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https://doi.org/10.1071/EN23049

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Environmental Chemistry

Rare earth elements binding humic acids: NICA–Donnan modelling

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Environmental context. Rare earth elements (REEs) are technologically critical elements released into the environment by various anthropogenic activities, and whose ecotoxicological impacts are still largely unknown. REE binding to natural organic matter (NOM) is key to understand their fate and bioavailability in the environment. With this work, it is now possible to predict REE binding to NOM in various environments using various speciation software (ECOSAT, ORCHESTRA, Visual MINTEQ).

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Handling Editor:
Stephen Lofts

Received: 1 May 2023
Accepted: 15 August 2023
Published: 22 September 2023

Cite this:
Otero-Fariña A *et al.* (2024)
Environmental Chemistry **21**, EN23049.
doi:10.1071/EN23049

ABSTRACT

Rationale. Understanding rare earth element (REE) speciation in different natural environments is important to evaluate their environmental risks because different chemical species of an element may have different bioavailability and toxicity. REEs have a great affinity for particulate and dissolved organic matter, particularly fulvic and humic acids (HAs). Thus, the use of humic ion binding models may help to understand and predict the behaviour and speciation of these species in surface waters, groundwaters and soils. **Methodology.** In this work, we used previously published experimental datasets to parameterise the NICA–Donnan model for REEs binding with HAs, using the model optimisation tool PEST-ORCHESTRA. We propose using linear free energy relationships (LFERs) to constrain the number of parameters to optimise. **Results.** We determined a coherent NICA–Donnan parameter set for the whole REEs series being compatible with available generic NICA–Donnan parameters for other metals. The impact of pH, ionic strength and REE/HA ratio as well as the presence of competitors (Fe^{3+}, Al^{3+} and Cu^{2+}) on model results is analysed. **Discussion.** We consolidate confidence in our derived NICA–Donnan parameters for REEs by comparing them with the Irving–Rossotti LFER. We also show the general applicability of this relationship to predict and constrain metal-binding parameters for the NICA–Donnan model. We discuss observed shortcomings and provide suggestions for potential improvement of NICA–Donnan modelling.

Keywords: humic acid, linear free energy relationships (LFER), NICA–Donnan model, rare earth elements, soil chemistry, organic matter, speciation, trace metals, water chemistry.

Introduction

Rare earth elements (REEs) have been increasingly used in the past decades. They are technologically critical elements used in high-tech products such as lasers, storage media for data handling, mobile phones, photovoltaic cells, catalysers in cars, permanent magnets in turbines, lodestones and ceramics manufacturing. Anthropogenic activities such as mining and industrial manufacturing, but also agriculture can increase the release of these emerging pollutants into the environment (Borgmann *et al.* 2005; Vukov *et al.* 2016; Liu *et al.* 2017). Despite confirmed ecotoxicological effects of REEs on various organisms (Gonzalez *et al.* 2014; González *et al.* 2015; Oral *et al.* 2017; Gwenzi *et al.* 2018; Pagano *et al.* 2019; Malhotra *et al.* 2020; Romero-Freire *et al.* 2018, 2021), the fate and behaviour of the REEs – and thus their impact on different ecosystems – are still quite unknown (Kouhail *et al.* 2019; Batley and Campbell 2022). Understanding their speciation in different natural environments is very important to evaluate their ecotoxicological risks

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Collection: Dedication to Edward Tipping because their different chemical species have different bioavailabilities and toxicities (Leybourne and Johannesson 2008; Migaszewski and Gałuszka 2015; Khan *et al.* 2016; Romero-Freire *et al.* 2019; Malhotra *et al.* 2020; Lachaux *et al.* 2022). REEs in natural waters or soils are often operationally distributed between (i) truly dissolved, (ii) colloidal and (iii) particulate fractions (Singhal *et al.* 2006). On both colloids and particulate fractions, REE partitioning has been attributed to adsorption to organic and mineral phases or precipitation. REE concentrations in the different phases depend on pH, ionic strength, redox conditions and types of minerals present in the environment, which impact the complexation of REEs with organic and inorganic ligands (Johannesson *et al.* 2004; Leybourne and Johannesson 2008; Pourret *et al.* 2010; Liu *et al.* 2017). Thus, solid–solution partitioning, mineral equilibria and solution speciation of REEs are critical factors to determine their solubility in soils, sediments and waters and thereby their environmental fate and diffusion, mobility, bioavailability and toxicity (Groenenberg and Lofts 2014).

REEs form a homogeneous group of elements, with coherent behaviour among the series, generally divided in three groups: light REEs (LREE, from La to Nd), middle REEs (MREE, from Nd to Tb) and heavy REEs (HREE, from Dy to Lu). They have a great affinity for particulate and dissolved organic matter, particularly humic and fulvic acids therein (Sonke and Salters 2006; Pourret *et al.* 2007; Marsac *et al.* 2011; Gangloff *et al.* 2014; Catrouillet *et al.* 2020). Humic ion binding models are powerful tools developed to understand and predict the behaviour and speciation of trace metals including REEs and radionuclides in surface waters, groundwaters and soils, and interactions of potentially toxic trace elements with biota (Groenenberg and Lofts 2014; Di Bonito *et al.* 2018). These models consider both the heterogeneous nature of the humic substances (HSs) and electrostatic interactions due to their negative charge. Humic acids (HAs) contain functional groups, mainly carboxylic and phenolic groups, that have a high affinity to bind trace metals. Binding site heterogeneity can be described, depending on the model, with a discrete (Model VI and VII (Tipping 1998; Lofts and Tipping 2011), Stockholm Humic Model (Gustafsson 2001)) or a continuous distribution, as in the Non-Ideal Competitive Adsorption (NICA)–Donnan model (Kinniburgh *et al.* 1999; Koopal *et al.* 2005). Binding parameters for all REEs have been determined for Model VII (Tipping *et al.* 2011) and recently refined by Marsac *et al.* (2021) by using previously published datasets (Sonke and Salters 2006; Pourret *et al.* 2007; Marsac *et al.* 2010). For NICA–Donnan (ND), to this day, only Eu and Dy parameters are available (Milne *et al.* 2003). Here, we use the same datasets used by Marsac *et al.* (2021) to derive ND model parameters for REEs binding with HA, using the model optimisation tool PEST-ORCHESTRA (Janot *et al.* 2017).

