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Speciation of rare earth elements in natural terrestrial waters: Assessing the role of dissolved organic matter from the modeling approach

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Abstract—Humic Ion-Binding Model V, which focuses on metal complexation with humic and fulvic acids, was modified to assess the role of dissolved natural organic matter in the speciation of rare earth elements (REEs) in natural terrestrial waters. Intrinsic equilibrium constants for cation-proton exchange with humic substances (i.e., pK_{MHA} for type A sites, consisting mainly of carboxylic acids), required by the model for each REE, were initially estimated using linear free-energy relationships between the first hydrolysis constants and stability constants for REE metal complexation with lactic and acetic acid. pK_{MHA} values were further refined by comparison of calculated Model V "fits" to published data sets describing complexation of Eu, Tb, and Dy with humic substances. A subroutine that allows for the simultaneous evaluation of REE complexation with inorganic ligands (e.g., Cl^-, F^-, OH^-, SO_4^{2-}, CO_3^{2-}, PO_4^{3-}), incorporating recently determined stability constants for REE complexes with these ligands, was also linked to Model V. Humic Ion-Binding Model V's ability to predict REE speciation with natural organic matter in natural waters was evaluated by comparing model results to "speciation" data determined previously with ultrafiltration techniques (i.e., organic acid–rich waters of the Nsimi-Zoetele catchment, Cameroon; dilute, circumneutral-pH waters of the Tamagawa River, Japan, and the Kalix River, northern Sweden). The model predictions compare well with the ultrafiltration studies, especially for the heavy REEs in circumneutral-pH river waters. Subsequent application of the model to world average river water predicts that organic matter complexes are the dominant form of dissolved REEs in bulk river waters draining the continents. Holding major solute, minor solute, and REE concentrations of world average river water constant while varying pH, the model suggests that organic matter complexes would dominate La, Eu, and Lu speciation within the pH ranges of 5.4 to 7.9, 4.8 to 7.3, and 4.9 to 6.9, respectively. For acidic waters, the model predicts that the free metal ion (Ln^{3+}) and sulfate complexes ($LnSO_4^+$) dominate, whereas in alkaline waters, carbonate complexes ($LnCO_3^+$ + $Ln[CO_3]_2^-$) are predicted to out-compete humic substances for dissolved REEs. Application of the modified Model V to a "model" groundwater suggests that natural organic matter complexes of REEs are insignificant. However, groundwaters with higher dissolved organic carbon concentrations than the "model" groundwater (i.e., >0.7 mg/L) would exhibit greater fractions of each REE complexed with organic matter. Sensitively analysis indicates that increasing ionic strength can weaken humate-REE interactions, and increasing the concentration of competitive cations such as Fe(III) and Al can lead to a decrease in the amount of REEs bound to dissolved organic matter. *Copyright © 2003 Elsevier Science Ltd*

1. INTRODUCTION

Rare earth elements (REEs) are commonly used as geochemical tracers in the study of many geologic processes because of their unique, chemically coherent behavior (e.g., Goldberg et al., 1963; Kay and Gast, 1973; Hanson, 1980; Elderfield and Greaves, 1982; Cullers and Graf, 1984; Sholkovitz and Elderfield, 1988; Sholkovitz et al., 1993). Furthermore, because the naturally occurring REEs exhibit similar ionic radii and identical charge to trivalent actinides (Am^{3+}, Cm^{3+}, Cf^{3+}), the REEs can be employed as chemical analogues for predicting the behavior of these radioactive elements in natural waters (Brookins, 1986; Choppin, 1986, 1989; Wood, 1990). However, the full exploitation of REEs in natural waters requires a comprehensive understanding of their aqueous geochemistry, including more quantitative information concerning their solution and surface complexation behavior. For example, although the REEs are strongly particle reactive, they also form strong solution complexes with some inorganic and organic ligands, including carbonate and phosphate ions and ethylenediaminetetraacetic acid (Cantrell and Byrne, 1987; Wood, 1990; Lee and Byrne, 1992, 1993; Millero, 1992; Takahashi et al., 1997; Lewis et al., 1998; Leybourne et al., 2000). Indeed, these and other investigations suggest that carbonate complexes dominate REE solution complexation in neutral- to alkaline-pH, natural (i.e., unpolluted) waters, whereas the free metal ion species (Ln^{3+}) and sulfate complexes are most important in acidic waters. Although stability constants describing the formation of REE phosphate complexes are similar in magnitude to those for some REE carbonate complexes (Lee and Byrne, 1992, 1993), equilibrium calculations indicate that phosphate ions likely affect dissolved REEs via precipitation of REE phosphate salts (e.g., Byrne and Kim, 1993; Johannesson et al., 1995).

Despite the growing understanding of REE complexation with inorganic ligands, little is known concerning REE complexation with naturally occurring organic ligands in natural waters. Significant efforts have been made toward the study of REE solution complexation behavior with a variety of well-characterized or synthetic organic ligands (e.g., Wood, 1993;

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Table 1. Model parameter definitions and their fixed values for fulvic and humic acids (based on Tipping, 1993).

	Fulvic acid	Humic acid
n_A: mol type A groups per g	4.7×10^{-3}	3.3×10^{-3}
pK_A: mid-range pK of type A group	3.3	4.0
pK_B: mid-range pK of type B group	9.6	8.6
ΔpK_A: "spread factor" for type A pK values	3.3	1.8
ΔpK_B: "spread factor" for type B pK values	5.5	3.4
P: defines $w = P\log_{10}I$	–103	–374
f_{pr}: proximity factor	0.4	0.5
Approximate molecular weight	1500	15000
Approximate molecular radius (nm)	0.8	1.72
pK_{MHB}: intrinsic equilibrium constants for the metal-proton exchange reaction at type B sites	$3.96pK_{MHA}$	$3pK_{MHA}$–3
pK_{MHA}: intrinsic equilibrium constants for the metal-proton exchange reaction at type A sites	Adjusted by metal-binding data	Adjusted by metal-binding data

Deberdt et al., 2000; Gammons and Wood, 2000; Wood et al., 2000; Zotov et al., 2002); however, these ligands are likely to differ dramatically from complex, natural organic matter. Dissolved natural organic matter typically includes poorly understood humic acids (HA) and fulvic acids (FA), amino acids and proteins, simple organic acids resulting from microbially mediated degradation of organic matter, biotically produced ligands such as siderophores, as well as other as yet unidentified naturally occurring organic ligands, all or none of which could conceivably complex the REEs (e.g., McKnight and Morel, 1980; Thurman, 1985; Bruland, 1989; Bruland et al., 1991; Xue et al., 1995; Achterberg et al., 1997; Leal and van den Berg, 1998; Brantley et al., 2001). Nevertheless, many investigators have argued that complexation of REEs with natural organic ligands, particularly surface complexation to organic-coated particulates, is likely to be important for REE speciation in natural waters (Byrne and Kim, 1990; Wood, 1993; McCarthy et al., 1998a, 1998b). In fact, these predictions have in large part been documented by recent ultrafiltration studies, which clearly demonstrate that REEs are strongly associated with organic matter in terrestrial waters (e.g., Tanizaki et al., 1992; Viers et al., 1997; Dupré et al., 1999; Ingri et al., 2000). Consequently, it is desirable to develop simulation models to predict the solution complexation of REEs with organic matter in natural waters that can be used as proxies for more time-consuming and expensive ultrafiltration techniques (e.g., Lead et al., 1997). However, it is imperative that these predictive models first be verified with ultrafiltration studies and/or other analytical techniques (e.g., electrochemical) before their widespread use in natural water systems. In this contribution, we present a modified version of a well-known metal–organic matter speciation code (Humic Ion-Binding Model V; Tipping, 1994), revised to allow predictions of complexation of the naturally occurring REEs with organic matter in natural waters. The ability of Model V to predict REE speciation is compared to previous ultrafiltration studies of REE speciation in natural waters (Tanizaki et al., 1992; Viers et al., 1997; Ingri et al., 2000), which demonstrates that the model can predict reasonably well the distribution of REEs with organic matter. It is critical to point out that the model described herein for REE speciation predictions is a first attempt to develop an easily employed predictive tool for REE complexation with organic ligands in natural water based on an existing code. The model is limited by the numerous assumptions inherent in the model (e.g., Tipping and Hurley, 1992; Tipping, 1994), the fact that the model considers only metal binding with the humic matter (HM) fraction of natural organic material, and perhaps most importantly the fact that the necessary model parameters have been determined for only a limited number of the 14 naturally occurring REEs, not the entire REE series. Nevertheless, despite these limitations, the model performs reasonably well in predicting REEs with natural organic matter on the basis of the comparisons with the ultrafiltration studies. Here, we use the term *organic matter–bound REE solution complex* to include REEs complexed to both low- and high–molecular weight (MW) natural organic matter, which have been considered dissolved and colloidal organic matter, respectively, by other investigations (Tanizaki et al., 1992; Viers et al., 1997; Ingri et al., 2000).

2. APPLICATION OF MODEL V TO THE REE SERIES

In terms of modeling REE speciation, addressing complexation with natural organic matter in existing aqueous speciation codes is problematic at best. For example, large naturally occurring organic molecules, such as FA and HA, contain numerous and chemically different potential metal binding sites, and thus it is difficult to define discrete equilibrium constants for each complexation reaction that can take place (Crawford, 1996). Furthermore, quantifying activity coefficients for these sites and metals bound to these sites as a function of ionic strength remains a difficult problem to solve. Typically, a sophisticated, discrete-site electrostatic organic binding model is employed to model metal–organic matter interactions, although other approaches have also been used (e.g., Glaus et al., 2000; Hummel et al., 2000). In the current study, a modified version of the discrete-site Humic Ion-Binding Model V, originally developed by Tipping and coworkers (Tipping and Hurley, 1992; Tipping, 1993, 1994), was employed to assess the role of dissolved organic matter in the speciation of REEs in natural waters. Model V is favored because (1) it has been widely validated for a variety of trace metals, including some of the REEs, by application to experimental data; and (2) most of the important model parameters (i.e., n_A, pK_A, pK_B, ΔpK_A, ΔpK_B, P, f_{pr}, pK_{MHB}) have been derived and fixed separately for HA and FA (Table 1). Consequently, only a single parameter, pK_{MHA}, is required to fit model predictions to metal-binding data (Tipping, 1993). The

Table 2. Experimental conditions for rare earth element–humic substance complexation.

Data source	Metal ion	Method	n	I(mol/L)	pH	[HA]t or [FA]t (mg/L)	[M]t (μmol/L)
Bidoglio et al. (1991)	Eu^{3+}		15	0.1	6.5	[FA]t: 1.0–32.2	20
	Eu^{3+}	TRLIF	19	0.1	5.5	[FA]t: 1.5–72.2	20
	Tb^{3+}		29	0.1	5.5	[FA]t: 0.76–75.2	20
Lead et al. (1998)	Eu^{3+}	Schubert's method	15	0.1	3.56–6.04	[FA]t: 25	0.015–0.14
		Equilibrium dialysis	16	0.005	2.0–7.43	[FA]t: 3	0.17
Moulin and Tits (1992)	Dy^{3+}	TRLIS	14	0.1	5.0	[HA]t: 0.54–8.67	2.0

n is the number of data points used in fitting Model V; I is ionic strength; [HA]t or [FA]t indicates total humic or fulvic acid concentration; [M]t is total metal ion concentration; TRLIF = time-resolved laser-induced fluorescence; TRLIS = time-resolved laser-induced spectrofluorometry.

single, adjustable parameter (pK_{MHA}) approach allows the model to be readily applied to most cases of metal-proton exchange with humic substances. Furthermore, this approach allows the model to be used for investigating metal interactions with both the more soluble, low-MW, fulvic-type organic fraction and the less soluble, higher MW, humic fraction (Tipping and Hurley, 1992; Tipping, 1993, 1994; Hamilton-Taylor et al., 2002). Application of the model to data for Cu^{2+}, Zn^{2+}, Ni^{2+}, Pb^{2+}, Cd^{2+}, Co^{2+}, Mn^{2+}, Ba^{2+}, Sr^{2+}, Ca^{2+}, Mg^{2+}, Eu^{3+}, U^{4+}, Pa^{4+}, Pu^{4+}, Np^{4+}, U^{4+}, Am^{3+}, and Cm^{3+} indicates that the model accurately predicts the complexation behavior of many metals with humic substances, including some REEs and a number of actinides (Tipping and Hurley, 1992; Tipping, 1993, 1994; Hamilton-Taylor et al., 2002). Furthermore, although Model V has recently been updated (i.e., Model VI), resulting in an overall improvement in the model's predictive abilities in many cases (e.g., Tipping, 1998; Tipping et al., 2002), no significant differences in the model's abilities to predict REE speciation have been identified (Lead et al., 1998).

