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## Does the long-term application of calcium superphosphate lead to an increase of the soil rare earth element contents?

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**Abstract:** In order to test whether the long-term application of calcium superphosphate leads to an increase of the soil rare earth element contents, superphosphate fertilized soils were sampled and compared with superphosphate-free soils. Spectrophotometer inductively coupled argon plasma atomic emission spectrophotometer (ICP-AES) was applied to quantify the rare earth elements (REEs). The total rare earth element contents in calcium superphosphate from Zhijin County, west part of Guizhou Province, China (produced by the sulphuric acid treatment of the apatites) are about 2.54 mg/g. Between 38 and 189 gREEs/hm<sup>2</sup> per year (available for plants, estimated by 2% citric acid) will be introduced into the soil solution when applying 320 kg superphosphate/hm<sup>2</sup> per year. The long-term application of the latter will increase the REE content by about 18% in the soil surface layer in these areas. A statistically significant increase of the content of the rare earths in some cultivated soils should not be neglected.

**Keywords:** rare earth elements; calcium superphosphate; soil

### Introduction

Rare earths are now widely applied in increasing quantities by Chinese agriculturists (Yu and Chen, 1995; Xu, 1997; Wen *et al.*, 2000) partly because China contains approximately 80% of the world's resource of rare earths and is a major producer of them for the world market (Brown *et al.*, 1990). Some reports during the last decade (Wen *et al.*, 2000; Jing and Qian, 2002; Chen and He, 2004) identify the rare earth element (REE) application as microfertilizers which increase the yield of a number of crops by 2.7%—28% and also improve the agricultural production quality. The same reports show that some of the rare earth elements (REEs) in elevated concentrations may inhibit plant growth (Zeng *et al.*, 2001; Hu *et al.*, 2002). Considerable work has shown that the application of rare earths with suitable dosages can improve crop growth and production (Guo, 1988; Brown *et al.*, 1990; Xu, 1997). The beneficial effects may be due to the stimulatory effects of these elements on nutrient uptake by plants or the increased synthesis of chlorophyll of the plant (Guo, 1988; Wang, 1988; Qi *et al.*, 1990).

However, the widespread application of rare earths has led to scattering and bio-accumulation in the environment, particularly in agricultural production, which leads to transfer through the food chain to the human body. Tong *et al.* (2004) have studied distribution characteristics of rare earth elements in children's scalp hair from a rare earths

mining area in southern China and found sixteen REEs contents in the samples from the mining area were significantly higher than those from the reference area, the scalp hair REEs contents may indicate not only quantitatively but also qualitatively (distribution pattern) the absorption of REEs from environmental exposure into human body. Velasco *et al.* (1979) suggested that, at high dosages, rare earths might become harmful in the environment. Rare earths can be taken up through the leaf surface of plants after spraying (Sun *et al.*, 1994), but normally uptake exclusively takes place via the roots. Concentrations of rare earths in plants seem to be extremely variable, and are dependent on the various species of plants and their corresponding habitats (Ichihashi *et al.*, 1992; Wyttenbach *et al.*, 1998). Plants growing on the rare earth-enriched soil show very high concentrations (Miekeley *et al.*, 1994). A body of literature has reported the distribution patterns of rare earths in native plants (Henke, 1977; Ichihashi *et al.*, 1992; Miekeley *et al.*, 1994; Wang *et al.*, 1997; Wyttenbach *et al.*, 1998). In addition, some data are available on the distribution of rare earths in field-grown crops after foliage dressing with fertilizer containing small amounts of rare earths (Zhang *et al.*, 1993; Liu *et al.*, 1997; Wang *et al.*, 2001). Such an application with low dosage, however, does not allow quantification of the accumulative effects of rare earths in the crops as a function of high doses. Since, up to now, Chinese agriculturists have used rare earth-containing fertilizers as base fertilizers together with N fertilizers

(Xu, 1997; Wen *et al.*, 2000), currently studies are only available on the combined effects of nitrogen and lanthanides (Xu and Wang, 2001). In addition, very little attention has been paid to the concentrations of heavy metals in the grains after years of application. In a literature survey, there were no data available on the dose-dependent accumulation of individual rare earths in field-grown crops, which is a key to assess the exposure to rare earths through agricultural application.

