Fractionation of Zn and Pb in bulk soil and size fractions of water-stable micro-aggregates of lead/zinc tailing soil under simulated acid rain

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Abstract

A typical lead/zinc tailing soil was collected from in Qixia Mountain located in the east of Nanjing City, China, and separated into four size fractions of water-stable micro-aggregates. Bulk soil and each size fractions of micro-aggregates were leached using the simulated acid rain made of a H₂SO₄ to HNO₃ mole ratio of 4:1 with pH 4.5 under the ratio for liquid to solid (5/1, 10/1 and 50/1) and the treatment time (6h, 12h, 24h and 48h). After the leaching of the simulated acid rain, modified BCR sequential extraction procedure was used to gain information on potential mobility of heavy metals in bulk samples and size fractions of water-stable micro-aggregates of tailing soil. The extractable contents decreased with the increase of leaching time, but increased significantly with the increase of ratio of liquid to solid. The extractable contents of Cu, Pb and Zn in the 250-50 μm and the <2 μm fraction were significant lower than them in the fraction of the >200 μm and the 50-2 μm fraction. Zn was found to be predominantly associated with the acid extractable and the residual fraction; Pb was predominantly associated with the reducible fraction; Cu was dominant in the reducible and the oxidizable fraction. The treatment time has no significant effects on the fractionation of Zn, Pb and Cu, but the increase of the ratio of liquid to solid increased the acid extractable fraction of Zn, Pb and Cu. The fractionation pattern of the metals (Zn, Pb and Cu) differed with the size fractions of water-stable micro-aggregates.

Keywords: Fractionation; heavy metal; tailing soil; micro-aggregates; simulated acid rain

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1. Introduction

Mining/smelting is one of the main sources of heavy metal pollution in the environment. Therefore, many researches have been done in different metal mines and surroundings on the release and accumulation, transportation and transformation, spatial distribution and bioavailability of the heavy metals, as well as the potential environmental risks of heavy metals [1-4]. The tailings generally contain higher concentration of heavy metals, which may be important sources of water pollution and of wind-borne, metal-containing dusts. For a certain contaminated tailing soils, soil properties and contaminant related parameters are fixed and unchangeable, so the variables affecting the release of metals are the rain and the organism such as microbes and wild plants.

Acid rain is considered as one of the major environmental issues in recent years due to the rapid economic development in China [5]. Some researchers reported that acid rain usually occurred in large areas mainly south of the Yangtze River, especially in the suburbs of industrial cities [6, 7]. Acid deposition can cause the deterioration of terrestrial and aquatic ecosystem, such as accelerating soil acidification, resulting in the activation of aluminum (Al) and toxic heavy metals and thus increasing their ecological risk [8]. Previous studies emphasized the impact of acid rain on metal solubility, and concluded that the pH of acid rain was the main factor altering the mobility and speciation of metals in soil [9-11]. Researches have confirmed that the concentration of heavy metals in soils was controlled by the particle sizes, as it was reported that accumulation of heavy metals was inversely related to particle size [12-14]. Whether does the acid rain affect the mobility and speciation of metals in soil? It is important for the research on the soil contamination around mine tailing soils. The metal distribution among the different soil components can be estimated using specific chemical reagents in order to discriminate the total metal content over various operationally defined fractions in the solid phase.

The objective of the present study is to study the release and fractionation of Zn and Pb in bulk samples and size fractions of water-stable micro-aggregates of lead/zinc tailing soil under simulated acid rain. It is important for modeling and policy implementation to know which particle sizes of mine tailing soils are dominant in release of pollutants under naturally acid rain leaching.