For the specific case of the REEs, Humic Ion-Binding Model V was initially applied to study Eu complexation with natural dissolved organic matter (Tipping, 1993). Tipping (1993) demonstrated that Model V accurately describes Eu complexation with HA over a wide range of solution compositions (i.e., pH 2.5–9.1, pI 0.5–3.5, HCO_3^- concentration up to 0.1 mol/L) and determined a representative pK_{MHA} value of 1.3 for Eu-HA binding. However, pK_{MHA} values derived from existing data to describe Eu complexation with FA exhibit a wide range (i.e., 0.49 and −0.11), which may reflect experimental error, actual differences between the fulvic isolates, and/or different types of model failures (Tipping, 1993). To rectify this issue and better constrain the pK_{MHA} value for Eu-FA complexation, we surveyed and evaluated other and more recent experimental data for Eu^{3+}-HM binding (i.e., Maes et al., 1988, 1991; Bidoglio et al., 1991; Dierckx et al., 1994; Lead et al., 1998). Briefly, the data of Maes et al. (1988) can be used to calibrate Model V, giving excellent results that closely resemble our adopted pK_{MHA} results for Eu (see below). However, this observation is expected because Tipping (1993) previously used these data to calibrate the model. Maes et al. (1991) provided the range and mean values for specific stability constants; however, because they chose not to include their experimental data, this study cannot be used to better constrain the pK_{MHA} values for Eu. The study by Dierckx et al. (1994) examined mixed complexation of Eu with HA and a competing ligand, which Model V does not consider. Furthermore, Glaus et al. (2000) questioned the data of Dierckx et al. (1994), noting that either EuHS or $EuHSL_2$ will form over the whole range of L (ligand) concentration investigated but observed no formation of $EuHSL_1$ complexes. Subsequently, Glaus et al. (2000) argued that the behavior of mixed ligand complexes reported by Dierckx et al. (1994) is apparently at odds with the common behavior of low-MW organic ligands (Sigel, 1973), and oxide-based surfaces (Schindler, 1990). Hence, because of these observations and the fact that Model V does not address mixed-ligand complexes, we have not considered the data of Dierckx et al. (1994) further. Therefore, to the best of our knowledge, only the data sets of Bidoglio et al. (1991) and Lead et al. (1998) can be used to further calibrate Model V and constrain pK_{MHA} values for Eu.

The experimental conditions used by Bidoglio et al. (1991) and Lead et al. (1998) are summarized in Table 2. Furthermore, the experimental data from these studies (data points) are compared to the results of Humic Ion-Binding Model V for Eu complexation with FA (solid curves, Fig. 1) on the basis of the experimental conditions presented in Table 2. Figure 1 clearly demonstrates that Model V simulates the experimental data reasonably well. Because of the good fit, the best-fit Model V calculated curves to the experimental data were subsequently used to obtain "best-fit" pK_{MHA} values for Eu with FA (i.e., pK_{MHA} values labeled in Figs. 1a and 1b). Table 3 summarizes the "best-fit" logK_{MHA} values and root mean square (rms) errors in pv (i.e., $-\log_{10}v$; v is moles of Eu bound per gram of FA) for Eu-FA complexation for the data sets of Tipping (1993), Bidoglio et al. (1991), and Lead et al. (1998). Table 3 demonstrates that the "best-fit" pK_{MHA} values are similar when the rms error values are low (e.g., compare data sets 3, 4, and 5). On the other hand, the substantially different and lower pK_{MHA} values of data sets 2 and 6 (Table 3) reflect poorer fits to the experimental data, as indicated by their high rms error values. Thus, it is our belief that the pK_{MHA} values of −0.11 and 0.1 obtained from data sets 2 and 6 should not be used in Humic Ion-Binding Model V simulations of Eu complexation with FA. Instead, on the basis of the low rms error values of data sets 3, 4, and 5, we submit that a pK_{MHA} value of 0.625 is a more representative value for Eu-FA complexation.

Determining representative pK_{MHA} values for complexation of REEs other than Eu with humic substances is more difficult because of the lack of experimental data. In fact, other than Eu, data describing the complexation of only Tb, Dy, and Sm complexation with humic substances exist in the readily available literature (Bidoglio et al., 1991; Moulin and Tits, 1992; Franz et al., 1997). The data sets for Sm complexation (i.e., Franz et al., 1997) were inconsistent with each other, suggest-

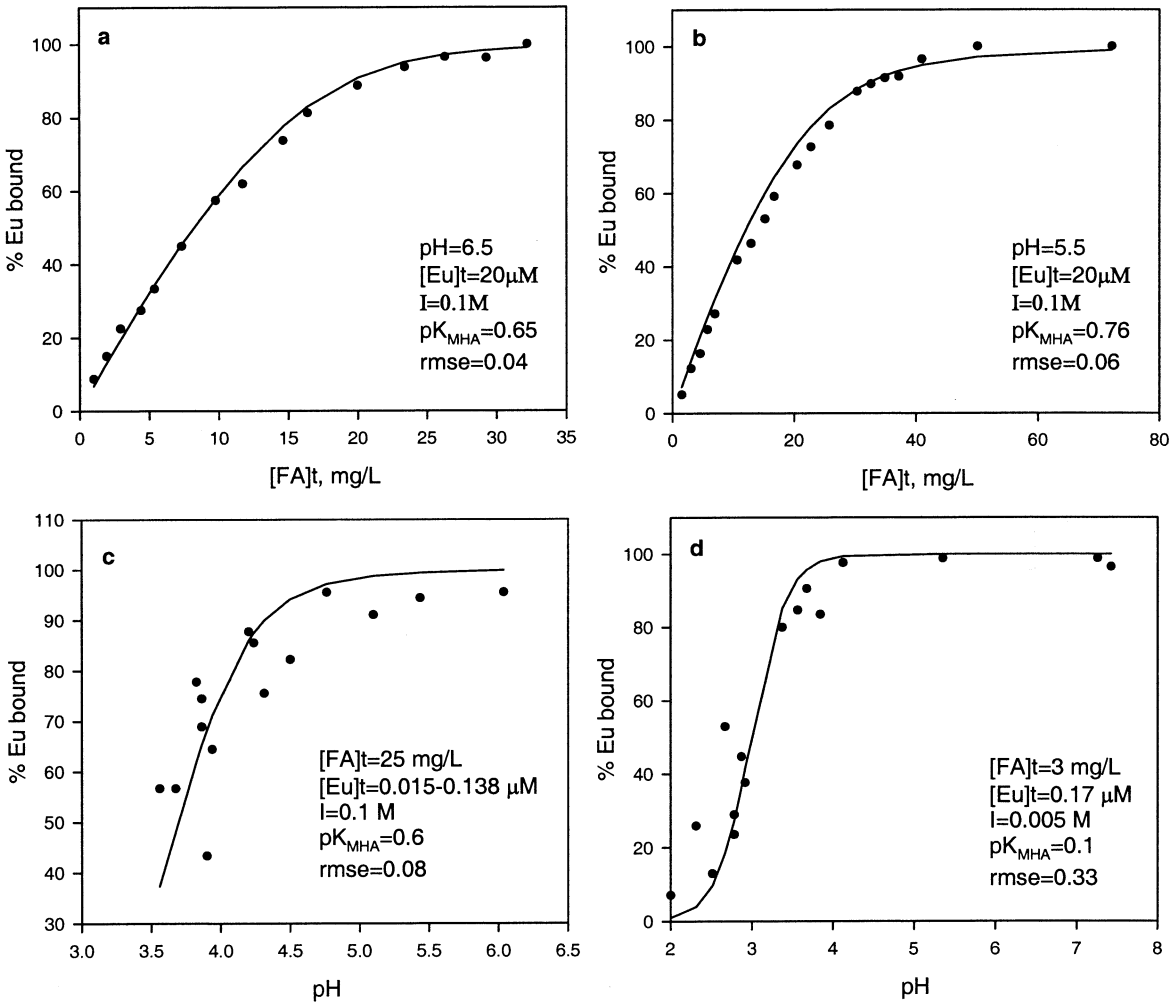

Fig. 1. Complexation of Eu with fulvic acid (FA). Points represent experimental data and the solid lines indicate the best model fits. Panels (a) and (b) show the dependence of %Eu bound to the total FA concentration for two pH conditions (Bidoglio et al., 1991). Panels (c) and (d) show the dependence of %Eu bound vs. pH (Lead et al., 1998).

ing that problems may have arisen during analysis. More specifically, in the study by Franz et al. (1997), the data obtained using cation-exchange methods differed between weakly and strongly acidic resins, and both cation-exchange methods employed by these investigators gave stability constants that were lower than that determined by electrophoresis. Because of these inconsistencies, only data sets describing Tb and Dy complexation, in addition to Eu, with humic substances (i.e., Bidoglio et al., 1991; Moulin and Tits, 1992) were used to evaluate the ability of Humic Ion-Binding Model V to reproduce the experimental data for REEs. Again, the experimental conditions used to obtain representative pK_{MHA} values for Tb and Dy data in these studies are shown in Table 2. Applying Humic Ion-Binding Model V to the experimental data of Bidoglio et al. (1991) and Moulin and Tits (1992) reveals relatively good model fits to the data for both Tb and Dy (Fig. 2; note the low rms errors for both Tb and Dy). Consequently, the relatively good reproduction by Model V of the experimental data for Tb

Table 3. Best-fit pK_{MHA} values and root mean square (rms) errors in pν for all data sets of Eu–fulvic acid complexation. p is standard notation for –log10, and ν represents the moles of Eu bound per gram of fulvic acid.

Data set	pK_{MHA}	rms error in pν	Reference
1	0.49	0.19	Tipping (1993)
2	–0.11	0.57	Tipping (1993)
3	0.65 (pH = 6.5)	0.04	Bidoglio et al. (1991)
4	0.76 (pH = 5.5)	0.06	Bidoglio et al. (1991)
5	0.60 (Schubert's method)	0.08	Lead et al. (1998)
6	0.10 (equilibrium dialysis)	0.33	Lead et al. (1998)

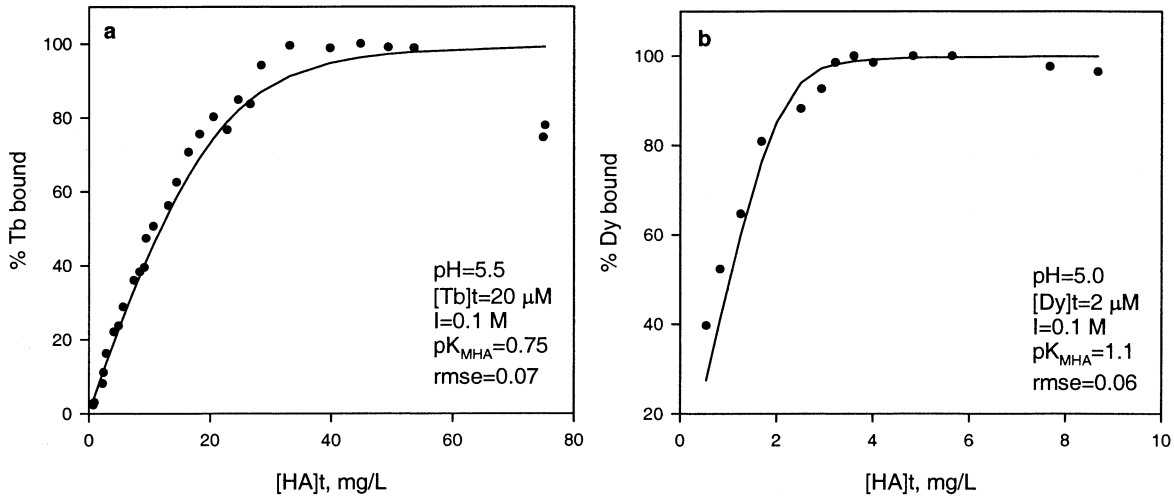

Fig. 2. Complexation of Tb and Dy with humic matter. Panel (a) shows complexation of Tb with fulvic acid (data from Bidoglio et al., 1991); and panel (b) shows complexation of Dy with humic acid (HA) (data from Moulin and Tits, 1992). Points represent experimental data and the solid lines are the model fits determined with Humic Ion-Binding Model V.

and Dy indicates that Model V can also be applied with confidence to predict complexation of other REEs besides Eu with natural humic substances. Our results are clearly in agreement with those of Tipping (1993) and Lead et al. (1998), who previously showed that Model V can predict REE complexation with humic materials. Furthermore, on the basis of the Model V fits to the experimental data for Tb and Dy, representative pK_{MHA} values for Tb-FA complexation and Dy-HA complexation are 0.75 and 1.0, respectively.

3. ESTIMATING pK_{MHA} VALUES FOR THE REE SERIES

As demonstrated above, application of Humic Ion-Binding Model V to experimental data from studies of REE complexation with humic substances produces good model fits to these experimental data (Figs. 1 and 2). Thus, Model V can be used to assess, to a first approximation, the role that dissolved organic matter plays in the speciation of REEs in natural waters. However, to apply Model V to simulate REE complexation with humic substances for the entire REE series, the pK_{MHA} value must be known for each of the naturally occurring REEs. As discussed above, the existing experimental data provide representative pK_{MHA} values only for Eu-HA, Eu-FA, Tb-FA, and Dy-HA complexation. Consequently, another indirect method is required to estimate appropriate pK_{MHA} values for the remaining REEs.

