



HAL
open science

Rare Earth Elements in wetlands

Mélanie Davranche, Gérard Gruau, Aline Dia, Martine Bouhnik-Le Coz, Remi Marsac, Mathieu Pédrot, Olivier Pourret

► **To cite this version:**

Mélanie Davranche, Gérard Gruau, Aline Dia, Martine Bouhnik-Le Coz, Remi Marsac, et al.. Rare Earth Elements in wetlands. Trace Elements in Waterlogged Soils and Sediments, Taylor & Francis Group/CRC Press, pp.135-162, 2017, 978-1-4822-4051-1. <10.1201/9781315372952-9>. <hal-02136493>

HAL Id: hal-02136493

<https://hal.science/hal-02136493v1>

Submitted on 22 May 2019

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization

Chapter 7 Rare Earth Elements in wetlands

Mélanie Davranche¹, Gérard Gruau¹, Aline Dia¹, Martine Le Coz-Bouhnik¹, Rémi Marsac², Mathieu Pédrot¹, Olivier Pourret³

¹: Géosciences Rennes UMR 6118, Université Rennes 1, CNRS, 35042 Rennes cedex, France

²: Institute of Technology, Institute for Nuclear Waste Disposal, D-76021 Karlsruhe, Germany

³: Institut Polytechnique LaSalle Beauvais, 19, rue Pierre Wagué, 60026 Beauvais Cedex - France

I. Introduction	1
II. Rare earth elements analysis	6
<i>II. 1. Analytical techniques</i>	6
II.1.1. Quadrupole-Inductively coupled plasma- mass spectrometer measurements: Q-ICP-MS	6
II. 1.2. High-resolution or sector field inductively coupled plasma mass spectrometer measurements: HR-ICP-MS or SF-ICP-MS	9
<i>II. 2. REE measurement in wetland soils, sediments and solution</i>	9
II. 2.1. Sample pre-treatment	9
II. 2.2. Separation and speciation of Rare Earth Elements	10
II. 2.2.1. Ultra filtration systems	11
II. 2.2.2. CE-ICP-MS	11
II. 2.2.3. SEC-ICP-MS and FFF-ICP-MS.	12
III. REE in waterlogged soil and sediments	12
<i>III. 1. REE signature of the solid fraction</i>	14
<i>III. 2. REE fingerprinting the paleoredoximorphic features in waterlogged soils</i>	15
IV. Biogeochemical factors controlling REE signature in wetlands waters	17
<i>IV. 1. Seasonal flooding and redox conditions</i>	18
<i>IV. 2. Colloidal control</i>	22
<i>IV. 3. Impact of biological parameters</i>	25
<i>IV. 4. Organic matter control</i>	26
V. REE as probes of water circulation pathways and trace element sources	30
V. REE impact on the human health and environment quality	36

I. Introduction

In the periodic table, rare earth elements represent a group of 15 elements, specifically the lanthanides (Table 7.1). They are often referred to as REE and share common physiochemical properties and therefore often occur together as elemental constituents of their host minerals.

Table 7.1 Yttrium and lanthanide (REE) symbols, atomic weight, and ionic radius for coordination number 6 (Shannon, 1976).

	symbol	Atomic Number (g mol ⁻¹)	Ionic radius (Å)
Yttrium	Y	88.9	0.9
lanthanum	La	138.9	1.03
cerium	Ce	140.1	1.01
praseodymium	Pr	140.9	0.99
neodymium	Nd	144.2	0.98
promethium	Pr		
smarium	Sm	150.4	0.96
europium	Eu	152	0.95
gadolinium	Ga	157.2	0.94
terbium	Tb	158.9	0.92
dysprosium	Dy	162.5	0.91
holmium	Ho	164.9	0.9
erbium	Er	167.3	0.89
terbium	Tb	168.9	0.88
ytterbium	Yb	173	0.87
Lutetium	Lu	175	0.86

The term “rare” is a carryover the metallurgical processes needed to isolate the individual metal species which are complex and low productive. As a result, lanthanide metals or metal oxides were difficult to obtain and are thus considered rare (Sonich-Mullin et al., 2013). Rare earth element form a coherent series of elements whose chemical properties display small but systematic changes with increasing atomic number. This chemical coherence is due to the gradual filling of their 4f electron shell. Because outer electrons (n = 5, 6) shield this inner shell, there are only minor differences in the chemical reactivity along the series (e.g., de Baar et al., 1991; McLennan, 1994). On the basis of their atomic number, REE are segregated into light (LREE) and heavy REE (HREE) with a division between Eu and Gd. Some authors distinguish middle REE (MREE) from Sm to Tb (e.g., Hannigan and Sholkovitch, 2001, Tang and

Johannesson 2003). This "weight" distinction is used to simplify the description and quantification of the inter-element relationship, typically ratios of normalized concentrations. Similarly, the anomalies of certain REE due to the Ce and Eu redox behavior, and the large anthropogenic emission of Gd are used to interpret geochemical processes.

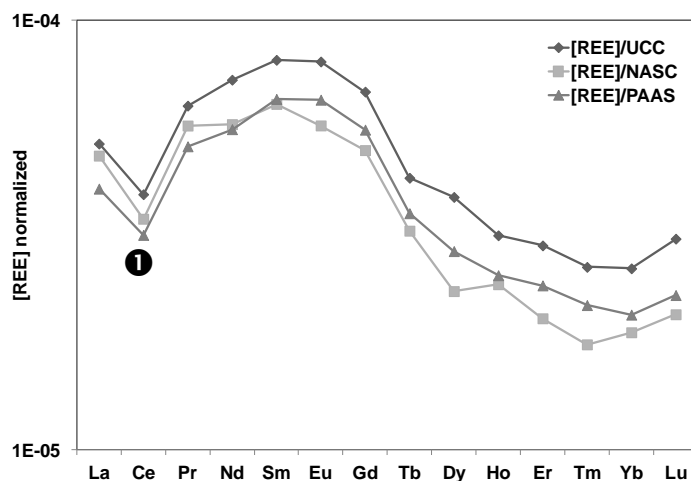


Figure 7.1 REE patterns normalized using the UCC, NASC and PAAS references. In **1**, a negative Ce anomaly is illustrated

In aquatic systems, with regards to their slight solubility, REE concentrations are low compared to their concentration in rocks. Numerous studies suggest that the solution and interface chemistry are the major controlling factors of the REE concentration in aquatic systems (Goldstein and Jacobsen, 1988; Elderfield et al., 1990; Sholkovitz, 1995). In solution, an important chemical property is that REE can form strong complexes with a number of different ligands. In general, REE³⁺ ions prefer the donor atoms in the following order O>N>S. The resulting chemical species tend to form mainly ionic bonds with REE within their unoccupied lower high-energy orbitals (Weber, 2008).

For the sake of convenience, the REE distribution in natural materials and water is usually illustrated by normalized REE patterns. Two geological reservoirs are used for the normalization, the upper continental crust and shales. The REE abundance is thereby normalized to the Post-Archean Australian Shale, PAAS (McLennan, 1989), North American shale composite, NASC (Gromet et al. 1984), or upper continental crust, UCC (Taylor et McLennan, 1985) (Table 7.1, Figure 7.1). A dominant systematic change is observed in the REE chemical properties, such as solution complexation, caused by the decrease in the ionic radius with an increasing atomic number. This change results in a systematic REE fractionation on the pattern called the "REE contraction". A normalized REE pattern allows for the recognition of an anomalous concentration for an individual REE as a positive or negative anomaly in an otherwise smooth pattern. This type of anomaly can occur in response to the redox behavior of Ce and Eu which can exist as a tetravalent or divalent state. Processes that convert Ce^{3+} to Ce^{4+} include biologically mediated oxidation (Moffett, 1990, 1994a, b) and abiotic oxidation on the surfaces of Mn oxides (Koeppenkastrop and De Carlo, 1992; Sholkovitz et al., 1994; Ohta and Kawabe, 2001). The reduction of Eu generally occurs at high temperatures and pressures, such as in hydrothermal fluids (e.g., Michard et al., 1983; German et al., 1990; Klinkhammer et al., 1994). The anomalous behaviors of Ce and Eu are quantified via Ce and Eu anomalies such as the Ce anomaly = $3Ce_N / (2La_N + 2Pr_N)$ or $2Ce_N / (La_N + Pr_N)$ and the Eu anomaly = $2Eu_N / (Sm_N + Gd_N)$ with N equal to the normalized abundance (Figure 7.1).

The REE pattern therefore results from the combination of several processes able to induce their fractionation. These processes are themselves controlled by several physicochemical mechanisms and parameters. In between, three processes can be distinguished: (i) precipitation/dissolution, (ii) sorption onto colloids and particles, and (iii) complexation in

solution with organic and inorganic ligands. The REE pattern therefore corresponds to the REE pattern for the mineral sources modified by the sorption/complexation constants of REE with ligands, colloids and particles. The result is highly diverse REE patterns that can be measured by a degree of depletion or enrichment relative to heavy REE (La/Yb or Sm/Yb ratios) or by whether or not anomalies are present.

Table 7.2 REE abundance in the various references used for the REE pattern normalization

	UCC		NASC		PAAS	
	ppm	μmol. L ⁻¹	ppm	μmol. L ⁻¹	ppm	μmol. L ⁻¹
La	30	216.0	32	230.4	38.2	275.0
Ce	64	456.8	73	521.0	79.6	568.1
Pr	7.1	50.4	7.9	56.1	8.83	62.7
Nd	26	180.3	33	228.8	33.9	235.0
Sm	4.5	29.9	5.7	37.9	5.55	36.9
Eu	0.88	5.8	1.24	8.2	1.08	7.1
Gd	3.8	24.2	5.2	33.1	4.66	29.6
Tb	0.64	4.0	0.85	5.3	0.774	4.9
Dy	3.5	21.5	5.8	35.7	4.68	28.8
Ho	0.8	4.9	1.04	6.3	0.991	6.0
Er	2.3	13.8	3.4	20.3	2.85	17.0
Tm	0.33	2.0	0.5	3.0	0.405	2.4
Yb	2.2	12.7	3.1	17.9	2.82	16.3
Lu	0.32	1.8	0.48	2.7	0.433	2.5

The coherent physicochemistry of REE allows their abundances and fractionation in rock to be used as a tracer and fingerprint for cosmochemical, geodynamic and petrogenetic processes (e.g., Henderson, 1984; Taylor and McLennan, 1985). The decrease in the quantification limit for REE analytical techniques such as ICP-MS also offers the opportunity for REE patterns to be used as a tracer for processes occurring in hydrosystems (ocean, surface and groundwater) (e.g. Goldberg et al., 1963; Elderfield and Greaves, 1982; De Baar et al., 1983; Byrne et Kim, 1990; German et al., 1991; Bau et al., 1997; Duncan and Shaw, 2004; Sholkovitz, 1993; Bau and Dulski, 1996; Dupré et al., 1996; Elbaz-Poulichet and Dupuy, 1999; Shiller et al., 2002; Fee et al., 1992; Möller and Bau, 1993; De Carlo and Green, 2002; Gammons et al., 2003; Johannesson

et al., 1995; 1996; 1997; Viers et al., 1997; Aubert et al., 2001; Janssen and Verweij, 2003). More specifically, REE fractionation patterns and abundances have been used to investigate the processes occurring in wetlands, such as the hydrology of the system, the mineral phases activated during water saturation, the trace element sources and the fine sorption processes occurring on wetland colloidal organic matter (Dia et al. 2000; Grybos et al. 2007, 2009; Pourret et al., 2007; 2010; Marsac et al., 2011; Davranche et al. 2011).

II. Rare earth elements analysis

II. 1. Analytical techniques

Rare earth elements are analyzed using several techniques such as NAA (neutron activation analysis) or TIMS (thermal ionization mass spectrometry). TIMS is a highly precise technique but this method requires laborious preparations. After acidic digestion, liquid column chromatography is used before analysis to separate REE from the solution. Since the 1990s, the development of ICP-MS (Inductively coupled plasma mass spectrometer) allows the direct determination of REE and thus became the most widely used technique. This method is used to introduce solutions with weak concentrations of REE while providing a low detection limit and is able to measure all REE simultaneously without any separation from the matrix.

II.1.1. Quadrupole-Inductively coupled plasma- mass spectrometer measurements: Q-ICP-MS

Ions produced in high temperature plasma are identified on the basis of the mass to charge ratio, m/z , which is characteristic of a given isotope. Each REE has at least one isotope that is free from isobaric overlap and the sensitivity is relatively uniform from ^{139}La to ^{175}Lu .

The major analytical problem encountered with Q-ICP-MS is the level of oxide formation in the plasma (Longerich et al., 1987; Jarvis et al., 1992) (Table 3). REE form a continuous group from

139 to 175 m/z, and the formation of light REE and barium oxide can produce significant middle REE interferences. In many cases, the LREE concentrations are higher than those for heavy REE, and the potential for interferences is increased. Refractory oxide ions are influenced by the plasma operating parameters. The oxide production level is close to 1 to 2%. The operating conditions are presented in Table 7.3. Mathematical corrections are required in order to suppress these spectroscopic interferences; these corrections are calculated as a function of the oxide level (Aries et al., 2000; Raut et al., 2005a, b). Previous studies have shown the importance of these corrections for accurate REE quantification. The choice of the measured isotopes and interferences that can be applied are summarized in Table 7.3.

Table 7.3 Preferred isotopes for REE analysis, isotopic abundance in %, oxides and hydroxides interference on analyte.

REE Element	Isotope Mass	Abundance (%)	oxide and hydroxide interferences
La	139	99.91	
Ce	140	88.48	
Pr	141	100	
Nd	146	17.19	
Sm	147-149	15	¹³⁰ BaOH
Eu	151-153	47.8-52.2	¹³⁵ BaO, ¹³⁷ BaO, ¹³⁶ BaOH,
Gd	157-158	15.65-24.84	¹⁴² CeO, ¹⁴² NdO, ¹⁴¹ PrO, ¹⁴¹ PrOH
Tb	159	100	¹⁴³ NdO
Dy	163	24.9	¹⁴⁷ SmO, ¹⁴⁶ NdOH,
Ho	165	100	¹⁴⁹ SmO
Er	166	33.6	¹⁵¹ EuO
Tm	169	100	
Yb	172-174	21.9-31.8	¹⁵⁷ GdOH
Lu	175	97.41	¹⁵⁹ TbO

Table 7.4 Instrument operating conditions

Plasma conditions	
RF Power	1450-1550W
Carrier Gas	15 L/min
Auxiliary argon flow	1 L/min
Nebulizer argon flow	0.9- 1.0 L/min
CeO ⁺ /Ce ⁺	1%
Ce ²⁺ /Ce ⁺	<2 %

Calibrations can usually be performed by using synthetic multi-elemental solutions prepared in

2% HNO₃. The quality of the blanks is fundamental because the level of concentrations for this technique is very low. Instrument drift is monitored and corrected by spiking each sample with an internal standard (In, Re, Rh, etc.) or by introducing it on-line using a peristaltic pump.

