



Geochemical evaluation of heavy metal migration in Pb–Zn tailings covered by different topsoils



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ABSTRACT

Heavy metal migration was evaluated in Pb–Zn tailings covered by different topsoil constructions. The four topsoil constructions each had different interlayers: one with direct topsoiling above the tailings (CT); the second had a limestone interlayer between the tailings and topsoil with two geotextile layers set above and below the interlayer (SLS); the third had a lime interlayer, also with two geotextile layers (SL); and the fourth had a clay interlayer with two geotextile layers (SC). The topsoils were evaluated in a 210-day laboratory column leaching experiments and in a 3-year field cover application at an abandoned Pb–Zn tailings pond (northeastern China). The contents of Pb, Zn and Cd in the soils, leachates, interlayers and leaves of *Amorpha fruticosa* L. were analysed by inductively coupled plasma optical emission spectroscopy (ICP-OES).

Results showed that the pH values of the leachates from the columns increased with time, from 6.5 to the range of 7.5 to 8.03, and the maximum in pH in C1 (tailings), C2 (CT), C3 (SLS), C4 (SL) and C5 (SC) appeared after the 180th day, at 7.85, 7.89, 7.78, 8.03, and 7.89, respectively. The topsoil effectively reduced the concentrations of Pb, Zn and Cd in the leachate, and the addition of a limestone or lime interlayer enhanced the efficiency, especially for Zn and Cd. The Pb, Zn and Cd concentrations in the topsoil that directly cover the tailings were appreciably less than the initial concentrations, resulting from the eluviation. The presence of a limestone or lime interlayer reduced the mobility of Zn and Cd, and a clay interlayer was effective in preventing the migration of Pb and Zn but had less impact on Cd.

During the 3-year field experiment, the pH values of the topsoil increased slightly with time, from 7.15 to the range of 7.67 to 8.20. At the end of the experiment, Pb, Zn and Cd concentrations in the topsoil at the SLS, SL and SC plots showed little change compared with the initial value in 2012. Acid-soluble Pb, Zn and Cd concentrations of the upper soil (0–0.1 m) at CT increased from 0.19, 1.95 and 0.11 mg kg⁻¹ in 2012 to 1.82, 32.87 and 0.56 mg kg⁻¹ in 2015, indicating that acid-soluble heavy metals migrated from tailings to topsoil. Acid-soluble Cd in topsoil and in the interlayer showed a small increase at plot SC, indicating that Cd may migrate through the clay layer to topsoil with pore water. The Pb contents in leaves at SLS and SL were 2.38 and 3.04 mg kg⁻¹, which were appreciably lower than at CT and SC, and the Zn and Cd contents in leaves at CT were 45.78 and 0.26 mg kg⁻¹, which were higher than at SLS, SL and SC. Topsoiling with an interlayer could be a reliable technique for preventing toxic elements from moving downward or upward during ecological restoration of tailings ponds.

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1. Introduction

Mining of minerals promotes rapid development of the economy, but it also causes serious environment pollution. Tailings are a major type of solid waste that is generated by the mining process, and they are discharged with water into tailings ponds to be stored. However, most of the tailings are left without any management after mine closure (Rashed, 2010). Toxic elements in tailings are prone to leaching into the surrounding environment by water and wind (Zanuzzi et al., 2009;

Rowe and Hosney, 2013). In addition, acid mine drainage (AMD) generated by sulphide oxidation may be a concern for ecological restoration of tailings ponds. Acidification enhances the mobility of heavy metals and causes failure of revegetation schemes (Yang et al., 2010; Gbadebo and Ekwue, 2014; Piyush et al., 2007; Marescotti et al., 2008).

Low nutrient content, poor physical structure and high levels of heavy metals in the tailings are the major problems for successful tailings pond reclamation (Tordoff et al., 2000). Dry cover and wet cover are two common techniques used in tailings pond remediation to prevent sulphide oxidation (Lu et al., 2013). Topsoiling is part of a dry cover application, and it plays a vital role in the success of vegetation. Topsoiling and vegetation can be a permanent and visually attractive solution for ecological

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restoration of tailings ponds, and they can be relatively inexpensive (Vangronsveld and Cunningham, 1998). However, reclaimed mine soils are man-made habitats, which may cause problems for establishing vegetation, and they are more vulnerable to heavy metal pollution (Wong, 2003). In addition, heavy metals in soil may be uptaken by plant roots and accumulated in above-ground tissues. Leaf deposition and degradation can thereby result in an increase in accumulation of metals in the topsoil, or they can become a part of the food chain (Mertens et al., 2004; Unterbrunner et al., 2007).

Many studies of heavy metal migration in reclaimed mine soil have been carried out (Kabas et al., 2012; Rodríguez-Jordá et al., 2012; Boruvka et al., 2012). A column experiment was conducted by D. Zhu et al. (1999) to evaluate the heavy metal leaching from mine tailings and contaminated soil covered by soil and plants. Although plants generally reduced the total amount of water leached from the column, the total mass of Zn and Cd leached was not impacted by plants. pH and heavy metals in topsoil are prone to be affected by the tailings substrate. The migration of soil water is a major transport pathway for pollution, and heavy metals may also move upwards to the topsoil due to evaporation and suction of soil (Dold and Fontboté, 2002). Cheong et al. (2012) evaluated the seasonal rainwater infiltration on ground and surface water quality in the abandoned Gyopung mine. It was concluded that 0.2 m thick topsoil on the tailings was not enough to prevent migration of heavy metals.

An interlayer including a capillary break layer, a low-permeable layer and a solidified layer between tailings and topsoil can effectively limit the water infiltration and mobility of metals. Materials such as paper mill by-products, coal ash, phosphate limestone wastes and sewage sludge are typically used in cover systems for tailings pond remediation projects (Pérez-López et al., 2007a; Bossé et al., 2013; Nason et al., 2014). Ahn et al. (2011) assessed a cover system on tailings, and a solidified layer of calcium silicate was efficient in reducing water infiltration, sulphide oxidation and acid generation. Heavy metals were stabilized as carbonate-bound phases, and sulphide minerals were surrounded by a calcium silicate matrix, preventing further reaction. Jia et al. (2014) assessed the effect of alkaline paper mill residuals on controlling the mobility of metals from the tailings, and the presence of the alkaline materials consistently reduced the mobility of Cd, Cr, Mn, Ni and Zn.

Quispe et al. (2013) tested a strategy for the treatment of acid mine drainage by addition of an alkaline cover of fly ash on two sulphide mine tailings ponds. The application of the fly ash cover significantly reduced the bioavailability of most of the elements, and the formation of the hardpan reduced the rate of sulphide oxidation. This remediation strategy is based on the self-isolation of the tailings by inducing the formation of a cemented layer by adding an alkaline layer (Chermak and Runnells, 1997; Quispe et al., 2013).

