Accumulation of Rare Earth Elements in Spinach and Soil under Condition of Using REE and Acid Rain Stress*

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Abstract: The content and distribution characteristics of REE in spinach and soil under using REE and acid rain stress were studied by pot experiments. The results show that the content of REE is 0.527～0.696 (μg·g^{-1}) in the above-ground portion of spinach, 2.668～3.003 (μg·g^{-1}) in the under-ground portion of spinach and 229.09～250.30 (μg·g^{-1}) in the soil. With the acidity of acid rain increasing, the leaching of REE in plants and soil is strengthened and the amount of REE reduces with decreasing of pH value. After REE are used, though plants show the selective absorption to Ce group elements (especially spraying on leaves), regardless under acid rain stress or using REE or not, the distribution model of REE in the above-ground and under-ground portion of plants is basically the same with the control. Plants also follow the Oddo-Harkins rule of the REE of distribution abundance, light rare earth elements is enriched, the minus of Eu is abnormal and admeasure of Ce is a rich model. The results show that REE in plants mainly come from soil and are affected by it.

Key words: rare earths; acid rain stress; spinach; soil

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There are many reports of studies on the effects on plants by acid rain[1～3] and utilization of REE[4～7] and a few studies on REE using as chemical adjustment to protecting plants from being damaged by acid rain stress under natural condition. This study was focused on the accumulation of REE in spinach and soil under acid rain stress and utilization of REE in agriculture.

1 Materials and Methods

Spinach olerace Huabo No. 1, an acid rain-sensitive plant commonly seen in the area where acid rain frequently happens[2], was selected for the pot-culture test. The soil for test was yellow soil, organic content in soil 3.69 %, pH 5.2. The REE for test were supplied by the Sangqiu Rare-Earth Fertilizer Plant, Henan Province. The composition of the REE is given in Table 1.

Simulating the ions concentration of nature rain in southwest of China (Table 2), and the solution was diluted by vitriol[8]. According to the average of nature rainfall in the

Table 1 Compositions of rare earth elements

Elements	Content/ %	Elements	Content/ %	Elements	Content/ %	Elements	Content/ %
La	21.32 - 22.87	Nd	12.85 - 14.57	En	< 0.086	Er	< 0.087
Ce	33.08 - 41.51	Sm	< 0.259	Tb	< 0.081	Yb	< 0.087
Pr	4.14 - 4.97	Dy	< 0.087	Ho	< 0.087	Lu	< 0.089
Y	< 0.078						

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growth period of spinach in this zone, the spinach was sprayed two times a week with each rainfall 10 mm. Four experimental groups (at pH 4.0, 3.5, 3.0, 2.5) and a group at pH 6.5, a group used REE at pH 6.5 and a control group (no REE treated) were included. The experiments consisted of 5 treatments: soaking the seeds with 0.03% and 0.05% REE (after soaking 16 h, dried in the shade then planted), and spraying on the leaves with 0.01%, 0.03%, 0.05% REE. 15 plants were planted in a 30 cm ×25 cm (diameter × high) culture pot, and each treatment was repeated 5 times. The plants were covered with a plastic shed in order to avoid the interfering from nature rain. In the seedling period of spinach, the contents of REE in the above-ground and under-ground portion of spinach and soil were measured respectively.

Table 2 Ion composition in acid rain ($\mu mol \cdot L^{-1}$)

K^+	Na^+	Ca^{2+}	Mg^{2+}	NH^+	H^+	SO_4^{2-}	NO_3^-	Cl^-	F^-
15	18	50	15.5	40.5	36.5	140	21	7.5	7

0.50 g sample was weighed and put in crucible, then burned at 550 ℃ in muffle furnace, extracted in 25 ml plastics tubes by nitric acid. 250 μg was put in them and solution was diluted by water to 24 ml. The REE were measured by the high resolution ICP-MS made by Germany Finnigan Mat Company.

