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Effects of Spraying Rare Earths on Contents of Rare Earth Elements and Effective Components in Tea

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Rare earth (RE) fertilizer is widely applied in China to increase the yield and the quality of crops including tea. However, the effects of spraying RE fertilizer on the contents of rare earth elements (REE) and effective components in tea are unknown. The results from basin and field experiments show that the values of the REE concentrations in new shoots of tea plants and the concentration of REE in the soil (REE/REEs) either from control basins or from treatment basins were smaller than those in other parts of tea plant and similar between control and treatment. The longer the interval between spraying RE fertilizer and picking the shoots of tea plants, the less the effects from spraying. About 80% ∑REE (the sum of the concentrations of 15 REE) in tea, whether it came from spraying or not, was insoluble in the infusion. About 10% the soluble REE of ∑REE in tea infusion was bound to polysaccharide, and the amount of REE bound polysaccharide decreased over time. At least a 25 day safety interval is needed between spraying and picking if the microelement fertilizer is used, in order to enhance tea output and to ensure tea safety.

KEYWORDS: Rare earth elements; fertilizer; components; tea; infusion

INTRODUCTION

In China, scientists have applied inorganic compounds of rare earths (RE) such as $RE(NO_3)_3$, which act as a microelement fertilizer, to agricultural crops and studied their effects on crop yield and quality. They have also studied cumulative concentrations of RE in the field since the 1970s (*1*−*5*). The results of agricultural experiments show that the applications can increase crop production by as much as50%, but these increases are typically in the range of 8−10%. According to analysis of the contents of individual rare earth elements (REE) in a field-grown maize after application of RE, the present dosage of RE (<0.23 kg ha^{-1} $year^{-1}$) currently applied in China can hardly affect the safety of maize growing in arable soil, even over a long period. Recent work has also proved that tea production could be evidently enhanced after spraying $RE(NO_3)_3$ at 300 mg/kg and a dosage of 0.225 kg ha^{-1} $year^{-1}$ on tea gardens (*6*, *7*). All of the results will inspire the use of the compound on tea gardens. It is known that REE are not necessary for plant and animal growth. Das et al. (*8*) reported that lanthanum has many chemical and physical characteristics in common with calcium. In particular, the ionic radius of La^{3+} (8.5×10^{-2}) is very close that of Ca^{2+} (9.2×10^{-2}). La^{3+} usually prevents the influx of Ca^{2+} and competes for available binding sites. REE will be toxic to animals at higher concentrations (*3*), but much research has proved that the REE are only slightly toxic to mammals (*3*, *9*) and hardly toxic to *Daphnia* at lower concentrations (*10*). However, tea is a simply prepared beverage, made by pouring boiling water onto the leaves. This is quite different from rice, wheat, and oil crops. Consumers are very concerned about the effects of spraying RE and different intervals on the contents of REE in tea if the fertilizer is used at the recommended dosage.

Tea is a common drink around the world, and its delicious flavor and health benefits are due to its components, such as polyphenols, amino acids, caffeine, and saccharide. To date, little is known about that the effects of spraying RE on the contents of the components in tea.

A number of studies have reported that REE are absorbed by plants and animals (*11*−*13*). They also found REE-bound polysaccharides in *Dicranopteris dichitima*, a plant with high REE residues. Recently, we reported that REE-bound polysaccharides were present in tea and that activities of the tea polysaccharide (TPS) bound REE (TPS-REE) with increased REE were higher than those of TPS-REE with lower levels of REE (*14*). Some elements found at higher contents, such as Ca^{2+}, Mg^{2+}, Zn^{2+}, and F^-, in tea have been well studied (*15*−*21*). However, reports on the contents of REE in tea, infusion and polysaccharide, and transportation characteristics of REE in the shoot to the different plant organs after spraying with RE fertilizer have not been presented.