2. Materials and methods

2.1. Soil collection and separation of water-stable micro-aggregates

Tailing soil was collected from a mining site named Qixia Mountain located in the east of Nanjing City, Jiangsu province in east China. The topsoil (0–15 cm) samples were collected, composited by mixing together and air-dried for further use. Bulk soil (100 g) was dispersed in distilled water (500mL) by physical, rather than chemical, dispersion. The >200μm (SF1) and 250-50 μm (SF2) fractions were obtained by wet sieving using a sieve stack consisting of 200- and 50-μm sieves and 50-2 μm (SF3) fraction was obtained by sedimentation, while the <2 μm (CS) fraction was obtained by centrifugation. Finally, all samples of separated particle fractions were dried at 50 °C using infrared radiation.

2.2. Simulated rain preparation and batch experiment

The mean pH of rainfall was about 4.65 and the mole ratio of SO$_4^{2-}$ and NO$_3^-$ in the acid rain ranged from 2.60 to 8.08 in Jiangsu Province [6]. Therefore, according to this chemical composition of the rainfall in local rain water, the simulated acid rains in this experiment were made of a H$_2$SO$_4$ to HNO$_3$ mole ratio of 4:1 with pH 4.5. Control group (C) was deionized water that saturated with CO$_2$ in air and stand for the normal rain.
The annual rainfall is around 1100 mm in the sampling areas, so it could be considered that the weight of rain/m²/year was about 1100 kg. If it was assumed that the thickness of tillage layer was 0.15 m and the soil bulk density was 1.5 g/cm³, the weight of rain/m² was 225 kg. So in the batch experiment, the ratio of liquid to solid was set as 5:1 to mean the leaching of natural acid rain of tillage layer soil per centiare per year.

The batch experiments were set as: 1) the simulated acid rains were made of H₂SO₄, HNO₃ and a H₂SO₄ to HNO₃ mole ratio of 8:1 and 4:1 with pH 4.5 with the ratio of 5:1 for liquid to solid for the treat time of 24 h for bulk soil; 2) the treatment time was set as 6 h, 12 h, 24 h and 48 h and the simulated acid rains were made of a H₂SO₄ to HNO₃ mole ratio of 4:1 with pH 4.5 with the ratio of 5:1 for liquid to solid for bulk soil; 2) the ratio of liquid to solid was set as 5:1 (S5), 10:1 (S10) and 50:1 (S50) and the simulated acid rains were made of a H₂SO₄ to HNO₃ mole ratio of 4:1 with pH 4.5 with 24 h treatment time for bulk soil and four size fractions.

Artificial acid rain solution was added into 2 g air-dried soil samples, and the mixture was agitated. pH of the mixture was measured and then centrifugally separated when batch finished. The centrifugal solution was passed through a 0.45 µm filter acidified to pH less than 2.0, and refrigerated in 4°C condition for further analysis. Metal concentrations were measured using ICP-OES (Perkin-Elmer SCIEX, Optima 5300). All the experiments were conducted in triplicates at room temperature 25 ºC.

2.3. Extraction of heavy metals by modified BCR sequential extraction procedure

Modified BCR sequential extraction procedure was used to gain information on potential mobility of heavy metals in bulk samples and size fractions of water-stable micro-aggregates of tailing soil after the leaching of simulated acid rain. Four operationally defined fractions are acid soluble fraction (F1, soluble and exchangeable fraction and bound to carbonates, 0.11 mol l⁻¹ CH₃COOH, for 16 h), reducible fraction (F2, bound to Fe/Mn oxides, 0.5 mol l⁻¹ NH₂OH•HCl, pH 1.5, for 16 h), oxidizable fraction (F3, bound to organic matter and sulphides, 30% H₂O₂ acidified with HNO₃ to pH 2 at 85 °C for 2 h, then followed by the extraction with 1 mol l⁻¹ CH₃COONH₄, pH 2-3, for 16 h) and residual fraction (R, digestion with aqua regia, ISO 11466). Between successive extraction steps, separation was performed by centrifugation at 3500 rpm for 20 min. The supernatant was decanted in polyethylene containers and stored in a refrigerator at about 4°C prior to analysis. Metal concentrations were measured using ICP-OES (Perkin-Elmer SCIEX, Optima 5300). All the experiments were conducted in triplicates.