2 Results and Discussion

2.1 Content and composition of REE in spinach and soil

The experimental results (Table 3) indicate that the content of REE in the above-ground portion of spinach is in the range of 0.527 ～ 0.696 $\mu g \cdot g^{-1}$, 2.668 ～ 3.003 $\mu g \cdot g^{-1}$ in the under-ground portion and 229.09～250.3 $\mu g \cdot g^{-1}$ in the soil. The admeasure results of REE in spinach are shown in Fig. 1 (a～f). After REE were applied, the content of REE in spinach tends to raise drastically with increasing concentration of REE (spraying was more notable than soaking), and reduces obviously with increasing acidity of acid rain compared to control, which indicates that the absorption and utilization of REE in spinach are affected by acid rain with increasing acidity of acid rain the absorption and utilization are reduced. The increase of REE in the above-ground portion is less than that in the under-ground portion, but the amount of REE increased in the above-ground portion is the most obviously. The absorption of REE by spinach focused on Ce group elements (La, Ce, Pr, Nd and Sm), and the next is Tb group elements (Eu, Gd, Tb, Dy), however the absorption to Yb group elements is relatively unobvious. This illustrated that the absorption of REE by spinach is not entirely but selectively. The distribution of REE in some plants under natural condition also show this characteristic[7,9].

Since REE absorbed by spinach selectively, especially for La, Ce, Pr, Nd, Sm (spraying on leaves), the ratio of these elements to the total of REE in plants was obviously larger than that of control. Even thus, the sequence of content of REE in plants is still coincident with that in control (Fig. 1), it is Ce > La > Nd > Pr > Sm. Whatever spraying or soaking with REE, the ratio of light REE to heavy REE (ΣLREE/ΣHREE) in above-ground portion of spinach is all obviously less than control (Table 3). But the ratio of ΣLREE/ΣHREE in under-ground portion of spinach is obviously more than that of control. Simultaneously in the same REE treatments, ΣLREE/ΣHREE is less in the above-ground portion of spinach than in the under-ground portion of spinach. One reason is the effect of the REE distribution in plant[5～7, 9, 11], and the other is the influence of acid rain which eluviates REE away directly from leaves.

Table 4 shows whatever the treatments are carried out by acid rain or using REE, the contents of REE in the above - ground and

Table 3 REE content (mg·kg^{-1}) and radio of LREE/HREE in spinach and soil

Treatments	Concentration/%	Site	Ratio and content	CK	pH 6.5	pH 4.0	pH 3.5	pH 3.0	pH 2.5
Spraying	0.01	Above-ground	∑LREE/∑HREE	13.57	10.31	11.31	11.86	11.90	12.86
			∑REE (μg·g^{-1})	0.554	0.611	0.591	0.566	0.555	0.527
		Under-ground	∑LREE/∑HREE	14.74	15.11	15.53	15.75	15.19	15.13
			∑REE (μg·g^{-1})	2.786	2.917	2.91	2.865	2.818	2.71
		Soil	∑LREE/∑HREE	10.71	9.89	13.44	10.18	10.63	15.04
			∑REE (μg·g^{-1})	238.34	242.8	236.11	239.09	237.76	229.09
	0.03	Above-ground	∑LREE/∑HREE	13.57	10.75	11.46	11.04	12.27	12.18
			∑REE (μg·g^{-1})	0.554	0.658	0.623	0.602	0.584	0.567
		Under-ground	∑LREE/∑HREE	14.74	13.69	14.69	15.22	15.08	14.69
			∑REE (μg·g^{-1})	2.786	2.837	2.873	2.888	2.751	2.668
		Soil	∑LREE/∑HREE	10.71	10.43	10.80	10.81	10.94	10.66
			∑REE (μg·g^{-1})	238.34	245.26	241.17	240.16	238.53	236.42
	0.05	Above-ground	∑LREE/∑HREE	13.57	10.22	10.91	11	11.56	10.15
			∑REE (μg·g^{-1})	0.554	0.696	0.679	0.648	0.628	0.591
		Under-ground	∑LREE/∑HREE	14.74	15.40	16.12	15.78	15.85	16.60
			∑REE (μg·g^{-1})	2.786	3.003	2.946	2.921	2.899	2.834
		Soil	∑LREE/∑HREE	10.71	7.68	7.87	7.89	8.37	8.44
			∑REE (μg·g^{-1})	238.34	250.3	246.74	243.88	243.5	238.71
Soaking	0.03	Above-ground	∑LREE/∑HREE	13.57	10.56	11.28	11.74	11.46	11.92
			∑REE (μg·g^{-1})	0.554	0.578	0.553	0.548	0.536	0.53
		Under-ground	∑LREE/∑HREE	14.74	14.80	14.71	15.93	15.60	16.20
			∑REE (μg·g^{-1})	2.786	2.845	2.829	2.794	2.773	2.718
		Soil	∑LREE/∑HREE	10.71	10.68	10.67	11.01	11.00	11.01
			∑REE (μg·g^{-1})	238.34	242.83	239.19	237.18	235.98	231.37
	0.05	Above-ground	∑LREE/∑HREE	13.57	9.37	11.14	11.71	11.83	12.52
			∑REE (μg·g^{-1})	0.554	0.602	0.583	0.572	0.552	0.541
		Under-ground	∑LREE/∑HREE	14.74	14.66	14.92	15.15	15.55	15.99
			∑REE (μg·g^{-1})	2.786	2.882	2.867	2.811	2.765	2.719
		Soil	∑LREE/∑HREE	10.71	10.77	10.65	10.57	10.69	10.81
			∑REE (μg·g^{-1})	238.34	242.57	238.37	235.19	236.81	232.8

