Effects of soil type on leaching and runoff transport of rare earth elements and phosphorus in laboratory experiments

Lingqing Wang · Tao Liang · Zhongyi Chong · Chaosheng Zhang

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Abstract
Introduction Through leaching experiments and simulated rainfall experiments, characteristics of vertical leaching of exogenous rare earth elements (REEs) and phosphorus (P) and their losses with surface runoff during simulated rainfall in different types of soils (terra nera soil, cinnamon soil, red soil, loess soil, and purple soil) were investigated.

Results and analyses Results of the leaching experiments showed that vertical transports of REEs and P were relatively low, with transport depths less than 6 cm. The vertical leaching rates of REEs and P in the different soils followed the order of purple soil > terra nera soil > red soil > cinnamon soil > loess soil. Results of the simulated rainfall experiments (83 mm h⁻¹) revealed that more than 92% of REEs and P transported with soil particles in runoff.

Conclusion The loss rates of REEs and P in surface runoff in the different soil types were in the order of loess soil > terra nera soil > cinnamon soil > red soil > purple soil. The total amounts of losses of REEs and P in runoff were significantly correlated.

Keywords Soil · Phosphorous · Rare earth elements · Simulated rainfall · Manure

1 Introduction

When excessive phosphate fertilizers are applied in the farmland soils for a long time, phosphorus input becomes greater than its demand, and the utilization efficiency of applied phosphorus (P) for crops can be as low as 10–25%, causing the enrichment of P in surface soils. There is an increasing concern of the environmental fate of P as it becomes the main source of eutrophication of many rivers and lakes (Sharpley et al. 2001). Agricultural non-point source P loss, while existing mainly in surface runoff, can also be significant in subsurface flow (Sims et al. 1998). It has been found that both P losses are affected by soil type (Heckrath et al. 1995). Phosphorus is a reactive solute but primarily exists as insoluble phosphate complexes in soils. Phosphates can be readily adsorbed by soil particles (clay mineral surfaces and amorphous oxy-hydroxides), precipitated by common soil cations (Al, Ca, Fe), or immobilized by microorganisms after a series of chemical, biological, and physical reactions. There are many studies on phosphorus losses from agricultural sources, their pathways, and rates (Haygarth et al. 1998), but the key mechanisms of phosphorus transport in different types of soils remain unclear.

Rare earth elements (REEs) have been successfully used as an important source tracer and applied extensively in the analyses of the sources of pollutants, mineral genesis and transfer, and soil erosion (Laveufa and Cornu 2009; Fernández-Caliani et al. 2009; Polyakov and Nearing 2004). Exogenous REEs can be rapidly adsorbed and immobilized on the solid surfaces of soils after application.
REEs have the potential to adsorb or precipitate phosphate anions, particularly when applied in halide forms to soils (Duddya 1980). Previous studies on REEs have focused on the improvement of crop yield and quality (Liang et al. 2005), differentiation of REEs in plants (Ding et al. 2006), REE distribution, adsorption and desorption (Zhu et al. 1996), speciation and biological availability (Song et al. 2003), and the alteration of soil properties after the application of agricultural rare earth fertilizers (Wang et al. 2005). However, the vertical transport and losses with surface runoff of REEs and P in different types of soils and their interactions have not been well understood.

This study is based on soil column leaching experiments and simulated rainfall experiments in order to investigate the vertical transport and loss of P with surface runoff when affected by exogenous REEs and to analyze the effects of soil types on the process of REEs and P transport. A total of five REEs (lanthanum La, neodymium Nd, samarium Sm, cerium Ce, and dysprosium Dy) were selected for this study.

## 2 Materials and methods

### 2.1 Materials

Composite soil samples were collected from farmland surface soils (0–25 cm deep) from various locations in China, which had been under rotational management with wheat and corn without a history of applications of REEs. The properties of the soils are presented in Table 1.

Chicken (*Gallus domesticus* L.) manure contains high concentrations of P. The samples used in this study were collected from Fangshan District, Beijing, with a total P concentration of 13,687.23 mg kg\(^{-1}\) after air drying. Both soil and fertilizer samples were sieved (following air drying) through a 2-mm nylon mesh.

The REE chlorides (REECl\(_3\)·6H\(_2\)O, purity up to 99.95%) were sieved through a 100-mesh sieve and hermetically preserved in desiccators for the following experiments.