The number of parameters to be optimised in the ND model fit is, however, generally too large to find an unconditional fit using titration and adsorption data. Parameter constraints could help reduce parameter uncertainty and obtain a coherent set of model parameters across different elements (Tipping 1998, 2002; Kinniburgh *et al.* 1999; van Riemsdijk *et al.* 2006; Lenoir *et al.* 2010). Here, we look for possibilities to constrain the fits using linear free energy relationships (or Gibbs energy relationships, LFERs) that, empirically, relate model parameters to thermodynamic constants. In this work we include: (i) the use of LFERs developed by Milne *et al.* (2003) who related ND parameters for metal cations to their first hydrolysis constants, and (ii) the evaluation of the applicability of the approach developed by Tipping *et al.* (2011) for binding constants in Humic Ion Binding Model VII to be applied for ND. The latter approach, based on the study of Carbonaro and Di Toro (2007) makes use of the Irving–Rossotti approach (Irving *et al.* 1956) and was recently extended for REEs by Marsac *et al.* (2021). Once the model parameters for different elements are obtained, it is also interesting to model data for competition experiments of the REEs with other metals (such as Fe^{3+}, Al^{3+} and Cu^{2+}) to test the coherency of the model parameters obtained for different elements. The present work aims to provide parameters to estimate REE binding to HA under various physicochemical conditions of pH, concentration and ionic strength (*I*), in the framework of an advanced humic ion binding model, NICA–Donnan. It will help the calculation of REE speciation in various environments and, therefore, provide better understanding of the environmental behaviour of these critical elements.

Materials and methods

NICA–Donnan model

The ND model is explained elsewhere in detail (Kinniburgh *et al.* 1999; Koopal *et al.* 2005). The NICA equation describes the local adsorption isotherm for specific binding of cations to the reactive sites of humic substances, while the Donnan model accounts for the electrostatic interactions. Briefly, the expression of the consistent NICA model for multi-component competitive binding, states that Q_i, the amount of a component i bound to the HS, at solution concentration c_i, is given by Eqn 1:

$$\begin{aligned} Q_i = {} & \frac{n_{i,1}}{n_{H,1}} \times Q_{\max,1} \frac{(\tilde{K}_{i,1}c_i)^{n_{i,1}}}{\sum_i (\tilde{K}_{i,1}c_i)^{n_{i,1}}} \\ & \times \frac{[\sum_i (\tilde{K}_{i,1}c_i)^{n_{i,1}}]^{p_1}}{1 + [\sum_i (\tilde{K}_{i,1}c_i)^{n_{i,1}}]^{p_1}} + \frac{n_{i,2}}{n_{H,2}} \\ & \times Q_{\max,2} \frac{(\tilde{K}_{i,2}c_i)^{n_{i,2}}}{\sum_i (\tilde{K}_{i,2}c_i)^{n_{i,2}}} \times \frac{[\sum_i (\tilde{K}_{i,2}c_i)^{n_{i,2}}]^{p_2}}{1 + [\sum_i (\tilde{K}_{i,2}c_i)^{n_{i,2}}]^{p_2}} \end{aligned} \tag{1}$$

In this framework, two types of functional groups are considered, Type 1 sites with a relative low affinity for cation binding (carboxylic type groups) and Type 2 sites with a relative high affinity for cation binding (phenolic type sites). $Q_{\max,i}$ corresponds to the maximum adsorption capacity of each type of site, n_i reflects the non-ideality of the system, related to lateral interactions and/or stoichiometric effects and is specific to each ion i ($0 < n_i \leq 1$, where 1 is the ideal case), p is the width of the affinity distribution for each type of site, and $\tilde{K}_i$ is the median of the distribution of each type of sites and the ion i.

Thus, from the NICA equation, four parameters are needed to describe the site density and site heterogeneity of the humic material with: $Q_{\max,1}$ and $Q_{\max,2}$ being the site densities (mol kg^{-1}), and p_1 and p_2 representing the heterogeneity of the Type 1 and Type 2 sites of the humic material, respectively. The other four parameters are needed to describe ion-specific binding (proton or metal): $\tilde{K}_{i,1}$, $\tilde{K}_{i,2}$, $n_{i,1}$ and $n_{i,2}$, which describe the median affinities and non-idealities of the ion binding, respectively.

This NICA equation can be combined with electrostatic interactions by using the local concentration of species i at the binding sites $c_{i,\mathrm{loc}}$ instead of the bulk concentration c_i. This has generally been done using the Donnan model, which considers that HSs behave as a homogeneously charged gel with a constant potential Ψ_D (V) in which the concentration of an ion $c_{i,\mathrm{D}}$ (mol L^{-1}) is related to its bulk solution concentration c_i (mol L^{-1}) according to the following equation:

$$c_{i,\mathrm{D}} = c_i \times \exp\left(\frac{-z_i F \psi_\mathrm{D}}{\mathrm{RT}}\right) \quad (2)$$

where F, R and T are the Faraday constant, gas constant and absolute temperature, respectively. In this electrostatic model, we consider that the charge of the HS particle Q is counteracted by the accumulation of counter-ions and the exclusion of co-ions within this Donnan gel of volume V_D (L kg^{-1}). The corresponding charge neutrality can be written as:

$$\frac{Q}{V_\mathrm{D}} + \sum_i z_i (c_{i,\mathrm{D}} - c_i) = 0 \quad (3)$$

The Donnan volume is needed to be able to solve these equations. It has been shown to evolve with I according to the following empirical equation (Benedetti *et al.* 1996):

$$\log V_\mathrm{D} = \alpha + \beta \log I \quad (4)$$

where α and β are empirical constants. Later, a simpler relationship was introduced, with only one empirical adjustable parameter that varies among HSs (Kinniburgh *et al.* 1999):

$$\log V_\mathrm{D} = b(1 - \log I) - 1 \quad (5)$$

where b is an empirical adjustable parameter that varies among HSs (Kinniburgh *et al.* 1999).

