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Effect of nutrient uptake by plant roots on the fate of REEs in soil

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Abstract

Concentrations of rare earth elements (REEs) and major ions in soil solutions were observed under different growth stages of soybean in order to evaluate the effect of nutrient uptake by plant roots on the mobility of REEs in soil–plant systems. Soybean plants were grown in pots, which were kept in a greenhouse for 84 days. The concentrations of major nutrient cations (K and Ca) in the soil solution decreased with the soybean growth. On the other hand, the concentrations of Al, Y, La, Ce, Nd, Gd, Dy, Er and Yb increased. Although no decrease of pH was observed, it was assumed that the REEs and Al were dissolved from the soil solid phase due to H^+ release from the plant roots for K^+ and Ca^{2+} uptake. Subsequently, the bioaccumulation of REEs in the soybean roots was observed in the maturing stage of the soybean. These results showed that the soybean roots could enhance the dissolution of REEs from the soil solid phase and they could also accumulate REEs through plant growth.

Keywords: Bioaccumulation; Metals; REEs; Soil solution; Transfer factor

1. Introduction

In recent years, rare earth elements (REEs) have become more widely used for industrial and agricultural purposes. The resulting environmental contamination by REEs is expected to grow rapidly in the near future. In agro-environments, although REEs have been considered non-essential metals because they have no established biological functions, millions of tonnes of fertilizers containing REEs are used in agriculture to increase crop production in China [1,2]. The accumulation of REEs in the roots of other higher plants (rice and wheat) has already been reported [1]. However, the effect of plant growth, which should have some influence on the behavior of REEs has not been studied yet. Previously, it was observed that soil pH, concentration levels of ions, and other chemical properties of soil were affected by plant roots during plant growth stages [3]. For example, when plant roots adsorb nutrient cations, the roots may release H^+ to maintain their electrical neutrality [4]. Soil pH near roots may, therefore, differ considerably from that a few millimeters away. The phenomenon should affect the mobility and the bioavailability of REEs in the soil environment, because soil pH affects REE dissolution [5].

Thus, in this study, we observed the uptake rates of REEs by soybean plant at different growth stages and we considered the effect of plant growth on their uptakes through the roots. Although soybean is a major crop, there were not many studies on the relationships between soybean and REEs compared to other major crops such as rice and wheat, thus we selected it for the present work. A pot cultivation experiment using soybean was carried out, and concentrations of REEs and other major cations in the soil solution and in the soybean plant were observed under different growth stages.

2. Materials and methods

Soil used was classified as volcanic ash soil (Andosol, pH (H_2O) 6.4). Fifteen pots were prepared for the experiment; each of them contained 2.5 kg of the air-dried soil.

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Soil water content was adjusted daily to field capacity (FC, 536 g H_2O kg^{-1} dry soil) with deionized water without water drainage. At 1 day before sowing, all pots were fertilized with a solution containing 5 mM of KNO_3, 1 mM of KH_2PO_4, 5 mM of $Ca(NO_3)_2 \cdot 4H_2O$ and 2 mM of $MgSO_4$ giving 158 mg of N, 53 mg of P_2O_5, 212 mg of K_2O, 210 mg of CaO and 66 mg of MgO per pot, respectively. Four soybean seeds (*Glycin max Merrill*) were sown into each of 12 pots. Three more pots were kept unplanted. After 2 weeks, seedlings were thinned to two per pot. The plants were grown in a greenhouse for 84 days under a normal day–light condition.

Soil solutions were collected at approximately 10-day intervals from selected pots using a plastic porous tube connected with a 15-mL plastic syringe. The tubes were buried in three planted pots and three unplanted pots, and 10–15 mL of solution were collected in each syringe 4 h after adjusting water content. Immediately after collection, each soil solution was filtered through a 0.22-μm membrane filter (Millipore, Steriflip-GP), and the pH and EC of the filtrate were measured. Transpiration was calculated by subtracting the water loss by evaporation of the three unplanted pots from the total loss of the planted pots.

Plants were sampled at 61 and 84 days after sowing. These sampling periods corresponded to the podding and maturing stages. After removing soil particles from the plant samples by rinsing thoroughly with deionized water, they were separated into leaves, stems, pods, seeds and roots. Due to aging of the plant at 84 days, we could not collect leaves then. The masses of the plant parts were recorded after drying at 80 °C in an electric oven. Plant material and soil samples collected from the pots were ground in an agate mill. Then, they were digested with a mixture of conc. HNO_3 and HF using a microwave digestion system (CEM Mars 5). The Y and lanthanides in each plant part, soil and soil solution samples were analysed by ICP-MS (Agilent, 7500a) and Al, K and Ca were determined by ICP-AES (Seiko Instruments, Vista-Pro).