### 2.2 Experimental design

1. **Soil column leaching experiments**

Polyvinyl chloride (PVC) tubes (external diameter=11 cm, internal diameter=10.5 cm, height=20 cm) were used in the column leaching experiments. A layer of medium-speed qualitative filter paper was placed at the bottom of each tube, using a perforated PVC disk (nine holes of 1 cm in diameter). A total of 900 g of each soil (column height=8 cm) was added to each tube. Then, a total of 225 g of each soil (column height = 2 cm) was mixed with 8.04 g chicken manure (equivalent to addition of 200 kg ha\(^{-1}\) total P), plus different kind of exogenous REEs, respectively. The doses of exogenous REEs are shown in Table 2, which were designed as ten times of the background values of REEs in the soils which was determined using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS, ELAN DRC-e, Perkin Elmer SCIEX).

Leaching experiments were conducted to assess P and REE transport in the soil columns over a 14-day period. For the initial leaching, a volume of 170 ml deionized water was added to each column and allowed to drain for 48 h. Care was taken to ensure that water was added slowly ensuring the aerobic conditions during the experiment. Then the columns were leached with 200 ml of deionized water every 48 h over a 12-day period, resulting in a total of 1,200 ml of added water. The PVC tubes were covered with plastic material after each addition of water to minimize evaporation. Leachate was collected every 48 h immediately prior to addition of water and stored at 4°C prior to analyses. Following the completion of the 14-day leaching experiment, soil samples were sliced into 2 cm
sections, dried, ground, and sieved through a 100-mesh sieve for analysis.

(2) Simulated rainfall experiments

The runoff boxes (Kleinman et al. 2002) were made of PVC, 1 m long, 20 cm wide, and 5 cm deep with back walls 2.5 cm higher than the soil surface. There were nine 5-mm drainage holes on the base. A V-shaped device was installed at the end of the runoff box to collect runoff samples. A cheese cloth was placed on the bottom of the box and 13 kg different types of soils, 84.06 g chicken manure (equivalent to addition of 200 kg ha$^{-1}$ total P), and RECl$_3$ (with a dosage ten times that of soil background values) were mixed and added into the runoff boxes, respectively (Table 2). A volume of 2 l of deionized water was sprinkled evenly on the soils. After 72 h, the artificial simulated rainfall experiments began at an intensity of 83 mm h$^{-1}$.

The slope angle of the runoff boxes was 10°. The simulated rainfall experiments were conducted by applying trough-type simulated rainfall machines placed 5.2 m above the soil surface. The speed of rainfall drops was close to that of natural rainfall and the rainfall intensity uniformity coefficient reached over 0.89. After runoff generation started, runoff samples were collected every 3 min in the initial 30 min. The runoff samples were immediately filtered (0.45 μm) and divided into water samples and soil particle samples.

During the experiment, rainfall intensity was strong and the duration was short. Therefore, the effect of evaporation during the rainfall process was not considered.

2.3 Laboratory and statistical analyses

Soil and manure samples were digested with HNO$_3$–HF–HClO$_4$ (Liang et al. 2005) for measurement of total P and REEs. Some properties of the soils used in this study such as extractable P and soil organic matter were determined using the method of Bao (Wang et al. 2005). The soil samples of soil column leaching experiments were extracted with the improved Hedley method (Hedley et al. 1982) to determine various REE forms. A subtraction method was used to determine the residual forms. Phosphorus concentrations in digested solutions and water samples were measured using Inductively Coupled Plasma-Optical Emission Spectrometry (OPTIMA 5300DV, Perkin Elmer), and REE concentrations in digested solutions and water samples were measured using ICP-MS (ELAN DRC-e, Perkin Elmer SCIEX).

Each experimental treatment was conducted in duplicate. National standard products, replicates, and blanks were applied to ensure accuracy of the results during all analyzing processes. The relative errors of the results were better than 1% on average.

Differences in REEs and P between treatment groups were assessed by Student’s t test in SPSS 13.0 for Windows (SPSS Inc., Chicago, USA). Associations between REEs and P were evaluated using Pearson’s correlation coefficient. Statistical inferences discussed below were considered using the significance level of $P<0.01$.

3 Results and analyses

3.1 The leaching characteristics of REEs and P in different types of soils

As the water in the soil columns did not reach saturation in the second day, the leachate was only collected from the fourth day of the leaching experiment. At that time, approximately 570 ml water had been added to the columns. Concentrations of REEs and P in the leachates are shown in Fig. 1. The declining trends of REEs and P concentrations with time in all the different types of soils were similar. However, the leaching rate (loss rate) of REEs and P in different types of soils were different: purple soil > terra nera soil > red soil > cinnamon soil > loess soil.

