



## Chemical dynamics of acidity and heavy metals in a mine water-polluted soil during decontamination using clean water

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### ABSTRACT

A column leaching experiment was conducted to investigate the chemical dynamics of the percolating water and washed soil during decontamination of an acidic mine water-polluted soil. The results show that leaching of the contaminated soil with clean water rapidly reduced soluble acidity and ion concentrations in the soils. However, only <20% of the total actual acidity in the soil column was eliminated after 30 leaching cycles. It is likely that the stored acidity continues to be released to the percolating water over a long period of time. During the column leaching, dissolved Cu and Pb were rapidly leached out, followed by mobilization of colloidal Cu and Pb from the exchangeable and the oxide-bound fractions as a result of reduced ionic strength in the soil solution. The soluble Fe contained in the soil was rare, probably because the soil pH was not sufficiently low; marked mobility of colloidal Fe took place after the ionic strength of the percolating water was weakened and the mobilized Fe was mainly derived from iron oxides. In contrast with Cu, Pb and Fe, the concentration of leachate Zn and Mn showed a continuously decreasing trend during the entire period of the experiment.

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### 1. Introduction

Soil contamination caused by acid mine drainage (AMD) is a significant environmental problem in some parts of the world, particularly in densely populated developing countries where human habitats are usually in close proximity to mine sites [1,2]. Water draining from coal and base metal mines frequently contains sulfuric acid and heavy metals at high levels [3], which could contaminate agricultural lands when the mine water or mine water-affected stream water is used for irrigation purposes. Entry of mine-originated contaminants into agricultural soils may also occur during heavy rainfall events that cause over-bank flooding. Elevated concentrations of heavy metals in the soils, accompanied with acidic pH, are likely to enhance uptake of heavy metals by plants [4,5], which poses a high health risk to the people who consume the contaminated agricultural products. Furthermore, with the decrease in capacity of soil to hold the contaminants, groundwater contamination becomes evident. This is particularly a problem where well water is a major source of drinking water [6].

Although methods such as chemical immobilization [7–9], phytoextraction [10,11] and intensive ex situ soil washing with various

extracting solutions [12,13] have been proposed for remediation of heavy metal-contaminated soils, leaching of contaminants with clean irrigation water remains the primary choice for clean-up of contaminated soils in broadacre agricultural lands in developing countries where costly remediation methods are not realistic options. Understanding chemical dynamics of the soil and percolating water during soil decontamination by clean water is needed for evaluating the effectiveness of clean water washing for decontamination of mine water-contaminated lands and for developing appropriate remediation strategies. There have been reports on water washing for decontamination of the soils contaminated by organic pollutants [14]. However, publications on the effects of water washing on heavy metal-contaminated soils are rare. In this study, a column leaching experiment was conducted to investigate the chemical dynamics of the percolating clean water and the soil within the soil column. The objectives were to understand the translocation and transformation of soil-borne contaminants and the chemical dynamics of the discharge water from the soil column.

### 2. Materials and methods

#### 2.1. The soil

The soil material used in this experiment was collected from a floodplain immediately downstream of the Guangdong Dabaoshan

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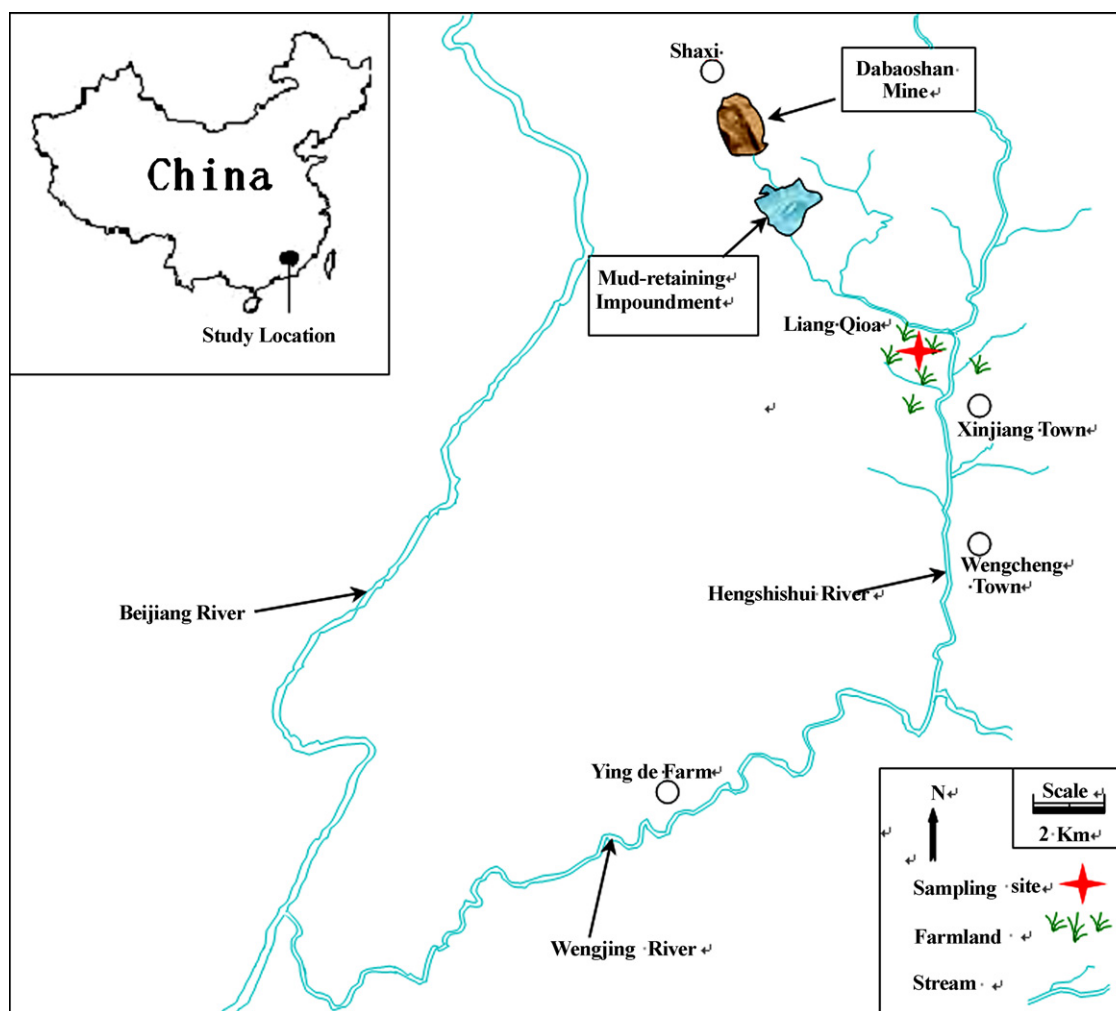


