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Evaluation of plant availability of rare earth elements in soils by chemical fractionation and multiple regression analysis

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Abstract

This case field study describes the distribution of rare earth elements (REEs) in different soil fractions obtained by a sequential extraction procedure and plant availability with single correlation and multiple regression analysis. Soil and plant samples were collected from a rural region of Beijing, China. Plant samples (corn, rice) were segmented into grain, stem, leaf and root. The results indicated that REE contents in different parts of plants followed the order: root > leaf > stem > grain. REEs in soils were extracted by a three-stage sequential extraction procedure into three fractions: water soluble, exchangeable and carbonate bound (B1), Fe–Mn oxide bound (B2), and organic matter and sulfide bound (B3). Chemical fractionation showed that the concentration of REEs in fraction B1 was close to or lower than 1% of the total REEs in soils, and in fractions B2 and B3 was in the range of 1.42–3.35 and 7.32–30.88% of total REEs in soil collected from corn fields, respectively. In soils from rice fields the concentration of REEs in fractions B1, B2 and B3 ranged from 0.58 to 1.05, 13.47 to 21.60 and 7.53 to 25.37% of total REEs, respectively. Correlation and multiple regression analysis indicated that total content of REEs in soils and the sum extracted with the sequential extraction procedure were poor indicators for REE uptake by plants. For La, Ce, Pr, Nd, Sm, Gd, Dy, Er, Yb and Y, consistently significant positive correlations existed between contents in fraction B1 and concentrations in leaves of corn ($r=0.5662$ – 0.7866) and rice ($r=0.5847$ – 0.8262). As for other parts of rice and corn, significant correlations were observed sparsely. Multiple regression analysis was utilized to obtain the ‘best’ regression equations for predicting plant uptake of REEs. The study demonstrated that the sequential extraction procedure applied, though operationally defined, could provide valuable information on plant uptake of REEs in soils. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Plant availability; Rare earth elements; Chemical fractionation

1. Introduction

In recent years, there has been much interest in and concern about the uptake of trace metals by plants from contaminated soils, because excess metals getting into the food chain through uptake by plants might be deleterious to the health of humans. Much work has been carried out to develop a method which could reliably estimate the plant availability and predict the uptake of trace metals by plants and thereby evaluate the potential health risk of these elements in a contaminated environment.

Metal availability depends on many factors such as plant species and soil properties (Soon and Bates, 1982; Sauerbeck and Hein, 1991; Davies, 1992; Smith, 1994). In soils, elements of interest are present in several

different forms and associated with various geochemical phases. Different fractions of soil metal vary considerably in their chemical reactivity and bioavailability. Generally, the water-soluble and exchangeable forms of metals are considered to be the most available to plants (Brummer, 1986; Petruzzelli, 1989; Shuman, 1991), and metals bound to organic matter are also found to be available to plants (LeClaire et al., 1984; Sims, 1986; Iyengar et al., 1981). So information about the physiochemical forms of the element is needed for understanding their environmental behavior. In recent years, the experimentally defined chemical fractionation procedures have been applied to identify plant-available forms of trace metals in soils (LeClaire et al., 1984; Shuman, 1985; Sims, 1986; Spevackova and Kucera, 1989; Sims and Kline, 1991; Qian et al., 1996). Although sequential extraction methods suffer from non-selectivity of extractants and trace element redistribution among phases during extraction (Shan and Chen, 1993), they

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are still considered useful for evaluation of bioavailability of trace metals in soils by many research workers (Sposito et al., 1982; LeClaire et al., 1984; Rappaport et al., 1986; Radogna, 1990; Tuin and Tels, 1990; Sims and Kline, 1991; Chlopecka and Adriano, 1996; Li and Shuman, 1996).

To date the sequential extraction procedures have not been standardized, of which the most widely used is that proposed by Tessier et al. (1979). Due to the need for establishing a common scheme for the sequential extraction as well as for the improvement of the quality of extractable trace metal determinations in soils and sediments, a three-stage sequential extraction procedure was proposed by a European working group coordinated and supported by the Community Bureau of Reference (BCR) (Quevauviller et al., 1993). BCR is now called the Standard Measurements and Testing Programme of the European Community (SMT). This method has been widely applied in studies on soils and sediments (Lopez-Sanchez et al., 1993; Thomas et al., 1994; Davison et al., 1994; McGrath, 1996). To our knowledge there is no report in the literature on the application of the BCR's sequential extraction procedure for evaluating plant availability of metals in soils. Until now sequential extraction procedures used were not very successful in predicting bioavailability, so the BCR procedure was used in this research work to fractionate the rare earth elements (REEs) in soils and to study the relationship between the speciation of REEs in soils and plant availability.