All of the experimental solutions used must be prepared with ultrapure analytical grade solution. Polyethylene and Teflon® vessels must have been previously decontaminated, and a clean room is recommended in order to obtain lower values for the blanks. The accurate and precise determination of the REE element concentration requires very low detection limits (DL). For the whole group of REE, the DL are typically between 0.01 and 0.1 ng mL⁻¹. These values are presented in Table 7.5.

Table 7.5 Detection limits in ng L⁻¹ (ppt), set values obtained on HP 7700x ICP-MS, calculated from the AFNOR standards and based on the blank measurement

Element	Isotope	Detection Limit (ppt)
La	139	0.15
Ce	140	0.14
Pr	141	0.06
Nd	146	0.16
Sm	147	0.23
Eu	153	0.10
Gd	157	0.22
Gd	158	0.13
Tb	159	0.04
Dy	163	0.17
Ho	165	0.05
Er	166	0.15
Tm	169	0.04
Yb	174	0.17

ICP-MS analysis normally includes three consecutive replicate measurements, producing a repeatability error less than 2%. To control the quality of the REE element measurements, certificated reference material is necessary. SLRS-4 followed by SLRS-5 standards (National Research Council –CNRC Canada) distributed without certificated values of REE can be used to analyze fresh water and soil solutions. Several studies have published REE concentrations (Yeghicheyan et al. 2002 and 2013; Lawrence et al., 2006; Heimburger et al., 2013). For peat

and organic material, no references are available, and therefore geological standards (USGS or NIST) and plant references (NIST1515, 1573a, etc.) are used (Ferrat et al., 2012).

II. 1.2. High-resolution or sector field inductively coupled plasma mass spectrometer measurements: HR-ICP-MS or SF-ICP-MS

HR-ICP-MS (high-resolution sector mass spectrometer) is more sensitive than Q-ICP-MS. This technique is used to analyze the REE concentration with high precision in aqueous samples. HR-ICP-MS is able to eliminate or reduce interferences due to mass overlap. Typically, HR-ICP-MS presents resolving powers for mass separation up to 10,000 and operates at preset resolution settings for low-, medium- or high-resolution.

To increase the precision of the REE measurements, a sample can be enriched with a pre-concentrated multi-spike REE solution, and the matrix can be removed using ion chromatography (Bakers et al., 2002; Rousseau et al., 2013). The level of the detection limit is very low, close to a pg L^{-1} (ppq) level.

II. 2. REE measurement in wetland soils, sediments and solution

II. 2.1. Sample pre-treatment

In water soil samples, the levels of the REE concentrations are close to the $\mu\text{g L}^{-1}$ to ng L^{-1} level (ppb to ppt). These solutions are rich in organic matter and Fe. Water samples must be collected and filtered using 0.22 μm or 0.45 μm filters (cellulose acetate membrane filters) that have previously been decontaminated. The water is sampled in acid-washed polyethylene bottles and is immediately acidified after filtration with ultrapure HNO_3 up to 2% to prevent iron oxide or hydroxide precipitation. Acidified samples are stored at 4°C. The level of dissolved organic carbon (DOC) must be controlled, as a high concentration affects the ICP-MS analysis. For a

high DOC concentration, the sample must be treated in order to eliminate the organic matter, after an acidic digestion with a mix of HNO_3 and H_2O_2 at 95°C on a hotplate or in a microwave furnace, and thus the sample is entirely solubilized.

In wetland soil and sediment samples, the levels of the REE concentrations are close to the mg kg^{-1} to $\mu\text{g kg}^{-1}$ (ppm to ppb) level. The organic-rich soil sample is dried at 20°C and then sieved at 2 mm. Dried soil samples (approximately 0.1-0.2g) are first digested in a HNO_3 and HF mixture in Teflon® containers using hot plate or microwave autoclave protocols. Then, two acidic digestions are needed to remove the excess of HF, and sometimes a H_2O_2 treatment is necessary. The dried residue is dissolved to a clear nitric acid solution (2%) for analysis. Finally, the sample is diluted by a factor ranging from 500 to 2000. The pre-treatment protocols are summarized in Figure 7.2.

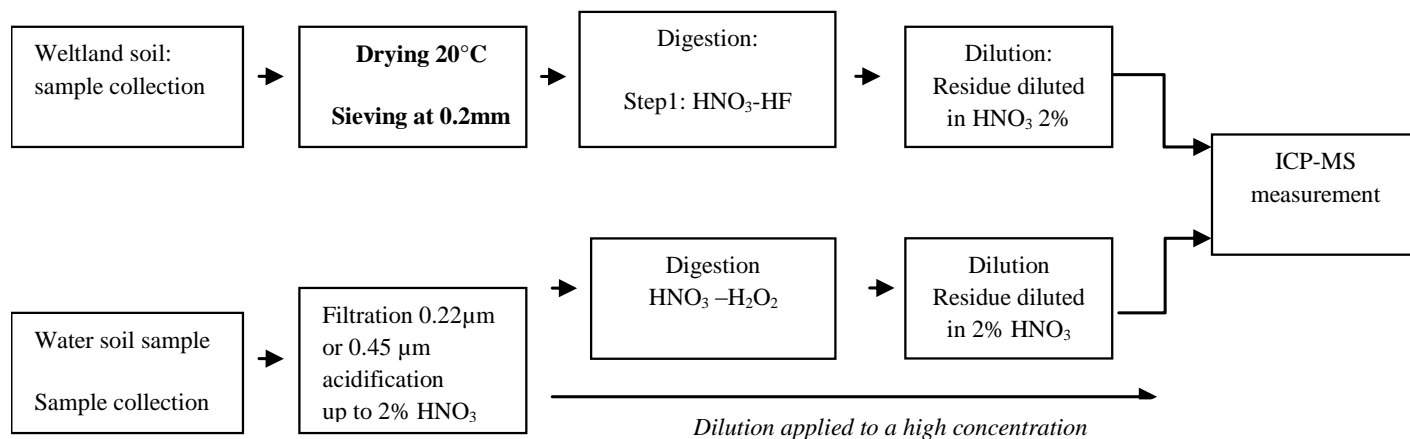


Figure 7.2 Pretreatment protocol for REE analysis in wetland soils and water soil samples

II. 2.2. Separation and speciation of Rare Earth Elements

REE concentrations in wetland solutions are strongly associated with dissolved and colloidal organic matter (e.g. Dia et al., 2000; Grybos et al., 2007, Pédrot et al., 2008). The reactive fraction of this soluble organic matter is mainly comprised of humic substances (Fulvic Acid and

Humic Acid), which are known to strongly bind metals and influence the sorption of trace metals onto the mineral surfaces (e.g. Avena and Koopal, 1998). It is therefore interesting to study and to precisely identify the distribution of REE in the different organic and inorganic fractions. Several technologies can be used to identify this distribution, such as capillary electrophoresis, field-flow fractionation and size exclusion coupled to ICP-MS or ultrafiltration systems.

II. 2.2.1. Ultra filtration systems

Ultrafiltration systems are used to study the control of organic-colloids on metal partitioning in water samples. To separate the colloidal bound elements from the non-colloidal elements, ultrafiltration experiments can be performed using centrifugal tubes at different molecular cut-off sizes (Amicon Ultra Millipore®, Vivaspin Sartorius®, Macrosep Pall®, etc.) equipped with permeable membranes of decreasing pore size ranging from 30-20-15-10-5-3 or 2 kDa, with $1 \text{ Da} = 1 \text{ g mol}^{-1}$. Each centrifugal filter device must be washed prior to use, in order to remove the glycerin protecting the membranes. Blank tests must be performed to determine possible contaminations (DOC and REE elements). The centrifugation speed is approximately 3000-4000 g; this is a function of the choice of ultrafiltration cells. The temperature must be controlled during centrifugation and the length of time is determined from the experiment.

According to the different cutoffs, REE-colloid complexes are retained by the ultrafiltration membrane while free ions and smaller complexes pass into the ultrafiltrate. The degree of metal-colloid complexation is usually determined from the metal concentration in the ultrafiltrate, relative to the original solution (e.g. Pourret et al., 2007; Pédrot et al., 2010; Vasuykovas et al., 2012).

II. 2.2.2. CE-ICP-MS

Capillary electrophoresis (CE) combined with inductively coupled plasma-mass spectrometry

(ICP-MS) is used as a speciation tool in order to investigate the complexation of humic acids with trivalent REE. CE separates the elements with a short separation time; ICP-MS has an excellent elemental selectivity with a high sensitivity. The main advantage of this speciation method is the simultaneous detection of metal that is either complexed and not by humic acid in only one analytical run. CE-ICP-MS studies are able to identify free and complexed HA-REE species and qualify the ligand effect (Sonke and Salters, 2005; Stern, 2007, Kautenburger, 2014).

II. 2.2.3. SEC-ICP-MS and FFF-ICP-MS.

SEC (size-exclusion chromatography) is usually used to separate natural organic matter over a column with a stationary phase using a porous gel material. The high molecular mass of the organic matter elutes first, followed by the smaller components. Coupled with UV detection and ICP-MS, SEC can be used to explore metal/organic matter complexation (Neubauer et al., 2013).

The FFF (field-flow fractionation) technique determines the continuous size distribution of colloids without the disadvantage of the stationary phase. It determines the size and REE-composition of the distinct types of colloids, information that usually cannot be acquired from standard ultrafiltration. FFF-ICP-MS is used to characterize REE-binding to colloids (Stolpe et al., 2012; Neubauer et al., 2013).

III. REE in waterlogged soil and sediments

Waterlogged soils and sediments are probably one of the most striking investigated surface environments involving the use of REE as efficient tracers of processes and/or matter sources.

Wetland and paddy soils are temporally or permanently flooded which involve the development of anoxic conditions and subsequent soil reduction. Both organic matter adsorption and Fe(III) oxyhydroxides reduction accompanying wetland soil flooding strongly control the mobility,

transfer and fate of REE in wetlands. (e.g. Grybos et al., 2007, 2009). Thereby, specific REE patterns that are displayed within these environments are related to the sources, but also to the prevailing reduction processes and associated organic matter and Fe dynamics.

Mihajlovic et al. (2014) who studied the REE distribution in wetland soil profile (Eutric Fluvisols, at the Wupper River, Germany) found very small differences between the total REE concentration and distribution between the different horizons as evidenced in Figure 7.3. Total REE concentrations and indicators of REE pattern fractionation (Eu/Eu^* , Ce/Ce^* , La/Yb ratio) do not evolve significantly. They explained these so small differences by the wetland soil flooding and the subsequent homogenization processes.

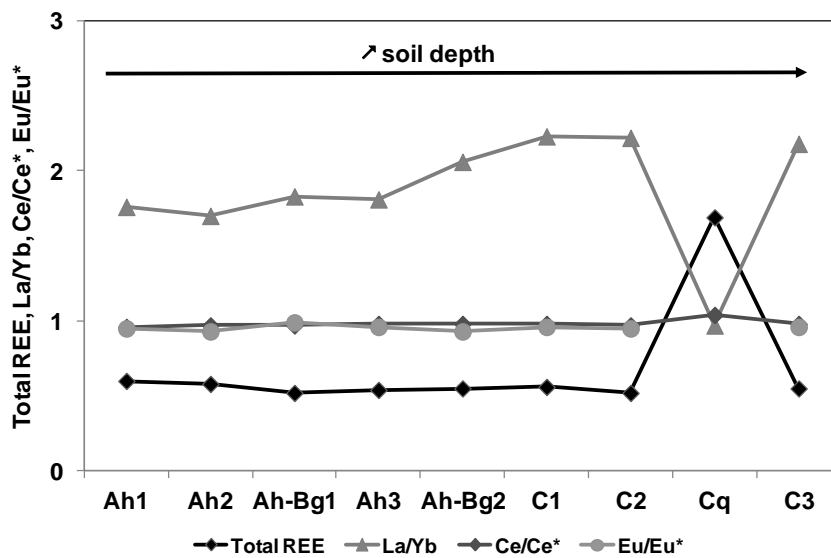


Figure 7.3 Evolution of the total REE concentration, La_{UCC}/Yb_{UCC} , Eu/Eu^* and Ce/Ce^* relative to the different soil horizons (Ah1, Ah2, Ah3, Ah-Bg, C1, C2, Cq, C, WRB classification) in Eutric Fluvisols, at the Wupper River, Germany (Mihajlovic et al., 2014).

Sequential extractions that are performed on soils wetland generally show -whatever the protocol- that REE dominate in the residual fraction, followed by the reducible and the oxidizable fraction, the exchangeable fraction being very low (Leybourne and Johannesson, 2008; Pédrot et al., 2008; Davranche et al., 2011; Mihajlovic et al., 2014).

III. 1. REE signature of the solid fraction

The REE patterns displayed by wetland soils or floodplain sediments could provide a large amount of information. The REE patterns of floodplain sediments taken from the Kaveri River basin (southern India) were discussed in terms of the REE behavior during sedimentary processes and as provenance tracers (Singh and Rajamani, 2001). As reported elsewhere (McLennan, 1989; Morey and Setterholm, 1997; Vital and Stattegger, 2000), this study clearly pointed out that fluvial sorting processes affect the REE distribution in the sediments. This type of physical sorting by fluvial processes could result in the accumulation of various minerals that are possibly enriched in REE. As a consequence, a REE-mediated provenance assessment study should be undertaken with sediments characterized by similar granulometric grades, because they would more closely reflect the source area (Singh and Rajamani, 2000). However, it should also be considered that a large amount of REE could be also present as surface coatings on grains in addition to those occurring within heavy minerals and clay minerals.

Paddy fields are usually distributed in flood plains along rivers and associated tributaries and valley floor plains incised by small rivers (Egashira et al., 1997; 2004), such as those occurring in the Mekong River. The REE content and associated patterns were studied, as well as the particle-size distribution and clay mineralogical composition, to estimate both the origin and fertility potentiality of the soil materials (Figure 7.4) (Egashira et al., 1997; Singh and Rajamani, 2000). The various REE patterns displayed in the paddy field samples along the Mekong River were divided into two groups establishing that the material origin was controlled by local composite materials and sediment carried by the Mekong River. This division was (i) confirmed through a mineralogical survey establishing differences in the origin and genesis of the soils, notably between the upper and lower areas, (ii) compared with indicators of soil potentiality such

as the exchangeable Ca or organic C content. However, conversely to samples recovered along the Mekong River (Egashira et al., 1997), unambiguously use of REE patterns was not possible to assess **the t soil** origins in floodplains of the Brahmaputra, Meghna and Ganges rivers in Bangladesh (Egashira et al., 2004). It is of prime importance to remember that whereas the REE composition in soils has mostly been considered as being inherited from the parent rock (Taylor and McLennan, 1984), given the low solubility and relative immobility of REE in the upper Earth's crust, the environmental parameters and processes involved in soil formation cannot be neglected nor can the anthropogenic inputs (e.g. manure, phosphate fertilizers or waste effluents...) (Tsumura and Yamasaki, 1993; Yuan et al., 2001; Protano and Riccobono, 2002).