Fig. 1. Map showing the sampling location of the soil used in the experiment.

Mine in the southern China region (Fig. 1). Underground mining of copper ores in the Dabaoshan Mine dates back at least to the Song Dynasty (about 1000 years ago). Since 1970s, large scale surface mining of iron ore has been in operation while smaller scale underground mining of copper, zinc and lead ores took place simultaneously. As a result of these mining activities, especially the involvement of illegal mining in recent decades, large amounts of sulfidic mine spoils have been left on the surface and thus are subject to rapid oxidation. A dam wall across the valley was constructed to intercept the floodwater and retain the mud being translocated from the mine spoil stockpiles on the top of the mountain. The mud-retaining impoundment behind the dam wall has been rapidly filled up with the sediments from the catchment due to severe soil erosion and no longer has any capacity to hold the mine water. Consequently, the overflowing acidic mine water enters into the downstream river reach.

The investigated soil was collected from the agricultural lands on the west bank of the Hengshishui River (refer to Fig. 1), which had been irrigated with acidic mine water for two decades. The soil sample used for the experiment had a pH of 4.3, which was much lower than that (pH > 6.6) in the soil on the east bank that was not affected by mine water [15]. Since the soils on both east and west banks were derived from the non-sulfidic fluvial sediments of the same sources, it is reasonable to assume that the

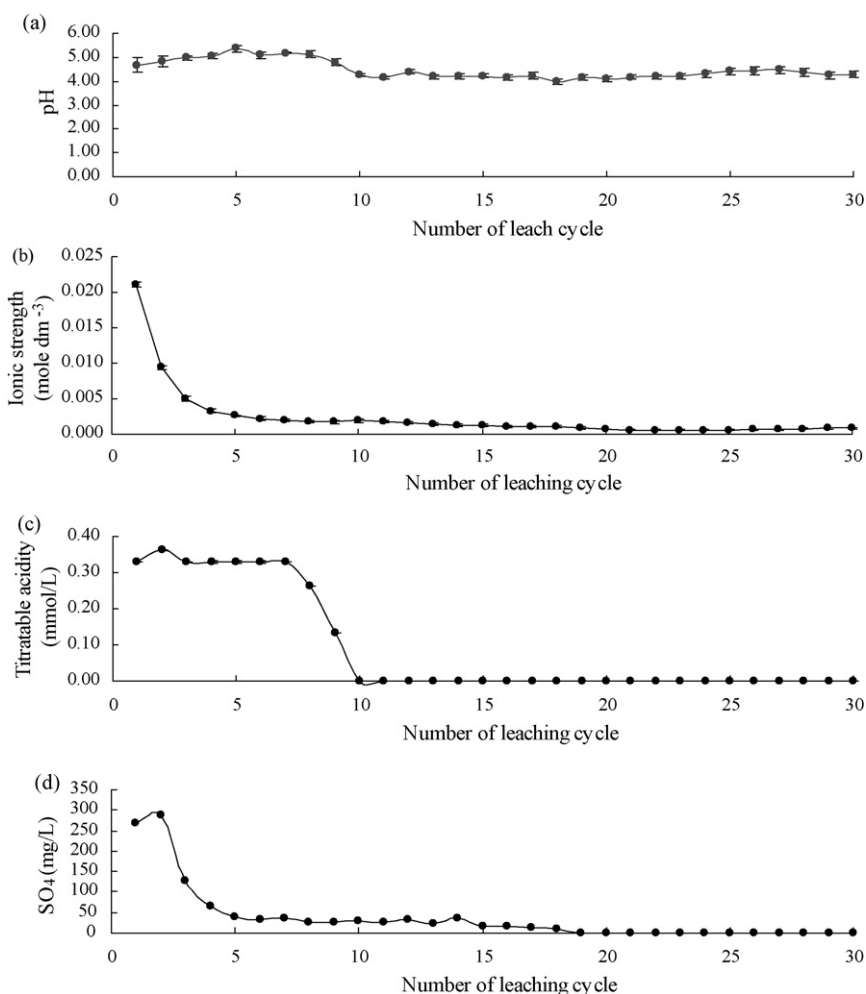
experimental soil was non-acidic prior to mine water irrigation. The experimental soil sample was taken from a depth of 0–30 cm. The soil was used for paddy rice cultivation when it was collected and locally known as subtropical paddy rice soil developed from fluvial sediments.

