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Mélanie Davranche, Gérard Gruau, Aline N. Dia, Rémi Marsac, Mathieu Pédrot, et al.. Biogeochemical factors affecting rare earth element distribution in shallow wetland groundwater. *Aquatic Geochemistry*, 2015, 21 (2-4), pp.197-215. 10.1007/s10498-014-9247-6 . hal-02265582

HAL Id: hal-02265582

<https://hal.science/hal-02265582>

Submitted on 10 Aug 2019

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Biogeochemical factors affecting rare earth element distribution in shallow wetland groundwater

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Abstract

Wetlands are specific areas able to regulate metals mobility in the environment. Among metals, rare earth elements (REE) appear to be particularly interesting because of the information that could be provided by the REE patterns. Moreover, as REE are becoming a matter of great economic interest, their significant release into the environment may be expected over the next few decades. Wetlands would then play a key role in the regulation of their concentration in the environment. This review demonstrated that REE are released in wetland bound to colloidal organic matter. During the flood season, the released REE concentrations are largely higher than those released during the wet period. This solubilisation is related to the organic matter desorption caused by the pH rise imposed by the reducing reactions. The resulting REE patterns depend on the heterogeneity of the humic acid (HA) binding sites and the presence of potential competitive cations, such as Fe(III) and Al(III). At high REE loading, REE are bound to HA carboxylic groups and the pattern exhibit a MREE downward concavity. At low loading, REE are bound to phenolic and chelate groups and the pattern exhibits a lanthanide contraction. At low loading, REE seem to act as cationic bridges between two organic molecules, whereas at high loading they seem to be engaged in strong multidentate bonding. Moreover, the REE patterns can be modified with the competitive cations amount and speciation. The prime factor governing all these processes is pH, which drives the organic colloid production, REE loading and solubility of competitive cations.

Keywords: rare earth elements, wetland, organic matter, colloids, sorption, Fe(III), Al(III), competition

1. Introduction

Rare earth elements represent a group of 15 elements, specifically the lanthanides. They are often referred to as REE. These 15 elements share common physiochemical properties and therefore often occur together. In aquatic systems, with regards to their slight solubility, REE concentrations are low compared to their

concentrations in rocks. Over the past few decades, REE became of critical importance to many high-tech products and medical applications, and therefore are of great economic interest (U.S. GAO 2010). In 2008, the consumption of REE oxides was approximately 129,000 t (Goonan 2011). The diverse applications of REE, and the intense use of fertilizers in agriculture (0.1 to 1% REE in natural phosphates, Otero et al. 2005) may lead to a significant release of REE into the environment (Cidu et al. 2013). As such, 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 soils and waters 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. Therefore, it appears especially important to assess and to fully understand the occurrence and fate of aqueous REE in the environment.

In aquatic systems, solution and interface chemistry appears to be the major factor controlling the REE concentration (e.g. Goldstein and Jacobsen 1988; Elderfield et al. 1990; Sholkovitz 1995). Rare earth elements can form strong complexes with a number of different ligands. Water is a strong ligand for trivalent (REE^{3+}) and therefore forms a hydration shell around the REE^{3+} ions. The number of water molecules that a REE^{3+} can bind varies between 8 and 9, depending on the element and species considered (Ohta et al. 2008). In aqueous environments, water molecules are only displaced if ligands with a small ionic radius are present at a high oxidation state and with high electronegativity. In general, REE^{3+} ions prefer donor atoms in the following order of affinity: $\text{O} > \text{N} > \text{S}$. 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 continental waters is usually illustrated by normalized REE patterns relative to the Upper Continental Crust (UCC) (Taylor et McLennan 1985). The REE patterns result 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 mineral sources that are modified by the sorption/complexation REE constants with ligands, colloids and particles. This results in a wide range of diverse REE patterns, which can be characterized by a depletion or enrichment degree relative to heavy REE (La/Yb or Sm/Yb ratios) or by

whether or not anomalies occur. More specifically, REE fractionation patterns and abundances have been used to investigate processes occurring in wetlands, such as the hydrological regime of the system, mineral phases activated during water saturation, trace element sources as well as fine sorption processes occurring onto 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). In turn, these studies have produced information that can be used to identify and discriminate the biogeochemical parameters that control their distribution in this type of surface environment.

The term wetland covers a number of various areas, the major common characteristic of which is the temporary or permanent water-saturation of the upper-most soil horizons. This permanent or temporary flooding induces the development of redox alternating or reducing conditions in soils and soils solutions (Ponnampereuma 1972). Under reducing conditions, soil organic matter is partly metabolized by microorganisms, which successively used O_2 , NO_3 , Mn and Fe-oxides and SO_4 as electron acceptors (Ponnampereuma 1972). In turn, Mn and Fe-oxides are reductively dissolved and released in solution with their respective metal/metalloid loading. Many authors have considered Mn and Fe-oxides to be a major parameter controlling trace metal mobility in wetland soils (Charlatchka and Cambier, 2000; Chuan et al. 1996; Davranche et al. 2003; Francis and Dodge 1990; Green et al. 2003; Quantin et al. 2001; Quantin et al. 2002). Several studies report positive correlations between Mn(II) and Fe(II) concentrations in wetland soil solutions and dissolved organic matter (DOC). For all of these reasons, wetlands are of particular interest in the environment, as well as in the flow regulation of many elements such as REE. Kohler et al. (2014), who studied the mobilization of several chemical elements in a boreal catchment, indicated that landscape effects and processes in riparian soils are dominant over purely chemical in-stream processes. As a result, Barroux et al. (2006) showed that in the Amazon River main stream and its major tributaries surrounded by many floodplains, the highest concentrations of REE are released in winter during water saturation and when reducing conditions are established. They calculated that during the high-water season, the maximum Nd flux is equal to $1,277 \text{ t yr}^{-1}$, constituting 30% of the required flux to the Atlantic Ocean (Tachikawa et al. 2003). Shiller (2010) suggested that the seasonal flooding of wetlands may be an important regulator of the REE concentrations in hydrosystems.

In this paper, we therefore discuss which biogeochemical factors and processes control the distribution and transfer of REE in wetland waters. First, we will consider the various REE patterns available in the literature and second, the different physicochemical mechanisms that account for the displayed variability.

2. Factors and processes controlling the distribution of REE released in wetland waters

A systematic evolution of the REE patterns is observed between those displayed in wetland soil/sediments, on the one hand, and in shallow wetland groundwater, on the other. Figure 1 shows the REE patterns for soil samples and soil solutions recovered from a peatland (Cotentin, France) and a riparian wetland (Pleine-Fougères, France), respectively. For both studied areas, the amount of REE in the soil is significantly higher than in solution. The soil REE patterns are flatter than the soil solution REE patterns which, for both wetlands, exhibit heavy REE (HREE) enrichment. This discrepancy indicates that the soil cannot be the one single factor controlling REE dynamics in waters flowing in wetlands. It seems reasonable to state that the REE dynamics in the water–soil system depend on: (i) the fractionation characteristics of the host rock/sediment, (ii) the weathering processes that might promote 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 dynamics.

2.1. 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. The gradual establishment of reducing conditions in wetland induces the release of redox-sensitive (or not) metals such as Fe or Mn, and Pb, Cd, etc., respectively but also large concentration of dissolved/colloidal organic matter (fraction <0.45 or 0.2 μm) (Hagedorn et al. 2000; Olivié-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 induced by reduction reactions (H^+ consumption). Organic matter can act as a major sink for trace metals due to its high binding capacity for metallic contaminants (Cabaniss and Shuman, 1988; Frimmel and Huber, 1996; Kalbitz and Wennrich, 1998). 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 therefore solubilized and its metal loading notably contains REE (Grybos et al. 2007; Pourret et al. 2007a; Pédrot et al. 2008; Shiller et al. 2010). Grybos et al. (2007) experimentally demonstrated that in wetland soil under reducing conditions, REE are mainly bound to dissolved organic matter in the solution. Moreover, using REE patterns as tracers of REE sources in wetland soils, Davranche et al. (2011) demonstrated that soil organic matter was the main source of

REE in solution. The flood period constitutes therefore the major input of REE into hydrosystems. Shiller (2010) calculated that the reducing conditions resulting from the spring flood of soil near Loch Vale (Colorado, USA) lead to an 8-fold increase in all REE concentrations.