Milne *et al.* (2001, 2003) compiled a large dataset of available acid/base titration and metal sorption data for HA and FA to derive their ND parameters for FA and HA proton and metal binding. First, the ND model was fitted to the individual HA titration data to obtain HA-specific ND proton parameters using Eqn 5 for the relationship between V_D and I. The averaged ND proton parameters were then used to fit the available data (various HAs) for each separate metal simultaneously. The 'generic' ND parameters thus obtained are now used in various speciation codes including ECOSAT, Visual MINTEQ and ORCHESTRA. Therefore, we followed the approach of Milne *et al.* for our newly derived REE parameters to be compatible with their generic parameter set.

Datasets used for parameterisation

Four datasets were used to calibrate the ND model parameters for REEs binding to HA, for a total of 55 different measurements (Sonke and Salters 2006; Pourret *et al.* 2007; Marsac *et al.* 2010, 2012). These datasets are the only ones that cover the whole REEs series, and over a wide range of pHs and metal loadings. They have already been used by Marsac *et al.* to calibrate the Models VI and VII HA-REEs parameters (Marsac *et al.* 2011, 2021). The experimental conditions under which these datasets were obtained are summarised below and in Table 1.

Sonke and Salters dataset

Sonke and Salters (2006) conducted REE-HA binding experiments for each of the 14 naturally present REEs separately. They used a standard Leonardite HA (a coal humic acid from the International Humic Substances Society, code 1S104H). REE binding to HA was studied with EDTA competition coupled with capillary electrophoresis-ICP-MS analysis. This study provides a dataset at low metal loadings and slightly acidic to basic pH values (6–9) in 0.1 M $NaNO_3$, and an extra series at pH 7 in 0.01 M $NaNO_3$ (Table 1).

Pourret *et al.* dataset

In contrast to the previous dataset, Pourret *et al.* (2007) conducted REE-HA binding experiments for all the REEs together. The experiments were performed at pH 2–10.5, fixed ionic strength (0.001 M $NaNO_3$) and concentration of REEs (50 µg L^{-1}), and three different concentrations of HA. The synthetic Aldrich HA was purified (PAHA) according to the protocol of Vermeer *et al.* (1998), using acid (HF and HCl) and resin (Dowex 50W-X8) washing steps to remove soluble minerals and trace metals, respectively. Truly dissolved REEs were separated from REEs bound to HA by ultrafiltration and measured by ICP-MS (Table 1).

Marsac *et al.* (2010) dataset

Marsac *et al.* (2010) used the ultrafiltration method of Pourret *et al.* (2007) to study metal loading effect on REEs

Table 1. Summary of the datasets used in this study to derive NICA parameters for REE.

Dataset	Sonke and Salters (2006)	Pourret *et al.* (2007)	Marsac *et al.* (2010)	Marsac *et al.* (2012)
Number of data points per REE	5	28	15	7
pH range	6–9	2.2–10.4	3	3–6
HA used	Leonardite HA	Purified Aldrich HA	Purified Aldrich HA	
HA concentration (mg L^{-1})	10	5; 10; 20	5–45	12.2
REE concentration (μg L^{-1})	12.5	50	2–120	110
REE/HA ratio (mg g^{-1})	2.5	2.5; 5; 10	0.2–12.6	9
Ionic strength, *I* (M)	0.01; 0.1	0.001	0.01	0.01
Experimental approach	EDTA competition coupled with capillary electrophoresis–inductively coupled plasma mass spectrometry (ICP-MS) analysis on single REE-HA system	Ultrafiltration on multi REE-HA system		

binding to the same PAHA. The PAHA solution was additionally purified by ultrafiltration at 10 kDa in order to remove potential small molecules that could pass through the ultrafiltration membrane in the REE-PAHA binding experiments (Marsac *et al.* 2010). They also performed their experiments with all the REEs together, under acidic conditions (pH 3) and constant ionic strength (*I*) of 0.01 M NaCl (Table 1), 10 times higher than that used by Pourret *et al.* (2007).

Marsac *et al.* (2012) dataset

Using the same experimental method as Marsac *et al.* (2010), Marsac *et al.* (2012) performed experiments at constant concentrations of REEs (Σ[REE] 10 μM), HA ([PAHA] 12.2 mg L^{-1}) and ionic strength (I = 0.01 M NaCl) but varying pH between 3 and 6.

In subsequent studies, Marsac *et al.* developed this dataset to investigate independently the effect of Fe, Al, and Cu on REE binding to PAHA (Marsac *et al.* 2012, 2013, 2021), using the same metal concentrations [Al/Fe/Cu] = 10 μM.

Parameterisation approach

ND fitting procedure

We used the generic ND proton parameters derived by Milne *et al.* (Milne *et al.* 2001, 2003) (values provided in Supplementary Table S1) and fitted only the metal ion binding parameters. We used the PEST-ORCHESTRA tool (Janot *et al.* 2017) to fit ND parameters for all REEs simultaneously.

Unconstrained optimisation of both $\log\tilde{K}$ and n for all REEs did not provide a good result (preliminary results not shown). Indeed, there was no expected trend in the $\log\tilde{K}_i$ values as observed in previous studies that showed at low REEs/HA ratios, when REEs bind to strong-affinity sites, $\log K_i$ increases along the REE series from La to Lu (Marsac *et al.* 2010; Yamamoto *et al.* 2010). Therefore, we followed the approach of Milne *et al.* (2003) to first constrain the NICA non-ideality parameter n, using the LFER in which n for each metal is related to its first hydrolysis constant:

$$n_1 = 0.14 - 0.055 \log K_{\mathrm{OH}} \quad (r^2 = 0.85) \tag{6}$$

$$n_2 = 0.76 n_1 \tag{7}$$

Using the latest REE hydrolysis constants $\log K_{\mathrm{OH}}$ from Klungness and Byrne (2000), we applied these equations to calculate n_i values for each of the REEs and better constrain the fit. By this, we optimised only two parameters, the metal affinity constants $\log\tilde{K}_{i,1}$ and $\log\tilde{K}_{i,2}$.