After collection from the field, the soil sample was oven-dried at 60 °C and then ground to pass a 2 mm sieve before it was analyzed and used for column leaching experiment.

## 2.2. Column leaching experiment

The experiment was performed in five replicates. For each column, 100 g of soil material (<2 mm fraction) were filled into a plastic tube with an inner diameter of 20 mm after filling 12 g of fine quartz sands on the bottom of the column. The total length of the soil column was about 300 mm. On the top of the soil column, 25 g of fine quartz sands were added to avoid direct disturbance of the soil when adding deionized water into the column. A double layer of nylon filter fabric was placed on the bottom of the column. 100 mL of deionized water was added into each column at a flow rate of 12.5 mL h<sup>-1</sup>.

Column leaching was performed daily. A total of 30 leaching cycles were completed for this study. The leachates were collected from the column bottom and used for determinations of various chemical parameters. Leachate samples were analyzed



**Fig. 2.** Change in (a) pH, (b) ionic strength, (c) titratable acidity and (d)  $\text{SO}_4^{2-}$  in leachate during the entire period of experiment (vertical error bars represent standard deviations from the means).

within 24–48 h after collection and stored in fridge before analysis.

After completion of the leaching experiment, the soil in the column was separated into three layers (0–5, 5–17.5 and 17.5–30 mm from the top to the bottom) and used for analysis of various chemical parameters.

### 2.3. Water analysis

The pH and EC in the leachate were measured using a calibrated pH and EC meter, respectively. Concentrations of various heavy metals were determined using an atomic absorption spectrometer (AAS). Sulfate was measured turbidimetrically [16]. Titratable acidity was determined by titrating an aliquot (20 mL) of leachate with a standardized NaOH solution (with a concentration ranging from 0.005 to 0.010 M, depending on leachate pH) to pH 5.5.

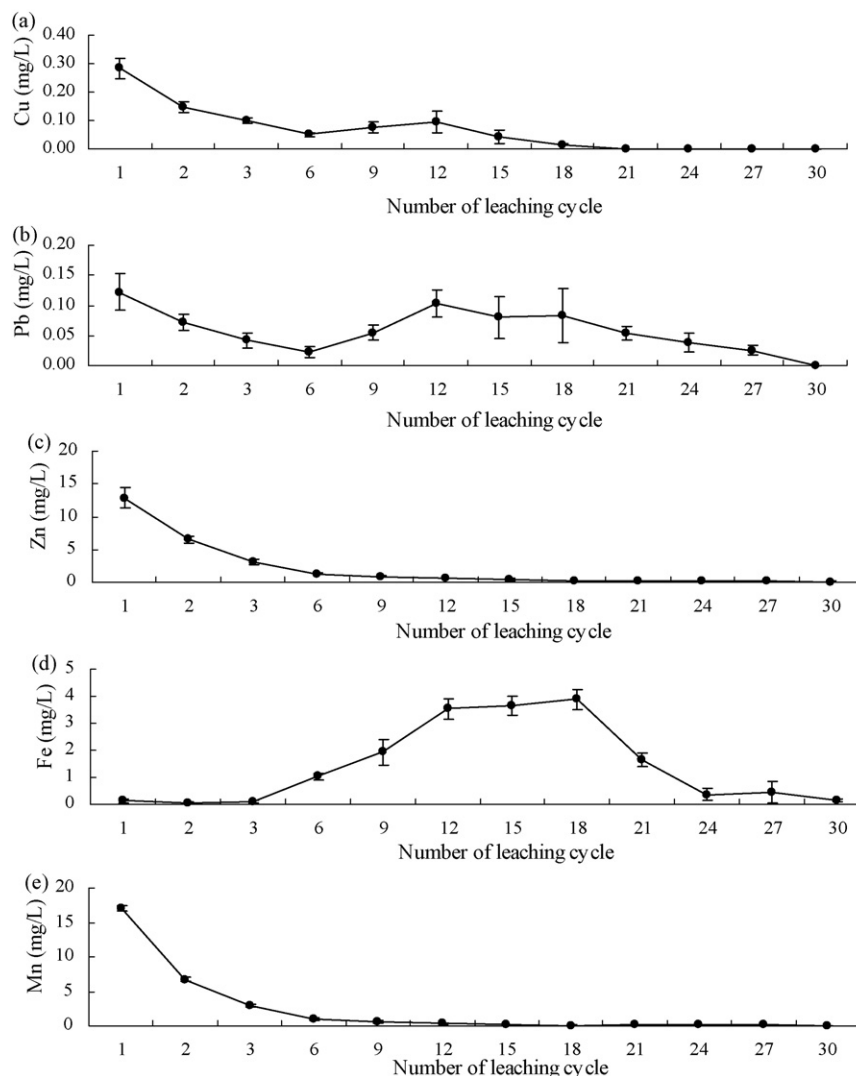
### 2.4. Soil analysis

The soil samples obtained following column leaching experiment were oven-dried at 60 °C and then ground to pass a 2 mm sieve. The leached soil samples, together with the original soil, were then analyzed for various parameters. Organic matter content was determined by Walkley–Black method [17]. Soil particle size anal-

