



Rare earth elements in soil and plant systems – A review

Germund Tyler*

Soil–Plant Research, Department of Ecology, Lund University, Ecology Building, SE-223 62 Lund, Sweden

Received 5 May 2003. Accepted in revised form 25 March 2004

Key words: lanthanide, plant, REE, review, soil

Abstract

The rare earth elements (REEs) form a chemically uniform group and include yttrium (Y), lanthanum (La) and the lanthanides cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and lutetium (Lu). Their average abundance in the Earth's crust range from $66 \mu\text{g g}^{-1}$ in Ce to $0.5 \mu\text{g g}^{-1}$ in Tm and $\ll 0.1 \mu\text{g g}^{-1}$ in Pm. Recent great improvements in more routine analytical technique, the use of REEs as fertilisers, at least in East Asian agriculture, and the importance of these elements as indicators in both pedological and physiological processes and reactions have contributed to an increased interest in these previously less considered elements in environmental sciences. This review of recent and current literature deals with REEs in primary and secondary soil minerals, concentrations in surface soils, factors influencing adsorption, solubility and transport in soils, including weathering and transformations of REE minerals, and vertical distribution in soil profiles. Reviewed and discussed are also concentrations, distribution and localisation of REEs in plants and plant organs, soil–plant relationships and interactions, effects on plant growth and crop production and their importance in plant physiology and biochemistry. The REEs are found, usually several elements together, as phosphates, carbonates and silicate minerals finely dispersed especially in magmatic and metamorphic rocks. REE concentrations in surface soils of humid climates, such as the A(E)-horizons of Podzols and Laterites, are usually lower than in the parent material, due to higher weathering and leaching rates than of the average soil constituents. Some fractionation may occur due to the formation of more element-specific secondary minerals. Transfer from soil to plant is usually low, but extreme accumulators are found, e.g., among several species of ferns. Roots have generally higher concentrations than shoots. Possible uptake mechanisms of REEs are discussed. Uptake is positively, though often weakly, correlated with soil acidity and easily soluble concentrations of the elements, but rarely well related to their total concentrations in the soil. Under certain conditions, low concentrations of at least some REEs seem to favour plant growth and productivity, but the physiological mechanisms are still not well understood. Some considerations concerning the boundary between essential and non-essential micro nutrients are discussed.

Introduction

Rare earth elements (REEs) include the 14 lanthanides: cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and lutetium (Lu). Moreover, lanthanum (La) belongs to the REEs; often yttrium (Y) is included as well. Their average abundance in the earth's

crust varies from $66 \mu\text{g g}^{-1}$ in Ce, $40 \mu\text{g g}^{-1}$ in Nd, and $35 \mu\text{g g}^{-1}$ in La to $0.5 \mu\text{g g}^{-1}$ in Tm, disregarding the extremely rare Pm. Several of the REEs are thus not very 'rare' and occur widely dispersed in a variety of forms, especially as accessory minerals in granites, pegmatites, gneisses and related common types of rocks (Greenwood and Earnshaw, 1984; NE, 1993). The abundance of Ce is almost the same as environmentally much more studied elements, such as Cu and Zn; the most scarce lanthanides, Lu and Tm,

*E-mail: germund.tyler@ekol.lu.se

are actually more abundant in the Earth's crust than Cd and Se.

No other group of elements in the periodic system displays such a great similarity as the REEs. They all usually form trivalent cations, though the divalent or the tetravalent oxidation state is known for most of them in chemical compounds. The effective ionic radius of the trivalent ions decreases gradually from La^{3+} (103.1) to Lu^{3+} (86.1). The radius of Y, however, is similar to that of Ho (90). The dissimilarities that do exist among the elements are partly controlled or dependent on these differences in effective ionic radii. The smaller ions at the end of the series form the most stable complexes with electronegative ligands, e.g., the chelate-forming oxalate.

Until recently, the REEs have neither been characterised as essential elements for life, nor as strongly toxic elements in the environment. Much less interest has, therefore, been paid to them than to several transition and other heavy metals. Until recently, their quantitative analysis in environmental materials has also presented great problems, at least on a more routine scale. The advancement of ICP-MS technique and the more common use of this technique in environmental and biological research since about 1990 has greatly facilitated their study.

Several interactions between REEs and biological systems are known. Many studies in Chinese agricultural science have suggested, indicated or even demonstrated that low concentrations of REEs may promote growth and productivity of several crops. Application of these elements, either to the seed or to the crop biomass is nowadays widely practised in Chinese agriculture, thus in a considerable part of the earth's cultivated soils. The physiological and eco-physiological mechanisms underlying their reactions have recently been given much attention.

However, there are conflicting evidence and opinions regarding the importance of REEs in pedology and biology. During the last decade much new information has appeared on the occurrence, behaviour and possible biological role of REEs in soil and plant systems. This paper originated from a demand to review the rapidly increasing knowledge in this field, with special emphasis on soil conditions of importance to the solubility, mobility and plant uptake of these elements and their suggested favourable effects on plant growth and vitality. The use of REE fertilisation in agriculture, and environmental concerns about REE pollution of the environment, will also be considered.

Definitions and abbreviations:

Some definitions and abbreviations used in the present study are given below.

Lanthanide(s): all elements from Ce to Lu in the periodic system;

REE(s): rare earth elements, comprising the lanthanides as well as La and Y;

Ln^{3+} : the trivalent cationic form of any REE;

LREE(s): 'light' rare earth elements, i.e. those with a lower mean atomic mass (weight) than ca 153 and a larger effective radius than 95 pm (La, Ce, Pr, Nd, Sm, and Eu);

HREE(s): 'heavy' rare earth elements, i.e. those with a higher mean atomic mass than ca 153 and a lower effective ion radius than 95 pm (Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu). Due to its low ion radius, Y is often included in this subgroup as well, in spite of its low atomic mass.

MREE(s): Sometimes used in the literature to designate REEs of intermediate mean atomic mass and ion radius. This subgroup is rarely well defined.

REEs in primary minerals and surface soils

The REEs are found, usually several together, in a variety of accessory minerals, such as phosphates, carbonates, fluorides and silicates and occur especially in pegmatites, granites and related metamorphic igneous rocks. They rarely form more continuous ore bodies. Some phosphate minerals may be rich in REEs. In xenotime, Y ions are often replaced by lanthanides with an emphasis on HREEs (Alex et al., 1998; Masau et al., 2000; Sabourdy et al., 1997). Monazite quite locally even forms bodies of economical importance (Forster, 1998), and apatites (fluoro-phosphates) may also contain REEs (Bauluz et al., 2000; Braun et al., 1993). Other REE-containing minerals are fluorites (Buhn et al., 2002; Gramaccioli et al., 1999; Ivanova et al., 1996), and fluoro-carbonates often containing Ba or Ca (Hong et al., 1999b). Of commercial importance is bastnaesite. The carbonatite pyrochlore may be rich in LREEs (Chakhmouradian, 1996).

Many silicate minerals, e.g. those of the epidot group, especially allanites (Braun et al., 1993; Ercit, 2002) may contain REEs, especially LREEs (Pan et al., 1994). The Zr mineral zircon may be enriched in HREEs (Pan et al., 1994). Other REE minerals are gadolinite and cerite, in the latter with Ce present in the tetravalent state. On weathering, secondary REE

Table 1. Mean concentrations of REEs in the earth's crust and a few examples of total concentrations in surface soils. All concentrations in $\mu\text{g g}^{-1}$ dry weight

Element	Earth's crust (means) ^a	77 soils in Japan (means) ^b	44 soils in China (means) ^c	30 topsoils of Swedish forests (ranges) ^d
Yttrium (Y)	31	–	22	4.9 –17.6
Lanthanum (La)	35	18	44	5.5 –33.2
Cerium (Ce)	66	40	86	11 –68
Prasaeodymium (Pr)	9.1	4.5	–	1.3 – 7.5
Neodymium (Nd)	40	18	36	9.3 –53
Samarium (Sm)	7.0	3.7	8.4	0.9 – 4.6
Europium (Eu)	2.1	1.0	–	0.22– 0.83
Gadolinium (Gd)	6.1	3.7	–	1.0 – 4.8
Terbium (Tb)	1.2	0.6	–	0.15– 0.65
Dysprosium (Dy)	4.5	3.3	–	0.9 – 3.7
Holmium (Ho)	1.3	0.7	–	0.20– 0.74
Erbium (Er)	3.5	2.0	–	0.63– 2.2
Thulium (Tm)	0.5	0.3	–	0.09– 0.33
Ytterbium (Yb)	3.1	2.0	–	0.60– 2.3
Lutetium (Lu)	0.8	0.3	–	0.09– 0.34

^aGreenwood and Earnshaw (1984)

^bUpland fields, paddies, forests, and open areas throughout Japan (Yoshida et al., 1998)

^cSoils representing eight main soil types (Ran and Liu, 1999)

^dA-horizons of non-fertilized forest Cambisols in south Sweden (Tyler and Olsson, 2002)

minerals such as hydrous phosphates and oxides may be formed. This will be treated later.

REE concentrations in surface soils vary according to parent material properties, history and weathering state of the soil, contents of organic matter (OM) and clay minerals, etc. Topsoil concentrations may, therefore, differ considerably. A few examples of total concentrations of REEs in surface soils are given in Table 1. As many soil-forming processes cause greater leaching losses of REEs than of the average soil mass, topsoil total concentrations of REEs in non-fertilised soils are often lower than in the parent material. LREEs are usually more abundant in soils than HREEs, just as in the earth's crust. Least abundant in soils (disregarding the almost non-existing Pm) are usually Tm, Lu, Tb, and Ho, with occurrences comparable to those of Mo.

