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Research Paper

Estimation of *WHAM7* constants for Ga^{III}, In^{III}, Sb^{III} and Bi^{III} from linear free energy relationships, and speciation calculations for natural waters

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Environmental context. Natural organic matter exerts a powerful control on chemical conditions in waters and soils, affecting pH and influencing the biological availability, transport and retention of metals. Modelling can help to predict these effects, but for many metals, model parameters are missing. We report parameters for four technology-critical elements in a chemical speciation model, and consider the chemistries of the elements in natural waters.

Abstract. We compiled the equilibrium constants for the interactions of the technology-critical elements (TCEs) Ga^{III}, In^{III}, Sb^{III} and Bi^{III} with ammonia, fluoride, hydroxyl and ligands with oxygen atoms. We then combined them with predictive equations to estimate parameters for Humic Ion-Binding Model VII, which permits the calculation of metal binding by natural organic matter (fulvic acid, FA, and humic acid, HA). Derived values of the Model VII parameter quantifying the interaction of metal ions with carboxyl-type groups (log K_{MA}) were among the highest estimated so far, as were the values for the parameter (ΔLK_2) that quantifies the tendency of the metal ion to interact with softer ligand atoms (N and S). The Windermere Humic Aqueous Model, version 7 (*WHAM7*), which incorporates Model VII, was then used to estimate the chemical speciation of each TCE element.

Additional keywords: antimony, bismuth, fulvic acid, gallium, humic acid, indium, technology-critical elements, Windermere Humic Aqueous Model.

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Introduction

Trace elements, including the platinum group elements (PGE), rare earth elements (REE), and others like Nb, Ta, Ga, In, Ge and Te, are often referred to as technology-critical elements or TCEs. The rate of their production and usage has particularly increased through their use in high-tech applications. The possible environmental and (eco)toxicological implications of this trend should be considered. An important control on their environmental behaviour may be binding by natural organic matter, but for most of the TCEs, we lack data describing metal-organic matter interactions, for example, by models such as *WHAM* (Tipping 1994, 2002) and NICA-Donnan (Kinniburgh et al. 1996; Milne et al. 2003).

The latest Humic Ion-Binding Model, version VII (Tipping et al. 2011) used with *WHAM* has two parameters to quantify the binding of each metal by humic substances. The first is log K_{MA}, which is the logarithm of the average binding constant for stronger weak acids (typically carboxyl), and the second is ΔLK_2, which accounts for the enhanced binding strength arising from interactions with softer ligand atoms (N and S). Values of log K_{MA} have been derived mainly from measured laboratory data; the parameterisation of Model VII used ~17 000 measured data points (pairs of bound and free metal ion concentrations) to describe the binding of protons and 40 metals by isolated fulvic and humic acids (FA and HA). Values of ΔLK_2 are, however, set from a linear equation involving the equilibrium constant for binding of the metal to NH_3 (K_{NH3}).

The question then arises, how to estimate model parameters for metals for which there is little or no direct binding data for humic substances, or for which there is no K_{NH3}. Tipping et al. (2011) applied the approach and findings of Carbonaro and Di Toro (2007) to analyse the Model VII results by plotting log K_{MA} against α_O, the slope of the equation of Irving and Rossotti (1956) for monodentate ligands with oxygen donor atoms (see Fig. 1). This provides a way to estimate log K_{MA} if equilibrium constants for the binding of the metal by such ligands are available. If there are no K_{NH3} values for the metal, then the equation of Hancock and Martell (1996), which relates log K_{NH3} to a linear equation involving log K_{OH} and log K_F (constants for metal binding by OH^- and F^-), might be applied.

In the present work, we describe the derivation of Model VII constants for three trivalent metals (Ga, In, Bi) and the metalloid Sb (referred to hereafter as a metal for ease of exposition) that are classified as technology critical (Gunn 2014; Hayes and

