We are IntechOpen,
the world's leading publisher of
Open Access books
Built by scientists, for scientists

6,900
Open access books available

186,000
International authors and editors

200M
Downloads

154
Countries delivered to

Our authors are among the

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities

CLARIVATE ANALYTICS
BOOK CITATION INDEX
INDEXED

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

Lanthanide Soil Chemistry and Its Importance in Understanding Soil Pathways: Mobility, Plant Uptake, and Soil Health

Michael Aide

Additional information is available at the end of the chapter

Abstract

The lanthanide elements or rare earth elements (REEs) are an active soil science research area, given their usage as micro-fertilizers, documented cases of environmental impact attributed to industry/mining, and their ability to identify lithologic discontinuities and reveal active soil processes. To fully understand REEs requires an understanding of their chemical reactivity, both for the individual elements and their behavior as a group of elements. The elements of the lanthanide series, including La and Y, may have subtle to very perceptible chemical differences that when viewed collectively reveal information that gives emphasis to soil processes that clarify soil behavior or soil genesis. This chapter concentrates on lanthanide soil chemistry and shows how the soil chemistry of REEs may support soil science investigations.

Keywords: rare earth elements, hydrolysis, complexation, adsorption, oxidation-reduction

1. The inorganic chemistry of the rare earth elements

In soil science the uniqueness and importance of the rare earth elements (REEs) arise because their respective concentrations as a function of atomic number have been employed to (i) assess soil genesis, (ii) augmenting soil fertility, (iii) evaluate anthropogenic impacts, and (iv) are sufficiently mobile to infer the intensity of key pedogenic processes. Soil mineralogy has documented that specific rare earth elements or collections of REE are present in specific minerals as a result of lattice isomorphic substitution or are unique minerals based on the presence of specific rare earth elements [1].

The rare earth elements (REE) are the 14 elements comprising the Lanthanide series: 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) [1, 2]. The Lanthanide series consists of unique elements characterized as having a ground state electronic configuration with at least one electron in the 4f electronic orbitals. Yttrium (Y) is frequently associated with the REEs because of its small ionic radius, approximately the same ionic radius as Ho. Lanthanum (La) is associated with the rare earth elements because of its Periodic Table position and its trivalent chemical affinity. Promethium undergoes rapid radioactive decay (half-life is 2.62 years) and its presence in the natural environment is virtually non-existent [1].

The lanthanide series is defined as elements having partially to filled 4f orbital ground state electronic configurations, with REE^{3+} species resulting from having three electrons removed from their d, s and f orbitals (**Table 1**). The number of f orbital electrons for each REE^{3+} species

Element	Atomic[1]		Ionic Radius[2]		Ground State
	Number	Weight	CN6	CN8	Configuration[1]
			10^{-12} meters		
Lanthanum (La)	57	138.9055	103.2	116	$[Xe]5d^16s^2$
Cerium (Ce)	58	140.12	101	114.3	$[Xe]4f^15d^16s^2$
Ce^{4+}			87	97	$[Xe]$
Praseodymium (Pr)	59	140.9077	99	112.6	$[Xe]4f^36s^2$
Neodymium (Nd)	60	144.24	98.3	110.9	$[Xe]4f^46s^2$
Promethium (Pm)	61	145	—	—	$[Xe]4f^56s^2$
Samarium (Sm)	62	150.36	95.8	107.9	$[Xe]4f^66s^2$
Europium (Eu)	63	151.96	94.7	106.6	$[Xe]4f^76s^2$
Eu^{2+}			117	125.0	$[Xe]$
Gadolinium (Gd)	64	157.25	93.8	105.3	$[Xe]4f^75d^16s^2$
Terbium (Tb)	65	158.9254	92.3	104.0	$[Xe]4f^96s^2$
Dysprosium (Dy)	66	162.50	91.2	102.7	$[Xe]4f^{10}6s^2$
Holmium (Ho)	67	164.9304	90.1	101.5	$[Xe]4f^{11}6s^2$
Erbium (Er)	68	167.26	89.0	100.4	$[Xe]4f^{12}6s^2$
Thulium (Tm)	69	168.93	88.0	99.4	$[Xe]4f^{13}6s^2$
Ytterbium (Yb)	70	173.04	86.8	98.5	$[Xe]4f^{14}6s^2$
Lutetium (Lu)	71	174.967	86.1	97.7	$[Xe]4f^{14}5d^16s^2$
Yttrium (Y^{3+})	39	88.9059	90.0	101.9	$[Kr]4d^15s^2$

[1]Greenwood and Earnshaw [1].
[2]Lee [2], Henderson [3].
CN6 is coordination number six and CN8 is coordination number eight.

Table 1. Chemical properties of the trivalent rare earth elements, including La and Y.

corresponds with their atomic number. Because the f-orbitals are mostly non-interactive, the REEs exhibit considerable ionic bonding character and are considered hard acids [1, 2].

Europium has a half-filled f-orbital, allowing stability for the Eu^{2+} species (**Table 1**); therefore, Eu is a lattice constituent in selected minerals important to igneous rook classification. Cerium exhibits oxidation-reduction behavior permitting either Ce^{3+} {$[Xe]4f^1$} or Ce^{4+} {$[Xe]$} to be present in the soil environment.

The influence of f-orbitals on the chemical attributes of the REEs observed by the regular decrease in the ionic radii on progression from La to Lu (**Table 1**). The so-called "Lanthanide Contraction" arises because of (i) the incomplete electric field shielding by the f-orbitals and (ii) unit increases in nuclear charge. The importance of the lanthanide contraction is revealed in greater chemical affinity for hydrolysis and greater stability of selected complexes on progression across the lanthanide series. The LREE are the light rare earth elements, comprised of the elements La to Eu, and the HREE are the heavy rare earth elements, comprised of the elements Gd to Lu.

The ionic radius is largely dependent on its atomic number, oxidation state, the coordination number (CN) and the radius of the anionic species. The ionic radii of REEs having octahedral coordination (CN 6) range from 103.2 pm for La to 86.1 pm for Lu (pm = picometer = 10^{-12} m) and the ionic radii of the REEs having cubic coordination (CN 8) range from 116.0 pm for La to 97.7 pm for Lu (**Table 1**).

2. Rare earth element rock and primary-secondary mineral abundances

Rock REE concentrations are predicated on rock type and source area. Most REE parent material compositions range from 0.1 to 100 mg/kg, thus REEs have moderate abundances. Typically, felsic's have greater REE concentrations than mafic's, with the LREE concentrations greater than the HREE concentrations. Similarly, argillaceous sediments have greater REE concentrations than limestones and sandstones.

The Oddo-Harkins rule states that an element with an even atomic number has a greater concentration than the next element in the Periodic Table. REEs typically obey the Oddo-Harkin rule. The PAAS, NASC, loess, and selected geochemical soil surveys usually reflect the Oddo-Harkin rule (**Table 2**).