REEs occur in many different primary and secondary forms in soils, as treated later. The share of the total content present in soil solution is certainly small. The sum concentrations of REEs in soil solutions from non-fertilised Australian soils ranged from $< 0.007 \mu\text{M}$ to $0.64 \mu\text{M}$, with a maximum of $0.13 \mu\text{M}$ ($18 \mu\text{g L}^{-1}$) in La and $0.51 \mu\text{M}$ ($71 \mu\text{g L}^{-1}$) in Ce (Diatloff et al., 1996). The percentage share of the total REE concentration, which was found in the soil solu-

tion of 30 forest Cambisols (most of them acid and low in clay), varied proportionally to the ionic radius; thus inversely to the atomic mass, from a mean of 0.019% in La and 0.018% in Ce to 0.011% in Lu (Tyler and Olsson, 2002). As a comparison, the corresponding percentage for Na was 0.38, for Zn 0.22, for Ca 0.067, for Al 0.017, for Fe 0.008 and for Ti 0.005%.

Factors influencing adsorption, solubility, and vertical transport in soils

Weathering and transformations of REE minerals

Soil formation in most humid or semihumid regions of the world seems to involve losses of REEs from the upper horizons, also compared to the average soil mass. In Podzols of cold-temperate regions, the eluvial (E)-horizon may be strongly depleted of REEs, and the loss of LREEs greater than of HREEs (Minarik et al., 1998; Ohlander et al., 2000; Tyler, 2004a). Experimental weathering/leaching sequences of granite soil at low pH may start with allanite, continue with apatite and end with feldspar dissolution (Harlavan and Erel, 2002). Granite weathering studied in New South Wales included a primary dissolution of allanite and apatite, and the formation of secondary LREE

phosphates. In the most highly weathered soils the secondary phosphates had also disappeared and Ce(IV) oxide had accumulated (Taunton et al., 2000a, b).

Early stages of soil alteration may give rise to extreme variations in abundance of different REEs, the mobility being functions of ionic radius and charge in solution, pH, Eh, water fluxes, and the nature of secondary intermediate minerals formed under different conditions (Price et al., 1991). In tropical laterites, the upper ferruginous horizons are depleted in REEs, whereas deeper horizons have accumulation zones, at different depths for the LREEs. The HREEs are also depleted in the upper horizons, mainly controlled by the dissolution of xenotime of the parent gneiss (Braun et al., 1998). Allanite, apatite and epidote dissolve during the first stages of laterite weathering (Braun et al., 1993).

Weathering and leaching sequences are partly controlled by soil microorganisms and the production, dissolution, movement and precipitation of organic compounds. Various microorganisms have a high capacity of biosorption of REE ions, such as Gd^{3+} (Andres et al., 2000). Mineral surfaces of REE phosphates may be covered by bacteria and fungal hyphae and both plant roots and microorganisms are often good producers of oxalic acid/oxalate, a highly efficient solubiliser of phosphate minerals. Oxalate can dominate REE speciation in slightly acid groundwater (Schijf and Byrne, 2001), and this is probably often true of soil solutions as well. Other explanations for enhanced metal release may be siderophore complexation at the mineral surface and the subsequent release to the soil solution or uptake by the cell. In a study of the soil bacterium *Arthrobacter* sp. (Brantley et al., 2001) HREEs were markedly fractionated, the uptake increasing from Ho to Lu.

The great diversity of organic compounds produced by microorganisms in litter decomposition is of great importance to the behaviour of REEs in soils. Soil organic matter (OM) has many negatively charged groups per unit dry weight and, thereby, a high capacity to adsorb or chelate divalent and trivalent cations (Wu et al., 2001a). In soil systems rich in OM, the amounts and shares of dissolved organic carbon (DOC) are of great importance to the mobility of the REEs. DOC accounted for 46–74% of the statistical variability in REE concentrations of the soil solutions, when A-horizons of 30 Swedish Cambisols were compared (Tyler and Olsson, 2002). In column experiments on Eu^{3+} adsorption and elution from sand, Eu was detected in the eluate only when DOM was intro-

duced to the system (Nagao et al., 1998). On the other hand, highly stable and immobile OM constitutes an efficient barrier to mobility and transport (Nikonov et al., 1999).

DOC concentrations are also of great importance to the REE concentrations in wells (Dia et al., 2000), rivers (Land et al., 1999; Neal et al., 2000; Åström and Corin, 2003), and in groundwater (McCarthy et al., 1998). In a river water, filtered on acidification to pH 3, > 95% of the REEs were complexed with organic compounds and two types of sites were probably involved. One of them was scarce but had a very high affinity for the elements and was of major significance at low REE concentrations. The other site was more abundant, had a lower affinity, but was more important at high REE levels (Dupré et al., 1999). Two types of binding sites of REE ions (La^{3+} , Ce^{3+} , Sm^{3+}) have been identified in fulvic acids extracted from soils (Gu et al., 2001). It seems likely that carboxylic groups are involved, maybe in various ways.

The stability of REE (Tb, Yb, and Gd) complexes with humic substances may be particularly high at moderately alkaline conditions (Dong et al., 2002). At comparable DOC concentrations in soil solution and runoff waters, pH is of great importance to REE solubility. Acid stream water from sulphate soils, originating from the oxidation of sulphide minerals, may be orders of magnitude richer in REEs than less acid water from 'normal' soils (Åström, 2001; Åström and Corin, 2003). Experimental release of La, Ce, Gd, and Y from a soil increased gradually with a decrease in pH from 7.5 to 3.5 (Cao et al., 2001). Calcium carbonate mixed into to a Cambisol A-horizon sample, yielding a soil solution pH-gradient from 5.2 to 7.8, caused a distinct decrease in the soil solution concentrations of Ce and Eu, and a less distinct decrease in the La, Pr, Nd, Sm, Gd, Dy, Er, Tm, Yb, and Lu concentrations (Tyler and Olsson, 2001a).

The primary and secondary properties of soils are, nevertheless, major factors influencing retention and release of REEs. Such factors and conditions of importance are high contents of clay minerals (Dong et al., 2001; Minarik et al., 1998), presence of secondary REE minerals such as certain phosphates (Braun et al., 1998; Wu et al., 2001b; Åström, 2001), high concentrations of phosphate or sulphate in the soil solution (Diatloff et al., 1993; Gu et al., 2000), and amounts and lability of REE-containing Fe-Mn-hydroxy compounds (Cao et al., 2001). Fluctuations in soil moisture, both strong desiccation (Wang et al., 2001a) and water-logging, change speciation and solu-

bility of REEs. Where leaching losses or accumulation of REEs will take place in a soil is, therefore, often less predictable.

Vertical distribution of REEs in soil profiles

Both total concentrations and amounts and fractions of different extractability in well-defined soil profiles may indicate the behaviour of elements during soil formation. The origin and age of the soil, the climate conditions under which it has developed, the influence of human cultivation and other activities, etc. are of importance. Less disturbed (natural or seminatural) soils of humid climates gradually lose many elements by weathering and leaching processes, leaving rather few elements to become relatively accumulated in the upper parts of the soil profile. This may be quite evident also in soils, which have only developed during some thousand years, as is the case of Swedish Podzols under cool-temperate conditions. In Podzol developed from granitic till in the very cool climate of North Sweden, much of the REEs had been lost, especially from the E-horizon (Land et al., 1999). However, the different REEs had become fractionated during weathering, and the degree of depletion decreased with increasing atomic number of the elements. Also the B-horizon had lost much REEs, though to a lesser extent. The LREEs were enriched in organic and sulphide fractions compared to the HREEs (Land et al., 1999). A related study of Podzol from the same region (Ohlander et al., 2000) likewise demonstrated great losses from the E-horizon and there were also losses of Sm and Nd from the B-horizon.

A ca 14000 y old Haplic Podzol from the very southern, temperate parts of Sweden had lost 40–50% of its total Y, La, Ce, Dy, Gd, Nd, Pr, Sm, Tm, and Yb from the E+B-horizons (0–90 cm depth). The total concentrations of most of these elements increased gradually from the upper E-horizon to the lowest part of the B-horizon (Tyler, 2004a). When 0.2 M HCl-extractable concentrations were considered, there was an increase of almost two orders of magnitude in all these elements within a vertical distance of 20–30 cm, from the lower E- to the middle part of the B-horizon, but no further appreciable changes down the profile. In an apparently podzolised soil from the Indiana Dunes, USA (Esser et al., 1991), La, Ce, Nd, Sm, Eu and Tb, originating from Fe-rich chlorite, had been leached from the E- and B-horizons, whereas Yb and Lu, more associated with Fe-oxides, were relatively enriched. In a French soil developed from granite (Aubert et al.,

2001), HREE depletion was greatest in the uppermost parts of the profile due to dissolution of phosphate minerals. At greater depth, zircon seemed to be important in controlling especially HREE enrichment. An Australian granodiorite had accumulated REEs in materials with intermediate weathering, reaching concentrations 2–3 times higher than in the unweathered rock (Nesbitt and Markovics, 1997).

Tropical lateritic soils have been studied in Cameroon. The upper, Fe-rich horizons were depleted in REEs in a Laterite developed from gneissic parent material. The REEs had accumulated at different levels in the basal saprolite; Ce just below the ferruginous horizons as the tetravalent CeO₂ and in hydrous phosphates (Braun et al., 1998). Other REEs were accumulated at slightly lower level in the profile. The HREEs were also depleted in the upper horizons, losses mainly being controlled by the dissolution of xenotime. In a lateritic profile derived from syenite (Braun et al., 1993), most of the REEs had been lost from the Fe-rich upper horizons and REEs were fractionated and redistributed with the fluctuations of the groundwater table.

Concentrations and distribution in plants

Concentrations of most elements in the above-ground biomass of vascular plants are usually quite low. There are rather many reports on plant concentrations in the scientific literature, though it might often be difficult to discriminate between amounts possibly present as not easily washable surface dust contamination or REEs contained in plaque around roots. Concentrations reported vary several orders of magnitude. Therefore, it is difficult to communicate any 'typical' concentrations of REEs in organs of vascular plants. Some examples are given in Table 2.