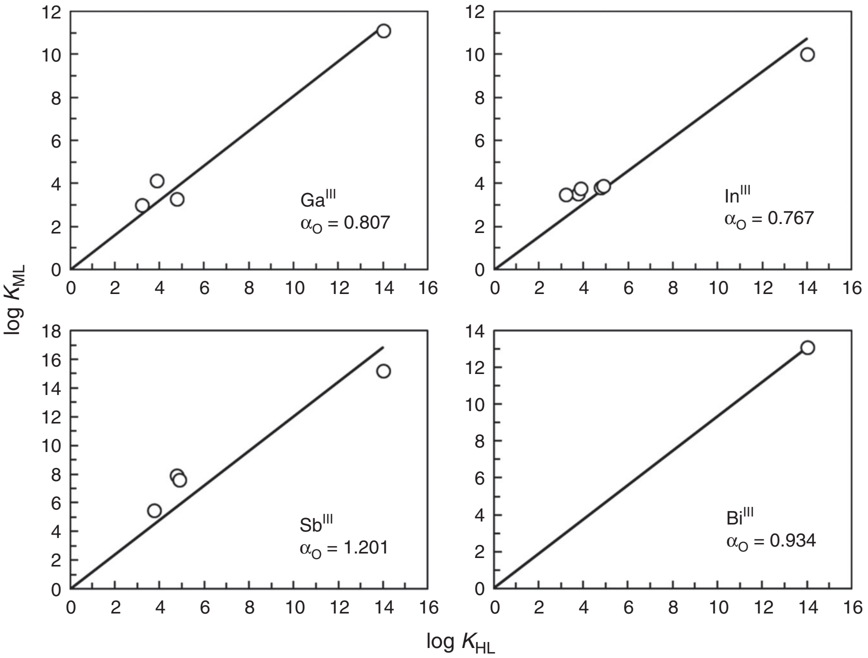

Fig. 1. Irving-Rossotti plots of log K_{ML} (metal binding) versus log K_{HL} (proton binding) for single oxygen ligands. Regressions are forced through (0,0). The Irving-Rossotti slopes (α_O) are shown in each panel.

McCullough 2018). This kind of exercise has been done previously for one of the metals studied here, In^{III}, by Tessier et al. (2014), and for some other metals by Stockdale et al. (2011*a*). After deriving the parameters, we used them within the speciation code *WHAM7* (UK Centre for Ecology and Hydrology 2019) to estimate how the metals are distributed among different chemical species in some representative natural waters.

Experimental

WHAM7

Chemical speciation calculations were performed using *WHAM* (UK Centre for Ecology and Hydrology 2019) incorporating Humic Ion-Binding Model VII (Tipping et al. 2011). This modelling takes into account the competitive complexation of protons, and major and trace cations, by organic and inorganic ligands, together with ionic strength effects.

The following is a brief description of Model VII. For detailed information about the assumptions of the model and the construction of its database, see the works by Tipping (1998, 2002) and Tipping et al. (2011). The model uses a structured formulation of discrete, chemically-plausible, binding sites for protons in HA and FA, to allow the creation of regular arrays of bidentate and tridentate binding sites for metals. The proton-binding sites comprise two types, A and B, the former being relatively strong acids (mainly carboxyl groups) and the latter relatively weak (e.g. phenolic). The A and B sites have ranges of values to represent heterogeneity. Metal aquo ions (Al^{3+}, Cu^{2+}, Zn^{2+} etc.) and their first hydrolysis products ($AlOH^{2+}$, $CuOH^+$, $ZnOH^+$ etc.) compete with each other, and with protons, for binding. The same intrinsic equilibrium constant (K_{MA}) for binding to type A sites is assumed to apply to the aquo ion and its first hydrolysis product. The constant (K_{MB}) for binding to type B sites has a fixed mathematical relationship to K_{MA}. The contributions to metal binding from rarer 'soft' ligand atoms are factored in through the model constant ΔLK_2 (see Eqn 4 below). The intrinsic equilibrium constants are modified by empirical electrostatic terms that take into account the attractive or repulsive interactions between ions and the charged macromolecule. Model parameters have been derived by fitting numerous equilibrium binding data for protons and 40 metals.

In *WHAM7*, the Model VII is combined with an inorganic speciation model, the species list and constants for which were given by Tipping (1994). The inorganic reactions in this database are restricted to monomeric complexes of metals. In the present work, we added species and constant for the four TCEs. The effects of ionic strength on the inorganic reactions are taken into account using the extended Debye-Hückel equation. Temperature effects on reactions between inorganic species are taken into account using published or estimated enthalpy data, but in the absence of experimental information, reactions involving humic substances are assumed to be independent of temperature. The *WHAM7* software also allows uncertainty in outputs to be estimated, by assigning ranges of values to the constants for metal binding by humic substances (i.e. log K_{MA} and ΔLK_2).

