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Review and Assessment of Organic and Inorganic Rare Earth Element Complexation in Soil, Surface Water, and Groundwater

Michael Aide

Abstract

The lanthanide elements, or rare earth elements (REEs), are an active research area, with increasing attention directed toward soil and water evaluation and protection. Rare earth element concentrations in surface and groundwaters may be appropriately evaluated by partitioning the REEs into (i) a dissolved fraction (REE^{3+} , hydrolysis, and simple anion complexation products) and (ii) REEs associated with inorganic and organic colloidal fractions. Given the total REE concentration and the organic, inorganic, and clastic composition, each fraction of REE concentration and the speciation within the fraction may be thermodynamically simulated to estimate (i) transport potential, (ii) biological availability, and (iii) system reactivity toward changes in pH, oxidation-reduction, chemical composition, mineralogy (facies) changes, or anthropogenic alteration. Chemical thermodynamic simulations using freely available USEPA software are presented to illustrate REE alterations attributed to pH changes, inorganic and organic adsorption, mineral precipitation, and oxidation-reduction. The purpose is to position researchers to better anticipate REE reactivity and transport potential in aquatic and soil resources.

Keywords: lanthanides, Minteq, aquatic resources, environmental degradation, thermodynamic simulation

1. Rare earth element: inorganic chemistry

The rare earth elements (REEs) 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]. Lanthanum (La) is associated with the rare earth elements because of its trivalent chemical affinity and periodic table position. The lanthanide series are elements characterized as having one or more electrons in the 4f electronic orbitals for their ground state configuration. Promethium undergoes rapid radioactive decay and is absent in the environment.

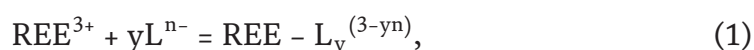
The typically trivalent REE elements have considerable ionic bonding character [1]. The chemical attributes of the REEs are influenced by the regular decrease

in the ionic radii on progression from La to Lu, the so-called lanthanide contraction. The “lanthanide contraction” occurs because of the incomplete electric field shielding by the f orbitals and increases in atomic number, supporting greater chemical affinity for hydrolysis and chelate/complex stability on progression across the lanthanide series [1]. 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. In some cases, The REEs have been partitioned as (i) the light REE (LREE includes La, Ce, Pr), (ii) the middle REE (MREE includes Nd, Sm, Eu, and Gd), and (iii) the heavy REE (HREE includes Tb to Lu).

2. Hydrolysis and complexation thermodynamic data

The hydrolysis of REE^{3+} species has been extensively investigated. The primary thermodynamic literature featuring data involving REE^{3+} hydrolysis and inorganic complexation reactions include Baes and Mesmer [2], Hummel et al. [3], Smith and Martel [4], Schijf and Byrne [5], Luo and Byrne [6], Cantrell and Byrne [7], Gramaccioli et al. [8], Lee and Byrne [9], and Millero [10]. Klungness and Byrne [11] noted that REE hydrolysis is more stable with increasing atomic number across the lanthanide series.

Inorganic complexation of the REE elements involves coordination with primarily anionic species, and it is expressed as.



where L^{n-} is an inorganic ligand with n ionic charge and y is the stoichiometric coefficient. For the lanthanide series, the dicarbonate complex becomes increasingly more stable with increasing atomic number [6, 7, 9]. Both hydrolysis and carbonate complexation show the expected increasing stability with increasing atomic number across the lanthanide series [12]. Aide [12] reviewed thermodynamic data concerning rare earth element hydrolysis.

Common low-molecular-weight organic complexes include acetic acid, phthalic acid, oxalic acid, lactic acid, malic acid, and citric acid. Humus components typically include fulvic and humic acids. The seminal literature featuring thermodynamic data involving REE^{3+} organic complexation include Gu et al. [13], Dong et al. [14], and Pourret et al. [15].

3. Distribution of rare earth elements in soils and earth materials

REE concentrations in soils, sediments, and other earth materials are dependent on their mineral assemblage and source area, with REE concentrations typically ranging from 0.1 to 100 mg/kg. In general, felsics have greater REE concentrations and greater LREE/HREE ratios than mafics. As expected, fine-grained clastic sediments frequently exhibit 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. The REEs typically obey the Oddo-Harkins rule. The Post-Archean Australian average shale (PAAS), North American shale composite (NASC), selective representative soil collections, and selected geochemical soil surveys usually reflect the Oddo-Harkins rule [16–18] (**Table 1**).