Modelling the competition experiments

Competition of Al^{3+}, Fe^{3+} and Cu^{2+} on REE-HA binding was modelled in ORCHESTRA (Meeussen 2003), using default ND parameters (Milne *et al.* 2003) and the Minteqv4 thermodynamic database (US-EPA 1999). In the experimental set-up, precipitation of Al/Fe hydroxides was expected at pH above 4.5 (Marsac *et al.* 2012, 2013, 2021). This phenomenon was considered in modelling by allowing precipitation of gibbsite ($\log K$ −8.291) and ferrihydrite ($\log K$ −3.191), respectively (Minteqv4 thermodynamic database).

Results and discussion

Determination of REE-specific affinity constants

The model parameters obtained for the whole REEs series are given in Table 2 and shown in black symbols in Fig. 1. The $\log\tilde{K}_1$ pattern shows the expected downward concavity for the MREEs (Marsac *et al.* 2010; Yamamoto *et al.* 2010). The optimised parameters for Eu compare well with those

Table 2. Summary of REE-HA ND binding parameters, REE hydrolysis constants and the Irving–Rossotti coefficients for REEs.

REE	$\log K_{\mathrm{OH}}$[A]	n_1[B]	n_2[B]	$\log\tilde{K}_{\mathrm{REE},1}$[C]	$\log\tilde{K}_{\mathrm{REE},2}$[C]	a_0[D]	β_0[D]
La	−8.81	0.62	0.47	1.59	2.86	0.30	1.02
Ce	−8.34	0.60	0.46	1.70	3.53	0.35	0.91
Pr	−8.32	0.60	0.45	1.80	3.92	0.34	0.99
Nd	−8.18	0.60	0.45	1.76	3.92	0.35	1.01
Sm	−7.84	0.57	0.43	1.76	4.02	0.38	0.97
Eu	−7.76	0.57	0.43	1.74	4.02	0.39	0.90
Gd	−7.83	0.57	0.43	1.55	4.06	0.38	0.83
Tb	−7.64	0.56	0.43	1.49	4.50	0.41	0.62
Dy	−7.59	0.56	0.42	1.40	4.95	0.42	0.56
Ho	−7.56	0.56	0.42	1.31	5.00	0.43	0.50
Er	−7.52	0.55	0.42	1.23	5.11	0.43	0.50
Tm	−7.39	0.55	0.42	1.25	5.41	0.45	0.43
Yb	−7.24	0.54	0.41	1.23	5.41	0.45	0.44
Lu	−7.27	0.54	0.41	1.21	5.58	0.45	0.45

[A] Klungness and Byrne (2000).
[B] Calculated from Eqns 6 and 7, Milne *et al.* (2003).
[C] Optimised using PEST-ORCHESTRA.
[D] Marsac *et al.* (2021).

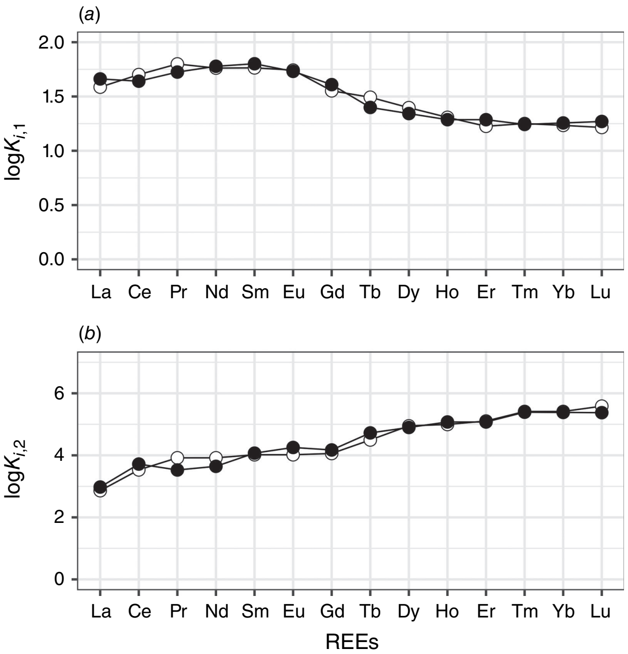

Fig. 1. NICA–Donnan median affinity constants for each of the REEs binding with the (*a*) Type 1 (carboxylic) and (*b*) Type 2 (phenolic) groups of HAs. Black symbols were obtained by fitting the experimental datasets with PEST-ORCHESTRA; white symbols were obtained by calculating $\log\tilde{K}_i$ according to the Irving–Rossotti approach and optimised using Eqn 8.

derived by Milne *et al.* (2003), with $\log\tilde{K}_{i,1}$ being close to that derived by Milne *et al.* (1.74 versus 1.92) but with somewhat higher $\log\tilde{K}_{i,2}$ than that obtained by Milne *et al.* (4.02 versus 3.43). These differences are possibly due to the use of other HAs in the study of Milne *et al.* compared with this study, together with natural variation in binding constants among various humic substances (Groenenberg *et al.* 2010). Differences for Dy are larger, with $\log\tilde{K}_{i,1}$ of 1.4 and 0.8 and $\log\tilde{K}_{i,2}$ of 4.95 and 3.9 obtained in our study versus those of Milne *et al.* respectively. The parameters for Dy published by Milne *et al.* (2003) are, however, not very reliable as they are based on a very small dataset for Dy binding to Aldrich HA with only six data points.

Modelled REE-HA binding versus measurements for the four datasets used for fitting are shown in Fig. 2. Most data points fell into the 0.3 log unit envelope around the 1:1 line between measured and calculated REE-HA binding, which is comparable with results for other metals (Milne *et al.* 2003) and indicative of a good fit. The relative importance of REE binding to Type 1 carboxylic versus Type 2 phenolic sites decreases from the LREEs to HREEs (Supplementary Fig. S1). Electrostatic binding in the Donnan volume decreases with increasing pH and becomes insignificant above pH 5 (Supplementary Fig. S1).

