

Metal loading effect on rare earth element binding to humic acid: Experimental and modelling evidence

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Abstract

The effect of metal loading on the binding of rare earth elements (REE) to humic acid (HA) was studied by combining ultrafiltration and Inductively Coupled Plasma Mass Spectrometry techniques. REE–HA complexation experiments were performed at pH 3 for REE/C molar ratios ranging from 4×10^{-4} to 2.7×10^{-2} . Results show that the relative amount of REE bound to HA strongly increases with decreasing REE/C. A middle-REE (MREE) downward concavity is shown by patterns at high metal loading, whereas patterns at low metal loading display a regular increase from La to Lu. Humic Ion Model VI modelling are close to the experimental data variations, provided that (i) the ΔLK_2 parameter (i.e. the Model VI parameter taken into account the presence of strong but low density binding sites) is allowed to increase regularly from La to Lu (from 1.1 to 2.1) and (ii) the published $\log K_{\text{MA}}$ values (i.e. the REE–HA binding constants specific to Model VI) are slightly modified, in particular with respect to heavy REE. Modelling approach provided evidence that $\log K_{\text{d}}^{\text{REE}}$ patterns with varying REE/C likely arises because REE binding to HA occurs through two types of binding sites in different density: (i) a few strong sites that preferentially complex the heavy REE and thus control the $\log K_{\text{d}}^{\text{REE}}$ patterns at low REE/C; (ii) a larger amount of weaker binding sites that preferentially complex the middle-REE and thus control the $\log K_{\text{d}}^{\text{REE}}$ pattern at high REE/C. Hence, metal loading exerts a major effect on HA-mediated REE binding, which could explain the diversity of published conditional constants for REE binding with HA. A literature survey suggests that the few strong sites activated at low REE/C could be multidentate carboxylic sites, or perhaps N-, or P-functional groups. Finally, an examination of the literature field data proposed that the described loading effect could account for much of the variation in REE patterns observed in natural organic-rich waters ($\text{DOC} > 5 \text{ mg L}^{-1}$ and $4 \leq \text{pH} \leq 7$).

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1. INTRODUCTION

There is now widespread evidence that rare earth elements (REE) in natural organic waters occur as organic complexes (Bidoglio et al., 1991; Glaus et al., 1995, 2000; Takahashi et al., 1997; Viers et al., 1997; Dia et al., 2000; Tang and Johannesson, 2003; Gruau et al., 2004; Pourret et al., 2007a,b; Yamamoto et al., 2005, in press; Sonke and Salters, 2006; Stern et al., 2007; Pédrot et al., 2008). This explains why the determination of conditional binding

constants of the REE by humic acids (HA) has recently become a major issue of REE hydrochemical studies (Tang and Johannesson, 2003; Yamamoto et al., 2005, in press; Sonke and Salters, 2006; Pourret et al., 2007a,b; Stern et al., 2007). Several recent studies showed that determining such constants is not an easy task because of the presence of a possible metal loading effect, leading to variations in the $\log K_{\text{d}}^{\text{REE}}$ patterns with variations in REE/HA ratio. Thus, Yamamoto et al. (2005, 2006) and Pourret et al. (2007b) reported a middle-REE (MREE) downward concavity in the $\log K_{\text{d}}^{\text{REE}}$ patterns from complexation experiments conducted at high metal loading (i.e. REE/C molar ratio ranging from 10^{-3} to 1.5×10^{-2} , with C corresponding to the amount of organic carbon). By contrast, Sonke and Salters (2006) and Stern et al. (2007) reported an overall increase of

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the $\log K_d^{\text{REE}}$ values from La to Lu (so-called lanthanide contraction effect) from experiments at much lower REE/C (10^{-4}). One possible explanation for this discrepancy is that the binding of the REE with HA occurs through the heterogeneity of the HA binding sites, having different stability constants and occurring in markedly distinct density. More specifically, the “lanthanide contraction effect” observed in low metal loading experiments could be due to the dominant binding of the REE to high affinity sites which, although occurring in the range of a few percent, would determine the $\log K_d^{\text{REE}}$ pattern under such low REE/C conditions. These sites, whose binding strength regularly increases with the REE atomic number, could be multidendate carboxylic sites, or phenolic, or aminocarboxylic sites as suggested by Stern et al. (2007) and Pourret and Martinez (2009). Alternatively, the MREE downward concavity observed at high metal loading could be due to the binding characteristics of high-density but weak sites, which would determine the HA binding under high REE/C conditions. These sites would complex the MREE much more efficiently than the LREE and the HREE, and could be attributed to carboxylic sites, which are known to be the main binding sites of REE in HA as demonstrated by NEXAFS analysis (C 1s-near edge X-ray absorption fine structure) of Eu–HA complexes at high Eu/C ratio (Plaschke et al., 2004).

The binding characteristics of different trace metals with HA were previously studied by adsorption isotherm experiments. These studies focused on the binding of Al (Kinniburgh et al., 1999), Ca, Cd, Cu (Benedetti et al., 1995), Am (Peters et al., 2001), As (Buschmann et al., 2004), Sb (Buschmann and Sigg, 2006), Pb and Cd (Abate and Masini, 2002) to humic substances (HS), evidenced an increase in the binding strength following the metal loading decrease, that can be related to HS surface site heterogeneity. Such non-linear binding was also observed by Hummel et al. (2000) for Eu complexation to HA. These studies agree with the hypothesis of a variation of the apparent $\log K_d^{\text{REE}}$ patterns with REE/C due to the heterogeneity of the HA binding sites occurring at different density. More recently, Yamamoto et al. (in press) demonstrated a regular and progressive evolution of the $\log K_d^{\text{REE}}$ patterns with decreasing metal loading, from a downward concave MREE distribution to a pattern showing the lanthanide contraction effect. However, this hypothesis still lacks corroboration from a comprehensive study involving experimental and modelling approaches.

In the present study, REE–HA binding experiments were performed simultaneously on the 14 naturally occurring REE over a wide range of REE/C molar ratio (ranging from 4×10^{-4} to 2.7×10^{-2}). Whereas the Sonke and Salters study used CE-ICP-MS at low REE/C and the Pourret et al. (2007a,b) study used ultrafiltration combined with ICP-MS, at high metal loading, all the here below presented data were obtained using same combined ultrafiltration and ICP-MS techniques. The experimental data are analysed to assess the variation in binding sites with changing REE/C using Humic ion binding Model VI (hereafter denoted as Model VI), developed by Tipping (1998). Finally, a compilation of 350 samples of organic-rich, river-, and soil-waters were pooling to show whether variations in REE pattern

displayed by natural organic-rich waters could be due to a metal loading effect.

2. MATERIALS AND METHODS

All chemicals used in this study were of analytical grade, with all experimental solutions being prepared with doubly-deionised water (Milli-Q system, Millipore™). Synthetic REE solutions were prepared from a nitrate REE standard (10 mg L^{-1} , Accu Trace™ Reference Standard). Polyethylene containers used to attain REE–HA complexation equilibrium were all previously soaked in 10% Ultrapure HNO_3 for 48 h at 60°C , then rinsed with deionised water for 24 h at 60°C to remove all REE contamination sources. All experiments were performed at room temperature, i.e. $20^\circ\text{C} \pm 2$.