3. Results and Discussion

3.1. Leaching heavy metals (Cu, Pb and Zn) in tailing soil under the treatment of simulated acid rain

The effects of treatment time on the extractable contents of Cu, Pb and Zn in bulk soil using simulated acid rain are shown in Fig. 1. The extractable contents of Zn were significant higher than them of Cu and Pb (Fig. 1). The total contents were 0.05% for Cu, 0.25% for Zn and 0.73% for Zn in bulk tailing soil. The percentage of extractable contents to the total contents was about 0.1% for Cu and Zn and about 0.01% for Pb. The extractable contents decreased when the extraction time was 48 h. This may result from readsoption for the long time extraction.

The extractable contents of Cu, Pb and Zn leached using simulated acid rain with different ratio of liquid to solid in bulk soil and size fractions of water-stable micro-aggregates are shown in Fig. 2. The extractable contents of Cu, Pb and Zn increased significantly with the increase of ratio of liquid to solid in bulk soil and size fractions of water-stable micro-aggregates (Fig. 2). Compared with bulk soil, the
extractable contents of Cu, Pb and Zn in the fraction of SF2 and CS were significant lower than them in the fraction of SF1 and SF3.

Fig. 1. Contents of Cu, Pb and Zn leached using simulated acid rain with different treatment time in bulk soil.

Fig. 2. Contents of Cu, Pb and Zn leached using simulated acid rain with different ratio of liquid to solid in bulk soil and size fractions of water-stable micro-aggregates

3.2 Fractionation of heavy metal (Cu, Pb and Zn) in RDSs and their potential mobility and bioavailability

The average percentage of metal contents for each fraction to its sum of the 4 extraction steps was calculated and the average fractionation pattern of the metals in the bulk tailing soil after leaching using simulated acid rain with different treatment time is given in Fig. 3. Fig. 3 shows that Zn was found to be predominantly associated with the acid extractable and the residual fraction; Pb was predominantly associated with the reducible fraction; Cu was dominant in the reducible and the oxidizable fraction. The acid extractable and the residual fractions are the most bioavailable species. So Zn is the most mobile elements and Pb has weak mobility. There were no significant changes in the fractionation of Zn, Pb and Cu after the treatment of the simulated acid rain with different treatment time.

The average fractionation pattern of the metals in the bulk tailing soil after leaching using simulated acid rain with different ratio of liquid to solid in bulk soil is given in Fig. 4. Fig. 4 shows that fractionation pattern of the metals (Zn, Pb and Cu) was similar to them in Fig. 3. The ratio of liquid to solid was set to mean the leaching effects of different volume natural acid rain. With the increase of the ratio of liquid to solid, the acid extractable fraction for all metals (Zn, Pb and Cu) increased.

Fig. 3. Fractionation of Cu, Pb and Zn leached using simulated acid rain with different treatment time in bulk soil.
The average fractionation pattern of Cu, Pb and Zn leached using simulated acid rain in bulk soil and size fractions of water-stable micro-aggregates is given in Fig. 5. Fig. 5 shows that fractionation pattern of the metals (Zn, Pb and Cu) differed with the size fractions of water-stable micro-aggregates. Compared with the bulk tailing soil, the average percentage of Pb in the reducible fraction decreased, and the residual fraction increased; there were obvious increase in the acid extractable fraction of Zn except for the size fractions of SF2; Cu had similar to Pb, but its acid extractable fraction increased. Compared with the control treatment groups, there were no significant changes in the average fractionation pattern of Cu, Pb and Zn in bulk soil and size fractions of water-stable micro-aggregates.

Fig. 4. Fractionation of Cu, Pb and Zn leached using simulated acid rain with different ratio of liquid to solid in bulk soil.

Fig. 5. Fractionation of Cu, Pb and Zn leached using simulated acid rain in bulk soil and size fractions of water-stable micro-aggregates.

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