ysis was conducted using a modified method of Gee and Bauder [18]. Mineral composition was determined by XRD method. 1:5 (soil:water) and 1:5 (soil:1 M  $\text{NH}_4\text{Cl}$ ) extracts were prepared by shaking 5 g of the soil with 25 mL of relevant extractants for 1 h in a horizontal rotating shaker. pH and EC in the water extract were measured by a calibrated pH and EC meter, respectively. Sulfate was measured turbidimetrically [16]. The water-extractable acidity, the  $\text{NH}_4\text{Cl}$ -extractable acidity and the total actual acidity (TAA) were determined by the methods of Lin et al. [19,20]. Concentrations of various heavy metals in water and in the 1 M  $\text{NH}_4\text{Cl}$  extracts were determined by AAS.

Ionic strength of each leachate was estimated from EC using the method of Simón and García [21]

The improved BCR sequential extraction procedure [22] was used to separate the following three fractions of a heavy metal in the soil: (a) 0.11 M  $\text{HCH}_3\text{COO}$ -extractable metal (termed as Fraction I), (b) 0.5 M  $\text{NH}_2\text{OH}\cdot\text{HCl}$ -extractable metal (termed as Fraction II) and (c) 1 M  $\text{NH}_2\text{CH}_3\text{COOH}$ -extractable metal after 30%  $\text{H}_2\text{O}_2$  digestion (termed as Fraction III). Details on the analytical procedure are described as follows: (1) a total of 40 mL of acetic acid was added to 1 g of soil and shaken overnight in a horizontal rotating shaker and then the mixture was centrifuged to separate the supernatant from the residue; (2) a total of 40 mL of hydroxylammonium chloride, adjusted with nitric acid to pH 1.5, was added to the residue from



**Fig. 3.** Change in (a) Cu, (b) Pb, (c) Zn, (d) Fe and (e) Mn in the leachate during the entire period of experiment (vertical error bars represent standard deviations from the means; the x-axes are not to scale).

(1) and the extraction performed as above; (3) the residue from (2) was treated twice with  $8.8 \text{ mol L}^{-1}$  hydrogen peroxide, evaporated to near dryness, then 50 mL of ammonium acetate, adjusted to pH 2 with nitric acid, was added and the extraction performed as above. Total metal was extracted by HF–HNO<sub>3</sub>–HClO<sub>4</sub> digestion. The concentration of a heavy metal in all the extracts was determined by AAS.

In the BCR system, Fraction I was thought to include water soluble, exchangeable and carbonate-bound metal; Fraction II was viewed to be in the forms bound to oxides of iron and manganese; and Fraction III was believed to include a metal bound to organic matter and sulfide minerals. In this study, water-extractable metal concentration is used to estimate soluble fraction of the metal; exchangeable metal is estimated by the difference between the NH<sub>4</sub>Cl-extractable metal concentration and the water-extractable metal concentration; carbonate-bound metal concentration is estimated by the difference between Fraction I and the NH<sub>4</sub>Cl-extractable metal concentration; Fraction II is used to estimate the concentration of the metal adsorbed to Fe and Mn oxides; since no metal sulfides were present in the soil, Fraction III is used to estimate the concentration of organic-bound metal. However, it is realized that the operationally defined metal fractions obtained from a sequential

extraction procedure are unlikely to be linked to metal speciation in an accurate manner. For example, our previous results showed that large amounts of “carbonate-bound” metals were detected for the soils with a pH below 5, which does not favour the presence of carbonates. It is likely that NH<sub>2</sub>OH·HCl can also extract tightly adsorbed exchangeable metals and also part of the oxide-bound metals. Therefore, caution should be taken in interpreting the metal fractionation data obtained from this method.

### 2.5. Statistical analysis and quality control

Duncan's multiple range tests were used for the statistical analysis of the analytical data. The detection limits of the ASS used for measurements of Cu, Pb, Zn, Fe and Mn were 0.01, 0.06, 0.01, 0.03 and 0.01 mg L<sup>-1</sup>, respectively. Repeatability analysis shows that the RSD (relative standard deviation) of various parameters was 2.74% (pH), 11.76% (ionic strength), 12.29% (Cu), 16.13% (Zn), 13.76% (Fe) and 22.67% (Mn) for leachate analysis (for data points that are 10 times greater than the detection limit) and 2.49% (Cu), 3.83% (Pb), 4.60% (Zn), 10.83% (Fe) and 2.68% (Mn) for the soil analysis.

### 3. Results

#### 3.1. Changes of chemical parameters in leachate over time

The mean pH of leachate increased with increasing number of leaching cycle and reached a peak in the 5th leaching cycle. Leachate pH started decreasing, with fluctuation, in the 9th leaching cycle. From the 10th to the 30th leaching cycle, leachate pH fluctuated between 3.97 and 4.46 (Fig. 2a).