In research on metal availability to plants, correlation and regression analysis were used to estimate the relationship between plant metal concentration and metal fractions from soils. Consistent correlations between specified metal fractions and plant metal concentrations were reported in some investigations. For instance, exchangeable and organically bound trace metals were found by some workers to be available to plants (LeClaire et al., 1984; Sims, 1986; Iyengar et al., 1981; Chlopecka and Adriano, 1996). In other studies, multiple regression analysis was used to study the relationship between soil metal fractions, and metal concentration in plants and soil pH (Sims and Kline, 1991; Davies, 1992). However, these studies mainly focused on heavy metals such as Cr, Cu, Ni, Pb, Zn, Mn, Cd, etc., and no paper appeared on the study of REE availability to plants. REEs might be introduced into the environment from anthropogenic sources such as utilization of REEs in industry, agriculture, forestry, etc. (Olmez and Gordon, 1985; Volokh et al., 1990; Kitto et al., 1992; Xiao and Huo, 1992). There have been some studies on the toxic effects of REEs (Haley, 1965; Venugopal and Luchey, 1975; Ji et al., 1985), and several ill-effects due to occupational and environmental exposure to REEs have also been reported (Sabbioni et al., 1982; Ding and Ma, 1984; Sax, 1984). Up to now there has been very

little information available for estimating the environmental impact of REEs. Therefore, it is important to obtain more knowledge of the environmental effects of REEs in order to predict any possible deleterious effect occasioned by their use.

The objectives of this research were to investigate the distribution of REEs in soils and to study the relationship between forms of REEs in soil and plant uptake. Multiple regression analysis using stepwise selection was applied to identify independent variables and their contribution to REE availability to cultivated corn and rice, based on the fraction data obtained by the BCR's sequential extraction procedure.

2. Materials and methods

Ten corn (*Zea mays* L.) and nine rice (*Oryza sativa*) samples were collected from rural areas of Beijing, China. All the samples were divided into grain, stem, leaf and root, washed thoroughly with deionized water, dried at 60°C for 48 h, ground to pass a 0.25 mm sieve. A portion of dried, ground plant sample (0.400 g) was digested with a mixture of 5 ml HNO₃ (68.0%) and 1 ml HClO₄ (72.0%) under high pressure for the determination of REEs.

The soil samples used in this study were collected from the corresponding sampling sites as plant samples. All the soil samples collected from corn fields and from rice fields (hereafter referred to simply as soil no. 1 and soil no. 2, respectively) were taken from the surface layer (0–20 cm) of cultivated soils. The soils were air-dried, ground and screened through a 1-mm nylon fiber sieve to remove stones, roots and other large particles. Precautions were taken to avoid contamination during sampling, drying, grinding and storage.

Soil pH was measured in a 1:1 soil/water mixture. Organic matter was determined by the Walkley–Black method (Nelson and Sommers, 1982). Cation exchange capacity (CEC) was determined by the method described by Rhoades (1982). Electric conductivity (EC) was determined in a 1:5 (w/v) soil/water mixture. Selected properties of the soils are presented in Table 1.

A three-stage procedure proposed by BCR was employed to extract REEs into three fractions (Table 2). They were specified as fraction B1: water soluble, exchangeable and carbonate bound; fraction B2: Fe–Mn oxide bound; and fraction B3: organic matter and sulfide bound. Extractions were performed for 0.500 g of dried soil samples in 50-ml polypropylene centrifuge tubes. All extractions were done on duplicate samples, and the average results were used for further analysis. Following each extraction, the mixture was centrifuged. The supernatant solutions were separated and the residues washed with deionized water, the washings being combined.

Table 1
Selected properties of studied soils

Sample	Geographical origin	Order	CEC (me/100 g)	EC ($\mu\text{S}/\text{cm}$)	pH (1:1)	Organic matter (%)
<i>Soil no. 1</i>						
1	Xiluyuan	Mollisols	12.6	130.9	7.63	1.63
2	Liqiao	Mollisols	14.0	168.3	7.71	1.17
3	Baihu	Mollisols	15.3	149.6	7.88	1.73
4	Shougang	Mollisols	13.6	118.5	7.82	2.76
5	Tongbei	Mollisols	18.7	143.4	7.69	2.00
6	Changyang	Mollisols	20.4	112.3	7.80	1.57
7	Chaobei	Mollisols	11.8	106.0	7.73	1.08
8	Gaodian	Mollisols	16.2	149.6	7.74	2.00
9	Xuxin	Mollisols	15.7	150.0	7.62	1.00
10	Chaoxi	Mollisols	19.9	87.3	7.36	0.87
<i>Soil no. 2</i>						
1	Yangfang	Mollisols	23.9	249.4	7.64	2.29
2	Chaoxi	Mollisols	12.7	112.2	7.94	0.86
3	Lidong	Mollisols	13.9	174.6	7.84	1.68
4	Qinghe	Mollisols	15.0	268.1	7.86	2.45
5	Ciqu	Mollisols	12.2	249.4	7.75	1.84
6	Qinghedong	Mollisols	11.8	268.1	7.85	2.26
7	Lishuiqiao	Mollisols	15.8	324.2	7.57	3.08
8	Lishui	Mollisols	18.3	205.8	7.95	1.73
9	Donglu	Mollisols	19.5	280.6	7.70	4.11