2.1. Humic acid

Purified humic acid (HA) was obtained from synthetic Aldrich humic acid (Aldrich™, H1, 675-2). The purification was performed with the protocol of Vermeer et al. (1998), except that a tangential ultrafiltration step was added to remove any possible HA molecules $<10 \text{ kDa}$ using a Labscale TFF system equipped with a Pellicon XL membrane (PLCGC10, Millipore™). Humic acid was freeze-dried and stored in a glass container. Prior to use, purified HA was solubilized overnight in a solution of 0.01 M NaCl at pH 10 to ensure complete dissolution (Vermeer et al., 1998).

2.2. Experimental set-up of the REE binding with HA

A standard batch equilibrium technique was used to study REE complexation with HA. The fourteen REE were added simultaneously to a solution of $5\text{--}40 \text{ mg L}^{-1}$ of HA and 10^{-2} M NaCl . The REE/C (metal loading) varied from 4×10^{-4} to 2.7×10^{-2} . REE–HA binding experiments were carried out at pH 3. This acidic pH was chosen to avoid total complexation of the REE with HA, and to prevent complexation of the REE inorganic fraction by OH^- and CO_3^{2-} . Regards to their low stability constants ($-0.66 < \log \beta < -0.41$ at 0.7 M ionic strength and 25°C) (Byrne and Sholkovitz, 1996), REE–Cl complexes were neglected. All inorganic REE can thus be confidently assumed to occur as free aqueous REE^{3+} species in all the experiments, and are modelled accordingly (Tang and Johannesson, 2003; Pourret et al., 2007a). According to Yamamoto et al. (2009, in press), Al and Fe form stable complexes with carboxylic sites within humic substances and cannot be excluded completely by purification of HA. Although humic acid was here purified with an acidic cation-exchange resin (Dionex 50) at pH 1, part of Al and Fe could effectively remain onto HA. Therefore, HA sites strongly bound with residual Fe and Al may be considered as not available for cation binding. Moreover, HA site density is generally evaluated by potentiometric titration carried out between pH 2 and 11 (e.g. Ritchie and Perdue, 2003). Considering the titration pH, titrations do not allow to remove this residual Fe and Al from HA surface. In consequence, the HA sites strongly bound with Fe and Al do not account for surface

site density. Therefore, the potential effect of residual Al and Fe on REE binding was not taken into account in this study. Prior to REE addition, the pH was adjusted directly to a value of 3 in the HA suspensions, which were then filtered to remove any potential precipitate. The dissolved organic carbon (DOC) concentration was then measured to assess the true HA concentration of the filtrate. Immediately following REE addition, a solution aliquot was systematically analysed to determine the exact REE concentration and thus the true REE/C of each experimental suspension.

Experimental suspensions were stirred for 48 h to reach equilibrium according to the protocol defined by Pourret et al. (2007b). The pH was monitored regularly with a combined Radiometer Red Rod electrode, calibrated with WTW standard solutions (pH 4 and 7). The accuracy of pH measurements was ± 0.05 pH units. At equilibrium (48 h), 10 mL of the suspension were sampled and ultra-filtered at 5 kDa to separate the REE–HA complexes from the remaining inorganic REE. Ultrafiltrations were carried out by centrifuging the suspension aliquots through 15 mL centrifugal tubes equipped with permeable membranes of 5 kDa pore size (Vivaspin 15RH12, Sartorius). All the membranes used were first washed with 0.15 mol L^{-1} HCl, then rinsed twice with MilliQ water to minimize contamination. Centrifugations were performed using a Jouan G4.12 centrifuge with swinging bucket rotor at 3000g for 30 min.

Dissolved organic carbon concentrations measured in the ultrafiltrates were systematically lower than or equal to 0.1 mg L^{-1} , a concentration corresponding to the blank value currently observed in our laboratory (e.g. Pourret et al., 2007b). The 10 kDa ultrafiltration step added in the HA purification protocol ensures that no organic molecules pass through the 5 kDa ultrafiltration cells. Previously, Pourret et al. (2007b) showed from mass balance calculations, that more than 98% of REE were recovered and that REE adsorption onto the membrane and the cell device was insignificant. Hence, the concentrations of REE complexed to HA correspond strictly to the difference between the initial REE concentration and the REE concentration in the <5 kDa ultrafiltrate.

The REE complexation with HA is described using the apparent partition coefficient K_d , as follows:

$$K_d(\text{ln}_i) = \frac{\mu\text{gln}_i \text{ adsorbed L}^{-1} / \text{g DOC}}{\mu\text{gln}_i^{3+} \text{ mL}^{-1}} \quad (1)$$

where $\text{ln}_i = \text{La to Lu}$.

2.3. Solution analysis

Rare earth element concentrations were determined at Rennes I University with an Agilent Technologies™ HP4500 ICP-MS instrument. All sample solutions were injected directly, except the initial suspensions, which were analysed to determine precisely the REE/C ratios for each experiment. The suspensions were first digested with sub-boiled nitric acid (HNO_3 14 N) at 100°C , then resolubilized in HNO_3 0.37 N after complete evaporation to avoid interferences with organic matter during mass analysis by ICP-MS. Quantitative analyses were performed using a

conventional external calibration procedure. Three external standard solutions with REE concentrations similar to the analysed samples were prepared from a multi-REE standard solution (Accu Trace™ Reference, 10 mg L^{-1} , USA). Indium was added to all samples as an internal standard at a concentration of $0.87 \mu\text{mol L}^{-1}$ (100 ppb) to correct for instrumental drift and possible matrix effects. Indium was also added to the external standard solutions. Calibration curves were calculated from measured REE/indium intensity ratios. As established from repeated analyses of multi-REE standard solution (Accu Trace™ Reference, USA) and the SLRS-4 water standard, the instrumental error on REE analysis is below 3%. Chemical blanks of all individual REE were all lower than detection limit (1 ng L^{-1}), and are thus negligible.

Dissolved organic carbon concentrations were determined using a Shimadzu 5000 TOC analyzer. The accuracy of DOC concentration measurements is estimated at $\pm 5\%$, as determined by repeated analysis of freshly prepared standard solutions (potassium biphtalate).

2.4. Humic ion binding Model VI

The Humic ion binding Model VI (Model VI) has been precisely described by Tipping (1998). This model is a discrete binding site model which takes into account electrostatic interactions. Eight sites are considered, divided into an equal number of Type A sites (the weak acidic group, commonly associated with carboxylic functional groups) and Type B sites (the strong acidic group, commonly associated with phenolic functional groups). There are n_A (mol g^{-1}) Type A sites and $n_A/2$ (mol g^{-1}) Type B sites. The thermodynamic properties of each site are described by intrinsic proton-binding constants ($\text{p}K_A$ or $\text{p}K_B$) and the spread of the values ($\Delta\text{p}K_A$ or $\Delta\text{p}K_B$). Cation binding is described by the intrinsic binding constant of a given cation with each type of site (namely, $\log K_{MA}$ and $\log K_{MB}$), together with a parameter (ΔLK_1) describing the spread of values around the median. By considering results from many datasets, a universal average value of ΔLK_1 was obtained for all cations, and a correlation established between $\log K_{MB}$ and $\log K_{MA}$ (Tipping, 1998). Model VI parameters used for REE binding to humic acid modelling (Tipping, 1998) are presented in Table 1.