The vertical distributions of REEs and P in soil columns of different types of soils are shown in Fig. 2. Figure 2(a) shows that the highest concentrations were observed at the surface (0-2 cm) where the exogenous REEs were added. At the layer of 2-4 cm, REE concentrations decreased rapidly, and they reached the background levels in soils at the depth of 4 cm and below. It indicated that it was difficult for REEs to transport vertically in all the different types of soils under study. By comparing the loss rate of REEs in the 0-2 cm layer of soils and the enrichment ratio

<table>
<thead>
<tr>
<th>Soil types</th>
<th>Cinnamon soil</th>
<th>Purple soil</th>
<th>Terra nera soil</th>
<th>Loess soil</th>
<th>Red soil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selected rare earth element</td>
<td>Ce</td>
<td>Dy</td>
<td>Sm</td>
<td>La</td>
<td>Nd</td>
</tr>
<tr>
<td>Selected rare earth element background value (mg kg$^{-1}$)</td>
<td>74.61</td>
<td>3.94</td>
<td>6.43</td>
<td>40.87</td>
<td>17.84</td>
</tr>
<tr>
<td>Rare earth chlorides</td>
<td>CeCl$_3$·6H$_2$O</td>
<td>DyCl$_3$·6H$_2$O</td>
<td>SmCl$_3$·6H$_2$O</td>
<td>LaCl$_3$·6H$_2$O</td>
<td>NdCl$_3$·6H$_2$O</td>
</tr>
<tr>
<td>Doses of rare earth chlorides in soil columns (g)</td>
<td>0.42</td>
<td>0.02</td>
<td>0.04</td>
<td>0.23</td>
<td>0.10</td>
</tr>
<tr>
<td>Doses of rare earth chlorides in soil boxes (g)</td>
<td>24.54</td>
<td>1.19</td>
<td>2.03</td>
<td>13.51</td>
<td>5.77</td>
</tr>
</tbody>
</table>
of REEs in soil samples at the depth of 4 cm and below, it was found that the vertical leaching rates of La, Ce, Nd, Sm, and Dy in different types of soils followed the order of purple soil > terra nera soil > red soil > cinnamon soil > loess soil. As shown in Fig. 2(b), similar to the vertical leaching characteristics of REEs, the vertical variation of P contents in different types of soils decreased with the increase of depth. In the 2-4 cm layer the P content decreased rapidly, reaching the level of the background concentrations in 4-6 cm layer and below. It indicated that it was also hard for P to transport in the different types of soils. The transport rate of P followed the same order of that of REEs. The reasons why losses of REEs and P in purple soil were strong may be because purple soil had low clay content and was highly permeable.

Table 3 shows the vertical distribution characteristics of different forms of REEs and P in different soil columns. The vertical distribution characteristics of different forms of REEs La, Ce, Nd, Sm, and Dy were similar to those of the total REEs. After leaching, the concentrations of different forms of La, Ce, Nd, Sm, and Dy decreased rapidly with the increasing depth of the soil profiles. The mean percentages (and ranges) of the different forms of REEs including double distilled water (DDW) extractable, NaHCO₃ extractable, NaOH extractable, HCl extractable, and residual were: 2.95% (0.41–11.77%), 17.79% (2.92–33.18%), 20.66% (2.52–44.24%), 20.91% (2.02–48.75%), and 37.68% (3.36–71.64%), respectively. The vertical distributions of different forms of P were similar to those of the total P. The different forms of P decreased rapidly with the increasing depth of the soil profile. The mean proportions (and ranges) of the different forms of P including DDW form, NaHCO₃ form, NaOH form, HCl form, and residual form were: 0.32% (0.01–0.88%), 3.19% (0.38–7.68%), 12.79% (0.07–37.29%), 6.92% (0.83–18.11%), and 76.78% (53.97–91.69%), respectively.

3.2 Characteristics of horizontal losses of REEs and P with surface runoff

During the rainfall, the amount of loose soil particles on the slope surface decreased gradually and the concentrations of REEs and P in runoff stabilized. Meanwhile, the concentrations of REEs and P fluctuated during the rainfall process which was affected by soil saturation, infiltration, splash erosion, etc.
Figures 3 and 4 illustrate the characteristics of losses of REEs and P with runoff in different types of soils in the simulated rainfall experiments. The losses of REEs and P in the beginning of runoff generation were high and then decreased rapidly with the increase of time. After 10 min, the losses of REEs and P decreased slowly and then the rates of losses stabilized. Due to the interactions between runoff water and soil, the water-soluble REEs and P reacted with the soil particles causing dynamic adsorption and desorption, which led to the fluctuation of concentrations of water-soluble REEs and P in the runoff.