The main purpose of the present work is to study the effects of spraying RE on the contents of REE and effective components

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Table 1. Contents of REE in the Soil from the Tea Garden (n = 3, $X \pm$ SD)

element	content (mg/kg)	%	element	content (mg/kg)	%
Y	9.75 ± 0.078	7.31	Dy	2.09 ± 0.002	1.57
La	25.75 ± 0.258	19.30	Ho	0.41 ± 0.089	0.31
Ce	56.89 ± 0.171	42.63	Er	1.20 ± 0.012	0.90
Pr	5.85 ± 0.058	4.38	Tm	0.20 ± 0.001	0.15
Nd	21.71 ± 0.239	16.27	Yb	1.41 ± 0.032	1.06
Sm	3.74 ± 0.037	2.80	Lu	0.21 ± 0.002	0.16
Eu	0.70 ± 0.005	0.52	ΣCe[a]	114.64	85.91
Gd	3.12 ± 0.062	2.34	ΣY[b]	18.80	14.09
Tb	0.41 ± 0.004	0.31	ΣREE[c]	133.44	100.00

[a] ΣCe = sum of the concentrations of light REE, La to Eu. [b] ΣY = sum of the concentrations of heavy REE, Gd to Lu and Y. [c] ΣREE = sum of the concentrations of 15 REE (the same in **Tables 2**–**4**).

in tea and the transportation characteristics of REE. This may clarify the action of RE, when used as a microelement fertilizer, and allow it to be used correctly in agriculture. Our particular interest in this work was to investigate the contents of REE in the tea infusion made from different treatments and to assess the potential safety effects of REE in the tea made from the plants sprayed with RE fertilizer.

MATERIALS AND METHODS

Basin Experiment. Prior to spraying of RE foliage fertilizer, the tea plants [*Camellia sinensis* (L.) O. Kuntze] were grown in basins (22 cm × 16 cm) for 12 months, one plant per basin. The soil in the basin was the same as that in the field experiment, and the contents and composition of REE in the soil are shown in **Table 1**. The plants were 2 years old, with an average height of 40 cm, and 24 plants were selected at random. On March 22, 2000, 12 plants were sprayed with water and the others were sprayed with the RE foliage fertilizer until they were soaked. The fertilizer concentration was 300 mg/kg. Thirty-five days after the application of the fertilizer, the plants were collected and immediately segmented into the root, stem, overyearing leaves, and new shoots. All samples were washed as follows: tap water, 0.02% nitric acid, tap water, and distilled water. After the final washing, all samples were immediately dried in an electric oven at 105 °C for 6 h and then at 80 °C for 6 h to a constant weight. The samples were then ground into powder for analysis.

Field Experiment. A tea garden representing general tea gardens was selected in the south (31° 22′ N, 116° 20′ E) of Anhui province, China, where tea plants are cultivated on a large scale. Tea plants usually begin to bud in early April in that location, and after 20 days, the new shoots can be picked and made into tea. The experimental site soil was red earth, with a pH of 5.80. The contents and composition of REE in the soil are shown in **Table 1**.

Rows of tea plants in the garden were selected at random for the experimental plots, with an area of 1.5 × 80 m^2 each. These included the four following treatments: treatment 0 (control), not sprayed with the RE fertilizer; treatment 1, sprayed with the RE on March 12 according to the methods recommended by the National Coordinate Network for RE Use on Agriculture in China until soaked; treatment 2, sprayed with the RE with the same methods on March 22; treatment 3, sprayed with the RE with the same methods on April 1. Each treatment was repeated five times (in different plots), and all of the plots received the same management.

Samples of young shoots, comprising ~93% two leaves and a bud, plus minor amounts of three leaves and a bud, were picked at each plot on April 16. The intervals between spraying and picking were 15, 25, and 35 days for treatment 3, 2, and 1, respectively. The samples from the same treatments were mixed adequately, cleaned, and aired, and then processed using conventional green tea manufacturing methods. The treated tea was selected at random for the analysis of contents of effective components and REE in the tea.

