Accessory publication

Humic ion-binding model VII: a revised parameterisation of cation-binding by humic substances

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Coding error concerning ΔLK_1 in Humic Ion-Binding Model VI

In Model VI, there are four carboxyl-type (type A) sites that can bind both protons and metals through monodentate complexation. In the original paper on Model VI (Tipping, 1998), ΔLK_1 was presented as a modifier of log K_{MA}, the intrinsic equilibrium constant for metal binding. Thus, for i = 1 to 4:

$$\log K_M(i) = \log K_{MA} + \{(2i - 5)/6\} \times \Delta LK_1 \quad (A1)$$

A similar pattern was imposed upon the proton binding reactions, but in terms of pK values, for i = 1 to 4

$$pK(i) = pK_A + \{(2i - 5)/6\} \times \Delta pK_A \quad (A2)$$

The computer code for Model VI was based on that for Model V, which used metal-proton exchange reactions,

$$LH + M = LM + H \quad (A3)$$

described by the constant pK_{MHA}, which is given by

$$pK_{MHA} = pK_A - \log K_{MA} \quad (A4)$$

Substituting (Eqn A1) and (Eqn A2) into (Eqn A4) we obtain

$$pK_{MH}(i) = pK_A + [\{(2i - 5)/6\} \times \Delta pK_A] - \log K_{MA} - [\{(2i - 5)/6\} \times \Delta LK_1] \quad (A5)$$

$$= pK_A - \log K_{MA} + [\{(2i - 5)/6\} \times (\Delta pK_A - \Delta LK_1)] \quad (A6)$$

$$= pK_{MHA} + [\{(2i - 5)/6\} \times (\Delta pK_A - \Delta LK_1)] \quad (A7)$$

In Model V, all the $pK_{MH}(i)$ terms were the same, and equal to pK_{MHA}, which is equivalent to forcing ΔpK_A and ΔLK_1 to be equal.

When parameterising Model VI, Tipping (1998)[1] claimed to have optimised ΔLK_1 and reported a single universal value of 2.8 for all metals, for FA and HA, and applying to both type A and type B sites. Because of the coding error, he in fact optimised the value of ($\Delta pK_A - \Delta LK_1$), i.e. this is the "parameter" that is universally equal to 2.8.

Therefore the values of ΔLK_1 that have actually been used in Model VI are

	FA	HA

Type A sites	3.3 - 2.8 = 0.5	2.1 - 2.8 = -0.7
Type B sites	4.9 - 2.8 = 2.1	3.6 - 2.8 = 0.8

The model is still consistent and the optimised parameters represent reported binding data. Therefore all calculations performed with the computer code provided by E Tipping and S Lofts will be correct, but will not refer to the model as described by Tipping (1998). Rather, they refer to the model in which ($\Delta pK_A - \Delta LK_1$) is constant.

When parameterising Model VII, it was found that adjustment of ΔLK_1, correctly applied, did not improve data fits. Consequently the parameter has been removed from the model. This is equivalent to setting it to zero. It can be noted that the average value of ΔLK_1 from the above table is 0.68, which compared to ΔpK_A is quite close to zero.

Reference

[1] E. Tipping, Humic Ion-Binding Model VI: an improved description of ion-binding by humic substances. *Aquatic Geochem.* **1998**, *4*, 3-48.

Data sources

The following pages describe the data sets used for fitting Humic Ion-Binding Model VII, including the fitting results. The data themselves are available at http://windermere.ceh.ac.uk/Aquatic_Processes/wham/.

Code	Reference	n	pI	pH	$-10^{-3}Z$	$10^3 n_A$	pKa	pKb	P	RMSD
HH-08	Lead et al. 1994	64	1.0-2.5	3.4-10.0	0.7-4.4	3.2	4.2	8.4	-171	0.077
HH-11	Robertson 1996	433	0.9-2.0	3.0-10.6	0.7-5.8	4.1	3.8	8.3	-274	0.117
HH-12	Schmeide 1999	669	0.5-3.0	3.0-10.4	0.5-5.7	3.7	3.5	7.9	-266	0.134
HH-13	Avena et al. 1999	250	0.9-2.2	3.2-10.3	0.6-4.0	2.9	4.3	8.7	-162	0.034
HH-14	Avena et al. 1999	252	1.0-2.4	3.4-10.4	1.2-5.3	3.5	3.8	7.2	-84	0.040
HH-15	Avena et al. 1999	255	0.9-2.3	3.3-10.3	1.3-4.9	3.3	3.5	7.3	-134	0.047
HH-16	Avena et al. 1999	251	0.9-2.5	3.3-10.3	0.5-3.2	2.5	4.4	9.1	-110	0.032
HH-17	Avena et al. 1999	252	1.0-2.5	3.4-10.4	1.0-5.7	3.8	4.0	7.1	-76	0.053
HH-18	Avena et al. 1999	254	1.0-2.3	3.4-10.4	0.6-4.5	3.0	4.4	7.8	-105	0.035
HH-19	Avena et al. 1999	251	0.9-2.4	3.3-10.3	0.5-3.5	2.4	4.4	8.3	-157	0.042
HH-22	Oste 2000	600	0.5-3.0	3.4-10.3	0.8-3.9	2.6	3.8	8.0	-349	0.078
HH-24	Masini et al. 2000	225	0.0-2.0	3.5-10.5	0.7-5.4	4.0	4.3	9.4	-270	0.074
HH-25	Plaza et al. 2005	121	0.5-2.0	3.3-10.4	0.8-5.8	4.5	4.1	9.4	-194	0.087
HH-26	Plaza et al. 2005	115	0.5-2.0	3.3-10.4	0.7-5.6	4.1	4.1	8.8	-210	0.096
HH-27	Fernandez et al. 2007	270	0.5-2.1	3.6-10.4	0.3-4.5	3.2	4.7	8.9	-178	0.059
HH-28	Zhou et al. 2005	50	0.3-1.3	3.6-10.1	1.0-6.1	4.1	4.3	8.0	-403	0.104
						3.4	4.1	8.3	-196	

Best average parameters:

$10^3 n_A$	3.4
pKa	4.1
pKb	8.3
DpKa	2.6
DpKb	3.1
P	-196

HH-08 Lead, J. R.; Hamilton-Taylor, J.; Hesketh, N.; Jones, M. N.; Wilkinson, A. E.; Tipping, E. A COMPARATIVE-STUDY OF PROTON AND ALKALINE-EARTH METAL-BINDING BY HUMIC SUBSTANCES . Anal. Chim. Acta 1994, 294, 319-327.

HH-11 Robertson, A. P. Goethite/humic acid interactions and their effect on copper(II) binding. Ph.D. Dissertation, Stanford University, CA, 1996.

HH-12 Schmeide, K.; Zänker, H.; Heise, K. H.; Nitsche, H. In Effects of humic substances on the migration of radionuclides: complexation and transport of actinides. First Technical Progress Report. Buckau, G., Ed.; Report FZKA 6124, Forschungszentrum Karlsruhe: Karlsruhe, 1998.

HH-13 Avena, M. J.; Koopal, L. K.; van Riemsdijk, W. H. J. Proton binding to humic acids: Electrostatic and intrinsic interactions. Colloid Interface Sci. 1999, 217, 37-48.

HH-14 Avena, M. J.; Koopal, L. K.; van Riemsdijk, W. H. J. Proton binding to humic acids: Electrostatic and intrinsic interactions. Colloid Interface Sci. 1999, 217, 37-48.

HH-15 Avena, M. J.; Koopal, L. K.; van Riemsdijk, W. H. J. Proton binding to humic acids: Electrostatic and intrinsic interactions. Colloid Interface Sci. 1999, 217, 37-48.

HH-16 Avena, M. J.; Koopal, L. K.; van Riemsdijk, W. H. J. Proton binding to humic acids: Electrostatic and intrinsic interactions. Colloid Interface Sci. 1999, 217, 37-48.

HH-17 Avena, M. J.; Koopal, L. K.; van Riemsdijk, W. H. J. Proton binding to humic acids: Electrostatic and intrinsic interactions. Colloid Interface Sci. 1999, 217, 37-48.

HH-18 Avena, M. J.; Koopal, L. K.; van Riemsdijk, W. H. J. Proton binding to humic acids: Electrostatic and intrinsic interactions. Colloid Interface Sci. 1999, 217, 37-48.

HH-19 Avena, M. J.; Koopal, L. K.; van Riemsdijk, W. H. J. Proton binding to humic acids: Electrostatic and intrinsic interactions. Colloid Interface Sci. 1999, 217, 37-48.