Linear free-energy relationships

To estimate K_{MA} for the four TCEs, we applied the following equations, which were derived by Tipping et al. (2011) by linear regression of fitted results for the binding of divalent and trivalent cations by FA and HA:

$$\log K_{MA,FA} = 3.81\alpha_O + 0.37 \qquad (1)$$

$$\log K_{MA,HA} = 3.51\alpha_O + 0.74 \qquad (2)$$

Values of α_O were obtained by plotting the logarithms of the equilibrium constants for metal binding by ligands with oxygen donor atoms (K_{ML}) against the logarithms of the corresponding equilibrium constants for proton binding (K_{HL}), and forcing the lines through the origin (see Fig. 1).

By definition within Model VII, the value of ΔLK_2 for each metal is given by

$$\Delta LK_2 = 0.58 \log K_{\mathrm{NH3}} \tag{3}$$

If K_{NH3} is not available from direct measurement or published estimation, it can be estimated from the following equation, owing to Hancock and Martell (1996):

$$\log K_{\mathrm{NH3}} = 0.881 \log K_{\mathrm{OH}} - 1.08 \log K_{\mathrm{F}} \tag{4}$$

This was derived from the equation reported by Drago et al. (1971), which predicts complexation constants in terms of the electrostatic, covalent and steric properties of Lewis acids and bases.

Data

We checked general non-critical (IUPAC) and critical databases (Baes and Mesmer 1976; www.nist.gov/srd/nist46) and, when possible, critical evaluations (Tuck 1983; Lothenbach et al. 1999; Filella and May 2003, 2005; Wood and Samson 2006; Kitamura et al. 2010). We consulted original publications when needed. Unfortunately, data for many of the reactions are missing, and available published data are sparse.

When possible, we obtained the required equilibrium constant values by processing the thermodynamic parameters of chemical reactions to achieve overall consistency using *JESS* (http://jess.murdoch.edu.au/jess_home.htm). *JESS* allows the ready calculation of sets of reliable equilibrium constants from all reaction data previously accumulated from the literature (May and Rowland 2018). The procedure involves an ordered Gaussian elimination to determine the so-called ‘basis species’ together with the linear combinations of reactions that are used to describe the whole chemical system. The ordering of the reactions depends on ‘weights’ assigned during compilation to each datum for the conditional equilibrium constants. Estimates of the relevant standard thermodynamic quantities (i.e. at 1 bar and infinite dilution), at 25 °C, are determined by least-squares regression using a well-established function (May 2000) based on the IUPAC-recommended specific ion interaction theory (SIT) equation to express, where possible, the effects of activity coefficient change. Where the original references are not given in the text below, they can be obtained from the *JESS* website.

Equilibrium constants for single oxygen organic ligands, needed to apply the Carbonaro and Di Toro (2007) approach, were obtained from the scarce published values (Sundén 1953; Wojtas 1975; Skorik and Artish 1985; Kulshrestha et al. 1987; Erim et al. 1990) with *JESS*. They are shown in Table 1. For the four metals studied here, the numbers of single oxygen organic ligands with binding data were generally fewer than those for the metals studied by Carbonaro and Di Toro (2007), although the latter authors also found only a few ligands for some metals.

Hydrolysis constants for Ga and In were taken to be the values recommended by Wood and Samson (2006). Values for Sb were from *JESS*, and those for Bi were taken from Kitamura et al. (2010). Values are shown in Table 2. It should be noted that $\mathrm{Sb^{III}}$ exists predominantly as $\mathrm{Sb(OH)_3}$ over a wide pH range (2–10) and it could be a matter of discussion whether the $\mathrm{Sb^{3+}}$ species really exists in solution. Lothenbach et al. (1999) considered it ‘probable’ that $\mathrm{Sb^{3+}}$ exists at low pH because the only published values for the first hydrolysis constant (Antonovich et al. 1977) agree well with results from Bond (1970) and Bond and Waugh (1970). Thus, we have included it in our study.

The equilibrium constants for the formation of $\mathrm{GaF^{2+}}$ and $\mathrm{InF^{+}}$ were taken from *JESS*, for $\mathrm{SbF^{2+}}$ the value given by Lothenbach et al. (1999) was preferred. For $\mathrm{BiF^{2+}}$, the *JESS* value was used, based on the only two published values (Loman and van Dalen 1967; Bond 1969). Values are shown in Table 2.

