Availability and Speciation of Cu, Zn, and Pb Added to Irrigated Desert Soil

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Abstract

Potential risks for human health and adverse effects on soil quality caused by accumulation of Cu, Zn, and Pb arising from the mining and smelting of heavy metals in northwestern China have long been recognized. An incubation experiment was conducted to study the availability and speciation of Cu, Zn, and Pb in the irrigated desert soil from the oasis regions of northwestern China. The quantities of Cu, Zn, and Pb extracted by NH_4NO_3 extractant increased with the quantities of Cu, Zn, and Pb added. At every metal concentration added, the quantities of heavy metals extracted by the NH_4NO_3 extractant decreased in the order: Cu>Zn>Pb. The sorption mechanism of Cu, Zn, and Pb was mainly not ion exchange, but specific sorption or precipitation. In lower added concentrations (100 mg/kg), most Cu and Pb was extracted in their reducible fraction and oxidizable fraction, probably because Cu and Pb mainly were sorbed to high energy sites. In higher added concentrations, most Cu, Zn, and Pb was extracted in its more mobile fraction (acetic acid soluble fraction), possibly because the irrigated desert soil contains high $CaCO_3$ and less organic matter. Acetic acid soluble fraction among Cu, Zn, and Pb at very initial concentrations was in the order: Zn>Cu>Pb; both reducible fraction and oxidizable fraction were in the order: Pb>Cu>Zn.

Keywords: availability, speciation, heavy metals, soil

Introduction

The input of heavy metals into soils is increasing as a result of the reuse of reclaimed sewage water for irrigation, the disposal of wastewater sludge and municipal refuse, industrial activities, and atmospheric fallout. Soils can be a sink, a source, or an interacting medium for heavy metal pollutants that affect human health and environment. The ecotoxicological significance of the environmental impact of heavy metal in soils is determined by its speciation and the nature and intensity of its association with particulate forms and solid-solution equilibria at the solid-water interface. It has long been accepted that total soil metal content alone is not a good measure of bioavailability and not a very useful tool to determine the potential risks associated with soil contamination [1]. Single step and sequential extraction have been widely used for determining availability and speciation of heavy metals in soil and the potential transfer of metals to plants, animals, and microorganisms. Speciation of heavy metals in soil depends on many factors, namely soil type, land use type, pH, CEC, redox potential, organic matter and oxides, and agricultural activity [2-8].

In northwestern China there is extensive mineral resource characterized by large quantities of ores containing copper, nickel, lead, zinc, iron, etc. Due to the shortage of irrigation water, it has a long history of using industrial and domestic wastewater to irrigate or partially irrigate croplands. The mining and smelting of heavy metals has created soil contamination problems of the greatest magnitude in the oasis, northwestern China [9-11].

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Table 1. Some physical and chemical properties of the irrigated desert soil used in this experiment.

Sand (%)	Silt (%)	Clay (%)	pH	CEC (cmol$_{(+)}$kg^{-1})	CaCO$_3$ (%)	OM (%)	Fe (%)	Mn (mg/kg)	Cu (mg/kg)	Zn (mg/kg)	Pb (mg/kg)
53.6	39.3	7.1	8.16	15.01	8.7	1.14	2.89	671	56.26	41.33	34.13

There is limited information on the availability and speciation of heavy metals in the irrigated desert soil from the oasis regions. This paper studied the availability and speciation of Cu, Zn, and Pb added to an irrigated desert soil from the oasis regions after a 180-day laboratory incubation.

Materials and Methods

Soils

Surface (0-15 cm) samples of the irrigated desert soil were collected from the oasis regions in the middle reaches of the Heihe river basin, northwestern China. The soil samples were air-dried, lightly ground and sieved through a < 2 mm sieve in preparation for the incubation experiments. Sand, silt, and clay were quantitatively measured by the pipette method; soil pH in water (1:1) was measured by a combined glass calomel electrode; organic matter content was measured using potassium dichromate oxidation; cation exchange capacity (CEC) was measured using the EDTA-ammonium acetate method [12]. Carbonate contents were determined using titration. Total iron, manganese, copper, zinc and lead in soil were extracted using an acid digestion mixture (HF+HClO$_4$+HNO$_3$) in an open system and was determined by atomic absorption spectrometer (Type M6MK2, Thermo Electron). Some physical and chemical properties of soils studied are presented in Table 1. Metals in soils (natural origin) can arise from parent material, agricultural activities, and continuous atmospheric deposition.