Table 2
Community Bureau of Reference (BCR) sequential extraction scheme for rare earth element (REE) fractionation in soil

Step ^a	Phases	Procedure
1	B1: water soluble, exchangeable and carbonate bound	0.1 M CH_3COOH , 20 ml, room temperature, shake for 16 h
2	B2: Fe–Mn oxide bound	0.1 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ (pH 2 with HNO_3), 20 ml, room temperature, shake for 16 h
3	B3: organic matter and sulfide bound	30% H_2O_2 , 5 ml, room temperature, 1 h, followed 85°C, 1 h, occasionally shake; add 5 ml 30% H_2O_2 , 85°C, 1 h; add 1 M NH_4OAc (pH 2 with HNO_3) 25 ml, room temperature, shake 16 h
Total ^b		$\text{HNO}_3 + \text{HF} + \text{HClO}_4$, 3 ml, under high pressure, 170°C

^a In steps 1–3, 0.500 g of soil sample was used.

^b Determination of the total content of individual REEs was performed independently by attacking 0.100 g soil (dry wt).

Before determination by inductively coupled plasma–mass spectrometry (ICP–MS), REEs in fraction B2 were separated from other metals by an ion-exchange column procedure. A portion of 15 ml of the extracting solutions was quantitatively transferred to 10×150 mm columns packed with 1×8 strong cation exchanger (60–100 mesh) at a flow rate of 0.5 ml/min. Then the column was successively rinsed with 50 ml of 1.0 mol l^{−1} HCl–0.01 mol l^{−1} tartaric acid and 70 ml of 1.0 mol l^{−1} HCl at the same flow rate to separate sample matrix of Ca, Mg, Al, Fe, Ti, Mn, etc. Finally, REEs were eluted with 100 ml of 4.0 mol l^{−1} HCl at a flow rate of 0.5 ml min^{−1}. In order to eliminate the interference of Cl[−] with the determination of REEs by ICP–MS, the eluate was heated on a hot plate to near dryness, then the residue was dissolved with 1% HNO_3 and transferred to 10-ml flasks for the final determination of REEs.

Total content of individual REE in soils was determined by attacking 0.100 g of dried soil with 3 ml of

$\text{HNO}_3\text{--HF--HClO}_4$ (1 + 1 + 1) mixture.

The contents of REEs in soil and plant samples were determined by ICP–MS (VG PlasmaQuard III). The operating conditions for the determination were optimized and ¹¹⁵In was used as an internal standard (Table 3). All reagents used were of analytical reagent grade or better. All statistical analyses were carried out on the Statistical Package for Social Science (SPSS).

3. Results and discussion

3.1. Soils

Accuracy of the elemental analysis was checked by the determination of REEs in the standard reference materials of soil and tea leaves. The results are listed in Table 4, and a good agreement was achieved between the data obtained by the present method and the

certified values for both soil and tea leaves. The range and mean of total content for each REE in the investigated soils are listed in Table 5. The fractionation of REEs in soil no. 1 and soil no. 2 obtained by the BCR sequential extraction procedure are given in Tables 6 and 7. The contents of Eu, Tb, Ho, Tm and Lu in fraction B1 were lower than the detection limit of ICP-MS. Therefore, these five elements were not taken into consideration during statistical analysis. For soil no. 1 the major part of the REEs was extracted in fraction B3. The average levels of REEs in fractions B1, B2 and B3 represented 0.29–0.63, 1.41–3.35 and 7.32–30.28% of total individual REE content in soils, respectively. Therefore, the following order could be arranged for the chemical fractions obtained for each REE:

Table 3
ICP-MS Operating conditions

<i>ICP system</i>	
Forward power	1350 W
Reflected power	< 5 W
Coolant argon flow rate	14 liter/min
Auxiliary gas flow rate	0.9 liter/min
Nebulizer gas flow rate	0.8 liter/min
Sample uptake rate	1.0 ml/min
Sampling depth	15 mm
<i>Mass spectrometer</i>	
Sampler (nickle) orifice	1.0 mm
Skimmer (nickle) orifice	0.7 mm
Third stage pressure	1.7×10^{-6} mbar
Data acquisition	range-scanning mode
Mass range	85–175 u
Total acquisition time	60 s

Table 4
Determination of rare earth elements (REEs) in the Certified Reference Materials GSS-1 (soil) and GBW-080001 (tea leaves) by ICP-MS