Equilibrium constants for the formation of $\mathrm{InCl^{2+}}$, $\mathrm{InCl_2{}^{+}}$ and $\mathrm{InCl_3}$ were those recommended by Wood and Samson (2006), and those for $\mathrm{BiCl^{2+}}$, $\mathrm{BiCl_2{}^{+}}$ and $\mathrm{BiCl_3}$ were from Kitamura et al. (2010). For $\mathrm{SbCl^{2+}}$ the value calculated by *JESS* was used. We could not find a reliable value for $\mathrm{GaCl^{2+}}$, and therefore it was approximated using the equation of Drago et al. (1971) (see above), using parameter values given by Martell and Hancock (1996). Equilibrium constants for the higher complexes of $\mathrm{Ga^{3+}}$ and $\mathrm{Sb^{3+}}$ with $\mathrm{Cl^-}$ were approximated by proportion to the values for $\mathrm{In^{3+}}$ and $\mathrm{Bi^{3+}}$. Values are shown in Table 2.

For Ga, In and Bi, values of $\log K_{\mathrm{NH3}}$ were obtained from (a) the estimates of Martell and Hancock (1996), based on the relationship between $\log K_{\mathrm{NH3}}$ and the difference between the logarithms of the constants for complexation by iminodiacetate and oxydiacetate (Mulla et al. 1985), and (b) from Eqn 4, and then averaged. For $\mathrm{Sb^{III}}$, only the value from Eqn 4 could be obtained.

The evaluation of the quality of the equilibrium constants chosen is a difficult task. It is important to note that there is not a generally accepted quality criterion in the field of equilibrium constants (Hummel et al. 2019); even in well-known critical equilibrium databases, sometimes formal quality assessment guidelines are lacking or rely on subjective criteria. However,

Table 1. Constant values for organic compounds with single oxygen ligand atoms, at I = 0 mol L^{-1} M and T = 25 °C

Values were taken from the JESS database, and extrapolation to I = 0 mol L^{-1} using the modified SIT equation (see *Methods*, *Data*). No values were available for $\mathrm{Bi^{III}}$

Ligand	$\mathrm{H^+}$	$\mathrm{Ga^{III}}$	$\mathrm{In^{III}}$	$\mathrm{Sb^{III}}$
Acetate	4.76	3.28	3.80	7.90
Formate	3.75		3.55	5.50
Glycolate	3.86	4.14	3.79	
Nitrite	3.20	3.01	3.50	
Propanoate	4.90		3.90	7.60

Table 2. Logarithms of equilibrium constants for reactions with inorganic ligands

M + nL = ML$_n$. Values were taken from the references given in the text (*Methods*, *Data*), or approximated (values in italics) from empirical relationships

Ligand	n	$\mathrm{Ga^{III}}$	$\mathrm{In^{III}}$	$\mathrm{Sb^{III}}$	$\mathrm{Bi^{III}}$
$\mathrm{OH^-}$	1	11.1	10.0	15.2	13.1
	2	20.7	20.2	29.3	25.4
	3	30.1	29.6	42.0	33.1
	4	40.3	33.9	44.3	34.3
$\mathrm{F^-}$	1	5.40	4.70	7.21	5.06
$\mathrm{Cl^-}$	1	*3.36*	2.75	3.35	3.61
	2	*5.26*	4.37	*5.24*	5.56
	3	*6.30*	5.00	*6.28*	6.98
$\mathrm{NH_3}$	1	4.03	3.87	5.60	5.53

irrespective of the criteria applied, assessing the formation of a given chemical species and providing a robust value for the corresponding equilibrium constant always require the existence of several independent studies on the system. When this is not the case, as for most of the systems considered here, it is not possible to effectively evaluate the likely accuracy of the data. Please note that, to avoid round-off errors, values in Tables 1–3 are given to a certain number of significant figures that do not necessarily reflect their true accuracy or precision. However, it is important to stress that, in spite of their limitations, we consider existing data adequate for the purpose of this study.

Calculations for natural waters

Generic compositions for some natural waters are shown in Table 4. We assumed that dissolved organic matter is 50 % carbon, with 65 % of sites active with respect to cation binding, represented by FA (Bryan et al. 2002). Thus, dissolved organic carbon (DOC) concentrations of 1 and 10 mg L^{-1} correspond to FA concentrations of 1.3 and 13.0 mg L^{-1} for speciation modelling. We investigated competition by dissolved Al and Fe^{III} species for metal binding by organic matter (see Tipping et al. 2002; Lofts et al. 2008) by comparing results with and without equilibrium with $Al(OH)_3$ and $Fe(OH)_3$, for freshwaters, and for seawaters by comparisons with and without average dissolved concentrations (Stockdale et al. 2011*b*).