Under oxidizing conditions, in the low water season, the exported flux of REE is low and is mainly controlled by the soil organic matter dynamics. Pourret et al. (2010) showed that REE speciation is controlled by colloidal organic matter present in wetland soil solution even under oxidizing conditions (Naizin, France; Table 1). REE speciation was determined from ultrafiltration with a pore-size between 30 and 5 kDa, and was supported by modeling calculations using Model VI (Tipping, 1998). Model VI is specific to cation binding with humic substances and its database is optimized for the binding parameters of REE-humic substances (Pourret et al. 2007a). The calculation demonstrated that the speciation of the REE was largely dominated by their binding with humic substances regardless of which water season was considered (Table 1).

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 2 shows that Eh decreases, whereas the Fe concentration increases in solution subsequently to the reductive solubilization of Fe(III). The establishment of the moderately reducing condition resulted in a rise in the dissolved REE concentration, but without any drastic modifications to the REE pattern (Fig. 2). The speciation of REE in the shallow groundwater was therefore not significantly modified between the oxidizing and reducing periods. Therefore, REE were bound to dissolved/colloidal organic matter occurring in the soil solutions and shallow groundwater under oxidizing and reducing conditions.

2.2. Colloidal control

In wetland soil solution or shallow groundwater, REE are closely associated with colloids (particles < 1 μ m). Studies performed on surface waters that drain wetlands, wetland solutions or shallow wetland groundwater from various types of boreal, tropical, Mediterranean or temperate wetlands, used ultrafiltration analysis and various pore sizes to demonstrate that REE are mainly concentrated in the high-molecular weight of the ultrafiltrated fraction of the solution, namely bound to the colloid phases (Viers et al. 1997; Dia et al. 2000; Tang et Johannesson 2003; Pourret al. 2007a-b; Pédrot et al. 2008; Cidu et al. 2013; Vasyukova et al. 2012; Neubauer et al. 2013). Vasyukova et al. (2012), who studied the distribution of 50 major and trace elements in Fe and organic-rich boreal surface waters (either draining wetlands or not) between the colloidal (1 kDa–0.22 μ m)

and truly dissolved (< 1 kDa) phases, showed that the association of REE with colloids increases with increasing pH.

If colloids are regarded as the main transfer and binding phases of REE in wetland solutions and waters, the Fe and organic matter phases are the major components of the colloids encountered and formed in wetlands or waterlogged soils. The term wetland covers a large diversity of areas 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 Fe-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 voltammetric titrations indicated that dissolved REE in Great Dismal Swamp waters are controlled by the complexation of REE with natural organic matter (Johannesson et al., 2004). Neubauer et al. (2013) applied Flow Field-Flow Fractionation analyses (FlowFFF) to waters 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, i.e. REE are bound to organic-rich colloids. Same results were obtained by Stolpe et al. (2013) using FFF separation for alaskan rivers water samples. This strong binding of REE by organic matter was confirmed by several field, experimental and modeling studies (Tang and Johannesson 2003; Johannesson et al. 2004; 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). Moreover, Davranche et al. (2011) demonstrated that Fe occurs mainly in wetland soils as amorphous Fe(III)-nanoparticles embedded within the organic matter which are poor in REE and trace elements. The controlling parameters of 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 the humid tropical watershed in Cameroon (Viers et al. 1997; Braun et al. 1998). Moreover Pédrot et al. (2008), who performed leaching experiments on wetland soils under oxidizing conditions, 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 are strongly related to the topography (Dia et al. 2000; Gruau et

al. 2004; Pourret al. 2010) (Fig. 3). Ultrafiltration analyses coupled to modeling calculations using Model VI indicated that REE are mainly bound to colloids, which are Fe enriched in the top of the catchment and organic-enriched at 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, Ce/Ce^* , ($Ce/Ce^* = 2Ce_{UCC}/[Pr_{UCC} + Nd_{UCC}]$) with the topography. Pédrot et al. (2014 under press) observed that this spatial variation is strongly correlated with the soil organic carbon/Fe ratio. From soil leaching experiments, they observed that for a low organic C/Fe ratio, the negative Ce anomaly amplitude in the soil solution was high, whereas for a high organic C/Fe ratio, the negative Ce anomaly was small or insignificant. Subsequent reductive dissolution experiments with ascorbate (as a reducing agent) on the soil sample with a low organic C/Fe ratio demonstrated that the REE pattern for the 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 wetland soils with a high organic C/Fe ratio, the REE patterns solubilized under reducing conditions did not exhibit any Ce anomaly. Davranche et al. (2004; 2005) demonstrated that the suppression of the Ce anomaly in organic-rich water is explained by the organic speciation of the REE. In this type of water, REE and Ce are bound to organic molecules. Although Fe and Mn could be present in the medium, this organic matter-mediated complexation prevents any Ce(III) scavenging/oxidation by Fe and Mn oxides from occurring. Therefore, in the bottomland, the REE signature is sourced in the organic matter in the uppermost soil and its solubilization as an organic colloid in the wetland soil solution.

Therefore along a toposequence, REE patterns, speciation and transfer are mainly controlled by organic colloids in bottom land soils (wetland soils) or Fe-rich colloids in the upland soil (well-drained soils). The composition, organic or Fe-rich, of such colloids is dependent on the soil composition. and on mechanisms that control colloid formation and transfer in solution such as, for instance, hydrodynamic conditions.

2.3 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 being 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 (Tyler 2004). Plants growing in sediments/waters with high elemental loading have developed tolerance or avoidance mechanisms (Freeman and Salt 2007). To avoid the uptake of metals and metalloids, they are able to excrete exudates by the roots, to bind elements in the roots and to leaf cells or to trap elements in the cell vacuole (Schaller et al. 2013). High amounts of chemical elements in plant tissues can also be accumulated through transpiration (Schaller et al. 2013). However, 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 (e.g. for La, about 700 ng g⁻¹ in fern (Matteuccia) and less than 10 ng g⁻¹ of La in Norway spruce needles (Ding et al., 2005))organs (leaves, roots), organs age (HREE amount decreased from the older to the younger leave, (Ding et al. 2005))and REE abundance in soils (Ding et al., 2006). In china, oncentrations up to 7000 ppm of LREE have been reported to accumulate in the leaves of the specific hyper-accumulator *Dicropteris dichotoma* (Shan et al. 2003). Nevertheless, the internal processes of plants can fractionated the REE (Ding et al., 2006; Lima e Cunha et al. 2006,; Stille, 2006; Brioschi et al., 2013). 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 (Akagi et al., 2002). However, further studies need to be carried out in order to confirm or dispel this hypothesis.

Therefore, the major biological mechanism that seems to account significantly for the behavior and distribution of REE in wetlands is an indirect mechanism, the bioreduction of Mn(IV) and Fe(III). This reaction which is mediated by the bacteria consortium occurring in wetlands, indirectly controls the organic matter solubility. The saturation of wetland soil with water promotes the use of Mn and Fe oxides as the electron

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 organic matter, with its REE loading, solubilization.