Soil Treatments

Soil samples (2 kg dry weight) were treated with mixed Cu(NO$_3$)$_2$, Zn(NO$_3$)$_2$, and Pb(NO$_3$)$_2$ solution containing the same concentrations of copper, zinc, and lead. Final soil concentration was 100, 250, 500, 1,000, 1,500, and 2,000 mg/kg for Cu; the concentration of Zn and Pb in soil was also the same as that of Cu. Copper, zinc, and lead ion solution used in this study was analytical grade and in the form of nitrate. The treated soils with Cu, Zn, and Pb were thoroughly mixed by hand. The moisture content of soils after treatments was 70% of water holding capacity. The soil samples were incubated in plastic boxes covered with plastic film at room temperature for 180 days. The soil samples were air-dried, lightly ground and sieved through < 2 mm sieve before being analyzed.

Single Extraction

The availability of Cu, Zn, and Pb was measured using 1 M NH$_4$NO$_3$. Twenty grams of soil samples were added to 50 ml 1 M NH$_4$NO$_3$ in 100 ml polypropylene centrifuge tubes and shaken at room temperature for 2 hours. The suspensions were then filtered through Whatman 42 filter paper. The filtrates were acidified with concentrated HNO$_3$ and stored at 4ºC prior to the analysis, and filtrates were measured for Cu, Zn, and Pb concentrations by atomic absorption spectrometer (AAS). There were three replicates for each treatment.

Sequential Extraction

Sequential extraction was carried out on air-dried hand-ground soils by the BCR extraction procedure developed within the Standards, Measurements and Testing Programme (formerly the Community Bureau of Reference, BCR) of the European Commission [13]. 1 g soil was extracted using the following sequential extraction procedure.

Firstly, soil samples were shaken at room temperature with 40 ml of 0.11 M acetic acid for 16 hours (overnight) in 100 ml polyethylene centrifuge tubes and centrifuged at 4,000 rpm for 10 min. The supernatant were then filtered through Whatman 42 and filter paper. This fraction (F1) corresponds to an exchangeable and specifically adsorbed fraction (acetic acid soluble fraction).

Secondly, the resulting residue was shaken at room temperature with 40 ml of 0.5 M hydroxylammonium chloride adjusted to pH 1.5 with high purity HNO$_3$ for 16 hours (overnight), centrifuged, and filtered. This fraction (F2) corresponds to Fe/Mn oxides and hydroxide-bound fraction (reducible fraction).

Thirdly, the residue was added to 10 ml of 8.8 M H$_2$O$_2$ adjusted to pH 2. The soil residue was digested at room temperature for 1 hour (vessel covered). The mixture was taken to dryness on a water bath heated to 85ºC for 1 hour; then the volume was reduced to < 1 ml (uncovered vessel). A second 10 ml H$_2$O$_2$ was then added and taken to dryness on a water bath at 85ºC with intermittent manual shaking. After cooling, 50 ml of 1 M NH$_4$OAc adjusted to pH 2 with HOAc were added to the dry residue to prevent the readsorption of extracted metals onto the oxidized solid residue. The mixture was extracted by shaking for 16 hours (overnight), followed by centrifugation and filtration as before. This fraction (F3) corresponds to primarily organically bound and sulfide metals (oxidizable fraction).

Table 2. Quantity of the extracted Cu, Zn, and Pb in using the NH$_4$NO$_3$ extractant.

Added metal concentration	Cu	Zn	Pb	Total (Cu+Zn+Pb)
	(mg/kg)			
100	4.114	0.788	0.561	5.463
250	20.372	2.757	0.852	23.979
500	47.741	8.595	1.279	57.614
1,000	107.092	33.337	4.103	144.532
1,500	178.125	106.123	11.561	295.806
2,000	231.054	222.327	32.105	485.455

Relative standard deviation (RSD) with the three replicates was almost all below 2% in all cases.