Geotextiles have also been extensively used in cover systems as hydraulic and pollution barriers in remediation projects at contaminated sites (Mazzieri et al., 2013; Hosney and Rowe, 2014). Hosney and Rowe (2013) investigated the field performance of three geosynthetic clay liner (GCL) products covered with local soil in a test cover over arsenic-rich tailings at a former gold mine in Nova Scotia. The GCL served as an effective barrier to arsenic migration, and the presence of a foundation layer between the tailings and GCL impeded the arsenic migrate from tailings into the GCL.

The effectiveness of a sealing cover system could vary from one site to another due to the characteristics of the tailings and covering materials, local climatic conditions and the type of topsoil construction. However, the relative role of these variables is presently unknown (Hosney and Rowe, 2013). In this study, a 210-day laboratory column leaching experiment and a 3-year field application were conducted to evaluate the migration of heavy metals at an abandoned Pb–Zn tailings pond (northeast China) covered by topsoil with different interlayers. The primary objective of this paper is to examine the changes of Pb, Zn and Cd in topsoil and to evaluate the performance of different topsoil constructions on heavy metal migration. The contents of Pb, Zn, and Cd in topsoil, leachates, interlayers and leaves of *Amorpha fruticosa* L. were evaluated.

2. Materials and methods

2.1. Site description and characterization of tailings

The Chaihe lead–zinc mine is located in Kaiyuan, Liaoning Province, northeast China. The study area has a temperate continental monsoon climate with an annual temperature of 5–7.3 °C, a mean annual precipitation of 678 mm and an evaporation of 1200 mm. The ore was processed by flotation to obtain zinc and lead (Hu et al., 2009). The tailings pond was abandoned for 22 years, and a small amount of weeds was growing on the surface. A 46 m high dam was constructed by the upstream embankment method. The total volume of tailings was approximately $2.284 \times 10^6 \text{ m}^3$. The tailings were discharged with water into the pond to be stockpiled, and they contained various heavy metals such as Pb, Zn, Cd, Cr and Hg.

The tailings pond was reclaimed in October 2012. The work contained dam strengthening, topsoiling, vegetation, and road and drainage construction. The tailings pond was covered by 0.3 m of soil, and the reclamation soil was dark brown and taken from the surrounding area. *A. fruticosa* L. was used for vegetation at a spacing of $1.5 \times 1.5 \text{ m}$. The study area was approximately 5400 m² and located in the northeast of the tailings pond (Fig. 1).

The field experiment was conducted at four plots. There was an interlayer between the tailings and the 0.3 m of topsoil at SLS, SL and SC (Fig. 1), and two geotextiles were set above and below the interlayer to prevent tailings from entering the interlayer materials and topsoil.

Two composite soil samples (0–0.1 m and 0.1–0.2 m in depth) were collected at four different sampling points in each plot at 1-, 1.5-, 2- and 3 year intervals after reclamation. Soil samples were air dried and passed through a 2 mm sieve.

Leaves of *A. fruticosa* L. around each soil sampling point were gathered and mixed into one composite sample. Leaves were washed in tap water and rinsed three times with distilled water. Leaves were dried at 40 °C to constant weight, and the dried leaves were ground and passed through a 2 mm sieve.

The mean values of selected heavy metal concentrations in tailings, reclaimed soil and clay were listed in Table 1. The concentrations of Pb, Zn, and Cd in tailings were 649.4 mg kg⁻¹, 2285 mg kg⁻¹, and 11.04 mg kg⁻¹, respectively, exceeding the thresholds of soil environment quality standards (GB15618–1995).

The tailings in the Chaihe lead–zinc mine belong to carbonate rock, and the gangue minerals were primarily dolomite (80–90%), quartz (6–8%) and calcite (1–2%); the tailings contained much soluble salt. The zinc minerals were primarily smithsonite, sphalerite and willemite, and the lead minerals were primarily cerussite, anglesite, galena and vanadinite. The total sulphur content in raw ore was 1.05% (Guo et al., 1988).

The net acid generation test (NAG) was used to predict the acid-forming potential of tailings. A sample of 2.5 g of tailings was soaked in 250 ml of 15% H₂O₂ for 24 h and then boiled for 1 h (Liao et al., 2007). The final NAG-pH was measured by a pH-meter (PHS-3C) after the mixture cooled to room temperature. The pH value of the tailings in the Chaihe lead–zinc mine was 8.23, and the NAG-pH of the tailings was 8.38, which implies non-acid-forming tailings.

2.2. Column experiments in the lab

Five leaching columns were made of PVC tubes (1.5 m high and 0.2 m in diameter). A conical cap was set in the bottom of the tube, and a 2 cm circular hole was drilled in the bottom cap to act as an exit port for leachate collection. A total of 7 holes (4 cm in diameter) were set at 0.2 m intervals on the tube for soil sampling at the end of the column leaching experiment (Fig. 2).

Tailings used in the column experiments were derived from the Chaihe Pb–Zn mine tailings pond. The tailings were carried back to the lab, air dried and mixed.

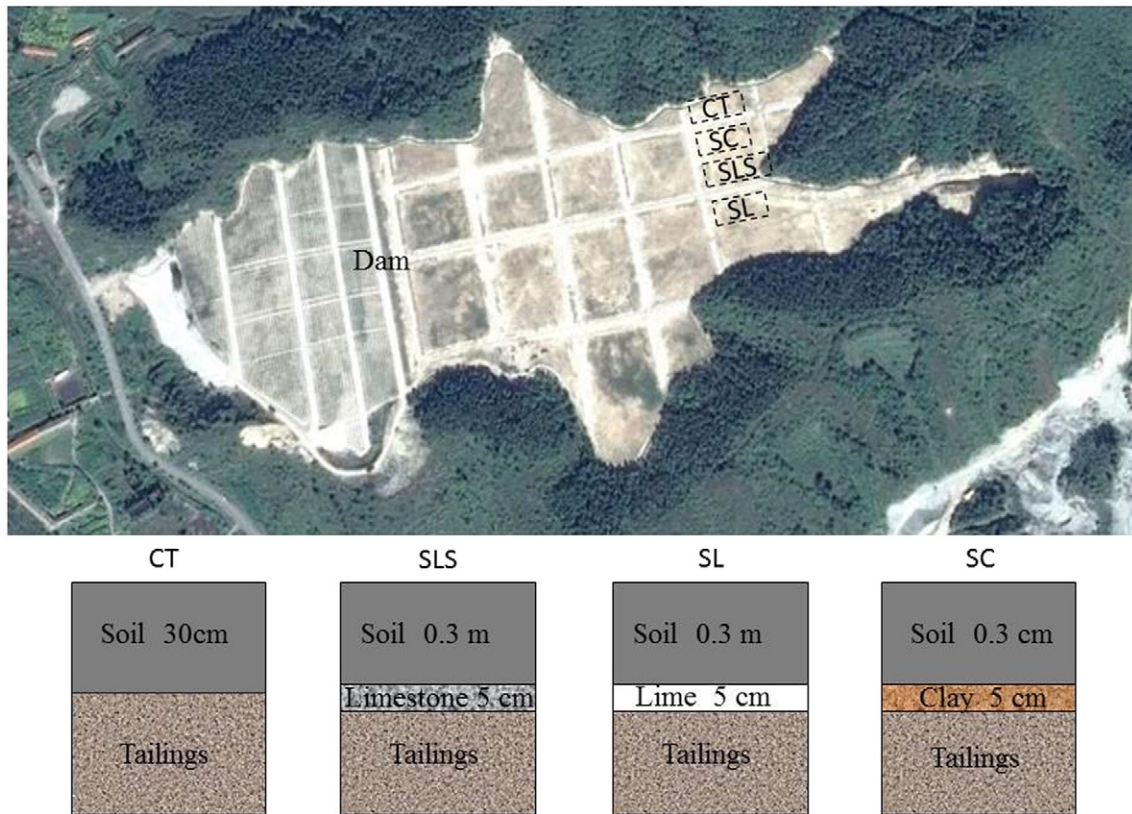


Fig. 1. Location and design of the different topsoil constructions in plots CT, SLS, SL and SC at the Chaihe tailings pond.

