Online Supporting Information

Table S1 contains a summary and explanation for the various equilibrium constants, '*K*', and their derivatives. The in-depth reader is recommended to start with the Sonke and Salters (2006) publication that details the experimental data and forms part I of a series of papers on lanthanide – humics complexation (*1*). Conditional binding constants in part I are indicated by subscript 'c', such as $K_{c,LaSRFA}$ for the reaction:

La + SRFA = LaSRFA

In part II (this study) we will compare trends in K_c values with trends in Model V binding parameters for individual sites, denoted simply by 'K' values. Be reminded that K values for the 20 individual Model V binding sites are determined by one overall intrinsic binding parameter, pK_{MHA}, which refers to a metal-proton exchange reaction for type A sites (see references (*2-4*) for more details).

Table S1. Explanation of symbols and abbreviations.

Symbols		explanation	remarks
family	example		
pK_{MH}			General term for Model V intrinsic binding parameter; M = metal, H = humics (both FA and HA)
	pK_{MHA}	pK_{MH} parameter for A sites (both FA and HA)	Essential Model V parameter that is typically fitted to experimental data.
	pK_{MHB}	pK_{MH} parameter for B sites (both FA and HA)	Not often used, nor fitted, as pK_{MHB} is found to be related to pK_{MHA}.
K and log*K*		Reaction quotient for metal – ligand complex formation: M + L = ML	K and logK refer to thermodynamic constants in general or to intrinsic constants for the 20 different sites in Model V
	$\log K_{LaEDTA}$	Ln + EDTA = LaEDTA	Thermodynamic constant for LaEDTA complexation.
	log*K*	M + A = MA (site A) M + B = MB (site B)	Log*K* is used for binding of metal M (such as Ln) to any of the model V sites (such as A, B, bidentate sites)
K_c and $\log K_c$		Conditional binding constant for: M + HS = MHS	Refers to Sonke and Salters (2006) publication (*1*)
	$\mathrm{Log}K_{c,LaSRFA}$	Conditional binding constant for lanthanum – SRFA complexation.	Example where metal and HS are specified.
$\Delta_L K$		$\log K_{LuL} - \log K_{LaL}$	Numerical difference in logK values between lutetium and lanthanum complexation by ligand L (such as EDTA).
	$\Delta_{HS} K_c$	$\log K_{c,LuHS} - \log K_{c,LaHS}$	HS indicates humic

			substances in general, while subscript 'c' indicates that conditional constants, instead of intrinsic or thermodynamic constants are being described.
	$\Delta_{EHA}K_c$	$\log K_{c,LuEHA} - \log K_{c,LaEHA}$	Here the particular HS is specified as EHA. 'c' refers to conditional constants of the Sonke and Salters 2006 paper (*1*).
	$\Delta_{EHA}K$	$\log K_{c,LuEHA} - \log K_{c,LaEHA}$	Here intrinsic K values are denoted, which means that Model V is being referred to, and EHA in particular.
	$\Delta_{FA}K$	$\log K_{LuFA} - \log K_{LaFA}$	Here intrinsic K values are denoted, which means that Model V is being referred to, and FA in general
	$\Delta_{HS}\, pK_{MHA}$	$\lvert pK_{LuHA} - pK_{LaHA} \rvert$	Here pK_{MHA} are evaluated for their lanthanide contraction effect. Note absolute value signs that force numbers to be positive.