Commonly occurring REE-bearing minerals include (i) fluorite (Ce replaces Ca), (ii) allanite (Ce), (iii) sphene (REE replace Ca), (iv) zircon (HREE replace Zr), (v) apatite (REE replace Ca), (vi) monazite ((CeLa) phosphate),

Element	PAAS ¹	NASC ¹	Soil ²	Chinese soils ³
mg/kg				
La	38.2	32	26.1	37.4
Ce	79.6	73	48.7	64.7
Pr	8.83	7.9	7.6	6.67
Nd	33.9	33	19.5	25.1
Sm	5.55	5.7	4.8	4.94
Eu	1.08	1.24	1.2	0.98
Gd	4.66	5.2	6.0	4.38
Tb	0.774	0.85	0.7	0.58
Dy	4.68	5.8	3.7	3.93
Ho	0.991	1.04	1.1	0.83
Er	2.85	3.4	1.6	2.42
Tm	0.405	0.5	0.5	0.35
Yb	2.82	3.1	2.1	2.32
Lu	0.433	0.48	0.3	0.35

¹Reported in McLennan [16].

²Reported in Kabata-Pendias [17].

³Reported in Liang et al. [18].

PAAS is Post-Archean Australian average shale; NASC is North American shale composite.

Table 1.
Rare earth element abundances for various parent materials.

(vii) xenotime (REE—phosphate), (viii) rhabdophane (Ce, REE—phosphate), and (ix) bastnaesite (REE fluorocarbonate). As with many mineral assemblies, the soil LREE concentrations are generally greater than the soil HREE; however, mineral assemblages featuring an abundance of zircon may differ in the LREE/HREE.

4. Rare earth element abundances in natural waters: river water

Natural waters include marine, river, lacustrine, and groundwater. Considerations for characterizing natural water REE concentrations include (1) the total REE concentration; (2) suspended minerals having adsorbed, occluded, or latticed REE; (3) organically complexed REE; and (4) soluble REE³⁺ and their hydrolytic and ion pair products. Liang et al. [18] cited literature references for river waters in China. 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-Harkins rule. These authors also compared rivers having either pristine and REE impaction because of REE mining activities (**Table 2**). The REE concentrations because of mining activity were intense, underscoring the environmental impact. Linear regression by the author of this manuscript of Liang et al. [18] river water data for dissolved and suspended REE load shows substantial correlation between the dissolved and suspended concentrations for all REEs. The linear relationship for the Yellow River segment [suspended matter = 317.86 (dissolved) –4.904 with $r^2 = 0.91$] and the Kundulum River segment [suspended matter = 0.787 (dissolved) +0.624 with $r^2 = 0.95$] infer that the respective suspended and dissolved REE concentrations arise from similar chemical adsorption relationships.

	Dissolved ($\mu\text{g L}^{-1}$)		Suspended matter ($\mu\text{g g}^{-1}$)	
	Yellow	Kundulum	Yellow	Kundulum
La	0.10	140	33.16	86.16
Ce	0.22	152	68.26	139.3
Pr	0.034	16.1	8.47	15.8
Nd	0.095	52.0	28.7	52.0
Sm	0.054	6.91	5.79	6.61
Eu	0.018	1.52	1.31	1.20
Gd	0.028	7.22	6.29	4.31
Tb	0.006	0.88	0.82	0.97
Dy	0.08	3.80	3.39	1.87
Ho	0.014	0.18	0.77	0.68
Er	0.03	2.34	2.25	1.36
Tm	0.007	0.24	0.25	0.22
Yb	0.032	1.48	1.76	1.01
Lu	0.006	0.21	0.25	0.22

Documented in Liang et al. [18].

Table 2.
Rare earth element concentrations documented for two Chinese rivers.

River waters typically have greater REE concentrations than marine waters because of their suspended load and a greater abundance of dissolved organic material [19–22]. Dupre et al. [19] observed that the REEs were primarily associated with suspended inorganic and organic colloids. Garcia et al. [20] studied river waters in Argentina draining predominately granitic landscapes, showing that high-rainfall periods effectively reduced or “diluted” REE concentrations. Andersson et al. [21] proposed that organic colloidal materials were largely responsible for REE transport in boreal Swedish river waters and that the LREE were more abundant than the HREE. Ingri et al. [22] demonstrated that the La concentrations in Swedish boreal river waters were seasonal and were associated with organic and Fe-oxyhydroxide inorganic colloidal material.

Gurumurthy et al. [23] documented 3 years of river discharge across south-western India and provided river water chemistry, including rare earth elements (**Table 3**). They observed that the rare earth elements showed higher concentrations during the monsoon season as opposed to the dry season, suggesting that soil leaching across the watersheds was important to the increased monsoonal river water concentrations. Cerium anomalies were observed, pH moderated adsorption-desorption reactions, and the dissolved oxygen concentrations were important in regulating the seasonality of the Ce anomalies. Rare earth element complexation was not highly significant in influencing the rare earth element concentrations.