Mean ionic strength sharply decreased from 0.0211 mol dm<sup>-3</sup> in the 1st leachate to 0.0026 mol dm<sup>-3</sup> in the 5th leachate. After initial rapid drop, ionic strength gently decreased, with minor fluctuation, from the 5th leaching cycle to 0.0008 mol dm<sup>-3</sup> in the last leaching cycle (30th leaching cycle) (Fig. 2b).

Titratable acidity maintained at high level (>0.3 mmol L<sup>-1</sup>) for the first seven leachates and then sharply dropped to non-detectable level in the 10th leachate. Titratable acidity maintained at non-detectable level for the leachates obtained from the 10th to the 30th leaching cycle (Fig. 2c).

After a slight increase from 267 mg L<sup>-1</sup> in the 1st leachate to 287 mg L<sup>-1</sup> in the 2nd leachate, sulfate concentration sharply dropped to 32 mg kg<sup>-1</sup> in the 6th leachate and then remained little change until the 14th leaching cycle. Sulfate concentration in the leachate decreased from the 14th leaching cycle to non-detectable level starting from the 19th leaching cycle until the end of the experiment (Fig. 2d).

Fig. 3 shows the changes in leachate Cu, Pb, Zn, Fe and Mn over time during the entire period of the experiment. Concentration of leachate Cu decreased from the 1st leaching cycle to the 6th leaching cycle and then slightly increased before decreasing again at the 12th leaching cycle. Leachate Cu become non-detectable after the 21st leaching cycle (Fig. 3a).

Variation of leachate Pb with increasing number of leaching cycle showed a similar pattern to Cu but it bounced back more remarkably than leachate Cu did from the 6th leaching cycle to the 12th leaching cycle and it took a longer time to drop to a non-detectable level (Fig. 3b).

Concentration of Zn sharply decreased from the 1st leaching cycle to the 6th leaching cycle and then gently decreased to a non-detectable level in the leachate obtained from the last leaching cycle (the 30th leaching cycle) (Fig. 3c).

Leachate Fe was at very low concentration (<0.15 mg L<sup>-1</sup>) during the first three leaching cycles. It increased sharply from the 3rd leaching cycle to the 12th leaching cycle (>3.5 mg L<sup>-1</sup>) and then maintained little change from the 12th leaching cycle to the 18th leaching cycle, followed by a sudden decrease to the 24th leaching cycle (<0.5 mg L<sup>-1</sup>). Leachate Fe then gently decreased from the 24th leaching cycle to the last leaching cycle (the 30th leaching cycle) (Fig. 3d).

The variation pattern of leachate Mn with increasing number of leaching cycle was very similar to Zn. It sharply decreased from the 1st leaching cycle to the 6th leaching cycle and then gently decreased to a non-detectable level in the leachate obtained from the last leaching cycle (the 30th leaching cycle) (Fig. 3e).

**Table 1**

Some basic characteristics of the soil used for the column leaching experiment.

Soil parameter	Value
pH	4.33
EC (dS m <sup>-1</sup> )	0.263
Organic matter content (%)	2.2
Major minerals	
Quartz (%)	40.0
Illite (%)	33.7
Kaolinite (%)	10.4
Montmorillonite (%)	8.9
Hematite (%)	3.6
Feldspar (%)	3.3
Particle size distribution	
Grain fraction <0.001 mm (%)	15
Grain fraction 0.001–0.005 mm (%)	17
Grain fraction 0.005–0.01 mm (%)	16
Grain fraction 0.01–0.05 mm (%)	28
Grain fraction >0.05 mm (%)	24
Total Cu (mg kg <sup>-1</sup> )	194.8
Total Pb (mg kg <sup>-1</sup> )	369.7
Total Zn (mg kg <sup>-1</sup> )	424.8
Total Cd (mg kg <sup>-1</sup> )	1.271
Total Fe (mg kg <sup>-1</sup> )	67968
Total Mn (mg kg <sup>-1</sup> )	131.7

#### 3.2. Soil chemical parameters

Some basic characteristics of the soil used for the column leaching experiment are given in Table 1. The pH, EC and organic matter content of the experimental soil were 4.33, 0.264 dS m<sup>-1</sup> and 2.2%, respectively. Major minerals contained in the soil sample were quartz, illite, kaolinite, montmorillonite, hematite and feldspar. The soil mainly consisted of soil particles with a diameter greater than 0.01 mm and the clay materials (<0.001 mm) accounted for about 15%. The soil contained substantial amounts of total iron (67968 mg kg<sup>-1</sup>). The total concentration of copper, lead, zinc, cadmium and manganese was 194.8, 369.7, 424.8, 1.271 and 131.7 mg kg<sup>-1</sup>, respectively.

After 30 leaching cycles, soil pH significantly increased, particularly for the top 5 cm of the soil column, where pH reached above 5. EC markedly dropped from 0.263 to <0.060 dS m<sup>-1</sup>. The water-extractable acidity markedly decreased from 19.3 to below 5 mmol kg<sup>-1</sup>. The NH<sub>4</sub>Cl-extractable acidity and TAA also decreased but the magnitude of decrease was much smaller, compared to the water-extractable acidity. There was a difference in each of the above parameters among the different soil layers; pH tended to decrease while EC and various forms of titratable acidity tended to increase with increasing depth along the soil column (Table 2).