under-ground portion of spinach and soil all accord with the selective model of rich Ce with the content of 38.27 %～43.20 % REE in the above-ground portion, 49.03 %～51.32 % in the under-grounder portion, and 50.2 %～54.32 % in soil, and then is La and Nd. The distribution of REE followed the Oddo-Harkins rule of the abundance of REE, namely the content of the rare earth elements with even atomic number is obviously more than that with odd atomic number. Though spinach mainly absorbed Ce group elements, it did not result in the great changes of abundance model of REE in plants, which is still similar to that in soil, so it indicates that the REE in plants mainly comes from soil and are influenced by soil.

2.2 Distribution of REE in spinach and soil

The admeasure results of REE in soil (Table 4) indicate that after applied REE the content of REE in each treated soil increases obviously compared to the control. With acidity of acid rain increasing, the content of REE in each tested soil reduced obviously, the content of REE was less than the control at pH 3.0

Table 4 Admeasure of REE in spinach and soil under using REE and acid rain stress

Treatments	Site	REE	CK	pH 6.5	pH 4.0	pH 3.5	pH 3.0	pH 2.5
Spraying 0.05 %REE	Above-ground	La	23.10	22.26	22.47	22.38	22.83	22.37
		Ce	41.70	39.87	41.34	41.96	42.75	42.70
		Pr	5.96	4.32	4.12	4.20	3.99	4.25
		Nd	17.33	18.44	18.52	18.36	18.30	18.67
		Pm						
		Sm	4.33	4.49	4.46	4.55	3.62	3.88
		Eu	0.72	1.00	0.86	0.70	0.72	0.74
		Gd	1.62	2.66	2.40	2.27	2.36	2.22
		Tb	0.18	0.33	0.34	0.35	0.18	0.18
		Dy	1.81	2.33	1.89	2.10	1.99	2.03
		Ho	0.36	0.50	0.51	0.35	0.36	0.18
		Er	1.26	1.50	1.37	1.22	1.27	1.11
		Tm	0.18	0.33	0.17	0.17	0.18	0.18
		Yb	1.08	1.33	1.20	1.05	1.09	1.11
		Lu	0.36	0.66	0.34	0.35	0.36	0.37
	Under-ground	La	20.06	20.71	21.08	20.99	21.32	21.81
		Ce	53.30	52.61	52.00	52.41	52.71	52.93
		Pr	6.35	5.99	6.35	6.03	6.11	5.79
		Nd	11.20	11.75	11.88	11.95	11.14	11.15
		Pm						
		Sm	2.40	2.46	2.48	2.40	2.45	2.36
		Eu	0.32	0.37	0.37	0.27	0.34	0.28
		Gd	1.54	1.47	1.32	1.44	1.41	1.31
		Tb	0.29	0.27	0.27	0.27	0.28	0.25
		Dy	1.72	1.57	1.63	1.64	1.59	1.52
		Ho	0.36	0.33	0.31	0.27	0.28	0.25
		Er	1.04	1.00	0.95	0.96	1.00	1.02