3. Results and discussion

3.1. Transfer factors of the REEs from the soil to the soybean plant

To evaluate the relationship between the transfer of REEs to the plants and the plant growth stage, we used transfer factor (TF). This parameter is defined as the ratio of the concentration of an element in the plant to that in the soil. The TF values obtained for each part of the soybean plants collected at the podding and maturing stages (61 and 84 days after sowing) are listed in Table 1.

The TF values of REEs in different parts of soybean plants for both growth stages followed the order: root > leaf > stem > seed ≥ pod. Among the plant parts, the REEs were mainly distributed in the roots. For example, at the podding stage, approximately 60–80% of the REEs adsorbed by the plants were in the roots, and 8–12% of them were in the leaves. Only a few percent of the REEs were distributed in the seeds.

When we compared TFs in roots between the two growth stages the value was two to three times higher in the maturing stage than in the podding stage. As dry weight of the roots only changed from 0.82 to 0.98 g, the big TF increases likely indicated the accumulation of REEs in the soybean roots was enhanced from podding to maturing stages.

Table 1
The transfer factor (TF) of REEs of each part of the soybean plant as sampled at 61 and 84 days

	61 days (podding stage)					84 days (maturing stage)			
	Roots	Leaves	Stems	Seeds	Pods	Roots	Stems	Seeds	Pods
Average plant dry weight (g)	0.82	1.97	1.56	1.65	1.65	0.98	1.19	5.73	1.58
TF of REEs									
Y	4.5E−02	2.3E−03	7.4E−04	4.3E−04	4.3E−04	1.1E−01	4.4E−03	1.7E−04	1.7E−03
La	6.4E−02	5.7E−03	1.3E−03	7.3E−04	5.5E−04	1.6E−01	1.3E−03	1.9E−04	4.3E−04
Ce	5.3E−02	4.7E−03	9.4E−04	1.6E−03	3.4E−04	1.5E−01	8.4E−04	4.3E−04	2.1E−04
Pr	5.2E−02	3.4E−03	9.4E−04	5.9E−04	3.5E−04	1.4E−01	6.0E−04	2.5E−04	1.2E−04
Nd	5.2E−02	3.2E−03	8.7E−04	5.3E−04	3.1E−04	1.3E−01	7.0E−04	1.3E−04	1.7E−04
Sm	4.5E−02	2.7E−03	8.6E−04	6.6E−04	3.4E−04	1.2E−01	3.1E−04	2.5E−04	1.2E−04
Eu	3.5E−02	3.3E−03	1.5E−03	9.0E−04	1.1E−03	1.1E−01	5.5E−04	5.5E−04	3.5E−04
Gd	4.5E−02	2.9E−03	8.7E−04	6.5E−04	3.9E−04	1.1E−01	4.7E−04	1.9E−04	1.3E−04
Tb	3.6E−02	2.9E−03	2.2E−03	3.0E−03	2.3E−03	1.0E−01	N.D.	1.0E−03	N.D.
Dy	4.1E−02	2.0E−03	6.5E−04	4.2E−04	3.0E−04	1.1E−01	3.0E−04	1.5E−04	9.4E−05
Ho	3.5E−02	2.1E−03	8.1E−04	6.6E−04	6.3E−04	9.7E−02	N.D.	1.0E−03	N.D.
Er	3.7E−02	1.7E−03	6.1E−04	4.2E−04	2.9E−04	9.9E−02	2.5E−04	2.4E−04	9.8E−05
Tm	2.8E−02	2.0E−03	1.1E−03	1.1E−03	1.2E−03	8.7E−02	N.D.	1.4E−03	N.D.
Yb	3.4E−02	1.5E−03	5.1E−04	3.9E−04	2.8E−04	9.1E−02	1.9E−04	2.0E−04	8.9E−05
Lu	4.0E−02	1.8E−03	9.2E−04	1.1E−03	1.2E−03	9.4E−02	N.D.	1.4E−03	N.D.

N.D.: the value was lower than the detection limit.