Neal [24] documented La, Ce, Pr, and yttrium (Y) concentrations in the upper River Severn catchments in Mid Wales. Over a 7-year interval, larger river water concentrations of La, Ce, Pr, and Y were associated with high-rainfall events and baseflow/return flow from land parcels having acidic soil pH values, suggesting that the surrounding terrestrial environment is important to REE river chemistry. Leybourne and Johannesson [25] described that the REE adsorption affinity for stream waters and sediments was pH-dependent, with deprotonation of surface

Southwestern Indian rivers (pmol L ⁻¹)				
Element	Bantwal	Gurupur	Mugeru	Shanthimugeru
La	854	793	1213	1136
Nd	759	765	1130	1096
Ce	1986	1867	2698	2658
Pr	198	189	291	276
Sm	162	159	216	229
Eu	46	44	62	62
Gd	148	134	209	211
Dy	112	105	166	174
Ho	27	28	34	36
Er	65	61	90	100
Tm	11	19	14	16
Yb	57	57	74	89
Documented in Gurumurthy et al. [23].				

Table 3.
Rare earth elements discharge-weighted mean averages of rare earth elements in river waters from southwestern India.

hydroxyl groups favoring REE adsorption at more alkaline pH intervals. With increasing pH, the adsorption potential may permit REE fractionation, with the adsorption affinity greatest for the LREE, less for the MREE, and least for the HREE. In Sweden, Ohlander et al. [26] recorded Sm/Nd ratios in the weathering of granitic till, noting Sm/Nd differences in the upper eluvial soil horizons relative to the deeper less weathered till. Weathering intensity differences and secondary preferential placement of Nd in the deeper less weathered till influenced adjacent stream compositions.

5. Rare earth element abundances in natural waters: groundwater

The total rare earth element concentrations in groundwater may be partitioned into (i) dissolved or free ion species that may include hydrolysis products and inorganic complexes, (ii) low-molecular-weight organic ligands and moderate- to large-molecular-weight chelates (e.g., humic and fulvic acids (FA)), and (iii) clastic colloids (e.g., phyllosilicates and Fe-oxyhydroxides) [27–33]. Groundwater may frequently exhibit a seasonal range in total REE concentrations [27]. Dia et al. [27] documented REE, dissolved organic carbon (DOC), and trace metals in well waters from a French catchment, noting that spatially distinct groundwaters may be partitioned based on DOC content and other hydrologic variables. Ultrafiltration of the distinct groundwaters reveals that the REE concentrations in the organic-rich waters were more associated with organic colloids, whereas the REEs in groundwaters having small DOC concentrations were more associated with inorganic colloids. Similarly, Pourret et al. [28], working with the same catchment as Dia et al. [27], employed ultrafiltration techniques and species modeling using the humic ion-binding model VI to show that (i) the smaller REE concentrations in ultrafiltration waters were attributed to the removal of REE-bearing organic colloids and (ii) modeling suggests that the lanthanum complexes were dominated by humic acids (80%) and subordinately with fulvic

acids (20%). Inorganic complexes were of greater importance in groundwaters having low DOC concentrations. Omonona and Okoghue [31] showed REE concentrations from Nigerian aquifers, demonstrating the region’s water REE chemical diversity (Table 4).

Adsorption reactions involving the REEs and aquifer materials are instrumental to understanding REE water concentrations and transport [34–41]. Rabung et al. [34] performed batch adsorption experiments involving Eu^{3+} on Ca-montmorillonite and Na-illite and showed Eu outer-sphere complexes at pH levels less than pH 4 on illite, whereas no outer-sphere complexes were observed with montmorillonite. For pH levels greater than pH 5, inner-sphere complexes were formed for both minerals. Coppin et al. [29] showed that lanthanide adsorption on smectite and kaolinite was pH and ionic strength dependent and demonstrated increased adsorption at higher ionic strengths near pH 5.5. At lower ionic strengths, REE adsorption onto smectite was weakly pH-dependent from 3 to pH 6, whereas REE adsorption was increasingly greater above pH 6. Kaolinite showed increased REE adsorption with increased pH. At the greater ionic strength, the heavy REEs exhibited greater adsorption, a feature consistent with lanthanide contraction.

Cteiner [42] observed monazite (NdPO_4) reactivity at low ionic strengths to estimate the influence of Cl^- , HCO_3^- , SO_4^{2-} , oxalate, and acetate on monazite solubility. At pH levels ranging from 6.0 to 6.5, Nd (oxalate) was the dominant species, followed by Nd^{3+} and NdSO_4^+ . Davranche et al. [37, 38] 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. [43] observed the strong competitive interaction between humic acids and carbonates for REE complexation, especially at increasing pH levels. Similarly, Wu et al. [36] described the strong competition involving EDTA and humic and fulvic acids, which effectively inhibited lanthanum adsorption onto goethite.

