Bull. Environ. Contam. Toxicol. (2003) 70:46–53
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DOI: 10.1007/s00128-002-0154-y

Bulletin of Environmental Contamination and Toxicology

# Changes in Form of Rare Earth Elements after Acid Rain Leaching Through Soil Column

Y. Zhang,[1] L. Dai,[2] X. Wang,[1] B. Du[1]

[1] State Key Laboratory of Pollution Control and Resources Reuse, School of Environment, Nanjing University, Nanjing 210093, People's Republic of China
[2] Center of Material Analysis, Nanjing University, Nanjing 210093, People's Republic of China

Received: 21 October 2001/Accepted: 16 August 2002

In China, Rare earth elements (REEs) are applied to cropland as micro-REEs fertilizers because of their ability to increase yields and improve qualities of crops (Guo et al. 1988). As a result, more and more REEs are moving into environment owing to their wide application in agriculture practice. It has been found that they might accumulate in soil, bioaccumulate in crops, and transfer into food chain, which improve REEs exposure to environment and made REEs a special pollution problem in China due to anthropology activity. Environmental effects of the exogenous REEs have received much attention from both environmental scientists and administrator. In recent years, a number of studies have been carried out on REEs accumulation of REEs and distribution (Yang et al. 1984). Acid rain is considered a global problem and has damaged aquatic ecosystems, crop, manmade materials, soil, and even human health. It also can alter physicochemical forms of metals in soils, which was influencing its distribution in soil, bioavailability, and mobility. Acidity of acid rain increased annually, and the strong acidic precipitation occurs more and more frequently in China, especially in the south (Hong, 1995). Several studies have been done on its effect on soil, crop and ecosystems. (Dong et al. 2000)

It is widely accepted that determining total content of heavy metals is insufficient to assess the environmental impact of metal in contaminated soils. The different fractions of metal in soil vary considerably in their chemical reactivity, lability, bioavailability, and susceptibility to leaching. Attempts have been made to assess mobilization and bioavailability of heavy metals in soils using certain sequential extraction procedures. Selective sequential extraction is a technique used to determine the solid-phase forms of metal in soil. Many different sequential extraction schemes have been proposed in literature. (Shumn, 1985; Davis-Cater and Shuman, 1993). The most widely used was proposed by Tessier et al. (1979). Although the sequential extraction methods suffer from non-selectivity and trace element redistribution among phases during extraction, they are still considered useful evaluation of leaching and bioavailability of trace metals in soil by many

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*Correspondence to:* X. Wang

research workers (Tuin and Tels, 1990). Based on the sequential extraction fractionation procedure described by Tessier et al. (1979), the REEs in soil were divided into (1) exchangeable (EXC), (2) bound to carbonates (CB) (3) bound to iron and manganese (FM), (4) bound to organic matter (OM), (5) residual (RE) fraction.

Few studies have been available about the effect of acid rain on the distribution, transformation and fate of the exogenous REEs in two different ways of pollution after acid rain leaching (Zhang et al. 2001). In this paper, pollution of soils with REEs was divided into two categories: instant pollution and accumulated pollution (Zhang et al., 2001). We studied the effect of acid rain on fraction changes of REEs in soil through column experiment where instant pollution and accumulated pollution was simulated. In this investigation, we selected the red soil purposely because it is major type of soil in acid rain area and cover large area in the south of China. The potential effects of acid rain on fractions of REEs in soil were studied to determine which kind of pollution would pose the greater threat to the environment. This was done by a comparative study of the changes in forms of REEs in soil columns after acid rain leaching.

## MATERIALS AND METHODS

The red soil (collected from Jiangxi, China) was taken from the surface (0-20cm). The soil was air dried, and ground to pass through a sieve (2mm) for the experiment. The solution containing REEs (1mg/ml) was prepared by using micro-REEs fertilizers. The physicochemical characterizations of soil and the constitutions of micro-REEs fertilizers were listed in table 1 and table 2.

Polyvinyl chloride columns (10cm inside diameter and 20cm in length) were adopted in this study. Each column was filled with soil (about 500g) to the height of 4cm so that the bulk density was similar to the bulk density in the fields. The columns were shaken during filling soil and water was aided to improve soil compacting. Details of filling columns were described as following:
Soil without adding exogenous REEs was filled in column Ⅰ, as a blank control. Column Ⅱ was filled with soil which has been incubated for equilibrium for 15 days after saturated with distilled water and added with 50ml REEs solution. It simulated instant pollution. Column Ⅲ was filled with untreated soil to the height of 3cm with another treated soil filling above to the height of 4cm, which was pretreated in the following procedure: The soil was flooded with distilled water, mixed with 50ml REEs solution and air-dried. The drying soil was ground, and sieved (2mm) to simulate accumulated pollution.