Tipping (1993) pointed out that linear free-energy relationships exist between pK_{MHA} values for metal–organic matter complexation and stability constants for simpler reactions, such as the first hydrolysis reaction for a given metal and metal–lactic acid (LA) and metal–acetic acid (AA) complexation. Table 4 lists pK_{MHA} values describing the complexation of numerous metals with HA and FA (data from Tipping, 1994). In addition, pK values for the first hydrolysis constant and complexation of these metals with LA and AA are also presented in Table 4 (data from Martell and Smith, 1977). The pK_{MHA} values and stability constants for hydrolysis and complexation with these simple organic acids for the various metals are plotted in Figure 3. Figure 3 demonstrates that relatively strong correlations exist between the pK_{MHA} values for metals listed in Table 4 and their first hydrolysis constants (MOH), as well as between the pK_{MHA} values and stability constants for the same metals with LA and AA (see also Tipping, 1993). The linear regression curves and correlation coefficients describing the relationships between the pK_{MHA} values for these metals as functions of their first hydrolysis constants and metal-LA and metal-AA stability constants are as follows:

$$pK_{MHA}\,(HA) = 0.66pK\,(LA) + 3.93 \qquad r = 0.93 \qquad (1)$$

$$pK_{MHA}\,(FA) = 0.77pK\,(LA) + 3.07 \qquad r = 0.93 \qquad (2)$$

$$pK_{MHA}\,(HA) = 0.29pK\,(MOH) + 3.8 \qquad r = 0.93 \qquad (3)$$

$$pK_{MHA}\,(FA) = 0.22pK\,(MOH) + 2.38 \qquad r = 0.89 \qquad (4)$$

$$pK_{MHA}\,(HA) = 1.1pK\,(AA) + 4.4 \qquad r = 0.79 \qquad (5)$$

$$pK_{MHA}\,(FA) = 0.85pK\,(AA) + 2.94 \qquad r = 0.85 \qquad (6)$$

Eqn. 1 to 6 were subsequently employed to estimate pK_{MHA} values for REE complexation with HA and FA (Table 5) using first hydrolysis constants for REEs (Klungness and Byrne, 2000) and stability constants for REE complexation with LA and AA (Martell and Smith, 1977).

Unfortunately, as Table 5 shows, some differences in the estimated pK_{MHA} values for the REEs are obtained depending on which equation (i.e., Eqn. 1 to 6) is employed. Because the correlation coefficients are high and each relationship described by Eqn. 1 to 6 is significant at the $> 98\%$ confidence level, it is difficult to determine which of these equations provide the best estimates of pK_{MHA} for the REEs. However, to establish which sets of linear free-energy estimated pK_{MHA} values for the REEs listed in Table 5 are more appropriate, we can compare them to the pK_{MHA} values for Eu-HA, Eu-FA, Tb-FA, and Dy-HA determined from the model fits to the experimental data (i.e., Figs. 1 and 2; Table 5). Using this approach, it is clear

Table 4. pK values for metal complexation with lactic acid (LA), acetic acid (AA), and the first hydrolysis product (MOH), and pK_{MHA} values for humic acid (HA) and fulvic acid (FA), used to obtain linear free-energy relationship equations between the pK_{MHA} and p*K* for these various ligands.

Metals	p*K* (LA)	p*K* (AA)	p*K* (MOH)	pK_{MHA} (HA)	pK_{MHA} (FA)
Mg^{2+}	–1.37	–1.27	—	3.3	2.2
Ca^{2+}	–1.45	–1.18	—	3.3	2.2
Sr^{2+}	–0.97	–1.14	—	2.8	—
Ba^{2+}	–0.71	–1.07	—	3.6	—
Th^{4+}	–5.50	—	–11.66	0.6	—
Mn^{2+}	–1.43	–1.40	–3.41	3.4	1.7
Co^{2+}	–1.90	–1.46	–4.35	2.7	1.7
Ni^{2+}	–2.22	–1.43	–4.14	2.7	1.4
Cu^{2+}	–3.02	–2.22	–6.48	1.5	0.8
Zn^{2+}	–2.22	–1.57	–5.04	2.3	1.3
Cd^{2+}	–1.70	–1.93	–3.92	2.7	1.5
Pb^{2+}	–2.78	–2.68	–6.29	1.7	0.9
Al^{3+}	—	—	–9.01	1.3	0.4
Fe^{2+}	—	–1.40	–4.50	2.1	—
Fe^{3+}	—	—	–11.81	0.8	—
Hg^{2+}	—	—	–10.6	0.2	—
UO_2^{2+}	—	—	–8.80	1.3	0.9
Am^{3+}	—	—	–7.6	1.2	0.3

The values of p*K* for acetate and lactate are from Martell and Smith (1977) at 25°C and zero ionic strength. The values of p*K* for MOH and the pK_{MHA} values for humic acid and fulvic acid were taken from Tipping (1994).

that the pK_{MHA} values estimated from the first hydrolysis constants (i.e., Eqn. 3 and 4) are too high (e.g., $pK_{MHA} \approx 1.05$ for Eu-FA complexation using Eqn. 4, and $pK_{MHA} \approx 0.63$ from the model fits; Figs. 1 and 2). On the other hand, pK_{MHA} values for Eu estimated using Eqn. 2 and 6 are more similar to the model fit estimates from the experimental data (Fig. 1). Similarly, the estimated pK_{MHA} values for Tb with FA calculated with Eqn. 6 (0.74) is almost identical to the value determined by fitting Model V to experimental data (i.e., 0.75; Fig. 2a). Consequently, we suggest that the linear free-energy estimates of pK_{MHA} for the REEs obtained with Eqn. 3 and 4 can be eliminated from further consideration.

In the case of Dy complexation with HA, the pK_{MHA} values estimated from the linear free-energy expressions (Eqn. 1, 3, and 5) are all high compared to the pK_{MHA} determined from fitting Model V to the experimental data (Fig. 2b), although those determined with Eqn. 1 and 5 are closer. Therefore, an additional approach is needed to help constrain which linear free-energy estimated pK_{MHA} values are most appropriate for Dy in particular and the REEs in general. To meet this objective, we can compare the linear free-energy estimated pK_{MHA} values for REEs to known pK_{MHA} values for other metal ions included in the database for Model V (e.g., Fe^{2+}, Cu^{2+}, Am^{3+}, Al^{3+}, and Fe^{3+}; Tipping, 1994). In other words, because K_{MHA} in Model V is an intrinsic constant and directly reflects the affinity of metal ions to complex with humic substances (Tipping and Hurley, 1992; Tipping, 1994), the pK_{MHA} values of these other metals can be used to constrain ranges of estimated pK_{MHA} values for REEs. By comparing the known conditional stability constants for FA with Fe^{2+}, Al^{3+}, and Eu^{3+}, Nordén et al. (1997) established that Eu^{3+} formed stronger complexes with FA than both Fe^{2+} and Al^{3+}. Takahashi et al. (1997) used a multitracer technique to simultaneously determine the stability constants of humate complexes with various metal ions. Their results show that stability constants of trivalent metal ions with humate are generally greater than those for divalent metal ions. Furthermore, the relative strength of stability constants for REEs and Fe^{3+} humate complexes are light REEs (LREEs) $<$ heavy REEs (HREEs) $<$ Fe^{3+} (Takahashi et al., 1997). Because Nd^{3+} and Am^{3+} have the same ionic radius and charge (Shannon, 1976), the pK_{MHA} value of Nd^{3+} should closely resemble that of Am^{3+}. Considering the pK_{MHA} values of Fe^{2+}, Cu^{2+}, Al^{3+}, Am^{3+}, and Fe^{3+} included in the Humic Ion-Binding Model V's database (Tipping, 1994) suggests that the pK_{MHA} values for the LREEs with HA and FA should be close to 1.3 and 0.2, respectively, and even smaller for the HREEs. In this sense, the estimated pK_{MHA} values for the REEs with Eqn. 1 and 2 are more appropriate than those estimated with Eqn. 5 and 6. Again, the pK_{MHA} values for the REEs estimated with Eqn. 3 and 4 are substantially higher than those suggested by considering the relative complexation strength of REEs and other metals, further supporting our previous decision to eliminate these values from consideration. Consequently, although this approach does not definitively determine a pK_{MHA} value for Dy complexation with HA, it does suggest that the pK_{MHA} values estimated with Eqn. 1 and 5 for HA and Eqn. 2 and 6 for FA (Table 5) represent relatively good first approximations of pK_{MHA} values for the REE series. Furthermore, it is well known that a coherence of interelement complexation behavior exists among the 15-member REE series (e.g., Lee and Byrne, 1992; Byrne and Li, 1995, and references therein). The pK_{MHA} values estimated with these four equations (Eqn. 1, 2, 5, and 6) exhibit interelement coherence across the REE series (Table 5). If, on the other hand, the individually determined pK_{MHA} values derived from the experimental data are used in REE speciation simulations, strong anomalous organic complexation behavior for Eu^{3+}, Tb^{3+}, and Dy^{3+} would be predicted. Thus, in this contribution, we adopt pK_{MHA} values that are average values of those estimated with Eqn. 1 and 5 for HA and Eqn. 2 and 6 for FA (Table 5). It is important to stress, however, that only additional experimental studies involving other members of the REE series will ultimately constrain the appropriate pK_{MHA} values.

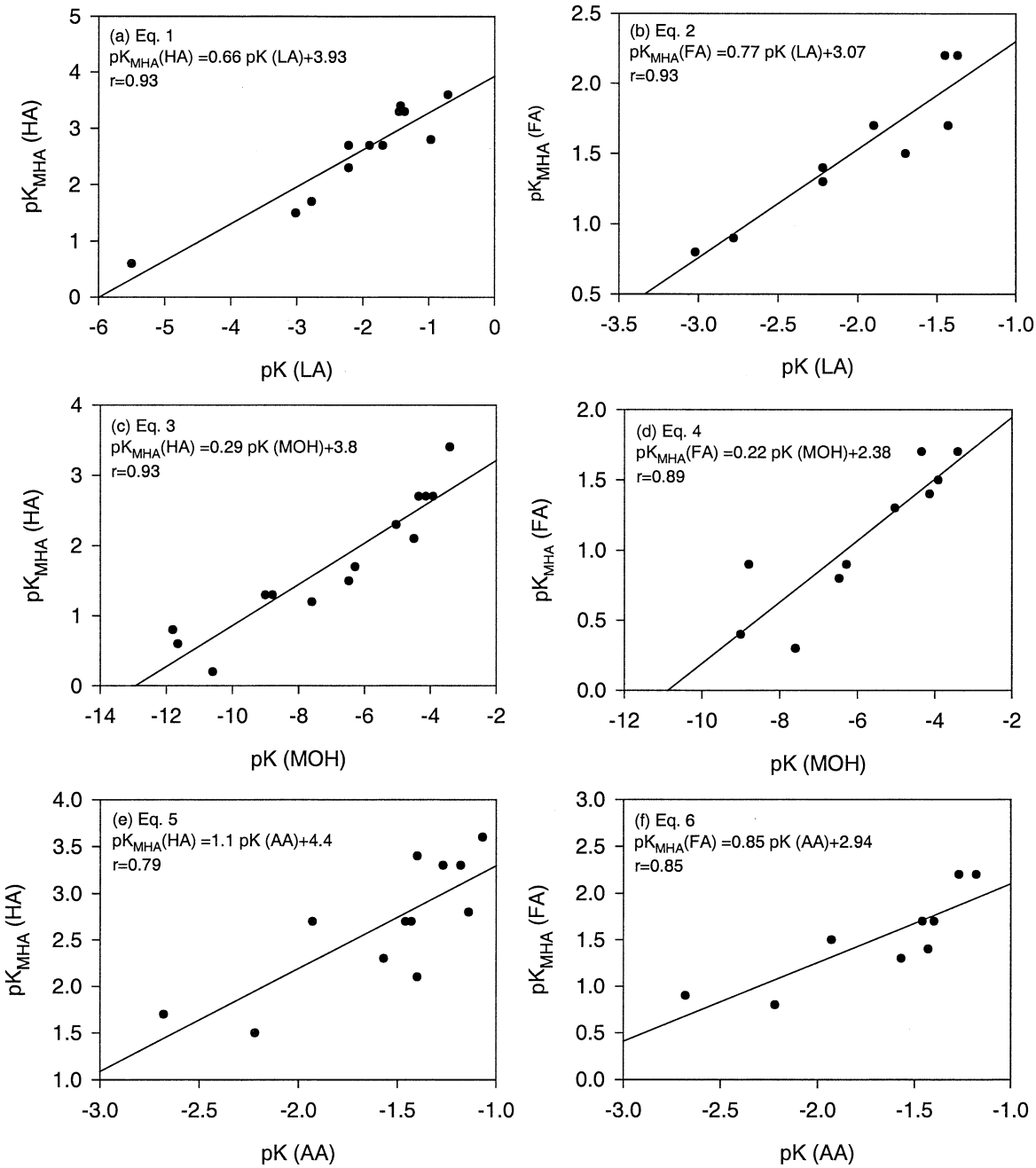

Fig. 3. Linear free-energy relationships between pK_{MHA} and stability constants for the first hydrolysis reaction and complexation with lactic acid (LA) and acetic acid (AA) for metals listed in Table 3. HA = humic acid; FA = fulvic acid; MOH = first hydrolysis product for metal M. The values for acetate and lactate are taken from Martell and Smith (1977), and the values for pK (MOH) and pK_{MHA} are from Tipping (1994).