The topsoil constructions in the columns are listed in Table 2. Columns C3, C4 and C5 consist of 0.95 m tailings covered by 0.5 m topsoil, with a 5 cm interlayer of limestone, lime and clay between the tailings and the soil. The interlayer materials were filled into a geotextile bag (cylindrical, approximately 0.2 m in diameter and 5 cm thick) to prevent movement of the materials.

The columns were irrigated with 2 L of deionized water (64 mm of rainfall, which corresponds to the average monthly precipitation in Chaihe) at a rainfall intensity of 29 ml/min (local maximum rainfall intensity: 150 L/s h m²) on a monthly basis over a period of 210 days. Filter paper was set on the top of the soil to prevent erosion. The leachate from the column was sampled once per month during the period from April to October 2013. The leachate was collected in a glass beaker with the opening covered with parafilm, and then it was filtered with a filter membrane (diameter 9 cm, pore size 0.45 μm). The pH of the leachate was determined every month using a pH metre (PHS-3C), and the concentrations of heavy metals in the leachate were measured by inductively coupled plasma optical emission spectroscopy (ICP-OES).

After the leaching column experiments were terminated, soil samples were obtained with a geotome at 7 different layers from each column. The interlayer materials in the geotextile bag were taken out from C3, C4 and C5. Samples were air dried and passed through a 2 mm sieve for chemical analysis.

Table 1
Mean values (± S.D.) of selected heavy metals concentration in raw materials (n = 3).

	Tailings	Soil	Clay
Cd(mg kg ⁻¹)	11.04 ± 0.07	0.46 ± 0.07	0.49 ± 0.02
Cr(mg kg ⁻¹)	0.74 ± 0.22	5.75 ± 0.21	5.75 ± 0.21
Cu(mg kg ⁻¹)	15.89 ± 0.25	10.17 ± 0.65	12.37 ± 0.74
Ni(mg kg ⁻¹)	1.73 ± 0.70	10.87 ± 0.37	13.52 ± 0.29
Pb(mg kg ⁻¹)	649.4 ± 2.0	15.04 ± 1.14	15.31 ± 1.58
Zn(mg kg ⁻¹)	2285 ± 36	53.82 ± 5.39	69.10 ± 8.26

2.3. Analytical methods

Soil pH values were measured by a pH metre (PHS-3C) (solid to water ratio = 1:2.5). For determination of the total content of heavy metals, soil samples were digested with a mixture of HCl–HNO₃–HF–HClO₄ (10:15:10:5, v/v). The acid-soluble fraction was extracted with 0.11 ml L⁻¹ of HOAc (Sahuquillo et al., 1999; Rauret et al., 1999). The concentrations of heavy metals in the extractants were measured by ICP-OES.

Heavy metal concentrations (Pb, Zn and Cd) in the Leaves of *A. fruticosa* L. were measured by ICP-OES after digestion of dry matter with a mixture of HNO₃–HClO₄, at 5:1 (v/v) (Allen, 1989). All samples were measured in triplicate, and the analytical error for selected trace elements was smaller than 3%.

3. Results and discussion

3.1. Leaching column experiment

3.1.1. Changes in pH and heavy metal concentrations of the leachate

The pH values of the leachates from the columns increased in the first four months (Fig. 3). The maximum of pH values in C1, C2, C3, C4 and C5, appearing on the 180th day, were 7.85, 7.89, 7.78, 8.03, and 7.89, respectively. The pH value of the leachate from C1 was slightly lower than those of the other columns, possibly due to the oxidation of sulphide minerals such as sphalerite and galena. In the initial flush of the experiment, low pH values of the leachates were due to the washing of pre-existing sulphide oxidation products (Pan et al., 2007). The increase of pH in the leachate during the experiment was probably caused by the dissolution of carbonate minerals in the tailings (Pan et al., 2007).

The highest Pb concentrations in the leachates from C1, C2, C4 and C5, occurring on the 30th day, were 0.053, 0.047, 0.031 and 0.037 mg L⁻¹, respectively. The Pb concentration in the leachate from

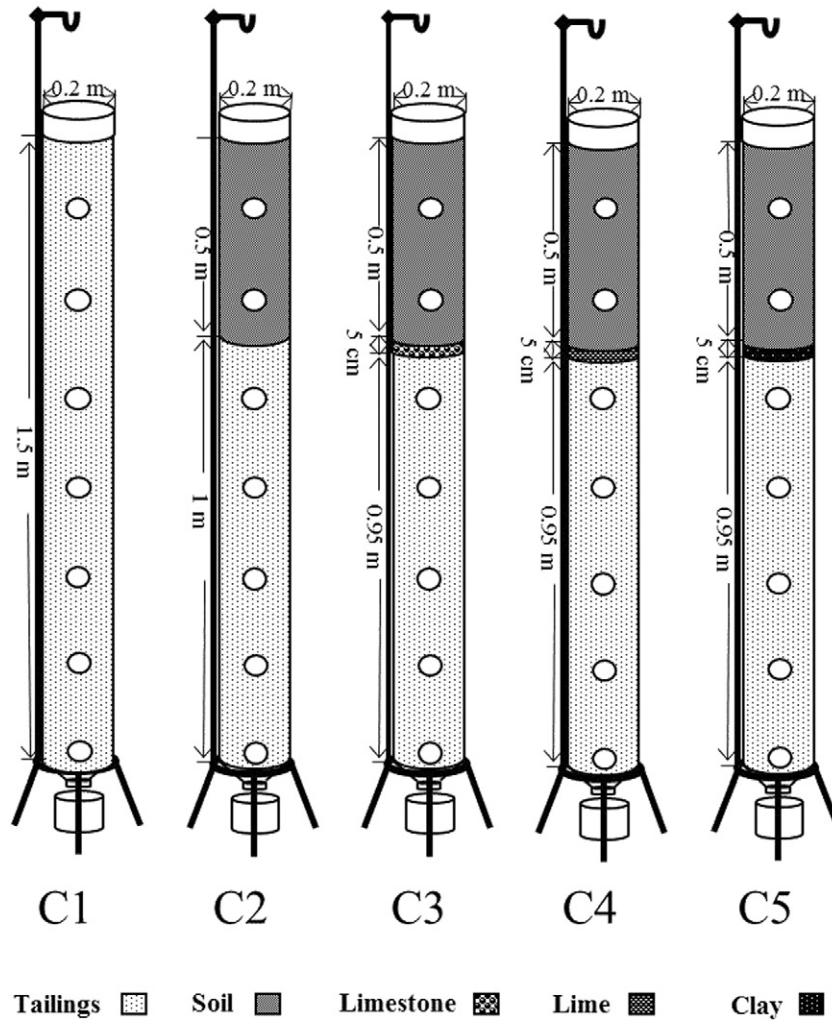


Fig. 2. Design of leaching columns.