HH-22 Oste, L. A.; Temminghoff, E. J. M.; Lexmond, T. M.; van Riemsdijk, W. H. Environ. Sci. Technol. 2001. [This study does not appear to have ever been published - it is not on Web of Science. The reference here is that listed in Chris Milne's paper of 2001.]

HH-24 Masini, J. C.; Abate, G.; Lima, E. C.; Hahn, L. C.; Nakamura, M. S.; Lichtig, J.; Nagatomy, H. R. Comparison of methodologies for determination of carboxylic and phenolic groups in humic acids. Anal. Chim. Acta 1998, 364, 223-233.

HH-25 Plaza C., Brunetti G., Senesi N., and Polo A. (2005) Proton binding to humic acids from organic amendments and amended soils by the NICA-Donnan model. Environ Sci Technol 39(17), 6692-6697.

HH-26 Plaza C., Brunetti G., Senesi N., and Polo A. (2005) Proton binding to humic acids from organic amendments and amended soils by the NICA-Donnan model. Environ Sci Technol 39(17), 6692-6697.

HH-27 Fernandez, J.M., Plaza, C., Sensei, N., Polo, A. 2007.Acid–base properties of humic substances from composted and thermally-dried sewage sludges and amended soils as determined by potentiometric titration and the NICA-Donnan model. Chemosphere 69, 630-635.

HH-28 ZHOU, P., YAN, H., AND GU, B. 2005. Competitive complexation of metal ions with humic substances. Chemosphere, 58, 1327-1337.

Code	Reference	Comments	n	pI	pH	$-10^{-3}Z$	$10^3 n_A$	pKa	pKb	P	RMSD
FH-01	Dempsey 1981		145	0.0-2.0	4.0-10.6	3.1-7.3	4.9	2.8	7.7	-103	0.081
FH-02	Dempsey 1981		101	0.0-2.0	3.7-10.4	2.8-6.5	5.2	3.2	9.8	-105	0.096
FH-05	Paxeus & Wedborg 1985		45	0.0-2.0	3.0-10.0	1.5-6.2	5.6	3.7	11.1	-77	0.088
FH-16	Christensen et al. 1998		620	0.9-2.2	3.5-10.7	2.7-8.0	6.3	3.4	10.1	-78	0.077
FH-17	Christensen et al. 1998		588	0.9-2.3	3.8-10.7	2.6-7.3	5.9	3.7	10.7	-52	0.068
FH-20	Higgo et al. 1998		869	1.0-2.6	2.3-10.9	1.9-7.6	4.9	3.0	7.4	-69	0.102
FH-21	Schmeide 1999		663	0.5-3.0	3.4-10.3	1.4-6.6	4.9	3.3	9.0	-222	0.111
FH-22	Avena et al. 1999		249	0.9-2.4	3.4-10.3	0.6-4.5	3.4	4.7	9.5	-184	0.156
FH-23	Pinheiro et al. 1999		255	1.0-2.0	3.6-10.4	1.2-7.2	5.5	4.3	9.2	-221	0.150
FH-25	Filius 2000		411	1.0-3.0	2.9-10.7	0.4-6.1	4.6	4.3	10.7	-79	0.094
FH-26	Gondar et al. 2005		211	1.0-2.3	3.9-10.2	1.9-5.9	5.0	3.4	9.4	-185	0.073
FH-27	Fernandez et al. 2007		285	0.5-2.0	3.3-10.4	1.1-6.9	5.5	4.1	10.4	-94	0.164
FH-28	Filius et al. 2000		66	1.0-2.0	3.5-10.4	2.1-6.7	5.4	3.7	10.3	-79	0.076
							5.2	3.7	9.6	-119	

Best average parameters:

$10^3 n_A$	5.2
pKa	3.7
pKb	9.6
DpKa	3.0
DpKb	4.5
P	-119

FH-01 Dempsey B. A. (1981) The protonation, calcium complexation and adsorption of a fractionated aquatic fulvic acid. Ph.D. thesis, Johns Hopkins University.

FH-02 Dempsey B. A. (1981) The protonation, calcium complexation and adsorption of a fractionated aquatic fulvic acid. Ph.D. thesis, Johns Hopkins University.

FH-05 Paxeus N. and Wedborg M. (1985) Acid-base properties of aquatic fulvic acid. Anal. Chim. Acta, 169, 87–98.

FH-16 Christensen, J. B.; Tipping, E.; Kinniburgh, D. G.; Grøn, C.; Christensen, T. H. Environ. Sci. Technol. 1998, 32, 3346-3355.

FH-17 Christensen, J. B.; Tipping, E.; Kinniburgh, D. G.; Grøn, C.; Christensen, T. H. Environ. Sci. Technol. 1998, 32, 3346-3355.

FH-20 Davis, J.; Higgo, J. J. W.; Moore, Y.; Milne, C. J. In Effects of humic substances on the migration of radionuclides: complexation and transport of actinides. Second Technical Progress Report; Buckau, G., Ed.; Report FZKA 6324, Forschungszentrum Karlsruhe: Karlsruhe, 1999.

FH-21 Schmeide, K.; Zänker, H.; Heise, K. H.; Nitsche, H. In Effects of humic substances on the migration of radionuclides: complexation and transport of actinides. First Technical Progress Report. Buckau, G., Ed.; Report FZKA 6124, Forschungszentrum Karlsruhe: Karlsruhe, 1998.

FH-22 Avena, M. J.; Koopal, L. K.; van Riemsdijk, W. H. J. Proton binding to humic acids: Electrostatic and intrinsic interactions. Colloid Interface Sci. 1999, 217, 37-48.

FH-23 Pinheiro, J. P.; Mota, A. M.; Benedetti, M. F. Environ. Sci. Technol. 1999, 33, 3398-3404.

FH-25 Filius, J. D. Wageningen Agricultural University, The Netherlands, unpublished results.

FH-26 Gondar D., Lopez R., Fiol S., Antelo J. M., and Arce F. (2005) Effect of soil depth on acid properties of humic substances extracted from an ombrotrophic peat bog in northwest Spain. 56(6), 793-801.

FH-27 Fernandez, J.M., Plaza, C., Sensei, N., Polo, A. 2007.Acid–base properties of humic substances from composted and thermally-dried sewage sludges and amended soils as determined by potentiometric titration and the NICA-Donnan model. Chemosphere 69, 630-635.

FH-28 Filius, J.D., Lumsdon, D.G., Meeussen, J.C.L., Hiemstra, T., Van Riemsdijk, W.H. 2000. Adsorption of fulvic acid on goethite . Geochimica et Cosmochimica Acta, 64, 51-60

Summary of data sets for metal binding

Metal	HA nDS	HA nDP	HA LKMA	HA RMSD	FA nDS	FA nDP	FA LKMA	FA RMSD
Ag	4	79	1.50	0.30	1	23	1.14	0.06
Al	4	100	2.67	0.16	4	117	2.69	0.19
Am	7	143	2.95	0.10	3	27	2.74	0.06
Ca	8	432	1.19	0.20	11	557	1.17	0.16
Cd	10	454	1.61	0.12	6	280	1.58	0.16
Ce	1	5	2.68	0.26	1	5	2.70	0.32
Cm	3	38	2.58	0.22	1	17	1.91	0.10
Co	2	257	1.51	0.36	8	484	1.32	0.33
Cr	1	31	2.52	0.15	0			
Cu	14	945	2.54	0.11	16	671	2.07	0.11
Dy	2	10	3.19	0.23	1	5	2.93	0.46
Er	1	4	3.03	0.50	1	3	3.09	0.46
Eu	5	256	2.97	0.27	10	325	2.61	0.39
FeIII	2	20	3.19	0.20	1	8	3.03	0.29
Gd	1	5	2.77	0.28	1	4	2.84	0.48
Hg	3	36	4.10	0.24	5	45	3.40	0.22
Ho	1	5	2.95	0.48	1	4	2.96	0.60
La	1	5	2.64	0.30	1	5	2.74	0.25
Lu	1	5	3.17	0.41	1	5	3.10	0.59
MeHg	4	112	0.53	0.40	1	3	0.39	0.03
Mg	1	11	0.98	0.17	2	45	1.01	0.28
Mn	2	12	2.21	0.07	1	2	1.67	0.00
Nd	1	5	2.68	0.24	1	41	2.71	0.36
Ni	2	445	1.60	0.50	5	160	1.41	0.14
Pb	10	399	2.39	0.16	10	613	2.14	0.15
Pr	1	5	2.69	0.26	1	5	2.74	0.33
Sc	1	4	3.61	0.11	0			
Sm	1	5	2.76	0.28	1	5	2.81	0.31
Sr	1	6	1.49	0.11	1	5	1.01	0.25
Tb	1	5	2.86	0.33	1	3	2.92	0.63
Th	2	11	3.41	0.16	0			
Tm	1	5	3.09	0.45	1	4	3.07	0.52
UO2	4	513	2.64	0.31	4	485	2.28	0.43
VO	0				1	12	2.51	0.11
Y	1	5	2.84	0.34	1	3	2.93	0.44
Yb	1	4	3.12	0.43	1	5	3.05	0.51
Zn	2	43	1.87	0.15	3	28	1.71	0.11
	107	*4420*			*108*	*4004*		