All speciation calculations were performed using the computer program WHAM-W (version 1.0, Tipping, 1994), which includes Humic Ion-Binding Model V. We modified the code by building a database for the REEs that includes our adopted pK_{MHA} values for REEs (Table 5) and well-accepted, infinite dilution (25°C) stability constants for inorganic complexes of the REEs (Lee and Byrne, 1992, 1993; Millero, 1992; Klungness and Byrne, 2000; Luo and Byrne, 2000).

4. EVALUATING MODEL V'S ABILITY TO PREDICT REE SPECIATION WITH NATURAL ORGANIC MATTER

4.1. Description of Natural Water Samples

To test the validity of Humic Ion-Binding Model V for predicting the speciation of the entire REE series with organic matter, we selected data from three previous studies in which REE speciation was evaluated using ultrafiltration techniques

Table 5. Summary of estimated values of pK_{MHA} for rare earth elements (REEs).

	pK_{MHA} (HA)				pK_{MHA} (FA)			
REEs	From Eqn. 1	From Eqn. 3	From Eqn. 5	Adopted estimated values	From Eqn. 2	From Eqn. 4	From Eqn. 6	Adopted estimated values
La	1.77	2.23	1.58	1.68	0.53	1.21	0.79	0.66
Ce	1.63	2.16	1.53	1.58	0.37	1.16	0.74	0.56
Pr	1.62	2.11	1.45	1.54	0.36	1.13	0.69	0.53
Nd	1.61	2.08	1.45	1.53	0.34	1.10	0.69	0.52
Sm	1.56	2.02	1.26	1.41	0.29	1.06	0.54	0.42
Eu	1.54	2.01	1.36	1.45	0.26	1.05	0.62	0.44
Gd	1.55	2.01	1.44	1.50	0.27	1.05	0.68	0.48
Tb	1.54	1.99	1.53	1.54	0.26	1.04	0.74	0.50
Dy	1.54	1.98	1.57	1.56	0.27	1.03	0.78	0.53
Ho	1.51	1.97	1.60	1.56	0.23	1.02	0.80	0.52
Er	1.50	1.96	1.62	1.56	0.21	1.01	0.81	0.51
Tm	1.48	1.94	1.59	1.54	0.20	1.00	0.79	0.50
Yb	1.46	1.92	1.57	1.52	0.17	0.98	0.78	0.48
Lu	1.41	1.91	1.57	1.49	0.10	0.98	0.78	0.44

HA = humic acid; FA = fulvic acid.

(Tanizaki et al., 1992; Viers et al., 1997; Ingri et al., 2000). These investigations examined the distributions of REEs between different-size fractions of organic matter vs. REEs thought to be in the "dissolved state" (i.e., free ions, simple inorganic, and/or organic complexes; <500 Da, 5 kDa, and 3 kDa, respectively). Tanizaki et al. (1992) and Ingri et al. (2000) focused on REE speciation in circumneutral-pH river waters, whereas Viers et al. (1997) studied REE speciation in organic-rich, acidic waters from a tropical wetland system. Major solutes, dissolved organic carbon (DOC), Fe, and Al concentrations for selected samples of these natural waters are summarized in Table 6, along with pH, ionic strength (I), and temperature data. The REE concentrations for these waters are presented in Table 7.

4.2. Nsimi-Zoetele Catchment, Cameroon

Waters from the Nsimi-Zoetele catchment, Cameroon, Africa, are organic-rich, acidic, natural waters (Viers et al., 1997; Table 6). Because most of the DOC was distributed in larger MW size fractions in these waters (MW > 5 kDa; Viers et al., 1997), in our model calculation, we assumed that DOC with MW > 5 kDa was HA and DOC with MW < 5 kDa consisted of simple organic acids. Using the major solute and REE data from Tables 6 and 7, respectively, Humic Ion-Binding Model V predicts that the majority of each REE should occur in these waters complexed with organic matter (e.g., LnHM accounts for ~63 to 95% of each REE; Table 8). The model calculations predict that the only important inorganic form of the REEs in these waters is the free metal ion (Ln^{3+}), which accounts for

Table 6. Major solute concentration (in μmol/kg, dissolved organic carbon [DOC] in mg/L) for selected water samples from the Nsimi-Zoetele catchment (Cameroon), the Tamagawa River (Japan), and the Kalix River (northern Sweden).

	Nsimi-Zoetele catchment[a]		Tamagawa River[b]		Kalix River[c] (Kamlunge)	
	Mengong	Mar2	S-2	S-4	May 7	May 14
T (°C)	21.8	22.6	22.1	13.9	3	3
pH	4.62	5.5	7.7	7.0	6.95	6.95
I (mol/L)	2×10^{-4}	3×10^{-4}	3.5×10^{-3}	3.0×10^{-3}	5.7×10^{-4}	5.6×10^{-4}
DOC	23.76	18.07	5.05	1.54	2.64	5.71
HCO_3^-	33	194	1290	1160	235	235
SO_4^{2-}	1.4	1.3	111.5	295	50	50
Cl^-	12.7	21.7	1048	758	42.3	42.3
NO_3^-	1.5	5.3	—	—	—	—
PO_4^{3-}	—	—	2.46	2.46	—	—
Na^+	67	151.4	1422	1010	78.3	78.3
K^+	9.6	23	174.4	103	15.4	15.4
Ca^{2+}	34.7	51.4	690	530	115	115
Mg^{2+}	25.9	47.5	288	213	45.3	45.3
Fe^{3+}	10.98	7.89	0.43	0.232	4.01	5.9
Al^{3+}	17.79	6.68	2.4	1.9	1.0	1.0

[a] Tanizaki et al. (1992).
[b] Viers et al. (1997).
[c] Ingri et al. (2000).

Table 7. Rare earth element concentrations in pmol/kg for selected water samples from the Nsimi-Zoetele catchment (Cameroon), the Tamagawa River (Japan), and the Kalix River (northern Sweden).

	Nsimi-Zoetele Catchment		Tamagawa River		Kalix River (Kamlunge)	
	Mengong	Mar2	S-2	S-4	May 7	May 14
La	2500	4140	156	86	374	1296
Ce	5910	8500	—	171	437	1970
Pr	680	1200	—	—	86.6	295
Nd	2770	4790	—	—	361	1213
Sm	520	880	37	13	58.1	190
Eu	—	—	9.9	4	16.5	41.0
Gd	350	640	—	—	—	—
Tb	50	110	12.6	3	—	—
Dy	360	540	—	—	48	140
Ho	70	110	—	—	—	30.4
Er	160	290	—	—	—	82.5
Tm	30	30	—	27	—	—
Yb	180	230	222	152	40.3	84.4
Lu	30	40	43	36	—	—

Data sources are the same as in Table 6.

the remainder of each REE (from a high of 37% for La in the Mengong sample to a low of 5% for Lu in sample Mar2; Table 8). The outstanding feature of our model predictions for waters of the Nsimi-Zoetele catchment basin is the general agreement with the findings of the ultrafiltration experiments of Viers et al. (1997) (Table 8). Both the model predictions and the ultrafiltration experiments of Viers et al. (1997) indicate that the REEs are chiefly bound to organic matter in the organic-rich, acidic natural waters of the Nsimi-Zoetele catchment. However, our model calculations predict that a lower proportion of each REE is complexed with organic matter in these waters compared to the ultrafiltration results (Table 8). This may reflect an underestimation of the pK_{MHA} values for the REEs in these specific natural waters. To improve the model predictions, the pK_{MHA} values could be calibrated to these specific natural waters using the data of Viers et al. (1997). However, considering the assumptions inherent in the speciation model and the adopted pK_{MHA} values (Table 5), the modified Humic Ion-Binding Model V captures, to a first approximation, the speciation of the REEs in these waters. Consequently, we suggest the relatively good agreement between our predicted results and the ultrafiltration studies as confirmation of the model's validity for applications to similar, low-pH, organic-rich natural waters. However, it is important to stress that because these waters are acidic and rich in organic matter, the general agreement between the measured (i.e., ultralfiltration) and predicted (Model V) REE speciation results may be fortuitous, reflecting the overwhelming abundance of organic ligands and the essential lack of effective competing ligands (e.g., CO_3^{2-}, PO_4^{3-}). The real test of the model's performance is discussed below for circumneutral-pH waters of low organic matter concentrations and significant carbonate alkalinity.

Table 8. Comparison between the percentage of rare earth element (REE)–humate complexes in samples from Nsimi- Zoetele catchment obtained by ultrafiltration experiments and by modeling calculations using Humic Ion-Binding Model V modified for REE speciation calculations.

	Mengong		Mar2	
% LnHM[a]	Ultrafiltration results[b]	Model predictions	Ultrafiltration results[b]	Model predictions
La	86.0	62.9	94.2	87.3
Ce	86.3	72.4	94.1	91.2
Pr	86.8	75.7	95.8	92.2
Nd	86.3	76.6	94.6	92.6
Sm	100	85.9	100	95.5
Gd	100	79.5	100	93.7
Tb	100	76.6	100	93.0
Dy	100	74.5	100	92.0
Ho	100	74.8	100	92.2
Er	68.8	75.1	100	92.5
Tm	100	76.6	100	92.8
Yb	100	78.3	100	93.4
Lu	100	81.1	100	94.5

[a] % LnHM represents percentage of each REE complexed with humic matter.
[b] Ultrafiltration results are calculated from Viers et al.'s (1997) experimental data as follows: % LnHM = 100 × (1–C_{Ln} in filtrate of 5 kDa/C_{Ln} in filtrate of 0.22 μm).

Table 9. Comparison between the percentage of rare earth element (REE)–humate complexes and the C_L/C_M values in samples from Tamagawa River obtained by ultrafiltration experiments and by modeling calculations.

	S-2		S-4	
	Ultrafiltration results	Model[a] predictions	Ultrafiltration results	Model[a] predictions
%LnHME				
La	86.6	99.1	87.5	94.7
Sm	89.1	99.4	84.7	98.2
Eu	94	99.1	85.5	97.2
Tb	81	97.9	82.2	94.1
Yb	97.2	95.3	89.7	88.6
Lu	97.4	96.3	93.1	91.5
C_L/C_M				
La	0.56	1.30	0.75	0.95
Sm	0.54	0.92	0.63	0.73
Eu	0.28	0.79	0.89	0.63
Tb	1.16	0.66	0.12	0.55
Yb	0.27	0.54	0.24	0.51
Lu	0.04	0.46	0.13	0.43

Ultrafiltration results are from Tanizaki et al.'s (1992) experimental data. % LnHM = 100× (1–C_{Ln} in filtrate of 500 Da/C_{Ln} in filtrate of 0.45 μm). C_L: REE concentration in larger molecular weight size (MW > 10 kDa). C_M: REE concentration in middle molecular weight size (MW 500 Da to 10 kDa).

[a] C_L/C_M ratios for model predictions reflect the ratio of each REE predicted to be complexed with humic acids vs. fulvic acids.

4.3. Tamagawa River, Japan

The organic-rich, acidic waters of the Nsimi-Zoetele catchment basin are somewhat unique in that the vast majority of natural terrestrial waters are broadly circumneutral in pH and contain substantially lower DOC concentrations. Consequently, to test the broader application of our modified version of Model V, we chose to examine the model's performance in circumneutral-pH river waters with low DOC values and typical competing ligand concentrations. Here, river waters of the Tamagawa River in Japan (pH 7.0–7.7) and the Kalix River in Sweden (pH 6.95) were chosen because REE speciation with organic matter was also previously examined in these waters using ultrafiltration techniques (Tanizaki et al., 1992; Ingri et al., 2001).

Tamagawa River waters have DOC concentrations that range from a low of 1.54 mg/L (sample S-4) to 5.05 mg/L (sample S-2, Table 6). In our model calculations, DOC of MW > 10 kDa was assumed to be HA, DOC of MW ranging between 500 Da and 10 kDa was considered FA, and DOC of MW < 500 Da was assumed to be simple organic acids. The Model V speciation calculations indicate that the REEs should occur in solution principally as humate-bound complexes (i.e., LnHM, both HA and FA). For example, for Tamagawa River sample S-4 (pH 7, DOC = 1.54 mg/L), the model predicts that REE–organic matter complexes should account for 89 to 98% of each REE in solution, whereas for sample S-2 (pH 7.7, DOC = 5.05 mg/L), the model predicts that between 95 and 99% of each REE occurs in solution complexed with organic matter (Table 9).