In a study comprising a variety of plant materials from a forest in Germany (Markert and Li, 1991) concentrations of all REEs were reported (Table 2). The plant/soil ratios (transfer factors) were 0.04–0.09. Somewhat lower concentrations were generally found in the grass *Agrostis capillaris* grown in soil from the A-horizon of an acid Cambisol (Tyler and Olsson, 2001b). Very low concentrations are reported for commercially grown vegetables, e.g., cabbage (*Brassica oleracea* var. *capitata*), even if values are recalculated on a dry weight basis to make them comparable with other data (Bibak et al., 1999; Table 2).

Table 2. Some examples of REE concentrations in above-ground biomass of plants, $\mu\text{g g}^{-1}$ dry weight

	Forest plants, Germany (ranges) ^a		Grass leaves (<i>Agrostis capillaris</i>) ^b	Cabbage ^c		Moss carpets south Sweden (ranges) ^d	
				mean	max.		
Yttrium	0.15	-0.25	0.030	0.0032	0.010	0.120	-0.134
Lanthanum	0.15	-0.25	0.110	0.014	0.114	0.248	-0.285
Cerium	0.25	-0.55	0.150	0.028	0.081	0.466	-0.519
Prasaeodymium	0.03	-0.06	0.017	0.0017	0.010	0.053	-0.059
Neodymium	0.10	-0.25	0.091	0.0054	0.033	0.373	-0.431
Samarium	0.02	-0.04	0.011	0.0006	0.0054	0.035	-0.037
Europium	0.005	-0.015	0.026	-	0.020	0.0093	-0.0106
Gadolinium	0.030	-0.060	0.010	0.0017	0.015	0.036	-0.039
Terbium	0.005	-0.015	0.0011	0.0002	0.0010	0.0048	-0.0052
Dysprosium	0.025	-0.050	0.0051	0.0007	0.0075	0.0235	-0.0253
Holmium	0.005	-0.015	0.0010	0.00014	0.0015	0.0045	-0.0049
Erbium	0.015	-0.030	0.0031	0.0003	0.0032	0.0127	-0.0139
Thulium	0.0025	-0.005	0.0029	0.00006	0.0004	0.0016	-0.0019
Ytterbium	0.015	-0.030	0.0019	0.0002	0.0016	0.0107	-0.0120
Lutetium	0.0025	-0.005	0.0003	0.0001	0.0005	0.0015	-0.0017

^a*Betula*, *Pinus sylvestris*, *Vaccinium vitis-idaea*, *V. myrtillus*, *Deschampsia flexuosa*, *Polytrichum*, *Sphagnum* (Markert and Li, 1991)

^bLeaves of the grass *Agrostis capillaris* grown in the A-horizon of a non-fertilized Cambiosol (Tyler and Olsson, 2001b)

^c*Brassica oleracea* var. *capitata* from 10 production areas in Denmark; concentrations recalculated to dry weight assuming 91% water content in fresh samples (data from Bibak et al., 1999)

^dThe three youngest segments in five carpets of *Hylocomium splendens* sampled autumn 2002 in abandoned semi-natural pastures in Scania, south Sweden (Tyler, unpublished data).

On the contrary, several pteridophytes (ferns) are known to be particular accumulators of REEs. Strong positive concentration anomalies of La and Ce were reported in at least 9 species of the genera *Dryopteris*, *Asplenium*, *Adiantum* and *Dicranopteris* in a Japanese study comprising 96 species of ferns (Ozaki et al., 2000). Leaf mesophyll tissue contained 10–40 $\mu\text{g g}^{-1}$ dry weight of La and 3–30 $\mu\text{g g}^{-1}$ of Ce in the accumulators, compared to 0.003–2.7 and 0.076–3.6 $\mu\text{g g}^{-1}$, respectively, in the other species studied. When accumulators and non-accumulators were compared, the latter contained relatively much more Y than other REEs (Ozaki et al., 2002). *Dicranopteris dichotoma* from a rare-earth area in China had total REE concentrations of 0.68–3.36 $\mu\text{g g}^{-1}$, though with an overrepresentation of the LREEs in the fern biomass compared to soil and also compared to other vascular plants studied (Wang et al., 1997).

In mosses and lichens, which accumulate elements from rainfall, dust and stemflow, *Hypogymnia physodes* was characterised by Markert and Deli (1991) as an accumulator of lanthanide elements up to a factor of ten compared to vascular plant forest species. Compared to total concentrations in soils, however, these data are also rather low, as was the case with the moss

Hylocomium splendens from south Sweden (Table 2). Lichens and mosses from arctic Canada had REE concentrations of one to three orders of magnitude lower than those of the continental crust (Chiarenzelli et al., 2001). Yttrium and La in Norwegian mosses were considered to originate mainly from windblown mineral particles (Berg et al., 1995). It is, however, likely that REEs in mosses of more densely inhabited areas also reflect a contribution from less specific human sources of pollution.

The distribution of REEs among main organs of vascular plants differs considerably. However, roots have usually higher concentrations than other plant organs, and this is only partly due to the fact that it might be difficult to liberate soil-growing roots from soil particles. Roots of maize and mungbean grown in solution culture accumulated 20–150 times higher La concentrations than their shoots (Diatloff et al., 1995a) and similar root/shoot ratios were measured in *Agrostis capillaris* grown in soil cultures, also after vigorous rinsing of the roots (Tyler and Olsson, 2001b). Many studies (e.g., Cao et al., 2000a; Li et al., 1998; Wen et al., 2001; Xu et al., 2002) have shown decreasing REE concentrations in the order: root > leaf > stem > grain or fruit in a variety of

crops, such as maize, wheat, rice and paprika. Also in trees, e.g. *Citrus* (Wutscher and Perkins, 1993), the highest REE concentrations are usually found in the roots. REEs in seven tropical tree species were also mainly accumulated in their roots, though Ce tended to be concentrated in the bark (Nakanishi et al., 1997).

Ageing leaf tissues often increase their concentrations of little demanded or non-essential elements, e.g. during the process of wilting. This is not only due to the circumstance that such tissue loses organic compounds and the more demanded or soluble elements by resorption or leaching. Concentrations of several REEs (La, Ce, Sm, Eu, Tb, Yb, Lu) in successive needle age classes of spruce (*Picea abies*), carefully surface-washed, increased almost linearly with age, as did e.g. Si (Wytenbach et al., 1994). A gradual, time-dependent incorporation of aerosol particles into cuticle and epiderm deposited on the needle surface can, however, rarely be excluded, when age series of plant organs are compared.

Solutions containing REEs sprayed on crops may be translocated in the plant tissues, and there are even indications that movements of REEs may take place from leaf to root, as studied in maize (Wang et al., 2001b). Generally however, the uptake rate of REEs from soil to root is much higher than the translocation rate from root to shoot (Hu et al., 2002). Rates also seem to differ considerably both between species and REE elements. Rates of translocation in paprika were similar for LREEs and HREEs, but in leaves of rape (*Brassica juncea*) they were one to two orders of magnitude higher for LREEs than for HREEs (Cao et al., 2000). In the fern *Dicranopteris linearis* the relative abundance of HREEs in the above-ground parts was lower than in the roots (Wei et al., 2001).

Much of the REE in roots is certainly located in the cortex or in the ferric plaque precipitate of the root surface. However, a study of root tips of rice and pea demonstrated La and Yb to be located to the xylem, and Yb also to the endoderm (Ishikawa et al., 1996). REE-containing silica particles in the cortex of *Matteuccia* roots had a similar composition to that of silicate minerals in the soil (Fu et al., 2002). Authors therefore considered it most likely that silicate minerals were incorporated into the root cortex and that the particles did not originate from a chemical precipitation of dissolved elements. It was also suggested that such incorporation might be a source of plant nutrition (Fu et al., 2002). In a study of the same species (Fu et al., 1998), however, the authors suggested that REEs in the fern, though originating

from silicates in the soil, had previously been in a dissolved state. Another Japanese study of several vascular plants (Fu et al., 2001) also indicated that *Sasa nipponica* and *Vicia villosa* take up free REEs and Si, rather than these elements directly from soil silicates. Most REEs and Si in *Taxodium japonicum* and *Thea sinensis* originated from a soluble fraction in the soil. The absorption of added Gd^{3+} by root tissue of maize seedlings was mainly due to precipitation, which decreased if Gd was supplied in complexed form as $Gd(DTPA)^{2-}$ (Quiquampoix et al., 1990). Deposits containing Gd and P were detected in the extracellular space. However, soluble Gd was present both in the cytoplasm and in the vacuole of roots treated with Gd, and this showed that Gd can reach the symplast.

Adsorption of Eu^{3+} on root surfaces, especially root hairs, of *Eichhornia crassipes* most likely takes place on carboxylate groups at hydration of Eu^{3+} (Kelley et al., 1999). In another study of this species by the same group (Kelley et al., 2000) authors concluded that carboxylic acids were responsible for binding of the intracellular portion of Eu^{3+} in the roots. In bacteria (*Pseudomonas aeruginosa*) both carboxylic and phosphate groups seem active in binding Eu^{3+} and binding sites are mainly extracellular (Texier et al., 2000).

REE fertilisation and effects on plant growth

As with most other heavy elements in solution, elevated concentrations of REEs, i.e. much above those which organisms are accustomed to, may cause toxic reactions and negative effects on plants. However, much evidence has accumulated in support of the view that small amounts of REEs may favour biomass production and growth of vascular plants. Mixtures of REEs in fertilisers are nowadays widely used in Chinese agriculture to improve crop nutrition (Xu et al., 2002) and has been in common use for about 20 years (Pang et al., 2002). Research trials have been conducted since 1972 (Buckingham et al., 1999). Doses of REEs up to $0.23 \text{ kg ha}^{-1} \text{ y}^{-1}$ are currently applied (Xu et al., 2002). In most cases, however, both La, several lanthanides, and probably Y are contained in the mixtures, making it difficult to conclude whether any single element is of particular importance or whether the effects are less element-specific, which seems most likely.