The artificial acid rainwater was prepared according to the composition analysis of rainwater in the Nanjing area and was adjusted to pH 3.0. A 4000ml volume of artificial acid rain was dripped on each column to simulate five years of rainfall. During the leaching, the layer of acid rain in the soil column was maintained 1 cm higher than the soil surface and effluent flow was kept with an average rate of 50ml/h. Acid rain was dripped 10 h/d for 8 days. Samples were collected at 500ml intervals.

**Table 1.** Physico-chemical proprieties of the red soils

| Soil | pH | Organic matter (g/kg) | Cation exchange capacity (cmol/kg) | Clay% (<0.002mm) |
|---|---|---|---|---|
| Red soil | 5.45 | 0.63 | 5.07 | 32.3 |

**Table 2.** The constitution of micro-rare earth elements fertilizer

| Element | Lanthanum | Cerium | Neodymium | Praseody-mium | Samarium |
|---|---|---|---|---|---|
| Content(%) | 26.85 | 46.44 | 18.53 | 7.32 | 0.86 |

**Table 3**. The sequential extraction scheme for REEs fraction

| Step | Fraction | Extraction reagents | sample :reagent | Extraction |
|---|---|---|---|---|
| 1 | EXC | 1 mol/l $Mg(NO_3)_2$ (pH7.0) | 1:2.5 | Shake 2h, 25℃ |
| 2 | CB | 1mol/l $NH_4OAC$ (pH5.0) | 1:10 | Shake 2h, 25℃ |
| 3 | FM | 0.04mol/l NH2OH•HCL in 25% HOAC | 1:10 | Water bath 96℃, 6h |
| 4 | OM | 30% $H_2O_2$<br>1mol/l $NH_4OAC$ | 1:8<br>1:10 | Water bath 85℃ 7h<br>Shake 2h, 25℃ |
| 5 | RE[1] | | | Burn 10 minute in oven 700℃ |

[1] Residue from step 4 was dried, and then added with 5 gram $Na_2O_2$ (Zhen and Shen, 1989).

After leaching, soil in the column was divided into 4 layers at even heights. The soil samples at each layer were collected in plastic bag, dried, ground and store in the drying bottle through the same procedure as treatment of soil. Samples of soil were collected and subjected to sequential extraction (Table 3) according to modification of the method by Tessier et al, (1979). Extractions were performed on 2 gram of dried soil samples in 50ml polyvinyl centrifuge tubes with mechanical shaking. Following each extraction, the mixture was centrifuged at 3000rpm for 30 minute. The supernatant was filtered through 0.45 μ m membrane filters. The solid residues were washed out with sub-boiling distilled water, and the obtained solutions were combined for analysis. All the extractions were done twice. The REEs concentration of the former five forms was measured by ICP-AES. In order to estimate the error in the procedure, a fractionation was also carried out for the recommended reference sample GSS-5, which were geological reference materials provided by the Institute of Geophysical and Geochemistry Prospecting (IGGP), Ministry of Geology and Mineral resources. Comparisons between the sum of various REE forms measured in this experiment and the total REEs concentrations of the reference samples showed a deviation < 8.9%. The results obtained by the parallel test of the same soil sample indicated that the mean relative error was less than 5%.

## RESULTS AND DISCUSSION

The exchangeable contents and organically bound trace metals were found to represent these that were available to plant by some researchers (Iyengar et al. 1981; Sims, 1986). In other studies, the exchangeable forms characterized the most mobile metal and immediately bioavailable forms. It is the most labile metal forms in the soil environment and has greater leaching potential than the other forms (Peruzzelli, 1989; Shuman, 1991). The RE fraction was held by the primary and secondary minerals with their crystal structure. The REEs in the RE fraction are not excepted to be released in solution over a reasonable time span under the conditions normally encountered in nature (Tessier et al., 1979). With this technique it is possible to determine the mobility and bioavailability of metal from soil solid phases. In this paper we focused on the change of the EXC and the RE fraction in order to compared the mobility and bioavailability of REEs for the two pollution ways. The concentration of Sm was very low in the micro-REEs fertilizers and those, not discussed.

