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The impact of iron plaque on La and Nd uptake and translocation in rice (*Oryza sativa* L.)

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ABSTRACT

The effect of root surface iron plaque formation on the uptake, transfer and accumulation of La and Nd in the rice root system was evaluated by using solution cultures. The results showed that La and Nd pollution stress inhibit formation of rice root surface iron plaques. The amount of La and Nd absorbed by the rice root surface iron plaque rose with the increase of La and Nd solution concentrations. Iron plaque formation on the rice root surface significantly decreases the La and Nd concentrations in rice roots and shoots. At growth solution La concentrations of 0.1, 0.5, and 1.0 mmol.L^{-1}, concentrations of La in rice roots with induced iron plaques decreased by 17.1%, 37.4%, and 31.2%, respectively, and concentrations of La in rice shoots decreased by 43.9%, 60.6%, and 27.0%, respectively, when compared to plants with non-induced iron plaques. Also, with Nd solution concentrations of 0.1, 0.5, and 1.0 mmol.L^{-1}, the Nd concentrations in rice roots and shoots of plants with induced iron plaques decreased by 21.0–31.7% and 22.7–47.5%, respectively when compared to plants with non-induced iron plaques. Iron plaque formation on the rice root surface affects the accumulation and transfer of La and Nd in rice roots. Accumulation of La and Nd was greater in rice roots than in rice shoots regardless of whether the plants had induced or non-induced iron plaques. Transfer coefficients of iron plague on rice root surface and root system under La treatments were both higher than those under Nd treatment. For rice roots and iron plaques on the root surface, the enrichment coefficient in the La treatment group was less than that in the Nd treatment group, while for rice shoots, the enrichment coefficient in the La treatment group was greater than that in the Nd treatment group. Clearly, the mechanisms governing the effect of iron plaque on La and Nd uptake and transfer in the rice root system are rather complicated.

1. Introduction

The rare earth elements (REEs) consist of seventeen chemical elements including the fifteen lanthanides (No. 57 to No. 71 in the periodic table) as well as scandium and yttrium [1]. Scandium and yttrium are considered rare earth elements because they exhibit chemical properties similar to the lanthanides. The abundance of REE in the earth's crust is 0.01534% by mass, and the most abundant REE, with a crustal content of 0.0046% by mass, followed by yttrium, neodymium and lanthanum. The atomic and ionic radii of lanthanides, as well as their capacity, decrease with the increase of atomic number. In other words, La is the most reactive element in the lanthanide series. Because of their unique characteristics, REEs are widely used in petroleum, chemical engineering, metallurgy, textiles, ceramics, glass, permanent magnets, etc. Mining, refining and the use of REEs can cause serious environmental problems [2–4]. Serkan and Michael showed that the use of rare earth catalysts in industrial production increased the concentration of REEs in industrial sewage discharged into the Rhine to 52 mg·kg^{-1}, resulting in the addition of 1.5 tons of La into the Arctic Ocean from the Rhine every year [5]. REEs were also accumulated in tobacco due to the use of rare earth fertilizer. Böhlandt et al. [6] found that the average concentrations of La in the air in smoking and non-smoking residences were 5.9 ng·m^{-3} and 0.2 ng·m^{-3}, respectively, while concentrations of Ce were 9.6 ng·m^{-3} and 0.4 ng·m^{-3}, respectively; for La and Ce, smoking residences contain 29.5 and 24 times the concentrations found in non-smoking residences, respectively. China is a major producer, consumer, and exporter of rare earth elements. Domestic rare earth resources are mainly distributed in Baotou and southern Jiangxi. Due to poor supervision during rare earth resource exploitation, mining plots surroundings were severely contaminated by sewage and industrial waste [7–8]. Li et al. [9] suggested that the rare earth content in the soil 10 km downwind from Baotou Steel Rare-Earth Hi-Tech Co. Ltd. of the Inner Mongolia Autonomous Region is 118 times that in the control group. The average soil REE content in mining areas in Jiangxi Province is 976.94 mg·kg^{-1}, 4.53 times the background value in Jiangxi Province and 5.09 times the domestic background value [10]. The average REE content of the well water is 0.033 mg·kg^{-1}, 10.55 times the concentration in control group well water. The average REE content in