REEs are usually applied annually in the form of seed dressing or as spray on the foliage of growing

crops. Direct application to soil has no or limited effects and is not recommended. The REEs are applied in soluble forms, mainly as nitrate, chloride, or complexed to a mix of amino acids. In 1995, REE fertilizer for agricultural production was predicted to cover over 16–20 mill. ha of land in China (Pang et al., 2002).

Problems with the rather extensive early Chinese literature reporting results of applied research on REE fertilisation are several. Much was mainly published in local journals and reports which are little available to the international public. Translations have often brought about ambiguities and lack of clarity, and details in experimental designs, methodologies, statistics, and results are often incompletely reported (Brown et al., 1990). The fertilisers used may also have contained other trace elements, such as Mo, which could have been responsible for some beneficial effects reported. Another problem of evaluating full-scale field trials is that N-compounds, such as urea, are usually sprayed together with the REEs, which makes it strictly possible only to evaluate effects of REEs together with effects of N (Xu et al., 2002). Moreover, reported dose–response relationships were almost lacking until quite recently (Wang et al., 2001). As with many other types of research, it must also be assumed that results showing negative or no effects, even if quite frequent, have been reported less often than results which demonstrate positive effects.

In the more recent literature positive, but also negative and no effects have been reported, differences possibly due to modes and rates of application, levels of other nutrients, crop type, etc. In a Chinese study on rice, La^{3+} promoted yields at 0.05–1.5 mg L^{-1} in nutrient solution, 0.05–0.75 mg L^{-1} increased root dry weight, and 0.05–6 mg L^{-1} increased the number of grains produced (Xie et al., 2002). In pot and field experiments, however, no influence on rice growth was measured in this study. In pot culture experiments on spinach, Ce^{3+} seemed to stimulate growth and increased the chlorophyll contents of the plants (Hong et al., 2002). In an Australian study (Diatloff et al., 1995c) 0.09 $\text{mg La}^{3+} \text{ L}^{-1}$ increased root growth of maize by 36%. A concentration of 0.026 mg L^{-1} increased mungbean root growth by 21%, but no effect of La on total dry matter yield was measurable in any of the species. From over 20 pot and 7 field experiments with La application to a number of crops and pastures it was concluded that, under certain conditions such as deficiency of water, La can have a positive effect on plant growth (Buckingham et al., 1999). Maize root elongation (but not dry matter pro-

duction) increased about two-fold at an application of Ce^{3+} , 0.088 mg L^{-1} (Diatloff et al., 1995b). Root growth of coconut palm in pot culture was favoured by La^{3+} , Pr^{3+} and Nd^{3+} at low rates of application (Wahid et al., 2000).

Negative effects on plants are, however, often reported at comparatively higher rates of REE application. Concentrations of 0.5–25 mg L^{-1} of La^{3+} or Ce^{3+} to a culture medium inhibited primary root elongation, decreased dry weight of roots and shoots and also the contents of Ca, Mg, K, Cu, and Zn in wheat seedlings. The degree of damage increased both with La and Ce concentration in the medium and with time of exposure (Hu et al., 2002). Neither foliar nor soil application of La and Ce to maize and mungbean in several experiments had any positive effect on shoot biomass production at rates recommended in Chinese agriculture (Diatloff et al., 1999). Higher rates caused foliar damage and reduced shoot dry weight, both if sprayed with La or Ce solutions or with a commercial REE fertiliser. In solution culture, La or Ce concentrations as low as 0.03 mg L^{-1} were toxic to mungbean. Maize was less sensitive, reductions being measured at > 0.7 mg L^{-1} of La or Ce. In another study of mungbean (Diatloff et al., 1995c) Ce^{3+} was more toxic than La^{3+} . Solution concentrations of 0.13 mg L^{-1} of Ce or 0.43 mg L^{-1} of La caused 50% reduction of root elongation. Maize was less sensitive than mungbean also in this study but the toxicity order was the opposite: 1.7 mg L^{-1} of Ce or 0.67 mg L^{-1} of La reduced root elongation by 50% at pH 5.5 in solution.

REEs in plant physiology and biochemistry

Cations of REEs have been utilised rather widely as aids in physiological research. Dy^{3+} and Eu^{3+} were used as probes for characterising Ca^{2+} binding sites in photosystem II of *Nicotiana tabacum* (Burda et al., 1995). Various lanthanide trivalent cations were utilised to probe the stacking arrangement of thylakoid membranes and the spatial distribution of protein complexes in photosystem I and II (Karukstis and Gruber, 1986; Mills and Hind, 1978). Gd^{3+} was utilised in studying Ca release channels in the endoplasmic reticulum of *Bryonia dioca*, which are effectively blocked by Gd^{3+} (Klusener et al., 1995). This ion was also used as an inhibitor of ion channels involved in xylem exudation in the symplast of roots (Schwenke and Wagner, 1992), as well as in several other studies on Ca channels in physiological research (Johannes et al.,

1992; Klusener et al., 1995). Other REE ions, e.g. La^{3+} , have also been used as blockers to test the importance of Ca channels in plants (Lewis and Spalding, 1998).

However, low concentrations of REE ions have been reported to promote physiological functions in plants. Replacement with REE ions of, e.g., Ca^{2+} in enzymes must not always inhibit its activity. Some lanthanide ions were able to replace endogenous Ca^{2+} of the hemoenzyme peroxidase in horseradish, retain the protein structure and its enzymatic activity. In contrast to other Ca^{2+} binding proteins, however, the affinity of this peroxidase for Ln^{3+} was lower than for Ca^{2+} , and Ln^{3+} was therefore easily replaced by Ca^{2+} (Morishima et al., 1986). Eu^{3+} was able to replace Ca^{2+} in calmodulin and still retain its ability to activate NAD-kinase from pea seedlings (Amann et al., 1992). Nd^{3+} , having an ion radius close to that of Ca^{2+} , seems to some extent able to replace Ca^{2+} in cell membranes of rape (*Brassica napus*) under conditions of Ca deficiency (Wei and Zhou, 2000). A combination of $0.5 \mu\text{M}$ Ce nitrate and $0.5 \mu\text{M}$ La nitrate was found to be effective in floral initiation of *Arabidopsis thaliana* (He and Loh, 2000). Low concentrations of LaCl_3 in the nutrient solution were reported to promote Mg-ATPase and the rate of phosphorylation in tobacco chloroplasts (Chen et al., 2001). The authors proposed that La^{3+} accelerated the photosynthetic light reactions at suitable concentration in vivo. LaCl_3 promoted the activation of ribulose biphosphate carboxylase (RuBPase) in tobacco (Chen et al., 2000). The activation effect of La^{3+} was greater than that of Gd^{3+} .

Other studies by Chinese physiologists indicated that REEs can increase the activities of photosystem II in the fern *Dicranopteris dichotoma* and bind to its chlorophyll (Hong et al., 1999a; 2001). Further studies of spinach actually suggested that Ce^{3+} could enter the chloroplast, bind easily to chlorophyll and might replace Mg^{2+} to form Ce-chlorophyll. Ce^{3+} obviously stimulated growth of spinach, increased its chlorophyll contents and photosynthetic rate.

These results on the effects of REE ions on plant photosynthesis partly contradict those of other related studies in this field which have demonstrated negative effects caused by these ions (e.g., Bakou et al., 1992; Bakou and Ghanotakis, 1993; Ghanotakis et al., 1985; Ono, 2000). The discrepancies might be at least partly due to different and often higher concentrations applied when studying inhibitory effects of REE ions,

but it cannot be excluded that differences in exposure and analytical techniques might contribute.

Several studies on interactions with REEs involved have been performed in microorganisms. Morrison and Cleland (1983) compared the relative effects of different REEs on yeast hexokinase, where LnATP complexes inhibit the reaction catalysed by this enzyme. The degree of inhibition increased with decreasing size of the REE ion and was much greater than with Mg^{2+} and Mn^{2+} . Terbium (Tb^{3+}) was a more potent inhibitor of yeast enolase occupying the same sites as those normally taken by Mg^{2+} , which thus were suggested to be carboxylic groups (Brewer et al., 1981).

The activities of nitrogen transforming soil bacteria were studied by incubation experiments in Chinese cultivated soils (Zhu et al., 2002). Nitrification in a red soil increased by 20% at $0.15 \text{ mg La g}^{-1}$ dry soil but decreased at higher rates of application. Ammonification rate was reduced between 0.06 and 1.2 mg La g^{-1} in well-drained soils, the variability depending on soil type, but in a paddy soil the amount of ammonium formed increased by 25 times at 0.9 mg La g^{-1} soil. Explanations for these great differences among soils are not apparent. However, incubation experiments with soils usually measure only the amounts of nitrate and ammonium remaining in the system at the end or at any other time during the test. Results are dependent on the delicate balance between formation and consumption of these nitrogen forms. The end product of the transformations which may accumulate in well-drained, circumneutral or slightly alkaline soil is usually nitrate, not ammonium, whereas the opposite may be true in water-logged or strongly acid soils.

Soil-plant relationships

Though some exceptions were reported above, concentrations of REEs in plants are usually very low compared to their total concentrations in soils. Transfer factors (TFs; the ratio concentration in plant/total concentration in their rhizosphere soil, both calculated on a dry weight basis) may give some idea about the relative availability of soil elements to plants. TFs of REEs in forest plants of NW Germany were as low as 0.04–0.09 (Markert and Li, 1991). These plants were at least partly rooted in a mineral soil substrate. Low TFs were also reported for vascular plants and fungal sporophores in Japanese forests (Yoshida and

Muramatsu, 1997). In a recent study (Tyler, 2004b) of ectomycorrhizal root tips of beech (*Fagus sylvatica*) in almost purely organic mor horizons of acid forest Podzol in south Sweden, the mean TFs of the light and intermediate REEs (Y, La, Ce to Tb) were 0.10–0.11, decreasing to 0.09 in Yb and Lu. The selectivity of REEs in the uptake by beech roots was thus quite small. A notable exception, however, was Eu, with a mean TF of 0.30 (range 0.27–0.34). This might indicate that Eu is at least partly taken up as a divalent cation, as TFs of Eu were more similar to those of other divalent than to trivalent cations in this study.