Ag

Code	n	pI	pH	p[M]	pNu	LKMA	RMSD	Comments
HAg_01	10	3	5.8-7.0	6.4-12.1	5.2-7.8	1.78	1.00	
HAg_02	22	1	6.5	3.3-4.8	3.0-3.9	1.50	0.07	
HAg_03	23	1	6.5	3.2-4.6	3.2-4.1	1.30	0.04	
HAg_04	24	1	6.5	3.2-5.2	3.1-4.3	1.41	0.08	
	79					**1.50**	**0.30**	
FAg_01	**23**	1	6.5	3.2-4.9	3.3-4.3	**1.14**	**0.06**	

HAg_01 Rader KJ, Shadi TS, Mahony JD, Di Toro DM (2005) Measuring the partitioning of silver to organic carbon using solubility enhancement. Env. Toxicol. Chem. 24, 2833-2838.
HAg_02 Sikora FJ, Stevenson FJ (1988) Silver complexation by humic substances - conditional stability-constants and nature of reactive sites. Geoderma 42, 353-363
HAg_03 Sikora FJ, Stevenson FJ (1988) Silver complexation by humic substances - conditional stability-constants and nature of reactive sites. Geoderma 42, 353-363
HAg_04 Sikora FJ, Stevenson FJ (1988) Silver complexation by humic substances - conditional stability-constants and nature of reactive sites. Geoderma 42, 353-363

FAg_01 Sikora FJ, Stevenson FJ (1988) Silver complexation by humic substances - conditional stability-constants and nature of reactive sites. Geoderma 42, 353-363

Al

Code	n	pI	pH	p[M]	pNu	LKMA	RMSD	Comments
HAl_01	58	1.0-2.0	3.0-5.4	*3.1-5.1*	*3.0-3.6*	3.32	0.21	proton displacement
HAl_02	12	1.0-2.0	3.3-4.3	3.4-3.6	2.9-3.4	2.83	0.11	
HAl_03	24	1.3-2.1	2.3-3.2	2.1-3.7	3.5-4.2	2.15	0.09	
HAl_04	6	1	2.9-4.7	4.5-5.0	3.9-4.6	2.36	0.24	
	100					**2.67**	**0.16**	
FAl_01	48	1	3.6-5.5	4.9-9.1	2.7-4.5	2.40	0.18	
FAl_02	8	2.5	4.7	5.0-5.5	2.7-3.1	2.81	0.08	
FAl_03								pH data, this set was coded by Milne, not used here
FAl_04	35	2.0-4.0	4.0-8.2	5.1-17.2	3.4-5.3	2.53	0.38	
FAl_05	26	2	3.5-4.9	3.7-5.3	2.6-3.1	3.01	0.1	
	117					**2.69**	**0.19**	

HAl_01 Tipping E, Backes CA, Hurley MA (1988) The complexation of protons, aluminium and calcium by aquatic humic substances: A model incorporating binding-site heterogeneity and macroionic effects. Water Res 22, 597-611.
HAl_02 Tipping E, Backes CA, Hurley MA (1988) The complexation of protons, aluminium and calcium by aquatic humic substances: A model incorporating binding-site heterogeneity and macroionic effects. Water Res 22, 597-611.
HAl_03 Lamber J, Buddrus J, Burba P (1995) Evaluation of conditional stability constants of dissolved aluminium/humic substance complexes by means of 27Al nuclear magnetic resonance. Fres. J. Anal. Chem. 351, 83-87.
HAl_04 Zhou P, Yan H, Gu B (2005) Competitive complexation of metal ions with humic substances Chemosphere 58, 1327–1337

FAl_01 Browne, B.A. & Driscoll, C.T. (1993). pH-dependent binding of aluminium by a fulvic acid. Environ. Sci. Technol. 27, 915-922.
FAl_02 Clarke N, Danielsson LG, Sparen A (1995) Studies of aluminium complexation to humic and fulvic acids using a method for the determination of quickly reacting aluminium. Water Air Soil Pollut. 84, 103-116.
FAl_03 Tipping E, Backes CA, Hurley MA (1988) The complexation of protons, aluminium and calcium by aquatic humic substances: A model incorporating binding-site heterogeneity and macroionic effects. Water Res 22, 597-611.
FAl_04 Sutheimer, S.H. & Cabaniss, S.E. (1997). Aluminium binding to humic substances determined by high performance cation exchange chromatography. Geochim. Cosmochim. Acta 61, 1-9.
FAl_05 Simonsson M (2000) Interactions of aluminium and fulvic acid in moderately acid solutions: stoichiometry of the H+/Al3+ exchange European Journal of Soil Science 51, 655-666.

Am

Code	n	pI	pH	p[M]	pNu	LKMA	RMSD	Comments
HAm_01	20	1.0	6.0	4.5-6.6	3.0-3.4	2.8	0.04	
HAm_02	20	1.0	6.0	4.9-6.5	2.8-3.3	3.21	0.07	
HAm_03	7	1.0	4.65	4.7-5.8	2.9-3.1	3.51	0.1	
HAm_04	4	1.0	4.65	4.8-5.3	3.0-3.3	3.04	0.16	
HAm_05	6	1.0	3.8	trace	trace	2.73	0.06	
HAm_06	25	1.0	5.0-6.0	4.2-6.6	3.1-3.8	2.36	0.15	
HAm_07	61	0.2-2.0	6	4.5-6.9	2.9-3.6	2.99	0.13	
	143					**2.95**	**0.10**	
FAm-01	8	1	4.7	4.9-5.7	3.1-3.2	2.81	0.06	
FAm-02	9	1	4.7	4.7-5.5	2.9-3.1	3.01	0.1	
FAm-03	10	1	6	4.4-6.1	2.9-3.3	2.4	0.03	
	27					**2.74**	**0.06**	

HAm_01 Kim, J.I., Rhee, D.S. & Buckau, G. (1991a). Complexation of Am(III) with humic acids of different origin. Radiochim. Acta 52/53, 49-55.
HAm_02 Kim, J.I., Rhee, D.S. & Buckau, G. (1991a). Complexation of Am(III) with humic acids of different origin. Radiochim. Acta 52/53, 49-55.
HAm_03 Moulin, V., Robouch, P. & Vitorge, P. (1987). Spectrophotometric study of the interaction between americium(III) and humic materials. Inorg. Chim. Acta 140, 303-306.
HAm_04 Moulin, V., Robouch, P. & Vitorge, P. (1987). Spectrophotometric study of the interaction between americium(III) and humic materials. Inorg. Chim. Acta 140, 303-306.
HAm_05 Torres, R.A. & Choppin, G.R. (1984). Europium(III) and americium(III) stability constants with humic acid. Radiochim. Acta 35, 143-148.
HAm_06 Kim, J.I., Rhee, D.S. & Buckau, G. (1991a). Complexation of Am(III) with humic acids of different origin. Radiochim. Acta 52/53, 49-55.
HAm_07 Czerwinski KR, Kim JI, Rhee DS, Buckau G (1996) Complexation of trivalent actined ions (Am3+, Cm3+) with humic acid: the effect of ionic strength. Radiochim. Acta 72, 179-187.

FAm-01 Moulin, V., Robouch, P. & Vitorge, P. (1987). Spectrophotometric study of the interaction between americium(III) and humic materials. Inorg. Chim. Acta 140, 303-306.
FAm-02 Moulin, V., Robouch, P. & Vitorge, P. (1987). Spectrophotometric study of the interaction between americium(III) and humic materials. Inorg. Chim. Acta 140, 303-306.
FAm-03 Buckau G, Kim JI, Klenze D, Rhee DS, Wimmer H (1992) A comparative spectroscopic study of the fulvate complexation of trivalent transuranium ions. Radiochim. Acta 57, 105-111.