Cation exchange and adsorption reactions involving cations and their hydrolytic products are dominant soil processes, including (i) multi-site cation exchange reactions, (ii) adsorption reactions with increasing degree of inner-sphere complexes

Element	Low	High ($\mu\text{g L}^{-1}$)	Mean
La	0.33	42.85	6.83
Ce	0.73	85.15	6.83
Nd	0.36	36.51	6.18
Pr	0.09	9.25	1.55
Sm	0.05	5.47	1.04
Eu	0.00	0.50	0.07
Gd	0.06	3.61	0.81
Dy	0.00	2.08	0.49
Ho	0.00	0.38	0.09
Er	0.01	0.94	0.23
Tm	0.00	0.12	0.03
Yb	0.00	0.80	0.18

Source: Omonona and Okoghue [31].

Table 4.
Rare earth element concentrations from selected aquifers in the Gboko area, Nigeria.

at pH levels greater than pH 5, (iii) REE affinity being reduced by increased ionic strength, and (iv) REE complexation affinity being greater at higher pH intervals. Davranche et al. [38] provided adsorption data on hydrous ferric oxides with REEs and REE-humate complexes. REE-humate complexes do not dissociate upon adsorption, with binding presumed to be anionic adsorption involving the humate portion of the complex. Pourret et al. [15] employed ultrafiltrate techniques to investigate La, Eu, and Lu synthetic humic acid complexation and modeled the datasets with the humic ion-binding model to demonstrate that the quantity of REE bonding increases with pH. The intensity of the REE-humic acid binding approached 100% near pH 4 for the highest humic acid concentration (20 mg L^{-1}). Rare earth complexes involving carbonate and especially dicarbonate speciation were effective competing anions in alkaline media with the effectiveness of carbonate complexation increasing from La to Lu.

6. Materials and methods

An aqua regia digestion was employed to obtain a near total estimation of elemental abundance associated with all but the most recalcitrant soil chemical environments. Aqua regia does not appreciably degrade quartz, albite, orthoclase, anatase, barite, monazite, sphene, chromite, ilmenite, rutile, and cassiterite; however, anorthite and phyllosilicates are partially digested. Homogenized samples (0.75 g) were equilibrated with 0.01 L of aqua regia (3 mole nitric acid/1 mole hydrochloric acid) in a 35°C incubator for 24 hours. Samples were shaken, centrifuged, and filtered ($0.45 \mu\text{m}$), with a known aliquot volume analyzed using inductively coupled plasma mass spectrometry (ICP-MS).

A hot water extraction was performed to recover only the most labile or potentially labile fractions. A hot water extraction involved equilibrating 0.5 g samples in 0.02 L distilled-deionized water at 80°C for 1 hour followed by $0.45 \mu\text{m}$ filtering and elemental determination using ICP-MS. In the water extract and the aqua regia digestion, selected samples were duplicated, and known reference materials were employed to guarantee analytical accuracy.

Using Minteq software [44] chemical speciation may be estimated from an internal Minteq thermochemical data for specified pH intervals. Establishing a reasonably constant ionic strength using the background solution chemistry [NO_3 , Cl, NH_4 , Ca, K, Mg, Na, SO_4 , PO_4] of subsurface tile-drainage effluent from the David M. Barton Agriculture Research Center [Missouri, USA], activity coefficients were calculated using the Debye-Huckel equation at 25°C.

7. Results and discussion

Soils of the Sharkey series (very-fine, smectitic, thermic chromic epiaquerts) have Ap-Bssg-Bssyg horizon sequences, and soils of the Lilbourn series (coarse-loamy, mixed, superactive, nonacid, thermic aeris fluvaquents) have Ap-C horizon sequences. The Sharkey and Lilbourn soil series are composed of Holocene fluvial sediments from the ancestral Mississippi/Ohio rivers in southeastern Missouri (USA). The clayey-textured Sharkey soil series shows greater REE concentrations than the coarse-textured Lilbourn series, and both series exhibit appreciably greater than unity LREE/HREE concentration ratios. In general, the REE distributions obey the Oddo-Harkins rule. REE water extract concentrations are an approximate estimate of soil REE activity. As expected, the water extract concentrations for the Sharkey and Lilbourn soil series are approximately two to three orders of magnitude smaller than the aqua regia digestion extract concentrations