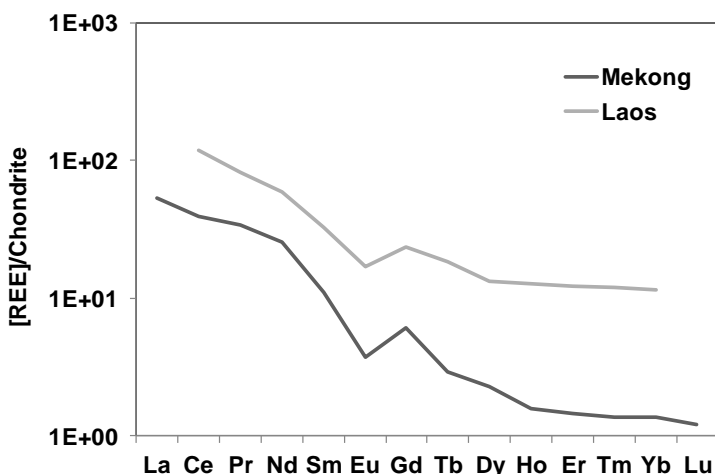


Figure 7.4 Chondrite-normalized REE patterns of a soil recovered in a low land of the Mekong River floodplain in Laos (Egashira et al., 1997) and a sediment collected in the floodplain of the Kaveri River basin in southern India (Singh and Rajamani, 2001).

III. 2. REE fingerprinting the paleoredoximorphic features in waterlogged soils

Wetlands and paddy soils are at the heart of alternating redox processes induced by waterlogging associated with the occurrence of large amounts of organic matter responsible for leaching, Fe-oxide dissolution or precipitation as oxide coatings, concretions or amorphous organo-mineral

colloidal phases.

Since both REE are strongly associated with Fe- and Mn-oxides and their fractionation is related to the drainage conditions, they are particularly interesting with regards to tracing the redox conditions, especially when considering Ce and Eu. However, all Eu fractionation must be precluded in the soils since the required reducing conditions that result in Eu reduction are far from the conditions possibly encountered within the soils (Bonnot-Courtois, 1981; Henderson, 1984; Panahi et al., 2000). By contrast, if the Eu anomaly cannot trace any redox processes occurring within the soils, the oxidation of Ce(III) to Ce(IV) can take place in soils, as previously established through field observations and experiments (Takahashi et al., 2000). This process results in the precipitation of the so-called cerianite (CeO_2) coupled with the reduction of Mn(IV) to Mn(III) on the surface of the Mn oxides (Ran and Liu, 1992; Bau, 1999; Ohta and Kawabe, 2001). Oxidative conditions allow for new Fe and Mn oxide precipitation preferentially incorporating Ce over REE, leading to the development of a positive Ce anomaly. Conversely, when reducing conditions prevail, notably during podzolisation, Fe-oxides are reduced by organic matter and Fe can be transferred within the organic complex, and then possibly precipitated again as ferrihydrite (Schwertmann and Fisher, 1973; Buurman and Jongmans, 2005; Sauer et al., 2007; Laveuf and Cornu, 2009). The newly precipitated Fe-rich phases might be enriched in HREE with regards to LREE, in response to the observed preferential transfer of HREE as organic complexes, but might also be enriched in MREE when the newly formed phases remain amorphous (Aubert et al., 2004). The dissolution of the Fe and Mn oxides, which releases all REE except Ce bound to cerianite, the dissolution of which is more dependent on pH than Eh, results in the persistence of the Ce anomaly, whereas Fe and Mn oxides disappear as shown by Koppi et al. (1996) in clayey areas bleached by flooding and drainage - and subsequent

degradation - in northern Australia. The Cerium anomaly resulting from cerianite precipitation could trace the redox processes (Koppi et al., 1996), keeping in mind that the relative contribution to the mobilization of REE that is made through redox conditions by primary minerals depends on both their initial proportion in the different pedological features possibly related to different redox processes, their relative mobilization during the redox process of concern, and their initial REE signatures (Laveuf et al., 2012).

IV. Biogeochemical factors controlling REE signature in wetlands waters

One of the critical questions concerning REE behavior in wetlands is whether REE concentrations are controlled by the sources or the physico-chemistry. Besides the specific characteristics of a specific site, it seems reasonable to state that the REE dynamics in the water–soil system depends on: (i) the fractionation characteristics of the host rock/sediment, (ii) the weathering process that might improve the dissolution of a mineral that is either depleted or enriched in REE, (iii) the water physicochemical characteristics (pH, Eh, organic and inorganic ligands, colloids/particles) and (iv) the water hydrodynamics. A systematic evolution in the REE pattern is thereby observed between the wetland soil/sediments and the soil solution or shallow groundwater. This evolution indicates that soil cannot be the one single factor controlling REE dynamics in wetland solutions (Figure 7.5). Several chemical and physical parameters either combined or not, have been advanced to explain this discrepancy.

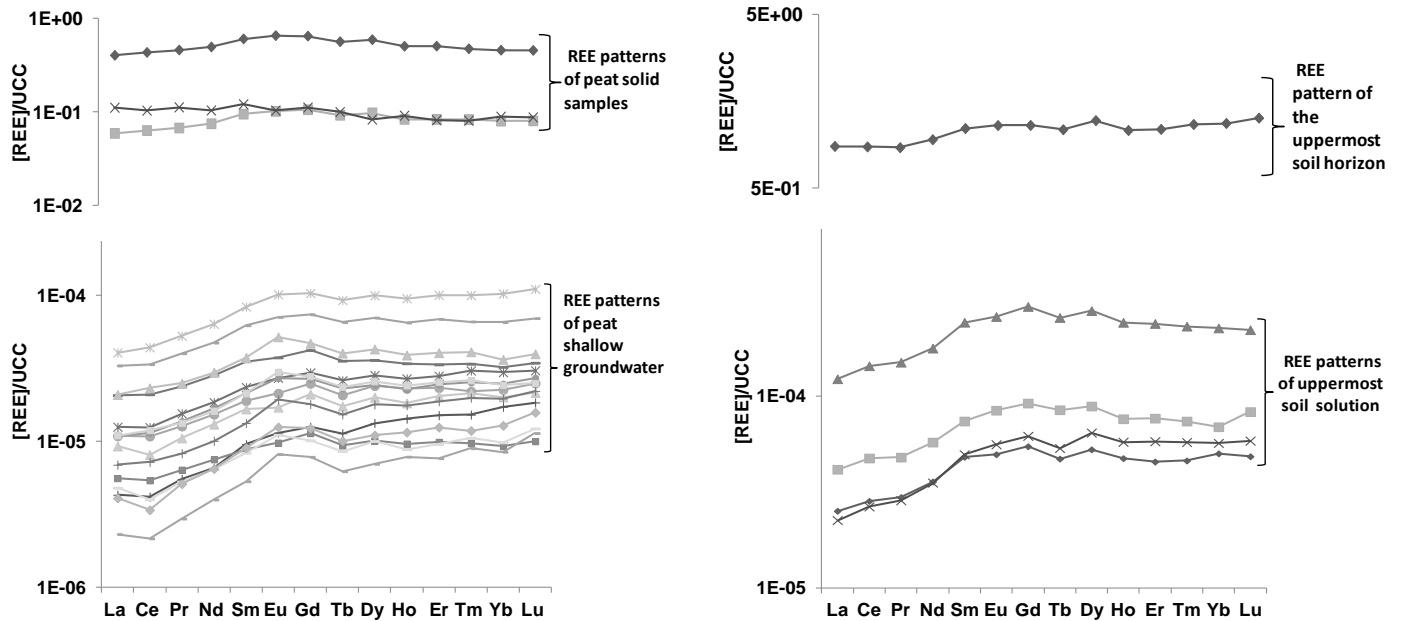


Figure 7.5 (a) REE patterns for a solid peat sample and peat solutions from the Cotentin marshland (France) (Auterives, 2007). (b) REE pattern for the uppermost soil horizon and its soil solution at various sampling dates from the riparian Le Home wetland (Brittany, France) (modified from Gruau et al., 2004). The peat and soil REE patterns are flat whereas the peat and wetland soil solution patterns exhibit a LREE depletion significant of a REE fractionation during their solubilization.

IV. 1. Seasonal flooding and redox conditions

In wetlands, redox conditions and their alternations are the main factors accounting for REE solubilization and mobilization in the environment. Many authors have therefore considered Mn and Fe-oxides reducing dissolution/precipitation as a major parameter controlling trace metal mobility in wetland soils (Charlatchka and Cambier, 2000; Chuan et al., 1996; Davranche et al., 2003; Francis & Dodge, 1990; Green et al., 2003; Quantin et al., 2001; Quantin et al., 2002). However, in the case of REE, Fe and Mn-oxides seem to just act indirectly. The gradual establishment of reducing conditions in wetlands results in the release of metals, either redox-sensitive or not, such as Fe or Mn, and Pb, Cd, etc. as well as a large concentration of dissolved/colloidal organic matter (fraction < 0.45 or 0.2 μm). Several studies report positive

correlations between Mn(II) and Fe(II) concentrations in wetland soil solutions and dissolved organic matter (DOC) (Hagedorn et al., 2000; Olivie-Lauquet et al., 2001; Gruau et al., 2004). Grybos et al. (2009) demonstrated that organic matter is mainly released as humic substances desorbed from soil minerals in response to the rise in pH caused by the reduction reactions (H^+ consumption). They also reported that the colloidal fraction of this organic matter strongly bound a large range of metals including REE. They experimentally demonstrated that the REE speciation was entirely dominated by their binding with the dissolved/colloidal organic fraction of the soil solution. This strong binding of REE by organic matter has been confirmed by several field, experimental and modeling studies (Tang and Johannesson, 2003, Sonke and Salters, 2006; Pourret et al., 2007a-b, Stern et al., 2007; Pédrot et al., 2008, Kerr et al., 2008; Marsac et al., 2011). Using REE patterns as a tracer for REE sources in wetland soil, Davranche et al. (2011) demonstrated that soil organic matter was the main source of REE and trace metals during wetland soil reduction. Iron was mainly present in the soil as amorphous Fe(III)-nanoparticles, which are poor in REE and trace elements, embedded within the organic matter. Therefore, in permanently or temporarily flooded wetlands, the establishment of reducing conditions produces an increase in pH (H^+ consumption by reductive reactions) which is responsible for the desorption of soil organic matter from the solid phases. This organic matter is solubilized with its metal loading constituted notably with REE (Grybos et al., 2007; Pourret et al., 2007; Pédrot et al., 2008; Shiller et al., 2010). During the flood period, REE are thus solubilized and transported to the hydrosystem mainly as organic colloidal phases. The flood period constitutes the major input of REE into hydrosystems. Shiller (2010) calculated that reducing conditions resulting from the spring flood of soil near the Loch Vale (Colorado, USA) led to an 8-fold increase in all REE concentrations. In the Amazon River main stream and its major tributaries surrounded by

many floodplains, the highest concentrations of REE are reported in winter during water saturation and when reducing conditions are established (Barroux et al., 2006). Tachikawa et al., (2003) calculated that during the high water season, the maximum Nd flux measurement is $1,277 \text{ t yr}^{-1}$, constituting 30% of the required flux to the Atlantic Ocean. Shiller (2010) suggests that the seasonal flooding of wetlands may be an important regulator of REE concentrations in hydrosystems.

Under oxidizing conditions, in the low water season, the exported flux of REE is low and mainly controlled by the dynamics of the soil organic matter. Pourret et al. (2010) showed that REE speciation is controlled by colloidal organic matter present in wetland soil solution even under oxidizing conditions. In the same way, Dia et al. (2000) did not observe any significant evolution in the REE patterns in shallow groundwater from the Naizin wetland (Brittany, France) between periods of oxidized and reduced conditions. Figure 7.5 shows that Eh decreases and the Fe concentration increases in solution subsequent to the reductive solubilization of Fe(III). The establishment of the moderately reducing condition caused a rise in the dissolved REE concentration but without any drastic modification of the REE pattern (Figure 7.6). The speciation of REE in the shallow groundwater was therefore not significantly modified between the oxidized and reduced periods. Thus, REE are bound to the dissolved/colloidal organic matter present in the soil solution and shallow groundwater under oxidizing and reducing conditions

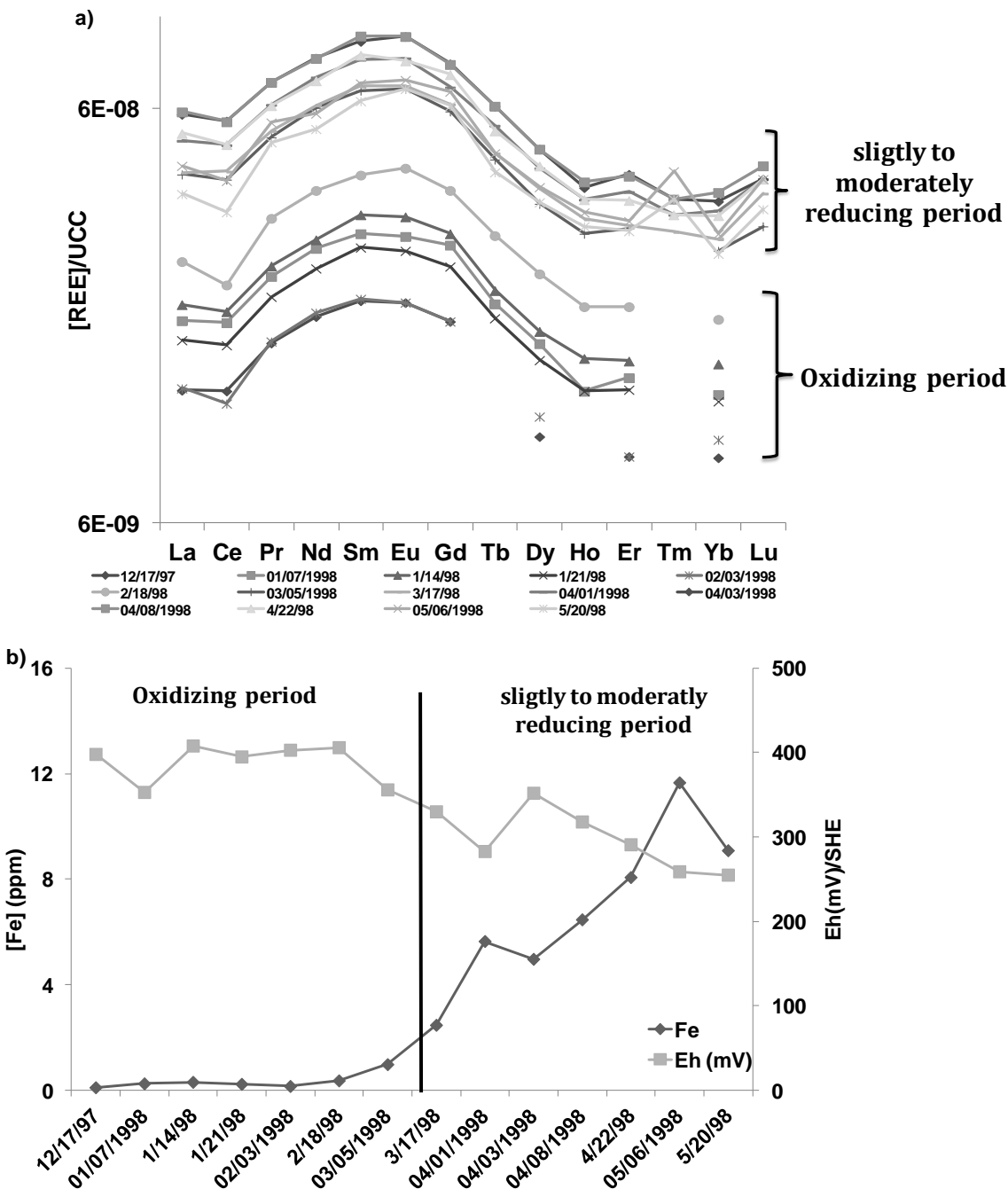


Figure 7.6 (a) Evolution of the REE pattern relative to time in shallow groundwater from the Naizin wetland (Brittany, France), (b) Evolution of the Eh and Fe concentration indicating the establishment of moderately reducing conditions and the reductive dissolution of soil Fe oxides (Dia et al., 2000). Although the redox conditions became moderately reduced, the REE pattern was not significantly modified suggesting no drastic change in the REE speciation.