We did not take into account complexation by fluoride or phosphate species, since they will not always be significant in speciation. Neither did we try to estimate complexation by carbonate or sulfate species, since equilibrium constants for the metals in question are mostly lacking. Thus, the calculations take account of solution reactions with OH^-, Cl^-, and dissolved organic matter (DOM). Since enthalpy data for the complexation reactions are not available, we assumed a temperature of 25 °C for the calculations.

Table 3. Model VII constants derived in this work

Metal	log K_{MA} HA	log K_{MA} FA	ΔLK_2
Ga^{III}	3.57	3.44	2.33
In^{III}	3.43	3.29	2.24
Sb^{III}	4.96	4.95	3.25
Bi^{III}	4.02	3.93	3.21

We assumed total dissolved concentrations of Ga, In, Sb and Bi all to be 0.1 nM, which is a rounded representative value based on the average freshwater values in the FOREGS database (http://weppi.gtk.fi/publ/foregsatlas/maps_table.php).

Output errors arising from uncertainty in parameter values were estimated with the *WHAM* software (Lofts and Tipping 2011).

Results

Irving-Rossotti plots of the data for the four metals, using the data of Table 1 and the log K_{OH} values for the first hydrolysis product (Table 2), are presented in Fig. 1. For Bi, only log K_{OH} was available, and so its Irving-Rossotti slope (α_O) was less certain; however, the log K_{OH} values for the other metals lay close to the regression lines (Fig. 1), which suggested that log K_{OH} alone provided a reasonable estimate of α_O. The derived values of log K_{MA} for FA and HA using Eqns 1 and 2 are given in Table 3. Also shown in Table 3 are the values of ΔLK_2 obtained by applying Eqn 3 using the log K_{NH3} values of Table 2. Comparisons of the log K_{MA} for FA and ΔLK_2 values with those for other metals are displayed in Fig. 2.

Errors in the log K_{MA} values arose first from uncertainties in the α_O values (Fig. 1), and second from scatter in the relationship between log K_{MA} and α_O in Eqns 1 and 2. From linear regression analysis for each metal (Fig. 1), the average error (95 % confidence interval) in α_O was ±0.15. The data from which the parameters in Eqns 1 and 2 were derived were plotted in Fig. 3 of Tipping et al. (2011). From linear regression analyses of these data, the average error (95 % confidence interval) in the prediction of log K_{MA} from α_O was found to be ±0.2 for log $K_{MA,FA}$ and ±0.3 for log $K_{MA,HA}$. We combined these errors for the four TCEs studied here, and assigned overall average errors of ±0.4 and ±0.5 respectively for the derived log $K_{MA,FA}$ and log $K_{MA,HA}$ values. Errors in ΔLK_2 have not been considered previously because a single value of log K_{NH3} was used for each estimation. The same applies to Sb here, but we used the average of two estimates of log K_{NH3} for Ga, In and Bi, and from these, an average error of ±0.15 in ΔLK_2 was estimated.

From the model outputs for natural water calculations (Table 5, Table S1, Supplementary Material), the following conclusions can be drawn:

(i) For Sb^{III} and Bi^{III}, nearly all the metal (>99.5 %) is complexed by DOM in all the natural waters considered. This also applies to In^{III} in the soft freshwaters (A, B, C, D),

Table 4. Generic natural water compositions

FW, freshwater; SW, seawater. The Al and Fe^{III} concentrations in FW-B, FW-D FW-F and FW-H are in equilibrium with the solid phases $Al(OH)_3$ and $Fe(OH)_3$

Solute	Unit	FW-A	FW-B	FW-C	FW-D	FW-E	FW-F	FW-G	FW-H	SW-A	SW-B
pH		6	6	6	6	8	8	8	8	8.2	8.2
DOC	mg L^{-1}	1	1	10	10	1	1	10	10	1	1
Na	mmol L^{-1}	0.1	0.1	0.1	0.1	5	5	5	5	468	468
Mg	mmol L^{-1}	0.02	0.02	0.02	0.02	0.5	0.5	0.5	0.5	53	53
K	mmol L^{-1}	0.01	0.01	0.01	0.01	0.1	0.1	0.1	0.1	10	10
Ca	mmol L^{-1}	0.04	0.04	0.04	0.04	1.5	1.5	1.5	1.5	10	10
Cl	mmol L^{-1}	0.1	0.1	0.1	0.1	5.0	5.0	5.0	5.0	545	545
SO_4	mmol L^{-1}	0.05	0.05	0.05	0.05	1.0	1.0	1.0	1.0	28	28
pCO_2	atm × 10^3	1	1	1	1	1	1	1	1	0.35	0.35
Al	µmol L^{-1}	0	0.76	0	7.3	0	0.54	0	0.54	0	0.01
Fe^{III}	µmol L^{-1}	0	0.074	0	0.72	0	0.017	0	0.16	0	0.001