The depletion rate (Kimoto et al. 2006) of the elements indicates the loss rate of REEs and P in different types of soils. This is calculated with the following formula (Kimoto et al. 2006):

\[
D = \frac{\sum (WiVi + PiMi)}{T \times 100}
\]

where \(D\) (%) is the depletion rate of an element; \(Wi\) (mg l\(^{-1}\)) is the concentration of the element in the \(i\)th water sample during the rainfall process; \(Vi\) (l) is the volume of runoff; \(Pi\) (mg kg\(^{-1}\)) is the concentration of the elements in the soil particles; \(Mi\) (kg) is the mass of soil particles; and \(T\) (g) is the total amount of the element in the soils after addition of exogenous REEs and P.

Table 4 shows the depletion rate of REEs and P in different types of soils. The loss rates of REEs and P in different types of soils with surface runoff was different: loess soil > terra nera soil > cinnamon soil > red soil > purple soil. Compared with the other soil types, the losses of REEs and P in loess soil with surface runoff were the greatest. This was possibly because that loess soil was porous and easily eroded, which caused the serious REEs and P loss.

### 4 Discussion

#### 4.1 Effects of soil type on vertical leaching of REEs and P

Experimental results in this study showed that it was difficult for REEs La, Ce, Nd, Sm, and Dy and P in soils to transport vertically. It was clear that concentrations of REEs...
and P in the first leachate were the highest and they decreased over the course of the experiment. This is because after REEs and P enter soils, they are immobilized by soil particles rapidly (Liang et al. 2005). Although there were dynamic adsorption and desorption in the leaching process, due to the dilution effect during leaching, the concentrations of water-soluble REEs and P became lower and lower. The adsorption of REEs and P in soils was affected by the soil texture, soil particle size, surface physicochemical properties, organic matter content, and pH, etc. The concentrations of these elements in the depth of 2–4 cm decreased rapidly and in the depth of 4–6 cm they were close to their background levels. According to previous studies, soils had strong capacity in retention and immobilization of REEs and P. It was found that over 99.5% of REEs and P were retained by soil particles after the exogenous rare earth elements were applied to soils, and only a very small amount remained in the soil solution (Jones 1997; Sharpley et al. 2001). The adsorption rate was affected by soil clay minerals, pH, oxidation–reduction potential, organic matter, and cation exchange capacity (Haygarth et al. 1998). Zhu et al. (1996) studied the migration of exogenous REEs through the leaching process in soil columns and performed numerical simulation. The results showed that Ce migrated downward approximately 1 cm every year in acid soils, 0.2 cm in neutral soils, and almost none in alkaline soils. Zhang et al. (2001) investigated Ce and Nd transport characteristics with the leaching experiment of soil columns, and it was found that even if the REEs amount reached 50% of the desorption rate of surface soils and the rainfall amount in the simulated rainfall experiments reached 1,000 mm, in most cases the migration depth of Ce and Nd was within 4 cm in nine different kinds of soils. In a few cases, the REEs were leached to a depth of 10 cm, but no $^{141}$Ce and $^{147}$Nd were detected in the leachate.

Similar to the transport characteristics of REEs, P in soils is hard to leach vertically. Soil particles react intensely with P making it hard for P transport in soils. The transport of P through soils with poor structure, such as in the soil

<table>
<thead>
<tr>
<th>Elements</th>
<th>Loess soil</th>
<th>Cinnamon soil</th>
<th>Red soil</th>
<th>Terra nera soil</th>
<th>Purple soil</th>
</tr>
</thead>
<tbody>
<tr>
<td>REEs</td>
<td>5.12</td>
<td>4.72</td>
<td>4.60</td>
<td>4.93</td>
<td>4.46</td>
</tr>
<tr>
<td>P</td>
<td>5.33</td>
<td>4.66</td>
<td>4.57</td>
<td>5.06</td>
<td>4.41</td>
</tr>
</tbody>
</table>
column experiment, is impeded by a variety of processes (Sims et al. 1998). There are two principal mechanisms for the vertical transport of P in soils; permeation flux, which occurs with interactions with soil particles at a slow speed; and preferential flow, which happens when water passes through the soil pores at a high speed (Cogger and Duxbury 1984). The leaching of P in soils is affected by many factors which are complicated and closely related, including climatic factors (rainfall, evaporation), soil factors (soil structure, content of organic matter, biological activity, pH, oxidation/reduction and permeability capacity for P), hydroographical factors (slope, groundwater level), as well as agricultural management factors (fertilizers and their quantity and application method, irrigation and rotation system; Welch et al. 2009; Hooda et al. 2000).