Even though the four datasets from which we derived the optimised model parameters cover a wide pH range, we observe a trend in model residuals (i.e. the difference between model prediction and experimental measurement)

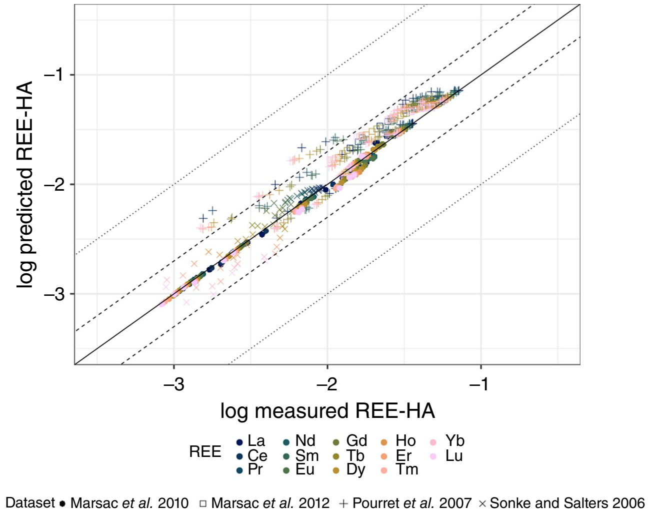

Fig. 2. Comparison between predicted and measured HA-bound REEs for the four datasets. Dashed and dotted lines respectively represent the 0.3 and 1 log unit envelope around the 1:1 (solid) line.

with pH. The distribution of residuals shows overprediction is largest at pH ≤ 3 and decreases with increasing pH until pH 6, after which at higher pH, the model increasingly underpredicts observations (Supplementary Fig. S2). This can also be seen in the results shown in Fig. 3. With increasing pH, metal cations become increasingly hydrolysed. In addition to the binding of the free metal cations, hydrolysed cations possibly also bind specifically to the reactive sites of HA. Specific binding of hydrolysed species to HA is not taken into account in the ND model, this being different from Models VI and VII for which specific adsorption of the first hydroxy species is included for all metal cations. In the ND model, hydrolysed species only interact with HA through electrostatic binding in the Donnan volume. Hydrolysis of REEs in the bulk solution starts to become important between pH ~7.3 for Lu, the most strongly hydrolysing lanthanide, and pH 8.8 for La (see $\log K_{\mathrm{OH}}$ values in Table 2). Specific binding as modelled in the ND model is related to the local concentration of the metal cation in the Donnan volume, which is different from that in the bulk solution. According to Eqn 2, accumulation of the free trivalent species in the Donnan volume is greater than that of the hydrolysed divalent and monovalent species. Speciation calculations for a fixed concentration of La and Lu in the bulk solution (Supplementary Fig. S3) show that the concentrations of hydrolysed species of Lu and La in the Donnan volume become larger at higher pH values compared with that for the bulk solution, i.e. at pH values higher than 8.5 for Lu and even higher than 10 for La. In cases where specific binding of hydrolysed metal species is important for metal cation binding to HA, this is expected to be relevant only at pH values higher than 8.5 for the REEs, especially the HREEs. Indeed, we see relatively large deviations between modelled and measured binding for these HREEs in the data from Sonke and Salters at pH 8.9 (Fig. 3*e*). However, similar deviations for these data were observed in modelling with Model VII (Marsac *et al.* 2021), which in contrast with NICA includes specific binding of hydrolysed species.

Fig. 3 shows the REE-HA pattern obtained for each of the parameterisation datasets. The shape of this pattern is generally well described by the ND model. However, the effect of the REE/HA concentration ratio on REE-HA binding prediction is not properly described by the model for the data of Pourret *et al.* (2007), with REE-HA binding being overestimated at high REE/HA ratios (HA concentration $5\,\mathrm{mg\,L^{-1}}$, Fig. 3*b*), and underestimated at the lowest REE/HA ratio (HA concentration $20\,\mathrm{mg\,L^{-1}}$, Fig. 3*d*). Marsac *et al.* (2010) noted that at high metal loadings, REEs were bound through high-density low-affinity sites, whereas at low loadings, strong-affinity sites became more important. Our ND calculations indeed show a slight increase in REE binding with Type 2 high-affinity sites (phenolic-type sites) with decreasing REE/HA ratio and vice versa: an accompanying decrease in the binding to low-affinity Type 1 sites (carboxylic-type sites) (Supplementary Fig. S4). This, however, did not lead to an accurate prediction of the REE/HA ratio-dependent behaviour observed in the data from Pourret *et al.* (2007). Kouhail, Benedetti and Reiller (2016) noted that the fulvic acid (FA) concentration impacted Eu-FA complexation using time-resolved luminescence spectroscopy. When increasing the FA concentration in solution while keeping the Eu concentration, pH and *I* at fixed levels, they observed the typical luminescence evolution of Eu complexed by humic substances in the low FA concentration range, but detected a second luminescence mode at higher FA concentrations. The first part – in the low FA concentration range – could be modelled adequately with the ND model. The second part at higher FA concentrations is possibly related to interparticle binding, a process not included in present humic ion binding models such as Model VII, SHM or ND. The FA concentration at which the luminescence pattern started to change decreased with increasing pH of the solution, with the concentration of Suwannee River FA (C_{SRFA}) < 100 mg/L at pH 4, C_{SRFA} < 40 mg/L and C_{SRFA} < 20 mg/L at pH 7. This pH dependence may explain that REEs binding to HA at different REE/HA ratios is well predicted by both ND (present study, Fig. 3*f*) and Model VII (Marsac *et al.* 2021) for the data of Marsac *et al.* (2010) that were measured at pH 3.