Comparison of the Model V predictions to the ultrafiltration results (Table 9) demonstrates a general agreement, especially for the HREEs. The model overpredicts the proportion of LREEs that occur in solution complexed with organic matter compared to the ultrafiltration study. However, keeping in mind the model assumptions, the speciation predictions agree relatively well with the measured (i.e., ultralfiltration) distribution of REEs with organics in these low-DOC, circumneutral-pH river waters. In addition, both the ultrafiltration study (Tanizaki et al., 1992) and our model calculations show that the C_L/C_M ratio (i.e., the ratio of the REE concentration in the MW > 10 kDa size fraction to that in the MW 500–10 kDa range) is < 1, which indicates that the REEs are mainly distributed in the smaller MW size fraction (Table 9). Furthermore, both the ultrafiltration study and our model calculations demonstrate that the C_L/C_M ratios generally decrease with increasing atomic number across the REE series, which suggests that the LREEs are relatively more strongly associated with colloidal size HA, whereas the HREEs are mainly complexed with "dissolved" FA. Consequently, these comparisons suggest that the modified Humic Ion-Binding Model V can predict, to a first approximation, the speciation of REEs with organic matter in dilute, circumneutral-pH, natural terrestrial waters.

4.4. Kalix River, Northern Sweden

The Kalix River has an average alkalinity of 235 μmol/kg, an average pH of 6.95, and an average DOC (<0.7 μmol/kg) concentration of 3.4 mg/L (Table 6; Ingri et al., 2000). According to Ingri et al.'s (2000) ultrafiltration studies, REEs in the Kalix River exhibit the following features: (1) the concentrations of REEs are strongly associated with the DOC concentrations; (2) the REEs are mainly distributed in the larger MW size fraction (i.e., colloidal size, MW > 3 kDa); (3) this colloidal fraction shows a flat to slightly enriched pattern of LREEs, whereas the "dissolved" fraction (MW < 3 kDa) is enriched in the HREEs; and (4) the REEs in the colloidal fraction are likely associated with a mixture of organic-rich and Fe-rich, inorganic materials/particulate (Ingri et al., 2000). For our model calculations, we assumed that DOC in the colloidal size consisted of HA molecules, whereas the DOC in "dissolved" fraction was composed of soluble and smaller FA molecules. Speciation of the REEs was calculated in two of the Kalix River samples (i.e., Kamlunge May 7 and May 14 samples, Tables 6 and 7). The model results indicate that nearly all of each REE is complexed with organic matter in the Kalix River. The model predictions agree with the previous ultrafiltration study, which suggested that REEs are controlled by the DOC concentration of Kalix River water. Because the recovery of REEs was ~65 to 80% for the ultrafiltration study (see data of Ingri et al., 2000) and because Model V predicts that almost all of each REE is complexed with organic matter in the river water, it is not reasonable to compare the percentages of LnHM obtained by the ultrafiltration experiments and our model predictions, as was done for the Nsimi-Zoetele and Tamagawa River waters (i.e., Tables 8 and 9). Instead, we compare our model results to the previous ultrafiltration data by defining a C_C/C_S ratio, which consists of the ratio of the concentration of a particular REE in the colloidal fraction to that in the solution fraction in the case of the ultralfiltration data and for our model calculations, represents the ratio of each REE complexed with larger sized HA vs. that complexed with smaller FA (Table 10).

Table 10. Comparison between the rare earth element (REE) C_C/C_S values in samples from Kalix River obtained by ultrafiltration experiments (Ingri et al., 2000) and by modeling calculations (this study).

	Kamlunge May 7		Kamlunge May 14	
C_C/C_S	Ultrafiltration results	Model[a] predictions	Ultrafiltration results	Model[a] predictions
La	15.56	3.05	12.17	9.99
Ce	14.57	2.95	10.92	8.26
Pr	10.98	3.13	9.63	8.62
Nd	10.47	3.10	10.37	8.43
Sm	3.58	3.24	6.82	8.17
Eu	1.66	2.79	2.80	7.13
Dy	4.78	2.58	6.43	7.13
Ho	—	—	3.32	6.35
Er	—	—	4.17	5.67
Yb	2.65	2.22	3.01	5.85

Ultrafiltration results are from Ingri et al.'s (2000) experimental data. C_C: REE concentration in the colloidal fraction (MW > 3 kDa). C_S: REE concentration in the solution fraction (MW < 3 kDa).

[a] C_C/C_S ratios for model predictions reflect the ratio of each REE predicted to be complexed with larger sized humic acids vs. smaller fulvic acids.

Table 11. Mean concentrations of major ions (mmol/kg), Fe and Al (μmol/kg), and rare earth elements (REEs) (pmol/kg) in world average river water.

Solute	Concentrations	Solute	Concentrations
HCO_3	0.957	La	655.2
SO_4	0.117	Ce	1351.4
NO_3	0.016	Nd	1010.6
Cl	0.22	Sm	235.3
Na	0.274	Eu	56.4
K	0.059	Gd	227.7
Ca	0.375	Dy	169.6
Mg	0.171	Er	90.2
Fe	12	Yb	78.3
Al	1.85	Lu	12.3

HCO_3, SO_4, NO_3, Cl, Na, K, Ca, Mg, and Fe (Livingstone, 1963); Al (Martin and Meybeck, 1979); and REEs (Goldstein and Jacobsen, 1988; Elderfield et al., 1990).

Although there are differences between the C_C/C_S ratios of our model calculations and the ultrafiltration results of Ingri et al. (2000), comparison of both demonstrates that the REEs are chiefly distributed in the colloidal (larger organic molecules) fraction. The measured C_C/C_S ratios (ultrafiltration) and the predicted C_C/C_S ratios (Model V) both decrease with increasing atomic number across the REE series, which indicates that LREEs are enriched in the colloidal fraction, whereas HREEs are enriched in the solution fraction. Pokrovsky and Schott (2002) demonstrated that the HREEs are strongly associated with soluble FA and are less affected by Fe-rich inorganic matter, whereas the LREEs are associated with colloidal HM and are strongly affected by Fe-rich inorganics. In our model calculations, we considered only the role of dissolved organic matter, not the effect of REE adsorption to an Fe-rich, inorganic phase. Table 10 demonstrates that the LREEs have much higher measured (by ultrafiltration) C_C/C_S ratios compared to the model predictions, whereas the HREEs exhibit similar C_C/C_S measured and predicted ratios. These differences may reflect the importance of LREE scavenging by Fe-rich inorganic phases compared to the affinity of HREE to form strong solution complexes. It is also possible that the pK_{MHA} values adopted here for Model V do not account for the differences between the ultrafiltration studies and the model calculations. Nevertheless, the comparisons in the Kalix River samples further support that Model V can predict, to a first approximation, the speciation of REEs with organic matter in dilute, circumneutral-pH, natural terrestrial waters.

5. REE SPECIATION CALCULATIONS FOR "AVERAGE" NATURAL WATERS

5.1. World Average River Water

The mean concentrations of major ions and Fe for world average river waters used in our calculations were obtained from Livingstone (1963), whereas the concentration for Al was taken from Martin and Meybeck (1979). These parameters are summarized in Table 11. The average value of DOC in major world rivers, as proposed by the SCOPE project (Degens, 1982), ranges between 4 and 6 mg/L. Thus, in our model calculations for world average river water, we chose a value of 5 mg/L for DOC and assumed that 80% of HM is FA, and ~20% is HA (Thurman, 1985). To estimate the REE concentration of world average river water, we calculated mean REE values for river water data from Goldstein and Jacobsen (1988) for 6 major world rivers and from Elderfield et al. (1990) for 15 world rivers (Table 11). Because the pH value of river water varies depending on the river and its corresponding catchment basin geology, and because pH is crucial to REE speciation, we performed REE speciation calculations for world average river water as a function of pH. In other words, the calculations were performed holding the major solute compositions constant (except HCO_3^- and CO_3^{2-}) and varying pH. These calculations can provide insights into the dominant dissolved forms in which the REEs are transported from the continents into oceans. The results are shown for La, Eu, and Lu in Figure 4. In each case, the LnHM species represents the percentage of each REE complexed with HA and FA.

Model V calculations predict that REEs occur as the free metal ion (Ln^{3+}) and sulfate complexes ($LnSO_4^+$) in low-pH river waters, and chiefly as carbonate complexes (i.e., $LnCO_3^+$ + $Ln[CO_3]_2^-$) in alkaline river waters (Fig. 4). To a first approximation, the results for strongly acidic and strongly alkaline river waters are consistent with earlier investigations of natural terrestrial waters (e.g., Lee and Byrne, 1992; Johannesson et al., 1994, 1996; Johannesson and Lyons, 1995). It is important to point out, however, that these previous studies did not include evaluations of REE complexation with organic matter. Hence, the agreement between Model V and the purely inorganic ligand speciation models for acid and alkaline waters should be viewed with caution until additional field and laboratory investigations validate or refute these models in these pH ranges.

The remarkable feature of our model calculations is that they predict that for river waters of circumneutral pH (the majority of world rivers; Brownlow, 1996), the REEs will chiefly occur in solution complexed with natural organic ligands (Fig. 4). Indeed, assuming major solute and REE concentrations identi-

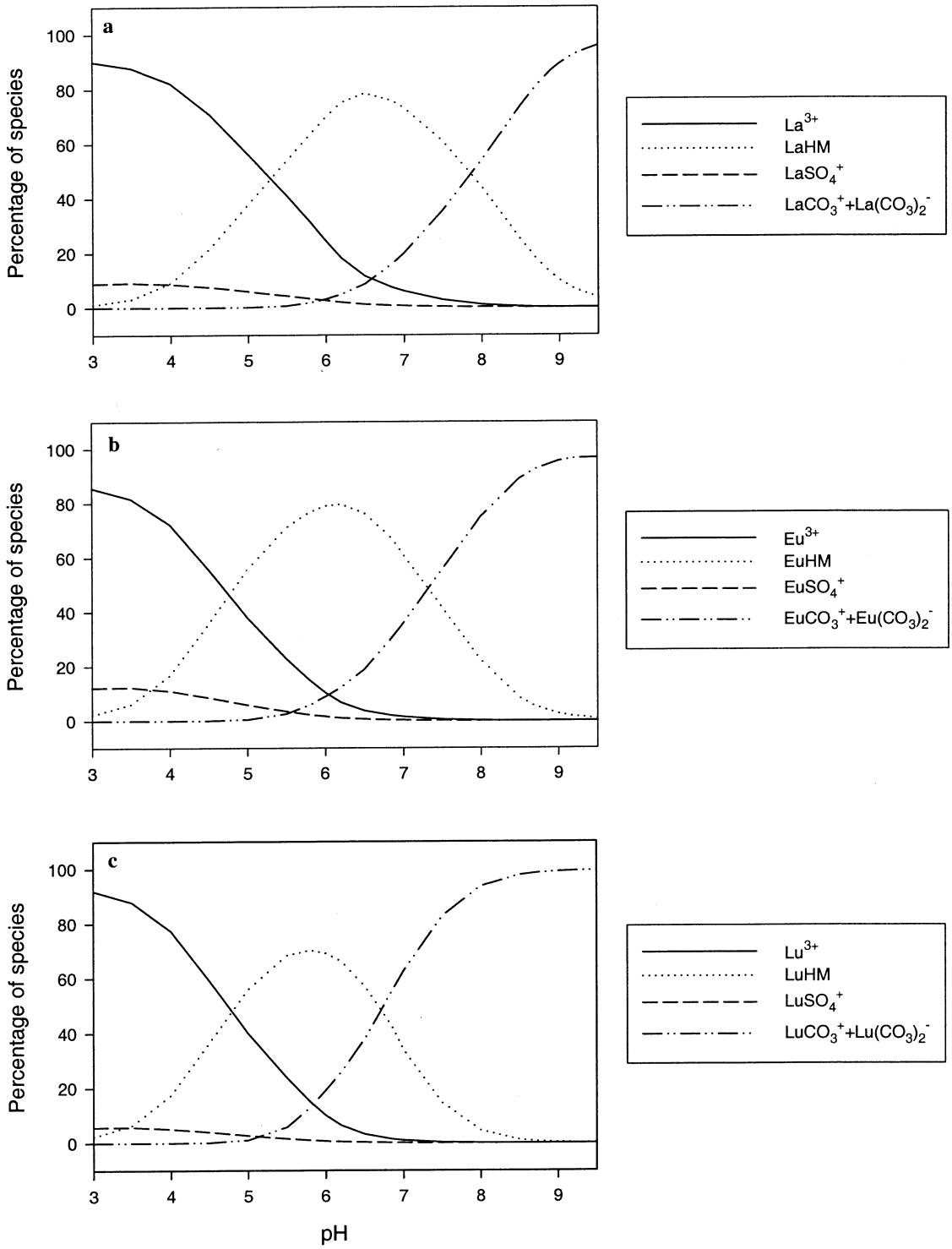

Fig. 4. Speciation of (a) La, (b) Eu, and (c) Lu in world average river water as a function of pH (dissolved organic carbon = 5 mg/L)

cal to world average river water (Table 11), the model predicts that LREEs (e.g., La) predominantly occur in solution as organic complexes in the pH range between 5.4 and 7.9, whereas HREEs (e.g., Lu) are primarily complexed with humic substances for pH between 4.8 and 6.7 (Fig. 4). The model also predicts that inorganic and organic ligands strongly compete with each other for REEs and that this competition varies with pH. As was the case with the circumneutral Tamagawa and Kalix Rivers, we suspect the model may overpredict the percentage of La complexed with organic matter in world average

river waters (i.e., the model does not account for colloidal Fe-rich inorganic phase). However, we suspect that the prediction for Lu is close to its actual speciation (Table 9).