Secondary minerals are (1) minerals formed after the rock enclosing the mineral was formed or (2) minerals that have chemically altered from primary minerals and have been transported. In some cases, REE are involved with isomorphic substitution or undergo adsorption reactions with phyllosilicates or oxyhydroxides. Precipitation reactions with fluoride, phosphate and carbonate may yield a variety of secondary REE minerals [6]. Cerianite (CeO_2) may form in oxic soil environments [7, 8].

Clark [6] provided a listing of important REE-bearing minerals, including (i) fluorite (CaF_2 where Y and Ce replace Ca), (ii) allanite [$(Ce,Ca,Y)_2(Al,Fe^{2+},Fe^{3+})_3(SO_4)_3OH$], (iii) sphene ($CaTiSiO_5$

| Element	PAAS[1]	NASC[1]	Loess[1]	Soil[2]
	mg/kg			
La	38.2	32	35.4	26.1
Ce	79.6	73	78.6	48.7
Pr	8.83	7.9	8.46	7.6
Nd	33.9	33	33.9	19.5
Sm	5.55	5.7	6.38	4.8
Eu	1.08	1.24	1.18	1.2
Gd	4.66	5.2	4.61	6.0
Tb	0.774	0.85	0.81	0.7
Dy	4.68	5.8	4.82	3.7
Ho	0.991	1.04	1.01	1.1
Er	2.85	3.4	2.85	1.6
Tm	0.405	0.5	bdl	0.5
Yb	2.82	3.1	2.71	2.1
Lu	0.433	0.48	bdl	0.3
Y	27	27	25	

[1]Reported in McLennan [4].
PAAS is Post-Archean Australian Average Shale, NASC is North American Shale Composite.
[2]Reported in Kabata-Pendias [5].
(bdl) is below detection limit.

Table 2. Rare earth element abundances for various parent materials.

where Y and REE replace Ca), (iv) Zircon ($ZrSiO_4$ where Y and HREE replace Zr), (v) apatite ($\Omega_5(XO_4)_3(F,OH,Cl)$; $\Omega + =Ca,Be,Ce,Pb$ and Y and REE replace Ca), (vi) monazite (($CeLa)PO_4$), (vii) xenotime (YPO_4 where REE replace Y), (viii) rhabdophane (($Ce,La)PO4$ and REE replace La), and (ix) bastnaesite (LaREE fluorocarbonate).

3. Rare earth element soil abundances

Rare earth element abundances in soils are influenced by (i) parent materials and organic matter contents, (ii) soil texture, (iii) pedogenic processes, and (iv) anthropogenic activities [5]. As with mineral assemblies, the soil LREE concentrations are generally greater than the soil HREE. Menfro soil series exists on uplands along the confluence of the Missouri and Mississippi Rivers (USA) and are developed in thick loess deposits. These well drained soils exhibit an A – E – Bt – C horizon sequence with acidification, Ca leaching and clay lessivage the dominant soil processes. The REE distribution shows that the light rare earth elements (La to Eu) are more abundant than the heavy REEs (Gd to Lu) and the distribution follows the Oddo-Harken rule. **Figures 1** and **2**
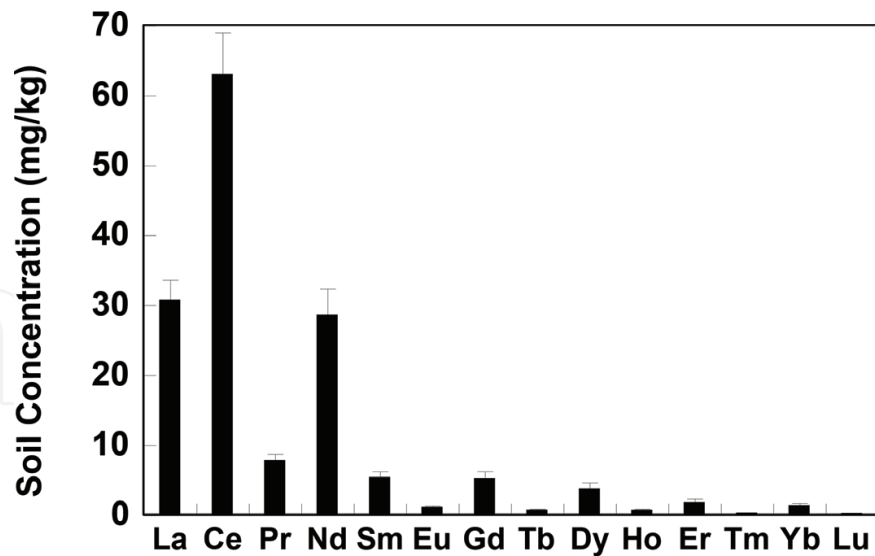
Figure 1. REE concentration distribution in two paired soil profiles of the Menfro series. (error bars are standard deviation). (Source: Data originally in [9]).
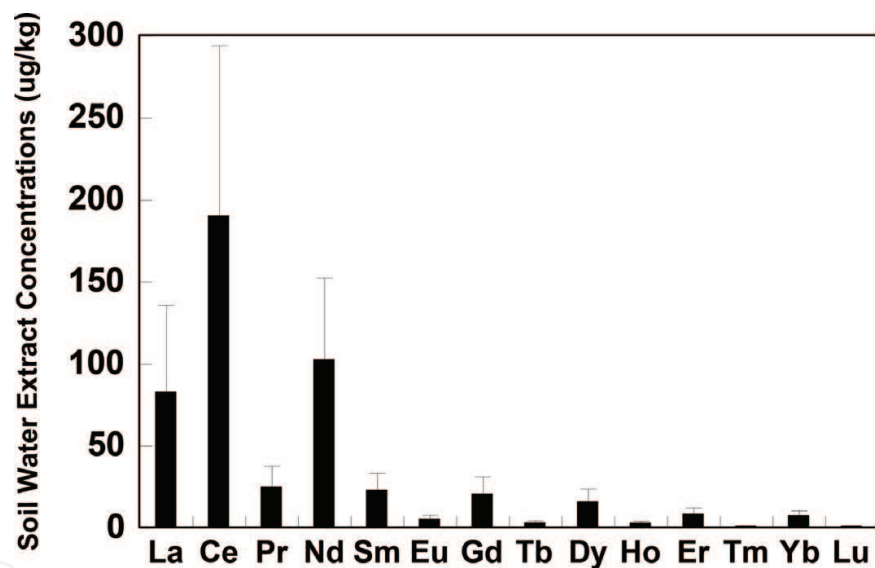
Figure 2. REE water extract concentration distribution in two paired soil profiles of the Menfro series (fine-silty, mixed, superactive, mesic Typic Hapludalfs). (error bars are standard deviation). (Source: Data originally in [9]).

The corresponding REE distribution from soil water extracts from the Menfro series closely correspond to the whole soil REE distribution.

