Effects of chemical amendment on heavy metal leachability and bioavailability of an acidic mine water-contaminated soil and growth of a vegetable

Chuxia Lin[A, B], Wenzhou Lu[B], Yong Liu[B], Yingqun Ma[B], Fengxian Wan[B] and Aisheng Chen[B]

[A]Australian Centre for Sustainable Catchments, University of Southern Queensland, Toowoomba QLD, Australia, Email Chuxia.Lin@usq.edu.au
[B]Centre for Ecological and Environmental Technologies, South China Agricultural University, Guangzhou, China.

Abstract
A pot experiment was conducted to examine the effects of acid neutralization treatment of a mine water-polluted soil on the leachability and bioavailability of the heavy metals in the soil, as well as the growth of a vegetable using the treated soils as growth media. The results show that the leachability of the soil-borne heavy metals can be effectively reduced after application of lime and red mud (pH 11.58, acid-neutralizing capacity of about 10 mole/kg). The amount of heavy metals extracted by the plant differed significantly among the different treatments despite that the soluble forms of the metals were consistently low or non-detectable for various treatments. This indicates that non-soluble heavy metal pools were more important sources for heavy metal uptake by the plant. The bioavailability of the heavy metals was not dependent on soil pH, at least for Cu, Zn and Cd. Soil pH might have certain effects on the uptake of Pb by the plant. The growth performance of the vegetable was significantly affected by the amount of red mud added to the soil, which does not appear to be related to soil pH conditions and heavy metal toxicity.

Key Words
Chemical amendment, heavy metal, metal mobility, soil contamination, acid mine drainage.

Introduction
Agricultural soils contaminated by acidic mine water tend to have elevated concentration of heavy metals, not only the total amount but also the soluble fraction. This could have significantly adverse impacts on the quality of crop and groundwater due to mobility of these metals from the soil to the crop plants and near-surface aquifers (Lin *et al.* 2005; Chen *et al.* 2007). Chemical amendments have been widely practised to remediate heavy metal-contaminated soils based on the general belief that they can immobilize the heavy metals and therefore reduce their export from the soil system (Lombi *et al.* 2002). In this study, a pot experiment was conducted to examine the growth performance of a vegetable and the chemical behaviours of a few heavy metals in a mine water-contaminated soil under acid-neutralizing treatments. The objective was to assess the effects of the acid neutralization on the leachability and bioavailability of the heavy metals in the soil.

Materials and methods
Experimental soil and crop plant
The soil used in this experiment was collected from a floodplain downsteam of the Dabaoshan Mine in the South China. The agricultural land had been irrigated with acidic mine water for two decades. The soil was abandoned due to severely acidic conditions when it was collected. The topsoil layer (0-30 cm) was sampled, air-dried and crushed to pass a 3 mm sieve before it was used for pot experiment. Some basic characteristics of the experimental soil are given in Table 1. The red mud used in the experiment had a pH of 11.58 and an acid-neutralizing capacity of about 10 mole/kg (Liu *et al.* 2007). *Brassica chinensis* L, a common vegetable species, was used as a test plant in the experiment.

Pot experiments
One control and 6 treatments (in triplicate) were set for the pot experiment. For all the 6 treatments, equal amount of 5 g hydrated lime (analytical grade) was used for each pot. From Treatment 1 (T1) to Treatment 6 (T6), 0, 1, 3, 5, 10, 20 g fresh red mud was used accordingly. One kilogram of the original soil was completely mixed with the additives and then put in a plastic pot (2 kg capacity). The control contained original soil without addition of hydrated lime and red mud. Prior to vegetable growth experiment, the soils were irrigated to keep the soil moisture content at field capacity level. This was done by placing each pot on a plastic tray containing a layer of water (at the very beginning, the dry soil needed to be wet by watering from top). After soil incubation for 20 days, the vegetable growth experiment commenced on July 20, 2005

and harvested on September 30, 2005. The pots were placed randomly in a green house with free ventilation. In each pot, three seedlings with two leaves were initially planted and only two healthier plants were remained in each pot by removing the weakest plant from the pot about two weeks after transplanting. In addition, a dose of compound fertilizer containing 0.2 g N, 0.2 g P and 0.2 g K was added to each pot twice, one at 25th day and another at 50th day following transplanting. At the first day of the growth experiment (i.e. after 20 days of soil incubation) and the harvest day (i.e. on September 30, 2005), soil samples were taken from each pot for chemical analysis.