The results of our REE speciation calculations for world average river water are especially significant if they accurately represent the distribution of REEs among inorganic and organic ligands in bulk river water draining the continents. Our model calculations suggest, for example, that dissolved REEs are chiefly transported in rivers to the oceans as dissolved organic ligand complexes and to a lesser extent as carbonate complexes. The model calculations predict, however, that REE carbonate complexes and REE complexes with FA become progressively more important with increasing atomic number across the REE series. Thus, the HREEs are likely to be truly distributed in solution, whereas the LREEs are strongly associated with colloids. Again, this result assumes that our best estimates for REE pK_{MHA} values are correct and that any other natural organic ligands present in solution form weaker complexes than carbonate complexes of REEs. It should be noted, however, that recent evidence suggests that siderophores produced by microbes on mineral surfaces strongly complex the REEs and may contribute to their mobilization in weathering solutions during chemical weathering (Brantley et al., 2001).

In summary, Model V predictions are consistent with the ultralfiltration studies discussed above and with previous studies that argue Fe-organic colloids are the principal carriers of REEs in the dissolved (i.e., $<0.22\ \mu$m) fraction of river waters (Sholkovitz, 1995; Sholkovitz et al., 1999; Andersson et al., 2001). Moreover, it is generally accepted that the highly fractionated REE pattern of seawater is linked to weathering processes on the continents; preferential scavenging of LREEs compared to HREEs in the low-salinity zone of estuaries; differential release from estuarine sediments; and solution and surface complexation reactions in rivers, estuaries, and the open oceans (Goldstein and Jacobsen, 1988; Elderfield et al., 1990; Sholkovitz, 1995; Sholkovitz and Szymczak, 2000). For the case of solution complexation, our model predictions suggest that dissolved organic ligand complexes of the REEs are at least as important as carbonate complexes in world rivers. The predicted importance at REE organic complexes in world rivers suggests that our understanding of REE cycling in the hydrosphere, where carbonate complexes have been presumed to dominate, may need revision.

5.2. "Model Groundwater"

Because groundwater compositions can vary significantly depending on the composition of aquifer source rocks and groundwater age (i.e., residence time in aquifer), it is difficult to choose a world average groundwater composition. However, Wood (1990), Lee and Byrne (1992), and Johannesson et al. (1996) evaluated REE speciation in a "model groundwater" of constant major anion composition closely resembling that of world average river water. Differences between major anion concentrations of Wood's (1990) "model groundwater" and world average river water (Table 11) include higher total NO_3^- in the "model groundwater" compared to world average river water (10^{-4} and $10^{-4.8}$ mol/kg, respectively) and higher ΣCO_3^{2-} concentrations in the "model groundwater" compared to world average river water (10^{-4} and $10^{-5.2}$ mol/kg, respectively; calculated using PHREEQE for pH 7 and 20°C). Both Wood (1990) and Johannesson et al. (1996) used the cation concentrations of world average river water, along with the anion values tabulated by Wood (1990), as a representative "model groundwater" in their REE speciation calculations. Similarly, we employ the mean values of major ions, minor ions (i.e., Fe, Al), and REEs of world average river water, along with the average groundwater DOC value of Leenheer et al. (1974), to predict REE speciation with natural organic matter in a slightly modified version of Wood's (1990) "model groundwater." Leenheer et al. (1974) reported an average DOC value of 0.7 mg/L for 100 groundwaters sampled from aquifers of diverse geological settings. Figure 5 shows the results of our REE speciation calculations for the slightly modified "model groundwater" as a function of pH.

The model predictions of REE speciation in the "model groundwater" using Model V are in general agreement with previous studies (Wood, 1990; Lee and Byrne, 1992; Johannesson et al., 1996). Again, these earlier investigations did not consider organic speciation of REEs, and consequently, direct comparison is not possible. Model V predicts that REE speciation in the "model groundwater" is grossly similar to that in world average river water (compare Figs. 4 and 5). The chief difference is that organically complexed REEs (LnHM) are predicted to be substantially less important in the "model groundwater" than in world average river waters, because of the lower mean groundwater DOC concentration compared to world average river water (i.e., 0.7 and 5 mg/L, respectively). In fact, LnHM complexes are predicted to be relatively insignificant in the "model groundwater" (Fig. 5). Overall, the model suggests that REEs mainly exist as free ions (Ln^{3+}) and sulfate complexes ($LnSO_4^+$) in acidic groundwaters, carbonate complexes ($LnCO_3^+ + Ln[CO_3]_2^-$) and free ions (Ln^{3+}) in neutral groundwaters, and as carbonate complexes ($LnCO_3^+ + Ln[CO_3]_2^-$) in alkaline groundwaters (Fig. 5). REE complexation by natural organic matter in groundwater-aquifer systems is therefore likely to be important only in organic-rich groundwaters, unless other organic ligands besides humic materials (e.g., siderophores; Brantley et al., 2001) are present in aquifers and complex the REEs.

6. SENSITIVITY ANALYSIS

6.1. The Uncertainty of pK_{MHA} Values

Although we chose to adopt what we consider to be the best overall estimates for pK_{MHA} values for REE complexation with humic substances based on existing data (Table 5), it should be clear that differences in the model predictions would result from use of different pK_{MHA} values estimated with Eqn. 1 to 6. Consequently, it is critical that additional experimental and laboratory studies be systematically conducted to obtain more reliable estimates of the pK_{MHA} values for each REE. The lack of available humate-binding data for most of the REEs is the chief limitation affecting overall Model V performance.

Nonetheless, we performed sensitivity analysis on world average river water by comparing model predictions using the pK_{MHA} values estimated with Eqn. 1 and 2 with those predicted with the pK_{MHA} values estimated with Eqn. 5 and 6. Again, because the pK_{MHA} values estimated with Eqn. 3 and 4 are

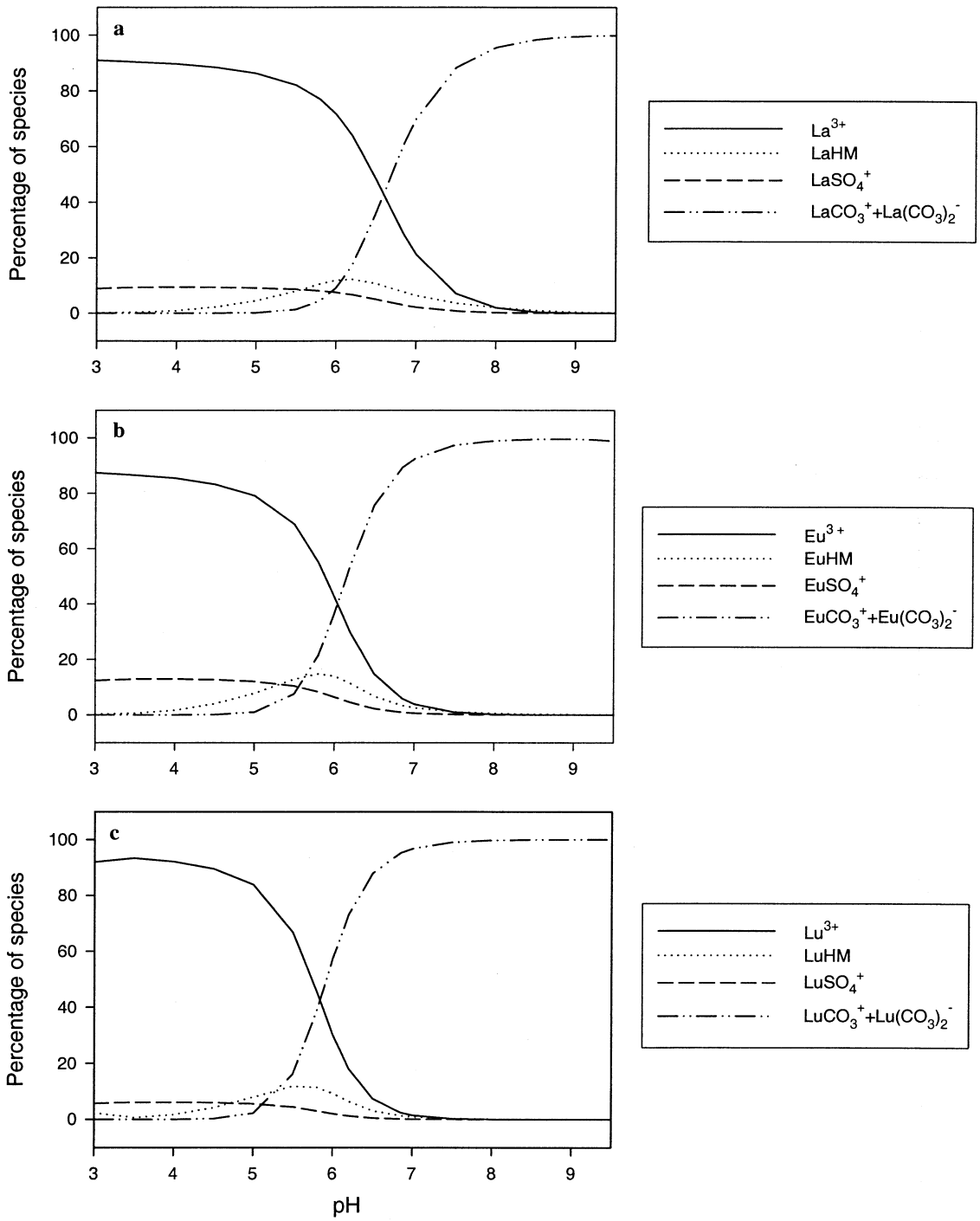

Fig. 5. Speciation of (a) La, (b) Eu, and (c) Lu in modified version of the "model" groundwater (Wood, 1990) as a function of pH (dissolved organic carbon = 0.7 mg/L, Leenheer et al., 1974)

considered to be too high compared to values determined with the experimental data (see section 3), they are not included in the sensitively analysis. It is our belief that because Eqn. 1 and 2 and Eqn. 5 and 6 span the range of "acceptable" pK_{MHA} values for the REEs on the basis of the linear free-energy approach and on the general agreement with the experimental data for Eu, Tb, and Dy, the actual pK_{MHA} values fall within this range of estimated values. With this in mind, Figure 6 shows the results of the speciation calculations for La, Eu, and Lu using the pK_{MHA} values estimated with Eqn. 1 and 2, whereas the results of speciation calculations using the pK_{MHA} values estimated with Eqn. 5 and 6 are presented in Figure 7. Overall, the results of the speciation calculations for both sets of pK_{MHA} values are grossly similar.

The differences in the predicted speciation of the REEs between the various estimated pK_{MHA} values of Table 5 chiefly

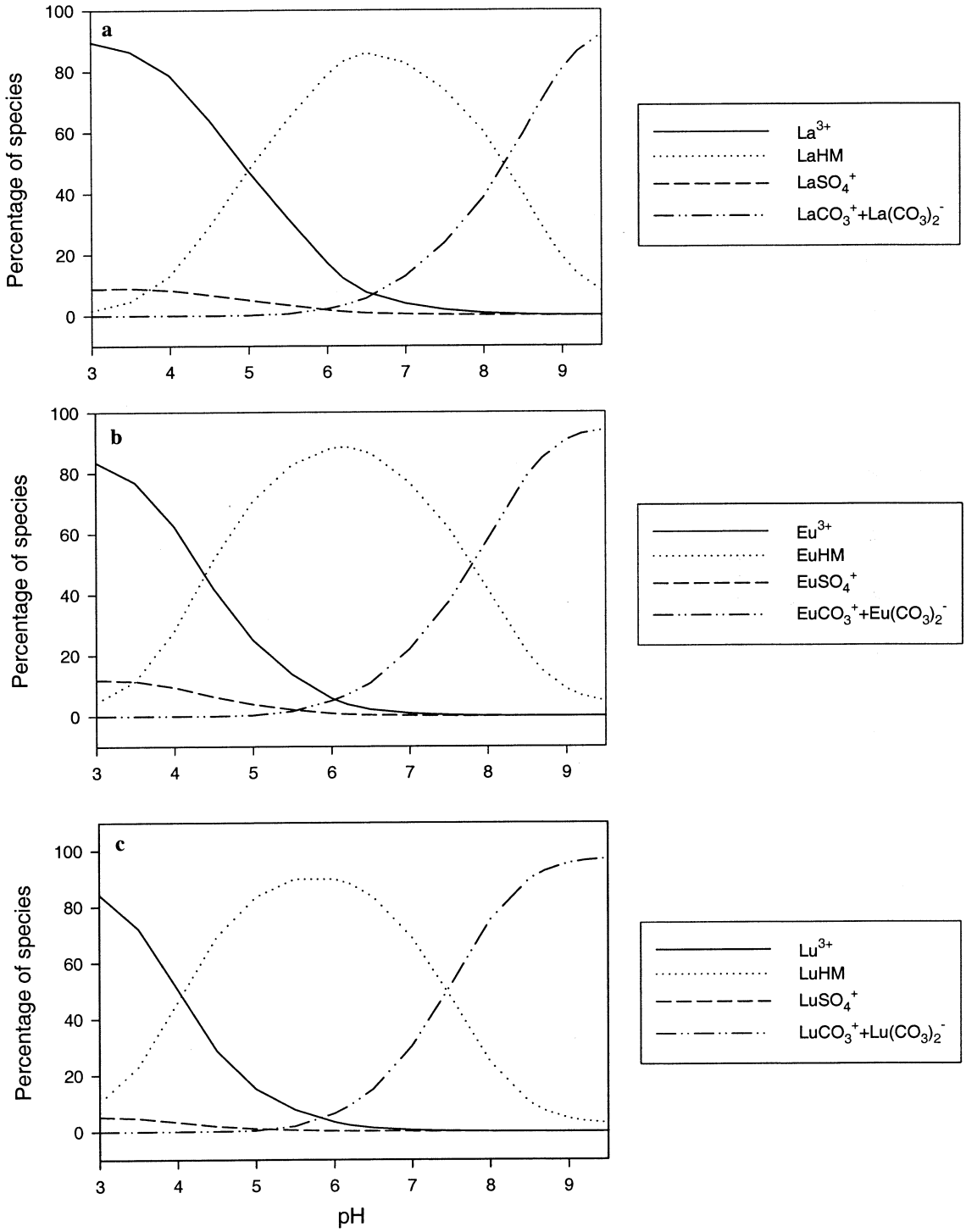

Fig. 6. Speciation of (a) La, (b) Eu, and (c) Lu in world average river water as a function of pH (dissolved organic carbon =5 mg/L; pK_{MHA} values estimated with Eqn. 1 and 2).