	Sharkey soil series						Lilbourn soil series			
	Soil (mg kg ⁻¹)			Water (µg kg ⁻¹)			Soil (mg kg ⁻¹)		Water (µg kg ⁻¹)	
	Ap	Bssg	Bssyg	Ap	Bssg	Bssyg	Ap	C4	Ap	C4
La	24.9	24.4	24.9	43	50	41	15.5	16.8	54.5	51.1
Ce	51.1	47.6	50.8	96.3	106	86.8	29.9	34.9	55.4	57.6
Pr	6.4	6.1	6.2	12	15	12	3.7	4.4	13.4	14.2
Nd	25.7	24.6	24.3	51	63	49	13.8	17.0	52.8	55.9
Sm	5.0	4.9	4.7	12	15	11	2.5	3.1	11.3	13.0
Eu	1.1	1.1	1.1	3	3	2	0.5	0.7	2.4	2.9
Gd	4.9	4.8	4.6	11	14	9.6	2.1	2.8	10.8	12.0
Tb	0.7	0.7	0.6	2	2	1	0.3	0.4	1.4	1.7
Dy	3.8	3.9	3.7	7.9	10	6.9	1.57	2.12	7.3	8.4
Ho	0.7	0.7	0.7	2	2	1	0.3	0.4	1.5	1.6
Er	1.9	1.9	1.8	5	6	4	0.8	1.1	4.3	4.5
Tm	0.3	0.3	0.2	1	1	0	0.1	0.1	0.6	0.6
Yb	1.4	1.4	1.3	4	5	3	0.6	0.9	3.9	4.1
Lu	0.2	0.2	0.2	1	1	0	0	0.1	0.6	0.6

Ap is the surface horizon and Bssg, Bssyg, and C4 are subsurface horizons. [unpublished soil data from the author of this manuscript].

Table 5.
Soil rare earth element abundances for soil (mg kg⁻¹) and water extract (µg kg⁻¹).

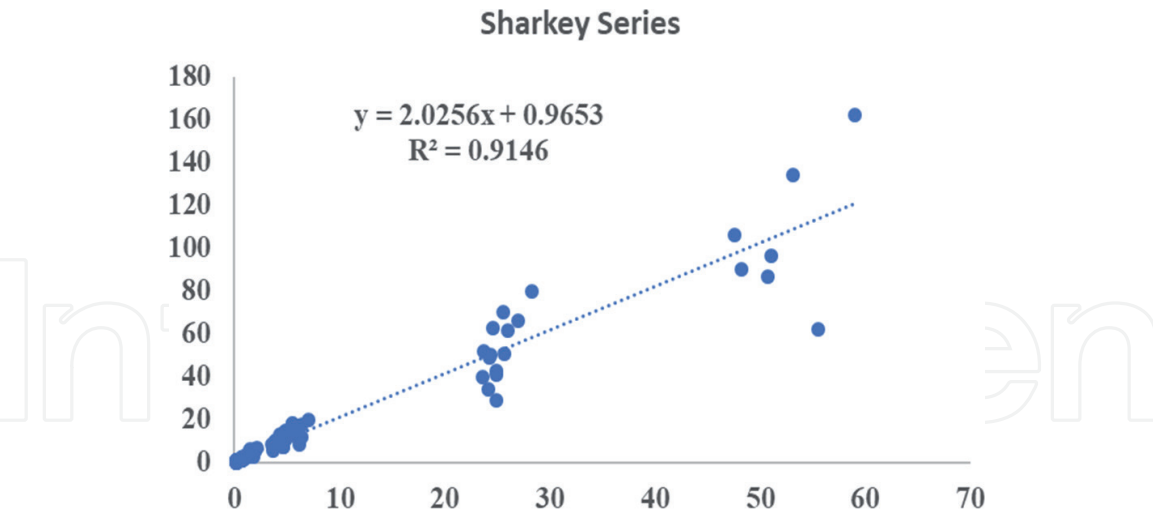


Figure 1.
The relationship between total rare earth element concentrations (x-axis with units of mg kg⁻¹) and water extractable rare earth element concentrations (y-axis with units of µg kg⁻¹) for the Sharkey soil series.

(Table 5). The REE distribution of the water extracts closely parallels the REE distribution of the aqua regia digestion distribution, inferring that (i) the REE release to water is influenced by the REE abundance regardless of atomic number and (ii) the water-absorbent partitioning is not strongly influenced by soil profile position (Figure 1).

The Kaintuck soil series in Missouri (coarse-loamy, siliceous, superactive, nonacid, mesic typic udifluvents) are very deep and well-drained floodplain soils formed from loamy alluvium and have an Ap-C horizon sequence. As with the Sharkey and Lilbourn

