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Transfer of REEs from nutrient solution to radish through fine roots and their distribution in the plant

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Abstract

In order to clarify transfer of rare earth elements (REEs, La through Lu) from soil solution to a plant and their distribution in the plant, a preliminary study on plant uptake of REEs was carried out using nutrient solution. Radish seedlings grown in a nutrient solution culture for about a month were transplanted to 120-mL plastic vessels containing nutrient solution spiked with 1, 5, 20 or 90 μg/L of each REE, respectively. The plant samples were in contact with the solution through their fine roots. After 1 d of contact, REEs in plant parts (fine roots, fleshy root and leaves) were measured by ICP-MS. The results showed that the concentrations of REEs in nutrient solution decreased for all REE concentration levels; these elements adsorbed quickly onto the fine roots. Concentration ratios of REEs in the fine roots decreased with increasing atomic number, which indicated that they competed for binding sites on roots. In the plant body, almost all of the absorbed REEs were distributed to the fine roots, while only small amounts of REEs were found in leaves. Chemical forms of REEs in the plant would affect their translocation mechanisms.

Keywords: Rare earth elements; Solution culture; Radish; ICP-MS

1. Introduction

Rare earth elements (REEs), La through Lu, are thought to be non-essential and/or toxic to animals and plants. As such, only limited attention has been paid by agricultural scientists to REE behavior in the earth's environment. However, studies have shown that REEs have been introduced into soil and water environments and the amounts are increasing due to more applications using REEs in industry and agriculture [1,2]. Some measurements of REEs in environmental samples, such as water, soil and plants have been reported [2–6]. In particular, inductively coupled plasma mass spectrometry (ICP-MS) allows researchers to measure low levels of REEs in such samples. ICP-MS also has the potential for providing reasonably complete REE patterns [7]. The REEs patterns are very useful in geological and environmental studies because REEs have very similar chemical behaviors; but as the number of f-electrons increases with atomic number within the lanthanide suite, chemical differences do occur from La through Lu.

The most stable oxidation state of REEs is the trivalent one under natural conditions so that these elements are adsorbed strongly on soil and rock surfaces or bound to organic substances [8]. Since solubilities of REEs are low, their bioavailabilities to plants from soil are low and usually only very small amounts of REEs are found in the edible part of crops [4,5,9,10]. Additionally the concentration ratio also depends on the plant species being grown and even in a plant, there is a significant difference in accumulation of REEs in different plant parts, such as fine roots and upper parts of the plant [6,10]. Most of the reported data have been obtained under field conditions so that it is difficult to get details of the uptake behavior of each REE by the plants due to the low concentrations of readily available REEs in soil.

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Recently, a multitracer technique was applied to understand the uptake mechanism of REEs by plants [11]. In this experiment, a multitracer solution without any nutrients was used to culture 11 plant species under a hydroponic condition for 1 week. Although grow rates of the plants have not been reported, very slow rates would be expected for these plants due to the lack of major nutrients, and, plants might not have been able to exhibit the usual behavior of their natural environment.

In this study, a multi-element technique with ICP-MS was applied to clarify the uptake behavior of REEs by plants under a typical hydroponic condition. The REEs concentrations were elevated from 1 to 90 μg/L for each REE, and the relationships between the concentrations of REEs in nutrient culture solution and the concentration ratios of each REE in plant parts were observed.

2. Experimental

2.1. Plant cultivation

Radish seedlings, 3 d after germination, were grown in a nutrient solution prepared from a commercially available nutrient powder, HYPONeX®, by dissolving it in deionized water (1:1000 in weight). The plants were placed in a greenhouse at 21 °C and exposed to normal daylight conditions for about 1 month. Then, new nutrient solution was prepared with added multi-element standard solution, XSTC-1 (SPEX CertiPrep Inc., USA) which included 10 mg/L of each REE, that is, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu. Concentrations were adjusted to 1, 5, 20 and 90 ng/mL of each REE, corresponding to 0. 014, 0.07, 0.28 and 1.26 mg/L in total REE concentrations, respectively, from the spiked nutrient solution. The solution pH was adjusted to about 4 with a 1 M NaOH solution. Then, a radish plant was transplanted to a 120-mL plastic vessel containing 50 mL of the adjusted REE concentration of spiked nutrient solution, prepared as described above.

2.2. Sample treatment

The plant samples were in contact with the solution through their fine roots [12]. The plants were carefully removed from the solution ($n = 3$ for each concentration). The nutrient solution was passed through a 0.22-μm filter. The concentrations of the REEs were measured by ICP-MS (Yokogawa, Agilent 7500a, Japan).