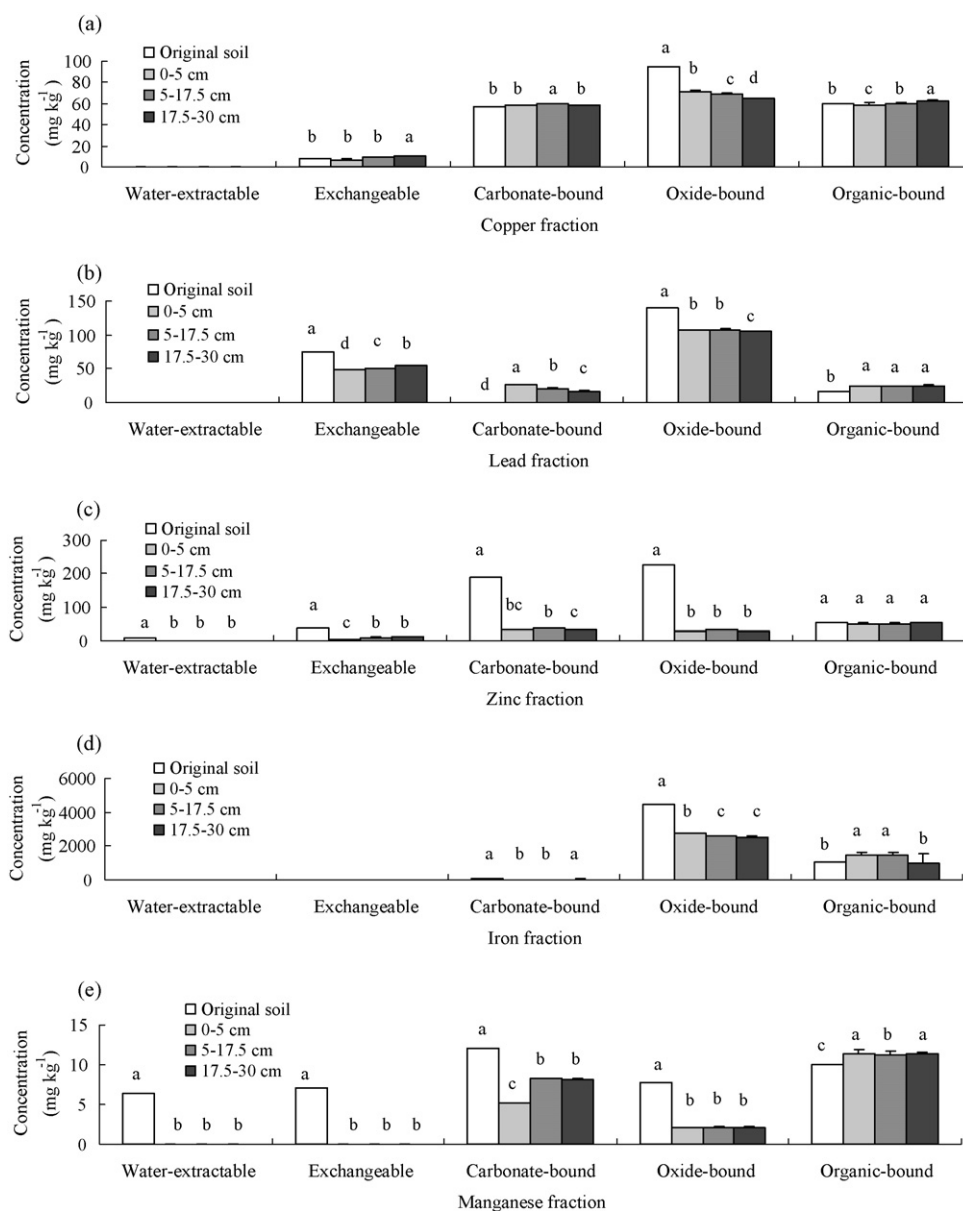
The concentration of the water-extractable Cu was 0.13 mg kg<sup>-1</sup> and non-detectable in the original soil and the washed soil, respectively. There was no significant difference in exchangeable Cu among the original soil, the 0–5 cm soil layer and the 5–17.5 cm soil layer, which contained significantly less exchangeable Cu than the 17.5–30 cm soil layer did. The carbonate-bound Cu was significantly higher in the 5–17.5 cm soil layer than in the original

**Table 2**

Comparison of pH, EC and various titratable acidity between the original soil and different layers of the leached soil column.

Parameter	Original	0–5 cm	5–17.5 cm	17.5–30 cm
pH	4.33 ± 0.35d	5.03 ± 0.02a	4.81 ± 0.03b	4.68 ± 0.02c
EC (dS m <sup>-1</sup> )	0.263 ± 0.000a	0.043 ± 0.003c	0.057 ± 0.002b	0.059 ± 0.001b
Water-extractable acidity (mmol kg <sup>-1</sup> )	19.3 ± 0.20a	2.47 ± 1.17d	4.12 ± 1.17c	4.95 ± 0.00b
NH <sub>4</sub> Cl-extractable acidity (mmol kg <sup>-1</sup> )	23.6 ± 0.11a	14.0 ± 1.17c	14.8 ± 0.00c	17.3 ± 1.17b
TAA (mmol kg <sup>-1</sup> )	40.1 ± 0.36a	29.0 ± 1.62d	31.8 ± 1.62c	35.5 ± 1.62b

Means with the same letters in the same row do not differ significantly at  $P > 0.05$ .