However, REE concentrations in plants are usually not closely related to variability of the total concentrations in their substrate soil. Total, as well as the sum of REEs extracted with a sequential extraction procedure, were poor indicators of REE uptake in rice and maize (Li et al., 1998), though a few individual elements correlated positively with their soluble+exchangeable soil fraction. The concentrations of La, Ce, Nd, Sm, Eu, Gd, Tb, Yb, and Lu in the leaves of six mainly woody plant species showed little or no agreement with concentrations in the soil or soil extracts (Wyttenbach et al., 1998). The concentration of REEs in 142 samples of fern leaves did not reflect the REE concentrations in their soils (Takada et al., 1998). The REE concentrations in *Vaccinium vitis-idaea* seemed largely independent of concentrations in the soil substrate (Markert, 1987).

The uptake and concentrations of REEs in plant tissues are, however, often better related to defined fractions of soil REEs. In a greenhouse study of winter wheat, 0.1 M HCl gave the best estimate of plant available REEs in the soil (Li et al., 2001). In a related study of the same crop (Zhang et al., 2000) a mixture of malic and citric acid was superior to five other extractants (HCl not used) to predict available REEs. Water-soluble, exchangeable, carbonate- or organic matter-bound REE fractions correlated with REE uptake in a pot experiment with alfalfa (Cao et al., 2000b), though differences among elements were observed. The uptake of La, Ce, Nd, Pr, and Yb was significantly related to exchangeable soil concentrations, uptake of La, Nd, and Yb to carbonate-bound concentrations, and uptake of La, Ce, Nd, Gd, and Dy to the organic matter-bound concentrations (Cao et al., 2000b). REEs in aqua regia extracts of *Citrus* soils correlated with concentrations in *Citrus* tree tissues (Wutscher and Perkins, 1993).

At some critical lower rate, depending on crop, soil type, etc., more REEs are often taken up in the tissues

of crops with soil application of REEs in fertilisers than from control soils. At 2 kg of total REEs applied ha^{-1} , the concentrations of La, Ce, Pr, Nd, and Gd increased in shoots of field-grown maize, whereas $> 10 \text{ kg ha}^{-1}$ were needed to increase concentrations in grains (Xu et al., 2002). A dose-dependent accumulation of REEs was measured in maize in a plot experiment at an early stage of plant development, but not at harvest, if $> 0.32 \text{ kg ha}^{-1}$ of REEs had been supplied to the soil (Wang et al., 2001b). Increases in root, leaf, and stem concentrations have also been measured in field-grown wheat, rice and vegetables following application of REE fertilisers (Wen et al., 2001).

Soil acidity may exert a profound influence on plant availability of mineral elements. A significant negative correlation was obtained between REE (especially La) concentration in roots and soil pH in a greenhouse study of wheat, both with and without fertilisers applied (Zhang and Shan, 2001). In another greenhouse study, relationships between soil solution chemistry and the uptake of 14 REEs were studied in *Agrostis capillaris* as influenced by soil acidity and application of CaCO_3 to an acid, unfertilised Cambisol (Tyler and Olsson, 2001b). The concentrations of all REEs, except Y, in the roots of the grass were inversely and linearly related ($P < 0.05$) to the pH of the soil solutions. In the shoots, only Eu was correlated to soil solution pH, but at $P < 0.001$ ($r = -0.88$). Inclusion of the soil solution concentration of the respective element in the statistical analysis increased the variability in shoot and root concentrations accounted for by soil solution properties only marginally; inclusion of DOC did not increase it at all.

Other soil factors than acidity and concentrations of the REEs are of possible importance to plant uptake of the elements, but seem to have been rather little studied. In solution culture containing 2 mg REEs L^{-1} (Y, La, and Gd), the uptake of La and Gd in wheat roots was inhibited following addition of sulphate, whereas the uptake of Y increased (Gu et al., 2000).

Environmental considerations

The use of REEs in various industries, especially their wide use in agriculture, has gradually been observed as a potential environmental problem in China (Hu et al., 2002). Most of the REEs applied as seed dressing or spray on growing crops will finally reach the soil. But the amounts applied annually are certainly

small compared to the total amounts present in the soil. Even if all REEs would end up and remain in the soil, thousands of years are needed to double the natural total soil pool at the recommended rates of application. It has to be considered, however, that REEs supplied as fertilisers are much more soluble and reactive than the average soil pool and therefore of more immediate environmental interest.

Moreover, the production and use of phosphate fertilisers may cause REE emissions both to the atmosphere and to the soil (Volokh et al., 1990). Superphosphate produced by sulphuric acid treatment of apatite from the Kola peninsula contains 2.6 mg REEs per g of the final product (Todorovsky et al., 1997). A normal P fertilisation of 300 kg ha⁻¹ y⁻¹ can thus contain more REEs as pollutant than intentionally applied in Chinese agriculture. In addition, REE-containing phosphogypsum, a main industrial waste of P fertiliser production, may also be used in agriculture, e.g., in Russia (Gorbunov et al., 1992).

Petroleum-cracking catalysts and their products in oil-fired power plants and oil refineries are other sources of REE pollution. The cracking products are produced from REE-rich minerals (bastnaesite and monazite). Marine sediments on the coast of California are clearly polluted by REEs from such activities (Olmez et al., 1991) and it is likely that this may be true for the surroundings of similar industry in other parts of the world.

Recent evidence indicates that a great many types of human activity, such as fossil-fuel combustion, waste incineration, metallurgic processes, etc., cause REE emissions to air, soil and water. Such dust emissions have, however, decreased considerably in Europe during the last decades due to improved emission control, closure of old-fashioned units and replacement by new technique. From measurements based on moss analysis it was demonstrated that the atmospheric deposition of all REEs over south Sweden decreased by a factor of 2.5–2.8 between 1972/75 and 1997/2000 (Rühling and Tyler, 2004). This was about the average decrease of all the 60 elements determined in this study.

Originating from the present, though limited knowledge, it seems unlikely that REE pollution may cause any large-scale severe environmental problems in the near future. The amounts and concentrations are usually too low compared to the ecotoxicity of these elements. It might, however, be possible that concentrations in soil or water may reach unfavourable levels quite locally around strong point sources. The large-

scale use of REEs in Chinese agriculture does not seem to be of great environmental concern at currently recommended application levels.

Discussion

Soil processes in humid climates normally cause a greater depletion of REEs than of the average soil constituents, resulting in lower concentrations per unit soil weight in topsoils than in subsoils and parent material. The A-(E)-horizons of both Laterites and Podzols are more depleted than the B-horizons. The E-horizon of some Podzols is almost lacking REEs in exchangeable or acid-leachable form. Secondary precipitates or minerals are formed along the REE transport down the soil profile and can sometimes give rise to locally higher concentrations of some REEs in deep horizons at particular stages of weathering.

Though fractionation processes of REEs have frequently been reported, both in soil and in plant systems, a general property common to most of these elements is that similarities dominate. When comparing concentrations in environmental materials, strong positive correlations are often measured between the different REE elements. A material with a higher concentration of La or Nd than otherwise related materials has very often a higher concentration of Gd, Yb, Lu, etc. This may be true of topsoils, plants and several other environmental materials. However, exceptions do exist. Fractionation of REEs, e.g., Ce and LREEs vs. HREEs in soils, may be caused by differences in weathering rates and the formation of more element-specific secondary minerals. REEs can also be fractionated in plant uptake from soils, or in the translocation process within the plant biomass. The transfer from soil to plant is usually low, and there is a tendency of decreasing TFs with increasing atomic mass (and decreasing ionic radius) of the REEs.

However, relationships between total concentrations in plants and in their substrate soils are usually weak, when variability in REE concentrations among soils and plants are compared. Soluble soil fractions can provide somewhat better predictions of plant uptake or concentrations, but other soil factors, such as pH or organic matter contents or properties, improve the predictions to some extent. Great species-specific differences in REE uptake also obstruct decisions of plant-available amounts of REEs in soils. Though still almost unknown, it is likely that interactions between soil, microorganisms and plant roots, such as mycor-

rhiza, may influence REE availability to plants. Exudation of low-molecular-weight organic acids, both by fungal hyphae and plant roots, promotes mineral weathering and dissolution by releasing acid and chelating compounds to the rhizosphere soil. It is well known that the dissolution of phosphate minerals is promoted by such processes and several such minerals contain REEs.

One problem when measuring and communicating element concentrations in plants is to define and decide what really belongs to the biomass and what should be removed from the biomass before digestion or extraction. Rain- or dry-deposited particles on the surface of leaves may enter the stomata or penetrate fissures in the cuticle and epiderm and gradually become part of the leaf biomass; possibly also utilised by the plant as a source of nutrient. This would be even more true of plant roots, around which compounds precipitate to gradually form a plaque containing hydroxy and organic complexes of Fe, Al and many other elements. To what extent constituents of this plaque gradually become available as a nutrient source is a matter of debate. As referred to earlier, mineral particles are also incorporated in the root tissue and its constituents may eventually become available to the plant. For these reasons, it is also a question of debate whether careful rinsing of fresh plant biomass in water only, or using detergents, which to a varying extent remove cuticle constituents on leaves or plaque on roots, should be used in sample preparation.