A correlation analysis was used to analyze the relationship between concentrations of REEs and P in the columns of different types of soils. The results are shown in Table 5. In columns of different types of soils, REEs were significantly correlated with P in both the leachates and soil column samples ($p \leq 0.01$). At the same time, different chemical speciation distributions of REEs and P in soil column samples also showed significant correlations ($p \leq 0.01$), which indicated that vertical leaching characteristics of REEs was similar to that of P.

4.2 Correlations between losses of REEs and P with the runoff

Under stable rainfall intensity, the relationship between sediment and runoff changed with time (Zhang et al. 2007). At the beginning of the simulated rainfall, the soils were loose and could be easily eroded. The soils were crushed and migrated due to the rain wash, which caused the loss of clay particles and the rapid increase of the concentrations of REEs and P in runoff (Song et al. 2003).

The experiment results in this study showed that, in different types of soils, most REEs (92–98%) and P (92–96%) transported with the fine soil particles in runoff, and only a small portions of REEs (2–8%) and P (4–8%) were lost in water samples. Exogenous REEs and P were adsorbed and immobilized rapidly on the surfaces of soil particles. Most REEs and P (80–99%) were lost with <0.1 mm fine soil particles, making soil erosion as one of the main ways for the losses of REEs and P with runoff.

Results of the correlation analyses on the losses of REEs and P in runoff from the different types of soils are shown in Table 6. Significant correlations between REEs and P were found in both water samples and sediment (soil particle) samples ($p \leq 0.01$).

The losses of REEs and P in runoff shared similar characters, with most of them adsorbed by soil particles and then migrated with surface runoff of soil erosion. Further studies are needed to investigate whether there are chemical reactions of REEs and P during the transport processes and the relationships between their chemical forms before and after rainfall.

5 Conclusion

The results demonstrated that it was hard for both REEs (La, Ce, Nd, Sm, and Dy) and P to transport vertically in soils. At the depth of 2–4 cm, REEs and P concentrations decreased rapidly, and they reached their background values at the depth of 4 cm and below. The vertical leaching rate of REEs and P in different types of soils followed the order of purple soil > terra nera soil > red soil > cinnamon soil > loess soil. There were significant correlations between the total amount of losses of REEs and P with runoff, the concentrations of REEs and P in water samples, and in soil particle samples. During simulated rainfall experiments with 10° slopes and a rainfall intensity of 83 mm h$^{-1}$, the majority of REEs and P transported with the fine soil particles in runoff, accounting for over 92% of total loss, whereas only a small portion of them were found in water samples. The losses of REEs and P with runoff in different types of soils were in the order of loess soil > terra nera soil > cinnamon soil > red soil > purple soil. Meanwhile, there were significant positive correlations between the losses of REEs (La, Nd, Ce, Dy, and Yb) and P in surface runoff in boxes of different soil types.

<table>
<thead>
<tr>
<th>Table 5</th>
<th>Pearson’s correlation coefficients between REEs and P in leaching processes ($n=6$, $p \leq 0.01$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Loess soil</td>
</tr>
<tr>
<td>Leachate</td>
<td>0.87</td>
</tr>
<tr>
<td>Soil column</td>
<td>0.86</td>
</tr>
<tr>
<td>DDW</td>
<td>0.94</td>
</tr>
<tr>
<td>NaHCO$_3$</td>
<td>0.59</td>
</tr>
<tr>
<td>NaOH</td>
<td>0.98</td>
</tr>
<tr>
<td>HCl</td>
<td>0.87</td>
</tr>
<tr>
<td>Residual forms</td>
<td>0.82</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 6</th>
<th>Pearson’s correlation coefficient between REEs and P in the simulated rainfall experiments ($n=10$, $p \leq 0.01$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>Loess soil</td>
</tr>
<tr>
<td>Water sample</td>
<td>0.91</td>
</tr>
<tr>
<td>Soil particles</td>
<td>0.83</td>
</tr>
<tr>
<td>Total amount</td>
<td>0.87</td>
</tr>
</tbody>
</table>
Acknowledgments In this study the laboratory simulated rainfall experiments were conducted at Fangshan Experimental Center of Beijing Normal University. The authors thank Professor Liu Baoyuan and Mr. Gao Xiaofei of Beijing Normal University for their help in the experiments.

References