Table S2. Summary of fitted pK_{MHA} values for the 11 lanthanide-HS datasets that were obtained for different pH, *I*, and HS source material. SRFA, Suwannee river fulvic acid; LHA, Leonardite coal humic acid; EHA, Elliot soil humic acid. Values in italics are fitted to non-linearly interpolated experimental data (using equation 9 in reference (*1*)), and were taken into account for averaging. Average pK_{MHA} values for one lanthanide (and one HS source) were calculated by first averaging pH sub-datasets at 0.1 mol L^{-1} I, followed by averaging *I* variations.

pH	6	7	8	9	7	7	9		
I	0.1	0.1	0.1	0.1	0.01	0.001	0.01	average	1sd
HS source	SRFA	SRFA	SRFA	SRFA	SRFA	SRFA		SRFA	
Sc			-0.58					-0.58	
Y	-0.03		-0.05					-0.03	
La	0.12	0.13	0.10	0.08	0.24	0.28		0.21	0.09
Ce	0.09	0.10	0.07	0.06	0.21	0.24		0.18	0.09
Pr	0.06	0.07	0.04	0.03	0.17	0.20		0.14	0.08
Nd	0.04	0.04	0.01	0.01	0.14	0.17		0.11	0.08
Sm	-0.02	-0.02	-0.04	-0.04	0.07	0.09		0.04	0.07
Eu	-0.05	-0.05	-0.07	-0.06	0.04	0.05		0.01	0.06
Gd	-0.08	-0.08	-0.10	-0.09	0.01	0.02		-0.02	0.06
Tb	-0.10	-0.11	-0.13	-0.11	-0.03	-0.02		-0.05	0.05
Dy	-0.13	-0.14	-0.16	-0.13	-0.06	-0.06		-0.09	0.05
Ho	-0.16	-0.17	-0.19	-0.16	-0.10	-0.10		-0.12	0.04
Er	-0.19	-0.20	-0.21	-0.18	-0.13	-0.14		-0.15	0.04
Tm	-0.21	-0.23	-0.24	-0.20	-0.16	-0.17		-0.19	0.03
Yb	-0.24	-0.26	-0.27	-0.23	-0.20	-0.21		-0.22	0.03
Lu	-0.27	-0.29	-0.30	-0.25	-0.23	-0.25		-0.25	0.02
$\Delta_{SRFA}K$	0.39	0.42	0.40	0.33	0.47	0.53		0.46	0.04
HS source	LHA	LHA	LHA	LHA	LHA		EHA	LHA	
Sc		-0.26	-0.18	-0.16	-0.28			-0.24	0.06
Y	0.50	0.58	0.56	0.56	0.85			0.70	0.21
La	0.75	0.86	0.86	0.84	1.16		1.58	0.99	0.24
Ce	0.71	0.82	0.82	0.80	1.11		1.53	0.95	0.23
Pr	0.67	0.77	0.77	0.76	1.07		1.47	0.90	0.23
Nd	0.63	0.73	0.73	0.72	1.02		1.42	0.86	0.22
Sm	0.55	0.64	0.64	0.63	0.92		1.31	0.77	0.22
Eu	0.51	0.60	0.59	0.59	0.88		1.26	0.73	0.21
Gd	0.48	0.56	0.55	0.55	0.83		1.21	0.68	0.21
Tb	0.44	0.51	0.51	0.51	0.78		1.15	0.64	0.21
Dy	0.40	0.47	0.46	0.47	0.74		1.10	0.59	0.20
Ho	0.36	0.42	0.42	0.43	0.69		1.04	0.55	0.20
Er	0.32	0.38	0.37	0.38	0.64		0.99	0.50	0.20
Tm	0.28	0.34	0.33	0.34	0.59		0.94	0.46	0.19
Yb	0.24	0.29	0.28	0.30	0.55		0.88	0.41	0.19
Lu	0.20	0.25	0.24	0.26	0.50		0.83	0.37	0.19
$\Delta_{HA}K$	0.55	0.61	0.62	0.58	0.66	0.75		0.60	0.04

Table S3. Summary of p*K* values for metal complexation with citric acid, NTA and EDTA at 0 ionic strength and 25 ˚C (*5*, *6*), and pK_{MHA} values for fulvic acid (FA) and humic acid (HA) (*7*). Linear free energy relationships between the pK values of these ligands and pK_{MHA} are shown in Figures S1-3.