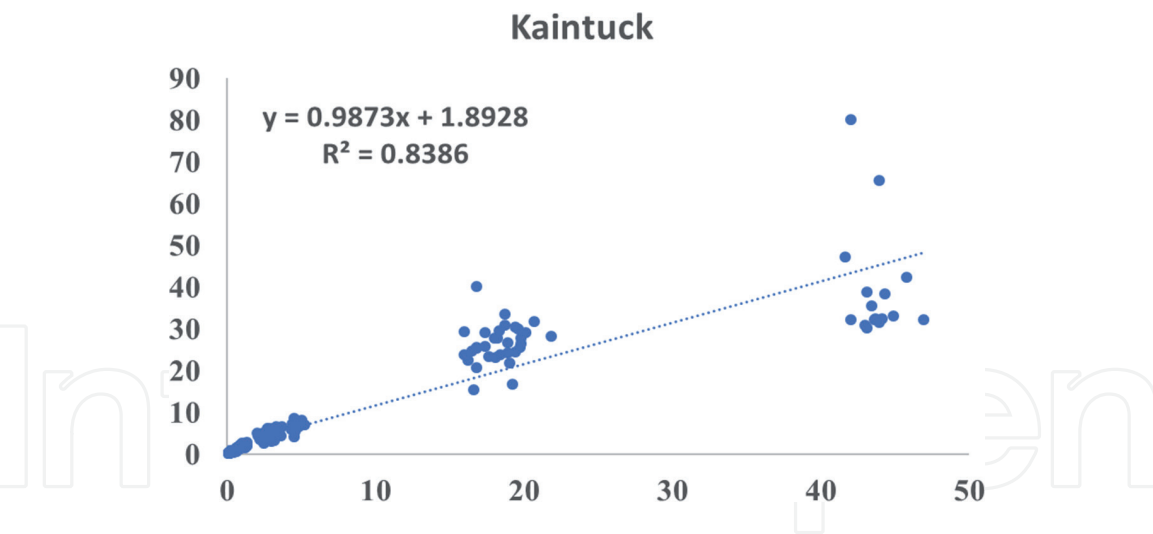


Figure 2.
The relationship between total rare earth element concentrations (x-axis with units of mg kg^{-1}) and water extractable rare earth element concentrations (y-axis with units of $\mu\text{g kg}^{-1}$) for the Kaintuck soil series.

	Ap	C1	C3	C5	C7	Ap	C1	C3	C5	C7
	Soil (mg kg^{-1})					Water ($\mu\text{g kg}^{-1}$)				
La	16.6	16.8	16.8	16.0	18.2	15.5	40.2	25.5	29.3	27.9
Ce	43.1	43.9	43.9	42.0	43.0	30.3	65.7	31.5	80.2	30.9
Pr	4.5	4.5	4.6	4.4	4.7	4.3	8.6	6.3	7.3	7.5
Nd	19.2	18.7	19.7	18.3	20.1	16.9	33.6	25.6	29.7	29.2
Sm	3.2	3.7	2.8	3.3	3.2	3.4	6.6	5.3	6.2	6.2
Eu	0.6	0.6	0.6	0.6	0.6	0.7	1.5	1.2	1.4	1.4
Gd	3.0	2.9	2.8	2.7	2.9	3.2	6.0	5.0	5.7	5.7
Tb	0.3	0.3	0.4	0.3	0.3	0.5	0.9	0.8	0.9	0.9
Dy	2.5	2.5	2.3	2.1	2.2	2.6	5.1	4.1	4.7	4.8
Ho	0.4	0.4	0.4	0.4	0.4	0.5	1.0	0.8	0.9	0.9
Er	1.2	1.3	1.2	1.1	1.2	1.5	3.0	2.2	2.5	2.5
Tm	0.1	0.1	0.1	0.1	0.1	0.2	0.4	0.3	0.3	0.3
Yb	0.9	1.0	0.9	0.8	0.8	1.3	2.6	1.8	2.1	2.0
Lu	0.1	0.1	0.1	0.1	0.1	0.3	0.5	0.3	0.3	0.3

Ap is the surface horizon and C1, C3, C5, and C7 are subsurface horizons. [unpublished soil data from the author of this manuscript].

Table 6.
Soil rare earth element abundances for the Kaintuck soil series (mg kg^{-1}) and associated water extract ($\mu\text{g kg}^{-1}$).

soil series, the release of REEs to the water is a function of REE abundance, regardless of atomic number. The regression slope for the Kaintuck soil series (Figure 2) is smaller than the corresponding Sharkey soil series (Figure 1), suggesting that the binding relationships involving REE release to water are slightly different (Table 6).

8. REE simulations involving inorganic and organic complexation

Background electrolyte concentrations were obtained from tile-drainage water at the David M. Barton Agriculture Research Center of Southeast Missouri State University. The background total elemental concentrations (mol kg-water^{-1})