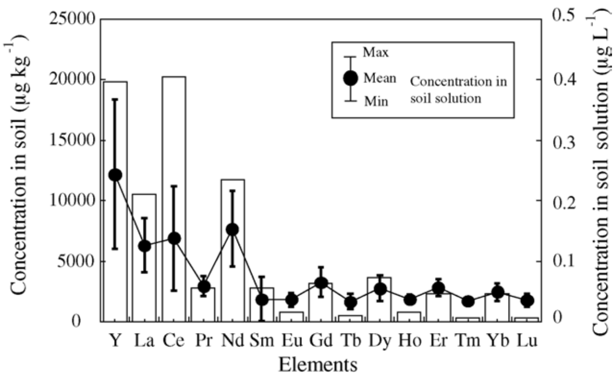

Fig. 1. Concentrations of REEs in the soil (bar) and the soil solution sampled from both the planted and unplanted pots (shaded circle).

3.2. The concentrations of REEs in the soil and in the soil solution

Fig. 1 shows the concentrations of REEs in the soil and the soil solution. In the soil, the concentration levels of REEs were 0.3–20 mg kg^{-1}, while levels of 0.02–0.4 μg L^{-1} were observed in the soil solution. The concentrations of REEs in the soil were two to three orders of magnitude higher than those in the soil solution, and covered a wide range. The REE concentration patterns of the soil solution were very close to those of the soil; the concentration of each REE in the soil and soil solution decreased as its atomic number increased.

The concentrations of Y, Nd and Eu and major elements, Al, K and Ca in the soil solutions plotted against days after sowing are shown in Fig. 2. During the 84 days period, the concentrations of Y and Nd in the soil solutions of the planted pots increased with plant growth, and were higher than those of the unplanted pots. Several REEs (La, Ce, Pr, Gd, Dy, Er and Yb) showed the same trend, however, no trend was clear for the other REEs such as Eu. Aluminum showed the same trend as the former elements, although its concentration level was one order of magnitude higher in the soil solution than the levels of REEs. On the other hand, the concentrations of K and Ca decreased with plant growth due to these elements being taken up by the plants as nutrients through the roots.

The concentrations of Al in the soil solutions of planted pots were negatively correlated with the concentrations of K and Ca (data not shown). It is well known that plant roots release H^+ on uptake of nutrient cations to maintain the ion balance in the plant [4]. The release of H^+ from plant roots would lead to dissolution of Al from the soil solid phase, consequently, the Al concentration in the soil solution increased. An increase of exchangeable Al of soil was clearly observed when the soybean plants were cultivated, although no significant pH change was observed in the studied soil (pH 6.0–6.5). Our results are close to those previously reported that the excess uptake of cations caused the enrichment of H^+ and the accumulation of dissolved Al at the root surface [6,7]. We think that some REEs might be released from the soil solid surface by the same mechanism as found for Al, because the dissolution of REEs should also be enhanced by the decrease of pH [2]. Since acidification by plant growth in the rhizosphere could occur for any plant species [4], the accumulation of REEs as observed in the present study would be found for any type of plant.

3.3. The effect of the concentration of REEs in the soil solution on their uptake by the plant roots

In order to identify the effect of the dissolved REEs in the soil solution on the soil–plant transfer of the REEs, we