Table 1. Some basic characteristics of the experimental soil.

Soil chemical parameter	Value
Organic matter content (%)	26.67
Total N (mg/kg)	860
Total P (mg/kg)	1640
Total K (mg/kg)	2110
Available N (mg/kg)	75.6
Available P (mg/kg)	50.57
Available K (mg/kg)	42.86
pH	3.49
EC (dS m^{-1})	0.970
Water-extractable acidity (mmol/kg)	1.5
NH_4Cl-extractable acidity (mmol/kg)	16.1
Total actual acidity (mmol/kg)	19.4

Chemical analysis

The plant materials were washed using deionized water, separated into root and the above-ground portion and then oven-dried at 70 ^oC to constant weight for hours to determine the dry biomass of the plant materials. The dried plant tissue was milled. Two grams of each milled plant sample were ignited (at 550^oC) in a Muffle furnace for 6 hours and then digested with 2 mol/L HCl (Long *et al.* 2002). Various heavy metals contained in the plant materials were determined by atomic absorption spectrometry. Soil samples were oven-dried at 60^oC for 1 day and then ground to pass a 2 mm sieve. 1:5 (soil:water) extracts was prepared. pH of the water extract was measured by a calibrated pH meter; water-extractable acidity was determined by titrating an aliquot of extract with a standardized NaOH solution to pH 5.5; concentrations of various heavy metals in the extract was determined by atomic absorption spectrometry;

Results

Changes in pH over time for the control and various treatments

Soil pH measured for the samples collected on the first day and last day of the pot experiment is given in Table 2. For the control, the mean pH of the soil was 3.49 and 3.89 for the first day and the 73rd day of the growth experiment, respectively. The mean soil pH of all the treatments was significantly higher than that of the control for all the sampling occasions. On the 1st day of the growth experiment, the soil pH increased from about 7.9 for T1 to 8.87 for T6.

Table 2. Variation of soil pH for various treatments during the period of experiment.

Treatment	First day	Last day
Control	3.49±0.01	3.89±0.02
T1	7.94±0.04	6.53±0.04
T2	8.45±0.11	7.60±0.12
T3	8.44±0.12	7.77±0.12
T4	8.46±0.05	7.87±0.05
T5	8.58±0.04	8.12±0.04
T6	8.87±0.04	8.35±0.04

Heavy metal concentration in the soils of the control and various treatments

After acid-neutralization treatments, water-extractable Cu, Pb and Cd become non-detectable except for Cu in T3 and T4. Water-extractable Zn was detected but markedly reduced, as compared to that in the control (Table 3).

Table 3. Concentration (mg/kg) of the water-extractable heavy metals for various treatments on the last day of experiment.

Treatment	Cu	Pb	Zn	Cd
Control	0.89±0.06	0.14±0.02	9.30±0.12	0.03±0.00
T1	nd	nd	0.29±0.10	nd
T2	nd	nd	0.32±0.01	nd
T3	0.27±0.06	nd	0.15±0.05	nd
T4	0.31±0.09	nd	0.13±0.02	nd
T5	nd	nd	0.14±0.05	nd
T6	nd	nd	0.42±0.12	nd

nd: not detectable

Biomass of the crop plants for the control and various treatments at harvest

The untreated soil did not support growth of the test plant. T2 had the best growth performance with a dry biomass of 21.2 mg/kg, followed by T3. There was no statistically significant difference in the dry biomass among T1, T4, T5 and T6 (Table 4).