IV. 2. Colloidal control

In wetland soil solution or shallow groundwater surrounded by wetlands, REE are closely associated with colloids. Studies performed on surface water that drains wetlands, wetland solution or shallow wetland groundwater from various type of boreal, tropical, Mediterranean or temperate wetlands, used an ultrafiltration analysis and various pore sizes to demonstrate that REE are mainly concentrated in the high molecular weight fraction, namely bound to the colloid phases (Viers et al., 1997; Dia et al., 2000; Tang and Johannesson 2003; Pourret al., 2007, Pédrot et al., 2008; Cidu et al., 2012; Vasyukova et al., 2012; Neubauer et al., 2013). If colloids are regarded as the main transfer and binding phases of REE in wetland solutions and waters, there is no real consensus on the nature of the REE carrier phases in the colloids themselves. The iron and organic matter phases are the major components of the colloids encountered and formed within wetlands or waterlogged soils. The term wetland covers a large diversity of areas that are subject to various hydrodynamic and climatic conditions which drastically influence the nature of the colloids released in solution. Andersson et al. (2006) demonstrated that in subarctic boreal rivers, draining organic-rich soils, two different REE colloid phases can be distinguished. During the sole spring flood, subsequent to soil saturation, small organic-rich colloids (~3 nm) are released. By contrast, large Fe-rich colloids (~12 nm) are formed during the winter and spring floods. Rare earth elements are bound to both C-rich and F-rich colloids. However, the amount of released REE is higher during the spring flood when organic-rich colloids are present. Moreover, the subsequent LREE-enriched REE pattern suggests that REE are released with the organic-rich colloids found in the litter of the organic-rich topsoil. In a temperate climate, in swamp water, speciation modeling and the voltammetric titrations all indicate that dissolved REE in the Great Dismal Swamp water are controlled by the REE complexation with natural

organic matter (Johannesson et al. 2004). Neubauer et al. (2013) applied Flow Field-Flow Fractionation analyses (FlowFFF) to water sampled in a small stream draining an unpolluted wetland (Tanner Moor) in Upper Austria to study the REE colloidal distribution. They showed that the REE size distribution corresponds to that of organic matter, namely that REE are bound to organic-rich colloids. Several authors, who studied temperate wetlands that are temporarily flooded from autumn until spring, have reached the same conclusions although they used different analyses or experimental methods (Pourret et al., 2007; Davranche et al., 2012). The controlling parameters for the REE distribution between organic and Fe-rich colloids probably does not account for climate or redox conditions. The same organic colloidal binding was demonstrated to dominate REE speciation in a humid tropical watershed in Cameroon (Viers et al., 1997; Braun et al., 1998). Pédrot et al. (2008), who performed leaching experiments on wetland soils under an oxidizing condition, provided evidence that REE speciation is dominated by their binding with organic colloids, such as under reducing conditions (Grybos et al., 2007). By contrast, it has been shown that REE patterns and therefore speciation in shallow groundwater along a catchment transect is strongly related to topography (Dia et al., 2000; Gruau et al., 2004; Pourret et al., 2010). These studies demonstrated that REE are mainly bound to colloids which are Fe enriched in the top of the catchment and organic-enriched in the bottom of the catchment where riparian wetlands are encountered (Pourret et al., 2010). The major feature of this evolution in the REE patterns is the decrease in the Ce anomaly with the topography. Pédrot et al. (2015) observed that this spatial variation is strongly correlated with the soil organic carbon/Fe ratio. They observed that for a low organic carbon/Fe ratio, the negative Ce anomaly amplitude in the soil solution is high, whereas for a high organic carbon/Fe ratio, the negative Ce anomaly is small or insignificant. They showed that REE pattern for soil Fe oxyhydroxides

exhibited a positive Ce anomaly and HREE enrichment, indicating that in the upland, the REE signature may be sourced in the Fe-oxyhydroxides in the upper soil horizons. Iron oxides are, indeed, able to present this positive Ce anomaly with regards to their capacity to oxidize Ce(III) in Ce(VI) and preferentially trap Ce(IV) compared to the other REE(III) (Bau, 1999; Davranche et al., 2005). By contrast, in soil with a high organic carbon/Fe ratio, the REE patterns obtained under reducing conditions did not exhibit any Ce anomaly suggesting that in the bottomland, the REE signature is sourced in the organic carbon in the uppermost soil which is solubilized as organic colloids in the wetland soil solution. These mechanisms are summarized in Figure 7.7. Therefore in wetlands, the patterns, speciation and transfer of REE are mainly controlled by colloids. The composition of these colloids (organic or Fe-rich) is dependent on the wetland soil composition, and on the mechanisms that themselves control the formation and transfer of colloids in solution such as, for instance, hydrodynamic conditions.

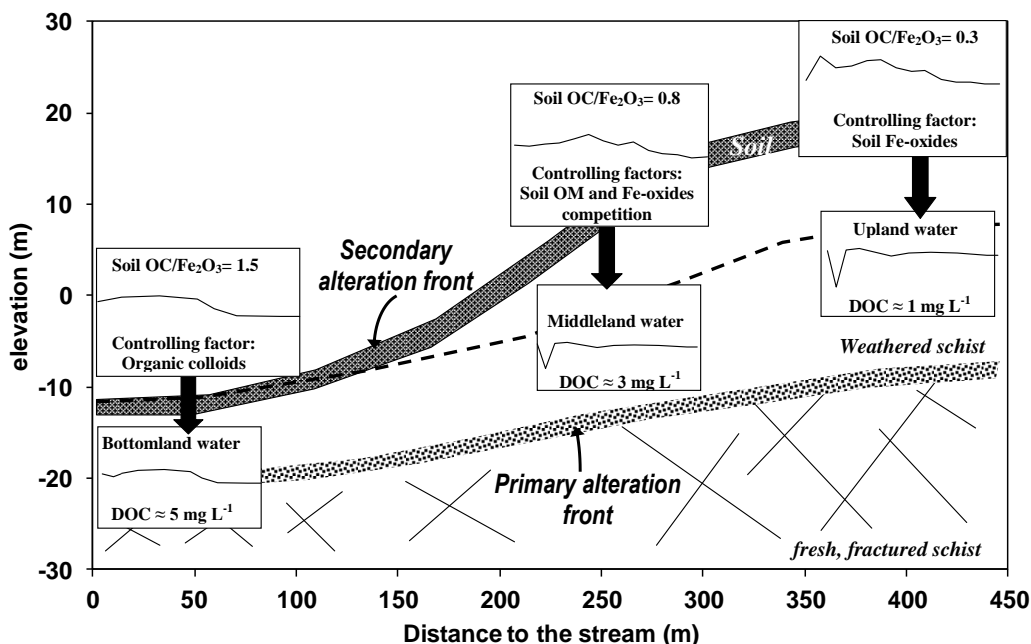


Figure 7.7 Sketch summarizing the processes responsible for the topography-related REE pattern in a theoretical catchment. In the top of the catchment, a negative Ce anomaly in the

shallow groundwater is sourced in the presence of Fe-oxide in the uppermost soil although the REE pattern is controlled by the solubilization of organic colloids in the bottomland occupied by riparian wetlands.

IV. 3. Impact of biological parameters

Biological parameters could potentially influence the REE distribution in wetland waters through direct and indirect mechanisms. Several authors have demonstrated the ability of the bacterial cell surface to bind REE (Takahashi et al., 2005; 2010; Ngwenya et al., 2009; 2010). The resulting REE pattern exhibits a tetrad effect and a prominent enrichment in HREE (from Er to Lu). Based on EXAFS evidence and modeling calculations, this shape was further attributed to the binding of REE as inner sphere complexes with carboxylic and multiple phosphate sites occurring on the surface cells (Takahashi et al., 2010; Ngwenya et al., 2010; Martinez et al., 2014). Simpson et al. (2007) suggested that bacterially derived biomass could constitute more than 50 % of the total soil organic carbon in aerobic soils. However, in wetlands, with regards to the temporary or permanent saturation of the soil, the bacterial activity is low, the nitrate respiratory or Mn and Fe reduction is less energetic compared to the O₂ respiratory in soil where aerobic conditions prevailed. A direct consequence is that organic molecules are transformed into humic substances rather than been degraded. The proportion of bacterial biomass as compared to humic ligand is therefore potentially lower than 50%. Moreover, bacteria and cells residues have also to compete with the soil organic ligand present in high amounts for REE binding. Therefore, it is unlikely that REE binding by bacterial cells could account significantly for the REE pattern and distribution. Another mechanism that can be inferred in the REE behavior in wetlands is the mechanism used by plants. The absorption of REE by plants is low (Lima e Cunha et al., 2012). The REE concentration varied from 1 to 500 ppm depending on the

plant species, organs and soil concentration. However, the internal processes of plants can fractionate the REE (Ding et al., 2006; Lima e Cunha et al., 2009). For example, Ding et al. (2006) observed MREE enrichment in the roots and MREE and HREE enrichment in the leaves. These results suggest that the REE patterns observed in the wetland solution could potentially be inherited from their fractionation in wetland plants. However, further studies need to be carried out in order to confirm or dispel this hypothesis.

Therefore, the major biological mechanism that seems account significantly for the behavior and distribution of REE in wetlands is the indirect bioreduction of Mn(IV) and Fe(III) which is mediated by the bacteria consortium occurring in wetlands. The saturation of wetland soil with water promotes the use of Mn and Fe oxides as the e- acceptor by the bacteria for their growth. This reduction involves the concomitant dissolution of Mn and Fe oxides and the rise in pH which is responsible for the release of REE in solution.

IV. 4. Organic matter control

In wetland soil solution or shallow groundwater, REE are mainly associated with organic colloids. However, two types of REE patterns are generally observed, a MREE downward concavity (Figure 7.8a) and a HREE enrichment (Figure 7.8b). Pourret et al. (2007) experimentally demonstrated that the distribution coefficient (K_d) between REE and humic acid (HA) increases for MREE at $\text{pH} < 7$ and at high REE concentrations with respect to HA (figure 8a). Between pH values from 6 to 9 and with a low REE concentration in regards to HA, Sonke and Salters (2006) observed a regular increase from La to Lu, i.e. a “lanthanide contraction” (Figures 7.8b). Marsac et al. (2010, 2011) demonstrated that this discrepancy between both kinds of REE patterns is explained by the combined effect of the metal loading and the surface

heterogeneity of HA. At low loading, REE are complexed to strong but less abundant HA sites, namely phenolic and/or multidendate sites. The resulting REE pattern exhibits a lanthanide contraction. By contrast at high metal loading, REE are complexed to weak but more abundant HA sites, the carboxylic group. The resulting REE pattern exhibits a MREE downward concavity.

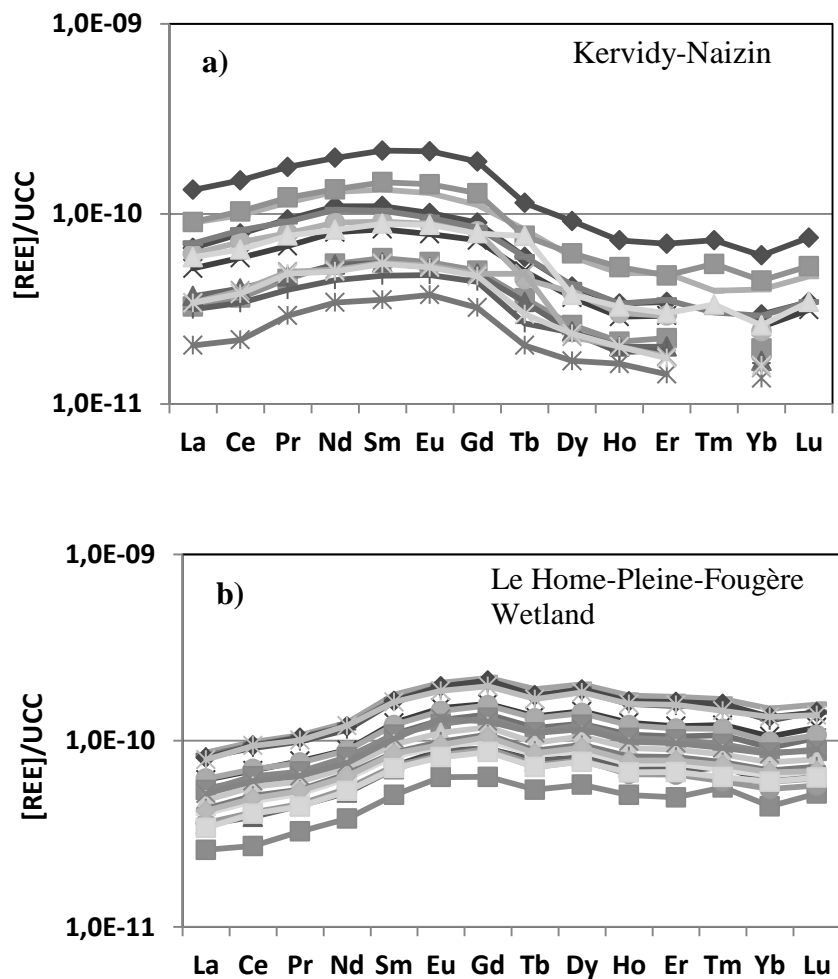


Figure 7.8 REE patterns in the dissolved fraction ($< 0.2 \mu\text{m}$) of the organic-rich shallow groundwater from the (a) Kervidy Naizin wetland (France) ($\text{DOC} \approx 15 \text{ ppm}$) and (b) The Le Home-Pleine Fougère wetland (France) ($\text{DOC} \approx 27 \text{ ppm}$). Both REE patterns are different although the modeling calculations using Model VI and ultrafiltration analysis showed that REE are bound to colloidal organic matter at around 90% (Gruau et al., 2004; Pourret et al., 2007).