4. Chemical reactivity of the rare earth elements in the soil environment

### 4.1. REE hydrolysis and complexation reactions

The hydrolysis of REE^{3+} species has been extensively investigated and numerous authors have published hydrolysis data [10–14]. For example, Eu^{3+} will undergo hydrolysis to

produce Eu(OH)$^{2+}$, Eu(OH)$_2^+$, Eu(OH)$_3$ and Eu(OH)$_4^-$, having log K° constants log K$_{11}$° = −7.64, log K$_{12}$° = −15.1, log K$_{13}$° = −23.7, log K$_{14}$° = −36.2, respectively [13]. Nd and Yb hydrolysis speciation as a function of pH illustrates that the Nd^{3+} and Yb^{3+} species are the dominant species in acidic and near-neutral pH environments, whereas the Nd and Yb mono- and di-hydroxy species are the dominant species in alkaline and Nd(OH)$_3$, Nd(OH)$_4^-$ Yb(OH)$_3$, and Yb(OH)$_4^-$ are the dominant species in strongly alkaline pH environments (**Figures 3** and **4**). The hydrolysis speciation of any REE^{3+} species is like that of Eu^{3+}, with a necessary understanding that the relative stabilities of the various REE hydrolytic species are more stable on transition with increasing atomic number across the Lanthanide series (**Table 3**).

Complexation of the REE elements involves coordination with primarily anionic species and typically is expressed as:

$$REE^{3+} + yL^{n-} = REE - L_y^{(3-yn)},$$
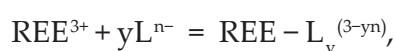
where L^{n-} is an inorganic ligand with n ionic charge and y is the stoichiometric coefficient. Common inorganic complexing species with REE^{3+} include NO$_3^-$, Cl$^-$, F$^-$, SO$_4^{2-}$, CO$_3^{2-}$, and HPO$_4^{2-}$. Carbonate and dicarbonate complexes exist, with carbonate complexes more prevalent in the LREEs and dicarbonate complexes more prevalent in the HREE [11, 16, 17]. Luo and Byrne [18] documented the carbonate complexing behavior of the REE. Cantrell and Byrne [16] estimated that 86% of the La speciation existed as a dicarbonate complex, whereas 98% of the Lu speciation occurred as the dicarbonate complex. Thus, for the Lanthanide Series, the dicarbonate complex becomes increasingly more stable with increasing atomic number. For illustration purposes, the La speciation involving carbonate complexes of water in equilibrium
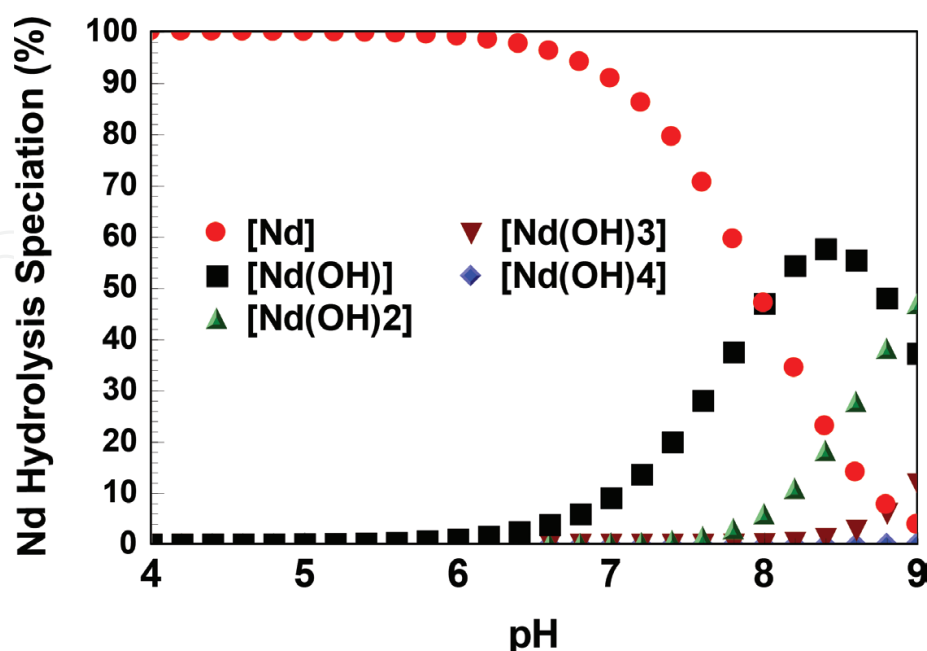
Figure 3. Aqueous hydroxyl speciation of Nd(III) over a pH interval. The Nd speciation involved concentrations without recourse to activity coefficients and overall formation quotients from Baes and Mesmer [10]. The total Nd concentration was 10^{-6} M.
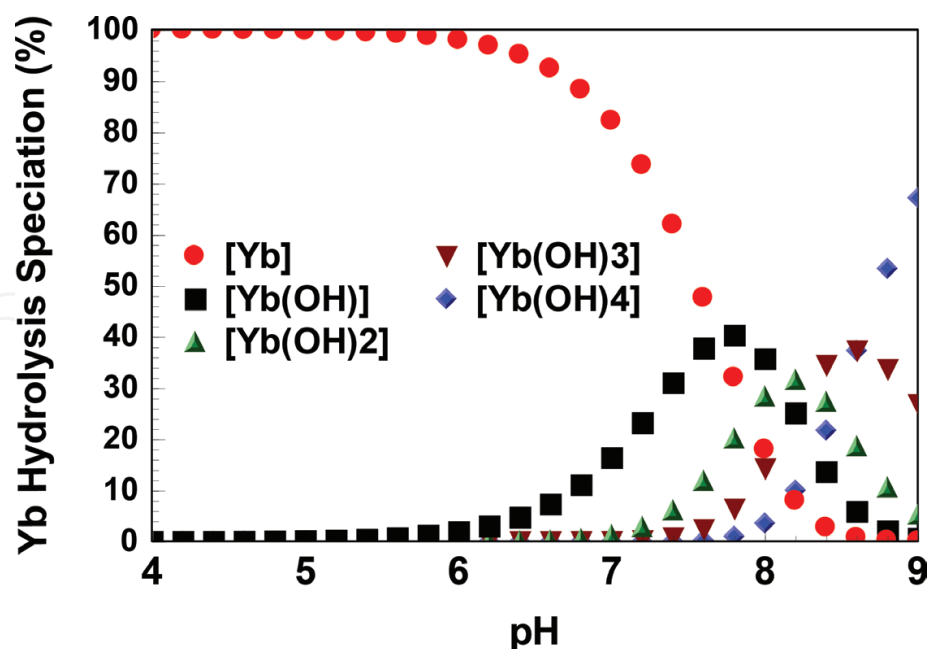
Figure 4. Aqueous hydroxyl speciation of Yb(III) over a pH interval. The Yb speciation involved concentrations without recourse to activity coefficients and overall formation quotients from Baes and Mesmer [10]. The total Yb concentration was 10^{-6} M.