Model simulations by Marsac *et al.* (2021), who modelled the same data of Pourret *et al.* (2007) using Model VII, show a similar trend to our ND simulations, with overestimation of REE-HA binding at low HA concentrations and underestimation of REE-HA binding at higher HA concentrations. The differences between their modelled concentrations at high and low HA concentrations are, however, less pronounced. An important difference in the experimental set-up between Pourret *et al.* (2007) and Marsac *et al.* (2010) is

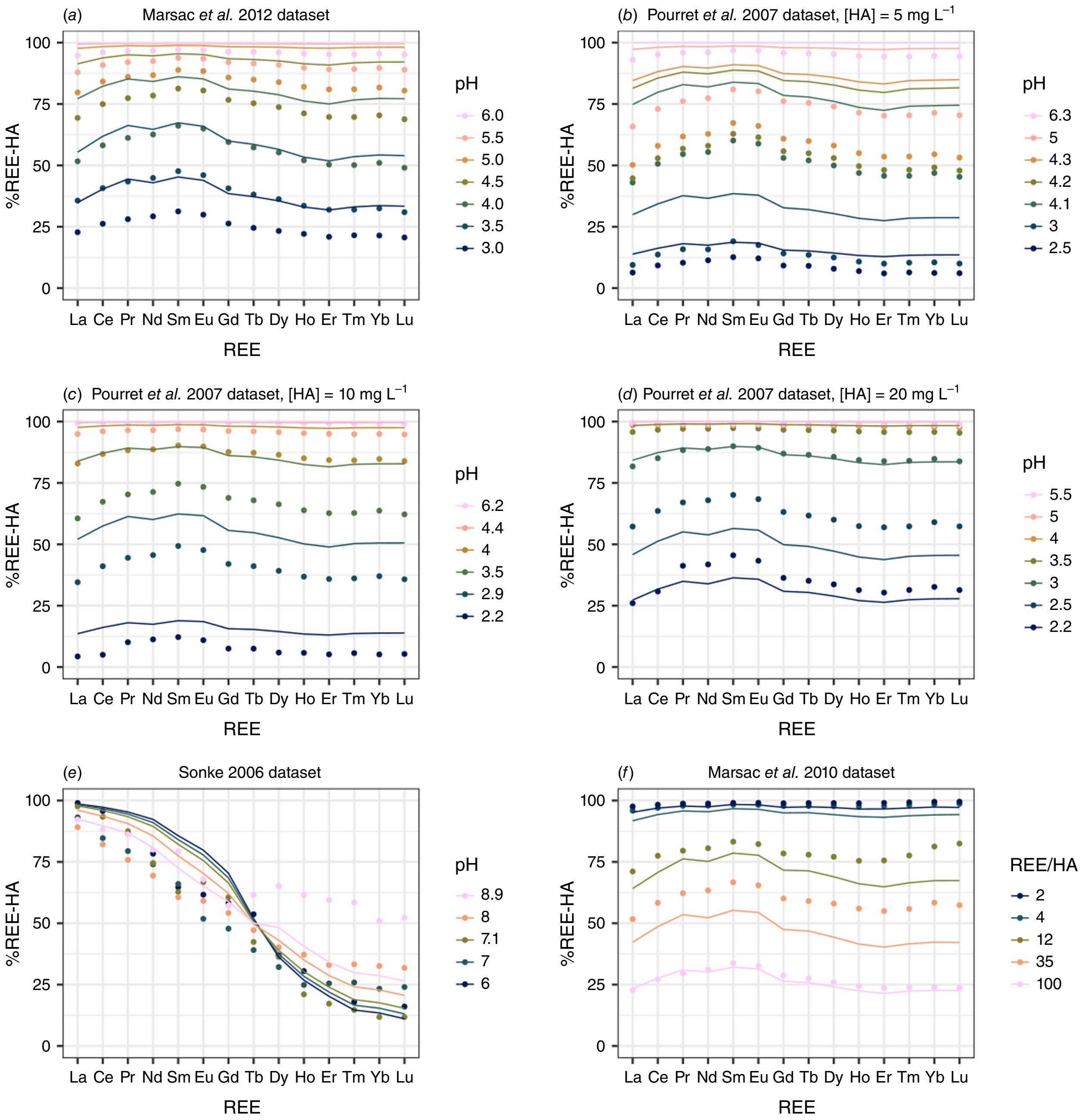

Fig. 3. REE-HA patterns, shown as percentage of REE bound to HA from dataset of Marsac *et al.* (2012) (*a*), Pourret *et al.* (2007) (*b*–*d*), Sonke and Salters (2006) (e), Marsac *et al.* (2010) (*f*); REE/HA values are given in mmol kg^{-1}, based on the La value for the whole series. Symbols are experimental data and lines results of calculation.

I imposed by the concentration of the background electrolyte $NaNO_3$ of 0.001 and 0.01 M respectively. The stronger deviations observed with the ND modelling compared with the simulations with Model VII at the low ionic strength for the Pourret *et al.* dataset may point in the direction of a discrepancy in the modelling of electrostatic interactions, which would have a stronger effect with the lower *I* in the experiments of Pourret *et al.* compared with the experiments with higher *I* of Marsac *et al.* (2010). According to Koopal *et al.* (2022), and as noted by Lenoir, Matynia and Manceau (2010) and Janot *et al.* (2017), the use of Eqn 5 (Kinniburgh *et al.* 1999), which relates the Donnan volume to the ionic strength, results in relatively strong electrostatic interactions. According to Eqn 2, a possible overestimation of the electrostatic potential will especially affect the electrostatic component in the binding of trivalent cations such as the REEs, because in the exponent of Eqn 2, the valence of the ion z is multiplied with the electrostatic potential.

At relatively high bulk concentrations as is the case with high REE/HA, this may lead to substantial overestimation of cation binding. It would be worthwhile investigating the use of Eqn 4, which leads to more realistic potentials than the Kinniburgh Eqn 5 (Janot *et al.* 2017; Koopal *et al.* 2022). However, we decided to stay with the one-parameter Kinniburgh Eqn 5 to have the newly derived REE parameters compatible with the generic parameters of Milne *et al.* (2001, 2003), which are used as the default ND parameters in the chemical speciation software ECOSAT, ORCHESTRA and Visual MINTEQ.