Ca

Code	n	pI	pH	p[M]	pNu	LKMA	RMSD	Comments
HCa_01	5	2.0	3.9-5.0	*3.0*	*3.3-3.8*	0.66	0.02	effect on pH
HCa_02	13	1.0	3.7-5.6	*1.5*	*3.0-3.6*	0.61	0.28	effect on pH
HCa_03	70	1.0	6.0-10.1	2.2-5.7	2.9-4.2	1.08	0.12	
HCa_04	18	1.1	8.2	3.4-6.9	3.1-5.1	1.18	0.17	
HCa_05								effect on pH / not used
HCa_06	285	0.7-1.7	4.8-10.0	6.2-8.6	4.2-5.5	1.21	0.39	
HCa_07	41	1.1	8.2	2.1-7.0	2.7-4.8	1.30	0.16	
HCa_08	117	1.5	5.1-8.1	3.0-5.9	2.6-4.2	1.55	0.18	
HCa_09	8	1.0	3.0-5.4	4.6-5.0	4.1-5.6	1.91	0.25	
	432					**1.19**	**0.20**	
FCa_01	30	1.0	5.0-9.0	2.0-3.2	2.7-3.6	0.79	0.06	
FCa_02	60	1.0	5.0-9.0	2.0-3.1	2.9-3.7	0.52	0.08	
FCa_03	42	1.0	3.0-9.9	*1.5*	*2.7-4.0*	0.51	0.20	proton displacement data
FCa_04	19	1.0-2.0	4.0-7.7	3.8-4.1	2.9-3.6	1.47	0.10	
FCa_05	2	1.0	3.5-5.0	5.3	4.9-5.6	1.58	0.06	
FCa_06	74	1.0-2.0	3.8-8.5	3.4-4.7	2.9-3.9	1.57	0.19	
FCa_07	87	1.0-2.0	3.5-8.0	3.4-4.6	3.0-4.6	1.55	0.20	
FCa_08	13	2.0	3.5-6.1	*2.5*	*2.7-3.2*	0.92	0.10	proton displacement data
FCa_09	54	1.0-2.0	3.7-6.9	9.0-11.1	8.4-10.0	1.35	0.37	
FCa_10	144	1-1.7	4.2-8.0	3.3-5.7	3.1-4.4	1.44	0.19	
FCa_11	32	1.0	6.5-8.5	2.8-4.8	2.7-4.2	1.17	0.20	
	557					**1.17**	**0.16**	

HCa_01 Tipping E, Backes CA, Hurley MA (1988) The complexation of protons, aluminium and calcium by aquatic humic substances: A model incorporating binding-site heterogeneity and macroionic effects. Water Res 22, 597-611.
HCa_02 Lead, J.R., Hamilton-Taylor, J., Hesketh, N., Jones, M.N., Wilkinson, A.E. & Tipping, E. (1994). A comparative study of proton and alkaline earth binding by humic substances. Anal. Chim. Acta 294, 319-327.
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HCa_04 Hering JG, Morel FMM (1988) Humic acid complexation of calcium and copper. Environ. Sci. Technol. 22, 1234-1237.
HCa_05 van Dijk H (1971) Cation binding by humic acids. Geoderma 5, 53-66.
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HCa_07 Hering JG, Morel FMM (1988) Humic acid complexation of calcium and copper. Environ. Sci. Technol. 22, 1234-1237.
HCa_08 Oste LA, Temminghoff EJM, Lexmond TM, Van Riemsdijk WH (2002) Measuring and Modeling Zinc and Cadmium Binding by Humic Acid Anal. Chem. 74, 856-862
HCa_09 Zhou P, Yan H, Gu B (2005) Competitive complexation of metal ions with humic substances Chemosphere 58, 1327–1337

FCa_01 Dempsey, B.A. (1981). The protonation, calcium complexation and adsorption of a fractionated aquatic fulvic acid. Ph.D. Thesis, Johns Hopkins University.
FCa_02 Dempsey, B.A. (1981). The protonation, calcium complexation and adsorption of a fractionated aquatic fulvic acid. Ph.D. Thesis, Johns Hopkins University.
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FCa_04 Marinsky, J.A., Reddy, M.M., Ephraim, J.H. & Mathuthu, A.S. (1992). Unpublished manuscript.
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FCa_06 Mathuthu, A.S. (1987). Ph.D. Thesis, State University of New York at Buffalo.
FCa_07 Mathuthu, A.S. (1987). Ph.D. Thesis, State University of New York at Buffalo.
FCa_08 Tipping E, Backes CA, Hurley MA (1988) The complexation of protons, aluminium and calcium by aquatic humic substances: A model incorporating binding-site heterogeneity and macroionic effects. Water Res 22, 597-611.
FCa_09 Higgo, J.J.W., Kinniburgh, D.G., Smith, B. & Tipping, E. (1993). Complexation of Co^{2+}, Ni^{2+}, $UO2^{2+}$ and Ca^{2+} by humic substances in groundwaters. Radiochim. Acta 61, 91-103.
FCa_10 Pinheiro JP, Mota AM, Benedetti MF (1999) Lead and Calcium Binding to Fulvic Acids: Salt Effect and Competition. Environ. Sci. Technol. 33, 3398-3404
FCa_11 Iglesias A, Lopez R, Fiol S, Antelo JM, Arce F (2003) Analysis of copper and calcium–fulvic acid complexation and competition effects Water Research 37, 3749–3755.

Cd

Code	n	pI	pH	p[M]	pNu	LKMA	RMSD	Comments
HCd_01	18	1.0	4.1-6.6	*2.8-5.4*	*2.9-3.8*	1.66	0.05	
HCd_02	56	1.7	5.0	3.3-8.4	2.9-6.0	1.62	0.17	
HCd_03	192	1.0	4.0-8.1	2.3-9.7	2.7-6.3	1.56	0.14	
HCd_04	10	1.0	4.5-6.5	4.1-5.6	4.1-5.4	1.28	0.25	
HCd_05	13	1.0	4.5-6.5	4.8-6.4	4.0-5.1	1.78	0.14	
HCd_06	14	1.0	5.0-6.0	4.1-5.0	3.0-3.5	1.68	0.11	
HCd_07	54	2.3	4.0-4.5	4.0-6.6	3.4-5.2	1.86	0.10	
HCd_08	18	2.0	4.5-6.5	4.7-6.9	4.0-5.8	1.39	0.08	
HCd_09	28	1.0	4.0-7.0	4.0-7.8	3.3-6.3	1.72	0.08	
HCd_10	51	1.0	5.5-6.0	3.7-7.5	3.2-5.4	1.54	0.07	
	454					**1.61**	**0.12**	
FCD_01	33	1	4.0-8.0	4.0-6.4	3.0-5.0	1.52	0.18	
FCD_02	27	1	4.0-8.0	4.3-6.1	3.0-4.8	1.70	0.15	
FCD_03	96	2	5.7-7.7	3.2-6.3	2.3-4.7	1.42	0.17	
FCD_04	70	1.0-2.0	3.6-7.9	3.1-4.2	2.7-4.5	1.64	0.19	
FCd_05	10	1	5.0	4.3-5.6	3.2-4.2	1.87	0.13	
FCd_06	44	1	5.5-6.0	3.5-6.5	3.3-5.5	1.30	0.13	
	280					**1.58**	**0.16**	

HCd_01 Stevenson, F.J. (1976). Stability constants of Cu2+, Pb2+, and Cd2+ complexes with humic acids. Soil Sci. Soc. Am. J. 40, 665-672.
HCd_02 Pinheiro JP, Mota AM, Simoes Goncalves ML (1994) Complexation study of humic acids with cadmium(II) and lead(II). Anal. Chim. Acta 284, 525-537.
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HCd_04 Fu G, Allen HE, Cao Y (1992) The importance of humic acids to proton and cadmium binding in sediments. Environ. Toxicol. Chem. 11, 1363-1372.
HCd_05 Fu G, Allen HE, Cao Y (1992) The importance of humic acids to proton and cadmium binding in sediments. Environ. Toxicol. Chem. 11, 1363-1372.
HCd_06 Lee, M.H., Choi, S.Y., Chung, K.H. & Moon, H. (1993). Complexation of cadmium(II) with humic acids: effects of pH and humic origin. Bull. Korean Chem. Soc. 14, 726-732.
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FCd_02 Saar, R.A. & Weber, J.H. (1979). Complexation of cadmium(II) with water- and soil-derived fulvic acids: effect of pH and fulvic acid concentration. Can. J. Chem. 57, 1263-1268.
FCd_03 Brady B, Pagenkopf GK (1978) Cadmium complaxation by soil fulvic acid. Can. J. Chem. 56, 2331-2336.
FCd_04 Mathuthu, A.S. & Ephraim, J.H. (1995). Binding of cadmium to Laurentide fulvic acid. Justification of the functionalities assigned to the predominant acidic moieties in the fulvic acid molecule. Talanta 42, 1803-1810.
FCd_05 Saar, R.A. & Weber, J.H. (1980). Comparison of spectrofluorometry and ion-selective electrode potentiometry for determination of complexes between fulvic acid and heavy-metal ions. Anal. Chem. 52, 2095-2100.
FCd_06 Gondar D, López R, Fiol S, Antelo JM, Arce F (2006) Cadmium, lead, and copper binding to humic acid and fulvic acid extracted from an ombrotrophic peat bog Geoderma 135, 196–203.