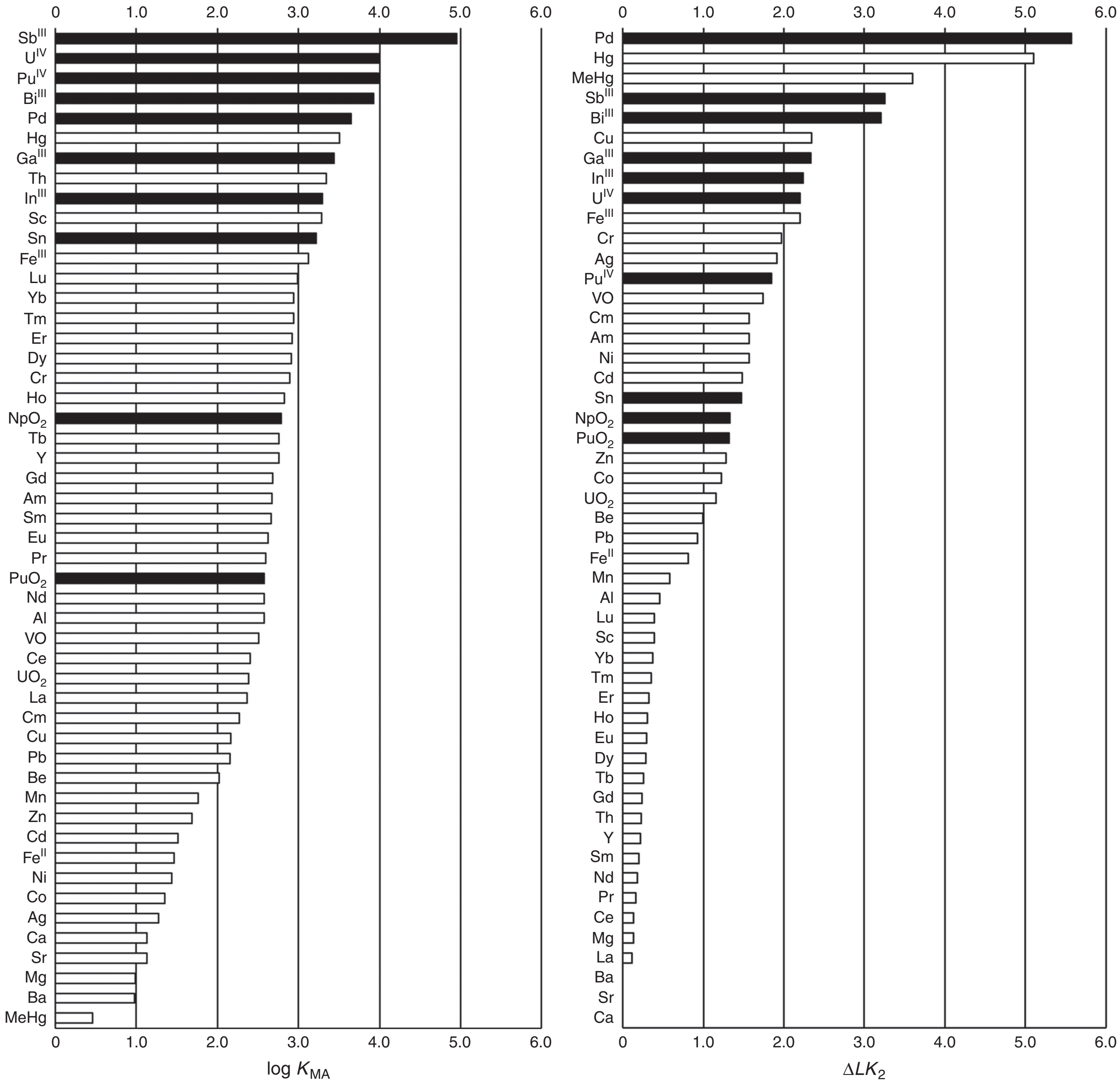

Fig. 2. Ranking of values of log K_{MA} for FA and ΔLK_2 (applies to both FA and HA). The black bars show data estimated by the methods used here, and include results for six metals (NpO$_2$, Pd, Pu^{IV}, PuO$_2$, Sn, U^{IV}) reported by Stockdale et al. (2011*a*).

but In^{III} complexation by DOM is less complete in the hard freshwaters and seawater. Of the four TCEs, Ga^{III} displays the weakest binding to DOM.