Model VI also takes into account the formation of bidentate and tridentate complexes by a proximity factor (ΔLK_2), which quantifies whether the binding sites are close enough to form multidentate sites. These multidentate sites can be considered as equivalent to strong sites, and may be compared to other strong sites formed by atoms such as N, P or S (Tipping, 2007). The occurrence of bidentate and tridentate sites is calculated probabilistically. The binding constant of the bidentate and tridentate sites are calculated by increasing the logarithms of monodendate site constants by $N \Delta\text{LK}_2$, where $N = 1$ and 2 for 9% and 0.9% of the bidentate sites, respectively, and $N = 1.5$ and 3 for 9% and 0.9% of the tridentate sites, respectively (Tipping, 2002). Thus, the ΔLK_2 parameter (so-called “the strong binding site term”) introduced in Model VI, can be used to model cation binding by the few strong sites.

Table 1
Model VI parameters used for REE binding to humic acid (Tipping, 1998).

Parameter	Description	Values
n_A	Amount of type A sites (mol g^{-1})	3.3×10^{-3}
n_B	Amount of type B sites (mol g^{-1})	$0.5 \times n_A$
pK_A	Intrinsic proton dissociation constant for type A sites	4.1
pK_B	Intrinsic proton dissociation constant for type B sites	8.8
ΔpK_A	Distribution terms that modifies pK_A	2.1
ΔpK_B	Distribution terms that modifies pK_B	3.6
$\log K_{MA}$	Intrinsic equilibrium constant for metal binding at type A sites	Fitted from experimental data
$\log K_{MB}$	Intrinsic equilibrium constant for metal binding at type B sites	$3.39 \log K_{MA} - 1.15$
ΔLK_1	Distribution term that modifies $\log K_{MA}$	2.8
ΔLK_2	Distribution term that modifies the strengths of bidentate and tridentate sites	Fitted from experimental data
P	Electrostatic parameter	−330
K_{sel}	Selectivity coefficient for counterion accumulation	1
M	Molecular weight	15,000 Da
r	Molecular radius	1.72 nm

3. RESULTS

All experimental data can be found in the [Supplementary file](#).

3.1. Experimental data

The influence of metal loading on REE complexation with HA is examined by considering the variation of the REE distribution coefficient ($\log K_d^{\text{REE}}$) patterns as a function of the REE/C (Fig. 1). Firstly, a variation in the

$\log K_d^{\text{REE}}$ value is observed from 4.8 to 6.6 for La, and from 4.8 to 7.3 for Lu over the range of tested REE/C (from 4×10^{-4} to 2.7×10^{-2}). Secondly, and more importantly, the suggested variation of the $\log K_d^{\text{REE}}$ patterns with changing REE/C is confirmed (see discussions in Pourret et al., 2007b; Stern et al., 2007). More specifically, $\log K_d^{\text{REE}}$ patterns at low REE/C display a continuous enrichment from La to Lu, a feature already reported by Sonke and Salters (2006) and Stern et al. (2007) for patterns obtained at similarly low REE/C. Conversely, $\log K_d^{\text{REE}}$ patterns at high REE/C show the typical downward concavity of the MREE earlier reported by Davranche et al. (2005), Yamamoto et al. (2005) and Pourret et al. (2007b) from high metal loading experiments. This $\log K_d^{\text{REE}}$ pattern variation can be quantified by means of the $\log(K_d^{\text{La}}/K_d^{\text{Sm}})$ and $\log(K_d^{\text{Gd}}/K_d^{\text{Yb}})$ (denoted below as $\log(\text{La}/\text{Sm})$ and $\log(\text{Gd}/\text{Yb})$, respectively). Indeed, the $\log K_d^{\text{REE}}$ patterns from low REE/C experiments – displaying the typical increase from La to Lu – are characterized by $\log(\text{La}/\text{Sm})$ and $\log(\text{Gd}/\text{Yb})$ values <0 , whereas patterns from high REE/C experiments – showing the characteristic downward concavity of the MREE – have $\log(\text{La}/\text{Sm})$ and $\log(\text{Gd}/\text{Yb})$ ratios <0 and >0 , respectively. As a whole, the $\log(\text{Gd}/\text{Yb})$ decreases more strongly with decreasing REE/C (from 0.11 for $\text{REE}/\text{C} = 2.7 \times 10^{-2}$ to −0.35 for $\text{REE}/\text{C} = 4 \times 10^{-4}$) than the $\log(\text{La}/\text{Sm})$ (from −0.24 for $\text{REE}/\text{C} = 2.7 \times 10^{-2}$ to −0.41 for $\text{REE}/\text{C} = 4 \times 10^{-4}$).

$\log K_d$ and $\log(\text{REE}/\text{C})$ display good negative linear correlations ($R^2 > 0.99$) when reported together (e.g. La, Lu; Fig. 2) within the tested REE/C range. The $\log K_d^{\text{REE}}$ increase with the decreasing metal loading demonstrated the non-linearity of the REE–HA binding involved by the HA binding site heterogeneity. Slopes of $\log K_d^{\text{REE}}$ versus $\log \text{REE}/\text{C}$ noted a_i ($i = \text{La to Lu}$) which corresponds to the non-linearity coefficient of the REE–HA binding increase regularly along the REE series, suggesting that HREE binding to HA is strongly influenced by the HA site heterogeneity (Fig. 3). Our results demonstrate that REE–HA binding occurs through high-density but weak HA sites at high metal loading, implying a concave $\log K_d^{\text{REE}}$ pattern.

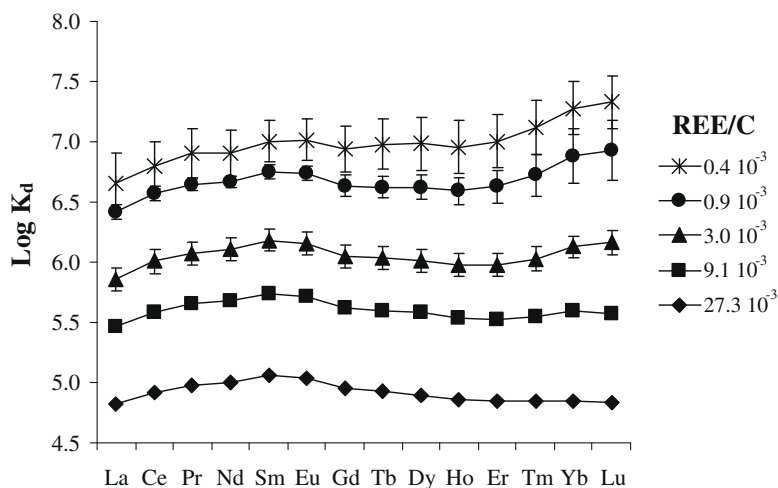


Fig. 1. Variation of $\log K_d^{\text{REE}}$ as a function of REE/C. Error bars correspond to standard deviation of triplicates.

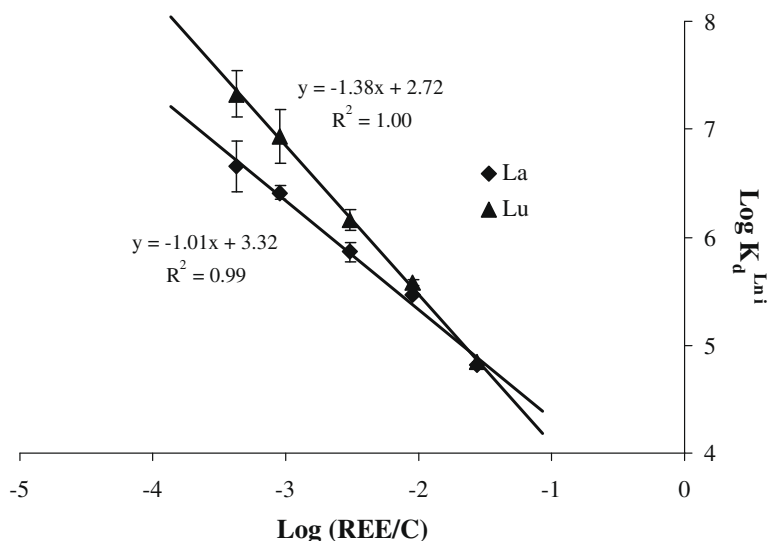


Fig. 2. Diagram illustrating negative linear correlations between $\log K_d$ and $\log(\text{REE}/C)$ for La and Lu. Error bars correspond to standard deviation of triplicates.