Xu *et al.* (2002) had reported that at a dosage of less than 10 kg/hm<sup>2</sup> of rare earths, no apparent accumulative concentrations of individual rare earths appeared in the maize grains. Under the experimental conditions, application of rare earth-containing fertilizer did not induce an increase in the concentrations of heavy metals in the grains. They concluded that the present dosage of rare earths (0.23 kg/(hm<sup>2</sup>·a)) currently applied in China can hardly affect the safety of maize grains in arable soil, even over a long period. But maybe the conclusion was not this case for some special areas. There is a kind of calcium superphosphate which is made from the apatites from Zhijin county, Guizhou province, the mean content of REEs is approximately 0.6%—1%. In the course of the sulphuric acid processing to produce phosphoric acid, 20%—40% of the REEs are transferred to H<sub>3</sub>PO<sub>4</sub>, phosphoric fertilizers and, consecutively, to the soil. In spite of the REEs' low toxicity, uncontrolled release of REEs into the environment cannot be tolerated. In the present paper the possibilities of transferring REEs from fertilizer to the soil solution and the long-term effect of phosphoric fertilizer application on the REE content in cultivated soils were examined.

## 1 Materials and methods

### 1.1 Site description

The investigated cultivated soil samples were collected from the Yina Village, Zhijin County, district of Bijie, west part of Guizhou Province, China, in karst landscape soil region. As a typical subtropical karst mountain plateau, general topography of the area ranges from 940 m to 1550 m above sea-level with a relative height of 300—400 m. The mean annual temperature is 14°C, the annual rain- and snowfall average is 1440 mm. The soil is of the chernozem-vertisol type. The fine-clay fraction is present in the surface layer (0—25 cm). Montmorillonite-type minerals are part of the clays; the humus content is about 4%; total N, 0.18%; P<sub>2</sub>O<sub>5</sub>, 1.8 mg/100g, and K<sub>2</sub>O, 25 mg/100g. The soil sorption capacity is relatively high, namely about 40 meq/100g, pH of the

water leach is about 6.5. The bedrock (below 110 cm) consists mainly of pliocene clays with about 13% carbonates and a pH of about 8 for the water leach. The ground water level is below 10 m.

### 1.2 Sampling

Samples of superphosphate with an overall phosphoric content, as P<sub>2</sub>O<sub>5</sub>, of 51.5% (produced by sulphuric acid treatment of the apatites) were studied. The sampling was undertaken in 2003 from the soil horizons (-10±2) cm and (-30±2) cm from two areas. To one of these areas superphosphate had been applied in the period 1980—2003 at an average amount of 320 kg/(hm<sup>2</sup>·a) along with nitrogen fertilizer (an average yearly rate of 250 kg/hm<sup>2</sup>). To the other area (cultivated by an elder peasant, situated approx. 1.5 km from the above described area) only nitrogen fertilizer had been applied for the same period at approximately the same amounts together with manure. The REE content in the nitrogen was below the detection limit (1.5 × 10<sup>-6</sup> g/g for each of the REEs) of the analytical method employed (no other REE source than the superphosphate in terms of our survey).

### 1.3 Sample preparation and chemical analysis

The analytical reagents used were of GR grade.

Air-dried superphosphate was treated with a 2% solution of citric acid, 1 mol/L HCl, with a mixture of conc. HCl and conc. HNO<sub>3</sub> using standard techniques (GB/T17767.2-1999) respectively for determination of the chemical forms of phosphorous in the fertilizer. Approximately 2 g of the sample were treated with 200 ml citric acid solution or with 100 ml 1 mol/L HCl under agitation for 30 min.

A complete dissolution of the fertilizer was obtained by treating about 2 g with 15 ml HNO<sub>3</sub> and 5 ml HCl under boiling. After dissolution 50 ml H<sub>2</sub>O were added and boiled again for 5 min.