Reagents. Pectinase and trypsin were imported and provided by Bio Life Science and Technology Co. LTP. The RE foliage fertilizer composed of La (61.49%), Ce (14.48%), Pr (5.78%), Nd (16.78%), Sm (1.06%), Gd (0.25%), and Eu (0.22%) was obtained from Shangqiu Rare Earth Elements and Microelements Fertilizer of Henan province (China). Gels of Sephadex G-75 and -150 were obtained from Pharmacia. All other chemicals used were of guaranteed grade.

Preparation of Tea and Tea Residue Samples. Five hundred grams of the green tea samples made from the different treatments was selected at random, ground, and kept in a desiccator for REE analysis.

One hundred grams of the green tea samples made from the different treatments was selected at random and infused with 5000 mL of boiling glassy doubly distilled water according to the procedure described by Wang et al. (*22*). The residue was centrifuged at 2500g for 20 min and dried at 103 °C to constant weight. The tea yield residue was calculated, and then the residue ground and kept in a desiccator for REE analysis. The amount of REE in the tea infusions from the different treatments was calculated as follows:

$$\text{REE in infusion} = \text{REE in tea} - \text{REE in tea residue} \times \text{residual yield (\%)}$$

Preparation and Purification of Polysaccharide. One hundred grams of the green tea sample from the different treatments was infused in 5000 mL of boiling deionized, distilled water. The tea extract was concentrated, sedimented by alcohol, and then centrifuged. The sediment was dissolved in hot deionized, distilled water. Trypsin was added and hydrolyzed at 38 °C for 36 h, and then boiling water stopped the enzymatic reaction. The mixture was dialyzed, and then pectinase was added and hydrolyzed at 40 °C and pH 4.0 for 18 h. It was dialyzed again before being sedimented by alcohol. The crude extract of polysaccharide was obtained by vacuum-drying at 60 °C. The crude extract was dissolved in water and separated through a Sephadex G-75 column and a Sephadex G-150 gel column. Thus, the purified polysaccharide was obtained and weighed, and then the yield rate was calculated. The detailed procedure was described in our earlier paper (*23*).

Analysis of Contents of REE and Effective Components in Different Samples. All samples were again dried in an electric oven at 80 °C for 8 h. Samples of 100−200 mg, except soil sample (100.0 mg), were microwave digested and then analyzed by inductively coupled plasma mass spectrometry (ICP-MS) (model POEMS, TJA Co.) following the same method described in a previous study (*24*).

The contents of amino acids, polyphenols, caffeine, and saccharide in tea have a great impact on tea quality and health function. They were analyzed according to the methods described by Wang et al. (*22*). The contents of the effective components are expressed on a dry weight basis.

Statistical Analysis. All data are presented on the basis of oven-dried weight and expressed as means ± SD for observation of the indicated number (n).

RESULTS AND DISCUSSION

Effects of Spraying RE on Distributions of REE in Different Organic Parts of Tea Plant. The values of REE concentration in the organic parts of tea plant normalized on the basis concentrations of REE in soil (REE/REEs) are summarized in **Figure 1**. The values of REE/REEs may reflect the absorption intensity of individual REE for different organic parts of tea plant. As shown in **Figure 1**, the concentrations of individual REE in different organic parts decrease in the order of root ≥ stem > leaf > new shoot. It is clear that spraying RE fertilizer influenced the concentrations of individual REE in root, stem, and leaves at 35 days after spraying in the basins. There is an apparent greater enrichment for light REE, especially La and Ce, in root, stem, and leaves from those treated as compared to those from the control. The increased REE in these parts is due to the easier transport of the individual REE absorbed from the RE fertilizer toward the bottom of the plant than toward the top (*25*).