	pK(EDTA)	pK(citrate)	pK(NTA)	pK_{MHA}(FA)	pK_{MHA}(HA)	pK_{MHA}(FA) citrate	pK_{MHA}(FA) NTA	pK_{MHA}(HA) EDTA
Ca	-12.4	-4.7	-7.6	2.2	3.3			
Mg	-10.6	-4.7	-6.5	2.2	3.3			
Ba	-9.6	-4.1	-5.9		3.6			
Sr	-10.5	-4.1	-6.3		2.8			
Zn	-18.3	-6.1	-12.0	1.3	2.3			
Mn	-15.6	-5.5	-8.7	1.7	3.4			
Cu	-20.5	-7.2	-14.2	0.8	1.5			
Ni	-20.4	-6.7	-12.8	1.4	2.7			
Pb	-19.8	-5.4	-12.6	0.9	1.7			
Cd	-18.2	-5.0	-11.1	1.5	2.7			
Hg	-23.5	-12.2	-15.9		0.2			
Fe(III)	-27.7	-13.5	-17.9		0.8			
Al	-18.9	-8.0	-13.4	0.4	1.3			
UO2	0.0	-8.7	-10.8	0.9	1.3			
Th	-26.7	-14.3	-15.0		0.6			
Co	-18.1	-6.3	-11.7	1.7	2.7			
Fe(II)	-16.1	-5.7	-9.6		2.1			
Am3+	-21.1	-9.7	-13.6	0.3	1.2			
Sc	-25.7		-14.7				0.53	0.82
Y	-20.7	-9.6	-13.4			0.28	0.81	1.68
La	-18.0	-9.1	-12.5			0.44	1.01	2.15
Ce	-18.6	-9.4	-12.7			0.35	0.96	2.05
Pr	-18.9	-9.6	-12.9			0.28	0.93	1.99
Nd	-19.2	-9.7	-13.1			0.25	0.88	1.95
Pm								
Sm	-19.7	-9.8	-13.3			0.22	0.83	1.86
Eu	-19.9	-9.8	-13.3			0.22	0.83	1.83
Gd	-20.0	-9.7	-13.3			0.25	0.82	1.81
Tb	-20.5	-9.7	-13.5			0.24	0.79	1.72
Dy	-20.9	-9.8	-13.6			0.22	0.76	1.65
Ho	-21.2	-9.8	-13.7			0.21	0.73	1.60
Er	-21.5	-9.8	-13.9			0.20	0.70	1.54
Tm	-22.0	-10.0	-14.1			0.16	0.67	1.47
Yb	-22.1	-10.0	-14.2			0.14	0.64	1.44
Lu	-22.4	-10.1	-14.3			0.13	0.61	1.40

Table S4. Chemical composition of an 'average world river' dissolved phase. Major element concentrations in μmol L^{-1}, DOM in mg L^{-1}, lanthanides in pmol L^{-1}.

parameter	Average world river	Reference
pH	Variable	
Na	240	(*8*)
K	44	(*8*)
Ca	594	(*8*)
Mg	245	(*8*)
HCO_3	798[a]	(*8*)
Cl	167	(*8*)
SO_4	175	(*8*)
PO_4	0.7	(*5*)
DOM	5	(*9*)
Reactive DOM	65%	(*2*)
FA %	100	(2)b
HA %	0	
Fe	1.18	(*10*)
Al	1.19	(*10*)
Y	449	(*10*)
La	864	(*10*)
Ce	1870	(*10*)
Pr	199	(*10*)
Nd	1054	(*10*)
Sm	239	(*10*)
Eu	64	(*10*)
Gd	254	(*10*)
Tb	35	(*10*)
Dy	185	(*10*)
Ho	43	(*10*)
Er	120	(*10*)
Tm	19.5	(*10*)
Yb	98	(*10*)
Lu	13.7	(*10*)

(a) the speciation code used (WinHumicV) uses total carbonate, '*TOT*CO3' as input parameter. Hence a slightly higher value for *TOT*CO3 of 1000 μmol L^{-1} was used, such that a [HCO_3^-] was ~ 798 μmol L^{-1} in the pH range 6-8.