The EXC fraction change of four kinds of REEs is given (Figure 1). In column I the percentage of Ce in the first layer was greater than those of unleached soil, which indicated the potential and bioavailability of the REEs would be increased under acid rain leaching. In column II, the percentage of Ce in the first layer was greater than that in other layers. This suggests the exogenous REEs were retained by the soil. It also can be concluded that leaching potential and bioavailability would be increased when the exogenous REEs went into the soil after leaching. The Ce concentration under the first layer was less altered compared with those of column I . In columnIII the percentage of Ce concentration decreased slowly with the depth of column. The percentage of Ce concentration in all layers of columnIII were higher than those of column I , which indicated the exogenous REEs have been migrated. By comparing the percentage of three REEs concentration in column II with columnIII, we found the EXC fraction in columnIII were greater than that in column II except for first layer, which meant the soil with accumulated pollution had greater leaching potential and bioavailability than soil with instant pollution. The results were in agreement with Zhang et al. (2001).

In column I the percentage of La and Nd in the first layer were greater than those of unleached soil. In column I the percentage of La and Nd decreased more rapidly from the first layer to the second layer than those of Ce. These observations are explained by the competitive adsorption and fraction action among REEs. Changes of La and Nd in the EXC fraction of column II and columnIII were similar to those of Ce.

In column I the percentage of Pr in the EXC fraction increased with the depth of column, which indicated Pr has more leaching potential and bioavailability than those of Ce, La, and Nd in the original soil under rain leaching. The percentage of Pr concentration in column II and columnIII were similar to those of La and Nd.

The RE fraction change of four kinds of REEs was given in Figure2. In uncontaminated soil the percentage of Ce changed a little, which indicated that Ce in the RE fraction wasn't released much under acid rain leaching. In instant pollution soil, the percentage of Ce significantly increased from first layer to second layer and increased slowly since second layer, which also meant the exogenous REEs were retained by the soil. In the accumulated pollution soil, the percentage of Ce concentration increased slowly with depth of column. The percentage of Ce concentration in all layers of columnIII were less than those of column I , which indicated the mobility and bioavailability of REEs would be increased in the contaminated soil. Comparing the percentage of Ce concentration in column II with columnIII, we found the RE fraction in column II were greater than that in columnIII, except for first layer. The results also suggested soil with accumulated pollution had greater leaching potential and bioavailability than soil with instant pollution.

The percentage of La and Nd in the RE fraction in the first layer of column I was less in leached relative than those of the unleaching soil . The percentage of La and Nd in the RE fraction in the first layer of column I was released more than those of Ce during acid rain leaching. These observations are explained by the competitive adsorption and fraction action among REEs. The change of La and Nd in the RE fraction of contaminated soils was similar to those of Ce.

Pr in the RE fraction of column I decreased rapidly compare with the original soil without leaching, which indicated that Pr in the RE fraction was released more than those of Ce, La and Nd under acid rain leaching. The percentage of Pr in column II and columnIII decreased more slowly with the depth of column compare with those of Ce, La and Nd, which meant the possible competitive adsorption might exist among these REEs in the soil.