All soil extracts were analyzed for Cu, Zn, and Pb by the atomic absorption spectrometer (Type M6MK2, Thermo Electron). There were three replicates for each treatment.

Results and Discussion

Copper, Zinc, and Lead Availability

The quantities of Cu, Zn, and Pb extracted with NH$_4$NO$_3$ were shown in Table 2. Results are the mean values of three replicate experiments. The relative standard deviation (RSD) associated with the three replicates was below 2% in all cases. As can be seen from Table 2, a large variation in the quantities of Cu, Zn, and Pb extracted from the irrigated desert soils by the NH$_4$NO$_3$ extractant. The quantities of Cu, Zn, and Pb extracted increased with the quantities of Cu, Zn, and Pb added. At every metal concentration added, the quantities of heavy metals extracted decreased in the order: Cu>Zn>Pb. The amount of available Cu was greater than Zn and Pb in the irrigated desert soil. These results were not in keeping with reports of greater sorption hysteresis of Cu than Zn in acid soils [14], very low desorption of copper from humic acids and soil oxides [15-16], and with Miller et al. [17] observation of preferential adsorption of Cu and Pb with respect to Cd and Zn. Probably this was an effect of less organic matter, and different sorption sequence of Cu, Zn, and Pb in the irrigated desert soil.

In all cases, the quantities of moveable Cu, Zn, and Pb did not exceed 12, 11.2, and 1.7% of their total quantities, respectively. The slight increase in the percentage of Cu, Zn, and Pb extracted with initial added concentration in this study is attributable to increased occupancy of binding sites, which reduces binding energy [14]. These results also showed that the sorption mechanism of Cu, Zn, and Pb was mainly not ion exchange, but specific sorption or precipitation due to alkali soil and high CaCO$_3$ content in the irrigated desert soil (Table 1).

Copper, Zinc, and Lead Speciation

The metal fractions in the sequential extraction scheme were shown in Figs. 1-3. Results were the mean values of three replicate experiments. The Relative Standard Deviation (RSD) associated with the three replicates was below 5% in all cases. Cu, Zn, and Pb in Zero-sample were mainly in the residual fraction. There were significant differences in the distribution of Cu, Zn, and Pb with the increase of initial Cu, Zn, and Pb concentrations. At low initial concentration, in most cases, smaller differences were seen in the distribution of Cu, Zn, and Pb among different fractions in the irrigated desert soil. On the other hand, at high initial Cu, Zn, and Pb concentrations larger differences were observed in most cases.

Every fraction of Cu and Pb increased with the increase of initial Cu, Zn, and Pb concentrations. Acetic acid soluble fraction (F1) and reducible fraction (F2) of Zn increased with the increase of initial Cu, Zn, and Pb concentrations;
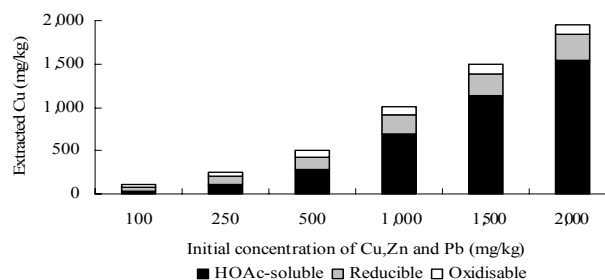

Fig. 1. Speciation of Cu in the irrigated desert soil at different initial added concentrations of Cu, Zn, and Pb.
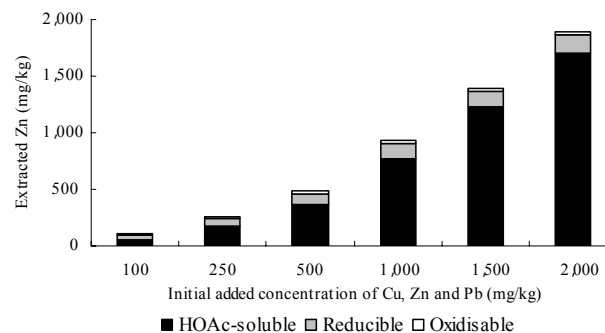