Preparation of the plant samples for ICP-MS was as follows. After rinsing the plant roots successively in two plastic cups containing about 300 mL of deionized water, the roots were gently wiped with paper towels, and the plants were separated into three parts, i.e., leaves, fleshy root and fine roots. The leaves and the fine roots were cut into 1–1.5 cm lengths and the fleshy root was sliced into disks approximately 1 mm thick. Each sample part was weighed (wet-weight), oven-dried at 60 °C for 72 h and weighed again (dry-weight). Then, the samples were incinerated at 450 °C for 3 h and the ash was dissolved in 10 mL of *aqua regia*. The acid mixture was evaporated to near dryness on a hotplate at 100 °C. The nearly dried residue was dissolved in 5 mL of 2% nitric acid. These acidic solutions were used for ICP-MS.

3. Results and discussion

3.1. Uptake of REEs by radish plants

In Fig. 1, contents of each REE retained in the spiked nutrient solution are plotted against REEs in increasing order of atomic number. As a blank sample, a plastic vessel with 50 mL of spiked nutrient solution without the plant was also measured and no REE fixation on the plastic vessel surface was found. Although REEs have very similar chemical properties, their ionic radii differ, so that they behave differently. Indeed, all the samples show a heavy REE enrichment pattern. The pattern is very close to that seen for filtered river waters normalized by average shale [13], the average shale is one of three commonly used sedimentary normalizing values for REEs [7]. Colloidal material, which was removed by filtration, had a shale-like or slight enriched light-REEs ratio [13], thus, heavy REE enrichment patterns were seen in the filtered river waters. In this study, the surface of the fine roots may be the main factor for this observed heavy REE-enrichment in the nutrient solution. Thus, a physicochemical reaction controls the pattern.

The pattern, that is, the retained REE contents increase with increasing atomic number, can be seen more clearly in Fig. 2. In the figure, relative content is defined as 'content of each REE retained in the solution after contact' divided by 'content of each REE added to the nutrient solution'. From

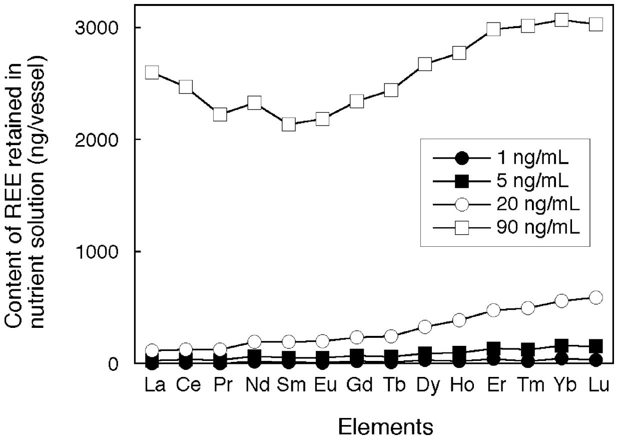

Fig. 1. Average REE contents retained in the nutrient solutions after contact with fine roots of radish plants. Symbols show each REE concentration in 50 mL of nutrient solutions at start.

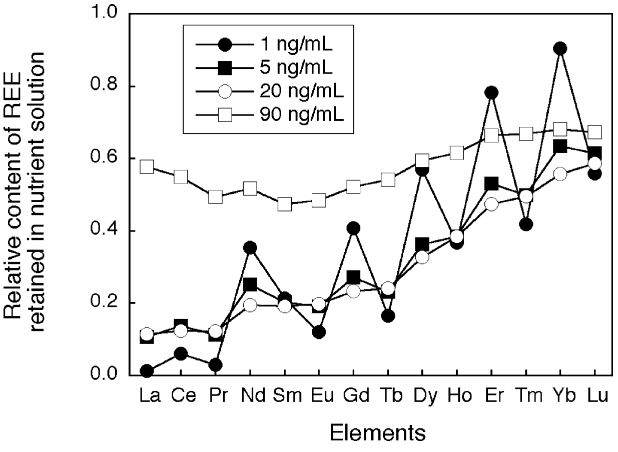

Fig. 2. Relative REE contents retained in the nutrient solutions before and after contact with fine roots of radish plants. Symbols show each REE concentration in 50 mL of nutrient solutions at start.

the results, about 90% of low REEs, such as La, Ce and Pr, are removed from the solution when each REE concentration is less than 20 ng/mL. The relative amount of retained REEs in nutrient solution is highly correlated with dry weight of fine roots. But, heavy REEs show higher retention in the solution indicating that there is an elemental fractionation from nutrient solution to fine roots.

In the authors' previous work [12], the same trend, that is, a slight increase from lower to heavier REEs, was observed when 10 ng/mL of REEs were present. The uptake behaviors of REEs into the plant roots are the same. However, it should be noted that the same radish species was used in the present and previous studies; it is necessary to check whether this pattern is also seen when other plant species are grown.