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rivers is 55.72 $mg \cdot kg^{-1}$, 8974.7 times the content in control group rivers. The daily average REE intake of local residents from crops and well water is 295.33 $g \cdot kg^{-1} \cdot d^{-1}$, much higher than the critical threshold for subclinical damage to humans [11]. Because of the high REE content of water and soil in the mining area, the average REE content of crops such as green vegetables and sweet potato is 10 to 20 times above the national hygienic standard [12].

Research has indicated that La accumulated in the rice root system can cause accumulation in the rice cytomembrane and affect the integrity of the plasma membrane. As a consequence, the physiological functions of the rice root may degrade [13]. Also, after prolonged, high-dosage exposure to La, the percentage of live sperm and the integrity of the perforatorium in mice decreased, and the frequency of sperm deformity increased [14]. In rats, $LaCl_3$ may cause severe degradation of learning, memory, and the ultrastructure of hippocampal neurons and synapses; the degree of damage increases with increasing La dosage [15]. One form of rare earth, partial Nd_2O_3, can move into rat lung tissue through non-tracheal exposure, causing acute lung injury for rat. Early symptoms include inflammation, which may lead to the formation of fiber cell nodules [16]. In rice, mitochondrion enzyme activity is passivized and restrained when the concentration of the rare earth compound neodymium trichloride reaches 40 to 60 $mg \cdot L^{-1}$ [17–18]. Researchers have used REE treatments, including La and Nd, on soybean, cucumber, maize, and mung bean crops, finding that high REE concentrations can significantly inhibit the germination of crop seeds and the growth of seedling roots [19]. Under the condition of severe contamination, growth of crop root system ceases completely. Other researchers studied the impact of REEs, such as La and Nd, on soil animal community structure in a plum garden. Their results showed that the number of animal classes and the number of soil animal communities decreased as the concentration of rare earth elements increased [20]. La^{3+} and Nd^{3+} can damage the ultrastructure of splenocyte and cause oxidative stress to splenic tissue. The degree of and mechanisms governing damage to mice may be related to the number of electrons in the REE 4f orbital [21]. Rare earth in the natural environment may enter the human body through the food chain, which affected human's health. Research has shown that when the daily intake of rare earth reached 6 to 6.7 mg, residents from mining areas in Southern Jiangxi Province experienced negative health effects [22].

The problem of rare earth entering the human body through the food chain becomes important in mining areas. At present, cleaning and recovery of heavy metal pollution from edaphophyte is the most studied approach. Many studies have shown that iron plaque on the plant root surface can inhibit the absorption and translocation of heavy metal elements [23]. Iron plaque on the rice root surface can lead to Cd, Pb, and Sb enrichment [24–25] and inhibit these elements from translocating towards the rice seedlings [26–27]. Because copper is passivated by iron on the root cortex, and aluminum precipitates with phosphate on the plant root surface, iron plaque on the root surface can reduce the toxicity of copper and aluminum [28–30]. However, some studies suggest that a small amount of iron plaque can accelerate plant absorption of heavy metal elements. Liu et al. [31] argued that iron plaque on the rice root system can promote the translocation of Pb into the root to a certain degree. In academic circles, researchers have mainly focused on the mechanisms by which iron plaque inhibits or promotes plant absorption of heavy metal and other hazardous substances. However, there has been little study of the impact of iron plaque on edaphophyte absorption and translocation of REEs. Although REE characteristics are similar to heavy metals, the mechanisms of passivation and restoration of iron plaque on the root surface are very complex and are affected by the physical and chemical properties of the iron plaque, the growth medium, and the condition of the plant. Because of these complexities, the impact of iron plaque on the absorption and translocation of REE is worth studying. The seventeen REEs have similar atomic structure and ionic radius, which is logical since they are paragenetic. Due to their comparatively high crustal contents, La and Nd exert great influence on the ecological environment in mining areas. In order to mitigate the impacts of REEs on environmental and human health, this paper presents hydroponic experiments on the impact of iron plaque on the absorption and translocation of La and Nd; the results herein provide a theoretical foundation for rare earth pollution control and prevention measures.