C1 showed a larger and more irregular variation compared with C2, C3, C4 and C5. Pb concentrations in the leachates from C1 on the 30th day and the 120th day were higher than the threshold of the surface water environmental quality standard (GB3838-2002) (0.05 mg L^{-1}). Pb concentrations in the leachates from C2, C4 and C5 showed similar variation, with the highest concentration at the start of the experiment, and they decreased to a low level on the 60th day and increased to approximately 0.02 mg L^{-1} on the 90th day. After the 120th day, the Pb concentration decreased steadily from 0.02 mg L^{-1} to 0.01 mg L^{-1} , and there were no significant differences between C2, C4 and C5. However, the Pb concentration in the leachate from C3 increased from the 120th to the 180th day and decreased to 0.004 mg L^{-1} on the 210th

day. The lower Pb concentrations in the leachates from C3, C4 and C5 were due to the high pH, and the topsoil with a lime or clay interlayer could reduce the oxygen transport and prevent the oxidation of sulphide minerals (sphalerite and galena).

The concentration of Zn in the leachate from C1 increased with time over a period of 120 days, and a maximum concentration of 5.98 mg L^{-1} was obtained on the 120th day, whereas it decreased steadily to approximately 3.3 mg L^{-1} on the 180th day. Changes in concentrations of Zn in the leachates from C4 were similar to those in the leachates from C5: the highest concentrations of both were obtained on the 30th day (3.88 and 5.34 mg L^{-1} , respectively), and they decreased sharply to 1.11 and 1.98 mg L^{-1} on the 60th day and then reached stable levels of 0.7 – 1.7 and 1.9 – 2.7 mg L^{-1} . This indicated that an interlayer of clay or lime reduced the Zn concentration over a short time frame.

After 60 days of leaching, the concentrations of Zn in the leachates from all of the columns exceeded the threshold of surface water environmental quality (GB3838-2002) (1 mg L^{-1}), and they follow the order $C4 < C3 < C5 < C2 < C1$. The concentrations of Zn in the leachates from C3 and C4 were close to the threshold and lower than the integrated wastewater discharge standard (GB8978-1996) (2 mg L^{-1}). This may be due to the high pH because Zn is sensitive to changes in pH (Hu et al., 1999), and it seems that the limestone and lime layers promote weak alkaline conditions, which reduced the Zn concentration.

The concentrations of Cd in the leachates from all of the columns were high at the start of the experiment, and they decreased to a low level on the 60th day. However, the concentration of Cd increased with time

Table 2
Topsoil reconstruction and maximum moisture capacity.

Column	Topsoil reconstruction	Maximum moisture capacity (%)
C1	1.5 m tailings	17.75
C2	1 m tailings + 0.5 m soil	23.57
C3	0.95 m tailings + geotextile + 5 cm limestone + geotextile + 0.5 m soil	24.50
C4	0.95 m tailings + geotextile + 5 cm lime + geotextile + 0.5 m soil	27.60
C5	0.95 m tailings + geotextile + 5 cm clay + geotextile + 0.5 m soil	24.54

Note: Maximum moisture capacity = (Input – Output) / Column volume.

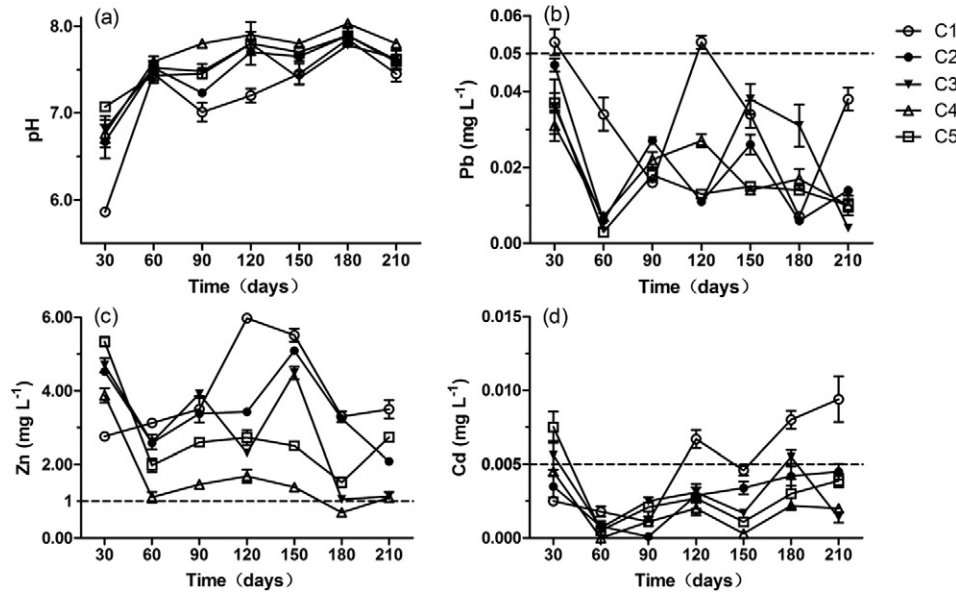


Fig. 3. Changes in pH and the concentrations of Pb, Zn, and Cd of leachates from each column. Mean values \pm S.D. are shown ($n = 3$). Note: – Level 4 standard of the surface water environmental quality (GB3838-2002).

after the 60th day, and the highest concentration of Cd in the leachate (0.0094 mg L^{-1}) was observed in C1 at the end of the experiment. The concentrations of Cd in the leachates followed the order $C3 < C4 < C5 < C2 < C1$, and the concentrations of Cd in the leachates from C2, C3, C4 and C5 did not exceed the threshold of the surface water environmental quality standard (GB3838-2002) (0.005 mg L^{-1}). However, there was a potential environmental risk because the concentration of Cd had a tendency to increase.

At the beginning of the experiment, the concentrations of selected metals in the leachates were higher, and pH values were lower, which was due to the washing of existing oxidation products, such that the metals adsorbed on the sulphide mineral surfaces may be released into solution (Hu et al., 1999). The increase in concentrations of Pb, Zn and Cd in the leachate from C1 indicated that the sulphide oxidation occurs during the test period.