Humic acids can be regarded as a group of discrete sites. It is thus possible to compare HA binding properties with the binding properties of organic ligand models. The REE pattern corresponding to the binding of REE with acetate (carboxylic group) exhibits a MREE downward concavity whereas catechol and NTA (phenolic and chelate group) exhibit a lanthanide contraction effect corresponding to both REE-HA patterns obtained respectively at high and low metal loadings (Figures 7.8 and 7.9). Figure 7.9d plots the evolution of the $\log(K_{Lu-organic\ ligand} / K_{La-organic\ ligand})$ relative to the average $\log K_{REE-organic\ ligand}$ for the 101 organic ligands compiled by Byrne and Li (1995). This figure shows that when the ligand is stronger, HREE are more strongly bound to the ligand compared to LREE. This result is supported by infra-red spectroscopy findings demonstrating that HREE, compared to LREE, are preferentially bound to aromatic functional groups of organic matter such as phenolic sites (Gangloff et al., 2014).

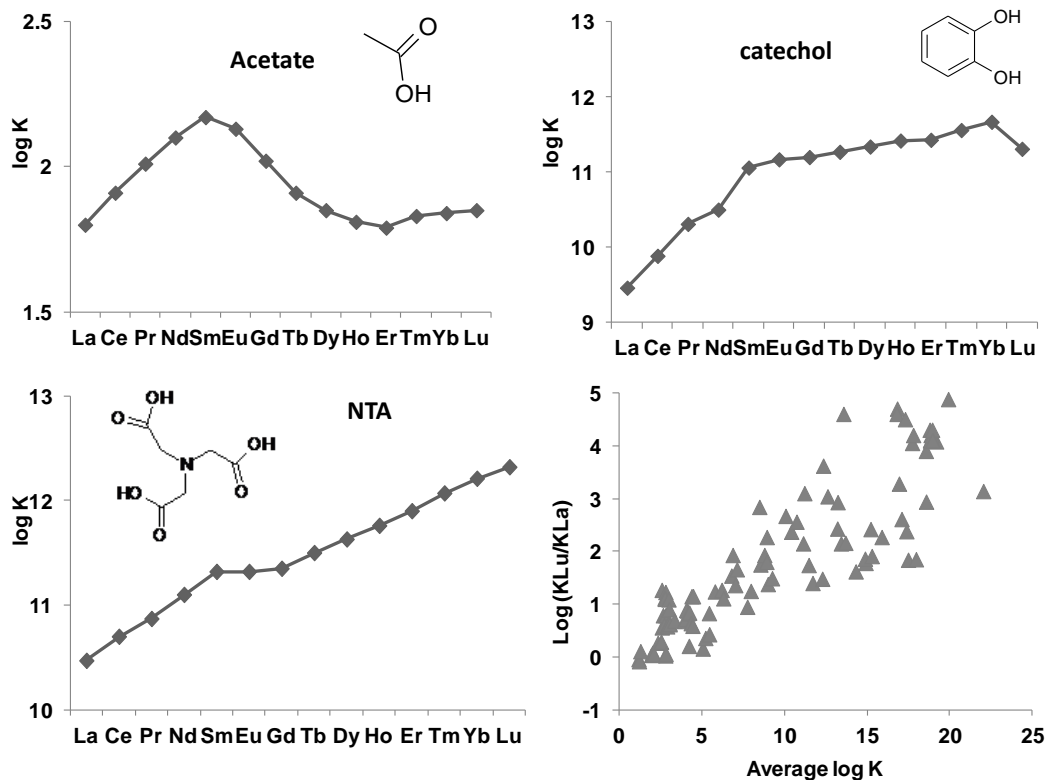


Figure 7.9 Log K REE pattern with (a) acetate, (b) catechol and (c) NTA, and (d) $\log(K_{Lu}/K_{La})$ relative to the average $\log K_{REE-organic\ ligand}$ for the 101 organic ligands compiled by Byrne and Li (1995).

In a second step, Marsac et al. (2011) used a modeling to provide evidence that HREE and LREE are not complexed to HA via the same functional sites. At high loading and acidic pH, LREE are bound to carboxylic groups and HREE to carboxylic and chelate groups. For circumneutral pH, LREE are bound to carboxylic groups and HREE via phenolic groups. The denticity of the REE-HA complex is also dependent on the metal loading (Marsac et al., 2011; 2014). More recently, Marsac et al. (2015) from EXAFS records suggest that at high loading, REE are bound to HA through bi-ligand complexes without any chelation effect in which REE act as cation bridge between two organic molecules whereas at low loading, REE are bound to HA via multi-carboxylic chelate ligands.

Competition between cations in solution in terms of their binding to HA also appeared to be another important controlling factor for the REE pattern developed in organic-rich wetland solution and shallow groundwater (Tang and Johannesson, 2003; Marsac et al., 2012; 2013). In natural water, the HA metal loading is generally imposed by other dissolved metals, such as Fe and Al, which occur in much higher concentrations than REE. Marsac et al. (2012; 2013) demonstrated that (i) Fe^{3+} competes more strongly with HREE than LREE, whereas Fe species formed at higher pH values (i.e. FeOH^{2+} or Fe polymer) compete equally with LREE and HREE, and that (ii) Al^{3+} has the same competitive effect on REE-HA binding as Fe^{3+} , but AlOH^{2+} competes mainly with LREE. Kohler et al. (2014) studied the mobilization of REE, Al, Fe and U in a boreal catchment. They demonstrated that organic matter controls their speciation in solution. However, the pH increases downstream from the catchment and involves the precipitation of Fe and Al as ferrihydrite and gibbsite, respectively. This selective removal of Al and Fe from the organic matter binding sites results in a higher La concentration downstream, namely a higher amount of La bound to colloidal organic matter present in the solution. Therefore the pH, which controls the chemical species of the competitor present in the solution, appears to drive this competition between trivalent cations and REE and the resulting REE pattern.

V. REE as probes of water circulation pathways and trace element sources

In recent years, REE have received much attention from hydrochemists because of their potential to be used as tracers or probes of water movement and water mixing (e.g. Smedley et al., 1991; Johannesson et al., 1997; Lawrence et al., 2006; Pourret et al., 2010; Siebert et al., 2012; Lu, 2014; Noack et al., 2014). In this respect, the discovery of a major difference in terms of the REE

signatures between organic-rich, wetland waters, and organic-poor surrounding groundwater (see previous sections of this chapter) could be extremely useful in detecting the contributions of wetland waters to stream and river waters, or in determining groundwater circulation pathways at the catchment scale. The most significant and useful difference here could be the lack of a Ce anomaly that characterizes the REE patterns in wetland waters, and which can be used to differentiate these waters from the less organic-rich, deeper groundwater that most commonly display profound negative Ce anomalies (see compilations in Gruau et al., 2004 and Pourret et al., 2010) (Figure 7.10).

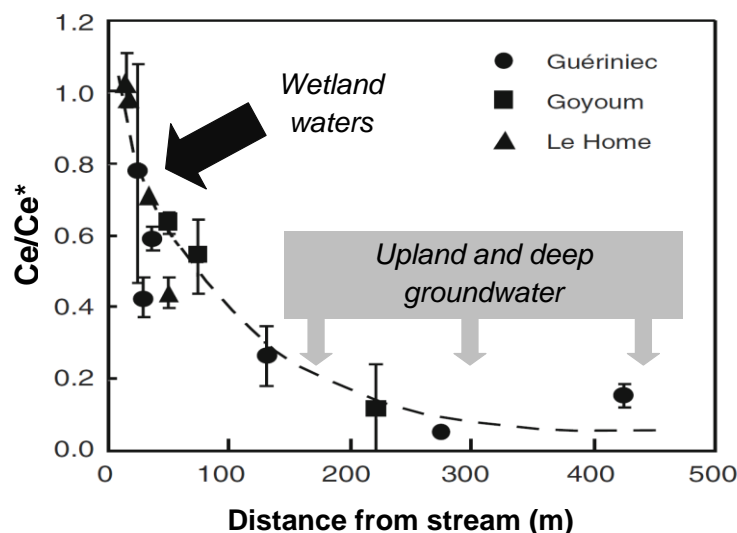


Figure 7.10 Strong difference in the negative Ce anomaly amplitude between wetland waters (reduced or non-reduced negative Ce anomaly) and deep/upland ground waters (deep negative Ce anomaly) as revealed by data from three toposequences located in Europe (Gueriniec; Le Home) and Africa (Goyoum).

This spatial variation in the negative Ce anomaly amplitude, which was earlier shown in this chapter to be due to the essentially organic speciation of REE in wetland waters, provides the basis for using REE patterns as a probe of the occurrence of a wetland water component in streams and rivers, notably during high flow periods when wetland domains and rivers and streams often become hydrologically connected to each other. This principle is illustrated in

Figure 7.11, which shows a conceptual model comparing high-flow and low-flow periods in a theoretical catchment developed on low-permeability basement rocks (e.g. shales or granites), and consisting of the juxtaposition of a poorly-drained bottomland domain (wetland area) and a well-drained upland domain. Because of the spatial difference in the Ce anomaly amplitude depicted in Figure 7.10, the model predicts that during low-flow periods, when most of the flow is expected to come from deep and upland groundwater because of the water table drawdown, REE patterns in stream waters should exhibit a deep negative Ce anomaly. By contrast, during high-flow periods, the connection between the wetland area and the stream induced by the rise in the water table should result in REE patterns showing much reduced negative Ce anomaly amplitudes.

This possibility of using the negative Ce anomaly amplitude as a probe to detect the occurrence of wetland water contributions in stream and river waters and to evaluate the temporal variability of this contribution has been tested in the Kervidy-Naizin catchment in western France, where extensive information exists regarding the spatial and temporal variability of the REE signatures in both organic-rich (wetland) and organic-poor groundwater (Gruau et al., unpublished). The test proved to be successful as the daily monitoring of the dissolved ($< 0.22 \mu\text{m}$) REE concentrations during almost one entire hydrological year (1999-2000) revealed strong Ce anomaly amplitude fluctuations (Figure 7.12). Systematic reductions in the Ce anomaly amplitude were observed in phase with the stream discharge and increases in the DOC concentration (Figure 7.12); two features that are known to correspond to wetland water inputs into the stream of this catchment (Olivié-Lauquet et al., 2001; Morel et al., 2009).

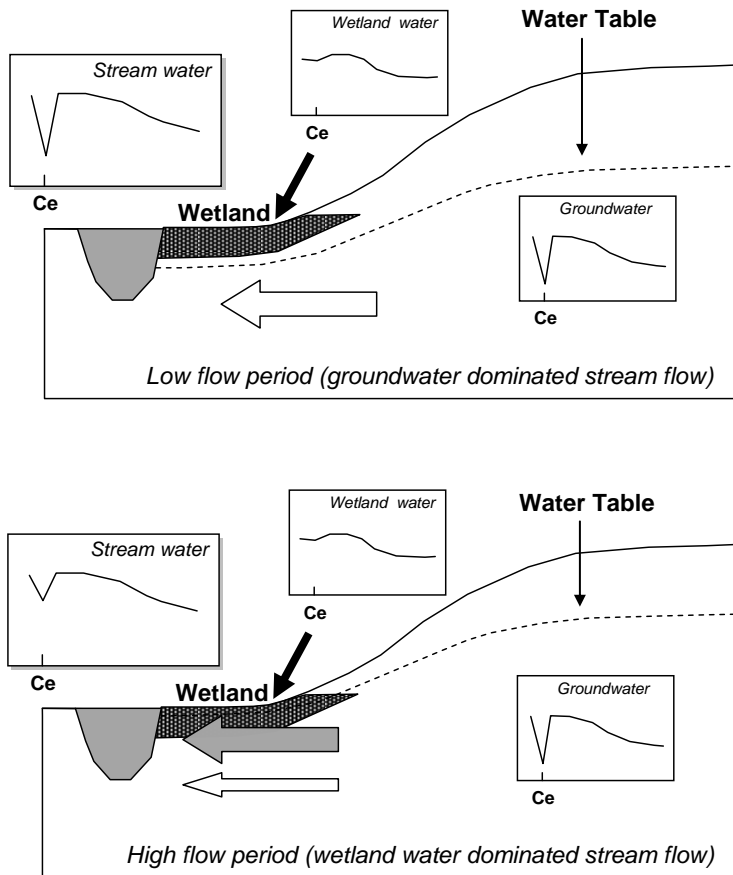


Figure 7.11 How the Ce anomaly amplitude in stream and river waters could be used to detect the contribution of a wetland water component and the possible temporal variability of this contribution.

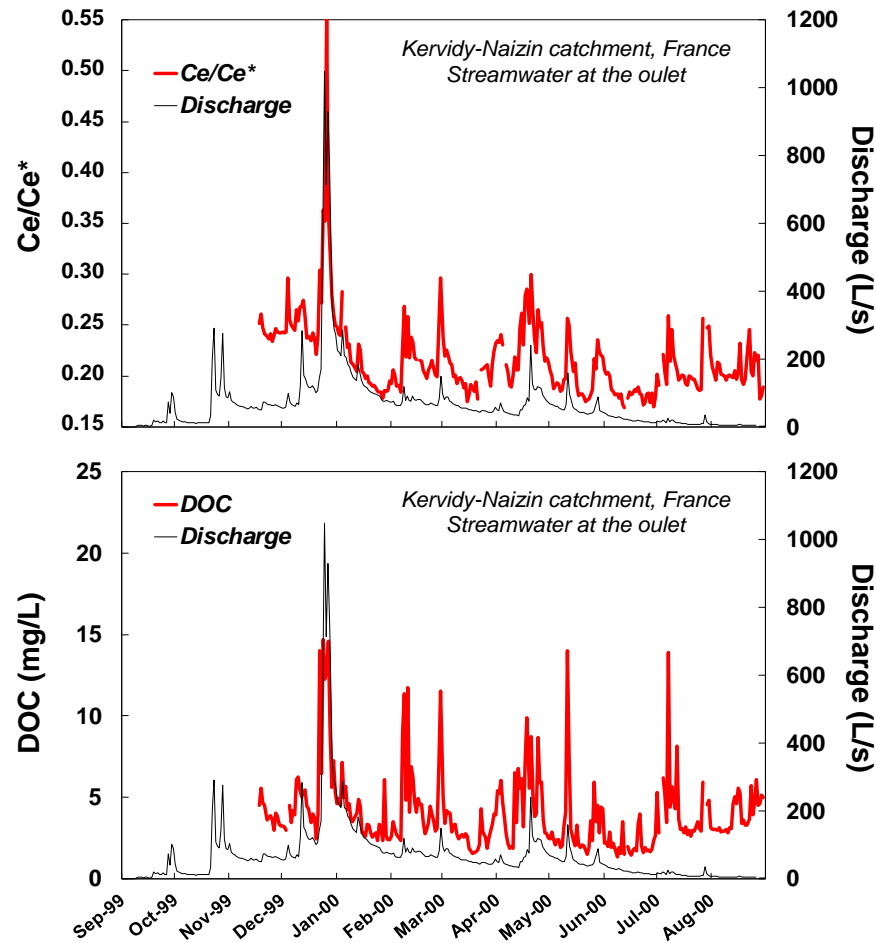


Figure 7.12 Synchronous Ce anomaly amplitude, discharge and DOC concentration variations in the stream at the outlet of the Kervidy-Naizin catchment during hydrological year 1999-2000.