Fig. 2. Speciation of Zn in the irrigated desert soil at different initial added concentrations of Cu, Zn, and Pb.
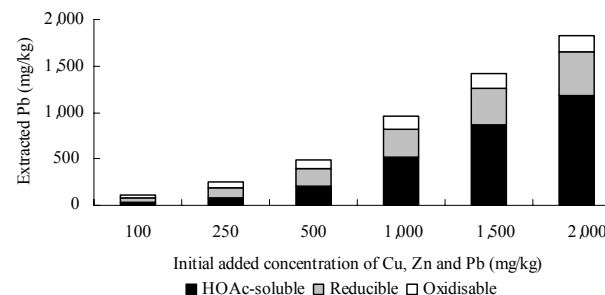

Fig. 3. Speciation of Pb in the irrigated desert soil at different initial added concentrations of Cu, Zn, and Pb.

oxidizable fraction (F3) of Zn increased with the increase of initial Cu, Zn, and Pb concentrations when initial Cu, Zn, and Pb concentrations < 1,000 mg/kg, while the difference of F3 is very small when initial Cu, Zn, and Pb concentrations >1,000 mg/kg, which suggested that Zn was readily transferred to acetic acid soluble fraction and reducible fraction. These results showed that Mn and Fe oxides acted as efficient sinks of Zn, although these metal fractions could be released under reducing conditions.

When initial concentrations of Cu, Zn, and Pb was 100 mg/kg, the quantity of different fractions of Cu and Pb was in the order: F2>F3>F1; the quantity of different fractions of Zn was in the order: F1>F2>F3, which suggested that mobility of Zn is high in the irrigated desert soils. Łukowski and Wiater [6] reported that the Cu content in particular fractions can be arranged quantitatively in order as follows: F2>F3>F1. When initial concentrations of Cu, Zn, and Pb was 250 mg/kg, the quantity of different fractions of Cu and Zn was in the order: F1>F2>F3; the quantity of different fractions of Pb was in the order: F2> F1>F3. This showed that the mobility of Cu and Zn was higher than Pb, which was readily bound to Mn and Fe oxides. The quantity of different fractions of Cu, Zn, and Pb was in the order: F1>F2>F3 when initial concentrations of Cu, Zn, and Pb ranged from 500 to 2,000 mg/kg. The acetic acid at lower pH should extract mostly from both exchangeable form and carbonate-bound fractions [18]. In lower added concentrations (100 mg/kg), most of Cu and Pb were extracted in their reducible fraction and oxidizable fraction probably because Cu and Pb mainly were sorbed to high energy sites. In higher added concentrations, most of Cu, Zn, and Pb were extracted in their more mobile fractions (acetic acid soluble fraction), possibly because the irrigated desert soil contains high $CaCO_3$ and less organic matter, indicating that the number of surface active sites responsible for the retention of more mobile fractions must be larger than the number of sites of high energy in the more resistant fractions [19].

Acetic acid soluble fraction (F1) among Cu, Zn, and Pb at very initial concentrations was in the order: Zn>Cu>Pb, indicating that the mobility of Zn is highest among Cu, Zn, and Pb. Reducible fraction (F2) among Cu , Zn, and Pb at very initial concentrations was in the order: Pb>Cu>Zn. Oxidizable fraction (F3) among Cu , Zn, and Pb at very initial concentrations was also in the order: Pb>Cu>Zn. This may be explained by differences in chemical characteristics among Cu, Zn, and Pb. Copper and lead can be preferentially combined with organic matter and Mn and Fe oxides compared with Zinc.

Conclusions

The quantities of Cu, Zn, and Pb extracted increased with the quantities of Cu, Zn, and Pb added. The amount of available Cu was greater than Zn and Pb in the irrigated desert soil. Every fraction of Cu and Pb increased with the increase of initial Cu, Zn, and Pb concentrations. Most of Cu, Zn, and Pb were extracted in their more mobile fraction (acetic acid soluble fraction) with increase of added concentrations of Cu, Zn, and Pb in the irrigated desert soil. The change of geochemical conditions might promote the release of Cu back into soil solution thus impacting organisms in the soils.

Acknowledgements

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