Element	GSS-1 ($\mu\text{g/g}$)		GBW-080001 (ng/g)	
	This method	Certified value	This method	Certified value
Y	25.66 ± 1.14	25 ± 4	790.64 ± 10.06	
La	37.02 ± 1.47	34 ± 4	1021.67 ± 30.64	1120 ± 100
Ce	70.00 ± 3.61	70 ± 5	1567.03 ± 36.20	1580 ± 180
Pr	7.58 ± 0.46	7.5 ± 0.5	214.28 ± 11.57	
Nd	24.85 ± 1.51	28 ± 3	814.76 ± 55.99	
Sm	5.36 ± 0.37	5.2 ± 0.4	179.67 ± 9.54	180^a
Eu	1.09 ± 0.07	1.0 ± 0.1	52.63 ± 3.80	
Gd	4.49 ± 0.32	4.6 ± 0.3	192.11 ± 14.06	
Tb	0.79 ± 0.06	0.75 ± 0.09	26.35 ± 1.57	
Dy	4.12 ± 0.25	4.6 ± 0.3	186.92 ± 9.43	
Ho	0.83 ± 0.06	0.87 ± 0.08	30.55 ± 2.12	
Er	2.60 ± 0.10	2.6 ± 0.2	75.11 ± 4.11	
Tm	0.42 ± 0.04	0.42 ± 0.33	13.18 ± 0.70	
Yb	2.37 ± 0.08	2.66 ± 0.33	104.55 ± 6.14	
Lu	0.36 ± 0.02	0.41 ± 0.06	12.36 ± 1.02	

^a Reference value.

$B3 > B2 > B1$. Generally, the concentration of REEs in fraction B3 was several times or even one order of magnitude higher than that in fraction B2.

As can be seen from Table 7, the average contents of REEs in fractions B1, B2 and B3 were in the range of 0.58 to 1.05, 13.47 to 20.52 and 7.53 to 25.37% of total REEs in soil no. 2, respectively. If comparing the REE distribution over fractions B1 and B3, there was little difference between soil no. 1 and soil no. 2. However, it should be pointed out that the average concentration of Y, La, Ce, Pr, Nd, Gd and Yb in fraction B2 for soil no. 2 was six to nine times that for soil no. 1, and even one order of magnitude greater for Sm and Dy as well.

In order to explain the reason for this large difference between B2 value for the two types of soils an experiment was carried out to determine the content of Fe and Mn in the B2 fraction for both soils. The results are

Table 5
Total content of each rare earth element (REE) in soils

Element	Concentration in soil no. 1 ($\mu\text{g/g}$ dry wt)		Concentration in soil no. 2 ($\mu\text{g/g}$ dry wt)	
	Range	Mean	Range	Mean
Y	14.03–20.09	17.12	13.24–18.24	16.49
La	22.06–40.47	27.56	19.12–23.94	21.30
Ce	46.98–73.67	56.15	44.18–53.19	49.00
Pr	5.20–8.90	6.47	4.60–6.07	5.39
Nd	20.50–32.56	24.39	18.07–23.91	21.59
Sm	3.67–6.33	4.72	3.96–4.86	4.33
Eu	0.89–1.54	1.19	0.83–1.13	1.00
Gd	3.76–5.33	4.41	3.46–4.65	3.96
Tb	0.55–0.95	0.72	0.52–0.65	0.57
Dy	2.70–4.55	3.54	2.71–3.62	3.12
Ho	0.65–0.92	0.78	0.47–0.72	0.61
Er	1.75–2.71	2.16	1.67–2.03	1.89
Tm	0.21–0.37	0.27	0.22–0.31	0.26
Yb	1.47–2.59	2.00	1.66–2.06	1.88
Lu	0.23–0.32	0.27	0.24–0.31	0.27

Table 6
The relative distribution of rare earth elements (REEs) among various fractions in soil no. 1 ($n = 10$)

Element	Content in fraction (%)					
	B1		B2		B3	
	Range	Average	Range	Average	Range	Average
Y	0.44–0.90	0.62	1.26–5.41	3.35	18.19–36.99	25.94
La	0.35–0.94	0.59	1.03–4.46	2.98	11.72–29.89	21.02
Ce	0.23–0.63	0.39	0.70–3.61	2.26	5.53–9.17	7.32
Pr	0.30–0.74	0.51	0.61–2.98	1.82	12.74–25.99	20.53
Nd	0.38–0.89	0.58	0.55–3.02	1.71	15.01–32.92	24.02
Sm	0.44–0.78	0.63	0.36–2.71	1.45	20.23–41.12	29.08
Gd	0.35–0.82	0.54	0.77–3.36	2.22	16.13–42.61	27.96
Dy	0.18–0.58	0.35	0.86–3.34	2.12	18.91–46.71	30.88
Er	0.19–0.47	0.29	0.65–2.89	1.72	19.69–34.27	25.90
Yb	0.18–0.47	0.31	0.67–2.48	1.42	19.06–40.61	27.23

Table 7

The relative distribution of rare earth elements (REEs) among various fractions in soil no. 2 ($n=9$)