Ce

Code	n	pI	pH	p[M]	pNu	LKMA	RMSD	Comments
HCe_01	**5**	1.0-2.0	6.0-9.0	10.7-13.7	5.0-5.1	**2.68**	**0.26**	
FCe_01	**5**	1.0-2.0	6.0-9.0	12.1-15.3	5.2-5.7	**2.70**	**0.32**	

HCe_01 Sonke J (2006) Lanthanide-Humic Substances Complexation. II. Calibration of Humic Ion-Binding Model V. Environ. Sci. Technol. 40, 7481-7487.
FCe_01 Sonke J (2006) Lanthanide-Humic Substances Complexation. II. Calibration of Humic Ion-Binding Model V. Environ. Sci. Technol. 40, 7481-7487.

Cm

Code	n	pI	pH	p[M]	pNu	LKMA	RMSD	Comments
HCm_01	4	1.0	6.0	7.2-7.9	4.0-4.6	2.16	0.12	
HCm_02	6	1.0	5.0	6.4-7.4	3.3-3.4	3.20	0.05	
HCm_03	28	0.7-3.0	6.0	6.5-8.1	3.2-5.1	2.39	0.48	
	38					**2.58**	**0.22**	
FCm_01	**17**	1	6	7.1-7.9	4.1-4.8	**1.91**	**0.10**	

HCm_01 Kim, J.I., Wimmer, H. & Klenze, R. (1991b). A study of curium(III) humate complexation by time resolved laser fluorescence spectroscopy (TRLFS). Radiochim. Acta 54, 35-41.
HCm_02 Moulin, V., Tits, J., Moulin, C., Decambox, P., Mauchien & de Ruty, O. (1992). Complexation behaviour of humic substances towards actinides and lanthanides studied by time-resoloved laser-induced spectrofluorometry. Radiochim. Acta 58/59, 121-128.
HCm_03 Czerwinski KR, Kim JI, Rhee DS, Buckau G (1996) Complexation of trivalent actined ions (Am3+, Cm3+) with humic acid: the effect of ionic strength. Radiochim. Acta 72, 179-187.

FCm_01 Buckau G, Kim JI, Klenze D, Rhee DS, Wimmer H (1992) A comparative spectroscopic study of the fulvate complexation of trivalent transuranium ions. Radiochim. Acta 57, 105-111.

Co

Code	n	pI	pH	p[M]	pNu	LKMA	RMSD	Comments
HCo_01	16	0.7-1.7	5.0-8.1	trace	trace	~1.43		data not used
HCo_02	42	1.0-2.0	4.7-6.8	3.5-8.2	2.8-5.6	1.50	0.15	
HCo_03								data not used
HCo_04	215	0.7-1.7	5.0-8.0	11.4-13.4	5.3-7.0	1.51	0.56	
	257					**1.51**	**0.36**	
FCo_01	2	1	3.5-5.0	5.1	4.3-4.9	1.69	0.05	
FCo_02	65	1.0-2.0	3.6-6.5	trace	trace	1.65	0.32	NB trace data
FCo_03	75	0.7-2.3	3.5-7.1	8.6-11.2	7.4-10.3	1.22	0.44	
FCo_04	54	0.7-2.3	6.5	8.9-11.1	7.8-8.6	1.17	0.31	
FCo_05	94	0.7-2.0	6.5-7.0	8.5-11.1	7.3-8.3	1.19	0.33	
FCo_06	63	0.7-2.3	6.7-7.3	8.6-10.4	7.0-8.0	1.10	0.27	
FCo_07	107	0.7-1.7	4.9-8.0	10.8-12.6	5.5-6.8	1.33	0.51	Fitted, but only pH up to 8
FCo_08	24	1	5.0-8.0	11.0-12.1	9.2-10.3	1.21	0.37	Fitted, but only pH up to 8
	484					**1.32**	**0.33**	

HCo_01 van Loon, L.R., Granacher, S. & Harduf, H. (1992). Equilibrium dialysis-ligand exchange: a novel method for determining conditional stability constants of radionuclide-humic acid complexes. Anal. Chim. Acta 268, 235-246.
HCo_02 Zachara, J.M., Resch, C.T. & Smith, S.C. (1994). Influence of humic substances on Co2+ sorption by a subsurface mineral separate and its mineralogic components. Geochim. Cosmochim. Acta 58, 553-566.
HCo_03 van Dijk H (1971) Cation binding by humic acids. Geoderma 5, 53-66.
HCo_04 Glaus MA, Hummel W, Van Loon LR (1997) PSI Bericht, 97-13: Experimental determination and modelling of trace metal-humate interactions: a pragmatic approach for applications in groundwater. Paul Scherrer Institute, Villigen, Switzerland.

FCo_01 Schnitzer M, Skinner SIM (1967) Organo-metallic interactions in soils. 7. Stability constants of Pb++-, Ni++-, Mn++-, Co++-, Ca++-, and Mg++-fulvic acid complexes. Soil Sci. 103, 247-252.
FCo_02 Ephraim, J.H., Marinsky, J.A. & Cramer, S.J. (1989b). Complex-forming properties of natural organic acids. Fulvic acid complexes with cobalt, zinc and europium. Talanta 36, 437-443.
FCo_03 Higgo, J.J.W., Kinniburgh, D.G., Smith, B. & Tipping, E. (1993). Complexation of Co2+, Ni2+, UO22+ and Ca2+ by humic substances in groundwaters. Radiochim. Acta 61, 91-103.
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FCo_08 Glaus MA, Hummel W, Van Loon LR (1997) PSI Bericht, 97-13: Experimental determination and modelling of trace metal-humate interactions: a pragmatic approach for applications in groundwater. Paul Scherrer Institute, Villigen, Switzerland.

Cr

Code	n	pI	pH	p[M]	pNu	LKMA	RMSD	Comments
HCr_01	**31**	2.0	3.3-4.3	4.4-6.6	3.3-4.3	**2.52**	**0.15**	

HCr_01 Fukushima M, Nakayasu K, Tanaka S, Nakamura H (1995) Chromium(III) binding abilities of humic acids. Anal. Chim. Acta 317, 195-206.

Cu

Code	n	pI	pH	p[M]	pNu	LKMA	RMSD	Comments
HCu_01	40	0.7-1.7	2.7-4.7	3.2-7.1	2.8-4.6	2.75	0.08	
HCu_02						2.64	0.07	
HCu_03	161	1.0-2.3	4.0-4.5	3.5-8.6	2.6-4.4	2.97	0.14	
HCu_04	102	1	4.0-8.0	3.4-14.0	3.5-6.0	2.23	0.24	
HCu_05	17	1	2.8-6.9	4.4-7.7	3.1-5.5	2.13	0.22	
HCu_06	18	0.3	8.25	8.6-9.8	3.7-4.0	2.46	0.02	
HCu_07								effect on pH - not used
HCu_08	303	1.0-2.0	4.1-6.1	2.6-11.0	2.2-4.8	2.72	0.08	
HCu_09	51	1.0	4.0-8.0	3.6-14.0	2.8-5.7	2.44	0.16	
HCu_10	85	2.5	3.9-8.3	4.2-11.3	2.7-4.4	2.37	0.11	
HCu_11	56	2.0	6.0-8.0	6.8-12.0	3.2-5.5	2.49	0.12	
HCu_12	6	1.3-1.8	2.0	1.9-2.7	3.3-3.9	2.50	0.06	
HCu_13	39	2.0	5.0	4.1-6.8	3.0-3.7	2.43	0.02	
HCu_14	67	1.0-2.0	4.1	4.0-9.4	2.9-4.8	2.84	0.06	
	945					**2.54**	**0.11**	
FCu_01	33	1.0	5.1-8.4	4.5-10.5	3.0-4.9	2.04	0.20	
FCu_02	22	2.3	6.0	4.7-9.2	2.8-4.7	2.00	0.14	
FCu_03	60	1.0	3.5-6.0	3.9-6.3	3.0-3.7	2.31	0.03	
FCu_04	2	1.0	3.5-5.0	5.3	3.2-4.0	2.35	0.09	
FCu_05	27	1.0	3.0-6.0	3.7-4.9	2.6-3.9	2.31	0.11	
FCu_06	24	1.0	6.2	5.1-8.5	3.3-4.5	1.98	0.02	
FCu_07	15	3.0	6.0	4.1-10.4	2.7-5.1	1.84	0.06	
FCu_08	17	1.0	3.3-7.1	4.4-6.5	2.9-4.5	2.02	0.15	
FCu_09	15	1.0	5.0	4.0-6.5	3.0-3.8	2.28	0.03	
FCu_10	60	1.0	4.0-8.0	3.0-13.4	3.0-5.6	2.14	0.14	
FCu_11	56	1.0	4.0-8.0	5.0-10.6	3.0-4.5	2.23	0.11	
FCu_12	51	1.0-3.0	6.0	3.8-9.2	2.3-4.7	1.91	0.15	
FCu_13	63	2.0	6.0-8.0	6.7-12.8	3.1-5.2	2.30	0.09	
FCu_14	89	1.0	4.5-6.0	4.2-8.6	3.0-5.1	1.81	0.14	
FCu_15	106	1.0	4.5-6.0	4.3-8.3	3.0-5.1	1.82	0.13	
FCu_16	31	1.0	5.5-6.5	4.3-8.7	3.1-4.9	1.73	0.11	
	671					**2.07**	**0.11**	