Topsoiling with or without an interlayer could effectively reduce the concentrations of Pb, Zn and Cd in the leachate by preventing sulphide oxidation, and topsoiling with a limestone or lime layer further reduced

the concentrations of Zn and Cd in the leachate. The carbonates in the tailings are sufficient to neutralize the acid generated from oxidation of sulphides, and the oxidation of sulphides in the tailings will not result in long-term lowering of the pH (Hu et al., 1999; Ma et al., 2009).

3.1.2. Changes in heavy metal concentrations of different column layers

Topsoil could be affected by underlying tailings via evaporation and suction of soil (Dold and Fontboté, 2002), and an interlayer could efficiently impede the migration of metals from tailings into the topsoil (Ahn et al., 2011; Hosney and Rowe, 2013). The remaining tailings and upper soils were analysed at the end of the column experiment (Table 3), and the mass loss of the tailings and upper soils due to leaching was calculated (Table 4).

As shown in Tables 3 and 4, the total concentrations of Pb, Zn and Cd in topsoil were appreciably lower than the initial concentration in C2. That was due to the strong eluviation, with soluble Pb, Zn and Cd moving downward with water.

Table 3
Total concentrations of Pb, Zn, Cd at different depths in the columns. Mean values \pm S.D. are shown ($n = 3$).

	Depth	C1	C2	C3	C4	C5
Pb	0.2 m	660.7 \pm 17.4	11.9 \pm 0.6	14.4 \pm 2.3	15.8 \pm 0.6	14.5 \pm 1.1
	0.4 m	644.6 \pm 28.5	11.6 \pm 5.0	15.6 \pm 0.3	14.2 \pm 1.1	12.4 \pm 2.2
	0.6 m	638.1 \pm 13.6	637 \pm 10.7	616.7 \pm 7.4	546.9 \pm 6.7	660.4 \pm 2.9
	0.8 m	675 \pm 12.8	627.4 \pm 5.5	666.8 \pm 5.2	704.1 \pm 13.8	657.1 \pm 23.4
	1.0 m	638.2 \pm 7.3	669.1 \pm 16.3	667.5 \pm 18.9	642.7 \pm 15.5	641.9 \pm 37.8
	1.2 m	618.7 \pm 23.7	651.9 \pm 13.7	639.1 \pm 8.9	664 \pm 18	647.6 \pm 18.7
	1.4 m	655.9 \pm 21.7	618.9 \pm 31.5	662.0 \pm 14.2	657.3 \pm 10.2	633.5 \pm 18.2
Zn	0.2 m	2247 \pm 14	46.9 \pm 0.9	53.5 \pm 13.7	53.5 \pm 14.0	40.1 \pm 3.1
	0.4 m	2209 \pm 46	40.4 \pm 3.7	39.3 \pm 3.8	41.9 \pm 16.2	27.9 \pm 7.9
	0.6 m	2165 \pm 18	2156 \pm 61	2156 \pm 54	2222 \pm 22	2206 \pm 10
	0.8 m	2302 \pm 17	2155 \pm 15	2316 \pm 20	2294 \pm 24	2238 \pm 20
	1.0 m	2196 \pm 16	2322 \pm 33	2370 \pm 37	2273 \pm 13	2296 \pm 55
	1.2 m	2242 \pm 73	2279 \pm 69	2312 \pm 67	2275 \pm 22	2277 \pm 15
	1.4 m	2262 \pm 18	2229 \pm 75	2286 \pm 80	2226 \pm 139	2280 \pm 3
Cd	0.2 m	10.36 \pm 0.15	0.07 \pm 0.06	0.37 \pm 0.10	0.42 \pm 0.12	0.53 \pm 0.06
	0.4 m	10.33 \pm 0.22	0.14 \pm 0.07	0.39 \pm 0.05	0.36 \pm 0.02	0.52 \pm 0.03
	0.6 m	10.24 \pm 0.09	10.84 \pm 0.38	10.64 \pm 0.21	10.56 \pm 0.18	10.80 \pm 0.25
	0.8 m	10.71 \pm 0.04	10.51 \pm 0.04	11.31 \pm 0.20	10.50 \pm 0.05	10.67 \pm 0.06
	1.0 m	10.30 \pm 0.13	10.91 \pm 0.16	11.04 \pm 0.24	10.37 \pm 0.15	10.40 \pm 0.18
	1.2 m	10.41 \pm 0.36	10.80 \pm 0.14	10.65 \pm 0.20	10.37 \pm 0.28	10.32 \pm 0.31
	1.4 m	10.69 \pm 0.12	10.45 \pm 0.30	10.63 \pm 0.20	10.43 \pm 0.29	10.32 \pm 0.24

Table 4

Mass loss (%) due to the column experiment.

	Depth	C1	C2	C3	C4	C5
Pb	0.2 m	-1.74	22.52	4.88	-5.16	4.10
	0.4 m	0.75	24.26	-3.61	5.66	18.46
	0.6 m	1.75	1.92	5.06	15.84	-1.69
	0.8 m	-3.96	3.41	-2.68	-8.44	-1.19
	1.0 m	1.74	-3.04	-2.79	1.04	1.17
	1.2 m	4.75	-0.38	1.59	-2.25	0.28
	1.4 m	-1.01	4.72	-1.95	-1.22	2.45
Zn	0.2 m	1.67	12.74	0.51	0.61	25.58
	0.4 m	3.40	24.93	26.96	22.17	48.26
	0.6 m	5.34	5.73	5.73	2.77	3.52
	0.8 m	-0.77	5.79	-1.36	-0.42	2.11
	1.0 m	3.97	-1.63	-3.77	0.54	-0.48
	1.2 m	1.91	0.26	-1.18	0.44	0.34
	1.4 m	1.05	2.50	-0.05	2.61	0.21
Cd	0.2 m	6.14	84.62	18.71	7.65	-14.69
	0.4 m	6.46	70.04	15.32	21.26	-12.26
	0.6 m	7.26	1.85	3.61	4.32	2.21
	0.8 m	2.95	4.82	-2.45	4.86	3.38
	1.0 m	6.68	1.17	0.04	6.05	5.77
	1.2 m	5.73	2.17	3.56	6.07	6.51
	1.4 m	3.17	5.39	3.71	5.49	6.54

The negative value indicated a net increase in mass. The negative value in the topsoil can be due to the effect of under tailings.

The total concentration of Pb at 0.4 m depth in C3 increased by 3.61%, which may be due to the release of soluble metals from the upper soil and retention at 0.4 m depth. The total concentrations of Cd in soil increased by 14.69% and 12.26% in soil at 0.2 m and 0.4 m depths in C5, indicating that Cd in the underlying tailings may move upward into the soil.

The total concentrations of Pb, Zn and Cd in tailings decreased at 0.6 m depth in each column. The total mass losses of Pb from tailings in C2, C3, C4 and C5 were 6.62%, -0.76%, 4.96% and 1.03% (the negative value indicated a net increase in mass); the total mass losses of Zn were 12.66%, -0.64%, 5.94% and 5.70%; and the total mass losses of Cd were 15.41%, 8.48%, 26.78% and 24.42%, respectively. The total mass losses of Pb, Zn and Cd from C2 were appreciably higher than those from C3, C4 and C5, of which C3 has the lowest mass losses. The presence of a lime interlayer could reduce the mobility of Zn and Cd, and a clay interlayer was effective in preventing the migration of Pb and Zn but had less impact on Cd. Lime can react with water and CO₂ to form a hardpan layer that could act as an oxygen and water diffusion barrier (Blowes et al., 1991; Pérez-López et al., 2007b; Lin, 1997). In addition, hydrated lime could stabilize the metals released from tailings and impede further dissolution.