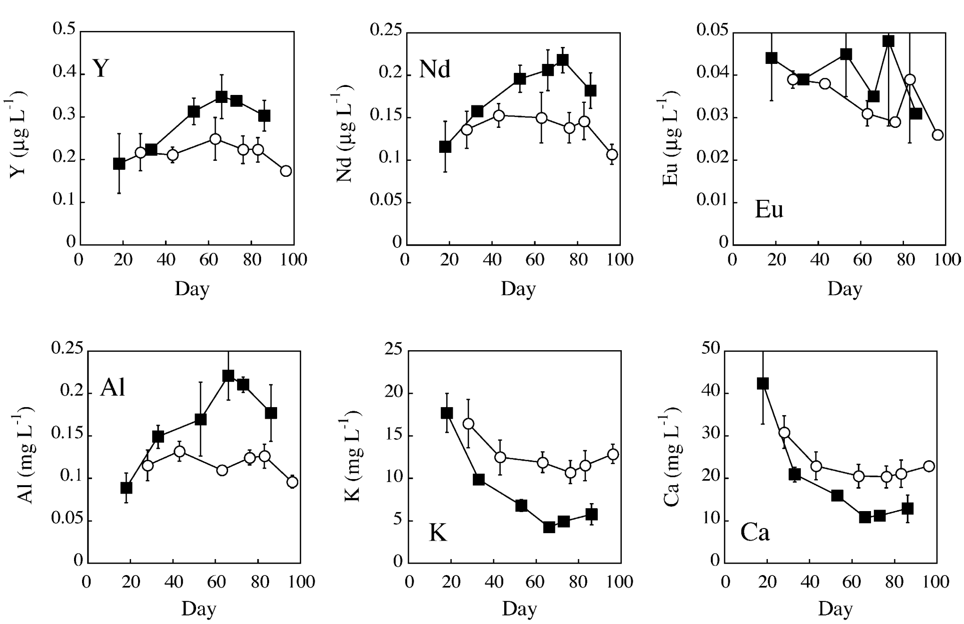

Fig. 2. Changes of the concentrations of Y (μg L^{-1}), Nd (μg L^{-1}), Eu (μg L^{-1}), Al (mg L^{-1}), K (mg L^{-1}) and Ca (mg L^{-1}) in the soil solution obtained from planted (■) and unplanted (○) pots with days after sowing. Error bars indicate the standard deviation of three different pots.

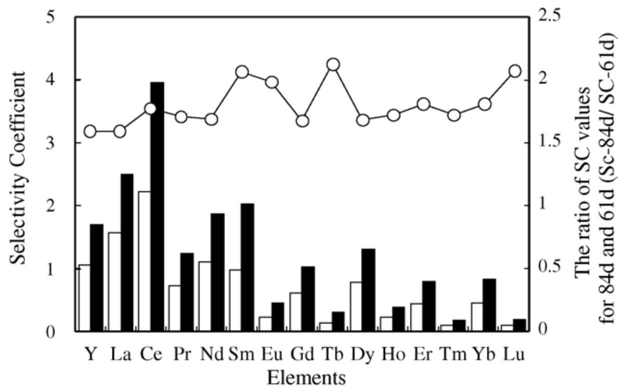

Fig. 3. The SC values of REEs obtained for the soybean roots sampled at 61 days (□; SC-61 d) and 84 days (■; SC-84 d) after sowing (left axis), and the bar (◯) indicates the ratio of SC values obtained for 84 days and those for 61 days (right axis).

calculated the mass flow using the data as shown in Fig. 2. The mass flow is the amount of REEs moved to the root surface with the water uptake, which was calculated for 0–61 and 0–84 days as follows:

$$M_x = \sum_x T_x \cdot C_x$$

where M_x is cumulative mass flow at day x, T_x the water transpired between two sampling dates $x-1$ and x (L per pot) and C_x is the concentration of the element in the soil solution on date x. C_x was approximated from linear interpolation of each sampling day.

The calculated mass flow values of REEs were 1.5–2 times larger in the maturing stage than in the podding stage (data not shown). The calculated mass flow values of REEs did not always correspond to the actual amounts of REEs in the plants; the ratios of the actual amounts of REEs in the plants to the mass flow values were 1–4 for the light-middle atomic weight REEs (Y–Sm) and 0.2–1 for the middle-heavy REEs (Eu–Lu). The ratios of the actual amounts of REEs in the plants to the mass flow values mean the selectivity coefficients (SCs) for the REEs by the soybean roots [8].

As shown in Fig. 3, the SCs for two sampling dates showed the same trend although the SCs of each REE were very different. The SCs for the REEs by the roots were 1.5–2 times higher in the maturing stage than in the podding stage (Fig. 3). The increase of the SCs indicated that the increase of TF of REEs in the roots at the maturing stage was not explained by the increased REE concentration in the soil solution only. The accumulation of REEs was observed for the maturing stage of soybean although the plant activity was not so high in this stage. Therefore, at the later growing stage, soybean roots possibly caused the enhanced sorption of REEs onto the root surface as adsorbent.

4. Conclusion

Wen et al. [1] reported accumulation of REEs in plant roots for rice and wheat. However, they just measured fully grown plants so it is difficult to identify any plant growth effect on the REE behavior in the soil environment. By collecting plant samples at different growth stages, we could observe the enhanced accumulation of REEs in the plant roots with the plant growth.

Especially in the later growth period, the increased dissolutions of some REEs from soil solid phase would lead to their accumulation in the roots. However, the accumulation of REEs in the roots was not explained by the increase of REEs in the soil solution only. Further studies are needed to understand the REE behavior in soil–plant systems.

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