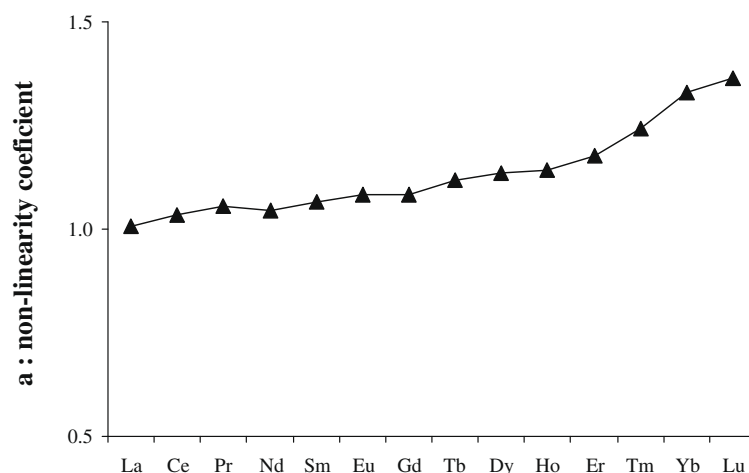


Fig. 3. Variation of “a” coefficient through the REE series. “a” is a measure of the non-linearity of the REE–HA binding isotherms, determined by the slope of $\log K_d^{\text{REE}}$ versus $\log(\text{REE}/C)$.

By contrast, at low metal loading, REE and notably HREE are preferentially bound to strong affinity but low density HA sites, which involves a regular $\log K_d^{\text{REE}}$ increase from La to Lu.

3.2. Calculating $\log K_{\text{MA}}$ and ΔLK_2 values

Calculations are performed using the computer program WHAM 6 (Version 6.0.13), which includes Model VI. We used a classic strategy that consists of adjusting the intrinsic parameters of the model to each REE simultaneously until the minimization of the root mean square error (rmse). We not only adjust $\log K_{\text{MA}}$ (i.e. the parameter that quantifies REE complexation via the high-density, low-affinity sites), but also the ΔLK_2 values. ΔLK_2 is the parameter that addresses the non-linearity of the cation–HA binding in Model VI and is used to increase HA strong site influence on the

binding. Tipping (2002) designate ΔLK_2 as “the strong binding site term”. This procedure is a unique feature of the present study, as all previous workers have considered this parameter as constant and equal to 0.29 for each individual REE (e.g. Pourret et al., 2007b). Pourret et al.’s (2007b) $\log K_{\text{MA}}$ dataset was used as initial $\log K_{\text{MA}}$ values. Considering that ΔLK_2 and $|a_i|$ coefficient represent both the non-linearity of the REE–HA binding and the subsequent HA site heterogeneity, ΔLK_2 values were optimized assuming a linear correlation with a_i . ($\Delta\text{LK}_2 = 2.98 \times a_i - 1.88$).

Table 2 reports the two sets of optimized $\log K_{\text{MA}}$ and ΔLK_2 values thus obtained for the 14 analysed REE. As indicated, by rmse values (<0.03), the fits can be considered of good quality. The optimized ΔLK_2 values are intermediate between the values for trivalent Al and Fe (0.46 and 2.20, respectively) determined by Tipping et al. (2002).

Table 2
log K_{MA} and ΔLK_2 values fitted from the experimental data using Model VI. The quality of the fit is determined by the rmse, calculated as $\sqrt{\text{mean}(\log v_{\text{exp}} - \log v_{\text{calc}})^2}$, where v is the amount of REE bound to HA per gram of DOC for experimental and modelled data, respectively. The log K_{MA} data published by Pourret et al. (2007b) are shown for comparison.

REE	log K_{MA}^a	log K_{MA}^b	ΔLK_2^b	rmse ^b
La	2.58	2.70	1.10	0.02
Ce	2.60	2.72	1.15	0.02
Pr	2.61	2.73	1.20	0.02
Nd	2.63	2.74	1.20	0.01
Sm	2.65	2.75	1.30	0.01
Eu	2.65	2.74	1.35	0.01
Gd	2.63	2.72	1.35	0.01
Tb	2.62	2.71	1.50	0.01
Dy	2.61	2.70	1.60	0.02
Ho	2.60	2.69	1.65	0.02
Er	2.60	2.69	1.70	0.01
Tm	2.59	2.67	1.90	0.01
Yb	2.60	2.65	2.05	0.02
Lu	2.60	2.64	2.10	0.02

^a Pourret et al. (2007b).
^b This study.

The new set of optimized log K_{MA} values is compared with the earlier dataset published by Pourret et al. (2007b) (Table 2). The new values are higher than the previous results by ca. 0.1 log unit. They are also distinguished by the presence of a slight but continuous decrease of log K_{MA} from Dy to Lu. The optimized log K_{MA} and ΔLK_2 values reported in Table 2 are used to draw the calculated La and Lu adsorption isotherm (Fig. 4a) as well as log (La/Sm) and log (Gd/Yb) variations vs. log (REE/C) (Fig. 4b). The comparison between calculated and experimental data shows a reasonably good fit which demonstrates the ability of Model VI to predict the REE–HA binding at high and low REE/C. In particular, calculated log (La/Sm) and log (Gd/Yb) decrease with decreasing log (REE/C), in the same way as the experimental values (Fig. 4b).

4. DISCUSSION

4.1. Comparison with the literature

In Model VI, the log K_{MA} values may be regarded as representing the binding characteristics of weak sites controlling REE complexation with HA at high REE/C.