		Tm	0.22	0.20	0.20	0.21	0.21	0.18
		Yb	1.01	1.03	0.95	0.96	1.00	0.99
		Lu	0.18	0.23	0.20	0.21	0.17	0.18
	Soil	La	19.30	19.26	19.60	19.36	20.05	19.87
		Ce	51.20	48.78	48.69	48.96	48.80	49.16
		Pr	4.18	4.10	4.15	3.96	4.12	3.95
		Nd	13.70	13.19	13.27	13.47	13.40	13.54
		Pm						
		Sm	2.57	2.66	2.52	2.49	2.45	2.39
		Eu	0.52	0.50	0.49	0.51	0.50	0.52
		Gd	2.24	2.43	2.27	2.24	1.97	1.71
		Tb	0.33	3.22	3.24	3.26	3.24	3.35
		Dy	2.34	2.25	2.12	2.27	2.01	2.08
		Ho	0.48	0.50	0.49	0.46	0.45	0.46
		Er	1.32	1.33	1.35	1.32	1.29	1.28
		Tm	0.22	0.21	0.21	0.21	0.20	0.20
		Yb	1.39	1.36	1.37	1.32	1.35	1.33
		Lu	0.22	0.22	0.22	0.18	0.16	0.17
Soaking 0.05 % REE	Above-ground	Er	23.10	22.26	22.47	22.38	22.83	22.37
		Ce	41.70	39.87	41.34	41.96	42.75	42.70
		Pr	5.96	4.32	4.12	4.20	3.99	4.25
		Nd	17.33	18.44	18.52	18.36	18.30	18.67
		Pm						
		Sm	4.33	4.49	4.46	4.55	3.62	3.88
		Eu	0.72	1.00	0.86	0.70	0.72	0.74
		Gd	1.62	2.66	2.40	2.27	2.36	2.22

	Tb	0.18	0.33	0.34	0.35	0.18	0.18
	Dy	1.81	2.33	1.89	2.10	1.99	2.03
	Ho	0.36	0.50	0.51	0.35	0.36	0.18
	Er	1.26	1.50	1.37	1.22	1.27	1.11
	Tm	0.18	0.33	0.17	0.17	0.18	0.18
	Yb	1.08	1.33	1.20	1.05	1.09	1.11
	Lu	0.36	0.66	0.34	0.35	0.36	0.37
Under-ground	La	20.06	20.23	20.33	20.28	20.29	20.19
	Ce	53.30	53.19	53.44	53.26	53.60	54.32
	Pr	6.35	6.25	6.28	6.15	6.15	5.88
	Nd	11.20	11.24	10.95	11.42	11.32	11.18
	Pm						
	Sm	2.40	2.36	2.37	2.38	2.35	2.28
	Eu	0.32	0.35	0.35	0.32	0.25	0.26
	Gd	1.54	1.53	1.50	1.46	1.52	1.36
	Tb	0.29	0.28	0.28	0.25	0.25	0.22
	Dy	1.72	1.77	1.74	1.71	1.66	1.66
	Ho	0.36	0.31	0.35	0.32	0.29	0.29
	Er	1.04	1.08	1.08	1.03	0.98	1.03
	Tm	0.22	0.21	0.21	0.21	0.18	0.18
	Yb	1.01	1.01	0.94	1.03	1.05	0.99
	Lu	0.18	0.21	0.17	0.18	0.11	0.15
Soil	La	23.10	25.00	25.33	25.77	25.96	25.21
	Ce	41.70	38.65	39.91	39.35	39.33	38.75
	Pr	5.96	4.45	3.98	3.70	4.14	4.23
	Nd	17.33	17.67	17.67	17.75	17.68	18.10
	Pm						
	Sm	4.33	4.17	3.83	4.17	4.14	3.89
	Eu	0.72	1.15	0.88	0.93	0.80	0.85
	Gd	1.62	2.44	2.36	2.16	2.23	2.54
	Tb	0.18	0.43	0.44	0.46	0.48	0.51
	Dy	1.81	2.30	2.21	2.47	2.23	2.20
	Ho	0.36	0.29	0.29	0.31	0.32	0.51
	Er	1.26	1.29	1.47	1.39	1.27	1.52
	Tm	0.18	0.29	0.15	0.15	0.16	0.17
	Yb	1.08	1.15	1.03	1.08	0.96	1.18
	Lu	0.36	0.72	0.44	0.31	0.32	0.34