Element	Content in fraction (%)					
	B1		B2		B3	
	Range	Average	Range	Average	Range	Average
Y	0.53–1.90	0.91	16.79–25.58	20.52	11.67–19.15	14.64
La	0.55–1.86	1.05	13.23–22.16	18.75	9.63–19.54	14.05
Ce	0.38–1.47	0.73	12.45–18.70	15.65	5.00–15.71	7.53
Pr	0.46–1.76	0.87	13.25–20.25	16.65	12.80–22.27	16.46
Nd	0.42–1.74	0.89	12.03–18.94	15.03	10.76–19.54	15.37
Sm	0.29–1.48	0.80	9.46–18.15	14.60	14.87–27.78	21.45
Gd	0.25–1.35	0.83	12.67–28.04	21.20	18.30–33.51	25.37
Dy	0.46–1.20	0.69	18.52–25.54	21.60	19.67–36.63	24.30
Er	0.37–1.01	0.59	10.60–20.0	14.50	14.78–34.87	24.47
Yb	0.30–1.00	0.58	10.85–1.13	13.47	17.89–35.57	22.83

Table 8

Content of Fe and Mn in fraction B2

Soil no. 1	Concentration ($\mu\text{g/g}$)		Soil no.2	Concentration ($\mu\text{g/g}$)	
	Fe	Mn		Fe	Mn
1	275.46	245.65	1	1010.5	55.86
2	263.95	169.75	2	684.06	120.95
3	136.10	187.43	3	844.10	69.21
4	255.15	100.17	4	1369.4	75.90
5	255.28	189.57	5	892.65	66.10
6	201.04	58.72	6	984.51	54.04
7	221.73	146.20	7	1021.4	66.23
8	200.85	163.14	8	525.71	166.84
9	177.25	208.12	9	1829.5	39.54
10	282.35	110.91			
Average	226.92	157.97		1018.0	79.42

Table 9

Concentration range and mean of rare earth elements (REEs) in parts of corn

Element	REE concentration (ng/g dry wt)							
	Grain		Stem		Leaf		Root	
	Range	Average	Range	Average	Range	Average	Range	Average
Y	0.75–3.78	1.47	15.24–27.65	20.71	63.13–150.53	105.20	184.15–1100.6	554.30
La	1.00–6.00	2.09	18.91–40.93	25.60	104.56–342.05	189.37	248.52–1774.4	837.90
Ce	1.77–11.47	3.95	34.38–65.58	47.80	212.22–632.88	379.71	512.00–3851.2	1814.7
Pr	< 1.26	1.97	4.12–8.59	6.14	22.44–73.00	41.78	63.56–408.60	195.11
Nd	0.85–5.27	1.02	16.24–34.52	24.15	80.20–249.50	143.92	215.51–1546.2	717.93
Sm	0.79–1.90		4.28–8.71	6.53	10.32–49.10	31.82	59.27–349.89	169.88
Eu	ND		1.11–3.59	2.22	2.63–8.62	5.89	9.41–63.62	31.37
Gd	< 1.15		3.32–8.35	5.91	18.74–52.06	30.49	33.96–305.15	146.17
Tb	ND		< 1.58	5.22	2.44–6.53	4.60	4.98–42.01	19.70
Dy	< 0.69		2.56–8.91	3.02	11.85–46.76	24.35	36.37–225.55	109.39
Ho	ND		< 2.10	3.04	2.66–9.69	4.58	4.75–41.78	19.80
Er	< 1.00		1.35–5.56		6.34–21.94	12.00	20.24–134.64	59.80
Tm	ND		< 1.11		1.56–3.04	2.37	2.23–18.41	8.58
Yb	< 1.00		2.02–4.26		8.16–17.90	13.45	15.27–124.70	55.35
Lu	ND		< 0.80		1.28–3.20	1.89	2.66–16.63	8.18

ND, not detected.

listed in Table 8. As can be seen, the average of Fe content in the B2 fraction for soil no. 2 was four to five times that for soil no. 1, although the corresponding Mn value was only half that for soil no. 1. According to the literature, REEs can be concentrated in Fe–Mn oxides during natural weathering, soil formation and sedimentation (Moeller, 1973). Therefore, a greater concentration of REEs in fraction B2 was expected to be observed for soil no. 2 than soil no. 1, which was in agreement with the experimental results. As far as the lower concentration of Mn in soil no. 2 is concerned, this might be ascribed to the reduction of pyrolusite ($\beta\text{-MnO}_2$, Mn^{4+}) or mangnrite ($\gamma\text{-MnOOH}$, Mn^{3+}) to rhodochrosite (MnCO_3 , Mn^{2+}) under anerobic conditions in the rice fields (Han and Banin, 1996). Moreover, the present information is too limited to enable detailed explanation of REE distribution among the different fractions of different types of soils.