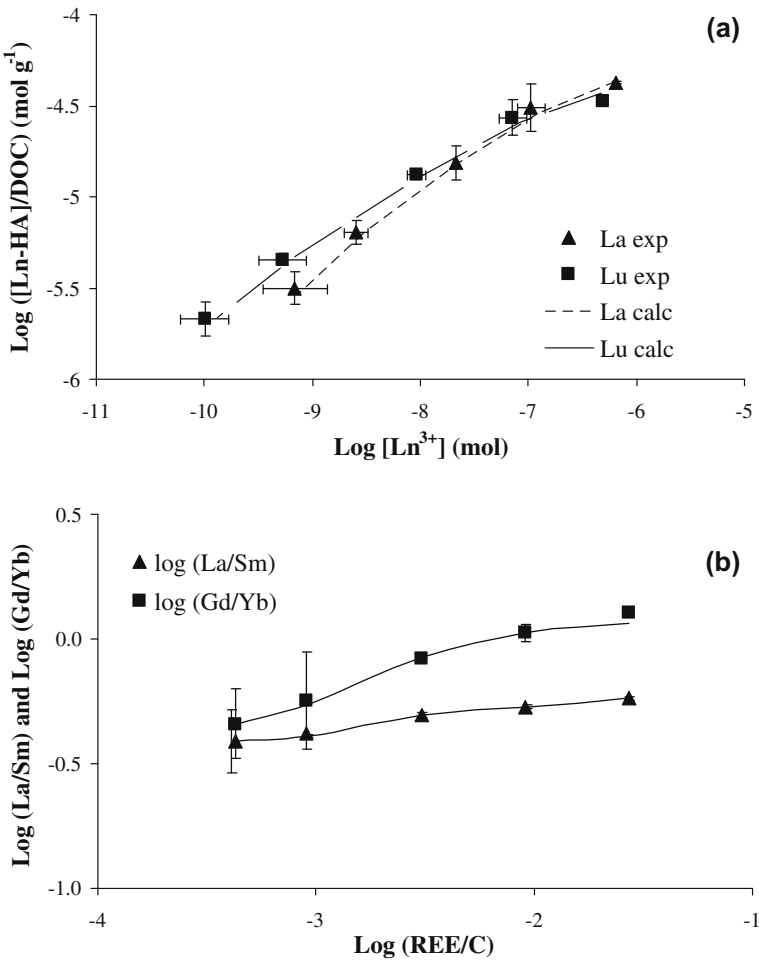


Fig. 4. Binding of REE by HA. (a) La–HA and Lu–HA binding isotherm, presented for La and Lu, and (b) Variation of log (La/Sm) and log (Gd/Yb) versus log (REE/C). Closed symbols and lines correspond to experimental data and best fits, respectively. Error bars correspond to standard deviation of triplicates.

Although, these values do not represent stability constants, the relative variation of $\log K_{MA}$ through the REE series likely reflects the ability of the weak sites to bind REE. Thus, the weak sites may be considered as preferentially complexing the MREE, whereas the strong sites, whose complexation constant depend on ΔLK_2 , may be regarded as preferentially complexing HREE rather than MREE or LREE.

In Fig. 5a, the optimized $\log K_{MA}$ values were compared with the $\log K_{MA}$ values reported earlier by Pourret et al. (2007b), as well as with the conditional stability constants ($\log \beta$) published by Yamamoto et al. (in press). Both published datasets were computed from high metal loading experiments ($3 \times 10^{-3} < \text{REE}/C < 3 \times 10^{-2}$) in which the REE behaviour should be determined by the weak sites. This comparison is interesting since the three datasets were obtained using different experimental techniques, namely: ultrafiltration in the present study and Pourret et al.'s datasets (2007b), as against solvent extraction for the dataset reported by Yamamoto et al. (in press). Quite clearly, the three data sets exhibit similar patterns, characterized by the same strong MREE downward concavity. The apparent decrease of the optimized $\log K_{MA}$ from Dy to Lu is a con-

sequence of the high ΔLK_2 values introduced into Model VI to accurately describe REE binding by HA. Optimized ΔLK_2 values computed from the new experimental data are not only different for each REE (varying from 1.1 to 2.1), but also much higher than the common value of 0.29 adopted by users of Model VI (i.e. Pourret et al., 2007b; Yamamoto et al., in press).

In Fig. 5b, $\log K$ pattern of REE–HA fewest and strongest site occurring in Model VI (i.e. 0.9% of T16 site, whose $\log K$ is increased by $3 \times \Delta LK_2$ in Tipping, 1998), noted $\log K(\text{REE-T16})$, is compared to that of $\log \beta$ reported by Sonke and Salters (2006) and Yamamoto et al. (in press) for low metal loading experiments. All patterns are characterized by a continuous increase from La to Lu. This similarity is considered as confirming that the ΔLK_2 values computed here can be used to model the role of strong sites controlling REE binding at low REE/C.

4.2. Impact of ΔLK_2 values on modelling results at high to low REE/C

To obtain further insight into the influence of the ΔLK_2 parameter in calculating REE complexation by HA using

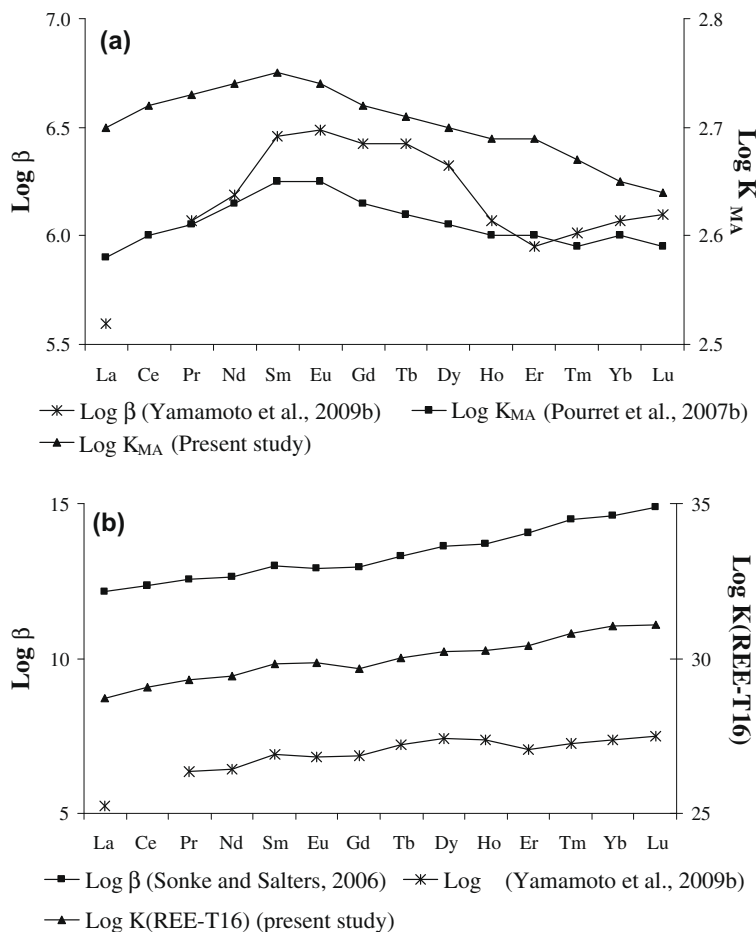


Fig. 5. REE patterns for apparent REE–HA binding constant obtained from (a) high REE/C experiments (weak sites) and (b) low REE/C experiments (strong sites). Data source: this study for $\log K_{MA}$ and $\log K(\text{REE-T16})$ ($\log K$ Model VI strongest site: 0.9% of T16 site); Sonke and Salters (2006) (Leonardite coal HA; pH 7); Pourret et al. (2007b) (Aldrich HA); Yamamoto et al. (2009b) (Suwannee River HA; pH 4.7).