Lanthanum speciation			
Species	pH 4	pH 6	pH 8
-log (activity) (% speciation at given pH)			
La ³⁺	7.02 (92.55%)	7.22 (60.62%)	8.50 (2%)
LaCl ²⁺	9.55 (0.15%)	9.75 (0.095%)	11.10
LaSO ₄ ⁺	7.75(0.01%)	10.66 (4.13%)	11.51 (0.34%)
LaNO ₃ ²⁺	9.86 (0.073%)	10.06 (0.047%)	11.32
LaH ₂ PO ₄ ²⁺	10.66 (0.012%)	10.93	14.09
LaHCO ₃ ²⁺	9.14 (0.389%)	7.52 (16.32%)	8.84 (0.63%)
LaCO ₃ ⁺	11.07	7.45 (12.84%)	6.78 (57.87%)
La(CO ₃) ₂ ⁻	—	9.85 (0.052%)	7.22 (21.22%)
LaOH ²⁺	—	10.03 (0.05%)	9.31 (0.21%)
FA ₂ -La ⁺	8.97 (0.35%)	7.74 (5.93%)	7.27 (17.74%)
Ytterbium speciation			
Species	pH 4	pH 6	pH 8
-log (activity) (% speciation at given pH)			
Yb ³⁺	10.36 (12.72%)	11.98 (0.31%)	14.31
YbCl ²⁺	13.01 (0.015%)	14.03	16.93
YbSO ₄ ⁺	11.18 (0.72%)	12.80 (0.017%)	14.91
Yb(SO ₄) ₂ ⁻¹	13.90	15.52	17.41
YbNO ₃ ²⁺	13.49	15.12	17.42
YbHPO ₄ ⁺	13.61	13.31	15.50
YbPO ₄	15.09	12.79 (0.016%)	12.98 (0.01%)
YbHCO ₃ ²⁺	12.28 (0.082%)	12.09 (0.14%)	14.45
YbCO ₃ ⁺	13.33	11.14 (0.79%)	11.50 (0.33%)
Yb(CO ₃) ₂ ⁻	18.62	12.62 (0.026%)	11.02 (0.99%)
YbOH ²⁺	13.60	13.22	13.55
FA ₂ -Yb ⁺	9.06 (86.44%)	9.00 (98.69%)	8.99 (98.66%)
Fulvic acid was set at 0.082 mg/L with estimated properties using the Stockholm Humic Model.			

Table 7.
La and Yb equilibria in a simulated natural water environment where La³⁺ or Yb³⁺ and their hydrolysis products are permitted speciation reactions with fulvic acid, carbonate, phosphate, sulfate, chloride, and nitrate complexes at three pH intervals and permitting precipitation of calcite, dolomite, and hydroxyapatite.

were (i) Ca²⁺ was 0.0032 mol kg⁻¹, (ii) CO₃ was 0.0079 mol kg⁻¹, (iii) Mg²⁺ was 0.0032 mol kg⁻¹, (iv) Na⁺ was 0.0025 mol kg⁻¹, (v) NH₄⁺ was 2.8 × 10⁻⁶ mol kg⁻¹, (vi) NO₃⁻ was 0.00032 mol kg⁻¹, (vii) PO₄ was 10⁻⁴ mol kg⁻¹, (viii) Cl⁻ was 10⁻³ mol kg⁻¹, (ix) DOC 4.16 × 10⁻⁶ mol kg⁻¹, (x) SO₄²⁻ was 10⁻⁴ mol kg⁻¹, (xi) La³⁺ was (when simulated) 3.1 × 10⁻⁷ mol kg⁻¹, and (xii) Yb³⁺ (when simulated) was 1.04 × 10⁻⁹ mol kg⁻¹. The ionic strength was 0.0158 mol kg⁻¹. In this simulation, hydroxyapatite, dolomite, and calcite were permitted to precipitate as finite solids. Lanthanum and ytterbium were simulated at pH 4, 6, and 8 to estimate hydrolysis, inorganic, and fulvic acid complexation. At pH 4, La³⁺ and LaHCO₃²⁺ are the dominant species (**Table 7**), whereas fulvic acid-La complex was estimated to be present at 0.35%. At pH 8, LaCO₃⁺ and La(CO₃)₂⁻ are the dominant species, with

REE	REE ³⁺	REE-phthalic	REE(OH) ²⁺	REE(CO ₃) ⁺	REE(CO ₃) ₂ ⁻
Percent of total REE					
La	0.99	18.8	0.20	48.28	31.25
Ce	0.51	—	0.31	52.49	45.82
Nd	0.22	10.90	0.19	37.67	50.93
Sm	0.12	3.97	0.23	31.39	64.24
Gd	0.14	3.83	0.27	30.29	64.90
Dy	0.06	1.22	0.21	20.10	78.31
Er	0.04	1.52	0.16	14.81	83.45
Yb	0.03	0.53	0.20	15.47	83.25

Concentration of phthalic acid (benzene-1,2-dicarboxylic acid) is 10⁻³ mol kg⁻¹. Total REE concentrations are 3.1 × 10⁻⁷ mol/kg.

Table 8.
REE complexation with phthalic acid at pH 8.3 in calcite-saturated water.