(b) 100% fulvic acid is not a recommended value by this author, but nevertheless frequently applied throughout this text.

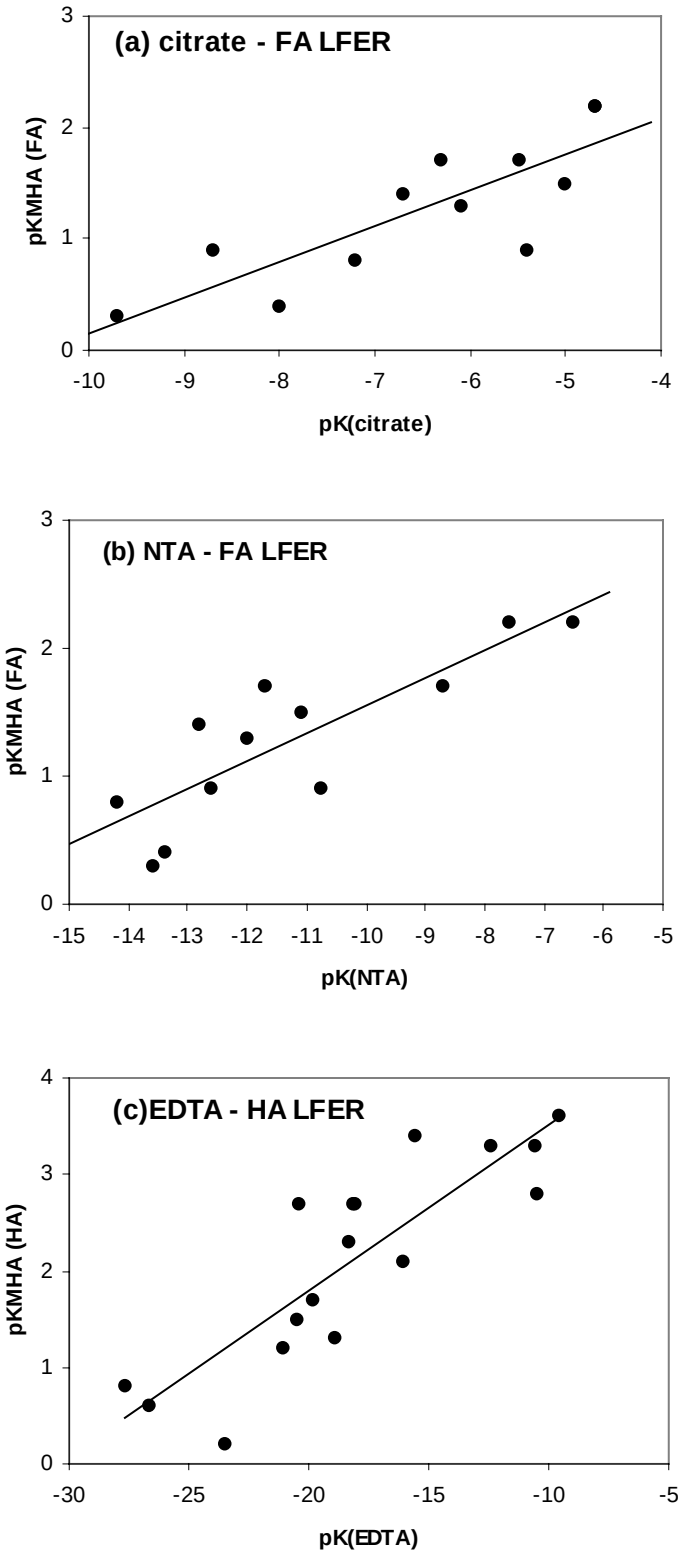

Figure S1(a-c). Linear free energy relationships (LFER) between pK_{MHA} and stability constants for citrate, NTA and EDTA (see also Table S2). FA = fulvic acid, HA = humic acid. Correlation coefficients, r, are 0.83, 0.84, and 0.86 for a, b, and c respectively.

References

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