HCu_01 Marinsky, J.A., Gupta, S. & Schindler, P. (1982). The interactions of Cu(II) ion with humic acid. J. Coll. Int. Sci. 89, 401-411.

HCu_02 Stevenson, F.J. (1976). Stability constants of Cu^{2+}, Pb^{2+}, and Cd^{2+} complexes with humic acids. Soil Sci. Soc. Am. J. 40, 665-672.

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HCu_04 Benedetti MF, Milne CJ, Kinniburgh DG, Van Riemsdijk WH, Koopal, LK (1995) metal-ion binding to humic substances: application of the non-ideal competitive adsorption model. Environ. Sci. Technol. 29, 446-457.

HCu_05 Town RM, Powell HKJ (1993) Ion-selective electrode potentiometric studies on the complexation of copper(II) by soil-derived humic and fulvic acids. Anal. Chim. Acta 279, 221-233.

HCu_06 Hering JG, Morel FMM (1988) Humic acid complexation of calcium and copper. Environ. Sci. Technol. 22, 1234-1237.

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HCu_08 Robertson AP (1996) Goethite/humic acid interactions and their effects on copper(II) binding. Ph D Dissertation, Stanford University, CA.

HCu_09 Christl I, Milne CJ, Kinniburgh DG, Kretzschmar R (2000) Relating ion-binding by fulvic and humic acids to chemical composition and molecular size: II. Metal binding. Environ. Sci. Technol. 35, 2512-2517

HCu_10 Oste LA unpublished; data supplied to CJ Milne

HCu_11 Christl I, Milne CJ, Kinniburgh DG, Kretzschmar R (2000) Relating ion-binding by fulvic and humic acids to chemical composition and molecular size: II. Metal binding. Environ. Sci. Technol. 35, 2512-2517

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FCu_11 possibly Filius JD unpublished; data supplied to CJ Milne

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FCu_13 Christl I, Metzger A, Heidmann I, Kretzschmar R (2005) Effect of Humic and Fulvic Acid Concentrations and Ionic Strength on Copper and Lead Binding Environ. Sci. Technol. 39, 5319-5326

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FCu_16 Iglesias A, Lopez R, Fiol S, Antelo JM, Arce F (2003) Analysis of copper and calcium–fulvic acid complexation and competition effects Water Research 37, 3749–3755.

Dy

Code	n	pI	pH	p[M]	pNu	LKMA	RMSD	Comments
HDy_01	5	1.0	5.0	5.8-6.5	3.9-4.3	3.43	0.04	
HDy_02	5	1.0-2.0	6.0-9.0	11.9-15.6	5.3-5.6	2.94	0.42	
	10					**3.19**	**0.23**	
FDy_01	**5**	1.0-2.0	6.0-8.9	13.5-17.3	5.8-6.7	**2.93**	**0.46**	

HDy_01 Moulin, V., Tits, J., Moulin, C., Decambox, P., Mauchien & de Ruty, O. (1992). Complexation behaviour of humic substances towards actinides and lanthanides studied by time-resoloved laser-induced spectrofluorometry. Radiochim. Acta 58/59, 121-128.
HDy_02 Sonke J (2006) Lanthanide-Humic Substances Complexation. II. Calibration of Humic Ion-Binding Model V. Environ. Sci. Technol. 40, 7481-7487.

FDy_01 Sonke J (2006) Lanthanide-Humic Substances Complexation. II. Calibration of Humic Ion-Binding Model V. Environ. Sci. Technol. 40, 7481-7487.

Er

Code	n	pI	pH	p[M]	pNu	LKMA	RMSD	Comments
HEr_01	**4**	1.0-2.0	7.0-9.0	13.8-16.2	5.3-5.9	**3.03**	**0.50**	
FEr_01	**3**	1.0-1.1	6.0-9.0	14.1-17.9	5.8-6.4	**3.09**	**0.46**	

HEr_01 Sonke J (2006) Lanthanide-Humic Substances Complexation. II. Calibration of Humic Ion-Binding Model V. Environ. Sci. Technol. 40, 7481-7487.

FEr_01 Sonke J (2006) Lanthanide-Humic Substances Complexation. II. Calibration of Humic Ion-Binding Model V. Environ. Sci. Technol. 40, 7481-7487.

Eu

Code	n	pI	pH	p[M]	pNu	LKMA	RMSD	Comments
HEu_01	8	1.3	4.5	5.0-6.6	3.7-4.3	2.51	0.08	
HEu_02	35	1.0	5.0-6.0	4.6-8.7	3.0-4.1	2.96	0.13	
HEu_03	40	1.0	8.9-9.1	15.6-19.6	4.5-8.1	3.37	0.11	
HEu_04	168	1.0-1.7	5.0-9.9	9.2-20.3	4.1-8.6	3.25	0.73	
HEu-05	5	1.0-2.0	6.0-9.0	11.1-14.6	5.2-5.3	2.77	0.28	
	256					**2.97**	**0.27**	
FEu_01	28	1.2-3.2	2.5-3.5	2.0-6.6	2.5-4.6	2.46	0.28	
FEu_02	54	0.5-2.0	3.5-5.3	11.2-15.7	7.2-8.2	3.20	0.39	
FEu_03	32	1	5.6-6.6	5.1-7.3	2.8-4.1	2.34	0.13	
FEu_04	13	1	2.9-6.3	13.0-15.8	11.1	2.42	0.45	
FEu_05	15	1	3.6-6.0	6.6-7.1	3.9-5.0	2.28	0.37	
FEu_06	17	2.3	2.0-7.4	6.9-8.7	4.2-5.8	2.71	0.50	
FEu_07	22	1	6	4.8-8.4	3.1-4.4	2.25	0.06	
FEu_08	89	1.0-1.7	5.0-9.9	12.8-20.3	6.2-8.3	2.98	0.59	
FEu_09	51	1.0-1.7	5.0-9.9	12.7-19.5	6.8-8.2	2.69	0.91	
FEu_10	4	1.0-2.0	6.0-8.0	5.6-6.1	12.8-15.0	2.78	0.22	
	325					**2.61**	**0.39**	

HEu_01 Carlsen, L., Bo, P. & Larsen, G. (1984) Radionuclide-humic acid interactions studied by dialysis. In Geochemical Behaviour of Radioactive Waste, ed. G.S. Barney, J.D. Navratil & W.W. Schulz, pp. 167-178. Washington, DC: American Chemical Society.
HEu_02 Caceci MS (1985) The interactions of humic acid with europium (III). Complexation strength as a function of load and pH. Radiochim Acta 39, 51-56.
HEu_03 Maes A, De Brabandere J, 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.
HEu_04 Glaus MA, Hummel W, Van Loon LR (1997) PSI Bericht, 97-13: Experimental determination and modelling of trace metal-humate interactions: a pragmatic approach for applications in groundwater. Paul Scherrer Institute, Villigen, Switzerland.
HEu-05 Sonke J (2006) Lanthanide-Humic Substances Complexation. II. Calibration of Humic Ion-Binding Model V. Environ. Sci. Technol. 40, 7481-7487.