(ii) In all four cases, metal not bound by DOM is complexed by OH$^-$; complexation by Cl$^-$ is negligible in all cases.

(iii) Free ion concentrations are all calculated to be small, the highest value being $10^{-18.1}$ for In^{3+} in a soft freshwater, the lowest being $10^{-40.9}$ for Sb^{3+} in a hard freshwater.

(iv) When significant binding by DOM occurs, there is substantial uncertainty in the calculated concentrations, reflecting the ranges of the Model VII parameter values. The uncertainties are shown in detail in Table S1. The uncertainty in the metal free ion concentration approaches four orders of magnitude in a few cases. This does not apply when the speciation is dominated by inorganic complexes, because the modelling did not include uncertainties in the thermodynamic constants for these reactions.

(v) Competition by Al and Fe^{III} can be substantial. It appreciably decreases the complexation of Ga^{III} by DOM, and increases free metal ion concentrations of all the TCE metals, by five to eight orders of magnitude, in soft freshwaters.

Discussion

The four metal species studied here have high equilibrium constants for reactions with monovalent oxygen-containing ligands (Table 1) and with OH$^-$ (Table 2), and therefore we calculated high values of the Model VII parameter log K_{MA} for each of them using Eqns 1 and 2. The log K_{MA} values are averages for the binding of the metals by the type A sites

Table 5. Calculated speciation results for generic natural waters, with total Ga^{III}, In^{III}, Sb^{III} and Bi^{III} concentrations of 0.1 nM

See Table 4 for pH and major solute concentrations. log [FI] = logarithm of free ion concentration, fr DOM = fraction of metal bound to DOM, fr OH = fraction of metal bound to OH$^-$

Metal	Variable	FW-A	FW-B	FW-C	FW-D	FW-E	FW-F	FW-G	FW-H	SW-A	SW-B
Ga^{III}	log [FI]	−24.02	−18.99	−26.23	−19.25	−26.23	−26.00	−27.13	−26.00	−26.27	−26.26
	fr DOM	1.00	0.82	1.00	0.98	0.41	0.00	0.93	0.01	0.02	0.00
	fr OH	0.00	0.18	0.00	0.02	0.59	1.00	0.07	0.99	0.98	1.00
In^{III}	log [FI]	−23.42	−18.06	−25.65	−19.10	−25.26	−22.30	−26.51	−23.28	−24.01	−22.50
	fr DOM	1.00	1.00	1.00	1.00	1.00	0.91	1.00	0.99	1.00	0.95
	fr OH	0.00	0.00	0.00	0.00	0.59	1.00	0.00	0.01	0.00	0.05
Sb^{III}	log [FI]	−37.80	−31.35	−40.02	−32.44	−39.64	−35.99	−40.89	−37.06	−38.39	−36.80
	fr DOM	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
	fr OH	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Bi^{III}	log [FI]	−30.87	−24.50	−33.09	−25.59	−32.71	−29.09	−33.97	−30.16	−31.47	−29.87
	fr DOM	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
	fr OH	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

assumed in the model; these were typically carboxyl groups, which are abundant in humic substances and natural organic matter in general. The high estimated affinities of the metals for the type A sites meant that the log K_{MA} values fell at the upper end of the distribution of the parameter across all metals (Fig. 2); the four trivalent TCE metals are all in the top eight strongest binders to FA.

Similar remarks applied to the Model VII ΔLK_2 parameter, which is proportional to the equilibrium constant for the complexation of the metal by NH_3. As shown by the equilibrium constants listed in Table 2, each of the four metals binds NH_3 strongly. Hence ΔLK_2 values were high, and again the four values fall within the top eight of the distribution for all metals (Fig. 2).

Our analysis has been very similar to that reported by Tessier et al. (2014), who estimated parameters for Humic Ion Binding Model VI. The parameter values for metal binding by the type A sites in the two models are not comparable, owing to different model formulations. The value found by Tessier et al. for ΔLK_2 was 2.2, which is very similar to our value of 2.24 (Table 3).