This use of the Ce anomaly amplitude variation as a probe of wetland water contributions to stream and river water flows could be regarded as having limited applicability, as the example presented relies on the daily monitoring of REE concentrations, which could be seen as a severe limitation for extrapolation to other river systems. However, comparable variations (i.e. decrease in the negative Ce anomaly amplitude along with an increase in the discharge and DOC concentrations) were observed at the Loch Vale catchment outlet in Colorado and in the Kalix River in Sweden based on weekly sampling (Ingri et al., 2010; Shiller, 2014), suggesting that the

method does not necessarily require a systematic daily monitoring frequency. Although possibly difficult to implement, this ability of the negative Ce anomaly to serve as a tool to identify the periods when the rivers and streams are becoming hydrologically connected to wetland soils is worth considering. For example, it could be used to show that some of the pollutants occurring at that time in the rivers and streams considered (e.g. some trace metals) have these soils as an ultimate source.

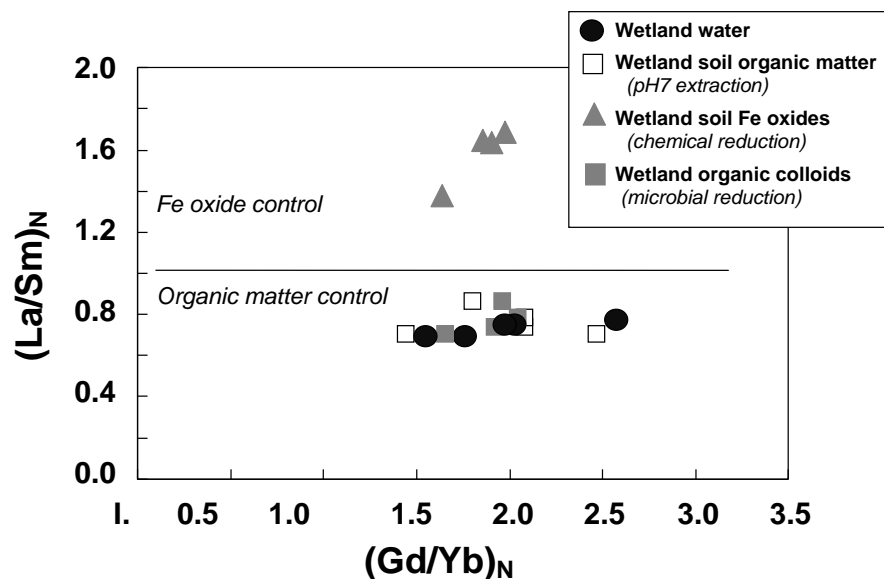


Figure 7.13 How the REE pattern can be used to determine the ultimate soil source of the REE and trace metals released during the reduction of wetland soils (Davranche et al., 2011).

Another domain in which REE can be used as a probe concerns the identification of soil components that host trace metals which are released during wetland/floodplain soil reduction. The release of trace metals such as Pb, Cr, Ni, Zn, Cd, and As during flooding and their subsequent reduction is a classical feature of floodplain/wetland soils (Schulz-Zunkel and Krueger, 2009; Du Laing et al., 2009). In this type of soil, several soil phases such as Mn(IV)-Fe(III)-oxyhydroxides, organic matter (OM) or mixed Fe-OM particles can host trace metals,

and one important question is to know which of these phases is(are) mobilized during the release process. Davranche et al. (2011) tackled this question by using REE as a probe of the activated phases. To do this, they used a wetland soil from the Kervidy Naizin catchment in France for which previous field monitoring data (Dia et al., 2001) revealed trace metal release during reduction. Their work was based on (i) the difference in the REE pattern between soil OM (relative MREE enrichment) and soil Fe(III) oxhydroxides (LREE enrichment) and (ii) the virtual absence of REE in the Fe components of the mixed Fe-OM particles. By performing different incubation laboratory experiments, Davranche et al. (2011) demonstrated that the REE fraction released in solution during the reduction of the studied soil had a pattern similar to that of the soil OM fraction, suggesting in turn that this fraction is the main source of REE and other trace metals that are released during the reduction of this soil (Figure 7.13).

The methodology developed by Davranche et al. (2011) is very promising with regards to the potential of REE to serve as a probe to identify the soil components from which trace metals are released during the reduction of wetland/floodplain soils. However, this use is clearly dependent on the occurrence of significant differences in the REE patterns between the end-members involved in the soil-water exchange process, a pre-requisite condition that should be evaluated in a greater number of sites.

V. REE impact on the human health and environment quality

Rare earth elements have been long considered as rare since the metallurgic extraction of individual elements is complicated and because of their low concentrations (ppb to ppt) in natural waters. However, over the past several decades, REE became of critical importance to many high-tech products and medical applications, and are therefore of great economic interest

(U.S. GAO, 2010). The global production of REE oxides increased from 10,000 t y⁻¹ in 1965 to > 80,000 t y⁻¹ in 2000 (Haxel et al., 2002). In 2008, the consumption of REE oxides was approximately 129,000 t (Goonan, 2011). The various applications of REE and the intense use of fertilizers in agriculture (0.1 to 1% REE in natural phosphate, Otero et al., 2005) may lead to a significant release of REE into the environment (Cidu et al., 2013). Kulaksiz and Bau (2011) showed abnormally high concentrations of Gd and La in the Rhine River (France). These authors highlighted that La was extremely mobile in this environment since La contamination was present more than 400 km after the source of the contamination. Tagami and Uchida (2006) provided evidence that REE are able to accumulate in soil and water and to bioaccumulate in the food chain. Sonich-Mullin et al. (2012) compiled the studies concerned with the specific human health effects of elevated REE concentrations. They only found a few studies which are, for the most part, dedicated to epidemiological data mixtures of REE rather than individual elements. These data indicate that the pulmonary toxicity of REE in humans may be a concern. Additionally, it has been shown that the larger, lighter (i.e. smaller atomic number), and less soluble REE are primarily deposited in the liver, while the smaller, heavier and more soluble REE are similar, in terms of their ionic radius, to divalent calcium and are primarily distributed to the bones. Therefore, it appears especially important to assess the occurrence and fate of aqueous REE in the environment.

Specifically concerning wetlands, previous concerns suggest that REE could be trapped by wetland soil components, notably organic matter. Their subsequent fate would thereby be controlled by the soil components and the behavior of the organic matter, which are themselves relative to the redox conditions prevailing in the wetland. Smuc et al. (2012) investigated the mobility of REE in contaminated paddy soil in Macedonia. Paddy soil can be considered as an

anthropogenic wetland, as the soils are regularly saturated. Although there were elevated REE concentrations in the soil, low amounts of REE occurred as soluble and exchangeable forms, as showed by the sequential extractions. The rice did not accumulate REE. Sequential extractions indicated that REE are mainly distributed in the organic and residual fractions, namely bound to soil organic matter and as minerals. Chen et al. (2014), who studied a series of paddy soil profiles with approximately 50, 300, 700 and 1000 years of paddy cultivation history, showed that paddy cultivation favors the accumulation of all REE in the soil profile. Several studies used sequential extractions of wetland soils under oxidizing conditions to demonstrate that REE are not very water soluble or exchangeable (Pédrot et al., 2008; Davranche et al., 2011; Mihajlovic et al., 2014). However under reducing conditions, when the organic phases of the soil are solubilized with their REE charge, REE are released into the wetland solution, and the question is now to know if the affinity between REE and organic ligands is strong enough to limit their bioavailability. Unfortunately, no ecotoxicology study is available to assess the potential bioavailability of REE bound to humic substances sourced in wetlands.

References

- Andersson K., Dahlgvist R., Turner D., Stolpe B., Larsson T., Ingri J., Andersson P. (2006) Colloidal rare earth elements in boreal river: Changing sources and distributions during the spring flood. *Geochim. Cosmochim. acta* 70, 3261–3274.
- Aries S., Valladon M., Polvé M., Dupré B. (2000) A routine method for oxide and hydroxide interference corrections in ICP-MS chemical analysis of environmental and geological samples. *Geostand. Newsl.* 24,19-31
- Aubert D., Stille P., 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.

Auterives C. (2007) Influence des flux d'eau souterraine entre une zone humide superficielle et un aquifère profond sur le fonctionnement hydrochimique des tourbières: exemple des marais du Cotentin, Basse-Normandie. Ph.D. thesis, University of Rennes I, France. Mémoires du CAREN 17, ISBN 2-914375-46-8, p. 261.

Avena, M.J., Koopal, L.K. (1999) Kinetics of humic acid adsorption at solid-water interfaces. *Environ. Sci. Technol.* 33, 2739-2744.

Baker J., Waight T., Ulfbeck D. (2002) Rapid and highly reproducible analysis of rare earth elements by multiple collector inductively coupled plasma mass spectrometry. *Geochim. Cosmochim. Acta*, 66, 3635-3646

Barroux G., Sonke J., Boaventura G., Viers J., Godderis Y., Bonnet M. P., Sondag F., Gardoll S., Lagane C., Seyler P. (2006) Seasonal dissolved rare earth element dynamics of the Amazon River main stem, its tributaries, and the Curuai' floodplain. *Geochem. Geophys. Geosyst.* 7, 1-18.

Bau M. (1999). Scavenging of dissolved yttrium and rare earths by precipitating iron oxyhydroxide: Experimental evidence for Ce oxidation, Y-Ho fractionation, and lanthanide tetrad effect. *Geochim. Cosmochim. Acta* 63, 67-77.

Bau M., Dulski P. (1999) Comparing yttrium and rare earths in hydrothermal fluids from the Mid-Atlantic Ridge: implications for Y and REE behaviour during nearvent mixing and for the Y/Ho ratio of Proterozoic seawater. *Chem. Geol.* 155, 77-90.

Bau M., Koschinsky A., Dulski P., Hein J. R. (1996) Comparison of the partitioning behaviours of yttrium, rare earth elements, and titanium between hydrogenetic marine ferromanganese

crusts and seawater. *Geochim. Cosmochim. Acta* 60, 1709-1725.

Bonnot-Courtois C. (1981) *Géochimie des terres rares dans les principaux milieux de formation et de sédimentation des argiles*. Thesis of the University Paris-Sud Orsay, Orsay (France), 217pp.

Braun J. J., Viers J., Dupré B., Polvé M., Ndam J., Muller J. P. (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.

Buurman P., Jongmans A.G. (2005) Podzolisation and soil organic matter dynamics. *Geoderma* 125, 71-83.

Byrne R. H. and Kim K.-H. (1990) Rare earth element scavenging in seawater. *Geochim. Cosmochim. Acta* 54, 2645-2656.

Byrne R. H., Li B. (1995) Comparative complexation behaviour of the rare earth elements. *Geochim. Cosmochim. Acta* 59, 4575–4589.

Charlatchka R., Cambier P. (2000). Influence of reducing conditions on solubility of trace metals in contaminated soils. *Water Air Soil Pollut.* 118, 143-167.

Chen L. M., Zhang G-L., Jin Z-D. (2014) Rare earth elements of a 1000-year paddy soil chronosequence: Implications for sediment provenances, parent material uniformity and pedological changes. *Geoderma*, 230–231, 274-279.

Chuan M.C., Shu G.Y., Liu A. (1996) Solubility of heavy metals in a contaminated soil: effect of redox potential and pH. *Water Air Soil Pollut.* 90, 543-556.

Cidu R., Antisari L. V., Biddau R., Buscaroli A., Carbone S., Da Pelo S., Dinelli E., Vianello G.,

- Zannoni D. (2013) Dynamics of rare earth elements in water–soil systems: The case study of the Pineta San Vitale (Ravenna, Italy). *Geoderma* 193-194, 52-67.
- Davranche M., Grybos M., Gruau G., Pédrot M., Dia A., Marsac R. (2011) Rare earth element patterns: A tool for identifying trace metal sources during wetland soil reduction. *Chem. geol.*, 284, 127-137.
- Davranche M., Bollinger J.-C., Bril H. (2003) Effect of reductive conditions on metal mobility from wasteland solids: an example from the Mortagne-du-Nord site (France). *Appl. Geochem.* 18, 383-394.
- Davranche M., Gruau G., Dia A., Marsac R., Pédrot M., Pourret O. (2015) Biogeochemical factors affecting rare earth element distribution in shallow wetland groundwater. *Aq. Geochem.*, 21, 197-215.
- Davranche M., Pourret O., Gruau G., Dia A., and Le Coz-Bouhnik M. (2005) Adsorption of REE(III)-humate complexes onto MnO₂: Experimental evidence for cerium anomaly and lanthanide tetrad effect suppression. *Geochim. Cosmochim. Acta* 69, 4825-4835.
- De Baar H. J. W., Bacon M. P., Brewer P. G. (1983) Rare-earth distributions with a positive Ce anomaly in the western North Atlantic Ocean. *Nature* 301, 324-327.
- De Baar H. J. W., Schijf J., Byrne R. H. (1991) Solution chemistry of the rare earth elements in seawater. *Eur. J. Solid State. Inorg. Chem.* 28, 357-373.
- De Carlo E. H., Green W. J. (2002) Rare earth elements in the water column of Lake Vanda, McMurdo Dry Valleys, Antarctica. *Geochim. Cosmochim. Acta* 66, 1323-1333.
- Dia A., Gruau G., Olivié-Lauquet G., Riou C., Molénat J., Curmi P. (2000) The distribution of rare-earths in groundwater: assessing the role of source-rock composition, redox changes and colloidal particles. *Geochim. Cosmochim. Acta* 64, 4131–4151.

Ding S. M., Liang T., Zhang C. S., Huang Z. C., Xie Y. N., Chen T. B. (2006) Fractionation Mechanisms of Rare Earth Elements (REEs) in Hydroponic Wheat: An Application for Metal Accumulation by Plants. *Environ. Sci. Technol.* 40, 2696-2691.

Du Laing G., Rinklebe J., Vandecasteele B., Meersa E., Tack F.M.G. (2009) Trace metal behaviour in estuarine and riverine floodplain soils and sediments: A review. *Sci. Tot. Environ.* 4007, 3972-3985.

Duncan T., Shaw T. J. (2003) The mobility of rare earth elements and redox sensitive elements in the groundwater/seawater mixing zone of a shallow coastal aquifer. *Aquat. Geochem.* 9, 233-255.

Dupré B., Gaillardet J., Rousseau D., Allègre C. J. (1996) Major and trace elements of river-borne material: The Congo Basin. *Geochim. Cosmochim. Acta* 60, 1301-1321.