Comparison with Irving–Rossotti approach

Marsac *et al.* (2021) used a different LFER than the one from Milne *et al.* (2003) to constrain their REE-HA binding parameters. They followed the work of Irving *et al.* (1956), who showed that the binding constant for monodentate binding of metals to oxygen ligands in organic acids (both carboxylic and phenolic) is related to the protonation constant of the ligand according to the linear correlation:

$$\log K_{\mathrm{ML}} = \alpha_0 \log K_{\mathrm{HL}} + \beta_0 \qquad (8)$$

with $\log K_{\mathrm{HL}}$ the equilibrium constant for proton–ligand formation, $\log K_{\mathrm{ML}}$ the equilibrium constant for metal–ligand complexation, and α_0 and β_0 metal-specific parameters.

Applicability to the ND model

Carbonaro and DiToro (2007) showed that β_0 is close to zero for most elements and can be neglected. Together with Tipping *et al.* (2011), they used this LFER to regress the values of $\log K_{\mathrm{MA}}$, the mean equilibrium constant for metal binding to the stronger acid sites of natural organic matter (NOM) in the WHAM (Windermere Humic Aqueous Model) humic ion binding Models V, VI and VII. To investigate the possibility of applying this approach to the ND model, we regressed the ND median metal binding constants $\log\tilde{K}_1$ and $\log\tilde{K}_2$ for 11 metals that were obtained by Milne *et al.* (2003) without constraints against the Irving–Rossotti slope α_0. Results are given in Fig. 4, together with nine other metals whose binding constants were also determined by Milne *et al.* (2003) by using constrains on parameter optimisation. With the $\log\tilde{K}_1$ of Al clearly deviating from the linear relationship, we excluded this metal from the regression, and obtained a good linear relationship, with R^2 of 0.89 and 0.90 for $\log\tilde{K}_1$ and $\log\tilde{K}_2$, respectively.

This observation allowed us to use the Irving–Rossotti approach to regularise ND parameters in a similar way as was done for Model VII (Tipping *et al.* 2011; Marsac *et al.* 2021).

Applicability to REEs

Carbonaro and DiToro (2007) found that β_0 significantly differed from 0 for several metal ions including Eu^{3+}. Later, Marsac *et al.* (2021) derived α_0 and β_0 values for the whole REE series. They found the following linear relationship between LFER parameters (α_0, β_0) and the binding constants $\log K_{\mathrm{MA}}$ of REEs:

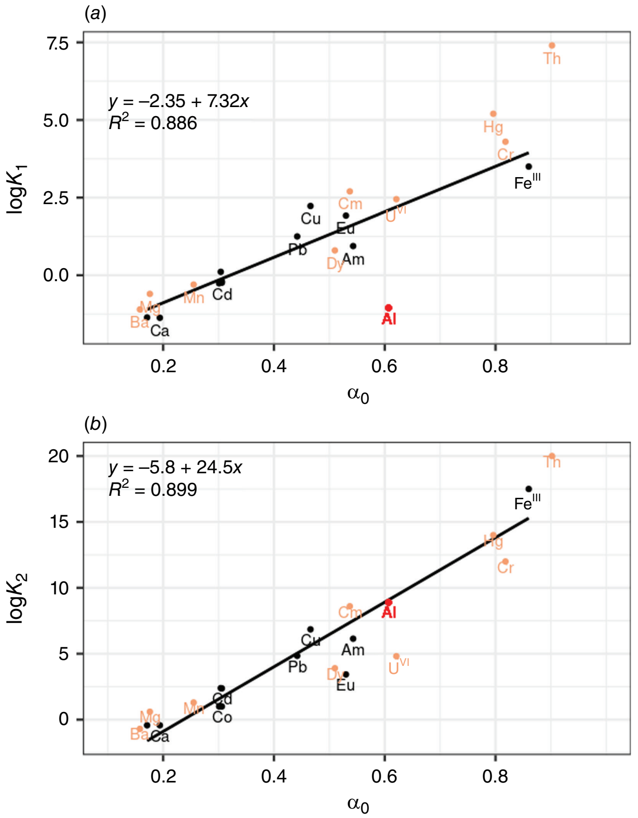

Fig. 4. Generic NICA–Donnan parameters $\log\tilde{K}_1$ (*a*) and $\log\tilde{K}_2$ (*b*) against the corresponding Irving–Rossotti slope a_0. Only the parameters determined by unconstrained optimisation by Milne *et al.* (2003) are included in the linear regression ($n = 11$, black symbols). Note that Al is not included in the linear regression, owing to large deviation of $\log\tilde{K}_{1,\mathrm{Al}}$ from the other metal parameters (red symbols). Other metals for which data were available but for which generic $\log K_i$ were determined applying constrains on the fit are shown for comparison ($n = 9$, orange symbols).

$$\log K_{\mathrm{Mi}} = U_i\alpha_0 + V_i\beta_0 + W_i, \qquad (9)$$

where U_i, V_i and W_i are parameters that must be optimised for each type of binding site.

Here, we fitted this LFER Eqn 9 to the $\log\tilde{K}_i$ values optimised above. For Type 1 sites, we obtained 2.71, 1.37 and −0.52 for U_1, V_1 and W_1, respectively. For Type 2 sites, we obtained 13.20, −0.74 and −0.24 for U_2, V_2 and W_2, respectively. As shown in Fig. 1 (grey symbols), the $\log\tilde{K}_i$ calculated using fitted Eqn 9 describe the patterns of the optimised $\log\tilde{K}_i$ rather well, which gives confidence in the optimised ND parameters for REEs. These results also show the potential of using the Irving–Rossotti approach to regularise existing ND parameters for other metals.

Prediction of cation competition effect on REE-HA binding

Modelling the effect of competitive cation binding (Fe^{3+}, Al^{3+}, Cu^{2+}) on REE binding to HA was performed using experimental datasets previously published (Marsac *et al.* 2012, 2013, 2021). Metal binding parameters used were the generic ND parameters (Milne *et al.* 2003), provided in Supplementary Table S1.