amount to changes in the breadth of the pH range over which REE organic complexes are expected to predominate (Figs. 6 and 7). More specifically, the pK_{MHA} values estimated with Eqn. 1 and 2 result in an expansion in the pH range over which REE–organic ligand complexes are predicted to dominate compared to our adopted, best estimated pK_{MHA} values, whereas the pK_{MHA} values estimated with Eqn. 5 and 6 predict a narrower pH range of REE organic complexation. These differences are significant, especially for the HREEs, and could conceivably lead to entirely different REE fractionation behavior and cycling in natural waters. However, it is critical to point out that for all REE pK_{MHA} values presented in Table 5 (except

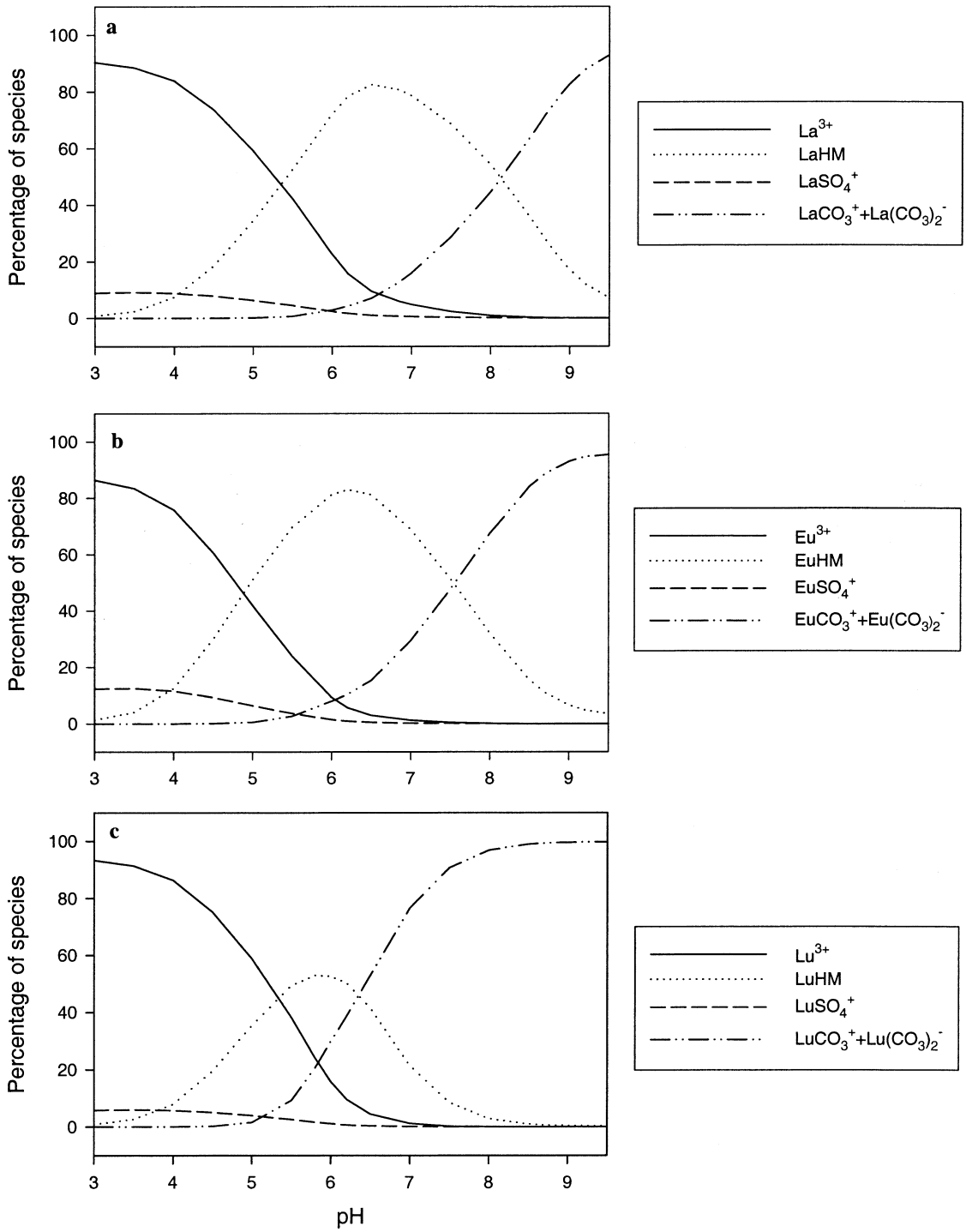

Fig. 7. Speciation of (a) La, (b) Eu, and (c) Lu in world average river water as a function of pH (dissolved organic carbon = 5 mg/L; pK_{MHA} values estimated from Eqn. 5 and 6).

those for Eqn. 3 and 4, which we have not considered; see above), Model V predicts that organic matter complexes dominate REE speciation in terrestrial surface waters at circumneutral pH values. Because the majority of natural waters are of circumneutral pH, the predicted dominance of REE–organic matter complexes may have profound consequences on our understanding of REE cycling in the hydrosphere if the model predictions are in fact verified with future field and laboratory studies.

6.2. The Effect of Ionic Strength

To assess the effect of ionic strength on REE-humate complexing, we performed sensitivity analysis on sample S-4 from

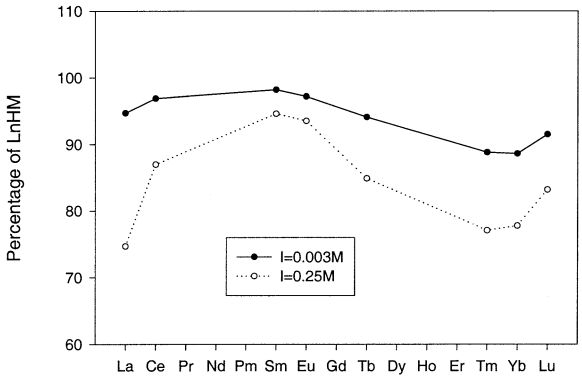

Fig. 8. Humate-bound complexes (LnHM) of rare earth elements for two different ionic strengths (sample S-4, dissolved organic carbon = 1.54 mg/L; Tanizaki et al., 1992)

the Tamagawa River (Fig. 8). In this case, the ionic strength effect was evaluated by changing the concentrations of only K and Na, while holding the concentrations of competitive inorganic ligands and competitive cations (Ca, Mg, Fe[III], and Al) constant. The results indicate that an increase in ionic strength weakens REE-humate complexing because of a decrease in the electrostatic term, such that the percentage of humate-bound complexes (LnHM) is predicted to decrease at higher ionic strength conditions (Fig. 8). For example, LnHM is predicated to account for 89 to 98% of each dissolved REE at $I = 0.003$ mol/kg but only 77 to 95% of each dissolved REE at $I = 0.25$ mol/kg (Fig. 8).

6.3. The Competitive Effect of Fe and Al

Because Fe(III) and Al occur in natural waters and because both complex strongly with humic substances (see section 3; Tanizaki et al., 1992; Dupré et al., 1999; Tipping et al., 2002), these metals are likely to compete with REEs in metal-humic complexing. To quantify the competitive effect of Fe(III) and Al on REE-humate complexation, we performed sensitivity analysis on sample S-4 from the Tamagawa River by changing the concentrations of Fe(III) and Al in the model calculations. More specifically, speciation calculations were performed for the REEs assuming no Fe(III) and Al in solution and using the measured concentrations of each of these metals. If Fe(III) and Al are not included in the model calculations, the results indicate that almost all of the REEs (i.e., >99% of each) will be bound to dissolved organic matter (Fig. 9). On the other hand, the LnHM species is predicted to account for 89 to 98% of each REEs when Fe(III) and Al are included in the model calculations. Consequently, these calculations indicate that cation competition can decrease the amount of REEs bound to dissolved organic matter in natural waters. These observations are in agreement with a previous study of Eu complexation (i.e., Nordén et al., 1997).

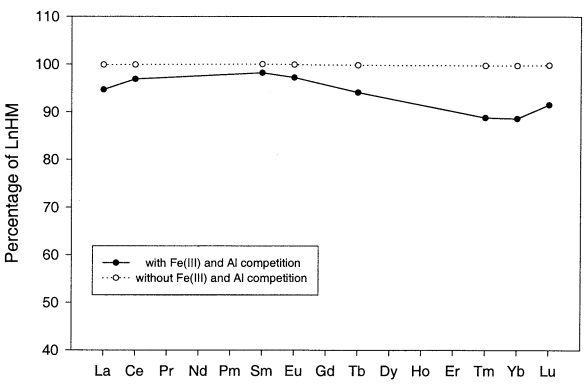

Fig. 9. Humate-bound complexes (LnHM) of rare earth elements varying with competitive cations (sample S-4, dissolved organic carbon = 1.54 mg/L; Tanizaki et al., 1992).

7. CONCLUSIONS

Our speciation calculations using Humic Ion-Binding Model V suggest that humic substances are important complexers of REEs in natural waters, effectively competing with inorganic ligands in many cases. The role humic substances play in complexing REEs depends on the pH, ionic strength, competitive cations, and the concentration of dissolved organic matter. The model calculations indicate that increasing ionic strength can weaken humate-REE interactions, and the increase in concentrations of competitive cations such as Fe(III) and Al can cause a decrease in the amount of REE bound to dissolved organic matter. However, the most important factor appears to be pH, followed by the concentrations of dissolved organic matter. For example, when pH is low, organic complexes of REEs will be important only in organic-rich waters (i.e., black waters). Otherwise, the model predicts that free ions (Ln^{3+}) and sulfate complexes dominate REE speciation. For circumneutral-pH waters, the model predicts that REEs will predominantly occur in solution as organic complexes. Remarkably, the model suggests that carbonate ions do not effectively compete with organic ligands for REEs in waters of circumneutral pH, even when DOC concentrations are relatively low. On the other hand, for alkaline waters, the model suggests that organic ligands do not effectively compete with carbonate ions for dissolved REEs.

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REFERENCES

Achterberg E. P., van den Berg C. M. G., Boussemart M., and Davison W. (1997) Speciation and cycling of trace metals in Esthwaite water: A productive English lake with seasonal deep-water anoxia. *Geochim. Cosmochim. Acta* **61,** 5233–5253.

Andersson PS., Dahlqvist R., Ingri J., and Gustafsson Ö. (2001) The isotope composition of Nd in a boreal river: A reflection of selective weathering and colloidal transport. *Geochim. Cosmochim. Acta* **65,** 521–527.

Bidoglio G., Grenthe I., Qi P., Robouch P., and Omenetto N. (1991) Complexation of Eu and Tb with fulvic acids as studied by time-resolved laser-induced fluorescence. *Talanta* **38,** 999–1008.

Brantley S. L., Liermann L., Bau M., and Wu S. (2001) Uptake of trace metals and rare earth elements from hornblende by a soil bacterium. *Geomicrobio. J.* **18,** 37–61.

Brookins D. G. (1986) Natural analogues for radwaste disposal: Elemental migration in igneous contact zones. *Chem. Geol.* **55,** 337–344.

Brownlow A. H. (1996) *Geochemistry*. Prentice Hall, Englewood Cliffs, NJ.

Bruland K. W. (1989) Complexation of zinc by natural organic ligands in the central North Pacific. *Limnol. Oceanogr.* **34,** 269–285.

Bruland K. W., Donat J. R., and Hutchins D. A. (1991) Interactive influences of bioactive trace metals on biological production in oceanic waters. *Limnol. Oceanogr.* **36,** 555–1577.