Egashira K., Fujii K., Yamasaki S., Virakornphanich P. (1997) Rare earth elements and clay minerals of paddy soils from the central region of the Mekong River, Laos. *Geoderma* 78, 237-249.

Egashira K., Aramaki K., Yoshimasa M., Takeda A., Yamasaki S. (2004) Rare earth elements and clay minerals of soils of the floodplains of three major rivers in Bangladesh. *Geoderma* 120, 7-15.

Elbaz-Poulichet F., Dupuy C. (1999) Behaviour of rare earth elements at the freshwater-seawater interface of two acid mine rivers: the Tinto and Odiel (Andalucia, Spain). *Appl. Geochem.* 14, 1063-1072.

Elderfield H. (1988) The oceanic chemistry of the rare earth elements in seawater. *Phil. Trans. R. Soc. Lond. A* 325, 105-126.

Elderfield H. and Greaves M. J. (1982) The rare earth elements in seawater. *Nature* 296, 214-219.

Elderfield H., Upstill-Goddard R. and Sholkovitz E.R. (1990) The rare earth elements in rivers, estuaries, and coastal seas and their significance to the composition of ocean waters. *Geochim. Cosmochim. Acta* 54, 971–991.

Fee J. A., Gaudette H. E., Lyons W. B., and Long D. T. (1992) Rare-earth element distribution in Lake Tyrrell groundwaters, Victoria, Australia. *Chem. Geol.* 96, 67-93.

Ferrat, M., Weiss, D. J., & Strekopytov, S. (2012). A single procedure for the accurate and precise quantification of the rare earth elements, Sc, Y, Th and Pb in dust and peat for provenance tracing in climate and environmental studies. *Talanta*, 93, 415-423.

Francis A.J., Dodge C.J. (1990). Anaerobic Microbial Remobilization of Toxic Metals Coprecipitated with Iron Oxide. *Environ. Sci. Technol.* 24, 373-378.

Freeman J. L., Salt D. E. (2007) The metal tolerance profile of *Thlaspi goesingense* is mimicked in *Arabidopsis thaliana* heterologously expressing serine acetyl-transferase. *Bio Med Central Plant Biology* 7, 63.

Gammons C. H., Wood S. A., Ponas J. P., Madison J. P. (2003) Geochemistry of the rare-earth elements and uranium in the acidic Berkeley Pit Lake, Butte, Montana. *Chem. Geol.* 198, 269-288.

Gangloff S., Stille P., Pierret M.-C., Weber T., Chabaux F. (2014) Characterization and evolution of dissolved organic matter in acidic forest soil and its impact on the mobility of major and trace elements (case of the Strengbach watershed). *Geochim. Cosmochim. Acta* 130, 21-41.

German C. R., Holiday B. P., Elderfield H. (1991) Redox cycling of rare earth elements in the

suboxic zone of the Black Sea. *Geochim. Cosmochim. Acta* 55, 3553-3558.

German C. R., Masuzawa T., Greaves M. J., Elderfield H., Edmond J. M. (1995) Dissolved rare earth elements in the Southern Ocean: Cerium oxidation and the influence of hydrography. *Geochim. Cosmochim. Acta* 59, 1551-1558.

Goldberg E. D., Koide M., Schmitt R. A., Smith R. H. (1963) Rare-earth distributions in the marine environment. *J. Geophys. Res.* 68, 4209-4217.

Goldstein S. J., Jacobsen S. B. (1988) Rare earth elements in river waters. *Earth Planet. Sci. Lett.* 89, 35-47.

Goonan, T.G. (2011) Rare earth elements — end use and recyclability: U.S. Geological Survey Scientific Investigations Report 2011-5094. (15 pp. available only at) <http://pubs.usgs.gov/sir/2011/5094/>.

Green C.H., Heil D.M., Cardon G.E., Butters G.L., Kelly E.F. (2003) Solubilization of Manganese and Trace Metals in Soils Affected by Acid Mine Runoff. *Journal of Environmental Quality* 32, 1323-1334.

Gromet L.P., Dymek R.F., Haskin L.A. and Korotev R.L. (1984). The "North American Shale Composite ": Its compilation, major and trace element characteristics. *Geochim. Cosmochim. Acta* 48, 2469-2482.

Gruau G., Dia A., Olivié-Lauquet G., Davranche M., Pinay G. (2004) Controls on the distribution of rare earth elements in shallow groundwaters. *Wat. Res.* 38, 3576-3586.

Grybos M., Davranche M., Gruau G., Petitjean P. (2007) Is trace metal release in wetland soils controlled by organic matter mobility or Fe-oxyhydroxide reduction? *J. Colloid Interface Sci.*, 314, 490–501.

Grybos M., Davranche M., Gruau G., Petitjean P., Pédrot M. (2009) Increasing pH drives

organic matter solubilization from wetland soils under reducing conditions. *Geoderma*, 154, 13-19.

Gupta, C. K. and N. Krishnamurthy. (2004) *Extractive Metallurgy of Rare Earths*. CRC Press.

Hagedorn F., Kaiser K., Feyen H., Schleppei P. (2000) Effect of redox conditions and flow processes on the mobility of dissolved organic carbon and nitrogen in a forest soil. *J. Environ. Qual.* 29, 288-297.

Hannigan R. E., Sholkovitz E. (2001) The development of middle rare earth element enrichments in freshwaters: weathering of phosphate minerals. *Chem. geol.* 175, 495-508.

Haskin L., Wildeman T., Haskin M. (1968) An accurate procedure for the determination of the rare earths by neutron activation. *Journal of Radioanalytical and Nuclear Chemistry* 1, 334-348.

Haxel, G.B., Hedrick, J.B., Orris, G.J. (2002) Rare earth elements. Critical resources for high technology. (US Geological Survey, Fact Sheet 087-02) <http://pubs.usgs.gov/fs/2002/fs087-02/>

Heimbürger, A., Tharaud, M., Monna, F., Losno, R., Desboeufs, K., Nguyen, E. B. (2013) SLRS-5 Elemental Concentrations of Thirty-Three Uncertified Elements Deduced from SLRS-5/SLRS-4 Ratios. *Geostand. Geoanal. Res.*, 37, 77-85.

Henderson P. (1984) Rare earth element geochemistry: Development in Geochemistry. Vol. 2. Elsevier, Amsterdam, 510pp.

Ingri J., Widerlund A., Land M., Gustafsson O., Andersson P., Ohlander B. (2000) Temporal variations in the fractionation of the rare earth elements in a boreal river; the role of colloidal particles. *Chem. geol.* 166, 23-45.

Janssen R. P. T., Verweij W. (2003) Geochemistry of some rare earth elements in groundwater, Vierlingsbeek, The Netherlands. *Wat. Res.* 37, 1320-1350.

Jarvis K.E., Gray A.L, Houk R.S. (1992) Handbook of inductively coupled plasma mass spectrometry; Glasgow : Blackie ; New York : Chapman and Hall, 380 p.

Johannesson K. H. and Hendry M. J. (2000) Rare earth element geochemistry of groundwaters from a thick till and clay-rich aquitard sequence, Saskatchewan, Canada. *Geochim. Cosmochim. Acta* 64, 1493-1509.

Johannesson K. H., Lyons W. B. (1995) Rare-earth element geochemistry of Colour Lake, an acidic freshwater lake on Axel Heiberg Island, Northwest Territories, Canada. *Chem. Geol.* 119, 209-223

Johannesson K. H., Lyons W. B., Yelken M. A., Gaudette H. E., Stetzenbach K. J. (1996) Geochemistry of the rare earth elements in hypersaline and dilute acidic natural terrestrial waters: complexation behavior and middle rare-earth element enrichments. *Chem. Geol.* 133, 125-144.

Johannesson K. H., Stetzenbach K. J., Hodge V. F. (1997) Rare earth elements as geochemical tracers of regional groundwater mixing. *Geochim. Cosmochim. Acta* 61, 3605-3618.

Johannesson K. H., Tang J., Daniels J. M., Bounds W. J., Burdige D. J. (2004) Rare earth element concentrations and speciation in organic-rich blackwaters of the Great Dismal Swamp, Virginia, USA. *Chem. geol.*, 209, 271–294

Johannesson K.H., Farnham I.M., Guo C., Stetzenbach K.J. (1999) Rare earth element fractionation and concentration variations along a groundwater flow path within a shallow basin-till aquifer, southern Nevada, USA. *Geochim. Cosmochim. Acta* 63, 2697-2708.

Johannesson K.H., Zhou X., Guo C., Stetzenbach K.J., Hodge, V.F. (2000) Origin of rare earth element signatures in groundwaters of circumneutral pH from southern Nevada and eastern California, USA. *Chem. Geol.* 164, 239-257.

Kautenburger R, Hein C, Sander JM, Beck HP (2014) Influence of metal loading and humic acid functional groups on the complexation behavior of trivalent lanthanides analyzed by CE-ICP-MS. *Anal. Chim. Acta*:816, 50-59

Kerr S. C., Shafer M. M., Overdier J., Armstrong D. E. (2008) Hydrologic and biogeochemical controls on trace element export from northern Wisconsin wetlands. *Biogeochem.* 89, 273–294.

Klinkhammer G., German C. R., Elderfield H., Greaves M. J., Mitra A. (1994) Rare earth elements in hydrothermal fluids and plume particulates by inductively coupled plasma mass spectrometry. *Mar. Chem.* 45, 179-186

Koepfenkastro D., De Carlo E. H. (1992) Sorption of rare-earth elements from seawater onto synthetic mineral particles: An experimental approach. *Chem. Geol.* 95, 251-263.

Kohler S. J., Lidman F., Laudon H. (2014) Landscape types and pH control organic matter mediated mobilization of Al, Fe, U and La in boreal catchments. *Geochim. Cosmochim. Acta* 135, 190-202.

Koppi A.J., Edis R., Field D.J., Geering H.R., Klessa D.A., Cockayne D.J.H. (1996) Rare earth element trends and cerium-uranium-manganese associations in weathered rock from Koongarra, Northern Territory, Australia. *Geochim. Cosmochim. Acta* 60,1695-1707.

Kulaksız S., Bau. M. (2011) Rare earth elements in the Rhine River, Germany: First case of anthropogenic lanthanum as a dissolved microcontaminant in the hydrosphere. *Environ.*

Internat., 37, 973-979

Laveuf C., Cornu S. (2009) A review of the potentiality of Rare Earth Element to trace pedogenetic processes. *Geoderma* 154, 1-12.

Laveuf C., Cornu S., Guilherme L.R.G., Guerin A., Juillot F. (2012) The impact of redox conditions on the rare earth element signature of redoximorphic features in a soil sequence developed from limestone. *Geoderma* 170, 25-38.

Lawrence M. G., Greig A., Collerson K. D., and Kamber B. S. (2006) Rare earth element and yttrium variability in South East Queensland waterways. *Aquat. Geochem.* 12, 39-72.

Lawrence M. G., Kamber B. S. (2006) The behaviour of the rare earth elements during estuarine mixing - revisited. *Mar. Chem.*, 100, 147-161.

Leybourne M.I., Johannesson K.H. (2008) Rare earth elements (REE) and yttrium in stream waters, stream sediments, and Fe–Mn oxyhydroxides: fractionation, speciation, and controls over REE + Y patterns in the surface environment. *Geochim. Cosmochim. Acta* 72, 5962–5983

Lima e Cunha M. C., Do Carmo M., Pereira V. P., Nardi L. V. S., Bastos Neto A. C., Vedana L. A., Formoso M. L. L. (2012) REE Distribution Pattern in Plants and Soils from Pitinga Mine—Amazon, Brazil. *Open J Geol.* 2, 253-259.

Lima e Cunha M. C., Pereira V. P., Bastos Neto A. C., Nardi L. V. S., Formoso M. L. L., Menegotto L. (2009) Bio-geoquímica dos Elementos Terras Raras Na Província Estanífera De Pitinga (AM). *Revista Brasileira de Geociências.* 39, 560-566.

Longerich H.P, Fryer B.J., Strong D.F., Kantipuly C.J.(1987) Effects of operating conditions on the determination of the rare earth elements by inductively coupled plasma-mass

spectrometry (ICP-MS), *Spectrochimica Acta Part B: Atom. Spectroscopy*, 42, 75-92

Lu, H.Y. (2014) Application of water chemistry as a hydrological tracer in a volcano catchment area: A case study of the Tatun Volcano Group, North Taiwan. *Journal of Hydrology*. 51, 825-837.

Marsac R., Davranche M., Gruau G., Bouhnik-Le Coz M., Dia A. (2011) An improved description of the interactions between rare earth elements and humic acids by modeling: PHREEQC-Model VI coupling. *Geochim. Cosmochim. Acta* 75, 5625-5637

Marsac, R., Davranche, M., Gruau, G., Dia, A., Pédrot, M., Le Coz-Bouhnik, M. and Briant, N. (2013) Effects of Fe competition on REE binding to humic acid: Origin of REE pattern variability in organic waters. *Chem. Geol.* 342, 119-127.

Marsac R., Davranche M., Gruau G., Dia A. (2010) Metal loading effect on rare earth element binding to humic acid: Experimental and modelling evidence. *Geochim. Cosmochim. Acta*, 74, 1749-1761.

Marsac R., Davranche M., Gruau G., Dia A., Bouhnik-Le Coz M. (2012). Aluminum competitive effect on rare earth elements binding to humic acid. *Geochim. Cosmochim. Acta*, 89, 1-9.

Marsac R., Davranche M., Morin G., Takahashi Y., Gruau G., Dia A. (2015) Impact of REE loading on REE-humate binding: Sm and Yb EXAFS evidence. *Chem. Geol.* 396, 218-227.

Martinez R. E., Pourret O., Takahashi Y. (2014) Modeling of rare earth element sorption to the Gram positive *Bacillus subtilis* bacteria surface. *J Colloid interface Sci.* 413, 106-111.

McLennan S. M. (1989) Rare earth elements in sedimentary rocks: Influence of provenance and sedimentary processes. *In* *Geochemistry and Mineralogy of Rare Earth Elements*, Vol. 21 (eds. B. R. Lipin and G. A. McKay), pp. 169-200. Mineralogical Society of America,

Washington, DC.

McLennan S. M. (1994) Rare earth element geochemistry and the "tetrad" effect. *Geochim. Cosmochim. Acta* 58, 2025-2033.

Michard A., Albarède F., Michard G., Minster J. F., Charlou J. L. (1983) Rare-earth elements and uranium in high-temperature solutions from East Pacific Rise hydrothermal vent field (13°N). *Nature* 303, 795-797.

Mihajlovic J., Stärk H-J., Rinklebe J. (2014) Geochemical fractions of rare earth elements in two floodplain soil profiles at the Wupper River, Germany. *Geoderma* 228–229, 160-172.

Moffett J. W. (1990) Microbially mediated cerium oxidation in sea water. *Nature* 345, 421-423.