Table 2. Effects of Spraying RE on Contents of REE in Tea Samples ($n = 3$, $X \pm SD$)

REE	treatment 0[a]		treatment 1[a]		treatment 2[a]		treatment 3[a]	
	µg/kg	%	µg/kg	%	µg/kg	%	µg/kg	%
Y	135 ± 12	6.59	141 ± 2	6.14	117 ± 2	4.84	121 ± 2	4.18
La	742 ± 12	36.20	863 ± 20	37.55	1003 ± 10	41.46	1302 ± 5	44.94
Ce	598 ± 14	29.17	644 ± 3	28.02	652 ± 2	26.95	670 ± 15	23.13
Pr	104 ± 1	5.07	114 ± 2	4.96	117 ± 3	4.84	154 ± 3	5.32
Nd	311 ± 11	15.17	361 ± 7	15.71	370 ± 16	15.30	472 ± 32	16.29
Sm	43 ± 2	2.10	48 ± 1	2.09	43 ± 2	1.78	51 ± 2	1.76
Eu	9 ± 1	0.44	11 ± 1	0.48	9 ± 1	0.37	11 ± 1	0.38
Gd	49 ± 2	2.39	47 ± 1	2.05	49 ± 1	2.03	54 ± 0	1.86
Tb	5 ± 1	0.24	6 ± 0	0.26	5 ± 1	0.21	6 ± 0	0.21
Dy	22 ± 2	1.07	26 ± 3	1.13	22 ± 1	0.91	22 ± 2	0.76
Ho	5 ± 1	0.24	5 ± 1	0.22	5 ± 0	0.21	5 ± 0	0.17
Er	12 ± 1	0.59	15 ± 1	0.65	12 ± 0	0.50	14 ± 2	0.48
Tm	2 ± 0	0.10	2 ± 0	0.09	2 ± 0	0.08	2 ± 0	0.07
Yb	11 ± 1	0.54	13 ± 1	0.57	11 ± 1	0.45	11 ± 2	0.38
Lu	2 ± 1	0.10	2 ± 0	0.09	2 ± 0	0.08	2 ± 0	0.07
ΣCe	1807	88.15	2041	88.82	2194	90.70	2660	91.82
ΣY	243	11.85	257	11.18	225	9.30	237	8.18
ΣREE	2050	100.00	2298	100.00	2419	100.00	2897	100.00

[a] Treatment 0 = tea garden never sprayed with RE; treatments 1–3 = experiment plots sprayed with RE on March 12, March 22, and April 1, respectively.

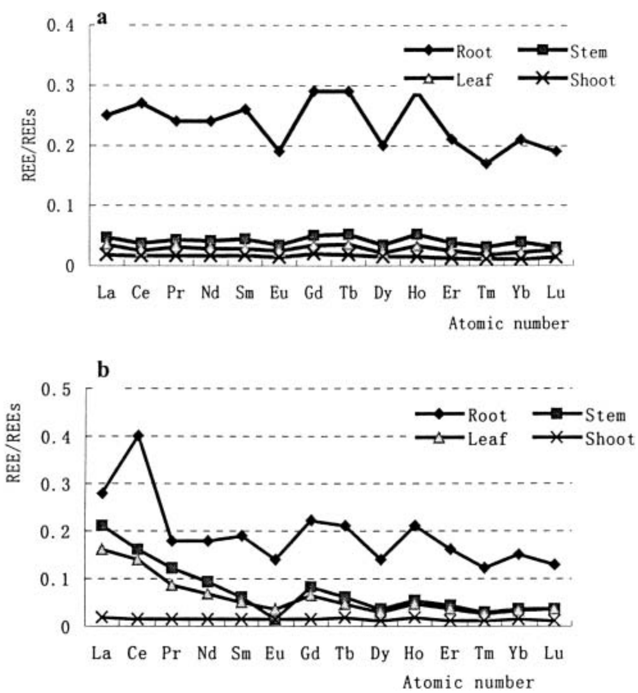

Figure 1. Effects of spraying RE fertilizer on values of REE/REEs, normalized on the basis of concentrations of REE in soil, in different parts of tea plants: (a) samples from control; (b) samples from treatment sprayed with the RE foliage fertilizer on March 22 until the plants were soaked. Fertilizer concentration was 300 mg/kg. At 35 days after the application of the fertilizer, the plants were collected and immediately segmented into the root, stem, overyearing leaves, and new shoot.