The 210-day leaching column experiment was only a short-term evaluation, and the simulated rainfall (64 mm) was irrigated once per month. Therefore, eluviation plays a strong role in the migration of heavy metals, and the concentrations of heavy metals in topsoil generally decreased. However, local climate conditions were different compared with lab conditions, and the effectiveness of different topsoil constructions under field conditions needs continuous monitoring.

3.2. Field experiment

3.2.1. Changes in pH values of soil

The pH values of tailings were 7.85–8.23, and the initial pH values of topsoil were 7.15–7.28, those of clay were 7.20–7.32, and those of lime were 12.65–12.81. During the three years of the field experiment, the pH values of topsoil at different plots varied in the range of 7.67–8.21 (Fig. 4a–b), and there was no significant difference between 0 and 0.1 m and 0.1–0.2 m. The pH values of topsoil at SL and SLS were slightly higher than at other plots, and the pH values of topsoil at 0–0.1 m increased with the reclamation time.

The increase in pH value at CT probably resulted from the movement of rainwater. Rainwater could infiltrate down into the tailings layer and move upward to the topsoil by evaporation and capillary action, thereby increasing the pH values of topsoil (Juwarkar et al., 2010; Ganjegunte et al., 2009). The pH values of topsoils with limestone or lime layers were appreciably higher than in other plots but still within the bounds of suitable pH for vegetation growth.

3.2.2. Changes in heavy metal concentrations of soil

3.2.2.1. Total concentration. Total concentrations of Pb, Zn and Cd in reclaimed soil are shown in Fig. 5. The mean concentrations of Pb, Zn and Cd in 2012 were 24.80, 86.18 and 2.42 mg kg⁻¹, respectively.

The total concentrations of Pb and Zn at 0–0.1 m soil were 32.89 and 102.37 mg kg⁻¹ at the SL plot in October 2013, and they increased to 63.18 and 182.40 mg kg⁻¹ in May 2014 then decreased to 22.68 and 74.37 mg kg⁻¹ in October 2014 (Fig. 5a–b).

The total concentrations of Cd in soil measured in 2015 were slightly lower at the SL and SC plots compared with those measured in 2012. The total concentrations of Cd in soil at 0–0.1 m depth fluctuated more easily than at 0.1–0.2 m, and the highest concentration (3.49 mg kg⁻¹) was observed in soil at 0.1–0.2 m depth at the CT plot in October 2015 (Fig. 5c, f).

After three years of the experiment, the total concentrations of Pb, Zn and Cd at plot CT were appreciably higher than the initial concentration in 2012, and the total concentrations of Pb, Zn and Cd at the SLS, SL and SC plots were similar or even lower than the concentrations in 2012 (Fig. 5a–f). These results imply a risk of heavy metal pollution for reclaimed soil in tailings ponds. However, the addition of an interlayer was effective in preventing the upward migration of heavy metals.

3.2.2.2. Acid-soluble fraction. At plot CT, after three years of the field experiment, the mean acid-soluble concentrations of Pb, Zn and Cd in topsoil increased appreciably (Fig. 6). The Pb concentration in 0–0.1 m soil increased from 0.19 mg kg⁻¹ in 2012 to 1.82 mg kg⁻¹ in 2015, the Zn concentration increased from 1.95 mg kg⁻¹ in 2012 to 32.87 mg kg⁻¹ in 2015, and the Cd concentration increased from 0.11 mg kg⁻¹ in 2012 to 0.56 mg kg⁻¹ in 2015. In the 0.1–0.2 m soil horizon, the highest concentrations of Pb, Zn and Cd were also observed in 2015: 1.91, 33.32 and 0.69 mg kg⁻¹, respectively. The acid-soluble concentrations of Pb, Zn and Cd at plot CT in 0.1–0.2 m soil were slightly higher than in 0–0.1 m soil. Acid-soluble concentrations of Pb, Zn and Cd were higher in

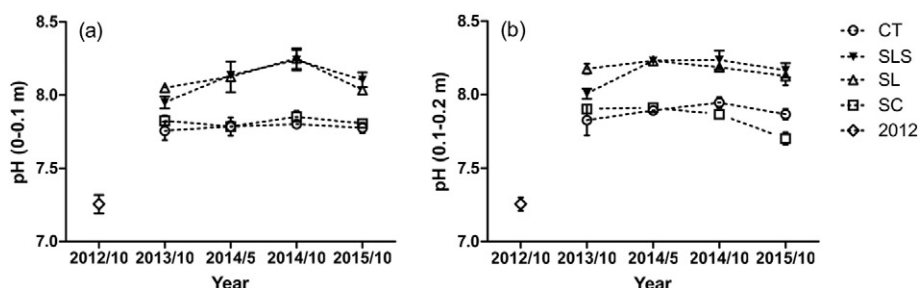


Fig. 4. Changes in the pH values of soil during the field experiment. (a) 0–0.1 m depth and (b) 0.1–0.2 m depth. Mean values \pm S.D. are shown ($n = 3$).