FEu_01 Dobbs, J.C., Susetyo, W., Knight,F.E., Castles, M.A. & Carreira, L.A. (1989). A novel approach to metal-humic complexation studies by lanthanide ion probe spectroscopy. Int. J. Environ. Anal. Chem. 37, 1-17.
FEu_02 Ephraim, J.H., Marinsky, J.A. & Cramer, S.J. (1989). Complex-forming properties of natural organic acids. Fulvic acid complexes with cobalt, zinc and europium. Talanta 36, 437-443.
FEu_03 Bidoglio G, Grenthe I, Qi P, Robouch P, Omenetto N (1991) Complexation of Eu and Tb with fulvic-acids as studied by time-resolved laser-indued fluorescence. Talanta 38, 999-1008.
FEu_04 Nordén, M., Ephraim, J.H. & Allard, B. (1993). The binding of strontium and europium by an aquatic fulvic acid - ion exchange distribution and ultrafiltration studies. Talanta 40, 1425-1432.
FEu_05 Lead, J.R., Hamilton-Taylor, J., Peters, A., Reiner, S & Tipping, E. (1998). Europium binding by fulvic acids. Anal. Chim. Acta. 369, 171-180.
FEu_06 Lead, J.R., Hamilton-Taylor, J., Peters, A., Reiner, S & Tipping, E. (1998). Europium binding by fulvic acids. Anal. Chim. Acta. 369, 171-180.
FEu_07 Shin HS, Lee BH, Yang HB, Yun SS, Moon H (1996) Bimodal normal distribution model for binding of trivalent europium by soil fulvic acid. J. Radioanal. Nucl. Chem. 209, 123-133.
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FEu_09 Glaus MA, Hummel W, Van Loon LR (1997) PSI Bericht, 97-13: Experimental determination and modelling of trace metal-humate interactions: a pragmatic approach for applications in groundwater. Paul Scherrer Institute, Villigen, Switzerland.
FEu_10 Sonke J (2006) Lanthanide-Humic Substances Complexation. II. Calibration of Humic Ion-Binding Model V. Environ. Sci. Technol. 40, 7481-7487.

FeIII

Code	n	pI	pH	p[M]	pNu	LKMA	RMSD	Comments
HFe3_01	10	0.2	3.6-8.2	7.1-21.9	2.7-5.7	3.45	0.37	Omitted the pH 12 point
HFe3_02	10	1.0-1.7	2	2.1-3.3	3.1-3.4	2.92	0.03	
	20					**3.19**	**0.20**	
FFe3_01	**8**	1.0	2.5	4.4-5.7	3.2-3.6	**3.03**	**0.29**	

HFe3_01 Liu XW, Millero FJ (1999) The solubility of iron hydroxide in sodium chloride solutions. Geochim. Cosmochim. Acta 63, 3487-3497.
HFe3_02 Ghabbour EA, Shaker M, El-Toukhy A, Abid IM, Davies G (2006) Thermodynamics of metal cation binding by a soil-derived humic acid: binding of Fe(III0, Pb(II), and Cu(II). Chemosphere 63, 477-483.

FFe3_01 Langfrod CH, Khan TR (1975) Kinetics and equilibrium binding of Fe3+ by a fulvic acid: a study by stopped flow methods. Can. J. Chem. 53, 2979-2984.

Gd

Code	n	pI	pH	p[M]	pNu	LKMA	RMSD	Comments
HGd_01	**5**	1.0-2.0	6.0-9.0	11.1-14.6	5.3-5.4	**2.77**	**0.28**	
FGd_01	**4**	1.0-1.1	6.0-9.0	12.8-16.6	5.6-6.2	**2.84**	**0.48**	

HGd_01 Sonke J (2006) Lanthanide-Humic Substances Complexation. II. Calibration of Humic Ion-Binding Model V. Environ. Sci. Technol. 40, 7481-7487.

FGd_01 Sonke J (2006) Lanthanide-Humic Substances Complexation. II. Calibration of Humic Ion-Binding Model V. Environ. Sci. Technol. 40, 7481-7487.

Hg

Code	n	pI	pH	p[M]	pNu	LKMA	RMSD	Comments
HHg_01	11	0.3	3.0-3.6	28.2-31.1	3.4-5.0	4.62	0.19	
HHg_02	6	0.3	4.1-5.0	30.9-34.0	3.1-4.0	4.94	0.44	
HHg_03	19	2	2.0	2.6-3.8	3.2-4.0	2.74	0.1	
	36					**4.10**	**0.24**	
FHg-01	2	1	3.0-4.0	5.0-6.4	2.8-2.9	3.81	0.06	
FHg-02	2	2	6	18.8-192	4.7-5.4	2.62	0.27	hydrophilic
FHg-03	4	2	4.0-6.0	18.9-19.4	3.7-5.5	3.89	0.37	hydrophobic
FHg-04	33	1	4.9-7.0	10.2-27.1	2.9-7.0	3.28	0.33	
FHg-05	4	1	4.0-7.2	24.3-29.8	6.3	3.39	0.08	
	45					**3.40**	**0.22**	

HHg_01 Khwaja AR, Bloom PR, Brezonik PL (2006) Binding constants of divalent mercury (Hg2+) in soil humic acids and soil organic matter. Environ. Sci. Technol. 40, 844-849.
HHg_02 Khwaja AR, Bloom PR, Brezonik PL (2006) Binding constants of divalent mercury (Hg2+) in soil humic acids and soil organic matter. Environ. Sci. Technol. 40, 844-849.
HHg_03 Ghabbour EA, Shaker M, El-Toukhy A, Abid IM, Davies G (2006) Thermodynamics of metal cation binding by a soil-derived humic acid. 2. Binding of Mn(II), Co(NH3)(3+)(6aq) and Hg(II). Chemosphere 64, 826-833.

FHg-01 Cheam, V., Gamble, D.S., 1974. Metal-fulvic acid chelation equilibrium in aqueous NaNO3 solution. Hg(II), Cd(II), and Cu(II) fulvate complexes. Can. J. Soil Sci. 54, 413-417.
FHg-02 Benoit, J.M., Mason, R.P., Gilmour, C.C., Aiken, G.R., 2001. Constants for mercury binding by dissolved organic matter isolates from the Florida Everglades. Geochim. Cosmochim. Acta 65, 4445-4451.
FHg-03 Benoit, J.M., Mason, R.P., Gilmour, C.C., Aiken, G.R., 2001. Constants for mercury binding by dissolved organic matter isolates from the Florida Everglades. Geochim. Cosmochim. Acta 65, 4445-4451.
FHg-04 Haitzer, M., Aiken, G.R., Ryan, J.N., 2002. Binding of mercury(II) to dissolved organic matter: the role of the mercury-to-DOM concentration ratio. Environ. Sci. Technol. 36, 3564-3570.
FHg-05 Haitzer, M., Aiken, G.R., Ryan, J.N., 2003. Binding of mercury(II) to aquatic humic substances: influence of pH and source of humic substances. Environ. Sci. Technol. 37, 2436-2441.

Ho

Code	n	pI	pH	p[M]	pNu	LKMA	RMSD	Comments
HHo_01	**5**	1.0-2.0	6.0-9.0	12.1-15.9	5.3-5.8	**2.95**	**0.48**	
FHo_01	**4**	1.0-1.1	6.0-9.0	13.8-17.5	5.9-7.0	**2.96**	**0.60**	

HHo_01 Sonke J (2006) Lanthanide-Humic Substances Complexation. II. Calibration of Humic Ion-Binding Model V. Environ. Sci. Technol. 40, 7481-7487.

FHo_01 Sonke J (2006) Lanthanide-Humic Substances Complexation. II. Calibration of Humic Ion-Binding Model V. Environ. Sci. Technol. 40, 7481-7487.

La

Code	n	pI	pH	p[M]	pNu	LKMA	RMSD	Comments
HLa_01	**5**	1.0-2.0	6.0-8.9	10.8-13.3	5.0-5.1	**2.64**	**0.30**	
FLa_01	**5**	1.0-2.0	6.0-9.0	12.3-14.9	5.2-5.4	**2.74**	**0.25**	

HLa_01 Sonke J (2006) Lanthanide-Humic Substances Complexation. II. Calibration of Humic Ion-Binding Model V. Environ. Sci. Technol. 40, 7481-7487.

FLa_01 Sonke J (2006) Lanthanide-Humic Substances Complexation. II. Calibration of Humic Ion-Binding Model V. Environ. Sci. Technol. 40, 7481-7487.

Lu

Code	n	pI	pH	p[M]	pNu	LKMA	RMSD	Comments
HLu_01	**5**	1.0-2.0	6.0-9.0	13.2-17.0	5.4-6.1	**3.17**	**0.41**	
FLu_01	**5**	1.0-2.0	6.0-9.0	15.0-18.6	6.2-7.7	**3.10**	**0.59**	

HLu_01 Sonke J (2006) Lanthanide-Humic Substances Complexation. II. Calibration of Humic Ion-Binding Model V. Environ. Sci. Technol. 40, 7481-7487.