Element	Log $Q_{1,1}$[1]	Infinite dilution stability constants			
		log CO_3	log $(CO_3)_2$	log Oxalate[3]	log HPO_4
La	−8.5	6.82	11.31	5.87	4.87
Ce	−8.3	6.95	11.50	5.97	4.98
Pr	−8.1	7.03	11.65	6.25	5.08
Nd	−8.0	7.13	11.80	6.31	5.18
Sm	−7.9	7.30	12.11	6.43	5.35
Eu	−7.8	7.37	12.24	6.52	5.42
Gd	−8.0	7.44	12.39	6.53	5.49
Tb	−7.9	7.50	12.52	6.63	5.54
Dy	−8.0	7.55	12.65	6.74	5.6
Ho	−8.0	7.59	12.77	6.77	5.64
Er	−7.9	7.63	12.88	6.83	5.68
Tm	−7.7	7.66	13.00	6.89	5.71
Yb	−7.7	7.67	13.08	6.95	5.73
Lu	−7.6	7.70	13.20	6.96	5.75
Y	−7.7			6.66	

[1]Q11 is the overall formation quotient for a hydrolysis product, $Ln(OH)^{2+}$.

[2]Baes and Mesmer [10].

[3]Carbonate-bicarbonate, phosphate, fluoride reported in Millero [11].

[4]Mono-oxalato complexation constants at infinite dilution from Schijf and Byrne [15].

Table 3. Hydrolysis and complexation constants for the La, REEs and Y.

with typical atmospheric concentrations of CO_2 are displayed in **Figure 5**. Similarly, the REE-Phosphate complex distribution as a pH function for La is displayed and shows that La^{3+} and $La(HPO_4)$ are the dominant species (**Figure 6**).

The hydrolysis, carbonate and EDTA ligand complex, and solubility products for La, Eu, and Lu (**Table 4**) show the expected trend of lanthanide contraction.

Millero [11] and Gramaccioli et al. [20] observed that REE-fluoride complexes obtained greater stability on transition from La to Lu. REE-phosphate precipitates have been implicated in limiting the mobility of the REE in soils and sediments [9].

4.2. Reactions involving organic complexation

Common organic complexes include: oxalic acid, malic acid and other low molecular weight organic acids and the semi-stable humus components fulvic and humic acids [15, 21–25]. Tyler and Olsson [26] reported that between 46 and 74% of the REEs extracted from the soil water of a Cambisol were associated with dissolved organic carbon. As with the inorganic REE complexes, organic REE complexes tend to show greater stability for the HREEs than the LREEs [15, 16].

Cteiner [27] observed monazite ($NdPO_4$) reactivity at low temperatures and low ionic strength to determine the influence of Cl^-, HCO_3^-, SO_4^{2-}, oxalate and acetate on solubility. At pH levels ranging from 6.0 to 6.5 Nd(oxalate) was the dominant species, followed by Nd^{3+} and $NdSO_4^+$. Gu et al. [21] independently proposed that organic materials may have multiple binding sites with a range of complexing bond strengths that strongly retain REE at low concentrations and provide non-specific REE retention at higher concentrations.
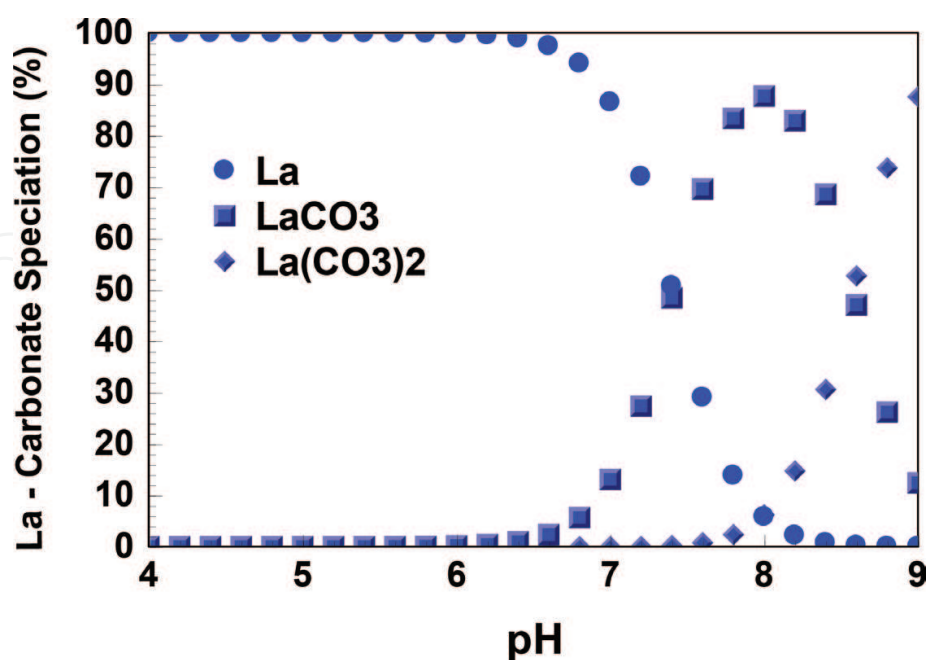
Figure 5. Aqueous hydroxyl and carbonate speciation of La(III). The La speciation involved concentrations with activity coefficients determined using by the Debye-Hückel equation. The carbonate complexation constants from Luo and Byrne [18] and acid dissociation constants for carbonic acid and bicarbonate from Essington [19].
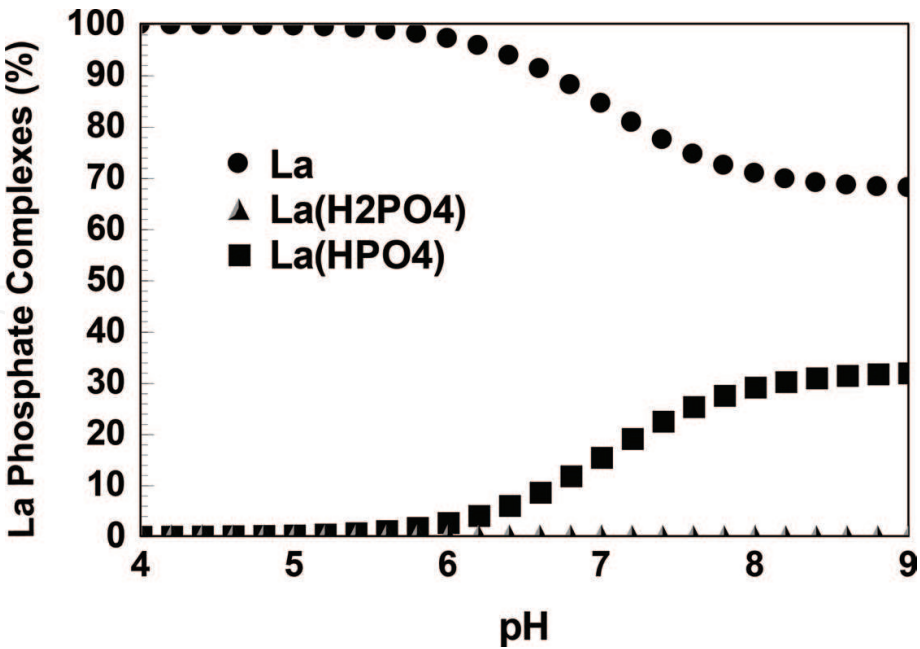
Figure 6. Aqueous carbonate speciation of La(III). The La speciation involved concentrations with activity coefficients determined using by the Debye-Hückel equation. The phosphate carbonate complexes are located in Millero [11].