Model VI, modelling calculations were performed at REE/C lower than present experimental ratios, using (i) the low and common ΔLK_2 value of 0.29 proposed by Tipping (1998) for each REE (simulation 1) and (ii) the optimized ΔLK_2 (simulation 2). In these simulations, the HA concentration, the pH and the ionic strength of the solution are kept constant and equal to 10 mg L^{-1} , 3, and 10^{-2} M NaCl , respectively. Rare earth element concentration ranges from 10^{-5} to 10^{-12} M . These simulations were carried out to determine quantitatively the bias introduced under low REE/C ratio conditions by using the ΔLK_2 value of 0.29. Moreover, this approach is also a way of emphasizing and quantifying the role of strong binding sites in controlling REE binding with HA at low to high REE/C ratio. The common use of the ΔLK_2 value of 0.29 leads to a huge underestimation of REE bound to HA when the REE/C becomes lower than ca. 10^{-4} , as compared to the predictions performed with the optimized ΔLK_2 values. For La, the underestimation ranges from ca. 0.4 log units for REE/C of ca. 10^{-4} up to ca. 1.5 for REE/C of ca. 10^{-7} . The underestimation is even higher for Lu: from ca. 1 log units for REE/C of ca. 10^{-4} up to ca. 3.5 for REE/C of ca. 10^{-7} . The higher underestimation obtained for Lu is

consistent with the fact that the optimized ΔLK_2 values, which must be introduced in Model VI to account for the strong REE binding sites, are much higher for Lu (2.1) than for La (1.1). In agreement with this behaviour, and as illustrated in Fig. 6, the use of a low and constant ΔLK_2 value of 0.29 as proposed by Tipping (1998) would lead to an underestimation of the fraction of the REE bound to HA under low REE/C conditions. More importantly, ΔLK_2 values of 0.29 would also produce a biased $\log K_d^{\text{REE}}$ pattern that remains concave whatever the metal loading.

4.3. Nature of the binding sites

Previous studies have shown that the downward concavity of $\log K_{\text{MA}}$ or/and $\log \beta$ patterns obtained from high REE/C experiments is also apparent in the patterns for simple organic compounds possessing carboxylic functional groups such as acetic acid (Fig. 7a; Yamamoto et al., 2005 and Pourret et al., 2007b). As stated above, the weak sites that control the binding of REE to humic substances at high REE/C are likely to be carboxylic functions, a hypothesis supported by the C 1s-NEXAFS analyses of saturated Eu–HA complexes published by Plaschke et al.

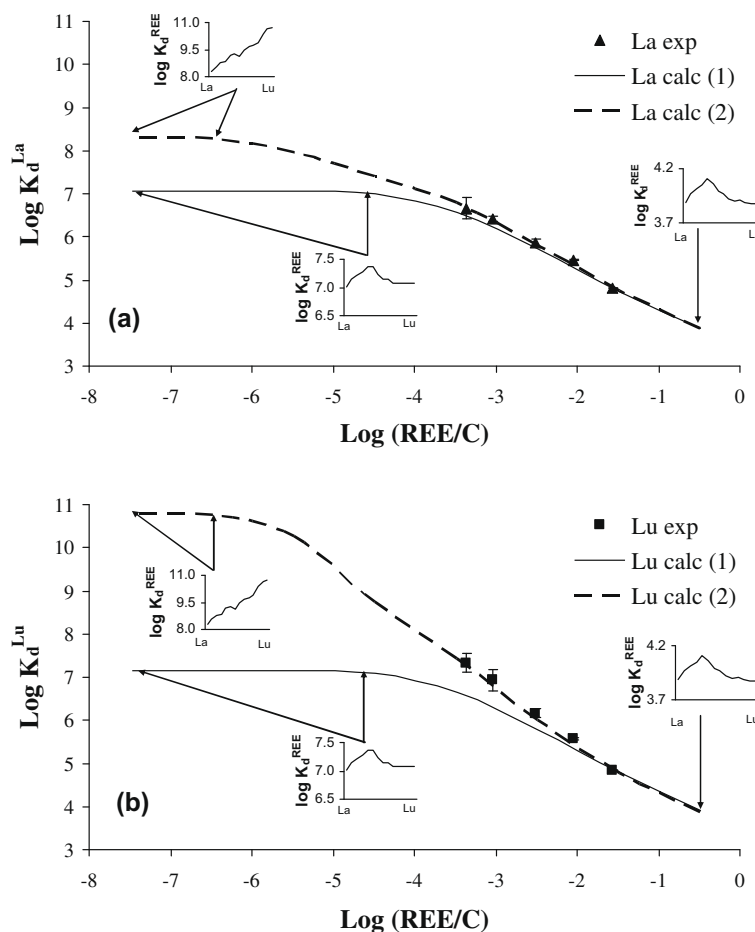


Fig. 6. Variation of (a) $\log K_d^{\text{La}}$ and (b) $\log K_d^{\text{Lu}}$ relative to the $\log(\text{REE/C})$, on a large range of metal loading. Comparison of Model VI prediction with (1) $\Delta\text{LK}_2 = 0.29$ (dashed line) and (2) with the optimized ΔLK_2 (bold dashed line). Symbols represent experimental data. Error bars correspond to standard deviation of triplicates.

(2004). This implies that simple organic compounds having carboxylic functional groups such as acetate (e.g. Byrne and Li, 1995) can be regarded as analogues of these weak sites.

A similar comparative approach may provide information about the nature of the strong sites. High-affinity sites in HA are generally thought to comprise phenolic functions and/or multidentate carboxylic (Takahashi et al., 1997; Stern et al., 2007; Pourret and Martinez, 2009). Amine sites are known to be involved in the complexation of Am (III) and Cu (II) by HA (Peters et al., 2001; Wu and Tanoue, 2001), so they could be also involved in strong binding sites. Due to the high pK_A of HA phenolic sites (around 9; Ritchie and Perdue, 2003), it is unlikely that strong sites correspond to phenolic sites given the low pH value (pH 3) of the present experiments. Stability constant patterns of REE-phosphate, REE-oxalic acid and REE-NTA complexes exhibit the same lanthanide contraction effect than the $\log K$ of the REE-HA strongest sites occurring in Model VI (REE-T16) complexes (Byrne and Sholkovitz, 1996; Schijf and Byrne, 2001; Takahashi et al., 2007; Fig. 7b). Rare earth element binding to oxalic acid and NTA occurs either through multicarboxylic sites or multicarboxylic N-

containing sites. Given the similarity of the stability constant patterns, the strong sites that control REE binding at low REE/C might be similar to simple multicarboxylic sites, or multicarboxylic sites containing amino or, possibly, phosphate binding groups.

Finally, the new $\log K_{MA}$ and $\log K$ (REE-T16) patterns were also compared with patterns of REE binding to bacteria cells (*Bacillus Subtilis*; Takahashi et al., 2007; see Fig. 7a). These patterns are interesting because they combine the binding features of the strong and weak sites of HA, namely a relative enrichment of the HREE and a middle downward concavity of the MREE. As observed in the present study, Takahashi et al. (2007) found that, with decreasing metal loading, the $\log K_d^{HREE}$ between the bacteria suspension and the experimental solution increased more strongly than the $\log K_d^{LREE}$ (Fig. 1, and Fig. 2 in Takahashi et al., 2007). More recently, Takahashi et al. (2008) demonstrated that the binding of the LREE and of the HREE at the surface of bacteria involved two types of sites: monodentate phosphate sites for the LREE and multidentate phosphate sites (alkylphosphates) for the HREE. Although bacteria cells cannot be compared to