3.2. Plants

REEs in the different parts of corn (Table 9) and rice (Table 10) show that the distributions of the REEs vary among different parts of plants, and the following order could be arranged for REEs in parts of corn and rice: root > leaf > stem > grain, which was also verified by other research (Kuang and Deng, 1981). The fact that REE concentrations in roots were much higher than that in other parts showed that the REEs could be accumulated and retained by the roots of corn and rice, so that only small portions of REEs reached other parts of plants. For both corn and rice samples, only Y, La, Ce, Pr and Nd in grains can be determined quantitatively,

Table 10
Concentration range and mean of rare earth elements (REEs) in parts of rice

Element	REE concentration (ng/g dry wt)							
	Grain		Stem		Leaf		Root	
	Range	Average	Range	Average	Range	Average	Range	Average
Y	0.68–1.70	1.08	16.00–149.64	55.47	90.40–282.04	195.03	2269.6–6665.3	4007.2
La	0.91–3.24	1.80	20.88–222.50	79.80	102.40–372.42	255.41	2701.5–7865.3	1731.3
Ce	1.61–5.58	3.56	34.91–434.76	143.75	181.75–716.04	491.35	5361.9–15080	10826
Pr	<0.99	1.55	6.33–50.16	18.15	25.67–84.58	59.11	587.0–1752.9	1231.0
Nd	1.07–3.01		13.50–175.30	60.07	90.64–288.02	200.50	2071.8–6457.4	4593.8
Sm	<0.78		3.83–29.73	14.47	9.92–50.42	30.57	451.64–1362.6	899.82
Eu	ND		1.89–9.28	6.07	6.44–15.89	11.37	89.76–302.00	193.76
Gd	<1.15		7.06–38.48	17.95	24.25–49.79	39.10	512.98–1460.3	931.52
Tb	ND		1.21–4.78	2.55	3.06–9.52	6.23	74.13–214.41	130.47
Dy	ND		4.10–27.24	10.31	15.94–54.69	35.34	347.46–1116.2	654.50
Ho	ND		0.72–5.09	2.07	5.20–10.85	7.49	73.67–228.83	136.60
Er	ND		2.33–13.82	5.84	15.85–33.45	23.07	197.21–646.71	385.22
Tm	ND		<2.85	5.48	1.50–4.94	3.14	29.25–94.58	57.76
Yb	ND		1.59–13.65		15.50–46.34	28.69	186.86–586.31	363.06
Lu	ND		<1.66		2.51–5.85	4.07	27.98–82.43	51.30

ND, not detected.

and the concentrations of other REEs are close to or below the detection limit. Compared with corn, REEs in rice were generally higher than that of corn. This result indicates that rice might have a comparatively higher ability to accumulate REEs.

3.3. Correlation between REE concentrations in different soil fractions and in parts of plants

Total contents of most REEs in soils correlated poorly with REE concentrations in each part of corn and rice. Total contents of La, Pr and Nd in soil no. 2 were inversely correlated with root uptake ($r = -0.7104^{**}$, -0.6334^{*} and -0.6735^{**} , respectively). A negative significant relationship between total contents of Yb and Y in soil no. 1 and plant concentrations in roots of corn was obtained ($r = -0.6131^{*}$ and -0.5865^{*} , respectively). Total content of Gd in soil no. 1 was negatively correlated with Gd uptake by stem of corn ($r = -0.6486^{**}$). Based on the above results it is apparent that total content of REE in soils can hardly predict plant REE uptake, which is in agreement with other reports (Sims, 1986; Iyengar et al., 1987; Sims and Kline, 1991). This could be interpreted by the general consideration that only a small fraction of the total metals in soils is available to plant uptake.

The relationships between the sum of extracted REEs by the BCR sequential extraction procedure and their plant uptake were also considered. Significant negative relationships between the sum of Pr, Gd and Er extracted from soil no. 1 and the concentration of the element of interest in leaves of corn were observed ($r = -0.6676^{**}$, -0.6579^{*} and -0.6702^{**} , respectively). In addition the sum of the Gd fraction from soil was also inversely

correlated with Gd content in stem of corn ($r = 0.6535^{**}$). In the case of La and Nd, the sum extracted from soil no. 2 was negatively correlated with La and Nd content in grain ($r = -0.6318^{*}$ and -0.6548^{*} , respectively). Generally, no significant correlation was obtained between the sum of REEs extracted and plant uptake. Therefore, the sum of REEs extracted is also a poor indicator of REE bioavailability to corn and rice.

Single correlation analysis was also performed to assess relationships between concentrations of REEs in different chemical fractions and uptake by each part of plants. The correlation coefficients obtained are listed in Tables 11 and 12.

For most REEs, including La, Ce, Pr, Nd, Sm, Gd, Dy, Er, Yb and Y, consistently significant positive correlations existed between the contents of REEs in fraction B1 and in leaves of corn ($r = 0.5662$ – 0.7866). A similar correlation existed for leaves of rice and the correlation coefficients ranged from 0.5847 to 0.8262. As far as the other parts of rice and corn are concerned, no significant correlations were observed. For La, Ce and Pr, plant uptake by the grain of rice was negatively correlated with the content in fraction B2. Positive correlations were obtained between uptake of Yb by rice stem and Yb content in fraction B1.