Teas, including black tea, green tea, and oolong tea, are made from the new shoots of the tea plant. Consumers are interested in the effects caused by spraying with RE fertilizer. They want to know the value of REE/REEs in the new shoots of tea plant after application of the fertilizer. **Figure 1** illustrates that the values of REE/REEs of individual REE in shoots are very small and almost unchanged between the treated tea plants and the controls.

According to the overall results from basin experiments, it is clear that the effects of spraying RE fertilizer on distributions of REE in new shoots were small at 35 days after application of the fertilizer. The values of REE/REEs in new shoots, whether from control or from treated basins, were smaller than those in other organic parts and similar between control and treated samples.

Table 3. Effects of Spraying RE on Contents of REE in Tea Infusion

REE	treatment 0[a]		treatment 1[a]		treatment 2[a]		treatment 3[a]	
	µg/kg[b]	%[c]	µg/kg	%	µg/kg	%	µg/kg	%
Y	37	27.41	32	22.70	20	17.09	35	28.93
La	130	17.52	143	16.57	218	21.73	445	34.18
Ce	174	29.10	141	21.89	194	29.75	223	33.28
Pr	26	25.00	22	19.30	6	5.13	47	30.52
Nd	73	23.47	77	21.33	44	11.89	167	35.38
Sm	12	27.91	8	16.67	6	13.95	18	35.29
Eu	1	11.11	4	36.36	1	11.11	4	36.36
Gd	16	32.65	6	12.77	11	22.45	17	31.48
Tb	1	20.00	1	16.77	1	20.00	1	16.67
Dy	5	22.73	7	26.92	4	18.18	4	18.18
Ho	2	40.00	ND[d]		2	40.00	2	40.00
Er	2	16.67	3	20.00	2	16.67	4	28.57
Tm	ND		ND		ND		ND	
Yb	2	18.18	3	23.08	2	18.18	4	36.36
Lu	ND		ND		ND		ND	
ΣCe	416	23.02	395	19.35	469	21.38	904	33.98
ΣY	65	26.75	52	20.23	42	18.67	67	28.27
ΣREE	481	23.46	447	19.45	511	21.12	971	33.52

[a] Treatment 0 = tea plants not sprayed with the RE; treatments 1–3 = plots sprayed with the RE on March 12, March 22, and April 1, respectively. [b] REE in infusion = REE in tea − REE in tea residue × the residual yield (%). [c] Weight percentage of REE in the tea infusion. The value is the amount of an element in the infusion divided by the amount of the element in the tea times 100. [d] No detectable amount.

Effects of Spraying RE on Contents of REE in Green Tea. The compositions of REE in soil were mainly Ce, La, and Nd (**Table 1**). The content of ∑Ce (light REE), which is composed of La, Ce, Pr, Nd, Sm, and Eu, was ∼86% of the ∑REE. The tea samples from control plots contained the same kinds of REE in the soil sample (**Table 2**). The compositions of REE in the tea samples were also mainly La, Ce, and Nd, but the composition proportion of La in ∑REE rose rapidly, whereas Ce was the reverse, compared to those in soil. The results indicated that tea plants absorbed selectively REE from soil, especially La.

Table 4. Effects of Spraying RE on Contents of REE in the Polysaccharide (n = 3, $X \pm$ SD)