3. Factor controlling the REE pattern variability in wetland water

As previously demonstrated, in shallow wetland groundwater, REE are mainly associated with organic colloids. However, although the speciation determination using modeling calculations (Model V, Model VI), voltametry and ultrafiltration showed that REE are bound to organic molecules at more than 90% (Fig. 4), several types of REE patterns can be observed (Gruau et al. 2004 ; Johannesson et al. 2004; Pourret et al. 2007a). The first REE pattern type, observed in acidic pH waters, displays a middle REE (MREE) enrichment compared to LREE and HREE (Figs. 4a, 4b and 4c). The REE pattern in the Great Dismal Swamp waters, for which Eu is determined, exhibit substantial negative Eu anomalies, Eu/Eu^* , ($Eu/Eu^* = \{2Eu_{UCC}/[Sm_{UCC} + Gd_{UCC}]\}$), which range from 1.07 to 0.44 (Fig. 4b). Pourret et al. (2007b) experimentally demonstrated that the distribution coefficients (K_d) between REE and humic acid (HA) increased for MREE at a $pH \leq 7$ and high REE concentrations with respect to HA (Fig. 5a). The second type of pattern exhibits an HREE enrichment (Fig. 4c). The same REE pattern was reproduced experimentally by both Sonke and Salters (2006) and Stern et al. (2007) from $pH = 6$ to 9 and a low REE concentration with respect to HA (Figs. 4c and 5b).

The first hypothesis, which was provided to explain both REE specific signatures this specific feature was that the REE patterns were controlled by the chemical weathering or the precipitation of specific minerals. Therefore, the MREE downward concavity was explained by the dissolution/leaching of Fe-iron oxides, apatite, rhadophane, etc. or the precipitation of LREE and HREE with phosphates (e.g. Johannesson and Lyons 1995; Byrne et al. 1996; Taunton et al. 2000). However, more recent studies have demonstrated that in organic-rich waters in which REE speciation is dominated by their binding with organic molecules, the REE pattern is controlled by the surface properties of the organic matter itself (e.g. Pourret et al. 2007b; Kautenburger 2009; Marsac et al. 2010; 2011; Kautenburger et al. 2014).

It important to note that many of these experimental studies concerns REE association with humic acid, and in particular, commercially available material Aldrich Humic Acid and Leonardite, both manufactured from coal. However, as previously demonstrated, the REE patterns are controlled by both functional surface sites distribution and composition. When surface sites of Leonardite and Aldrich are compared to those of humic acids extracted from organic soils, no drastic differences appear (e.g. Leonardite: 7.46 and 2.31 meq g^{-1} C for

carboxylic and phenolic groups, respectively against for Elliot soil: 8.28 and 1.87 meq g⁻¹ C for carboxylic group and phenolic groups, respectively) (Ritchie and Perdue, 2003). Furthermore, even if humic acid represent 15% of DOC in wetlands versus 10% of DOC in rivers (Thurman, 1985), it is well known that fulvic acids are generally much more abundant in natural waters. However, for experimental convenience such as product availability and REE-humic complexes separation from solution, humic acid remains generally chosen. If fulvic acids are more soluble than humic acids, both present higher abundance of carboxylic weak sites than phenolic strong sites and the sorption mechanisms on their surface are identical. The REE pattern resulting from binding with fulvic acids would therefore not differ from those corresponding to humic acids-mediated binding. The only carboxylic/phenolic site ratio between humic and fulvic acids could weakly modify the REE pattern developed when identical physico-chemical conditions prevail.

3.1. REE loading and HA surface heterogeneity

Marsac et al. (2010; 2011) demonstrate that the discrepancy between these two types of REE patterns is explained by the combined effect of 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 multidentate/chelating sites. The resulting REE patterns show a lanthanide contraction. By contrast, at high metal loading, REE are complexed to weak but more abundant HA sites, namely the carboxylic group. The resulting REE pattern exhibits a MREE downward concavity. These authors developed two approaches to obtain this result. In a first step, they compared their experimental log K_d REE-HA patterns with the pattern for the stability constants (log K) of REE-organic model ligands. Humic acids can be considered as a group of discrete sites. The major sites identified on the HA surface are the carboxylic and phenolic groups, which can form monodentate or multidentate complexes. Using this simplified representation, HA binding properties can be compared with the binding properties of model organic ligands. Figure 6 displays the pattern of the log K REE-carboxylic model ligand, namely acetic acid (Fig. 6a), the REE-phenolic model ligand, namely catechol (Fig. 6b) and the REE-chelate ligand model, namely nitrilotriacetic acid (NTA) (Fig. 6c) (Byrne and Li 1995). The REE patterns corresponding to the binding of REE with acetate (carboxylic group) exhibit a MREE downward concavity, whereas catechol and NTA (phenolic and chelate group) exhibit a lanthanide contraction effect corresponding to both REE-HA patterns obtained at high and low metal loading, respectively. Figure 6d 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). The ratio La/Lu is a useful tool to fingerprint the shape of the REE pattern. This ratio 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 results which demonstrate that HREE are preferentially bound to strong organic matter aromatic functional groups such as phenolic sites compared to LREE (Gangloff et al. 2014).

In a second step, Marsac et al. (2011) used a modeling approach to confirm this hypothesis and to gain access to the REE speciation on each HA site. They combined Model VI, a model specific to cation-humic acid binding (Tipping 1998) with PHREEQC, a generic speciation model (Parkhurst and Appelo 1999). This coupling allowed to dissociate the binding parameter of the carboxylic and phenolic sites ($\log K_{M_a}$ and $\log K_{M_b}$), which were previously linked by a linear relationship in Model VI. This linear relationship between both parameters means that the REE have to be bound to the HA phenolic groups via a MREE downward concavity pattern, which does not correspond to the pattern developed with the corresponding single organic ligand, catechol, as shown in Figure 6. This is the reason why this relationship was removed. This coupling also allowed to access the distribution of the REE onto each binding group described in PHREEQC-Model VI. Simulations of the experimental datasets available in the literature (Sonke and Salters 2005; Pourret et al. 2007b; Marsac et al. 2010; 2011) provided 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. At a circumneutral pH, LREE are bound to carboxylic groups and HREE via phenolic groups (Fig. 7). The denticity of the REE-HA complex is also dependent on the metal loading. Using PHREEQC-Model VI, the simulations showed that the average number of HA groups coordinated to REE increased with decreasing metal loading (Marsac et al. 2011; 2014). More recently, Kautenburger et al. (2014) studied the binding of REE to modified HA with blocked phenolic or carboxylic sites. The data obtained suggests that REE binding to strong sites can be assumed to be chelating complexes consisting of a combination of phenolic and carboxylic groups. Marsac et al. (2014, submitted) obtained EXAFS records on Yb-HA complexes synthesized at low and high loadings. Their results showed that at a low loading, REE are bound to HA through bi-ligand complexes without any chelation effect in which REE act as a cation bridge between two organic molecules. By contrast, at high loading, REE are bound to HA via multi-carboxylic chelate ligands.