The calculations for natural waters are restricted and necessarily tentative considering the assumptions we have made, i.e. the neglect of interactions with carbonate, sulfate, fluoride and phosphate, and the assumption of a temperature of 25 °C. However, hopefully they provide some initial insight into how these metals might behave in the natural environment. They suggest that significant binding of the four TCE metals by DOM would take place in soft waters of pH 6, and that competition by Al and Fe^{III} would be significant. Tipping et al. (2002) noted that such competition effects are especially strong for high affinity trace metals present at low total concentrations, which is the case here; at higher concentrations of the TCEs, competition would be less. The calculations suggest that at higher pH (hard freshwater and seawater), the strong hydrolysis of the TCE metals means that binding by DOM is reduced, and is negligible in some circumstances. Our finding that most or essentially all of the In^{III} is complexed by DOM in soft freshwaters is in agreement with the speciation calculations, using *WHAM6*, of Tessier et al. (2014). More direct evidence for the interaction of the TCEs with natural organic matter is limited, with just very few dedicated studies available for Ga^{III}, In^{III} and Bi^{III} (Eskenazy 1967; O'Shea and Mancy 1978; Lippold et al. 2005; Hagvall et al. 2014; Martin et al. 2017; Rotureau et al. 2019). However, in the only case where dedicated attention has been paid, as it is in the case of antimony (Filella 2011; Filella and Williams 2012), evidence points to significant trivalent TCEs binding by natural organic matter in the aquatic environment.

The low calculated binding of Ga^{III}, and to some extent the lower binding of In^{III}, by DOM at higher pH depend crucially on the modelling assumption that only the first hydrolysis product of any metal can bind to natural organic matter. This has been assumed in the development of the *WHAM* modelling system, ever since the introduction of Humic Ion Binding Model V, and was based initially on the superior fitting of Cu^{II} data at pH > 7 that could be achieved using the assumption. Otherwise, experimental data nearly always refer to conditions in which hydrolysis is avoided or minimised, and so the idea is not well tested. That it is not obviously wrong is evidenced by the results of Stockdale et al. (2013) who found that the binding by HA to Th^{IV}, which hydrolyses strongly, at high pH could be reasonably modelled under the assumption of binding only of Th^{4+} and ThOH^{3+}.

The constants estimated here for the binding of Ga^{III}, In^{III}, Sb^{III} and Bi^{III} by humic substances, obtained through the application of empirical non-thermodynamic relationships, are inevitably more uncertain than the values derived from direct measurements of metal binding. Consequently, speciation predictions for the four metals can only be approximate, as demonstrated by the wide ranges of predicted free metal ion concentrations and solution species presented in Table S1 (Supplementary Material). Therefore, the predictions must be regarded with due circumspection, and are perhaps best-regarded as scoping calculations which suggest possible behaviours of the metals in different environmental systems.

To reduce uncertainty, there is a need for comprehensive data describing the interactions of these TCEs with humic substances or DOM, in terms of bound and free concentrations, covering wide ranges, and under different conditions of pH and ionic strength. Studies to clarify the calculated competition between binding and hydrolysis would be especially welcome. However, measurement of the binding to humic substances of metals, like those studied here, is difficult, because free ion concentrations are small, owing to both the humic binding and extensive hydrolysis. The necessary speciation measurements therefore present a considerable analytical chemistry challenge. Until appropriate methodologies are devised and applied, constants for many strongly-complexing metals will have to be estimated by the methods used here, as illustrated by the black bars in Fig. 2.

Finally, we can use the constants derived here to consider the possible ecotoxicology of the four TCEs. From the study of Tipping et al. (2019), it would not be expected that any of the four metals would be strongly toxic, when bound to aquatic organisms, because they are classified as either hard (Ga, In) or borderline/intermediate (Sb, Bi) in the hardness-softness scale (Hancock and Martell 1996), whereas the most toxic bound metals (e.g., Ag, Cd, Hg) are soft. The extent to which the metals can bind to organisms, and thereby create a metabolic body burden, is important, and may be restricted by the competing hydrolysis reactions (see above). These considerations may explain why the median lethal concentration (96-h LC50) of Ga, Sb, and In were each greater than 1 mg L^{-1}, which indicated relatively low toxicity, while those of Cu and Cd were less than 0.1 mg L^{-1}, in acute toxicity tests with a freshwater swamp shrimp in moderately hard water with pH 7.4–8.1 (Yang 2014). Further work in this area might make use of the present results.

Supplementary material

WHAM outputs for natural water calculations are available on the Journal's website.

Conflicts of interest

The authors declare no conflicts of interest.

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