The role of dissolved organic matter and element mobility is an active area of research. In a plot experiment, the release of La, Ce, Gd and Y decreased gradually as the pH of the soil was

Reaction	log β, Ksp, Log K
$La^{3+} + OH^- = La(OH)^{2+}$ \	−9.1
$La^{3+} + 2OH^- = La(OH)_2^+$	−17.9
$La(OH)_{3(s)} = La^{3+} + 3OH^-$	−20.3
$Eu^{3+} + OH^- = La(OH)^{2+}$	−8.4
$Eu^{3+} + 4OH^- = La(OH)_4^-$	−26.2
$Eu(OH)_{3(s)} = Eu^{3+} + 3OH^-$	−24.5
$Lu^{3+} + OH^- = Lu(OH)^{2+}$	−8.0
$La(OH)_{3(s)} = Lu^{3+} + 3OH^-$	−25.1
$La^{3+} + CO_3^{2-} = [La(CO_3)]^+$	5.00
$Eu^{3+} + CO_3^{2-} = [Eu(CO_3)]^+$	5.76
$Lu^{3+} + CO_3^{2-} = [Lu(CO_3)]^+$	6.02
$La^{3+} + EDTA^{4-} = [La(EDTA)$	]⁻14.48
$Eu^{3+} + EDTA^{4-} = [Eu(EDTA)]$	⁻16.23
$Lu^{3+} + EDTA^{4-} = [Lu(EDTA)]$	⁻18.19

Source: Smith and Martell [14].

Table 4. Selected constants involving lanthanum, europium and lutetium with hydroxide, carbonate and EDTA (ethylenediaminetetraacetate).

raised from strongly acidic to alkaline pH ranges [28]. Davranche et al. [29] demonstrated that REEs and humic acid complexes frequently dominate soil aqueous systems, especially in near-neutral pH levels and at greater dissolved organic carbon concentrations. Pourret et al. [30] observed the strong competitive interaction between humic acids and carbonates for REE complexation, especially at increasing pH levels. Similarly, Wu et al. [24] described the strong competition from EDTA, humic and fulvic acids influencing lanthanum adsorption onto goethite as a pH function.

5. Exchange and adsorption reactions

Cation exchange and adsorption reactions involving cations and their hydrolytic products are dominant soil processes. Aide and Aide [9] reviewed REE reactions in the soil environment, including REE adsorption. Numerous studies cited in this review produced similar REE adsorption conclusions, including: (i) cation exchange reactions are largely associated with basal planar surfaces and pH-dependent silanol and aluminol reactions at edge positions, (ii) predominance of outer-sphere complexes occur at pH levels less than 4 and an increasing degree of inner sphere complexes at pH levels greater than 5, (iii) cation exchange was consistent with one electrostatic and non-specific site and one specific complexation site involving edge aluminol groups, (iv) REE affinity was reduced by increases in the ionic strength, (v) REE complexation affinity was greater at higher pH intervals. Conversely Tertre et al. [31] demonstrated the inner-sphere nature of aluminol sites on kaolinite and montmorillonite. Tang and Johannesson [32] noting that REE adsorption was more pronounced at greater pH intervals. At lower pH intervals, adsorption was attributed to REE^{3+} species whereas at greater pH intervals adsorption was attributed to REE^{3+} and REE-carbonate species. The adsorption constants increased regularly with an increase in REE atomic number.

6. Rare earth elements and soil availability

Tyler [33] reviewed the importance of REE in soils and plants in which he underscored the recent contributions of Chinese soil scientists in addressing REEs as plant promoting elements. Tyler acknowledged that the traditional definitions of plant essential nutrients may be challenged because of recent research involving the REEs and other elements. Pang et al. [34] documented the increasing use of REE-bearing fertilizers in China. More research needs to be performed to accurately assess whether any of the REEs are "plant essential" or simply supportive of plant growth and development.

Rare earth elements frequently have been shown to have greater concentrations in plant roots than leaves or above-ground woody tissue [35–37]. Li et al. [38] demonstrated that a 0.1 M HCl based extraction protocol effectively indicated REE plant availability. Lanthanum and to a lesser degree the other REEs exhibited root concentrations that were inversely proportional to the soil pH [36]. Using nutrient solutions, Gu et al. [39] demonstrated that sulfate inhibited REE uptake. Zhang et al. [40] reported that a mixture of malic acid and citric acid was effective in estimating REE plant availability. Cao et al. (200b) showed that water-soluble,

exchangeable, and carbonate-organic fractions resulting from a selective-sequential extraction protocol were effective predictors of REE uptake in alfalfa (*Medicago sativa.* L). Wu et al. [25] isolated sap from xylem from non-hyperaccumulating REE plants to discover that aspartic acid, asparagine, histidine and glutamic acid were correlated with La and Y xylem transport.

Tyler and Olsson [41] showed that the majority of the REE were 40–50% removed from the A and E horizons of a Swedish Haplic Podzol. In a subsequent investigation Tyler [42] performed a *Fagus sylvatica* growth study and demonstrated only incidental REE uptake, except for Eu which was preferentially accumulated, mostly likely as Eu^{2+}. Soil liming has been shown to reduce REE concentrations in soil solution [43]. Tyler and Olsson [35] documented substantial REE plant uptake of grass grown in a Cambisol.

Aide (unpublished research) employed a 45 mμ filtered water leach extraction on a series of Endoaqualfs (poorly drained Alfisols) and Eutrochepts (somewhat poorly-drained Inceptisols) in southeastern Missouri to show REE availability (**Figure 7**). Cerium was consistently the most abundant REE leached from the soils, followed by La and Nd. The LREE had greater leachate concentrations than the HREE. REE compliance with the Oddo-Harkin's rule was consistently observed.