3.2. Competitive cations

Competition between cations and REE in solution in terms of their binding to HA also appear to be another important controlling factor on the REE patterns developed in shallow organic-rich wetland groundwater (Tang and Johannesson 2003; Marsac et al. 2012; 2013). By contrast to laboratory experiments, in which the REE/HA ratio can vary from 10^{-4} to 10^{-2} mol REE/mol organic C, REE/HA ratios are often very low in natural waters, ranging from 10^{-6} to 10^{-4} mol REE/mol organic C (Tang and Johannesson 2010). In natural waters, the HA metal loading is therefore generally imposed by other dissolved metals, such as Fe and Al, which occur in much higher concentrations than REE. Marsac et al. (2012; 2013) used REE-Al(III) and REE-Fe(III) competitive complexation experiments for HA and the modeling of experimental datasets with PHREEQC-Model VI to demonstrate that (i) Fe^{3+} competes more strongly with HREE than LREE, whereas Fe(III) species formed at higher pH values (i.e. FeOH^{2+} or Fe polymer) compete equally with LREE and HREE (Figs. 8b and 8c). For Al(III), they show that Al^{3+} has the same competitive effect on REE-HA binding as Fe^{3+} , but at higher pH values, AlOH^{2+} mainly competes with LREE (Figs. 8a and 8b). In turn, since the HA binding sites for the REE are previously estimated, this effect of competition on the REE patterns gives information about the own binding sites of Fe and Al. Thereby, at acidic pH values, Fe(III) as Fe^{3+} is bound with carboxylic and multidendate sites and Al(III), Al^{3+} is bound to phenolic and multidendate sites (Figs. 8a and 8c). At a circumneutral pH, Fe(III) as FeOH^{2+} is bound to all HA binding sites and Al(III) as AlOH^{2+} is mainly bound to carboxylic sites. The effect of competition on the REE patterns appears to be totally dependent on the speciation of Al(III) and Fe(III) with respect to the physicochemical conditions. For example, in wetland solutions with an acidic pH < 5 and low REE loading, the theoretical REE pattern without any competitive cations should exhibit HREE enrichment (lanthanide contraction). However, when Fe(III) and Al(III) are present as Fe^{3+} and Al^{3+} in such acidic water, the REE pattern should exhibit a MREE downward concavity. This MREE enrichment is subsequently produced by the competition of Fe^{3+} and Al^{3+} with LREE for their binding to weak carboxylic sites and with HREE for their binding with phenolic and strong chelating sites. By contrast, in wetland solutions at a circumneutral pH and high REE loading, the presence Fe(III) as hydrolyzed species (FeOH^{2+} or Fe polymer) should not modify the MREE downward concavity pattern since FeOH^{2+} competes for all REE. Only the amount of REE bound to HA should decrease (Fig. 8d). Furthermore, for the same wetland solution at neutral pH and high REE loading, the presence of Al(III) as AlOH^{2+} should modify the MREE downward concavity to a HREE enriched pattern since Al competes with LREE for the carboxylic sites (Fig. 8b). Kohler et al. (2014) studied the mobilization of REE, Al, Fe and U in a boreal catchment and demonstrated that organic matter controls their speciation in solution. However, the increase in pH downstream from the catchment promotes the precipitation of Fe and Al as

ferrihydrate and gibbsite, respectively. This selective removal of Al and Fe from the organic matter binding sites results in a higher La concentration downstream, i.e. a higher amount of La bound to colloidal organic matter occurring in solution. Therefore the pH, which controls the chemical species of the competitor cations present in the solution, appears to be the major driver of this competition between trivalent cations and REE.

4. Conclusions

With regards to the hydrodynamic conditions prevailing in wetlands, the biogeochemical process occurring in these specific areas strongly influence the mobility and speciation of many elements in solution. Among them, REE is a unique group of elements in terms of the information that can be supplied by the REE patterns. REE patterns and abundances thereby can be used to discriminate between the most important mechanisms that occur. This review demonstrates that organic matter, pH and reducing conditions are the main factors controlling REE behavior in wetland areas. The first operator is soil organic matter. This organic matter strongly binds REE. The heterogeneity of the functional groups present on its surface results in a specific REE pattern in the solution in which organic matter is solubilized. However, this REE pattern is dependent on the other potential competitive cations, notably the trivalent cations that are able to compete with REE for the organic matter binding sites, namely Fe(III) and Al(III). The second operator is pH, which occurs at several steps. First, not only does pH control the solubility and speciation of REE, but also that of their competitors - Fe and Al - and therefore their ability to compete with REE. Second, pH is responsible for the solubilization of soil organic matter as organic colloids by controlling its adsorption/desorption from the soil solid phases. Last, reducing conditions appear to be a second order operator. The establishment of reducing conditions subsequent to wetland soil saturation drastically increases the amount of organic matter and its REE loading in shallow groundwater. However, reduction acts indirectly through the increase in pH caused by H^+ consumption in the reducing reactions. When the conditions become progressively reducing, the increase in pH promotes organic matter desorption as colloids from the soil matrix, and potentially a decrease in the amount of competitive Al by its precipitation as gibbsite, for example. This results in a strong release of REE, the speciation of which is dominated by their binding to organic colloids.

Acknowledgments. This research was funded by the French ANR, through the “Programme Jeunes Chercheuses
- Jeunes Chercheurs”/“SURFREE: Rare earth element partitioning at the solid-water interface: Impact on REE
geochemical behavior and tracing properties”. Dr. Sara Mullin is acknowledged for post-editing the English
style.

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Table and figure captions

Table 1

REE speciation in shallow groundwater from the Naizin (France) riparian wetland (Pourret et al. 2010). Calculations were performed using Model VI and the optimized data produced by Pourret et al. (2007a).

Fig. 1. a) REE patterns for a solid peat sample and peat solutions from the Cotentin marshlands (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 reflecting REE fractionation during their solubilization.

Fig. 2. a) REE pattern evolution relative to time in the 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 that no drastic REE speciation change occurs.

Fig. 3. Evolution of the REE pattern in shallow groundwater relative to the topography in the Mercy sub-catchment (Brittany, France) (Pourret et al. 2010).

Fig. 4. UCC normalized REE patterns in the dissolved fraction ($< 0.2 \mu\text{m}$) of the organic-rich wetland solutions from the a) Kervidy Naizin wetland (France) (DOC ≈ 15 ppm), c) Great Diswal swamp (USA) (DOC from 5.3 to 115 ppm) and c) Le Home-Pleine Fougères wetland (France) (DOC ≈ 27 ppm). The REE patterns are different although the modeling calculations using Model V, Model VI, Voltammetry and ultrafiltration analysis showed that REE are bound at more than 90% to colloidal organic matter (Gruau et al., 2004; Johannesson et al., 2005; Pourret et al., 2007a).

Fig. 5. (a) Log K_d REE pattern on the colloidal HA surface at pH = 6 (Pourret et al., 2007b). (b) Apparent log β REE-HA at pH = 6 (Sonke and Salters, 2006).

Fig. 6. Pattern of log K REE with (a) acetate, (b) catechol and (c) NTA. (d) log(KLu-organic ligand/KLa-organic ligand) relative to the average log KREE-organic ligand for the 101 organic ligands compiled by Byrne and Li (1995).

Fig. 7. Evolution of REE speciation on the HA site described in PHREEQC-Model VI relative to the pH at high loading.

Fig. 8. REE-HA log K_d pattern in the high loading condition and Al(III) or Fe(III)/REE ratio = 1, a) with and without Al(III) at pH 3, b) with and without Al(III) at pH 6, c) with and without Fe(III) at pH = 3 and d) with and without Fe(III) at pH = 6. Figure modified from Marsac et al. (2012).