**Fig. 4.** Comparison of various fractions of (a) Cu, (b) Pb, (c) Zn, (d) Fe and (e) Mn among the original soil and the three layers of the leached soil column (Means with the same letters for the same metal fraction do not differ significantly at  $P > 0.05$ ).

soil and the other two layers of the washed soil, which showed no significant difference in carbonate-bound Cu among each other. The oxide-bound Cu was significantly higher in the original soil than in the washed soil; within the soil column, significant difference in oxide-bound Cu existed among the three different soil layers; there was a trend that the concentration of oxide-bound Cu decreased with increasing depth. The organic-bound Cu in the original soil was significantly higher than that in the 0–5 cm soil layer, not significantly different from that in the 5–17.5 cm soil layer, and significantly lower than that in the 17.5 cm soil layer (Fig. 4a).

The concentration of the water-extractable Pb was  $0.161 \text{ mg kg}^{-1}$  in the original soil. However, water-extractable Pb was not detected for any layers of the washed soil. The exchangeable Pb was significantly higher in the original soil than in the washed soil; within the soil column, significant difference in the exchangeable Pb existed among the three different soil layers; there was a trend that the concentration of the exchangeable Pb increased with increasing depth. The carbonate-bound Pb was not detected in the original soil; there was significant difference

in carbonate-bound Pb among the three different soil layers; the concentration of the carbonate-bound Pb decreased with increasing depth of the soil column. The oxide-bound Pb was significantly higher in the original soil than in the washed soil; within the washed soil column, there was no significant difference in oxide-bound Pb between 0–5 cm soil layer and the 5–17.5 cm soil layer; both contained significantly higher oxide-bound Pb than the 17.5–30 cm soil layer did. The organic-bound Pb was significantly lower in the original soil than in the washed soil; within the washed soil column, there was no significant difference in organic-bound Pb among the three different soil layers (Fig. 4b).

Various forms of Zn were significantly higher in the original soil than those in the washed soil, except for the organic-bound Zn, which showed no significant difference between the original soil and the washed soil. For the water-extractable and oxide-bound Zn, there was no significant difference among the three different layers of the soil column. For the exchangeable Zn, there was no significant difference between the 5–17.5 cm soil layer and the 17.5–30 cm soil layer; both contained significantly higher exchangeable Zn than the

0–5 cm soil layer did. For carbonate-bound Zn, there was a significant difference among the three different soil layers and they were in the following decreasing order: the 5–17.5 cm soil layer > 0–5 cm soil layer > 17.5–30 cm soil layer (Fig. 4c).

Both forms of the water-extractable Fe and exchangeable Fe were not detected. The carbonate-bound Fe in the original soil was significantly higher than that in the 0–5 cm soil layer and the 5–17.5 cm soil layer, and not significantly different from that in the 17.5–30 cm soil layer. The oxide-bound Fe was significantly higher in the original soil than in the washed soil. Within the washed soil column, the oxide-bound Fe was significantly higher in the 0–5 cm soil layer than in the two lower soil layers, which did not differ in the oxide-bound Fe from each other. The organic-bound Fe in the original soil was significantly lower than that in either the 0–5 cm soil layer or the 5–17.5 cm soil layer, and not significantly different from that in the 17.5–30 cm soil layer (Fig. 4d).

Various forms of Mn were significantly higher in the original soil than in the washed soil, except for organic-bound Mn, which was significantly lower in the original soil than in any of the three layers of the washed soil. Both the water-extractable Mn and exchangeable Mn were not detected in the washed soil column. There was a tendency that carbonate-bound Mn increased with increasing depth of the soil column. There was no significant difference in oxide-bound Mn among the three layers of the washed soil column (Fig. 4e).

#### 4. Discussion

The increase in pH from the 1st leaching cycle to the 5th leaching cycle indicates a gradual reduction of  $H^+$  that entered the percolating water from the soil during this period. However, the leachate maintained at a high level ( $>0.3 \text{ mmol L}^{-1}$ ) of titratable acidity during the same period. This suggests that, during this period, the soluble acidity in the leachate consisted predominantly of acidic metal cations rather than  $H^+$ . Since there was a decrease in all heavy metals concentration analysed during the same period, heavy metal ions might contribute little to the titratable acidity. Therefore, the maintenance of a stable level of titratable acidity during the 1st–5th leaching cycles while the pH rose ( $H^+$  activity decreased) with increasing number of leaching cycle suggests that soluble Al ions dominated the titratable acidity in these leachates. Our unpublished data show that the mean concentration of water-extractable Al in the soils was  $4.22 \text{ mg/kg}$  ( $n = 56$ ) in the study area. Titratable acidity dropped to very low level at the 10th leaching cycle when the leachate pH decreased to a level that was even lower than that in the first leachate. This indicates that the soluble acidic metal cations was nearly depleted while the retained  $H^+$  was increasingly released from the soil to the percolating water. It is interesting to note that leachate pH remained at a level below 5 at least until the last leaching cycle (the 30th leaching cycle) of this experiment despite that the corresponding titratable acidity was very low.