	treatment 0[a]		treatment 1[a]		treatment 2[a]		treatment 3[a]	
REE	μg/kg	%[b]	μg/kg	%	μg/kg	%	μg/kg	%
Y	31 ± 3	2.60	88 ± 1	8.25	80 ± 5	13.20	136 ± 3	13.21
La	670 ± 21	15.98	1612 ± 6	33.82	1960 ± 33	29.67	1820 ± 5	13.91
Ce	280 ± 17	4.99	244 ± 4	5.19	272 ± 11	4.63	652 ± 2	9.94
Pr	51 ± 3	6.08	65 ± 2	8.86	40 ± 3	22.00	244 ± 3	17.65
Nd	284 ± 10	12.06	196 ± 5	7.64	228 ± 15	17.10	732 ± 7	14.90
Sm	21 ± 1	5.43	24 ± 1	9.00	21 ± 2	11.55	61 ± 4	11.52
Eu	22 ± 2	68.2	26 ± 2	19.5	11 ± 1	36.30	15 ± 1	12.75
Gd	61 ± 5	11.82	25 ± 1	12.5	54 ± 5	16.20	70 ± 2	14.00
Tb	ND[c]		8 ± 2	24.00	12 ± 1	39.60	7 ± 1	23.80
Dy	ND		5 ± 1	2.14	11 ± 2	9.08	23 ± 1	19.55
Ho	ND		ND		ND		ND	
Er	ND		ND		ND		ND	
Tm	ND		ND		ND		ND	
Yb	ND		11 ± 1	11.00	13 ± 1	21.45	13 ± 1	11.05
Lu	ND		ND		ND		ND	
ΣCe	1328	9.90	2167	16.46	2532	17.82	3524	13.25
ΣY	92	4.39	137	7.90	170	13.36	249	12.64
ΣREE	1420	9.15	2304	15.46	2702	17.45	3773	13.21

[a] Treatment 0 = tea plants not sprayed with the RE; treatments 1–3 = plots sprayed with the RE on March 12, March 22, and April 1, respectively. [b] Percentage of REE in the tea infusion binding to polysaccharide. The value was calculated from the amount of an element in polysaccharide divided by the amount of the element in the infusion, multiplied the polysaccharide yield by 100. [c] No detectable amount.

According to the data in **Table 2**, the ΣREE in tea from the plot sprayed with RE increased by 41.32% when compared with that in tea from the control plot when the interval between spraying and picking was 15 days (treatment 3). It increased by only 12.10% when the interval was 35 days (treatment 1). This shows that REE in tea shoots were transported downward and that the interval is critical in order to lessen the content of REE in tea from spraying RE on tea gardens and to ensure the safety of the tea.

Effects of spraying RE on the contents of REE in the teas (treatments 1−3) show that tea plants largely absorbed ΣCe compared to the absorption of ΣY (heavy REE), which is composed of Gd to Lu and Y. They also show that the content of ΣCe reduced gradually with the increasing interval, but the content of ΣY remained almost unchanged. This suggests also that ΣCe in tea plants may move easily from leaves to the other parts of the plant.

Effects of Spraying RE on Contents of Soluble REE in Tea. The commercial value of tea lies in its delicious infusion made with hot water. The contents of the REE in the infusion will always be very important. Naturally, concern about the effects of spraying RE and the amount of REE in a tea infusion has led to increasing interest in whether RE fertilizers will be used in tea cultivation. **Table 3** shows that REE in tea, whether from tea plants in a natural plot or from tea plants sprayed with RE, were primarily insoluble in infusion. The ΣREE in the infusions were only 19−34% of the ΣREE in the tea. About 34% of ΣREE in the tea were soluble in the infusion when the interval between spraying and picking was 15 days (treatment 3). The amount was ∼19% when the interval was 35 days (treatment 1). The amount of ΣREE in the tea infusion for treatment 1 was smaller than that in control (**Table 3**), suggesting that REE in tea from tea plants sprayed with RE mainly existed as an insoluble substance in hot water and remained in the tea residues when the interval was 35 days. It is necessary that there should be an interval of 35 days between spraying and picking in order to ensure the safety of tea.

Effects of Spraying RE on Contents of REE in Tea Polysaccharide. **Table 4** shows an amount of 9.15−17.45% ΣREE in tea infusion was bound to polysaccharide. The transfer ratios of ΣREE from tea infusion into polysaccharide were 13.21, 17.45, and 15.46%, respectively, when the intervals were 15, 25, and 35 days. This shows that the amount of REE in the infusion transferring into polysaccharide was small, and it was the largest when the interval was 25 days. The contents of REE in polysaccharide are shown in **Table 4**. The results show that ΣCe was the main contents of REE in the polysaccharide. ΣCe was >93% of the ΣREE in polysaccharide whether made from tea plants in a control plot or made from tea plants sprayed with RE. The effect of spraying RE on the compositions of REE in polysaccharide was small.