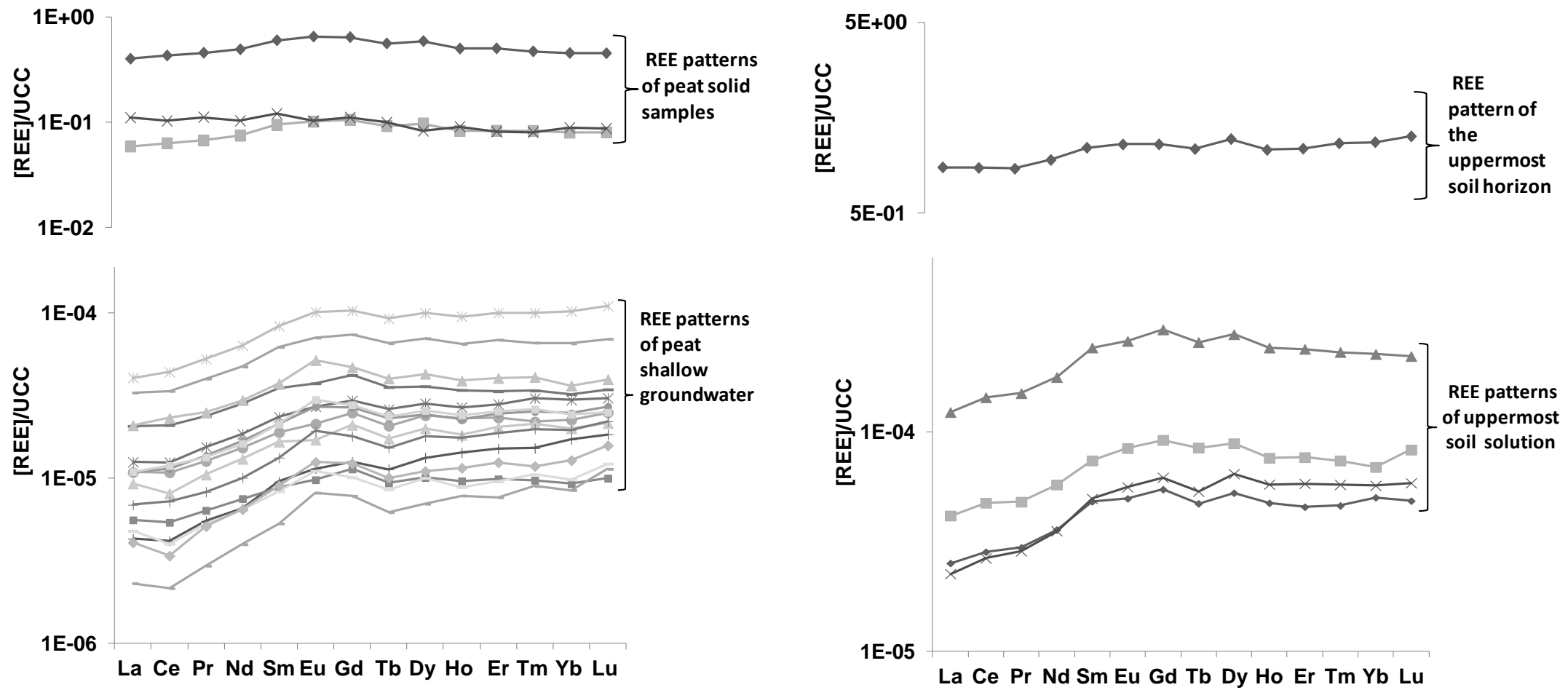


Fig. 1. a) REE patterns for a solid peat sample and peat solutions from the Cotentin marshlands (France) (Auterives, 2007). b) REE pattern for the uppermost soil horizon and its soil solution at various sampling dates from the riparian Le Home wetland (Brittany, France) (modified from Gruau et al., 2004). The peat and soil REE patterns are flat, whereas the peat and wetland soil solution patterns exhibit a LREE depletion reflecting REE fractionation during their solubilization.

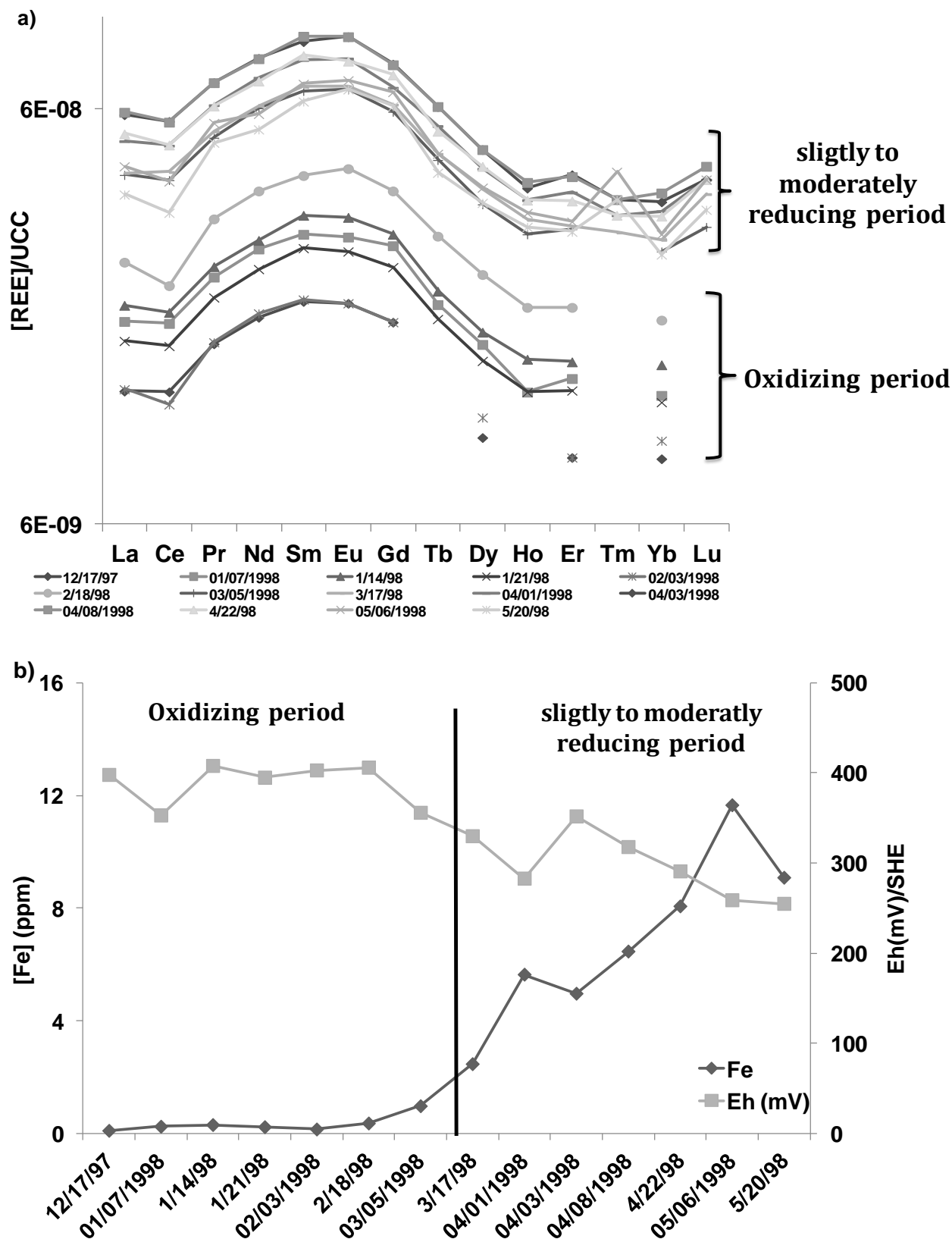


Fig. 2. a) REE pattern evolution relative to time in the shallow groundwater from the Naizin wetland (Brittany, France), b) Evolution of the Eh and Fe concentration indicating the establishment of moderately reducing conditions and the reductive dissolution of soil Fe oxides (Dia et al., 2000). Although the redox conditions became moderately reduced, the REE pattern was not significantly modified, suggesting that no drastic REE speciation change occurs.