Water leaching of the REEs from the superphosphate was performed by treating 100 g of the sample with 5 L de-ionized water for 30 min in a water bath. The filtrate was further concentrated to 25 ml and the precipitate formed was dissolved in a mixture of 25 ml HCl and 25 ml HNO<sub>3</sub>.

The dried soil samples were sieved through a 2-mm sieve; the fraction with a size < 2 mm were ground to < 0.5 mm in a ceramic mortar. Approximately 1 g of the material was then treated with a mixture of 1 ml HClO<sub>4</sub>, 5 ml HNO<sub>3</sub> and 3 ml H<sub>2</sub>SO<sub>4</sub>. The filtered solution was diluted to 100 ml with de-ionized water. Before the analysis of the solution was filtered through a 0.45 μm membrane filter (Ichihashi *et al.*, 1992).

Quantification of Y, La, Ce and Nd in the final solution was performed with a spectrophotometer inductively coupled argon plasma atomic emission spectrophotometer (ICP-AES) at the Table 1 analytical conditions. Four parallel samples from each type were chemically treated as described above; each final solution was measured in triplicate and the averaged mean values are represented in this paper.

**Table 1 Instrument settings and measurement conditions**

Items	Conditions
Generator power	1200 W and frequency 27 MHz
Argon gas flow rates(coolant)	15 dm <sup>3</sup> /min
Plasma	1 dm <sup>3</sup> /min
Carrier	1 dm <sup>3</sup> /min
Sample uptake rate	1.6 cm <sup>3</sup> /min
The analytical wavelengths, nm	Y, 371.03; La, 408.76; Ce, 413.38; Nd, 406.11
Ion-sampling depth	Adjusted to obtain maximum signal intensity
Ion-lens settings	Adjusted to obtain maximum signal intensity and resolution

The accuracy of the analytical method was verified through the standard material. Three parallel samples of this material were treated as described above. No systematic errors were found.

The mean REE content in phosphate-fertilized and phosphate-unfertilized soils were compared using a *t*-test (at a probability level of 95%) after a preliminary verification (employing an *F*-test) for homogeneity of the respective standard deviations of the analytical results.

## 2 Results and discussion

The REE content in the solutions obtained by treating the superphosphate with water and with diluted acids is summarized in Table 2. In study No.4 a complete dissolution of the fertilizer is ensured, hence the data represent the overall content of the elements studied, which amounts to 2.26 mg/g. The investigated REEs (Y, La, Ce, Nd) represent about 89% of the total REE content of the apatites (Liu, 2003). The total REE content in the studied superphosphate of about 2.54 mg/g is 2–3 times below the REE content in the fertilizer forecast on the basis of the average REE content in the apatite, the apatite/H<sub>3</sub>PO<sub>4</sub> transfer coefficient and the stoichiometry of the fertilizer production process. Dilute citric and hydrochloric acid are commonly used as reagents modelling the soil solution action on the

fertilizers introduced into a soil. From the REE leaching data using these acids (Table 2) 320 kg/(hm<sup>2</sup>·a) of superphosphate is a source of 38–189 g REE available for the plants per hectare per year; the upper limit of this interval is close to the lower limit of the optimum REE fertilizer. The results of determinations of REE content in the soil samples studied are given in Fig.1. The statistical analysis shows the deeper layer of phosphate free fertilized soil is enriched in Y, La and Nd by about 20% in comparison with the surface zone. A probable reason is that the natural REE content in the soil (about 79 mg/kg) which is not affected by the application with other REEs. The use of superphosphate fertilizers leads to an increase in the soil REE content. Significant differences exist between the Y-, Ce- and Nd-content in 10-cm layers of the superphosphate fertilized and non-fertilized soils; for the 30-cm layer the difference is significant for all the REEs studied. The differences in the mean values for the individual REEs are 0–50% in the surface layer and a little lower (10%–30%) in the deeper one. The total REE content in the 0- to 30-cm layer of the phosphate fertilized soil is about 18% higher than that in the phosphate-free fertilized soil.