Table 5. Effects of RE on Contents of Effective Components in Tea (n = 4, $X \pm$ SD)

	treatment 0[a]	treatment 1[a]	treatment 2[a]	treatment 3[a]
amino acids (%)	5.46 ± 0.22	5.53 ± 0.28	5.17 ± 0.31	5.07 ± 0.31
polyphenols (%)	17.20 ± 0.41	21.08 ± 0.76	22.10 ± 0.81	22.40 ± 0.85
caffeine (%)	3.34 ± 0.29	2.56 ± 0.11	2.51 ± 0.31	2.53 ± 0.41
water soluble sugar (%)	2.77 ± 0.14	3.58 ± 0.28	3.48 ± 0.32	3.79 ± 0.41
water extraction (%)	39.85 ± 3.08	39.11 ± 2.77	40.01 ± 2.01	40.59 ± 3.10

[a] Treatment 0 = tea garden never sprayed with RE; treatments 1–3 = experiment plots sprayed with RE on March 12, March 22, and April 1, respectively.

Effects of Spraying RE on the Effective Components in Tea. Tea quality and health benefits are dependent on components in the tea, such as amino acids, which relate directly to the tea's taste. The amount of polyphenols is related to the tea's thickness and its health benefits. **Table 5** shows that the components produced by nitrogen metabolism, such as amino acid and caffeine, decreased in treatments 1−3, whereas the other components produced by carbon metabolism, such as sugar and polyphenols, increased in treatments 1−3. The amount of polyphenols in tea from treatments 1−3 increased by 22.56, 28.56, and 30.23%, respectively, when compared with treatment 0. The amount of caffeine in tea in treatments 1−3 decreased by 23.35, 24.85, and 24.25%, respectively, in comparison with that in treatment 0. Our prior experiments found that spraying the RE fertilizer on a tea garden can enhance photosynthesis in the tea plant and increase tea output (*7*). The data in **Table 5** show that the contents of the components related to photosynthesis in tea samples made from plants from a field sprayed with the RE fertilizer were increased, which may indicate that photosynthesis is enhanced by REE.

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LITERATURE CITED

(1) Guo, B. S.; Zhu, W. M.; Xiong, B. K. *Rare Earths in Agriculture*; China Agricultural Science and Technology Press: Beijing, China, 1988; pp 1−22.

(2) Guo, B. S. Progress in application study of rare earth to biology. *Chinese Rare Earths* **1998**, *1*, 64−68.

(3) Ni, J. Z. *Bioinorganic Chemistry of Rare Earth Elements*; Science Press: Beijing, China, 1995; pp 13−37.

(4) Hong, F. H.; Wei, Z. G.; Zhao, G. W. Effect of lanthanum on aged seed germination of rice. *Biol. Trace Elem. Res.* **2000**, *1*, 260−268.

(5) Xu, X. K.; Zhu, W. Z.; Wang, Z. J.; Witkamp, G. J. Distributions of rare earths and heavy metals in field-frown maize after application of rare earth-containing fertilizer. *Sci. Total Environ.* **2002**, *293*, 97−105.

(6) Wang, D. F.; Wang, C. H. Progress in application study of rare earth to tea plants. *Chinese Rare Earths* **1996**, *4*, 46−50.

(7) Wang, D. F.; Shao, X. G.; Wang, C. H.; Fang, N. H.; Zhao, G. W. Analysis on effects of spraying rare earths in tea garden on tea output and quality. *Acta Agron. Sin.* **2000**, *4*, 455−461.

(8) Das, T.; Sharma, A.; Geata, T. Effects of lanthanum in cellular systems. *Biol. Trace Elem. Res.* **1988**, *18*, 201−228.