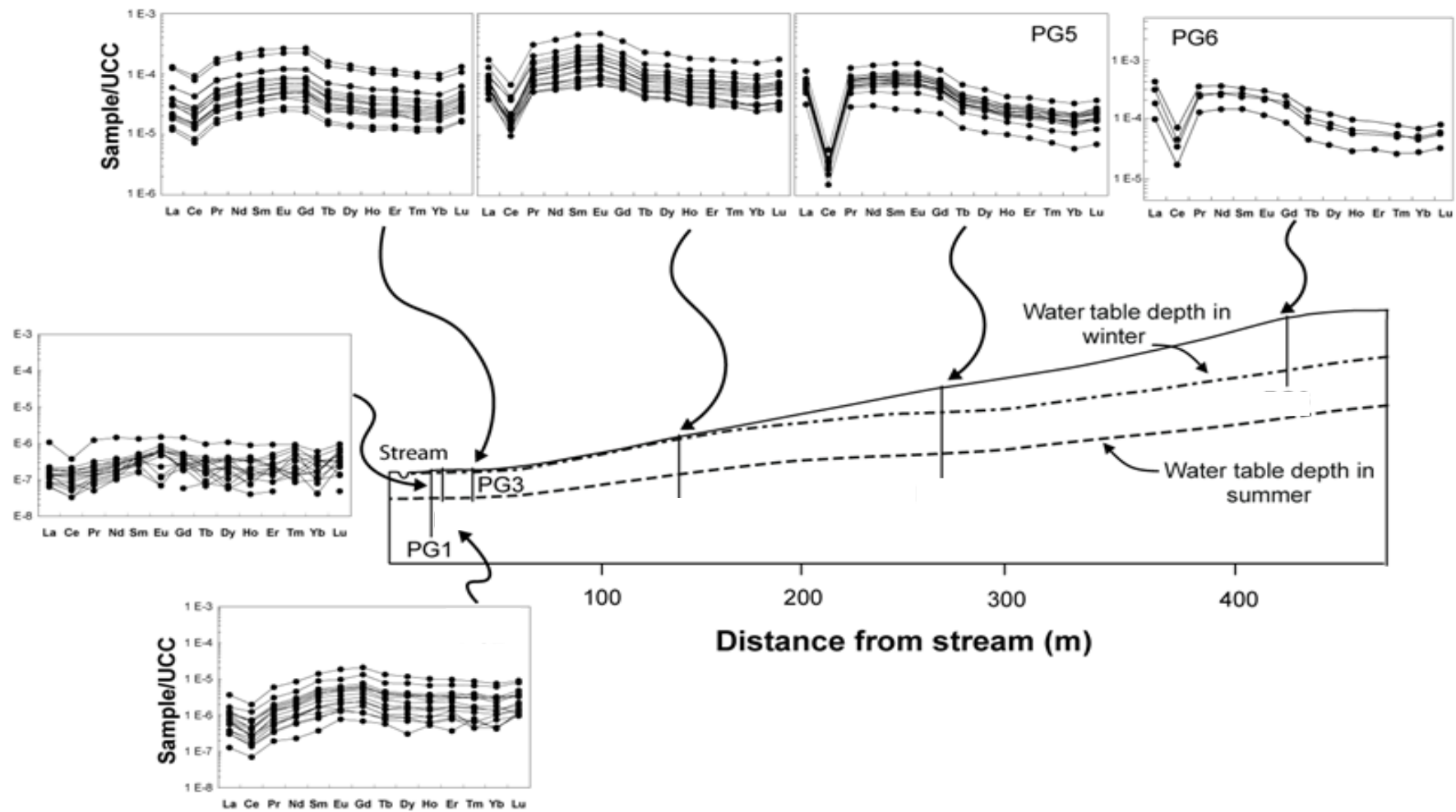


Fig. 3. Evolution of the REE pattern in shallow groundwater relative to the topography in the Mercy sub-catchment (Brittany, France) (Pourret et al. 2010).

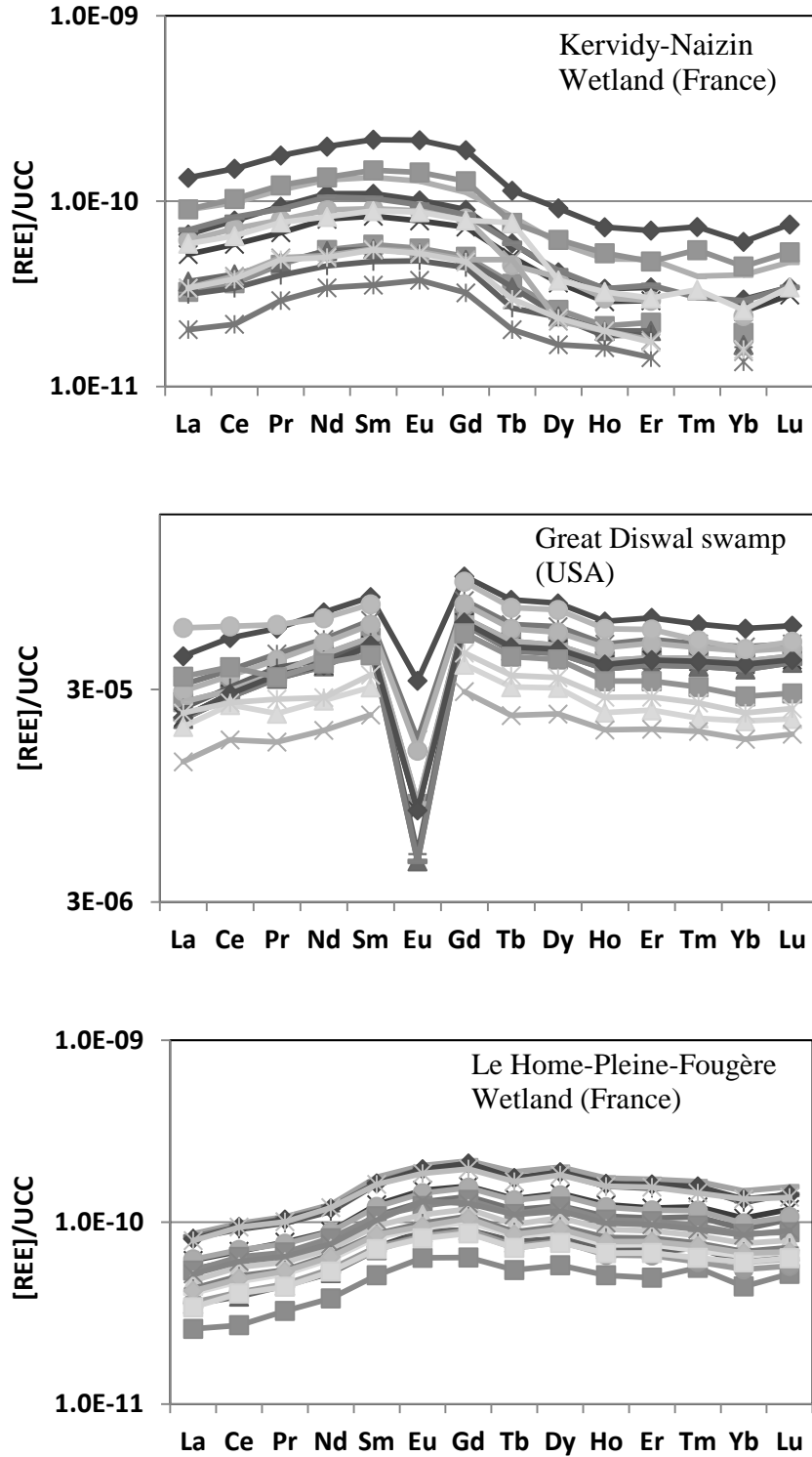


Fig. 4. UCC normalized REE patterns in the dissolved fraction ($< 0.2 \mu m$) of the organic-rich wetland solutions from the a) Kervidy Naizin wetland (France) (DOC ≈ 15 ppm), c) Great Diswal swamp (USA) (DOC from 5.3 to 115 ppm) and c) Le Home-Pleine Fougères wetland (France) (DOC ≈ 27 ppm). The REE patterns are different although the modeling calculations using Model V, Model VI, Voltammetry and ultrafiltration analysis showed that REE are bound at more than 90% to colloidal organic matter (Gruau et al., 2004; Johannesson et al., 2005; Pourret et al., 2007a).