Table 4. Dry biomass (mg/kg) of the crop plants for the control and various treatments at harvest.

Treatment	Above-ground portion	Underground portion
Control	0.00d	0.00d
T1	4.38±1.08bc	0.02±0.01cd
T2	21.2±7.48a	0.04±0.01cd
T3	13.16±9.41ab	0.15±0.12bcd
T4	7.32±1.84bc	0.26±0.09ab
T5	4.03±1.12bc	0.2±0.06abc
T6	5.29±0.66bc	0.32±0.046a

Means with the same letters in the same column do not differ significantly at P >0.05

Heavy metal concentration in the soils of the control and various treatments

The degree of heavy metal accumulation in the plant tissue in relation to the amount of added red mud varied among different metals. Pb showed a trend to decrease with increasing amount of added red mud but other metals exhibited no clear relationship between the amount of added red mud and the metal concentration in the tissue (Table 5).

Table 5. Heavy metal concentration (mg/kg) of plant tissue for the control and various treatments at harvest.

Treatment	Cu	Pb	Zn	Cd
T1	34.91±2.69bc	4.26±1.05a	58.96±1.09bc	3.25±1.08abc
T2	31.92±0.69c	3.56±0.35a	65.06±2.37abc	0.90±0.24d
T3	40.33±1.3abc	3.08±0.10ab	72.19±6.66ab	0.97±0.52cd
T4	33.95±3.26bc	3.42±0.51ab	62.58±1.62abc	1.28±0.35cd
T5	44.9±5.58abc	3.36±0.34ab	66.27±5.18abc	2.80±0.21abcd
T6	32.33±13.24c	2.84±0.71ab	46.31±9.78bc	1.43±0.49bcd

Means with the same letters in the same column do not differ significantly at P >0.05

Discussion

The results obtained from this experiment suggests that the leachability of the heavy metals in the soil, as indicated by elimination or significant reduction in water-extractable forms of the metals, can be effectively reduced after amendment of the soil with the acid-neutralizing agents. This is attributable to the maintenance of a high soil pH during the period of the experiment.

The much better growth performance of the vegetable in T2 and T3, compared to those of other treatments, either higher or lower dose of added red mud, suggests that addition of appropriate amount of acid-neutralizing agents is extremely important in terms of achieving remediation goals. It is unknown that T1 had such poor growth performance despite that its soil pH ranged from 6.53 to 7.94, which is even more optimal for the growth of *Brassica chinensis* L. (Huxley, 1992), compared to the soil pH in T2 and T3.

The significant difference in heavy metal uptake by the crop plant among the different treatments is not related to the status of soluble heavy metal pools since the concentration of the heavy metals in the soils was consistently very low or non-detectable for all the treatments. This suggests that the certain non-soluble heavy metal pools played a significant role in supplying heavy metals for the plant uptake. Further work is required to investigate the mechanisms responsible for this. Under the current experimental conditions, the bioavailability of the heavy metals was not dependent on soil pH, at least for Cu, Zn and Cd. Soil pH might have certain impacts on the uptake of Pb by the plant but this requires further work to confirm it.

Conclusion

The leachability of the soil-borne heavy metals can be effectively reduced after application of lime and red mud. The amount of heavy metals extracted by the plant differed significantly among the different treatments despite that the soluble forms of the metals were consistently low or non-detectable for various treatments. It is evident that that non-soluble heavy metal pools were more important sources for heavy metal uptake by the plant. The bioavailability of the heavy metals was not dependent on soil pH, at least for Cu, Zn and Cd. Soil pH might have certain effects on the uptake of Pb by the plant. The growth performance of the vegetable was significantly affected by the amount of red mud added to the soil, which does not appear to be related to soil pH conditions and heavy metal toxicity.

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