Moffett J. W. (1994a) A radiotracer study of cerium and manganese uptake onto suspended particles in Chesapeake Bay. *Geochim. Cosmochim. Acta* 58, 695- 703.

Moffett J. W. (1994b) The relationship between cerium and manganese oxidation in the marine environment. *Limnol. Oceanogr.* 39, 1309-1318.

Möller P., Bau M. (1993) Rare-earth patterns with positive cerium anomaly in alkaline waters from Lake Van, Turkey. *Earth Planet. Sci. Lett.* 117, 671-676.

Morel, B., Durand, P., Jaffrezic, A., Gruau, G. and Molénat, J. (2009) Sources of dissolved organic carbon during stormflow in a headwater agricultural catchment, *Hydrol. Process.* 23, 2888–2901.

Morey G.B., Setterholm D.R. (1997) Rare earth elements in weathering profiles and sediments of Minnesota : Implications for provenance studies. *J. Sed. Res.* 67, 105-115.

Neubauer E., Kammer F. V. D., Hofmann T. (2013) Using FLOWFFF and HPSEC to determine trace metal colloid associations in wetland runoff. *Wat. Res.* 47, 2757-2769.

- Ngwenya B. T., Magennis M., Olive M., Mosselmans J. F. W., Ellam R. M. (2010) Discrete site surface complexation constant for lanthanide adsorption to bacteria as determined by experiments and linear free energy relationship. *Environ. Sci Technol.* 44, 650-656.
- Ngwenya BT, Mosselmans J. F. W., Magennis M., Atkinson K.D., Tournay J., Olive V., Ellam R. M. (2009) Macroscopic and spectroscopic analysis of lanthanide adsorption to bacterial cells *Geochim. Cosmochim. Acta* 73, 3134-3147.
- Noack C.W., Dzombak D.A., Karamalidis A.K. (2014) Rare Earth Element Distributions and Trends in Natural Waters with a Focus on Groundwater. *Environ. Sci. Technol.* 48, 4317–4326.
- Ohta A., Kawabe I. (2001) REE(III) adsorption onto Mn dioxide (δ -MnO₂) and Fe oxyhydroxide: Ce(III) oxidation by δ -MnO₂. *Geochim. Cosmochim. Acta* 65, 695-703.
- Olivié-Lauquet G., Allard T., Benedetti M., Muller J.-P. (1999) Chemical distribution of trivalent iron in riverine material from a tropical ecosystem: a quantitative EPR study. *Wat. Res.* 33, 2726-2734.
- Olivié-Lauquet G., Gruau G., Dia A., Riou C., Jaffrezic A., and Henin O. (2001) Release of trace elements in wetlands: role of seasonal variability. *Wat. Res.* 35, 943-952.
- Oral R., Bustamante P., Warnau M., D'Ambra A., Guida M., Pagano G. (2010) Cytogenetic and developmental toxicity of cerium and lanthanum to sea urchin embryos. *Chemosphere*, 81 194–198.
- Otero, N., Vitoria, L., Soler, A., Canals, A. (2005) Fertilizer characterization: major, trace and rare earth elements. *Appl. Geochem.* 20, 1473–1488.
- Panahi A., Young G.M., Rainbird R.H. (2000) Behavior of major and trace elements (including

REE) during Paleoproterozoic pedogenesis and diagenetic alteration of an Archean granite near Ville Marie, Quebec, Canada. *Geochim. Cosmochim. Acta* 64, 2199-2220.

Parkhurst D.L., Appelo C.A.J. (1999) User's guide to PHREEQC (Version 2) - a computer program for speciation, batch reaction, one-dimensional transport and inverse geochemical calculation. Water-resources Investigation Report 99-4259, USGS, Denver, Colorado, p. 312.

Pédrot M., Dia A., Davranche M., Bouhnik-Le Coz M., Henin O., Gruau G. (2008) Insights into colloid-mediated trace element release at soil/water interface. *J. Colloid Interface Sci.* 325, 187-197.

Pédrot M., Dia A., Davranche M., Gruau G. (2015) Upper soil horizons control the rare earth element patterns in shallow groundwaters. *Geoderma*, 239-240, 84-96.

Ponnamperuma F.N. (1972) The chemistry of submerged soils. *Advances in Agronomy* 24:29-96.

Pourret O., Davranche M., Gruau G., Dia A. (2007a) Organic complexation of rare earth elements in natural waters: evaluating model calculations from ultrafiltration data. *Geochim. Cosmochim. Acta* 71, 2718-2735.

Pourret O., Davranche M., Gruau G., Dia A. (2007b) Rare earth complexation by humic acid. *Chem. Geol.* 243, 128-141.

Pourret O., Gruau G., Dia A., Davranche M., Molénat J. (2010) Colloidal control on the distribution of rare earth elements in shallow groundwaters, *Aquat. Geochem.* 16, 31-59

Protano G., Riccobono F. (2002) High contents of rare earth elements in stream waters of a Cu-Pb-Zn mining area. *Environ. Pollut.* 117, 499-514.

Quantin C., Becquer T., Berthelin J. (2002) Mn-oxide: a major source of easily mobilisable Co

and Ni under reducing conditions in New Caledonia Ferralsols. *Comptes Rendus Geoscience* 334, 273-278.

Quantin C., Becquer T., Rouiller J.H., Berthelin J. (2001) Oxide weathering and trace metal release by bacterial reduction in a New Caledonia Ferralsol. *Biogeochem.* 53, 323-340.

Ran Y., Liu Z. (1992) Specific adsorption of trivalent La, Ce and Y by soils and ferromanganese oxides and its mechanism. *Pedosphere* 2, 13-22.

Raut N. M., Huang L.S., Lin K.C., Aggarwal S. K. (2005a) Uncertainty propagation through correction methodology for the determination of rare earth elements by quadrupole based inductively coupled plasma mass spectrometry. *Anal. Chim. Acta*, 530, 91-103

Raut N.M., Huang L.S., Aggarwal S.K., Lin K.C. (2005b) Mathematical correction for polyatomic isobaric spectral interferences in determination of lanthanides by inductively coupled plasma-mass spectrometry. *J. Chinese Chem. Soc.*, 52,589-597

Rousseau, T. C., Sonke, J. E., Chmeleff, J., Candaudap, F., Lacan, F., Boaventura, G., Jeandel, C. (2013) Rare earth element analysis in natural waters by multiple isotope dilution–sector field ICP-MS. *J. Anal. Atomic Spect.*, 28, 573-584.

Sauer D., Sponagel H., Sommer M., Giani L., Jahn R., Stahr K. (2007) Podzol : soil of the year 2007. A review on its genesis, occurrence, and functions. *Journal of Plant Nutrition and Soil Science* 170, 581-597.

Schaller J., Vymazal J., Brackhage C. (2013) Retention of resources (metals, metalloids and rare earth elements) by autochthonously/allochthonously dominated wetlands: A review. *Eco. Eng.* 53, 106-114.

Schulz-Zunkel C., Krueger F. (2009) Trace Metal Dynamics in Floodplain Soils of the River

Elbe: A Review. *Journal of Environmental Quality*. 38, 1349-1362.

Schwertmann U., Fisher W.R. (1973) Natural “amorphous” ferric hydroxide. *Geoderma* 10, 237-247.

Shannon R. D. (1976) Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr.* A32, 751-767.

Shiller A. M. (2002) Seasonality of dissolved rare earth elements in the Lower Mississippi River. *Geochem. Geophys. Geosyst.* 3, 1068.

Shiller A. M. (2010) Dissolved rare earth elements in a seasonally snow-covered, alpine/subalpine watershed, Loch Vale, Colorado. *Geochim. Cosmochim. Acta*, 74, 2040-2052.

Sholkovitz E. R. (1993) The geochemistry of rare earth elements in the Amazon River estuary. *Geochim. Cosmochim. Acta* 57, 2181-2190

Sholkovitz E. R., Landing W. M., Lewis B. L. (1994) Ocean particle chemistry: The fractionation of rare earth elements between suspended particles and seawater. *Geochim. Cosmochim. Acta* 58, 1567-1579.

Sholkovitz E.R. (1995) The aquatic chemistry of the rare earth elements in rivers and estuaries. *Aq. Geochem.* 1, 1-34.

Siebert C., Rosenthal E., Möller P., Rödiger T., Meiler M. (2012) The hydrochemical identification of groundwater flowing to the Bet She’an-Harod multiaquifer system (Lower Jordan Valley) by rare earth elements, yttrium, stable isotopes (H, O) and Tritium. *Appl. Geochem.* 27, 703–714.

Simpson A. J., Simpson M. J., Smith E., Kellher B. P. (2007) Microbially derived inputs to soil

- organic matter: are current estimates too low. *Environ. Sci. Technol.* 41, 8070-8076.
- Singh P., Rajamani V. (2001) REE geochemistry of recent clastic sediments from the Kaveri floodplains, southern India: Implications to source area weathering and sedimentary processes. *Geochim. Cosmochim. Acta* 65, 3093-3108.
- Smedley P. (1991) The geochemistry of rare earth elements in groundwater from the Carnmenellis area, southwest England. *Geochim. Cosmochim. Acta* 55, 2267-2779.
- Šmuc N. R., Dolenc T., Serafimovski T., Dolenc M., Vrhovnik P. (2012) Geochemical characteristics of rare earth elements (REEs) in the paddy soil and rice (*Oryza sativa* L.) system of Kočani Field, Republic of Macedonia. *Geoderma*, 183–184, 1-11.
- Sonich-Mullin C. (2012) Rare Earth Elements: A Review of Production, Processing, Recycling, and Associated Environmental Issues. Office of research and development, EPA/600/R-12/572, 135p, USA.
- Sonke J. E., Salters V. J. M. (2006) Lanthanide–humic substances complexation. I. Experimental evidence for a lanthanide contraction effect. *Geochim. Cosmochim. Acta* 70, 1495–1506.
- Stern J. C., Sonke J. E., Salters V. J. M. (2007) A capillary electrophoresis-ICP-MS study of rare earth elements complexation by humic acids. *Chem. Geol.* 246, 170-180.
- Stolpe, B., Guo, L., Shiller, A. M. (2013). Binding and transport of rare earth elements by organic and iron-rich nanocolloids in Alaskan rivers, as revealed by field-flow fractionation and ICP-MS. *Geochim. Cosmochim. Acta*, 106, 446-462.
- Tachikawa, K., Athias, V., Jeandel, C. (2003) Neodymium budget in the modern ocean and paleo-oceanographic implications. *J. Geophys. Res.* 108, 0148-0227.
- Tagami K., Uchida S. (2006) Transfer of REEs from nutrient solution to radish through fine

roots and their distribution in the plant. *J. Alloys. Compd.* 408, 409–412.

Takahashi Y., Shimizu H., Usui A., Kagi H., Nomura M. (2000) Direct observation of tetravalent cerium in ferromanganese nodules and crust by X-ray absorption near-edge structure (XANES). *Geochim. Cosmochim. Acta* 64, 2829-2835.

Takahashi Y., Châtellier X., Hattori K. H., Kato K., Fortin D. (2005) Adsorption of rare earth elements onto bacterial cell walls and its implication for REE sorption onto natural microbial mats. *Chem. Geol.* 219, 53-67.

Takahashi Y., Yamamoto M., Yamamoto Y., Tanaka K. (2010) EXAFS study on the cause of enrichment of heavy REEs on bacterial cell surfaces. *Geochim. Cosmochim. Acta* 74, 5443-5462.

Tang J., Johannesson K. H. (2003) Speciation of rare earth elements in natural terrestrial waters: Assessing the role of dissolved organic matter from the modeling approach. *Geochim. Cosmochim. Acta* 67, 2321-2339.

Tang J., Johannesson K.H. (2005) Rare earth element concentrations, speciation and fractionation along groundwater flow paths: the Carrizo sand (Texas) and Upper Floridan aquifers. *Rare Earth Elem. Groundwater Flow Syst.* 51, 223-251.

Tang J., Johannesson K.H. (2010) Ligand extraction of rare earth elements from aquifer sediments: Implications for rare earth element complexation with organic matter in natural waters. *Geochim. Cosmochim. Acta* 74, 6690-6705.

Taylor S. R., McLennan S. M. (1985) *The Continental Crust: Its Composition and Evolution.* Blackwell Science Publishers Taylor and McLennan, 1985

Tipping E. (1998) Humic ion-binding model VI: an improved description of the interactions of

protons and metal ions with humic substances. *Aquat. Geochem.* 4, 3–48.

Tsumura A., Yamasaki S. (1993) Behaviour of uranium, thorium and lanthanides in paddy fields.

Radioisotopes 42, 265-272.

U.S. GAO. United States Government Accountability Office Rare earth materials in the defense supply chain GAO-10-617R (2010) Available: <http://www.gao.gov/new.items/d10617r.pdf>

Vasyukova E., Pokrovsky O., Viers J., Dupré B. (2012) New operational method of testing colloid complexation with metals in natural waters. *Appl. Geochem.*, 27, 1226-1237.

Viers J., Dupré B., Polvé M., Schott J., Dandurand J.-L., Braun J.J. (1997) Chemical weathering in the drainage basin of a tropical watershed (Nsimi–Zoetele site, Cameroon): comparison between organic poor and organic-rich waters. *Chem. Geol.* 140, 181–206.

Vital H., and Stattegger K. (2000) Major and trace elements of stream sediments from the lowermost Amazon River. *Chem. Geol.* 168,151–168.

Weber R. (2008) An experimental study of fractionation of the rare earth elements in poplar plants (*populus eugenei*) grown in a calcium-bearing smectite soil. Master's Thesis, Kansas State University, Manhattan. 50p

Yeghicheyan, D, Bossy, C, Bouhnik Le Coz, M, Douchet, C, Granier, G, Heimbürger, A, Lacan, F, Lanzanova, A, Rousseau, T, Seidel, J, Tharaud, M, Candaudap, F, Chmeleff, J, Cloquet, C, Delpoux, S, Labatut, M, Losno, R, Pradoux, C, Sivry, Y, Sonke, J (2013) A Compilation of Silicon, Rare Earth Element and Twenty-One other Trace Element Concentrations in the Natural River Water Reference Material SLRS-5 (NRC-CNRC). *Geos. Geoanal. Res.* 37, 449-467.

Yeghicheyan, D, Carignan, J, Valladon, M, Coz, M, Cornec, F, Castrec-Rouelle, M, Robert, M, Aquilina, L, Aubry, E, Churlaud, C, Dia, A, Deberdt, S, Dupré, B, Freydier, R, Gruau, G,

Hénin, O, Kersabiec, A, Macé, J, Marin, L, Morin, N (2001) Compilation of Silicon and Thirty One Trace Elements Measured in the Natural River Water Reference Material SLRS-4 (NRC-CNRC). *Geos. Newsletter* 25, 465-474.

Yuan D., Shan X.Q., Huai Q., Wen B., Zhu X. (2001) Uptake and distribution of rare earth elements in rice seeds cultured in fertilizer solution of rare earth elements. *Chemosphere* 43, 33-44.