Loell et al. [44] employed total and EDTA extractions to infer bioavailability and reported that Ce had the greatest total concentration and the lowest bioavailability, whereas Y had the highest availability expression. Using regression analysis, the REE bioavailability was a function of pH, clay content, organic carbon and the total REE concentration. Mihajlovic et al. [45] observed the vertical distribution of REE in marshland soils using selective sequential extractions and documented that the residual fraction exhibited the largest REE abundance, followed by the reducible fraction. They also reported that the LREE were more abundant than the HREE, that the HREE exhibited the greater tendency to leach because of complex formation and the HREE were relatively more abundant in the exchangeable/available fractions.
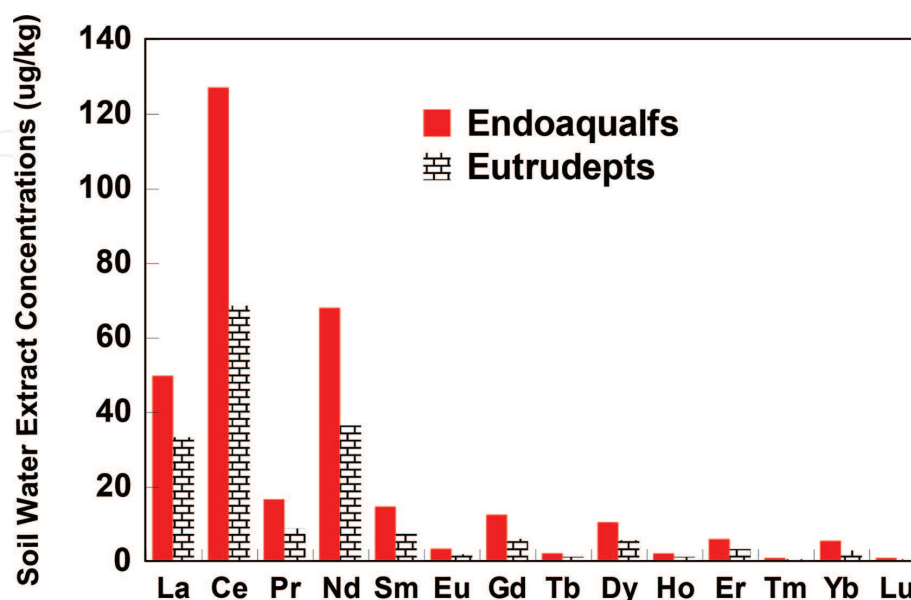
Figure 7. Soil water extract concentrations from two great groups in Missouri. The Endoaqualfs represent 27 observations, whereas the Eutrudepts represent 24 observations.

Selective, sequential extractions have been used to estimate REE plant uptake potential [40, 46–48]. Brantley et al. [49] reinforced the microbial component for REE availability, an area of research that is largely missing within the literature.

## 7. Rare earth elements and soil development

The importance of the REEs rests with their "signature", which may be defined as either the actual REE concentrations, when displayed by atomic number. Analysis of the REE signatures typically involves identifying evidence of fractionation, i.e., LREE and HREE ratios, La/Yb ratios, Nd/Sm ratios, and the presence of Ce or Eu anomalies. REE signatures have been compared to reveal (i) lithologic discontinuities [9], (ii) the presence of eolian or anthropogenic additions [50], (iii) estimates of the weathering intensities and elemental loss rates of soils [33], and (4) oxidation–reduction conditions in soil [9, 51]. Wang et al. [52] observed that greater soil water contents supported greater overland water flow, in which greater quantities of REE and P were transported. Similarly, Wu et al. [48] observed that apatite and calcium phosphate fertilizers altered the speciation and availability of selected REEs.

In a review of literature, Aide and Aide [9] reiterated numerous studies indicating REE migration in soil profiles. A summarization of the key REE soil transformations are (i) CO_2 and organic matter displace REEs as carbonate complexes and chelates in near surface horizons to support their accumulation in deeper soil horizons because of exchangeable, adsorption or precipitation reactions, (ii) HREE were enriched in the deeper soil horizons to a greater degree than the LREE, whereas other studies have indicated that the LREE were more readily transported to deeper soil horizons, (iii) apatite weathering supports the relatively rapid mobilization of the LREEs, whereas the weathering resistance mineral 'zircon' limits the mobilization of HREEs, (iv) similarities involving the REE signatures among the soil horizons and the host rock have been used to support arguments for parent material uniformity, whereas differences involving the REE signatures among the soil horizons and the host rock have been used to infer lithologic discontinuities (v) argillic (illuvial) horizons may have greater concentrations of LREE than the near-surface horizons (eluvial) inferring that phyllosilicate adsorption is an important soil process, (vi) crystalline Fe-oxyhydroxide and labile organic fractions accumulated HREEs than the LREEs, whereas the soil organic matter fraction representing humic acids and fulvic acids preferentially accumulated LREEs.

As an example, recent unpolished data from the authors of this manuscript follow. The Alred soil series (Loamy-skeletal over clayey, siliceous, semiactive, mesic Typic Paleudalfs) demonstrates differences in the rare earth element signatures to isolate lithologic discontinuities. The Alred series is a deep, well-drained collection of soils formed in cherty hillslope sediments (loess) and the underlying clayey limestone residuum. The eluvial (overlying loess mantle) and the illuvial (hill slope sediments derived from limestone residuum) differ significantly in their respective rare earth element concentrations, suggesting the REE differences are inherited (**Figure 8**).

The overcup series consists very deep, poorly drained, very slowly permeable soils that formed in alluvium (Fine, smectitic, thermic Vertic Albaqualfs). Aide (unpublished data) separated the
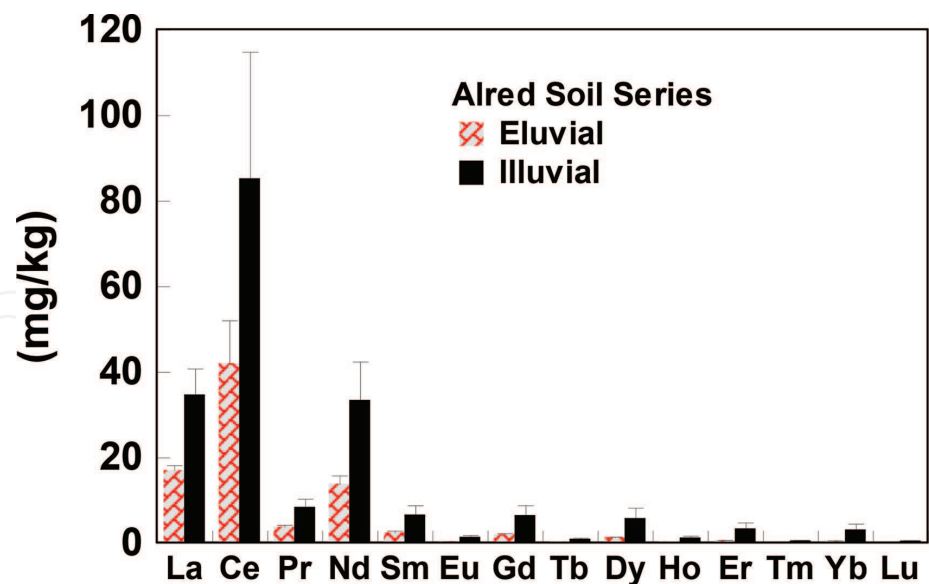
Figure 8. The rare earth element distributions for the eluvial and illuvial horizons of the Alred soil series (Cape Girardeau County, Missouri, USA). Error bars are the standard deviation).