The great differences reported in plant concentrations of REEs, even between species of the same or related genera, such as in ferns, are far from unique. Differences amounting to several orders of magnitude have previously been demonstrated for many other scarce or rare elements, in vascular plants, fungi and other biological groups. If the element is considered essential or non-essential to life seems to be of less importance to its uptake and does not constitute a criterion of far-reaching accumulation in certain species at normal soil concentrations. Cadmium, traditionally considered non-essential to life, accumulates in fine roots of some vascular plants and in the biomass of several macrofungi. It may reach concentrations (by weight) of two–three orders of magnitude above those of their soil substrate. Selenium may be accumulated by species of *Astragalus* to concentrations, which are toxic to grazing animals. Plants on acid soils take up much Rb and Cs. Strongly inverse, pH-related Rb/K ratios characterise plants on acid to circumneutral soils (Drobner and Tyler, 1998) and such ratios are con-

served throughout the food-web in forest ecosystems (Folkeson et al., 1990). Sporophores of the fungus *Clitocybe odora* contained a thousand times more Cu per unit dry weight than species of *Gomphidius* in a similar site (Tyler, 1980) and concentrations of V in *Amanita muscaria* are two–three orders of magnitude higher than in other *Amanita* species. The list could be extended with several more examples.

Such differences are often explained by confusion by the uptake mechanisms of a non-essential element with a chemically related essential element. However, a great preference for an assumed non-essential element is often difficult to account for, e.g. in the case of Cd and Zn in some organisms, where TF values of Cd are much greater than of Zn. A real demand or positive function of the ‘wrong’ element has to be assumed before detailed studies might contradict such an assumption. The positive effects reported for LREEs or REE mixtures on plant quality, growth rate or productivity seem to be partly crop-specific and probably dependent on nutrient status of the particular crop. As seems to be the case with Rb *versus* K, REE ions with an effective radius close to that of Ca^{2+} might partly be able to replace or interact positively with Ca in various physiological functions, though Ca is one of the most abundant cations in soils, even compared to plant demands. Other positive interactions or partial substitutions are possible as well, but the problem is, most likely, more complicated and really deserves further studies.

We have to accept a circumstance that the boundary between essential and non-essential elements is not as distinct as was considered in traditional plant physiology and ecophysiology. There is a less well-defined and maybe large intermediate group of elements, such as the REEs, which can be favourable, though not absolutely essential to life, under some conditions, at certain concentrations or amounts, in some chemical form(s) and at least to some species of organisms, including vascular plants. Essentiality of elements has actually been studied in a quite limited number of plant species compared to the enormous total diversity of the plant kingdom. Demand for a particular element is considered to need a long evolutionary development. Vascular plants have developed during a large part of the geological history of the earth; pteridophytes during hundreds of million years and angiosperms, nowadays comprising at least 250 000 species, appeared more than one hundred million years ago. There seems to have been plenty of time

available also for the development of physiological diversity.

References

- Alex P, Suri A K and Gupta C K 1998 Processing of xenotime concentrate. *Hydrometallurgy* 50, 331–338.
- Amann B T, Mulqueen P and Horrocks W D 1992 A continuous spectrophotometric assay for the activation of plant NAD kinase by calmodulin, calcium(II), and europium(III) ions. *J. Biochem. Biophys. Meth.* 25, 207–217.
- Andres Y, Thouand G, Boualam M and Mergeay M 2000 Factors influencing the biosorption of gadolinium by micro-organisms and its mobilisation from sand. *Appl. Microbiol. Biot.* 54, 262–267.
- Åström M 2001 Abundance and fractionation patterns of rare earth elements in streams affected by acid sulphate soils. *Chem. Geol.* 175, 249–258.
- Åström M and Corin N 2003 Distribution of rare earth elements in anionic, cationic and particulate fractions in boreal humus-rich streams affected by acid sulphate soils. *Water Res.* 37, 273–280.
- Aubert D, Stille P and Probst A 2001 REE fractionation during granite weathering and removal by waters and suspended loads: Sr and Nd isotopic evidence. *Geochim. Cosmochim. Acta.* 65, 387–406.
- Bakou A, Buser C, Dandulakis G, Brudvig G and Ghanotakis DF 1992 Calcium binding sites of photosystem II as probed by lanthanides. *Biochim. Biophys. Acta* 1099, 131–136.
- Bakou A and Ghanotakis D F 1993 Substitution of lanthanides at the calcium site(s) in Photosystem II affects electron transport from tyrosine Z to P680 positive. *Biochim. Biophys. Acta* 1141, 303–308.
- Bauluz B, Mayayo M J, Fernandez-Nieto C and Lopez J M G 2000 Geochemistry of Precambrian and Paleozoic siliciclastic rocks from the Iberian Range (NE Spain): implications for source-area weathering, sorting, provenance, and tectonic setting. *Chem. Geol.* 168, 135–150.
- Berg T, Royset O, Steinnes E and Vadset M 1995 Atmospheric trace-element deposition – principal component analysis of ICP-MS data from moss samples. *Environ. Pollut.* 88, 67–77.
- Bibak A, Stürup S, Knudsen L and Gundersen V 1999 Concentrations of 63 elements in cabbage and sprouts in Denmark. *Commun. Soil Sci. Plan* 30, 2409–2418.
- Brantley S L, Liermann L, Bau M and Wu S 2001 Uptake of trace elements and rare earth elements from hornblende by a soil bacterium. *Geomicrobiol. J.* 18, 37–61.
- Braun J J, Pagel M, Herbillon A and Rosin C 1993 Mobilization and redistribution of REEs and thorium in a syenitic lateritic profile – a mass-balance study. *Geochim. Cosmochim. Acta* 57, 4419–4434.
- Braun J J, Viers J, Dupre B, Polve M, Ndam J and Muller JP 1998 Solid/liquid REE fractionation in the lateritic system of Goyoum, east Cameroon: The implication for the present dynamics of the soil covers of the humid tropical regions. *Geochim. Cosmochim. Acta* 62, 273–299.
- Brewer J M, Carreira L A, Irwin R M and Elliott J I 1981 Binding of terbium III to yeast enolase. *J. Inorg. Biochem.* 14, 33–44.
- Brown P H, Rathjen A H, Graham R D and Tribe D E 1990 Rare earth elements in biological systems. *In Handbook on the Physics and Chemistry of Rare Earths* (eds. Gschneidner Jr and Eyring L) 13, 423–453. Elsevier Science Publishers, Amsterdam.
- Buckingham S, Maheswaran J, Meehan B and Peverill K 1999 The role of applications of rare earth elements in enhancement of crop and pasture production. *Rare Earths '98, Mater. Sci. Forum* 315, 339–347.
- Buhn B, Rankin A H, Schneider J and Dulski P 2002 The nature of orthomagmatic, carbonatitic fluids precipitating REE, Sr-rich fluorite: fluid-inclusion evidence from the Okorusu fluorite deposit, Namibia. *Chem. Geol.* 186, 75–98.
- Burda K, Strzalka K and Schmid GH 1995 Europium- and dysprosium-ions as probes for the study of calcium binding sites in photosystem II. *Z. Naturforsch. C* 50, 220–230.
- Cao X D, Chen Y, Gu Z M and Wang X R 2000a Determination of trace rare earth elements in plant and soil samples by inductively coupled plasma-mass spectrometry. *Int. J. Environ. An. Ch* 76, 295–309.
- Cao X D, Wang X R and Zhao G W 2000b Assessment of the bioavailability of rare earth elements in soils by chemical fractionation and multiple regression analysis. *Chemosphere* 40, 23–28.
- Cao X D, Chen Y, Wang X R and Deng X H 2001 Effects of redox potential and pH value on the release of rare earth elements from soil. *Chemosphere* 44, 655–661.
- Chakhmouradian A R 1996 On the development of niobium and rare earth minerals in the monticellite–calcite carbonatite of the Oka complex, Quebec. *Can. Mineral.* 34, 479–484.
- Chen W J, Gu Y H, Zhao G W, Tao Y, Luo, J P and Hu T D 2000 Effects of rare earth ions on activity of RuBpCase in tobacco. *Plant Sci.* 152, 145–151.
- Chen W J, Tao Y, Gu Y H and Zhao G W 2001 Effect of lanthanide chloride on photosynthesis and dry matter accumulation in tobacco seedlings. *Biol. Trace Elem. Res.* 79, 169–176.
- Chiarenzelli J, Aspler L, Dunn C, Cousens B, Ozarko D and Powis K 2001 Multi-element and rare earth element composition of lichens, mosses and vascular plants from the Central Barrenland, Nunavut, Canada. *Appl. Geochem.* 16, 245–270.
- Dia A, Gruau G, Olivie-Lauquet G, Riou C, Molénat J and Curmi P 2000 The distribution of rare earth elements in groundwaters: Assessing the role of source-rock composition, redox changes and colloidal particles. *Geochim. Cosmochim. Acta* 64, 4131–4151.
- Diatloff E, Asher C J and Smith F W 1993 Use of geochem-PC to predict rare-earth element (REE) species in nutrient solutions. *Plant Soil* 156, 251–254.
- Diatloff E, Smith F W and Asher C J 1995a Rare-earth elements and plant growth. 2. Responses of corn and mungbean to low concentrations of lanthanum in dilute, continuously flowing nutrient solutions. *J. Plant Nutr.* 18, 1977–1989.
- Diatloff E, Smith F W and Asher C J 1995b Rare-earth elements and plant growth. 3. Responses of corn and mungbean to low concentrations of cerium in dilute, continuously flowing nutrient solutions. *J. Plant Nutr.* 18, 1991–2003.
- Diatloff E, Smith F W and Asher C J 1995c Rare-earth elements and plant growth. 1. Effects of lanthanum and cerium on root elongation of corn and mungbean. *J. Plant Nutr.* 18, 1963–1976.
- Diatloff E, Asher C J and Smith F W 1996 Concentrations of rare earth elements in some Australian soils. *Aust. J. Soil Res.* 34, 735–747.
- Diatloff E, Asher C J and Smith FW 1999 The effects of rare earth elements on the growth and nutrition of plants. *Rare Earths '98, Mater. Sci. Forum* 315, 354–360.
- Dong M W, Li W J and Tao Z Y 2002 Use of the ion exchange method for the determination of stability constants of trivalent metal complexes with humic and fulvic acids II. Tb^{3+} , Yb^{3+} and