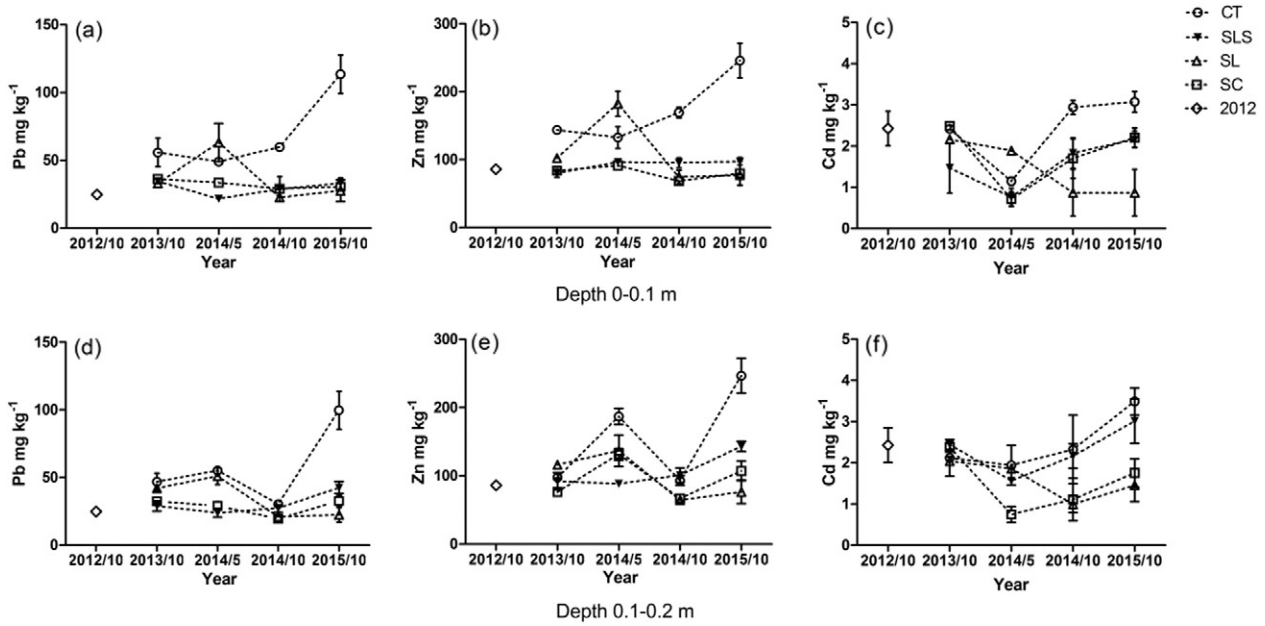


Fig. 5. Changes in total concentrations of Pb, Zn and Cd in soil in different plots. (a) Pb at 0–0.1 m depth, (b) Zn at 0–0.1 m depth, (c) Cd at 0–0.1 m depth, (d) Pb at 0.1–0.2 m depth, (e) Zn at 0.1–0.2 m depth, (f) Cd at 0.1–0.2 m depth. Mean values \pm S.D. are shown ($n = 3$).

May than in October, indicating that heavy metal concentrations in the surface soil were susceptible to rainwater infiltration and evaporation and that heavy metals in surface soil may move downward in the rainy season and move upward in the dry season, enriching the surface soil (Dold and Fontboté, 2002).

During the three years of the field experiment, the acid-soluble concentrations of Pb, Zn and Cd at plots SL and SC changed less compared with those at plot CT. At plot SL, the highest acid-soluble concentrations of Pb, Zn and Cd were observed in May 2014: 1.18, 22.70 and 0.45 mg kg^{-1} . At plot SC, the acid-soluble concentrations of Zn and Cd (0–0.1 m) in 2013 were ten-fold and five-fold higher, respectively, than in 2012. However, after three years of the experiment, the acid-soluble concentrations of Pb and Zn at plot SC did not increase compared with the initial concentration, whereas acid-soluble Cd exhibited

a small increase at plot SC, indicating that Cd may migrate through the clay layer to the topsoil with pore water.

At plot SLS, the acid-soluble concentrations of Pb, Zn and Cd were near the original level during the first two years, but they showed an appreciable increase in 2015. The limestone layer was efficient as a capillary break layer during the first two years of field application, and the long-term efficiency in the field needs further monitoring.

3.2.3. Heavy metal contents in interlayer

The Pb, Zn and Cd contents in interlayer materials (clay and lime) were measured after three years of the field experiment (Table 5). The total contents of Pb, Zn and Cd in the lime layer increased 28-fold, 45-fold and 10-fold, respectively. However, the soluble contents of Pb, Zn and Cd in the lime-layer showed little change. This was likely because

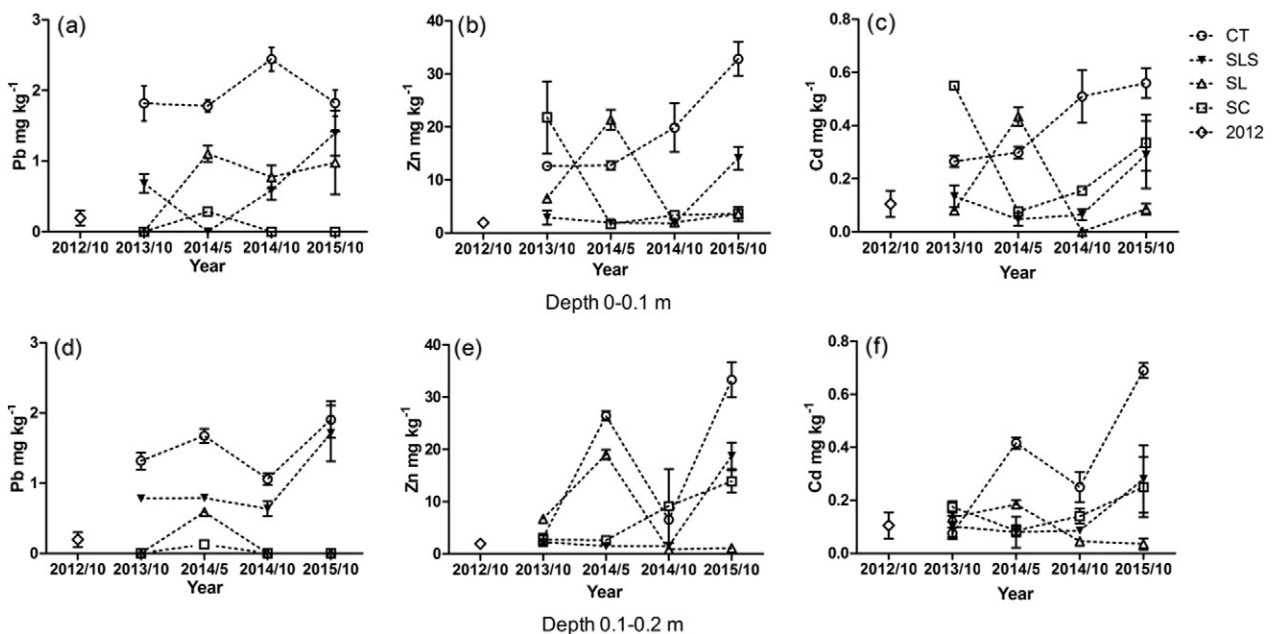


Fig. 6. Changes in acid-soluble Pb, Zn and Cd concentrations of soil in different plots. (a) Soluble Pb at 0–0.1 m depth, (b) soluble Zn at 0–0.1 m depth, (c) soluble Cd at 0–0.1 m depth, (d) soluble Pb at 0.1–0.2 m depth, (e) soluble Zn at 0.1–0.2 m depth, (f) soluble Cd at 0.1–0.2 m depth. Mean values \pm S.D. are shown ($n = 3$).

Table 5

Total and soluble concentrations of Pb, Zn, and Cd at different interlayers. Mean values \pm S.D. are shown ($n = 3$).

Interlayer materials		Lime		Clay	
		2012	2015	2012	2015
Pb	Total	9.16 \pm 0.95	255.85 \pm 17.21	20.65 \pm 1.34	29.65 \pm 1.09
	Soluble	n.m.	n.m.	n.m.	n.m.
Zn	Total	10.7 \pm 1.23	491.24 \pm 23.20	51.38 \pm 3.62	96.92 \pm 7.52
	Soluble	0.71 \pm 0.23	3.9 \pm 1.02	11.24 \pm 1.11	15.37 \pm 0.56
Cd	Total	0.54 \pm 0.13	5.66 \pm 1.50	1.51 \pm 0.37	1.98 \pm 0.64
	Soluble	0.07 \pm 0.04	0.12 \pm 0.06	0.17 \pm 0.07	0.65 \pm 0.16

Note: n.m. is not measurable.

the tailings provided the water needs for hydration of the interlayer, and heavy metals in the porewater were stabilized by hydrated lime ($\text{Ca}(\text{OH})_2$) or co-precipitated with calcium carbonate (Ahn et al., 2011; Bolan et al., 2014).