and 2.5. Compared to soaking, the content of REE was more in the former than in the latter, the variation was relatively apparent.

Under acid rain stress and using REE in the experiments, the REE content in the above-ground and under-ground portion of plants decreased gradually with reducing pH value of acid rain. The reason was that (1) Under the acid rain stress, excess H^+ ion entered plant cells, which resulted in the acidification of cells, and changed the inter-environment of leaves cells. Acid rain also affected the conductivity of leaves, causing the exosmosis of many electrolytes (including REE ions). Acid rain stress also influences anti-oxidation enzyme systems of plants, and decreases the ability of eliminating active-oxygen in cells, so the balance system between active-oxygen producing and eliminating is broken, the balance moves to accumulation. The accumulation of active-oxidation finally causes the damaged of the structures of plant cell membrane systems, which results in the changes of the infiltration pressure, so it is hard for REE ions to enter plant cells. Further increase of acid rain stress can cause the lipolysis of the plant cell membrane systems[8,10], so they lost their normal physiological function, and REE ions are hard to accumulate in membrane under this condition. (2) REE itself has a dualism of longitu-

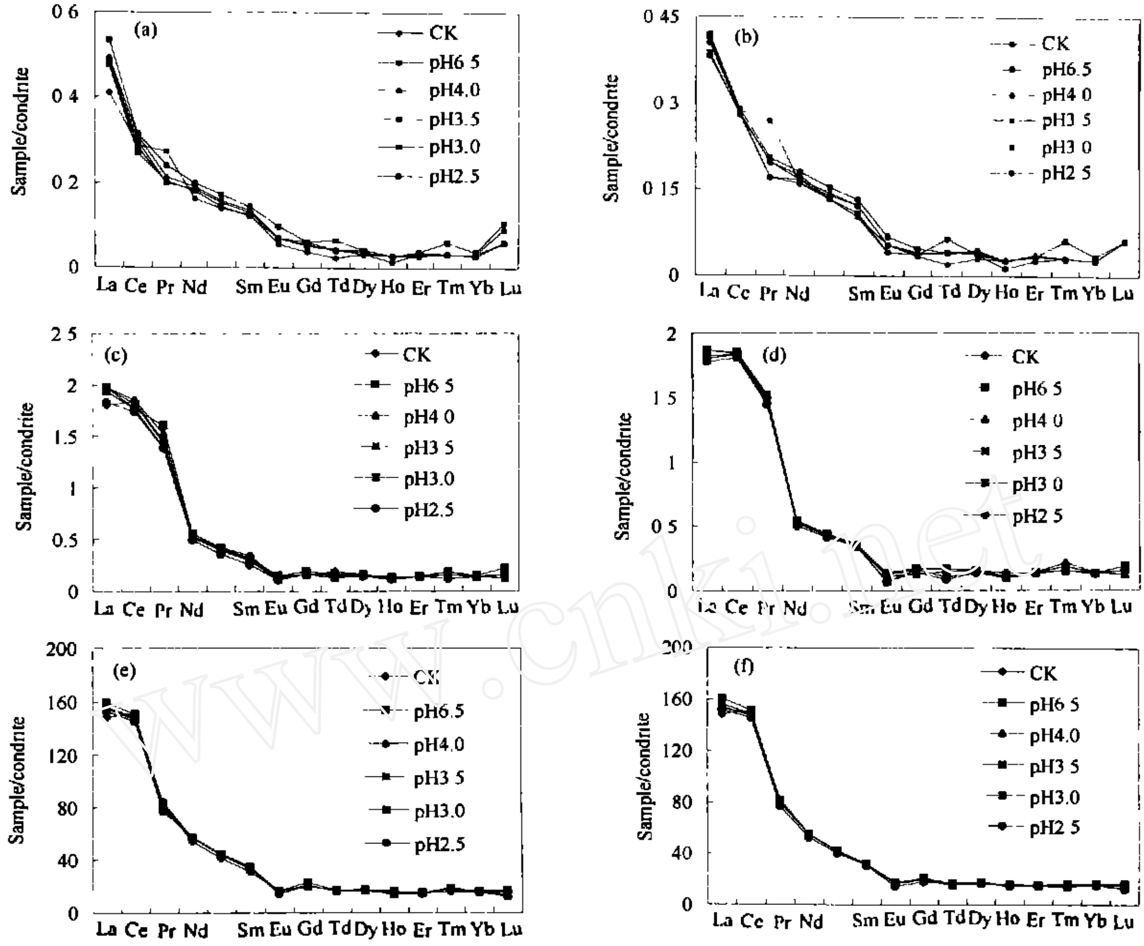

Fig. 1 Distribution of REE in spinach and soil under using REE and acid rain stress (0.03 % REE)
(a) Above ground, spraying; (b) Above ground, soaking; (c) Under ground, spraying;
(d) Under ground; (e) In soil, spraying; (f) In soil, soaking

dinal eluviation and crosswise movement[11~13]. Because of the effect of acid rain, the REE in soil are replaced by the excess H^+ ions brought by acid rain and are washed away by the eluviation of acid rain. Because of the interposition of the H^+ ion of acid rain, the REE can exert their dualism downright, resulting in the decrease of REE which was able to be absorbed by roots in soil. (3) Acid rain itself can eluviate and run off the minor-elements and organic substances in plants (especially in leaves) [1], and it is one of the factors for losing REE in plants. The effect abovementioned brought about the decrease of REE in spinach with the increase of acid rain stress, and the secondary reason also causes the REE reducing with decreasing pH value of acid rain.