The metals extracted with CH_3COOH in the first step were predominantly water soluble, exchangeable, and bound to carbonate forms. The first two forms of metals in soils were generally considered as the most mobile and immediately bioavailable forms of metals in soils (Brummer, 1986; Petruzzelli, 1989; Shuman, 1991). As for metals bound to carbonate, Viets (1962) supposed them to be relatively unavailable to plants. However,

Table 11

Correlation matrix (*r*) for rare earth elements (REEs) in soil fractions and REE concentrations in corn tissues

Element	Fraction	Grain	Stem	Leaf	Root
Y	B1	0.7451**	−0.0563	0.6667**	−0.3792
	B2	0.0342	0.3714	−0.4128	0.3144
	B3	−0.0588	0.1913	0.4568	−0.0474
La	B1	0.5072	0.3389	0.7866**	−0.3787
	B2	0.1269	0.1237	−0.2848	0.2910
	B3	−0.0476	0.2024	−0.5098	0.0461
Ce	B1	0.2800	0.4325	0.5685*	−0.3927
	B2	−0.0236	0.2904	−0.3044	0.2646
	B3	0.2476	−0.5247	−0.5482	−0.2042
Pr	B1		0.2729	0.6788**	−0.4014
	B2		0.3731	−0.3156	0.3266
	B3		0.3200	−0.6676**	0.0222
Nd	B1	0.3789	0.0168	0.6545**	−0.5474
	B2	0.0287	0.3270	−0.3015	0.3262
	B3	0.1561	0.2393	−0.5033	0.0131
Sm	B1		−0.1465	0.5662*	0.3847
	B2		0.6460**	0.1764	0.0598
	B3		−0.0695	−0.4537	0.0691
Gd	B1		−0.2072	0.7576**	−0.1890
	B2		−0.5552	−0.4760	0.2851
	B3		0.6133**	−0.6579**	−0.1491
Dy	B1		0.2921	0.7005**	−0.3981
	B2		0.2000	−0.3299	0.4176
	B3		0.4470	−0.4992	0.1642
Er	B1		0.2873	0.6584**	−0.5086
	B2		−0.0354	0.0174	0.3067
	B3		0.4470	−0.7046**	−0.0476
Yb	B1		−0.1965	0.6488**	0.0064
	B2		0.4265	−0.1808	0.3920
	B3		0.0001	−0.3937	−0.0013

**, * Significance at 5 and 10% levels, respectively.

Table 12

Correlation matrix (*r*) for rare earth elements (REEs) in soil fractions and REE concentrations in rice tissues

Element	Fraction	Grain	Stem	Leaf	Root
Y	B1	0.0067	0.1097	0.7203**	0.4242
	B2	−0.1091	−0.5071	−0.2542	0.1702
	B3	−0.4233	−0.1169	−0.2301	−0.1389
La	B1	−0.1142	0.1788	0.7539**	0.0583
	B2	−0.7130**	−0.1346	−0.0466	0.4863
	B3	−0.5156	−0.1396	−0.2007	0.2362
Ce	B1	−0.0009	0.1404	0.7827**	0.2191
	B2	−0.8122**	−0.3826	−0.1797	0.4571
	B3	−0.0027	−0.2741	−0.0476	0.0160
Pr	B1		0.2743	0.8262**	0.0951
	B2		−0.4256	−0.2180	0.2456
	B3		−0.5610	−0.5210	−0.1872
Nd	B1	0.1066	−0.0247	0.6691**	0.1389
	B2	−0.5300	−0.3962	−0.1004	0.1602
	B3	−0.6379*	−0.2712	−0.2426	0.2085
Sm	B1		0.2976	−0.6989**	0.2665
	B2		−0.3654	−0.1237	0.5488
	B3		−0.2503	−0.4443	−0.1164
Gd	B1		0.2075	0.6146*	0.0014
	B2		−0.2628	−0.2797	0.0340
	B3		−0.1188	−0.0928	−0.1206
Dy	B1		−0.1530	0.5903*	0.3808
	B2		−0.1672	−0.0766	−0.3182
	B3		0.2488	0.0290	0.0383
Er	B1		−0.0549	0.6671**	0.4903
	B2		−0.6762**	−0.2655	0.2427
	B3		−0.3722	−0.3924	−0.4081
Yb	B1		0.3991	0.6023*	0.6971**
	B2		−0.3342	−0.0714	0.5966*
	B3		−0.6069*	0.3140	0.0788

**, * Significance at 5 and 10% levels, respectively.

Xian et al. (1989) thought that metals associated with carbonates were also easily released to solution when soil pH was sufficiently low to dissolve the carbonates. The behavior of metal association with distinct geochemical phases is strongly dependent on the physico-chemical conditions of soil, such as pH. Plant root could secrete many kinds of organic acids during root physiological activities (Qu et al., 1995). As metabolic products of plant root, the organic acids secreted by plant root would lower the pH of the rhizosphere. Sarong et al. (1989) reported that pH of the rhizosphere is obviously lower than that of bulk soil. The low pH could solute more metals easily available for plant uptake. The CH₃COOH extractant used in the first step of the present method is found in the nature of organic acids secreted by plant root, and the REE forms extracted by CH₃COOH may be considerably similar to the part of REEs that was available to the plant. To some extent this may account for the experimental results.