(9) Haley, T. J. Toxicity. In *Handbook on the Physics and Chemistry of Rare Earths*; Schneider, K. A., Jr., Eyring, L., Eds.; North-Holland: Amsterdam, The Netherlands, 1979; pp 553−585.

(10) Barry, M. J.; Meehan, B. J. The acute and chronic of lanthanum to *Daphnia carinata. Chemosphere* **2000**, *41*, 1669−1674.

(11) Guo, F. O.; Wang, Y. Q.; Chen, M. REE bound polysaccharides on leaves of *Dicranopteris dichitima* by Maa. *Sci. China (Ser. 8)* **1998**, *14*, 266−267.

(12) Chen, W. J.; Gu, Y. H.; Zhao, G. W. Effects of rare earth ions on activity of RuBPcase in tobacco. *Plant Sci.* **2000**, *152*, 145−151.

(13) Chen, C. Y.; Zhang, P.; Chai, Z. F. Distribution of some rare earth elements and their binding species with proteins in human liver studied by instrumental neutron activation analysis combined with biochemical techniques. *Anal. Chim. Acta* **2001**, *439*, 19−27.

(14) Wang, D. F.; Wang, C. H.; Zhao, G. W.; Wei, Z. G.; Tao, Y.; Liang, X. G. Composition, Ccaracteristic and activity of rare earth elements-bound polysaccharide from tea. *Biosci., Biotechnol., Biochem.* **2001**, *9*, 1987−1992.

(15) Tsushida, T.; Takeo, T. Zinc, copper, lead and cadmium contents in green tea. *J. Sci. Food Agric.* **1977**, *28*, 255−261.

(16) Cao, J.; Zhao, Y.; Liu, W. Safety evalution and fluorine concentration of Pu'er brick tea and bianxiao brick tea. *Food Chem. Toxicol.* **1998**, *36*, 1061−1063.

(17) Mierzwa, J.; Sun, Y. C.; Chung, Y. T.; Yang, M. H. Comparative determination of Ba, Cu, Fe, Pb and Zn in tea leaves by slurry sampling electro thermal atomic absorption and liquid sampling inductively coupled plasma atomic emission spectrometry. *Talanta* **1998**, *7*, 1263−1270.

(18) Ozdemir, Y.; Gücer, S. Speciation of manganese in tea leaves and tea infusions. *Food Chem.* **1999**, *61*, 313−317.

(19) Herrador, M. A.; Gonzalez, A. G. Pattern recognition procedures for differentiation of green, black and oolong teas according to their metal content from inductively coupled plasma atomic emission spectrometry. *Talanta* **2001**, *53*, 1249−1257.

(20) Fernández-Caceres, P. L.; Martin M. J.; Pablos F.; González A. G. Differentiation of tea (*Camellia sinensis*) varieties and their geographical origin according to their metal content. *J. Agric. Food Chem.* **2001**, *49*, 4775−4779.

(21) Fernández-Caceres, P. L.; Pablos, F.; Martin, M. J.; González, A. G. Mutli-elements analysis of tea beverages by inductively coupled plasma atomic emission spectrometry. *Food Chem.* **2002**, *76*, 483−489.

(22) Wang, D. F.; Lu, F. D. *Basic Experiment and Study Skill on Tea Biochemistry*; Science Technology and Document Press: Beijing, China, 1997; pp 6−21, 66−68.

(23) Wang, D. F.; Wang, C. H.; Li, J.; Zhao, G. W. Components and activity of polysaccharides from coarse tea. *J. Agric. Food Chem.* **2001**, *49*, 507−510.

(24) Cao, X. D.; Zhao, G. W.; Yin, M. Determination of ultra trace rare earth elements in tea by inductively coupled plasma mass spectrometry with microwave digestion and AG50W-X8 action exchange chromatography. *Analyst* **1998**, *123*, 1115−1119.

(25) Diatloff, E.; Smith, F. W.; Asher, C. J. Rare earth elements and plant growth: I. Effects of lanthanum and cerium on root elongation of corn and mungbean. *J. Plant Nutr.* **1995**, *18*, 1963−1976.

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