Comparison between the leached soil column and the original soil (the non leached soil) shows that water washing significantly reduced various forms of acidity and ion concentrations in the soils, especially in the upper layer of the soil column. However, the retained acidity still remained high in the soil after 30 leaching cycle (Table 2). This stored acidity is expected to be a source of soluble acidity that is continuously released to the percolating water through transformation of retained acidity into soluble  $H^+$  upon  $H^+$  removal by clean water in each leaching cycle. After 30 leaching cycles, about 23%, 20% and 12% of the total acidity in the 0–5 cm layer, the 5–17.5 cm layer and the 17.5–30 cm layer, respectively were eliminated by the washing water. This suggests that the release of  $H^+$  from the soil could be a long-lasting process if the acidic mine water-contaminated soils are decontaminated solely by clean water.

The sharp drop in ionic strength from the 1st leaching cycle to the 5th leaching cycle reflects the rapid removal of the soil-borne soluble ions by the percolating clean water. This was evident for sulfate, Cu, Pb, Zn and Mn. It is worthwhile to note that leachate Pb concentration re-increased from the 6th leaching cycle to the 12th leaching cycle. The higher level of leachate Pb from 7th leaching cycle to the 27th leaching cycle, relative to leachate Pb for the 6th leaching cycle was probably caused by the release of retained Pb to the percolating water. Since ionic strength was very low during this period, it is likely that the Pb carried by the leachates was in forms of non or low charges, i.e. colloidal forms. It has been widely reported that ionic strength of solutions had a significant impact on the mobilization of colloids; decrease in ionic strength favoured the mobility of colloids [23–27]. The increase in leachate Pb concentration from the 7th leaching cycle to the 27th leaching cycle could be related to the decreased ionic strength, which enhanced mobilization of colloidal Pb during the same period. The mobilized Pb appeared to be derived from the exchangeable fraction and the oxide-bound fraction since the concentration of these two fractions was lower in the leached soil column than in the original soil (non leached soil) (Fig. 4b). However, the concentration of the carbonate-bound and organic-bound Pb increased after column leaching, suggesting that transformation of exchangeable and oxide-bound Pb into the carbonate-bound and organic-bound Pb might occur during the column leaching. The increase in Pb concentration in the leachates obtained after 6th leaching cycle corresponded with very low ionic strength, indicating that the leachate Pb was likely to be predominantly in colloidal forms. Therefore, during this period colloid transport might be a more important mode of Pb mobility, compared to free ion transport.

Similar to Pb, leachate Cu also increased from the 6th leaching cycle to the 12th leaching cycle. However, the magnitude and duration of Cu rebound was smaller and shorter, relative to leachate Pb. By comparison, Cu mobility was mainly through dissolution of soluble Cu in the soil. The major form of mobilized colloidal Cu was oxide-bound Cu. Other Cu fractions showed little change after leaching.

The low concentration of Fe in the first three leachates indicated that soluble Fe was rare, probably because the soil pH was not sufficiently low. The sharp increase in leachate Fe concentration from the 3rd leaching cycle to the 12th leaching cycle also reflected intensified mobilization of colloidal Fe as a result of ionic strength weakening. The sudden decrease in leachate Fe from the 18th leaching cycle to the 24th leaching cycle was probably due to the reduced availability of Fe-bearing colloids. The mobilized Fe was mainly derived from iron oxides. The carbonate-bound Fe also contributed to leachate Fe. It is likely that part of the mobilized Fe was re-immobilized to form organic-bound Fe during leaching since the leached soil had a higher concentration of organic-bound Fe, compared to the original soil (the non leached soil).

In contrast with Cu, Pb and Fe, the concentration of leachate Zn and Mn showed a continuously decreasing trend during the entire period of the experiment; the concentration of various Zn and Mn fractions in the soil significantly decreased after water washing, except for organic-bound Zn and Mn fractions.

#### 5. Conclusion

The research findings obtained from this study have implications for remediation of acidic mine water-contaminated soils. Leaching of acidic mine water-contaminated soils with clean irrigation water can rapidly remove the labile fractions of acids and heavy metals from the soils at the cost of temporary groundwater contamination. After this initial flushing, mobility of the remaining heavy metals becomes insignificant. However, only less than

20% of the total actual acidity in the soil column was eliminated by the washing water after 30 leaching cycles. It is expected that the stored acidity continue to be a source of soluble acidity that is released to the percolating water over a long period of time if water washing is the only measure for decontamination of the acidic mine water-contaminated soils. Different patterns were observed for mobilization of soil-borne heavy metals during the column leaching. The dissolved Cu and Pb were rapidly leached out, followed by mobilization of colloidal forms as a result of reduced ionic strength in the soil solution. The soluble Fe contained in the soil was rare, probably because the soil pH was not sufficiently low; marked mobility of colloidal Fe took place after the ionic strength of the percolating water was weakened and the mobilized Fe was mainly derived from iron oxides. In contrast with Cu, Pb and Fe, the concentration of leachate Zn and Mn showed a continuously decreasing trend during the entire period of the experiment; the concentration of various Zn and Mn fractions in the soil significantly decreased after water washing, except for organic-bound Zn and Mn fractions.

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