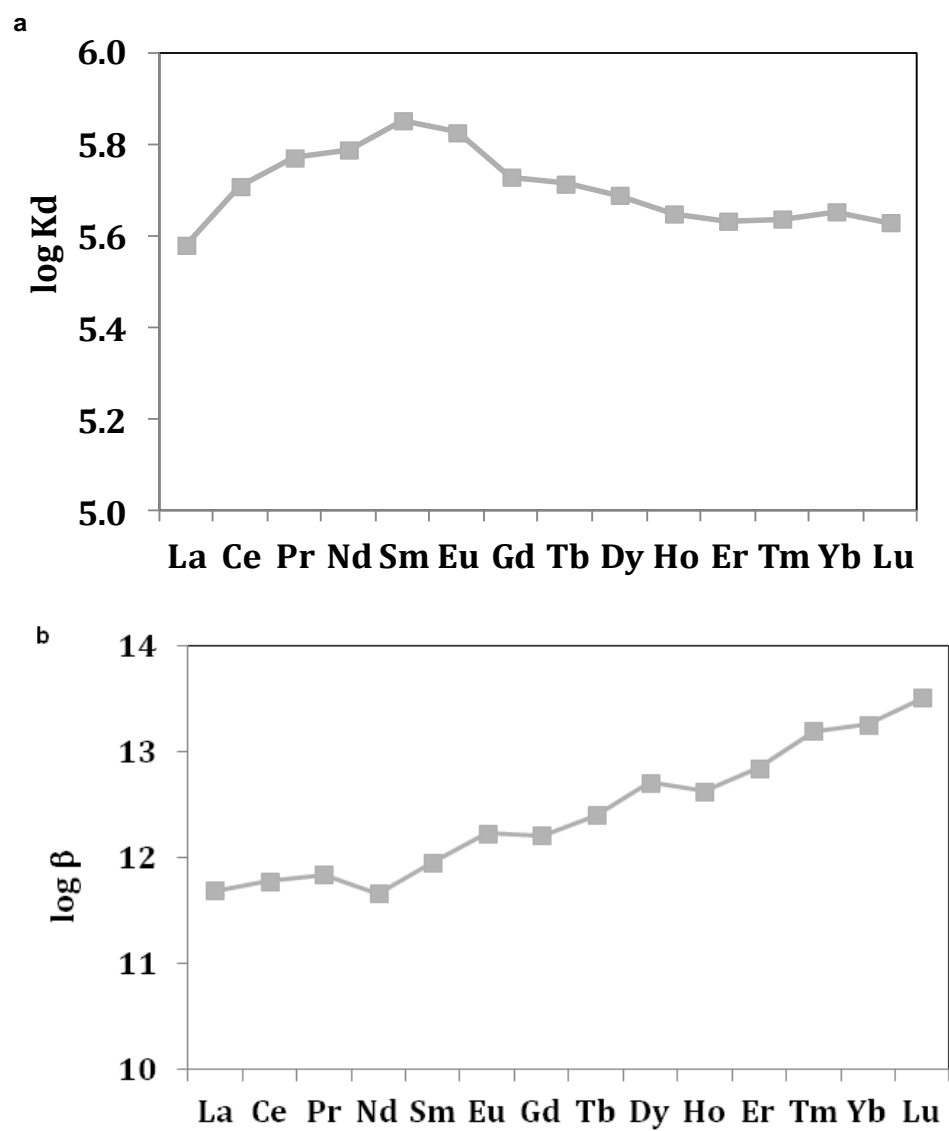


Fig. 5. (a) Log Kd REE pattern on the colloidal HA surface at pH = 6 (Pourret et al., 2007b). (b) Apparent log β REE-HA at pH = 6 (Sonke and Salters, 2006).

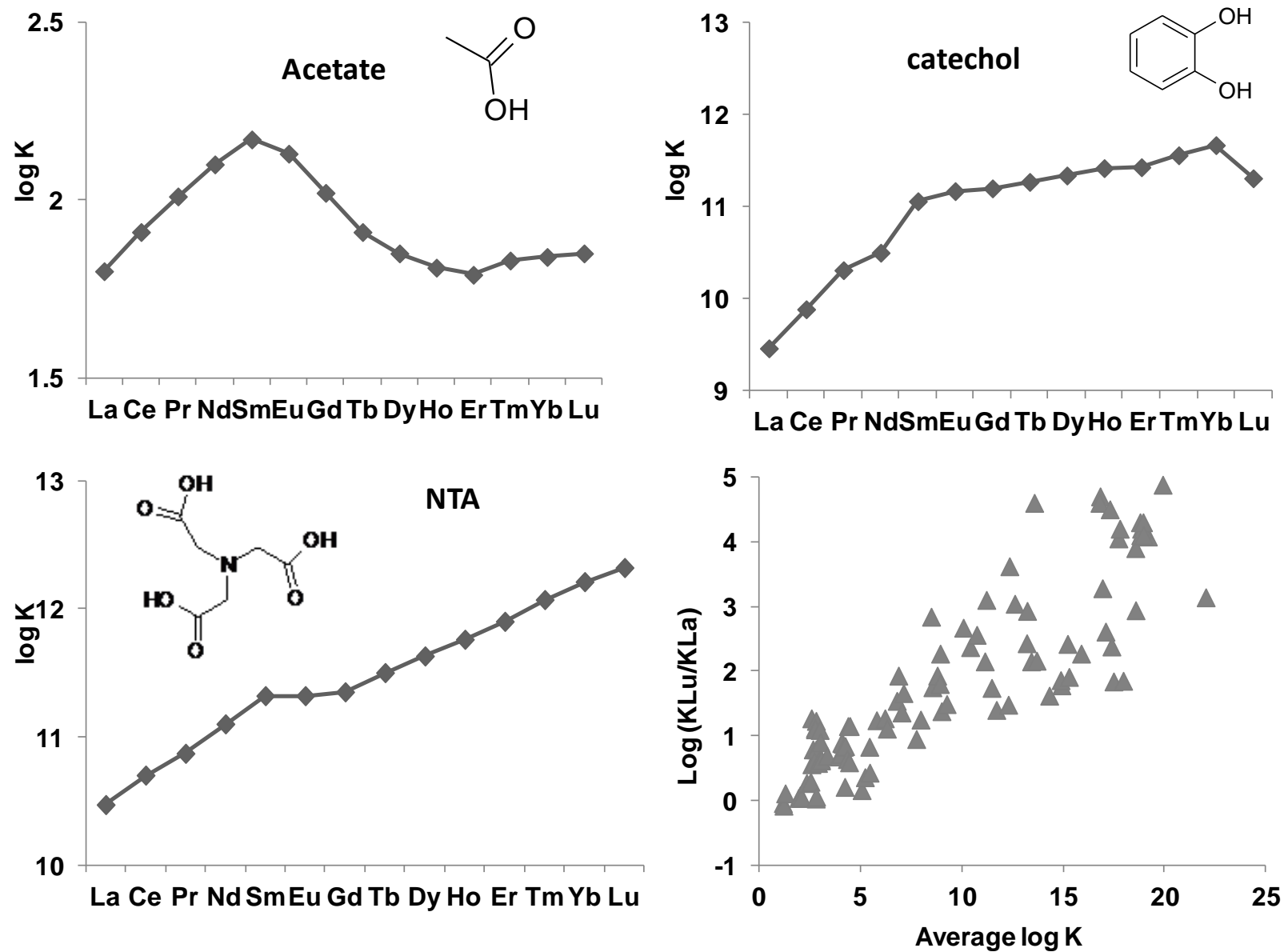


Fig. 6. Pattern of $\log K$ REE with (a) acetate, (b) catechol and (c) NTA. (d) $\log(K_{\text{Lu-organic ligand}}/K_{\text{La-organic ligand}})$ relative to the average $\log K_{\text{REE-organic ligand}}$ for the 101 organic ligands compiled by Byrne and Li (1995).