In order to obtain the most consistently significant regression equation for estimating plant uptake for the REEs, the data were put through a stepwise multiple regression with chemical fractionation as potential independent variables. The consistently significant regression equations for REEs are listed in Tables 13 and 14.

It can be seen from the above results that positive correlation between the concentration of Y, La, Ce, Pr, Nd, Sm, Gd, Dy, Er and Yb in fraction B1 of both soil no. 1 and soil no. 2 and various parts of plants was found. It seems that REEs in B1 might play an important role in the process of REE uptake by plant. The fractions obtained by the sequential extraction procedure proposed by BCR, though operationally defined, in combination with a stepwise multiple regression can still provide valuable information on plant uptake of REEs. However, these data are incomplete for quantitatively predicting the plant uptake of REEs in soils. Soil is a complicated system and the interactions between biota and soil are intricate. More detailed

Table 13

Regression equations between concentrations of rare earth elements (REEs) in corn and in soil fractions

Element ^a	Regression equation	r ²
Y	C _{lf} = 106.29 + 0.66B1 – 0.016B3 C _{gr} = 0.021 + 0.74B1	0.6536** 0.5552**
La	C _{lf} = 218.01 + 1.04B1 – 0.035B3	0.8063**
Ce	C _{lf} = 94.44 + 1.33B1	0.3232*
Pr	C _{lf} = 86.65 + 1.09B1 – 0.062B3	0.7911**
Nd	C _{lf} = 18.94 + 0.90B1	0.4284**
Sm	C _{lf} = –8.37 + 1.38B1 C _{st} = 4.20 + 0.036B2	0.3206* 0.4173**
Gd	C _{lf} = 33.80 + 0.99B1 – 0.022B3 C _{st} = 0.64 + 0.0044B3	0.7676** 0.3761*
Dy	C _{lf} = 28.99 + 1.47B1 – 0.022B3	0.7586**
Er	C _{lf} = 42.59 + 0.76B1 – 0.14B2 – 0.055B3	0.8342**
Yb	C _{lf} = 13.42 + 1.42B1 – 0.016B3	0.6255**

**, * Significance at 5 and 10% levels, respectively.

^a C_{lf}, C_{gr}, C_{st}, concentration (ng/g dry wt) of REEs in leaf, grain and stem of corn, respectively.

Table 14

Regression equations between concentrations of rare earth elements (REEs) in rice and in soil fractions

Element ^a	Regression equation	r ²
Y	C _{lf} = 87.68 + 0.717B1	0.5189**
La	C _{lf} = 71.21 + 0.83B1 C _{gr} = 6.85 – 0.0013B2	0.5084** 0.5683**
Ce	C _{lf} = 151.16 + 0.96B1 C _{gr} = 13.05 – 0.0012B2	0.6127** 0.6597**
Pr	C _{lf} = 20.74 + 0.83B1	0.6827**
Nd	C _{st} = 94.06 + 0.56B1 C _{gr} = 3.77 – 6.71B3	0.4477** 0.4069*
Sm	C _{lf} = 8.25 + 0.65B1	0.4884**
Gd	C _{lf} = –11.79 + 0.66B1 + 0.029B3	0.7625**
Dy	C _{lf} = 18.37 + 0.77B1	0.3448*
Er	C _{lf} = 11.76 + 1.01B1 C _{st} = 18.29 – 0.064B3	0.4451** 0.4571**
Yb	C _{lf} = 19.64 + 0.82B1 C _{st} = 13.49 – 0.019B3 C _{rt} = –447.08 + 18.93B1 + 2.45B2	0.3771* 0.3683* 0.7352**

**, * Significance at 5 and 10% levels, respectively.

^a C_{lf}, C_{gr}, C_{st}, C_{rt}, concentration (ng/g dry wt) of REE in leaf, grain, stem and root of rice, respectively.

information is, therefore, needed to quantitatively predict soil REE availability to plants.

4. Summary

Based on the foregoing discussion, it is apparent that total content of individual REEs was a poor indicator of uptake by plants as was the sum of REEs extracted with the BCR procedure. However, for the REEs studied, a stepwise multiple regression procedure using fractions obtained with the BCR sequential extraction procedure as independent variables could predict REEs uptake by plants. The CH₃COOH extractable fraction B1 of REEs

in Mollisol soils might play an important role in the process of REE uptake by plants. However, it is still difficult to quantitatively predict the REEs bioavailability to plants. Further research is required to develop more accurate speciation analysis methods so that well-defined or even true species can be determined convincingly. Then, the relationship between the speciation of REEs in soil and their bioavailability could be established.

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