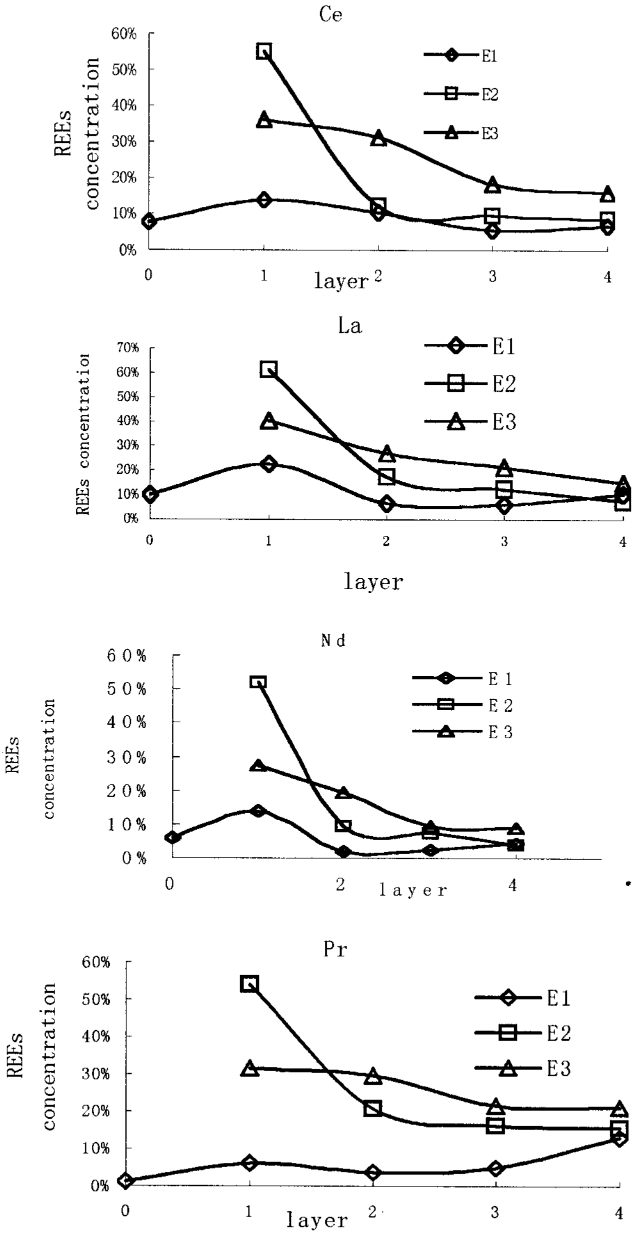

**Figure 1**. The EXC fraction change of four kinds of REEs in the red soil
E1, E2, E3 represent the EXC fraction in column I ,column II,columnIII. 0,1,2,3, and 4 of abscissa represent original soil without leaching, 0-1cm, 1-2cm, 2-3cm, 3-4cm depth in the soil column respectively.

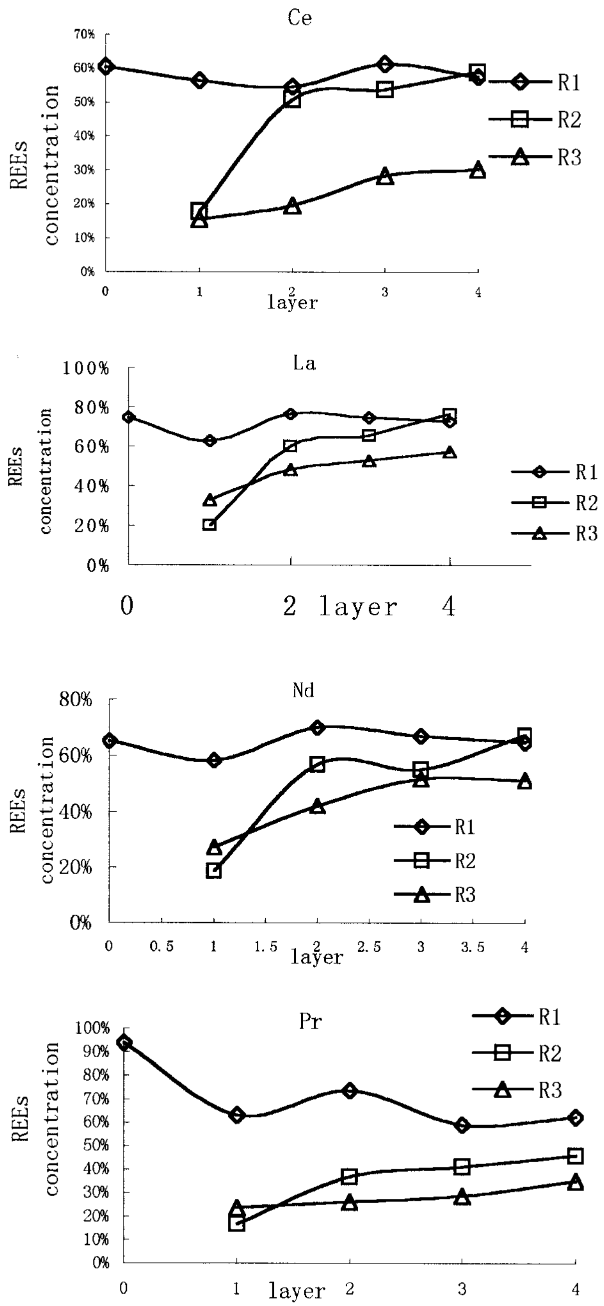

**Figure 2**. The RE fraction change of four kinds of REEs in the red soil

R1, R2, R3 represent the RE fraction in column I ,column II,columnIII. 0,1,2,3, and 4 of abscissa represent original soil without leaching, 0-1cm, 1-2cm, 2-3cm, 3-4cm depth in the soil column respectively.

*Acknowledgment* This work was supported by the National Natural Science Foundation of P. R. China.

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