As this hardpan layer became gradually stabilized, the diffusion of heavy metals into topsoil was limited during the three years of the field experiment, and this interlayer acted as an oxygen and water infiltration barrier under the field conditions (Ahn et al., 2011; Quispe et al., 2013).

The total contents of Pb, Zn and Cd in clay were 29.65 mg kg^{-1} , 96.92 mg kg^{-1} and 1.98 mg kg^{-1} after three years in the field (Table 5). These were appreciably lower than in lime, but the soluble contents of Zn and Cd in clay were higher. The increase of soluble Zn and Cd in clay indicates that heavy metals could migrate up to the clay-layer from the tailings with pore water and adsorb to the clay surface. That is consistent with the findings of Hosney and Rowe (2013).

There was no obvious migration of Pb, Zn and Cd to the topsoil in plots SLS, SL and SC, although the three years of the field experiment was only a short-term evaluation. The increase of soluble Zn and Cd in the clay layer indicates that the construction of a clay layer in direct contact with tailings is not enough for a long-term remediation strategy under local climate conditions. However, no migration of Pb to the interlayer, indicated that the mobility of Pb was lower than those of Zn and Cd.

Both the 210-day column experiment and the 3-year field experiment showed that the Cd content in topsoil above the clay-layer increased. This was likely because Cd was more prone to migration to topsoil with pore water. The column leaching experiment verified that topsoiling could improve leachate water quality: the concentrations of Pb, Zn and Cd in topsoil decreased under the direct topsoiling condition and increased under the field condition. That was due to the strong eluviation as the simulated rainfall (2 L water) was irrigated once a month. Therefore, the eluviation has a strong effect on migration of heavy metals, and heavy metal concentrations in topsoil generally decreased. However, the heavy metals moved upward to the topsoil due to evaporation and capillary forces under field conditions.

3.2.4. Heavy metal contents in leaves

The increase in heavy metal contents in leaves may lead to heavy metal enrichment in surface soil (Qin et al., 2006). The Pb contents in

leaves at SLS and SL were 2.38 mg kg^{-1} and 3.04 mg kg^{-1} , which were appreciably lower than at CT and SC (Fig. 7).

The Zn and Cd contents in leaves at CT were 45.78 and 0.26 mg kg^{-1} , respectively, which were higher than at SLS, SL and SC. The Zn contents in leaves at SLS, SL and SC were similar, and the Cd contents in leaves followed the order $\text{CT} > \text{SL} > \text{SC} > \text{SLS}$. After tailings pond reclamation, where diversified trees or even crops are planted, long-term site monitoring and assessment should be made to ensure that toxic elements are not transferred into topsoil and accumulated in plants.

The aim of tailings pond reclamation is pollution source control. Generally, erosion control could be achieved through simple topsoiling and vegetation. However, the problem of release of contaminative elements still exists, and thus the reclamation model needs further improvement.

4. Conclusions

Topsoil construction would mitigate heavy metal migration by preventing water infiltration and maintaining water in the topsoil layer. The maximum moisture capacity of C2 (23.57%) was appreciably higher than that of C1 (17.75%), and the addition of an interlayer was more effective.

The topsoil effectively reduced the concentrations of Pb, Zn and Cd in the leachate, and the addition of a limestone or lime interlayer enhanced the efficiency, especially for Zn and Cd. The pH values of the leachates from the columns increased with time, and the maximum pH values in C1, C2, C3, C4 and C5, appearing on the 180th day, were 7.85, 7.89, 7.78, 8.03, and 7.89, respectively.

After the 210-day column experiment, the total concentrations of Pb, Zn and Cd in topsoil in C2 were appreciably lower than the initial concentration as a result of the eluviation. The presence of a limestone or lime interlayer reduced the mobility of Zn and Cd, and a clay interlayer was effective in preventing the migration of Pb and Zn, but it had less impact on Cd.

During the 3-year field experiment, the pH values in the topsoil increased slightly with time in the range of 7.67 to 8.20. At the end of the experiment, the Pb, Zn and Cd concentrations in the topsoil at SLS, SL and SC were similar or even lower than the initial values in 2012. Acid-soluble Pb, Zn and Cd concentrations in the upper soil (0–0.1 m) at CT increased from 0.19, 1.95 and 0.11 mg kg^{-1} in 2012 to 1.82, 32.87 and 0.56 mg kg^{-1} in 2015. The acid-soluble Pb and Zn in soil at SL and SC were not significantly increased with respect to the initial concentrations in 2012, whereas acid-soluble Cd in topsoil and the interlayer at plot SC showed small increases, indicating that Cd may migrate through the clay layer to topsoil with pore water. The Pb contents in leaves at SLS and SL were 2.38 and 3.04 mg kg^{-1} , respectively, which are appreciably lower than at CT and SC. The Zn and Cd contents in leaves at CT were 45.78 and 0.26 mg kg^{-1} , which are higher than at SLS, SL and SC.

These results showed that topsoiling with an interlayer was an effective technique for preventing heavy metal migration in the tailings pond. However, many factors, such as soil properties (grain size distribution, hydraulic conductivity, water retention, etc.), local precipitation,

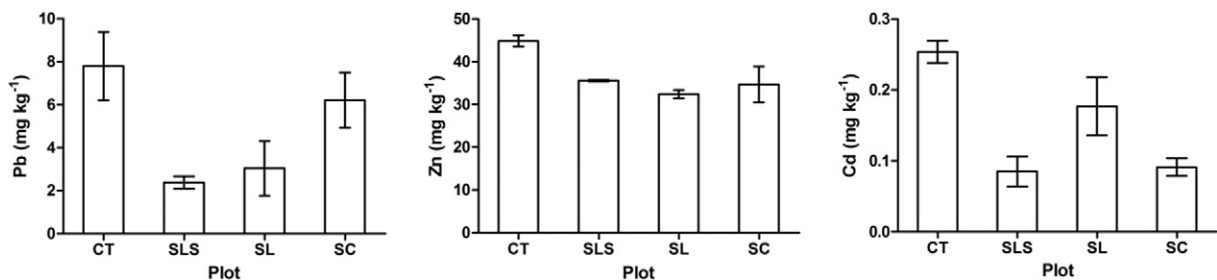


Fig. 7. Changes in Pb, Zn and Cd contents in *Amorpha fruticosa* L. leaves.

soil resources and the objective of tailings pond reclamation, must be considered for topsoil construction. Therefore, it is difficult to form a unified technical standard for tailings pond reclamation and project acceptance. A reclamation model containing particular topsoil construction parameters (thickness, slope, etc.) for tailings ponds is necessary.

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