Species	Percent of species
Lanthanum	
Fulvic acid-La ⁺	5.6
LaCO ₃ ⁺	56.8
La(CO ₃) ₂ ⁻	35.8
Cerium	
Fulvic acid-Ce ⁺	2.9
CeCO ₃ ⁺	51.6
Ce(CO ₃) ₂ ⁻	43.9
Neodymium	
Fulvic acid-Nd ⁺	5.2
NdCO ₃ ⁺	40.7
Nd(CO ₃) ₂ ⁻	53.6
Samarium	
Fulvic acid-Sm ⁺	7.0
SmCO ₃ ⁺	30.9
Sm(CO ₃) ₂ ⁻	61.7
Gadolinium	
Fulvic acid-Gd ⁺	3.9
GdCO ₃ ⁺	30.8
Gd(CO ₃) ₂ ⁻	64.3
Dysprosium	
Fulvic acid-Dy ⁺	0.8
DyCO ₃ ⁺	20.6
Dy(CO ₃) ₂ ⁻	78.3
Erbium	
Fulvic Acid-Er ⁺	0.5
ErCO ₃ ⁺	15.3

Species	Percent of species
Er(CO ₃) ₂ ⁻	83.9
Ytterbium	
Fulvic acid-Yb ⁺	1.3
YbCO ₃ ⁺	15.7
Yb(CO ₃) ₂ ⁻	82.2

All rare earth element concentrations are initially set as 0.31×10^{-7} mol/kg. Ionic strength was estimated at 3.85×10^{-3} mol/L. Fulvic acid was set at 0.082 mg/L with estimated properties using the Stockholm Humic Model.

Table 9. Simulation of the partitioning of selected rare earth elements between carbonate complexes and fulvic acid in stream waters in equilibrium with ordered dolomite and hydroxyapatite.

the fulvic acid-La complex being estimated to be present at 17.7%. At pH 4, Yb³⁺ and fulvic acid-Yb are the dominant species (**Table 7**), with the fulvic acid-Yb complex showing 86% of the total Yb concentration. At pH 8, the fulvic acid-Yb complex was estimated to be present at 99% of the total Yb concentration.

The REEs were simulated in the presence of phthalic acid (10^{-3} mol kg⁻¹) at pH 8.3. In this simulation dolomite, calcite, and hydroxyapatite were permitted to precipitate (**Table 8**). The REE—phthalic acid complexes as a percentage of the total REE concentration—was greatest for La and declined with increasing atomic number. The REE concentrations of REE(CO₃)⁺ and REE(CO₃)₂⁻ were the most extensive species, with the concentration of REE(CO₃)⁺ declining with increasing atomic number and the concentration of REE(CO₃)₂⁻ increasing with atomic number.

The simulation of the REE partitioning between carbonate complexes and fulvic acid in stream waters in equilibrium with ordered dolomite and hydroxyapatite was performed (**Table 9**). The fulvic acid-REE complexes generally represented less than 10% of the total REE concentration. Conversely, the concentrations of REECO₃⁺ and REE(CO₃)₂⁻ declined and increased, respectively, on progression with increasing atomic number.

9. Evolution of REE studies and needs

Kautenburger et al. [45] demonstrated that (i) humic acid and (ii) humic acid with partially blocked phenolic OH and COOH groups supported different complex stability constants, showing that humic acids with a high concentration of strong binding sites can be responsible for increased REE mobility because of dissolved negatively charged metal-humate complexes. Marang et al. [46] investigated the competitive behavior of Cu and Ca on Eu binding with sedimentary humic acid. Copper²⁺ and Eu³⁺ were shown to exhibit direct competition with humic acid, whereas Ca²⁺ competition was indirect and attributed to simple electrostatic interactions. Sonke [47] evaluated complexation of river, coal, and soil humic acid binding of rare earth elements. Upon progression from La to Lu, the observed increase in complex stability is consistent with lanthanide contraction and supports the premise that organic matter outcompetes carbonate complexation, even in alkaline environments, and that REE fractionation in aquatic environments is common.

Aosai et al. [48] employed nanofiltration membranes to estimate organic colloids in deep groundwaters. Ramirez-Guinart et al. [49] observed soil sorption and desorption of Sm were predicated on the Sm concentration, with dilute Sm concentrations exhibiting higher sorption and reduced desorption. Sorption of Sm was influenced by

pH and soil organic matter solubility, and the soil phases of organic matter, presence of carbonates, and clay separated were important predictors of Sm mobility.

10. Future research needs

Our collective understanding of rare earth element activity in surface and groundwater requires a more fundamental examination of (i) REE partitioning within the aqueous phase, including complexation and adsorption reactions involving organic and inorganic colloids; (ii) partitioning involving REE in the aqueous phase and the surrounding solid phases constituting the river bed and aquifer skeleton; (iii) the influence of temperature, Eh (pe), pH, and ionic strength; and (iv) a greater and more accurate thermodynamic database of organic and inorganic species.

We also need a more significant database of rare earth element abundances in surface and groundwaters to gauge the extent of environmental impact and to serve as a reference for future REE environmental impact in water. Key areas of extensive groundwater and surface water across North and South America, Europe, Africa, and Asia have not received any preliminary documentation of their rare earth element composition.

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