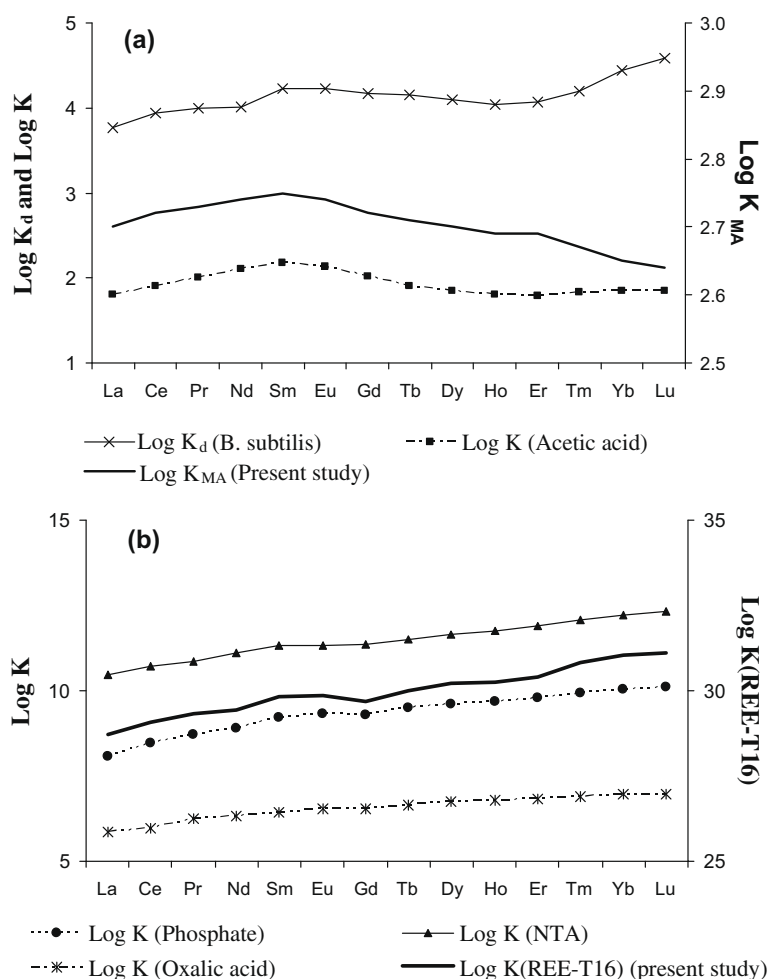


Fig. 7. REE patterns comparing the $\log K_{MA}$ obtained in this study and $\log K$ published for acetic acid and bacteria cells (*Bacillus Subtilis*) (a), as well $\log K$ (REE-T16), $\log K$ Model VI strongest site (0.9% of T16 site);(this study) and $\log K$ of NTA, oxalic acid and phosphate complexes (b). Data source: this study, Byrne and Li (1995), Schijf and Byrne (2001), Takahashi et al. (2007).

HA, it is a striking observation that similar variations in metal loading led to similar changes in REE binding capacity and a similar fractionation of REE distribution patterns.

To conclude, this literature review suggests that the few strong sites activated at low REE/C in REE binding with HA could be multidentate carboxylic sites, or perhaps N-, or P-functional groups. The identification of the exact nature of these sites clearly remains a challenging issue. To solve this problem, further detailed high-resolution spectroscopic investigations of REE–HA complexes involving, for example, EXAFS studies are required.

4.4. Is there any evidence for a metal loading effect in natural organic-rich waters?

There is now ample evidence that humic substances (HS) control REE speciation in natural organic-rich waters (Bidoglio et al., 1991; Takahashi et al., 1997; Glaus et al., 1995, 2000; Viers et al., 1997; Dia et al., 2000; Gruau et al., 2004; Johannesson et al., 2004; Davranche et al., 2005, 2008; Yamamoto et al., 2005, 2006, in press; Sonke and Salters, 2006; Pourret et al., 2007a,b; Stern et al., 2007; Pédrot et al., 2008). Speciation studies show that nearly 100% of the REE occur as organic complexes in such waters (Viers et al., 1997; Dia et al., 2000; Tang and Johannesson, 2003; Gruau et al., 2004; Johannesson et al., 2004; Pourret et al., 2007b; Pédrot et al., 2008). Yet, REE patterns are highly variable in these waters. As shown on Fig. 8, which presents a compilation of REE data for $<0.2\ \mu\text{m}$ filtered organic-rich waters, $\log(\text{La}/\text{Sm})_{\text{UCC}}$ and $\log(\text{Gd}/\text{Yb})_{\text{UCC}}$ values vary by ca. 0.5 and 0.8 log units in such waters, respectively, reflecting strong fractionation of the REE patterns. All the waters compiled in Fig. 8 have DOC concentrations $>5\ \text{mg L}^{-1}$, and pH values in the range 4–7. This implies that the REE pattern in these waters must be controlled, at least in part, by the binding affinities

of the organic molecules REE binding sites. Given the results presented in this study, we are led to pose the following question: could the variation in REE pattern displayed by natural organic-rich waters be due to the metal loading effect?

Addressing this question is not a trivial task because of the pH dependence of the metal loading effect, and the chemical composition variability of these waters. Nevertheless, we can note the following two features which allow us to consider this possibility. Fig. 8 presents a compilation of 350 samples of organic-rich, river-, and soil-waters. Besides the strong variability of the REE pattern, Fig. 8 shows that organic-rich waters are not randomly distributed when plotted in a $\log(\text{La}/\text{Sm})_{\text{UCC}}$ versus $\log(\text{Gd}/\text{Yb})_{\text{UCC}}$ diagram. Indeed, the data points are almost entirely restricted to the upper and lower left-hand corners of the diagram, illustrating that REE patterns in organic-rich waters range from patterns showing a MREE downward concavity to patterns showing a continuous enrichment from La to Lu. Only a very small number of waters (7 out of a total of 350) display patterns exhibiting a continuous enrichment from Lu to La, or showing a MREE upward concavity. This non-random distribution of REE patterns in organic-rich waters was already pointed out by Pourret et al. (2007b), although based on a compilation pooling a far more limited number of waters (Fig. 6 in Pourret et al., 2007b). Fig. 9a and b plotting $\log(\text{La}/\text{Sm})_{\text{UCC}}$ and $\log(\text{Gd}/\text{Yb})_{\text{UCC}}$ against $\log(\text{REE}/\text{C})$, respectively, display both $(\text{La}/\text{Sm})_{\text{UCC}}$ and $\log(\text{Gd}/\text{Yb})_{\text{UCC}}$ decrease with decreasing metal loading which is consistent with the present experimental results, HREE–HS and MREE–HS binding being favoured at low and high metal loading, respectively. Therefore, natural waters with low REE/C should exhibit an HREE-enriched REE pattern, by contrast to high REE/C waters which should display a MREE-enriched REE pattern. The dispersion of data ob-

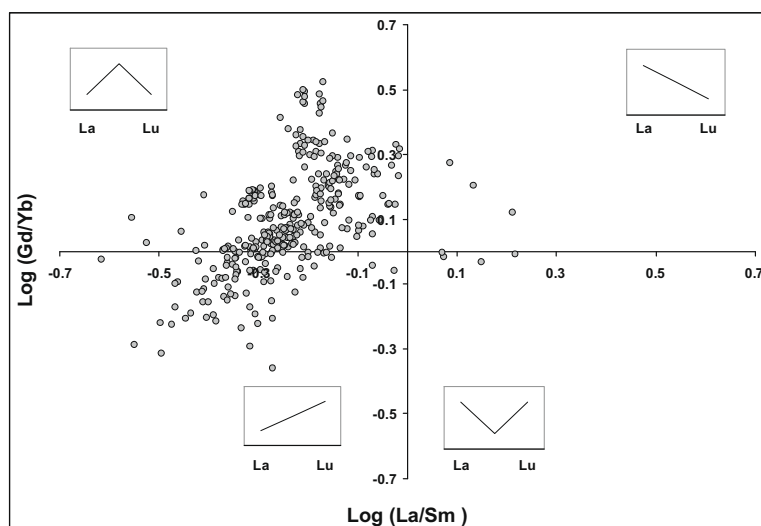


Fig. 8. Literature compilation of $\log(\text{Gd}/\text{Yb})_{\text{UCC}}$ versus $\log(\text{La}/\text{Sm})_{\text{UCC}}$, illustrating coherent variations of REE pattern, in natural organic-rich river- and soil-waters. The REE patterns indicate the types of REE pattern specific to each corner of the diagram. Data sources: Dia et al. (2000), Viers et al. (2000), Gaillardet et al. (2004), Gruau et al. (2004), Tosiani et al. (2004), Auterives (2007).