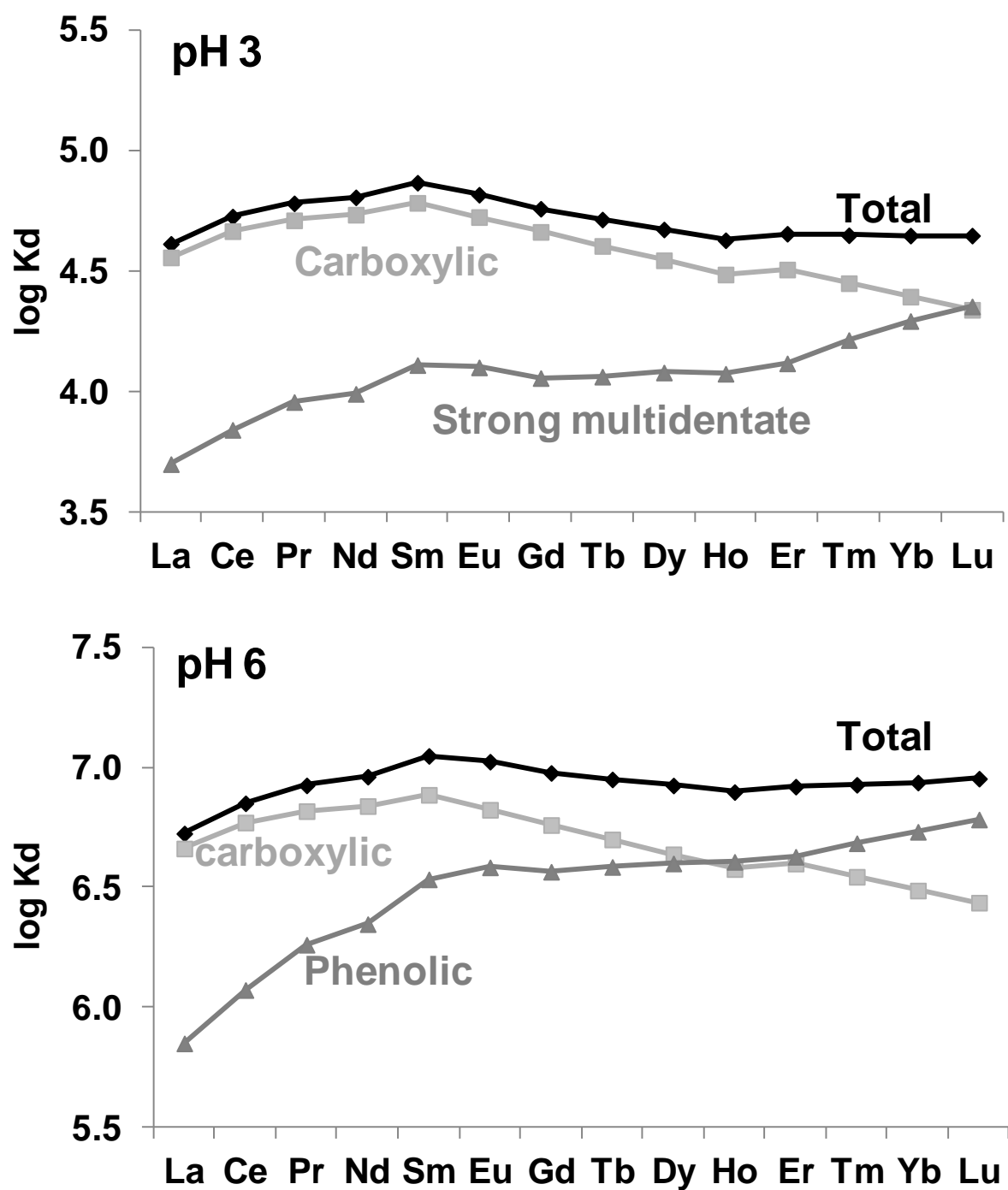


Fig. 7. Evolution of REE speciation on the HA site described in PHREEQC-Model VI relative to the pH at high loading.

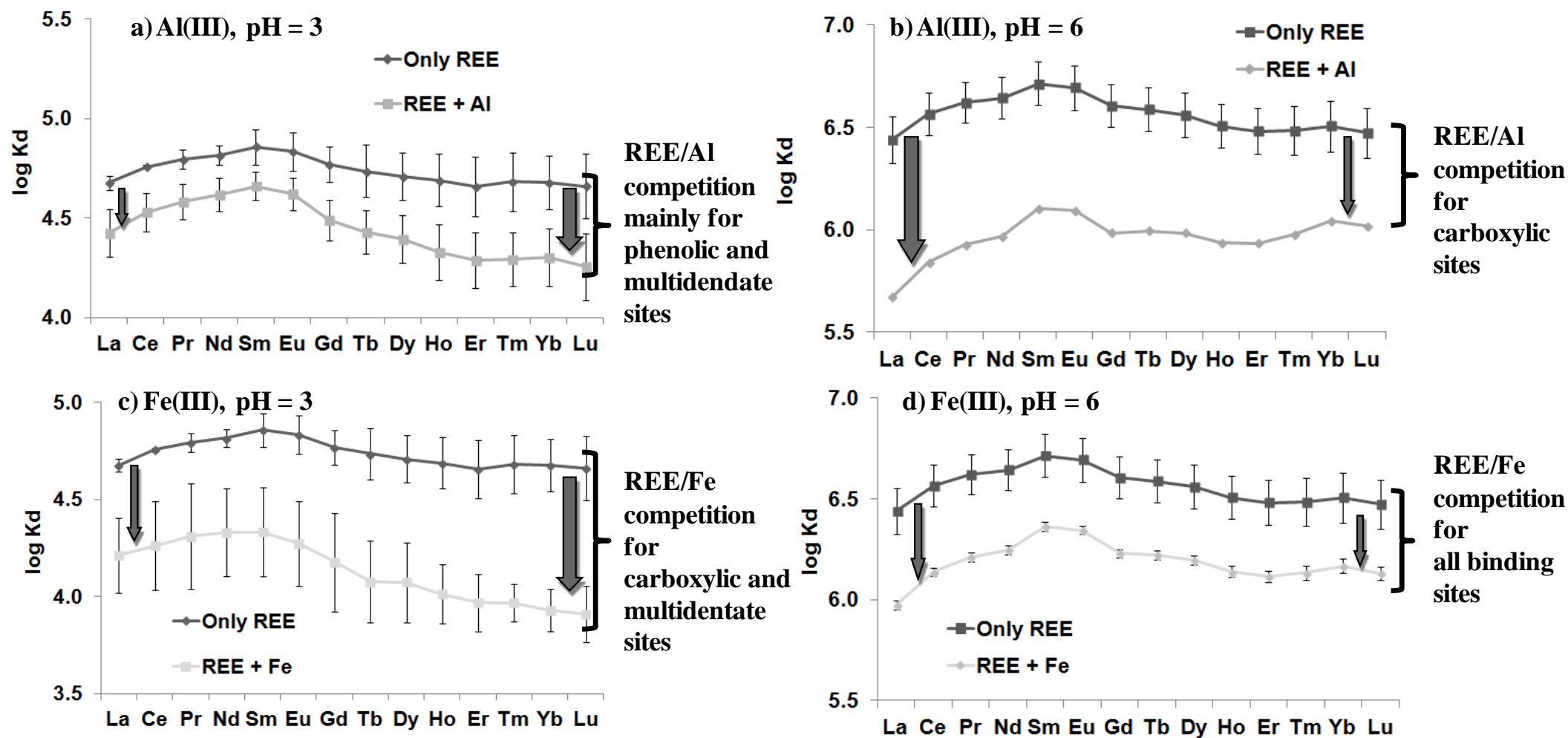


Fig. 8. REE-HA log Kd pattern in the high loading condition and Al(III) or Fe(III)/REE ratio = 1, a) with and without Al(III) at pH 3, b) with and without Al(III) at pH 6, c) with and without Fe(III) at pH = 3 and d) with and without Fe(III) at pH = 6. Figure modified from Marsac et al. (2012).

Species % (in shallow wetland groundwater)	La³⁺	LaSO₄	La-HS	Other species
November (beginning of the saturated season)	0.0	0.0	100	0.0
May (beginning of the unsaturated season)	7.0	0.5	92.5	0.0

Table 1

REE speciation in shallow groundwater from the Naizin (France) riparian wetland (Pourret et al. 2010). Calculations were performed using Model VI and the optimized data produced by Pourret et al. (2007a).