soil horizons into their sand, silt and clay fractions, then determined the REE distribution using aqua regia digestion with ICP-MS. Selecting La for presentation, the La concentrations for the Ap through Btg2 horizons are rather evenly partitioned among the textural separates, with the clay separate showing slightly greater La abundance (**Figure 9**). The other REE elements show similar patterns. The Btg3 and Btg4 separates have greater La expression, especially for the sand separate. The Btg3 horizons are marked by a significant increase in sand-sized glabules
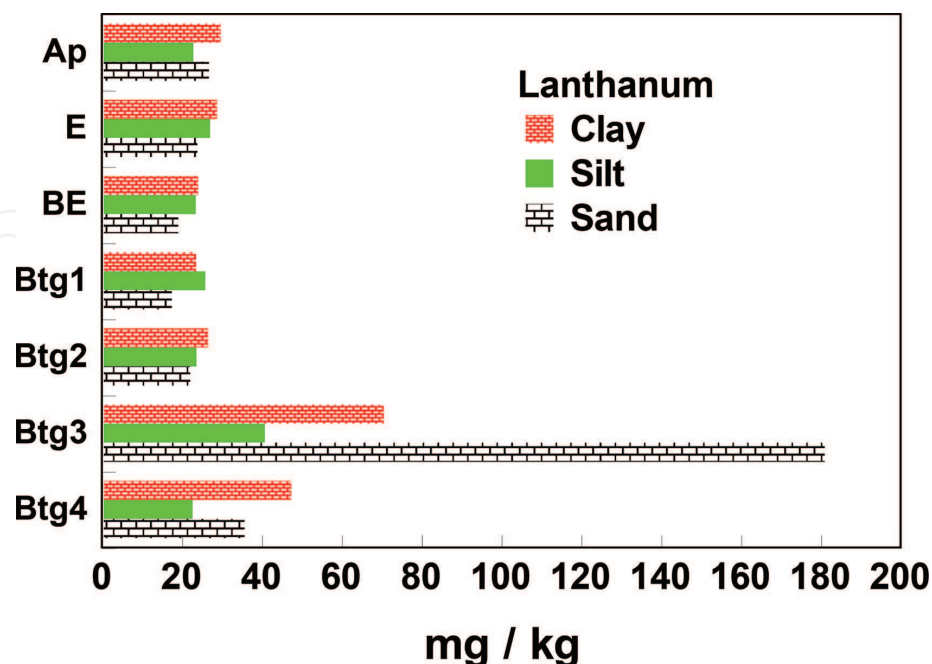
Figure 9. Rare earth element distribution by particle size for the Overcup soil series.

(nodules of Fe- and Mn-oxyhydroxides) and an abrupt increase in pH from an acidic to alkaline regime. Thus, oxidation-reduction and pH appear to be the controlling variables.

8. Future research needs

Future research needs include; (i) understanding of the REE-microbiological interactions, especially in the rhizosphere, (ii) are the REE elements plant essential elements or growth promoting entities, (iii) more complex models (along with thermodynamic data) to better simulate the soil environment, and (iv) anticipate REE impacts to the soil environment because of increasing industrial REE utilization.

Author details

Michael Aide

Address all correspondence to: mtaide@semo.edu

Southeast Missouri State University, USA

References

[1] Greenwood NN, Earnshaw A. Chemistry of the Elements. NY: Pergamon Press; 1984

[2] Lee JD. Concise Inorganic Chemistry. NY: Chapman and Hall; 1992

[3] Henderson P. General geochemical properties and abundances of the rare earth elements. In: Henderson P, editor. Rare Earth Element Geochemistry. NY: Elsevier; 1984. pp. 1-29

[4] McLennan SM. Rare earth elements in sedimentary rocks: Influence of provenance and sedimentary processes. In: Lipin BR, McKay GA, editors. Geochemistry and Mineralogy of Rare Earth Elements. Reviews in Mineralogy. Vol. 21. Washington DC: Mineralogical Society of America; 1989

[5] Kabata-Pendias A. Trace Elements in Soils and Plants. New York: CRC Press; 2001

[6] Clark AM. Mineralogy of the rare earth elements. In: Henderson P, editor. Rare Earth Element Geochemistry. NY: Elsevier; 1984. pp. 33-54

[7] Bau M. Scavenging of dissolved yttrium and rare earths by precipitating iron oxyhydroxide: Experimental evidence for Ce oxidation, Y-Ho fractionation, and lanthanide tetrad effect. Geochimica et Cosmochimica Acta. 1999;**63**:67-77

[8] Ohta A, Kawabe I. REE(III) adsorption onto Mn dioxide (δ-MnO_2) and Fe oxyhydroxide: Ce(III) oxidation by δ-MnO_2. Geochimica et Cosmochimica Acta. 2001;**65**:695-703

[9] Aide MT, Aide CC. Rare earth elements: Their importance in understanding soil genesis. International Scholarly Research Network (ISRN Soil Science). 2012;**2012**: Article ID783876. DOI: 10.5402/2012/783876

[10] Baes CF, Mesmer RE. The Hydrolysis of Cations. NY: John Wiley and Sons; 1976

[11] Millero FJ. Stability constants for the formation of rare earth inorganic complexes as a function of ionic strength. Geochimica et Cosmochimica Acta. 1992;**56**:3123-3132

[12] Klungness GD, Byrne RH. Comparative hydrolysis behavior of rare earth elements and yttrium: The influence of temperature and ionic strength. Polydron. 2000;**19**:99-107

[13] Hummel E, Berner U, Curti E, Thoenen A. Nagra/PSI Chemical Thermodynamic Data Base. Wettingen, Switzerland: Nagra; 2008

[14] Smith R, Martell A. Critical Stability Constants, Volumes 1 and 4. Inorganic Complexes. New York: Plenum Press; 1976

[15] Schijf J, Byrne RH. Stability constants for mono- and dioxalato-complexes of Y and the REE, potentially important species in groundwaters and surface freshwaters. Geochimica et Cosmochimica Acta. 2001;**65**:1037-1046

[16] Cantrell KJ, Byrne RH. Rare earth element complexation by carbonate and oxalate ions. Geochimica et Cosmochimica Acta. 1987;**51**:597-605

[17] Lee JH, Byrne RH. Complexation of trivalent rare earth elements (Ce, Eu, Gd, Tb, Yb) by carbonate ions. Geochimica et Cosmochimica Acta. 1993;**57**:295-302

[18] Luo YR, Byrne RH. Carbonate complexation of yttrium and rare earth elements in natural waters. Geochimica et Cosmochimica Acta. 2004;**68**:691-699

[19] Essington ME. Soil and Water Chemistry: An Integrative Approach. Boca Raton, FL: CRC Press; 2004