The average content of REE in aerolite particle commended by Baynton[14] was adopted as the standard coefficient to standardize the contents of REE in plants and soil. The abundance model obtained from the average content of every elements (Fig. 1) indicates: Whatever acid rain and REE are used or not, the distribution curves of REE in the above-ground portion (Fig. 1 (a, b)) and under-ground portion (Fig. 1 (c, d)) and in the soil (Fig. 1 (e, f)) leans to right in LREE, and they are obviously LREE enrichment. But variation of the distribution of HREE is less in the curve, the curves tends to plain, which shows the deficit.

The values of ΣLREE/ΣHREE are 9.37 %～13.57 % in the above-ground portion, 13.69 %～16.60 % in the under-ground portion, and 7.68 %～16.6 % in the soil, which show that the enrichment of LREE is very apparent.

Under the leaching of acid rain, the contents of REE in plants are reduced, and the contents of REE which can be absorbed by plants from soil also decreases gradually. If only the relationship of plants-soil is considered, a conclusion may be drawn that the acid rain should enlarge the environment holding capability of REE in acid rain area.

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Effect of Ce^{3+} on Free Cytoplasmic Calcium of Cells

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Abstract: The effect of Ce^{3+} on free cytoplasmic calcium of hepatocytes and V79 cells was studied with microfluorometry. The results show that the free cytoplasmic calcium increases in low dose and increases significantly in high dose of Ce^{3+}. These results suggest that Ce^{3+} might enhance the influx of Ca^{2+} and be toxic to hepatocytes in high dose.

Key words: rare earths; cerium; free cytoplasmic calcium; hepatocytes; microfluorometry

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