served in Figs. 8 and 9 may be attributed to two major uncertainties. (i) The metal loading should be expressed as $\log (M/C)$ where M represents the sum of the dissolved cations that compete with REE for HS surface sites. However, because metallic nano-oxides (Fe or Al) may be included in the $<0.2 \mu\text{m}$ water fraction, (e.g. Pokrovsky et al., 2006; Pédrot et al., 2008), $\log (M/C)$ could be overestimated. By contrast, published chemical water compositions often lack the entire cation content, which consequence could be an underestimation of the $\log (M/C)$. (ii) REE distribution may also be strongly influenced by the surface functional group heterogeneity and density of the different HS types. Although these uncertainties, REE distributions in Figs. 8 and 9 do correspond to the expected distributions if the REE pattern shape prevailing in organic-rich waters is controlled by a metal loading effect.

Thus, the special fractionation of REE patterns in natural organic-rich waters suggests that the metal loading effect could be the cause of the marked variability of REE patterns that characterize these systems. As a whole, the present investigation, when combined with results from previous studies by Yamamoto et al. (2005, in press), Sonke and Salters (2006), Stern et al. (2007) and Pourret et al. (2007b) demonstrates that: (i) HA binding site heterogeneity (strong and weak sites) directly influences the REE com-

plexation patterns, and (ii) this latter point may be explained by a loading effect: at low metal loading, stronger sites are favoured yielding HREE-enriched REE patterns, whereas, at high metal loading, the more abundant weaker sites dominate complexation leading to REE patterns with MREE downward concavity.

5. CONCLUSIONS

The effect of metal loading on the binding of the rare earth elements (REE) to humic acid (HA) was studied by combining ultrafiltration and Inductively Coupled Plasma Mass Spectrometry techniques. REE–HA binding experiments were performed at pH 3 for REE/C ranging from 4×10^{-4} to 2.7×10^{-2} , using a standard batch equilibration method. Results show that the relative amount of REE bound to HA strongly increases with decreasing REE/C. Moreover, a middle-REE (MREE) downward concavity is displayed by $\log K_d^{\text{REE}}$ patterns at high metal loading, whereas patterns at low metal loading exhibit a regular increase from La to Lu. These results demonstrate that the variability of REE–HA binding patterns published so far (Yamamoto et al., 2005, 2006, in press; Sonke and Salters, 2006; Pourret et al., 2007b; Stern et al., 2007) is not an artefact resulting from the use of different analytical

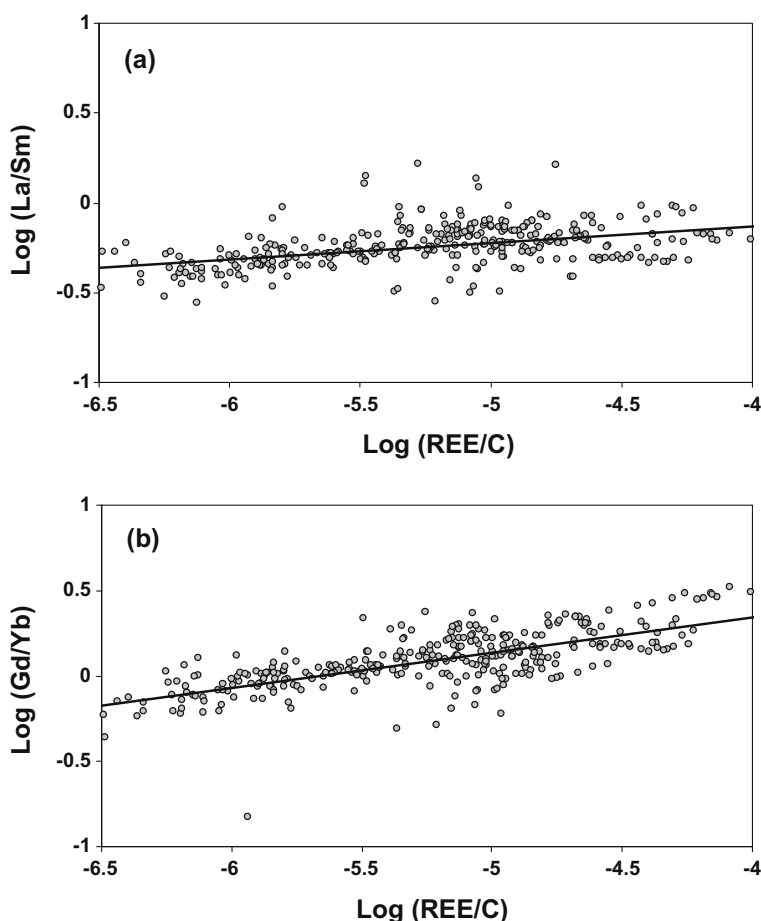


Fig. 9. (a) $\log (\text{La/Sm})_{\text{UCC}}$ and (b) $\log (\text{Gd/Yb})_{\text{UCC}}$ versus $\log \text{REE/C}$ for the data compiled in Fig. 8. Solid line represents the linear relationship.

procedures. The variability of patterns is real, reflecting the presence of two types of sites in HA surface, each occurring in markedly distinct proportions and each having different binding affinities for the REE. The resulting metal loading effect explains the variation of $\log K_d^{\text{REE}}$ patterns with changing REE/C.

Calculations performed using Model VI show that the two types of sites involved in the binding of REE with HA can be defined by the Model VI intrinsic $\log K_{\text{MA}}$ and ΔLK_2 parameters, ΔLK_2 parameter being free to vary among the REE series. Optimization of both parameters provides evidence that high-density but weak sites determine the distribution of REE to HA at high REE/C, favouring the complexation of the MREE. By contrast, the few strong sites determine the distribution of REE to HA at low REE/C, favouring the HREE complexation. A literature review suggests that the few strong sites activated at low REE/C could be multidentate carboxylic sites, or perhaps N-, or P-functional groups, whereas the weak sites involved at high metal loading are likely to be monodentate carboxylic sites. Application of Model VI to the experimental data shows that this model closely reproduces the observed variations. Hence, this model is a very powerful tool for studying and taking into account the loading effect that controls REE binding by HA.

Finally, confronting the variability of REE patterns in natural organic-rich waters and their metal loading level, expressed as REE/C, shows that the loading effect discussed here could explain part of the shape variability of REE patterns observed in these waters. Overall, our results suggest that further factors, such as competitive cations and/or colloidal nano-oxides, should be considered to improve the metal loading effect accuracy. Also the variability of humic substances chemical composition should be considered to explain the diversity of the binding sites that may be involved in REE complexation mediated by organic matter. These other factors should be taken into account to model and thus better understand REE cycling and transport in natural systems. Once again, Model VI may provide a reliable and powerful tool for this purpose.

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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.gca.2009.12.006](https://doi.org/10.1016/j.gca.2009.12.006).

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