3.2. Distributions of REEs in radish plant

Distributions of REEs absorbed by the plant were measured. Since all REEs show the same trend, total REE amount was used for the distribution. The absorbed total REEs are shown in Fig. 3, plotted against the REE concentration in nutrient solution. All REEs are retained mainly on the fine roots. The REE bio-accumulation in fine roots, fleshy root and leaves increases with increasing REE concentration in the nutrient solution. The correlation between concentrations of total REE in plant parts and that in nutrient solution appears to be relatively linear. However, the plant ability to take up REEs should have an upper limit, otherwise all plants would have an ability to accumulate REEs at high levels which is not true [10]. An example has been reported using aquatic flora [1]; when the REE concentration was more than 3.6 mg/L, the concentration ratio, i.e., the bio-accumulated REEs in plant parts to the REEs in the culture solutions, reached constant values. It is difficult to compare the present results with reported data [1], however, the concentrations used at this time were not high enough to limit plant ability to take up REEs.

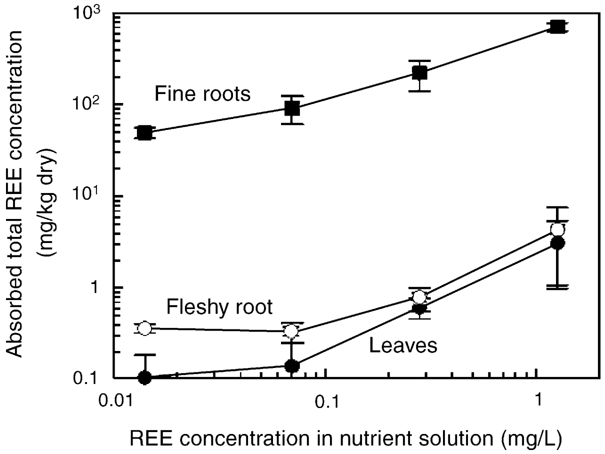

Fig. 3. Average of absorbed total REE concentration in plant samples ($n = 3$) plotted against concentrations of all REEs in nutrient solutions (0.014–1.26 μg/mL). Error bars show standard deviation (1 sigma) of three replicates.

Although plants grown in soil under natural conditions sometimes show a different trend, REEs are usually retained on the roots [5,10]. It is considered that REEs are transported into cells via proteins for Ca due to their physicochemical similarities to Ca. Among the REEs, the ionic radius of Ce is closest to that of Ca, so that it is expected that Ce should show the highest accumulation ratio in plant parts. Thus, concentration ratio, 'each REE amount in plant parts (mg/kg dry)' divided by 'average of each REE amount in nutrient solution' was calculated for the samples collected from 20 to 90 ng/mL spiked nutrient solutions (Fig. 4). The average concentration of initial and final concentrations was used because it was apparent that each REE was removed from the nutrient solution by the plant.

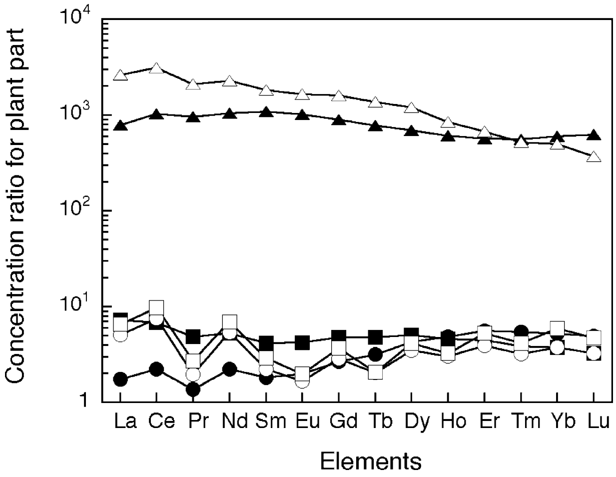

Fig. 4. Concentration ratios of REEs in plant parts. For plants collected from 20 ng/mL nutrient solutions: open circle, leaves; open square, fleshy root and open triangle, fine roots. For plants collected from 90 ng/mL nutrient solutions: shaded circle, leaves; shaded square, fleshy root and shaded triangle, fine roots.

The concentration ratio of Ce is the highest in the roots as expected, however, the concentration ratios of REEs for leaves show a slight increase with increasing atomic number, except for light REEs. Transfer ratios of REEs from roots to leaves were higher in light REEs than in heavy REEs [10], however, the present results exhibit the opposite trend, probably because nutrient solution contact time in the present study was short. Thus, it is considered that REEs bound to proteins on root surfaces can pass fairly slowly through the root surface to the xylem for translocation and this depends on their ionic radius. The high concentration ratio of light REEs can support the hypothesis, however, to clarify the fractionation effect for REEs, further studies on bio-accumulation mechanisms on root surfaces and physicochemical forms of REEs in the plant when translocation occurs are necessary.

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