[20] Gramaccioli CM, Diella V, Demartin F. The role of fluoride complexes in REE geochemistry and the importance of 4f electrons: Some examples in minerals. European Journal of Mineralogy. 1999;**11**:983-992

[21] Gu ZM, Wang XR, Gu XY, Cheng J, Wang LS, Dai LM, Cao M. Determination of stability constants for rare earth elements and fulvic acids extracted from different soils. Talanta. 2001;**53**:1163-1170

[22] Dong WM, Wang XK, Bian XY, Wang AX, Du JZ, Tao ZY. 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. Applied Radiation and Isotopes. 2001;**54**:603-610

[23] Dong MW, Li WJ, Tao ZY. Use of the ion exchange method for the determination of stability constants of trivalent metal complexes with humic and fulvic acids II. Tb3+, Yb3+ and Gd3+ complexes in weakly alkaline conditions. Applied Radiation and Isotopes. 2002;**56**:967-974

[24] Wu ZH, Luo J, Guo HY, Wang XR, Yang CS. Adsorption isotherms of lanthanum to soil constituents and effects of pH, EDTA and fulvic acid on adsorption of lanthanum onto goethite and humic acid. Chemical Speciation & Bioavailability. 2001;**13**:75-81

[25] Wu J, Chen A, Peng S, Wei Z, Liu G. Identification and application of amino acids as chelators in phytoremediation of rare earth elements lanthanum and yttrium. Plant and Soil. 2013;**373**:329-338

[26] Tyler G, Olsson T. Conditions related to solubility of rare and minor elements in forest soils. Journal of Plant Nutrition and Soil Science. 2002;**165**:594-601

[27] Cteiner ZS. The influence of pH and temperature on the aqueous geochemistry of neodymium in near surface conditions. Environmental Monitoring and Assessment. 2009;**151**:279-287

[28] Cao XD, Chen Y, Wang XR, Deng XH. Effects of redox potential and pH value on the release of rare earth elements from soil. Chemosphere. 2001;**44**:655-661

[29] Davranche M, Pourret O, Gruau G, Dia A, Le Coz-Bouhnik M. Competitive binding of REE to humic acid and manganese oxide: Impact of reaction kinetics on development of cerium anomaly and REE adsorption. Chemical Geology. 2008;**247**:154-170

[30] Pourret O, Davranche M, Gruau G, Dia A. Competition between humic acid and carbonates for rare earth elements complexation. Journal of Colloid and Interface Science. 2007;**305**:25-31

[31] Tertre E, Berger G, Giffaut E, Loubet M, Catalette H. Europium retention onto clay minerals from 25 to 150°C: Experimental measurements, spectroscopic features and sorption modeling. Geochimica et Cosmochimica Acta. 2006;**70**:4563-4578

[32] Tang J, Johannesson KH. Adsorption of rare earth elements onto Carrizo sand: Experimental investigations and modeling with surface complexation. Geochimica et Cosmochimica Acta. 2005;**69**:5247-5261

[33] Tyler G. Rare earth elements in soil and plant systems – A review. Plant and Soil. 2004;**267**:191-206

[34] Pang X, Li DC, Peng A. Application of rare-earth elements in the agriculture of China and its environmental behavior in soil. Environemental Science and Pollution Research. 2002;**9**:143-148

[35] Tyler G, Olsson T. Plant uptake of major and minor elements as influenced by soil acidity and liming. Plant and Soil. 2001;**230**:307-321

[36] Zhang SZ, Shan XQ. Speciation of rare earth elements in soils and accumulation in wheat with rare earth fertilizer application. Environmental Pollution. 2001;**112**:395-405

[37] Li FL, Shan XQ, Zhang TH, Zhang SZ. Evaluation of plant availability of rare earth elements in soils by chemical fractionation and multiple regression analysis. Environmental Pollution. 1998;**102**:269-277

[38] Li FL, Shan XQ, Zhang SZ. Evaluation of single extractants for assessing plant availability of rare earth elements in soils. Communications in Soil Science and Plant Analysis. 2001;**32**:2577-2587

[39] Gu ZM, Wang XR, Cheng J, Wang LS, Dai LM. Effects of sulfate on speciation and bioavailability of rare earth elements in nutrient solution. Chemical Speciation & Bioavailability. 2000;**12**:53-58

[40] Zhang SZ, Shan XQ, Li FL. Low-molecular-weight-organic-acids as extractant to predict bioavailability of rare earth elements. International Journal of Environmental Analytical Chemistry. 2000;**76**:283-294

[41] Tyler G. Vertical distribution of major, minor, and rare elements in a Haplic Podzol. Geoderma. 2004;**119**:277-290

[42] Tyler G. Ionic change, radius, and potential control root/soil concentration ratios of fifty cationic elements in the organic horizon of a beech (*Fagus sylvatica*) forest Podzol. Science of the Total Environment. 2004;**329**:231-239

[43] Tyler G, Olsson T. Concentrations of 60 elements in the soil solution as related to the soil acidity. European Journal of Soil Science. 2001;**52**:151-165

[44] Loell M, Albrecht C, Felix-Henningsen P. Rare earth elements and relation between their potential bioavailability and soil properties, Nidda catchment (Central Germany). Plant and Soil. 2011;**239**:303-317

[45] Mihajlovic J, Giani L, Stark H-J, Rinklebe J. Concentrations and geochemical fractions of rare earth elements in two different marsh soil profiles at the North Sea, Germany. Journal of Soils and Sediments. 2014;**14**:1417-1433

[46] Cao XD, Wang XR, Zhao GW. Assessment of the bioavailability of rare earth elements in soils by chemical fractionation and multiple regression analysis. Chemosphere. 2000;**40**: 23-28

[47] Ding S, Liang T, Zhang C, Yan J, Zhang Z. Accumulation and fractionation of rare earth elements (REEs) in wheat: Controlled by phosphate precipitation, cell wall absorption and solution complexation. The Journal of Experimental Biology. 2005;**56**:2765-2775

[48] Wu ZH, Wang XR, Zhang YF, Dai LM, Chen YJ. Effects of apatite and calcium oxyphosphate on speciation and bioavailability of exogenous rare earth elements in the soil-plant system. Chemical Specification and Bioavailability. 2001b;**13**:49-56

[49] Brantley SL, Liermann L, Bau M, Wu S. Uptake of trace elements and rare earth elements from hornblende by a soil bacterium. Geomicrobiology Journal. 2001;**18**:37-61

[50] Aide MT, Aide CC, Dolde J, Guffey C. Geochemical indicators of external additions to soils in big bend National Park, Texas. Soil Science. 2002;**168**:200-208

[51] Aide MT. Elemental composition of soil nodules from two Alfisols on an alluvial terrace in Missouri. Soil Science. 2005;**170**:1022-1033

[52] Wang L, Liang T, Wang W, Zhang C. Effects of antecedent soil moisture on losses of rare earth elements and phosphorus runoff. Environment and Earth Science. 2012;**66**:2379-2385