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

Byrne R. H. and Kim K.-H. (1993) Rare earth precipitation and coprecipitation behavior: The limiting role of PO_4^{3-} ion dissolved REE concentrations in seawater. *Geochim. Cosmochim. Acta* **57,** 519–526.

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

Cantrell K. J. and Byrne R. H. (1987) Rare earth element complexation by carbonate and oxalate ions. *Geochim. Cosmochim. Acta* **51,** 597–605.

Choppin G. R. (1986) Speciation of trivalent f elements in natural waters. *J. Less-Common Met.* **126,** 307–313.

Choppin G. R. (1989) Soluble rare earth and actinide species in seawater. *Mar. Chem.* **28,** 19–26.

Crawford M. B. (1996) PHREEQEV: The incorporation of a version of Model V for organic complexation in aqueous solutions into the speciation code PHREEQE. *Comput. Geosci.* **22,** 109–116.

Cullers R. L. and Graf J. L. (1984) Rare earth elements in igneous rocks of the continental crust: Intermediate and silicic rocks-ore petrogenesis. In *Rare Earth Element Geochemistry* (ed. P. Henderson), pp. 275–316. Elsevier, New York.

Deberdt S., Castet S., Danderand J.-L., and Harrichoury J.-C. (2000) Potentiometric study of Gd- and Yb-acetate complexing in the temperature range 25-80°C. *Chem. Geol.* **167,** 75–88.

Degens E. T. (1982) Transport of carbon and minerals in major world rivers, part 1. Proceeding of a workshop arranged by Scientific Committee on Problems of the Environment. (SCOPE) and the United Nations Environment Programme. (UNEP) at Hamburg University. March 8-12.

Dierckx A., Maes A., and Vancluysen J. (1994) Mixed complex formation of Eu^{3+} with humic acid and a competing ligand. *Radiochim. Acta* **66/67,** 149–156.

Dupré L., Viers J., Dandurand J.-L., Polve M., Bénézeth P., Vervier P., and Braun J.-J. (1999) Major and trace elements associated with colloids in organic-rich river waters: Ultrafiltration of natural and spiked solutions. *Chem. Geol.* **160,** 63–80.

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

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

Franz C., Herrmann G., and Trautmann N. (1997) Complexation of samarium(III) and americium(III) with humic acid at very low metal concentrations. *Radiochim. Acta* **77,** 177–181.

Gammons C. H. and Wood S. A. (2000) The aqueous geochemistry of REE. Part 8: Solubility of ytterbium oxalate and the stability of Yb(III)-oxalate complexes in water at 25°C to 80°C. *Chem. Geol.* **166,** 103–124.

Glaus M. A., Hummel W., and Van Loon L. R. (2000) Trace metal-humate interactions. I. Experimental determination of conditional stability constants. *Appl. Geochem.* **15,** 953–973.

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

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

Hamilton-Taylor J., Postill A. S., Tipping E., and Harper M. P. (2002) Laboratory measurements and modeling of metal-humic interactions under estuarine conditions. *Geochim. Cosmochim. Acta* **66,** 403–415.

Hanson G. N. (1980) Rare earth elements in petrogenetic studies of igneous systems. *Ann. Rev. Earth Planet. Sci.* **8,** 371–406.

Hummel W., Glaus M. A., and Van Loon L. R. (2000) Trace metal-humate interactions. II. The "conservative roof" model and its application. *Appl. Geochem.* **15,** 975–1001.

Ingri J., Winderlund A., Land M., Gustafsson Ö., Andersson P., and Ölander B. (2000) Temporal variation in the fractionation of the rare earth elements in a boreal river; the role of colloidal particles. *Chem. Geol.* **166,** 23–45.

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

Johannesson K. H., Lyons W. B., and Bird D. A. (1994) Rare earth element concentrations and speciation in alkaline lakes from the western USA. *Geophys. Res. Lett.* **21,** 773–776.

Johannesson K. H., Lyons W. B., Stetzenbach K. J., and Byrne R. H. (1995) The solubility control of rare earth elements in natural terrestrial waters and the significance of PO_4^{3-} and CO_3^{2-} in limiting dissolved rare earth concentrations: A review of recent information. *Aquat. Geochem.* **1,** 157–173.

Johannesson K. H., Stetzenbach K. J., Hodge V. F., and Lyons W. B. (1996) Rare earth element complexation behavior in circumneutral pH groundwaters; assessing the role of carbonate and phosphate ions. *Earth Planet. Sci. Lett.* **139,** 305–320.

Kay R. W. and Gast P. W. (1973) The rare earth content and origin of alkali-rich basalts. *J. Geol.* **81,** 653–682.

Klungness G. D. and Byrne R. H. (2000) Comparative hydrolysis behavior of the rare earths and yttrium: The influence of temperature and ionic strength. *Polyhedron* **19,** 99–107.

Lead J. R., Davison W., Hamilton-Taylor J., and Buffle J. (1997) Characterizing colloidal material in natural waters. *Aquat. Geochem.* **3,** 213–232.

Lead J. R., Hamilton-Taylor J., Peters A., Reiner S., and Tipping E. (1998) Europium binding by fulvic acids. *Anal. Chim. Acta* **369,** 171–180.

Leal M. F. C. and van den Berg C. M. G. (1998) Evidence for strong copper(I) complexation by organic ligands in seawater. *Aquat. Geochem.* **4,** 49–75.

Lee J. H. and Byrne R. H. (1992) Examination of comparative rare earth element complexation behavior using linear free-energy relationships. *Geochim. Cosmochim. Acta* **56,** 1127–1137.

Lee J. H. and Byrne R. H. (1993) Complexation of trivalent rare earth elements (Ce, Eu, Gd, Tb, Yb) by carbonate ions. *Geochim. Cosmochim. Acta* **57,** 295–302.

Leenheer A., Malcolm R. L., McKinley P. W., and Eccles L. A. (1974) Occurrence of dissolved organic carbon in selected groundwater samples in the United States. *U. S. Geol. Surv. J. Res.* **2,** 361–369.

Lewis A. J., Komninou A., Yardley B. W. D., and Palmer M. R. (1998) Rare earth element speciation in geothermal fluids from Yellowstone National Park, Wyoming, USA. *Geochim. Cosmochim. Acta* **62,** 657–663.

Leybourne M. I., Goodfellow W. D., Boyle D. R., and Hall G. M. (2000) Rapid development of negative Ce anomalies in surface waters and contrasting REE patterns in groundwaters associated with Zn-Pb massive sulfide deposits. *Appl. Geochem.* **15,** 695–723.

Livingstone D. A. (1963) Chemical composition of rivers and lakes. In Data of Geochemistry: U.S. Geol. Survey Prof. (ed. M. Fleischer), paper 440, pp. G1-G64.

Luo Y. R. and Byrne R. H. (2000) The ionic strength dependence of rare earth and yttrium fluoride complexation at 25°C. *J. Solution Chem.* **29,** 1089–1099.

Maes A., De Brabandere J., and Cremers A. (1988) A modified Schubert method for the measurement of the stability of europium humic acid complexes in alkaline conditions. *Radiochim. Acta* **44/45,** 51–57.

Maes A., De Brabandere J., and Cremers A. (1991) Complexation of Eu^{3+} and Am^{3+} with humic substances. *Radiochim. Acta* **52/53,** 41–47.

Martell A. E. and Smith R. M. (1977) *Critical stability constants, vol. 3: Other organic ligands*. Plenum, New York.

Martin J.-M. and Meybeck M. (1979) Elemental mass-balance of material carried by major world rivers. *Mar. Chem.* **7,** 173–206.

McCarthy J. F., Sanford W. E., and Stafford P. L. (1998a) Lanthanide field tracers demonstrate enhanced transport of transuranic radionuclides by natural organic matter. *Environ. Sci. Technol.* **32,** 3901–3906.

McCarthy J. F., Czerwinski K. R., Sanford W. E., Jardine P. M., and Marsh J. D. (1998b) Mobilization of transuranic radionuclides from disposal trenches by natural organic matter. *J. Contam. Hydrol.* **30,** 49–77.

McKnight D. M. and Morel F. M. M. (1980) Copper complexes by siderophores from filamentous blue-green algae. *Limnol. Oceanogr.* **25,** 62–71.

Millero F. J. (1992) Stability constants for the formation of rare earth inorganic complexes as a function of ionic strength. *Geochim. Cosmochim. Acta* **56,** 3123–3132.

Moulin V. and Tits J. (1992) Complexation behaviour of humic substances towards actinides and lanthanides studied by time-resolved laser-induced spectrofluorometry. *Radiochim. Acta* **58/59,** 121–128.

Nordén M., Ephraim J. H., and Allard B. (1997) Europium complexation by an aquatic fulvic acid—Effects of competing ions. *Talanta* **44,** 781–786.

Pokrovsky O. S. and Schott J. (in press) Iron colloids/organic matter associated transport of major and trace elements in small boreal rivers and their estuaries. (NW Russia). *Chem. Geol* **190,** 141–179.

Schindler P. W. (1990) Coadsorption of metal ions and organic ligands: Formation of ternary surface complexes. In *Mineral-Water Interface Geochemistry.* (eds. M. F. Hochella, Jr., and A. F. White), *Rev. Mineral.* **23,** 281–307. Mineralogical Society of America, Washington, DC.

Shannon R. D. (1976) Revised effective ionic radii and systematic studies of interatomic distances in halides and chalogenides. *Acta Crystallogr., Sect. A* **32,** 751–767.

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

Sholkovitz E. R. and Elderfield H. (1988) The cycling of dissolved rare earth elements in Chesapeake Bay. *Global Biogeochem. Cycles* **2,** 157–176.

Sholkovitz E. R. and Szymczak R. (2000) The estuarine chemistry of rare earth elements: Comparison of the Amazon, Fly, Sepik and the Gulf of Papua systems. *Earth Planet. Sci. Lett.* **179,** 299–309.

Sholkovitz E. R., Church T. M., and Arimoto R. (1993) Rare earth element composition of precipitation, precipitation particles, and aerosols. *J. Geophys. Res.* **98,** 20587–20599.

Sholkovitz E. R., Elderfield H., Szymczak R., and Casey K. (1999) Island weathering: River sources of rare earth elements to the western Pacific Ocean. *Mar. Chem.* **68,** 39–57.

Sigel H. (1973) Metal Ions in Biological Systems, vol. 2: Mixed-ligand complexes (ed. H. Sigel). Marcel Dekker, New York.

Takahashi Y., Minai Y., Ambe S., Makide Y., Ambe F., and Tominaga T. (1997) Simultaneous determination of stability constants of humate complexes with various metal ions using multitracer technique. *Sci. Tot. Environ.* **198,** 61–71.

Tanizaki Y., Shimokawa T., and Nakamura M. (1992) Physicochemical speciation of trace elements in river waters by size fractionation. *Environ. Sci. Tech.* **26,** 1433–1444.

Thurman E. M. (1985) *Organic Geochemistry of Natural Waters*. Nijhoff/Junk, Dordrechtthe, Netherlands.

Tipping E. (1993) Modelling the binding of Europium and Actinides by humic substances. *Radiochim. Acta* **62,** 141–152.

Tipping E. (1994) WHAM—A chemical equilibrium model and computer code for waters, sediments, and soils incorporating a discrete site/electrostatic model of ion-binding by humic substances. *Comput. Geosci.* **20,** 973–1023.

Tipping E. (1998) Humic Ion-Binding Model VI: An improved description of the interactions of protons and metal ions with humic substances. *Aquat. Geochem.* **4,** 3–48.

Tipping E. and Hurley M. A. (1992) A unifying model of cation binding by humic substances. *Geochim. Cosmochim. Acta* **56,** 3627–3641.

Tipping E., Rey-Castro C., Bryan S. E., and Hamilton-Taylor J. (2002) Al(III) and Fe(III) binding by humic substances in freshwaters and implications for trace metal speciation. *Geochim. Cosmochim. Acta* **66,** 3211–3224.

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

Wood S. A. (1990) The aqueous geochemistry of the rare-earth elements and yttrium; 1, review of available low-temperature data for inorganic complexes and the inorganic REE speciation of natural waters. *Chem. Geol.* **82,** 159–186.

Wood S. A. (1993) The aqueous geochemistry of the rare earth elements: Critical stability constants for complexes with simple carboxylic acids at 25°C and 1 bar and their application to nuclear waste management. *Eng. Geol.* **34,** 229–259.

Wood S. A., Wesolowski D. J., and Palmer D. A. (2000) The aqueous geochemistry of the rare earth elements IX. A potentiometric study of Nd^{3+} complexation with acetate in 0.1 molal NaCl solution at 25°C to 225°C. *Chem. Geol.* **167,** 231–253.

Xue H. B., Kistler D., and Sigg L. (1995) Competition of copper and zinc for strong ligands in a eutrophic lake. *Limnol. Oceanogr.* **40,** 1142–1152.

Zotov A. V., Tagirov B. R., Diakonov I. I., and Ragnarsdottir K. V. (2002) A potentiometric study of Eu^{3+} complexation with acetate ligand from 25 to 170°C at P_{sat}. *Geochim. Cosmochim. Acta* **66,** 3599–3613.