- Gd³⁺ complexes in weakly alkaline conditions. Appl. Radiat. Isotopes 56, 967–974.
- Dong W M, Wang X K, Bian X Y, Wang A X, Du J Z and Tao Z Y 2001 Comparative study on sorption/desorption of radioeuropium on alumina, bentonite and red earth: effects of pH, ionic strength, fulvic acid, and iron oxides in red earth. Appl. Radiat. Isotopes 54, 603–610.
- Drobner U and Tyler G 1998 Conditions controlling relative uptake of potassium and rubidium by plants from soils. Plant Soil 201, 285–293.
- Dupré B, Viers J, Dandurand J L, Polve M, Benezeth P, Vervier P and Braun J J 1999 Major and trace elements associated with colloids in organic-rich river waters: ultrafiltration of natural and spiked solutions. Chem. Geol. 160, 63–80.
- Ercit T S 2002 The mess that is 'allanite'. Can. Mineral. 40, 1411–1419.
- Esser K B, Bockheim, J G and Helmke P A 1991 Trace element distribution in soils formed in the Indiana Dunes USA. Soil Sci. 152, 340–350.
- Folkesson L, Nyholm N E I and Tyler G 1990 Influence of acidity and other soil properties on metal concentrations in forest plants and animals. Sci. Total Environ. 96, 211–233.
- Forster H J 1998 The chemical composition of REE-Y-Th-U-rich accessory minerals in peraluminous granites of the Erzgebirge–Fichtelgebirge region, Germany. Part II: Xenotime. Am. Mineral. 83, 1302–1315.
- Fu F F, Akagi T and Shinotsuka K 1998 Distribution pattern of rare earth elements in fern – Implication for intake of fresh silicate particles by plants. Biol. Trace Elem. Res. 64, 13–26.
- Fu F F, Akagi T, Yabuki S and Iwaki M 2001 The variation of REE (rare earth elements) pattern in soil-grown plants: a new proxy for the source of rare earth elements and silicon in plants. Plant Soil 235, 53–64.
- Fu F F, Akagi T and Yabuki S 2002 Origin of silica particles found in the cortex of Matteuccia roots. Soil Sci. Soc. Am. J. 66, 1265–1271.
- Ghanotakis D F, Babcock G T and Yocum C F 1985 Structure of the oxygen-evolving complex of photosystem II Calcium and lanthanum compete for sites on the oxidizing side of photosystem II which control the binding of water-soluble polypeptides and regulate the activity of the manganese complex. Biochim. Biophys. Acta 809, 173–180.
- Gorbunov A V, Frontasyeva M V, Gundorina S F, Onischenko T L, Maksjuta B B and Pal C S 1992 Effect of agricultural use of phosphogypsum on trace elements in soils and vegetation. Sci. Total Environ. 122, 337–346.
- Gramaccioli C M, Diella V and Demartin F 1999 The role of fluoride complexes in REE geochemistry and the importance of 4f electrons: some examples in minerals. Eur. J. Mineral. 11, 983–992.
- Greenwood N N and Earnshaw A 1984 Chemistry of the elements. Pergamon Press, Oxford.
- Gu Z M, Wang X R, Cheng J, Wang L S and Dai L M 2000 Effects of sulfate on speciation and bioavailability of rare earth elements in nutrient solution. Chem. Spec. Bioavailab. 12, 53–58.
- Gu Z M, Wang X R, Gu X Y, Cheng J, Wang L S, Dai L M and Cao M 2001 Determination of stability constants for rare earth elements and fulvic acids extracted from different soils. Talanta 53, 1163–1170.
- Harlavan Y and Erel Y 2002 The release of Pb and REE from granitoids by the dissolution of accessory phases. Geochim. Cosmochim. Acta 66, 837–848.
- He Y W and Loh C S 2000 Cerium and lanthanum promote floral initiation and reproductive growth of *Arabidopsis thaliana*. Plant Sci. 159, 117–124.
- Hong F S, Wei Z G, Tao Y, Wan S K, Yang Y T, Cao X D and Zhao G W 1999a Distribution of rare earth elements and structure characterization of chlorophyll-lanthanum in a natural plant fern *Dicranopteris dichotoma*. Acta Bot. Sin. 41, 851–854.
- Hong F S, Wei Z G and Zhao G W 2001 Studies of bound form on rare earths in a natural plant fern *Dicranopteris dichotoma* by spectroscopy. Chem. J. Chinese U 22, 1790–1794.
- Hong F S, Wang L, Meng X X, Wei Z and Zhao G W 2002 The effect of cerium (III) on the chlorophyll formation in spinach. Biol. Trace. Elem. Res. 89, 263–276.
- Hong W X, He S Y, Huang S H, Wang Y, Hou H Q and Zhu X K 1999b A Raman spectral studies of rare-earth (REE) fluoro-carbonate minerals. Spectrosc. Spect. Anal. 19, 546–549.
- Hu X, Ding Z H, Chen Y J, Wang X R and Dai L M 2002 Bioaccumulation of lanthanum and cerium and their effects on the growth of wheat (*Triticum aestivum* L.) seedlings. Chemosphere 48, 621–629.
- Ishikawa S, Wagatsuma T and Ikarashi T 1996 Comparative toxicity of Al³⁺, Yb³⁺, and La³⁺ to root tip cells differing in tolerance to high Al³⁺ in terms of ionic potentials of dehydrated trivalent cations. Soil Sci. Plant Nutr. 42, 613–625.
- Ivanova G F, Cherkasova E V and Naumov V B 1996 Mineral composition and formation conditions of the Piatang tin-tungsten deposit, south China. Geol. Ore. Deposit. 38, 137–150.
- Johannes E, Brosnan J M and Sanders D 1992 Calcium channels in the vacuolar membrane of plants – multiple pathways for intracellular calcium mobilization. Philos. T. Roy. Soc. B 338, 105–112.
- Karukstis K K and Gruber S M 1986 Effect of trivalent lanthanide cations on chlorophyll fluorescence and thylakoid membrane stacking. Biochim. Biophys. Acta 851, 322–326.
- Kelley C, Curtis A J, Uno, J K and Berman C L 2000 Spectroscopic studies of the interaction of Eu(III) with roots of water hyacinth. Water Air Soil Poll. 119, 171–176.
- Kelley C, Mielke R E, Dimaquibo D, Curtis A J and Dewitt J G 1999 Adsorption of Eu(III) onto roots of water hyacinth. Environ. Sci. Technol. 33, 1439–1443.
- Klusener B, Boheim G, Liss H, Engelberth J and Weiler E W 1995 Gadolinium-sensitive, voltage-dependent calcium-release channels in the endoplasmic reticulum of a higher-plant mechanoreceptor organ. Embo J. 14, 2708–2714.
- Land M, Ohlander B, Ingri J and Thunberg J 1999 Solid speciation and fractionation of rare earth elements in a spodosol profile from northern Sweden as revealed by sequential extraction. Chem. Geol. 160, 121–138.
- Lewis B D and Spalding E P 1998 Nonselective block by La³⁺ of *Arabidopsis* ion channels involved in signal transduction. J. Membrane Biol. 162, 81–90.
- Li F L, Shan X Q, Zhang T H and Zhang S Z 1998 Evaluation of plant availability of rare earth elements in soils by chemical fractionation and multiple regression analysis. Environ. Pollut. 102, 269–277.
- Li F L, Shan X Q and Zhang S Z 2001 Evaluation of single extractants for assessing plant availability of rare earth elements in soils. Commun. Soil Sci. Plan. 32, 2577–2587.
- Markert B 1987 The pattern of distribution of lanthanide elements in soils and plants. Phytochemistry 26, 3167–3170.
- Markert B and Deli Z 1991 Inorganic chemical investigations in the forest biosphere reserve near Kalinin, USSR. 2. The distribution of lanthanide elements in the vegetation cover. Vegetatio 97, 57–62.