2. Materials and methods

2.1. Experimental rice

The experimental rice seed, named Jiahua-1, is a local type of mid-maturation japonica rice grown in Jinhua, Zhejiang Province. Whole grains of consistent size were selected and 30% hydrogen peroxide (H_2O_2) was used to sterilize them for 15 min. The grains were washed three times using deionized water, and were sowed in soaked perlite, and allowed to grow for twenty days. When the rice seedlings developed four leaf pieces, healthy seedlings with consistent growth were selected and transplanted to PVC pots with a diameter of 7.5 cm and a height of 14 cm for further study. Each pot grown one rice seedling; the nutrient solution was changed twice a week. The compositions of the nutrient solutions are shown in Table 1; solution pH was adjusted to 5.5 using 0.1 $mol \cdot L^{-1}$ KOH or HCl, as needed. In plants showing crystalline salt formation on the rice surface, a nutrient solution of 1/3 concentration was used during pot cultivation.

2.2. Experimental design

A total of 56 pots of rice were cultivated in phytotron. The growth conditions were as follows: sunlight duration = 14 $h \cdot d^{-1}$, illumination intensity = 260 to 350 $\mu mol \cdot (m^2 \cdot s)^{-1}$, relative humidity = ~5%, and temperature = ~25 °C. When the length of the rice root reached about 15 cm, the nutrient solution was poured away in 28 pots of rice, soaked them with distilled water for 12 h, treated them with 40 ppm ferrous sulfate (Fe_2SO_4) solution for 36 h, and finally discarded the sulfate solution and treated the plants using a 1/3-concentration nutrient solution for 48 h. These 28 pots of rice comprise the iron-plaque-induced group (hereafter referred to as the induced group), and the other 28 pots are non iron-plaque-induced group (hereafter referred to as the control group). Half of these 56 pots of rice were treated with lanthanum nitrate ($La(NO_3)_3$) solutions and another half with neodymium nitrate ($Nd(NO_3)_3$) solutions. Both treatments consisted of four concentrations of 0.0 (CK), 0.1, 0.5 and 1.0 $mmol \cdot L^{-1}$, and each concentration was replicated for four times. After ten days of lanthanum nitrate and neodymium nitrate treatments, all rice plants were harvested and divided into two parts: aboveground and underground.

2.3. Sample treatment and analysis

After harvesting, the iron plaque on the root system was extracted by using the DCB (dithionite-citrate-bicarbonate) method. Specific procedures were as follows: the rice roots were washed using distilled water, dried using absorbent paper, and separated from the rest of the plant. The roots were soaked in a 100-ml beaker containing 30 ml of a mixed 0.03 $mol \cdot L^{-1}$ trisodium citrate ($Na_3C_6H_5O_7 \cdot 2H_2O$) and

Table 1
Nutrient solution composition for rice.

Nutriment	Concentrations/$mg \cdot L^{-1}$	Nutriment	Concentrations/$mg \cdot L^{-1}$
$CaCl_2$	444	$MnSO_4 \cdot 1H_2O$	0.85
NH_4NO_3	402	H_3BO_3	0.62
$MgSO_4 \cdot 7H_2O$	368	$ZnSO_4 \cdot 7H_2O$	0.29
K_2SO_4	348	$CuSO_4 \cdot 5H_2O$	0.25
KH_2PO_4	180	$Na_2MoO_4 \cdot 2H_2O$	0.12
Fe EDTA	21	$CoSO_4 \cdot 7H_2O$	0.053
NaCl	5.85		

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