The modelled and measured pH edge impact of parameterisation on REE binding to HA is shown in Fig. 5 for Eu. Results show that, using generic parameters, binding of Eu to HA is overpredicted at all pH in the absence and presence of all competitors. Experimental results show no effect of Cu^{2+} on REE-HA binding, in contrast to the trivalent Al^{3+} and Fe^{3+}, which, when present in the system, lead to a significant decrease in REE-HA binding.

The use of the generic ND model parameters from Milne *et al.* (2003) to describe this competition effect seems to have quite strong limitations, as the addition of the three cations in the modelling only leads to a slight decrease in the calculated amount of Eu-HA binding. We thus used the LFER determined above (Fig. 4) to update the Fe and Al ND parameters proposed by Milne *et al.* (2003): $\log\tilde{K}_{1,\mathrm{Fe}}$ was shifted from 3.5 to 3.95, $\log\tilde{K}_{1,\mathrm{Al}}$ from -1.05 to 2.09 and $\log\tilde{K}_{2,\mathrm{Al}}$ from 8.89 to 9.07. Results of Eu binding to HA are shown in Fig. 5. The slight increase of $\log\tilde{K}_{1,\mathrm{Fe}}$ has no impact on Eu or on Fe binding (Supplementary Fig. S5). However, the substantial increase of $\log\tilde{K}_{1,\mathrm{Al}}$ has a significant impact on Al complexation to HA (Supplementary Fig. S5), and thus on REE binding, as shown in Fig. 5 for Eu, although Eu complexation is still overestimated for the whole pH range studied.

This overestimation of REE binding to HA by the ND model across a large range of pH values, even in the presence of competitors, could possibly be due to the generic site densities Q_i of Milne *et al.* (2003) being too high for the specific HA (PAHA) used in this study. Adapting proton-binding parameters to the specific HA used in these experiments could be a way to increase the accuracy of the results. However, this has not been tested as this was outside the scope of this study. Indeed, the goal of the present work was to determine generic REE-HA binding parameters compatible with the generic parameters of Milne *et al.* (2003) that can be applied in a wide range of environmental conditions (type of HA as well as pH, ionic strength or REE/HA concentrations), to be able to predict REE behaviour in such environments. We consistently captured the shapes of REEs patterns and the impact of various environmental parameters, which gives us confidence in the derived parameters.

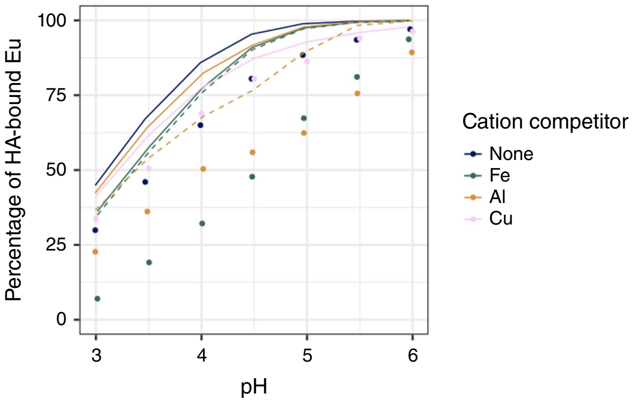

Fig. 5. pH edge of Eu binding to HA dependence on the competitor present: Fe^{3+}, Al^{3+}, Cu^{2+} or none. Points are experimental results (Marsac *et al.* 2021) and lines are model predictions: solid lines with generic parameters and dashed lines with updated parameters according to the Irving–Rossotti approach and regression given in Fig. 4.

Another explanation for the discrepancies between experimental and modelling results of the competition experiments could be the fact that the specific binding of the Al and Fe hydroxy species ($AlOH^{2+}$, $FeOH^{2+}$) to HA is not taken into account in the ND model. In the present ND model, these hydrolysed species only interact with HA through electrostatic binding in the Donnan volume. Including the specific binding of hydroxy species in ND, as within Model VII, is worthwhile considering as the modelling of strong hydrolysing trivalent species (e.g. Al, Fe) with ND is known to be inferior compared with the modelling of the less strongly hydrolysing divalent species (Milne *et al.* 2003).

Conclusions

Recently, several datasets from the literature were collected to calibrate the advanced humic ion binding model for the prediction of REE binding to HA Model VII (Marsac *et al.* 2021). The present work provides parameters to model REE binding to HA under various pH, concentration and ionic strength physico-chemical conditions, in the framework of another advanced humic ion binding model, the NICA–Donnan model. At the moment, such advanced models are the best option to predict metal ion binding to HSs (Koopal *et al.* 2020). The present work will thus make it possible to calculate REE speciation in various environments with ND using chemical speciation software (ECOSAT, ORCHESTRA and Visual MINTEQ).

This work also showed the potential of the Irving–Rossotti approach to estimate and constrain metal binding parameters for the NICA–Donnan model. Here, we showed that it can also be applied for ND parameter estimation of REEs when using the extended Irving–Rosotti approach (Marsac *et al.* 2021).

Supplementary material

Supplementary material is available online.

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Data availability. The data that support this study will be shared upon reasonable request to the corresponding author.

Conflicts of interest. The authors declare no conflicts of interest.

Declaration of funding. This work was supported by the French National Research Agency through the national program 'Investissements d'avenir' (reference ANR-10LABX-21–01/LABEX RESSOURCES 21).

Acknowledgements. We dedicate this paper to Professor Edward Tipping for his major scientific contributions in the field of the chemistry of humic substances and metals and the development of humic ion binding models, for his helpfulness and for being inspiring to us. This manuscript benefited from the constructive comments of two anonymous reviewers.

Author contributions. A. Otero-Fariña: conceptualisation, investigation, formal analysis, writing – original draft. N. Janot: conceptualisation, investigation, visualisation, writing – original draft; writing – review and editing. R. Marsac: resources, writing – review and editing. C. Catrouillet: writing – review and editing. J. E. Groenenberg: conceptualisation, methodology, investigation, resources, writing – review and editing, supervision.

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