- Markert B and Li ZD 1991 Natural background concentrations of rare-earth elements in a forest ecosystem. *Sci. Total Environ.* 103, 27–35.
- Masau M, Cerny P and Chapman R 2000 Dysprosian xenotime-(Y) from the Annie Claim no.3 granitic pegmatite, southeastern Manitoba, Canada: Evidence of the tetrad effect? *Can. Mineral* 38, 899–905.
- McCarthy J F, Sanford W E and Stafford P L 1998 Lanthanide field tracers demonstrate enhanced transport of transuranic radionuclides by natural organic matter. *Environ. Sci. Technol.* 32, 3901–3906.
- Mills J D and Hind G 1978 Use of the fluorescent lanthanide terbium ion as a probe for cation binding sites associated with isolated chloroplast thylakoid membranes. *Photochem. Photobiol.* 28, 67–74.
- Minarik L, Zigova A, Bendl J, Skrivan P and St'astny M 1998 The behaviour of rare earth elements and Y during the rock weathering and soil formation in the Ricany granite massif, Central Bohemia. *Sci. Total Environ.* 215, 101–111.
- Morishima I, Kurono M and Shiro Y 1986 Presence of endogenous calcium ion in horseradish peroxidase. Elucidation of metal-binding site by substitutions of divalent and lanthanide ions for calcium and use of metal-induced NMR proton and calcium-113 resonances. *J. Biol. Chem.* 261, 9391–9399.
- Morrison J F and Cleland W W 1983 Lanthanide ATP complexes determination of their dissociation constants and mechanism of action as inhibitors of yeast hexo kinase. *Biochemistry-US* 22, 5507–5513.
- Nagao S, Rao R R, Killely R W D and Young J L 1998 Migration behaviour of Eu(III) in sandy soil in the presence of dissolved organic materials. *Radiochim. Acta* 82, 205–211.
- Nakanishi T M, Takahashi J and Yagi H 1997 Rare earth element, Al, and Sc partition between soil and Caatinga wood grown in north-east Brazil by instrumental neutron activation analysis. *Biol. Trace Elem. Res.* 60, 163–174.
- NE1993 Nationalencyklopedin (National Encyclopedia of Sweden) vol.12. Höganäs, Sweden.
- Neal C, Jarvie H P, Whitton B A and Gemmill J 2000 The water quality of the River Wear, north-east England. *Sci. Total Environ.* 251/252, 153–172.
- Nesbitt H W and Markovics G 1997 Weathering of granodioritic crust, long-term storage of elements in weathering profiles, and petrogenesis of siliciclastic sediments. *Geochim. Cosmochim. Acta* 61, 1653–1670.
- Nikonov V V, Lukina N V and Frontasyeva M V 1999 Trace elements in Al-Fe-humus podzolic soils subjected to aerial pollution from the copper-nickel production industry in conditions of varying lithogenic background. *Eurasian. Soil Sci.* 32, 338–349.
- Ohlander B, Ingri J, Land M and Schönberg H 2000 Change of Sm-Nd isotope composition during weathering of till. *Geochim. Cosmochim. Acta* 64, 813–820.
- Olmez I, Sholkovitz E R, Hermann D and Eganhouse R P 1991 Rare-earth elements in sediments off southern California – a new anthropogenic indicator. *Environ. Sci. Technol.* 25, 310–316.
- Ono T 2000 Effects of lanthanide substitution at Ca²⁺-site on the properties of the oxygen evolving center of Photosystem II. *J. Inorg. Biochem.* 82, 85–91.
- Ozaki T, Ambe S, Enomoto S, Minai Y, Yoshida S and Makide Y 2002 Multitracer study of the uptake mechanism of yttrium and rare earth elements by autumn fern. *Radiochim. Acta* 90, 303–307.
- Ozaki T, Enomoto S, Minai Y, Ambe S and Makide Y 2000 A survey of trace elements in pteridophytes. *Biol. Trace Elem. Res.* 74, 259–273.
- Pan Y M, Fleet M E and Barnett R L 1994 Rare-earth mineralogy and geochemistry of the Mattagami lake volcanogenic massive sulfide deposit, Quebec. *Can. Mineral.* 32, 133–147.
- Pang X, Li DC and Peng A 2002 Application of rare-earth elements in the agriculture of China and its environmental behavior in soil. *Environ. Sci. Pollut. R* 9, 143–148.
- Price R C, Gray C M, Wilson R E, Frey F A and Taylor S R 1991 The effects of weathering on rare-earth element, Y and Ba abundances in Tertiary basalts from southeastern Australia. *Chem. Geol.* 93, 245–265.
- Quiquampoix H, Ratcliffe R G, Ratkovic S and Vucinic Z 1990 Proton and phosphorus-31 NMR investigation of gadolinium uptake in maize roots. *J. Inorg. Biochem.* 38, 265–276.
- Ran Y and Liu Z 1999 Contents and distribution of rare earth elements in main types of soil in China. *J. Rare Earth* 17, 213–217.
- Rühling Å and Tyler G 2004 Changes in the atmospheric deposition of sixty elements between 1975 and 2000 in south Sweden, as measured by moss analysis. *Environ. Pollut.* (accepted).
- Sabourdy G, Sagon JP and Pastier P 1997 The chemical composition of xenotime from the Limousin region, Massif-Central, France. *Can. Mineral.* 35, 937–946.
- Schijf J and Byrne RH 2001 Stability constants for mono- and dioxalato-complexes of Y and the REE, potentially important species in groundwaters and surface freshwaters. *Geochim. Cosmochim. Acta* 65, 1037–1046.
- Schwenke H and Wagner E 1992 A new concept of root exudation. *Plant Cell Environ.* 15, 289–299.
- Takada J, Sumino T, Tanaka Y, Nishimura K and Akaboshi M 1998 Correlation between terbium and the other rare earth element contents in fern leaves. *J. Radioanal. Nucl. Ch* 236, 35–38.
- Taunton A E, Welch S A and Banfield J F 2000a Microbial controls on phosphate and lanthanide distributions during granite weathering and soil formation. *Chem. Geol.* 169, 371–382.
- Taunton A E, Welch S A and Banfield J F 2000b Geomicrobiological controls on light rare earth element, Y and Ba distributions during granite weathering and soil formation. *J. Alloy Compd.* 303, 30–36.
- Texier A C, Andres Y, Illemassene M and Le Cloirec P 2000 Characterization of lanthanide ions binding sites in the cell wall of *Pseudomonas aeruginosa*. *Environ. Sci. Technol.* 34, 610–615.
- Todorovsky D S, Minkova N L and Bakalova D P 1997 Effect of the application of superphosphate on rare earths' content in the soil. *Sci. Total Environ.* 203, 13–16.
- Tyler G 1980 Metals in sporophores of basidiomycetes. *T. Brit. Mycol. Soc.* 74, 41–49.
- Tyler G 2004a Vertical distribution of major, minor, and rare elements in a Haplic Podzol. *Geoderma* 119, 277–290.
- Tyler, G 2004b Ionic charge, radius, and potential control root/soil concentration ratios of fifty cationic elements in the organic horizon of a beech (*Fagus sylvatica*) forest Podzol. *Sci. Total Environ.* (accepted).
- Tyler, G and Olsson T 2001a Concentrations of 60 elements in the soil solution as related to the soil acidity. *Eur. J. Soil Sci.* 52, 151–165.
- Tyler, G and Olsson T 2001b Plant uptake of major and minor elements as influenced by soil acidity and liming. *Plant Soil* 230, 307–321.
- Tyler, G and Olsson T 2002 Conditions related to solubility of rare and minor elements in forest soils. *J. Plant Nutr. Soil Sci.* 165, 594–601.
- Volokh A A, Gorbunov A V, Gundorina S F, Revich B A, Frontasyeva M V and Pal CS 1990 Phosphorus fertilizer pro-

- duction as a source of rare-earth elements pollution of the environment. *Sci. Total Environ.* 95, 141–148.
- Wahid P A, Valiathan M S, Kamalam N V, Eapen J T, Vijayalakshmi S, Prabhu R K and Mahalingam T R 2000 Effect of rare earth elements on growth and nutrition of coconut palm and root competition for these elements between the palm and *Calotropis gigantea*. *J. Plant Nutr.* 23, 329–338.
- Wang Y Q, Sun J X, Chen H M and Guo F Q 1997 Determination of the contents and distribution characteristics of REE in natural plants by NAA. *J. Radioanal Nucl. Ch* 219, 99–103.
- Wang Z W, Shan X Q and Zhang S Z 2001a Comparison of speciation and bioavailability of rare earth elements between wet rhizosphere soil and air-dried bulk soil. *Anal. Chim. Acta* 441, 147–156.
- Wang Z J, Liu D F, Lu P and Wang C X 2001b Accumulation of rare earth elements in corn after agricultural application. *J. Environ. Qual.* 30, 37–45.
- Wei Y Z and Zhou X B 2000 Effect of neodymium on physiological activities in oilseed rape during calcium starvation. *J. Rare Earth* 18, 57–61.
- Wei Z G, Yin M, Zhang X, Hong F S, Li B, Tao Y, Zhao G W and Yan C H 2001 Rare earth elements in naturally grown fern *Dicranopteris linearis* in relation to their variation in soils in South-Jiangxi region (Southern China). *Environ. Pollut.* 114, 345–355.
- Wen B, Yuan D A, Shan X Q, Li F L and Zhang S Z 2001 The influence of rare earth element fertilizer application on the distribution and bioaccumulation of rare earth elements in plants under field conditions. *Chem. Spec. Bioavailab.* 13, 39–48.
- Wu Z H, Luo J, Guo H Y, Wang X R and Yang C S 2001a Adsorption isotherms of lanthanum to soil constituents and effects of pH, EDTA and fulvic acid on adsorption of lanthanum onto goethite and humic acid. *Chem. Spec. Bioavailab.* 13, 75–81.
- Wu Z H, Wang X R, Zhang Y F, Dai L M and Chen Y J 2001b Effects of apatite and calcium oxyphosphate on speciation and bioavailability of exogenous rare earth elements in the soil–plant system. *Chem. Spec. Bioavailab.* 13, 49–56.
- Wutscher H K and Perkins R E 1993 Acid extractable rare-earth elements in Florida Citrus soils and trees. *Commun. Soil Sci. Plan.* 24, 2059–2068.
- Wytenbach A, Furrer V, Schleppe P and Tobler L 1998 Rare earth elements in soil and in soil-grown plants. *Plant Soil* 199, 267–273.
- Wytenbach A, Schleppe P, Bucher J, Furrer V and Tobler L 1994 The accumulation of the rare-earth elements and of scandium in successive needle age classes of Norway spruce. *Biol. Trace Elem. Res.* 41, 13–29.
- Xie Z B, Zhu J G, Chu H Y, Zhang Y L, Zeng Q, Ma H L and Cao Z H 2002 Effect of lanthanum on rice production, nutrient uptake, and distribution. *J. Plant Nutr.* 25, 2315–2331.
- Xu X K, Zhu W Z, Wang Z J and Witkamp G J 2002 Distribution of rare earths and heavy metals in field-grown maize after application of rare earth-containing fertilizer. *Sci. Total Environ.* 293, 97–105.
- Yoshida S and Muramatsu Y 1997 Determination of major and trace elements in mushroom, plant and soil samples collected from Japanese forests. *Int. J. Environ. An. Ch* 67, 49–58.
- Yoshida S, Maramutsu Y, Tagami K and Uchida S 1998 Concentrations of lanthanide elements, Th, and U in 77 Japanese surface soils. *Environ. Int.* 24, 275–286.
- Zhang S Z, Shan X Q and Li F L 2000 Low-molecular-weight-organic-acids as extractant to predict plant bioavailability of rare earth elements. *Int. J. Environ. An. Ch* 76, 283–294.
- Zhang S Z and Shan X Q 2001 Speciation of rare earth elements in soil and accumulation by wheat with rare earth fertilizer application. *Environ. Pollut.* 112, 395–405.
- Zhu J G, Chu H Y, Xie Z B and Yagi K 2002 Effects of lanthanum on nitrification and ammonification in three Chinese soils. *Nutr. Cycl. Agroecosys.* 63, 309–314.

Section editor: H. Lambers