DJ (<i>n</i> = 10)	Inert	Non-hazardous	Hazardous	
As	0.43 ± 0.12	0.26 ± 0.05	0.13 ± 0.07	0.50	2.00	25.0	<1
Cd	NA	NA	NA	0.04	1.00	5.00	<1
Cr	0.26 ± 0.08	0.19 ± 0.07	0.16 ± 0.05	0.50	10.0	70.0	<1
Cu	1.06 ± 0.35	0.78 ± 0.46	2.13 ± 0.46	2.00	50.0	100	<1
Pb	0.19 ± 0.04	0.13 ± 0.07	0.17 ± 0.05	0.50	10.0	50.0	<1
Zn	0.23 ± 0.08	0.36 ± 0.12	0.27 ± 0.09	4.00	50.0	200	<1
F ⁻	7.11 ± 1.23	4.75 ± 1.87	3.06 ± 0.56	10	150	500	
Cl ⁻	4.54 ± 1.34	4.36 ± 1.54	5.78 ± 0.77	800	15,000	25,000	
SO ₄ ²⁻	5.27 ± 1.86	18.4 ± 3.9	5.78 ± 1.34	1000	20,000	50,000	

NA—below the limit of detection

$$Lr = \frac{\text{Heavy metal concentration in the leachates/}}{\text{Heavy metal concentration in the soil}}$$

According to Table 9, the leaching rates of all the selected heavy metal are less than 1 %. When compared with the contents of heavy metals in the leachates with the waste acceptance criteria for landfilling stated in the Annex 2 of the Council Decision (2003/33/CE), the concentrations of the selected heavy metals were lower than the limit values.

International sediment quality guidelines (SQGs) calculations, such as effects range low (ERL) and effects range median (ERM), were applied to assess the biological toxicity of heavy metals (As, Cd, Cr, Cu, Pb and Zn) in soil. The ERM values are chemical concentrations above which adverse effects are likely to occur, while the ERL values represent the contents lower than the potential adverse effect concentrations (Long et al. 1995). The incidence of toxicity is determined among samples in which none of the samples is higher than the ERL values (<ERL values), in which one or increasing numbers of chemicals exceed ERL values, but none is lower than ERM values (>ERL values and <ERM values), and in which one or increasing numbers of substances exceed ERM concentration (>ERM values) (Pekey et al. 2004). The ERL and ERM values for the heavy metals are given in Table 1. The concentrations of Cd, Cr, Pb and Zn in all the selected samples are lower than ERL, which suggested that the adverse biological effects are expected to be negligible. For As and Cu, 65 and 46 %, respectively, those are in the middle range, which indicated that occasional adverse biological effects are predicted. None of the samples exceed the ERM values.

According to the results of the sequential chemical extraction procedures, heavy metals in soil are associated with different species. The partition behaviors of heavy

metals could be employed as an indication to evaluate the potential ecological risk (Dellantonio et al. 2008; Rath et al. 2009). The risk assessment code (RAC) classified that heavy metals could be regarded as safe (no risk) to the ecosystem when the exchangeable and carbonate bound are less than 1 % of the total values. In contrast, once the fractions of exchangeable and carbonate bound of any of these heavy metals are more than 50 % of the totals values, these heavy metals could be resulted in a strong environmental impacts (very high risk). Meanwhile, 1–10, 11–30 and 31–50 % of RAC values could be regarded as low risk, medium risk and high risk, respectively (Perin et al. 1985). According to the fractionation profiles of the selected heavy metals (Fig. 2), the RAC values of the selected heavy metals reveal that these heavy metals could pose a medium risk to the ecosystem. Therefore, the environmental impacts induced by heavy metals in mining activities areas soil deserve further concern.

Conclusions

The concentrations of heavy metals increase with increasing mining duration, which indicated that the mining activities are the important sources for the heavy metal pollution in soil. The fractionation profiles are various among different heavy metals. For As, Cd, Cr and Zn, the proportions of residual bound, organic matter bound and exchangeable bound increase with increasing mining duration. Based on the leaching experiment, the concentrations of the selected heavy metals were lower than the limit values. According to the international sediment quality guidelines (SQGs) calculations, the adverse biological effects caused by Cd, Cr, Pb and Zn of all samples are expected to be negligible. For As and Cu, occasional adverse biological effects are predicted. Based on the risk

assessment code (RAC), the RAC values of the selected heavy metals reveal that these heavy metals could pose a medium risk to the ecosystem. Therefore, the environmental impacts induced by heavy metals in the selected mining activities areas soil may be caused if no counter-measures are adopted.

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