**Table 2 REEs(Y, La, Ce, Nd) conversion to solution as a result of water and acidic treatment the superphosphate**

No.	Reagent	REE	
		A <sup>a</sup>	B <sup>b</sup> , %
1	Water	<0.07	<3.1
2	Citric acid (2%)	0.12 ± 0.02	5.3 ± 0.8
3	1 mol/L HCl	0.59 ± 0.08	26.1 ± 3.5
4	Conc. HCl + conc. HNO <sub>3</sub>	2.26 ± 0.01	100

Notes: a. The mass of the REE passed to the solution, mg/g fertilizer, averaged mean values and confidential interval at 95% probability level; b. B=100 × A/m, where m is the mass of the REE in the fertilizer, mg/g; the value is obtained from experiment 4

Zhou(2003) studied on the residues rare earth fertilizer in the soil and found REEs obviously enriched in the soil after application of rare earth fertilizer, but different REEs showed different accumulation, a significant increase in the concentration of La, Ce and Nd in the soil. These findings are similar to the results of this paper.

The REEs more commonly used are Ce, La, Pr, Nd, Sm and Y. Recent widespread applications of REEs in agricultural activities include forestry, animal husbandry and aquaculture. REEs are contained in bactericides, microelement fertilizers and animal feeds (Sun *et al.*, 1994). The main element-pollutants in

phosphogypsum used in agriculture are fluorine, sulphur, strontium and the REEs. There is a tendency for strontium and the REEs to scatter or accumulate in soil and the water environment (Gorbunov *et al.*, 1992). The REEs enter the human body mainly via ingestion of contaminated food and inhalation of airborne dust particles bearing REEs. While REEs taken into the human body are mostly excreted, a small amount may enter the bloodstream through ion exchange and can be deposited in various organs (Koeberl and Bayer, 1992). It has been predicted that the industrial and agricultural usage of REEs and the

resulting environmental contamination by REEs will grow rapidly in the next few decades (Volokh *et al.*, 1990). Prolonged occupational, environmental and dietary exposure to REEs may adversely affect human health. A number of diseases have preliminarily been associated with exposure to REEs, Y and Sc can lead to cancer, Sm and Tb tend to accumulate in a human's liver (Sabbioni *et al.*, 1982; Ding and Ma, 1984). The oral LD<sub>50</sub>-values in rats for REE-nitrates are all between about 900 and 1750 mg/kg body weight (Slooff *et al.*, 1993).

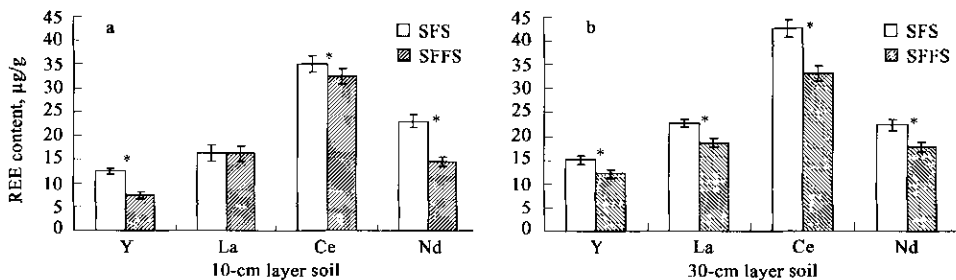


Fig.1 Difference between REE content in superphosphate fertilized(SFS) and superphosphate-free soil(SFFS) at 10-cm layer(a) and 30-cm layer(b), \* denotes the difference is significant at a probability level of 95%

### 3 Conclusions

The REE content in a superphosphate produced by sulphuric acid processing of apatites is about 2.54 mg/g. Between 38 and 189 gREEs/ (hm<sup>2</sup>·a)(available for plants) will be introduced into the soil solution when applying 320 kg/(hm<sup>2</sup>·a) of superphosphate. The long-term application of the latter will increase the REE content in the soil surface layer by about 18%. A comparison between the REE content in the superphosphate studied and its increase in the fertilized soils suggests that the REEs have obviously accumulated in the soils and their washing by rainwater, etc. is negligible. The very low solubility of the REE phosphates is the most probable reason for such an effect. In certain areas, it is worth paying more attention to a significant increase of REE content after the long-term application of the superphosphate in the soil.

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