FLu_01 Sonke J (2006) Lanthanide-Humic Substances Complexation. II. Calibration of Humic Ion-Binding Model V. Environ. Sci. Technol. 40, 7481-7487.

MeHg

Code	n	pI	pH	p[M]	pNu	LKMA	RMSD	Comments
HMeHg_01	4	4	7	12.0-15.0	4.6-5.4	0.02	0.40	
HMeHg_02	3	4	7	12.0-14.0	4.6-5.1	0.39	0.06	
HMeHg_03	54	3	3.5-9.2	10.4-13.6	6.1-7.4	0.99	0.46	
HMeHg_04	51	3	3.5-9.2	9.8-13.5	6.3-8.1	0.7	0.67	
	112					**0.53**	**0.40**	
FMeHg_01	**3**	4	7	12.0-14.0	4.7-5.3	**0.39**	**0.03**	

HMeHg_01 Hintelmann, H., Welbourn, P.M. & Evans, R.D. (1995). Binding of methylmercury compounds by humic and fulvic acids. Wat. Air Soil Pollut. 80, 1031-1034.
HMeHg_02 Hintelmann, H., Welbourn, P.M. & Evans, R.D. (1995). Binding of methylmercury compounds by humic and fulvic acids. Wat. Air Soil Pollut. 80, 1031-1034.
HMeHg_03 Amirbahman A, Reid AL, Kahl JS, Arnold C (2002) Association of methylmercury with dissolved humic acids. Environ. Sci. Technol. 36, 690-695.
HMeHg_04 Amirbahman A, Reid AL, Kahl JS, Arnold C (2002) Association of methylmercury with dissolved humic acids. Environ. Sci. Technol. 36, 690-695.

FMeHg_01 Hintelmann, H., Welbourn, P.M. & Evans, R.D. (1995). Binding of methylmercury compounds by humic and fulvic acids. Wat. Air Soil Pollut. 80, 1031-1034.

Mg

Code	n	pI	pH	p[M]	pNu	LKMA	RMSD	Comments
HMg_01	**11**	1	3.6-7.2	1.5	2.9-3.5	**0.98**	**0.17**	proton displacement
FMg_01	2	1	3.5-5.0	5	5.1-5.3	1.44	0.28	
FMg_02	43	1	3.1-10.0	1.5	2.7-4.0	0.58	0.28	proton displacement
	45					**1.01**	**0.28**	

HMg_01 Lead, J.R., Hamilton-Taylor, J., Hesketh, N., Jones, M.N., Wilkinson, A.E. & Tipping, E. (1994). A comparative study of proton and alkaline earth binding by humic substances. Anal. Chim. Acta 294, 319-327.

FMg_01 Schnitzer M, Skinner SIM (1967) Organo-metallic interactions in soils. 7. Stability constants of Pb++-, Ni++-, Mn++-, Co++-, Ca++-, and Mg++-fulvic acid complexes. Soil Sci. 103, 247-252.
FMg_02 Lead, J.R., Hamilton-Taylor, J., Hesketh, N., Jones, M.N., Wilkinson, A.E. & Tipping, E. (1994). A comparative study of proton and alkaline earth binding by humic substances. Anal. Chim. Acta 294, 319-327.

Mn

Code	n	pI	pH	p[M]	pNu	LKMA	RMSD	Comments
HMn_02	6	1.3-1.7	2.0	2.2-2.9	3.6-4.4	2.24	0.07	
HMn_03	6	1.2-1.8	2.0	2.2-2.9	3.8-4.5	2.18	0.07	
	12					**2.21**	**0.07**	
FMn_01	**2**	1	3.5-5.0	5.2-5.3	4.6-5.4	**1.67**	**0.00**	

HMn_02 Ghabbour EA, Shaker M, El-Toukhy A, Abid IM, Davies G (2006) Thermodynamics of metal cation binding by a soil-derived humic acid. 2. Binding of Mn(II), Co(NH3)(3+)(6aq) and Hg(II). Chemosphere 64, 826-833.
HMn_03 Ghabbour EA, Shaker M, El-Toukhy A, Abid IM, Davies G (2006) Thermodynamics of metal cation binding by a soil-derived humic acid. 2. Binding of Mn(II), Co(NH3)(3+)(6aq) and Hg(II). Chemosphere 64, 826-833.

FMn_01 Schnitzer M, Skinner SIM (1967) Organo-metallic interactions in soils. 7. Stability constants of Pb++-, Ni++-, Mn++-, Co++-, Ca++-, and Mg++-fulvic acid complexes. Soil Sci. 103, 247-252.

Nd

Code	n	pI	pH	p[M]	pNu	LKMA	RMSD	Comments
HNd_01	**5**	1.0-2.0	6.0-8.9	10.6-14.0	5.1-5.2	**2.68**	**0.24**	
FNd_01	**41**	1.0-3.0	6.0-9.0	12.4-17.7	4.8-7.2	**2.71**	**0.36**	

HNd_01 Sonke J (2006) Lanthanide-Humic Substances Complexation. II. Calibration of Humic Ion-Binding Model V. Environ. Sci. Technol. 40, 7481-7487.

FNd_01 Sonke J (2006) Lanthanide-Humic Substances Complexation. II. Calibration of Humic Ion-Binding Model V. Environ. Sci. Technol. 40, 7481-7487.

Ni

Code	n	pI	pH	p[M]	pNu	LKMA	RMSD	Comments
HNi_01								proton displacement - not used
HNi_02	437	1.0-1.7	5.0-9.9	9.2-20.3	4.1-8.6	1.49	0.71	
HNi_03	8	1.0	2.9-5.8	4.9-5.4	4.2-4.8	1.7	0.29	
	445					**1.60**	**0.50**	
FNI_01	2	1	3.5-5.0	5.1-5.3	3.9-4.4	1.89	0.04	
FNI_02	52	0.7-2.0	6.6-7.8	8.2-10.0	6.3-7.1	1.19	0.20	
FNI_03	50	0.7-2.0	6.7-7.2	8.2-10.2	6.3-6.8	1.20	0.18	
FNI_04	50	0.7-2.0	6.6-7.0	8.2-10.0	6.4-7.1	1.14	0.16	
FNI_05	6	1	9.8	15.1-15.5	8.5-8.7	1.63	0.12	
	160					**1.41**	**0.14**	

HNi_01 van Dijk H (1971) Cation binding by humic acids. Geoderma 5, 53-66.
HNi_02 Glaus MA, Hummel W, Van Loon LR (1997) PSI Bericht, 97-13: Experimental determination and modelling of trace metal-humate interactions: a pragmatic approach for applications in groundwater. Paul Scherrer Institute, Villigen, Switzerland.
HNi_03 Zhou P, Yan H, Gu B (2005) Competitive complexation of metal ions with humic substances Chemosphere 58, 1327–1337

FNi_01 Schnitzer M, Skinner SIM (1967) Organo-metallic interactions in soils. 7. Stability constants of Pb++-, Ni++-, Mn++-, Co++-, Ca++-, and Mg++-fulvic acid complexes. Soil Sci. 103, 247-252.
FNi_02 Higgo, J.J.W., Kinniburgh, D.G., Smith, B. & Tipping, E. (1993). Complexation of Co2+, Ni2+, UO22+ and Ca2+ by humic substances in groundwaters. Radiochim. Acta 61, 91-103.
FNi_03 Higgo, J.J.W., Kinniburgh, D.G., Smith, B. & Tipping, E. (1993). Complexation of Co2+, Ni2+, UO22+ and Ca2+ by humic substances in groundwaters. Radiochim. Acta 61, 91-103.
FNi_04 Higgo, J.J.W., Kinniburgh, D.G., Smith, B. & Tipping, E. (1993). Complexation of Co2+, Ni2+, UO22+ and Ca2+ by humic substances in groundwaters. Radiochim. Acta 61, 91-103.
FNi_05 Glaus MA, Hummel W, Van Loon LR (1997) PSI Bericht, 97-13: Experimental determination and modelling of trace metal-humate interactions: a pragmatic approach for applications in groundwater. Paul Scherrer Institute, Villigen, Switzerland.

Pb

Code	n	pI	pH	p[M]	pNu	LKMA	RMSD	Comments
HPb_01	62	1	3.2-6.5	3.0-10.0	2.8-3.6	2.62	0.11	proton displacement
HPb_02	6	1.0	5.0	5.1-5.2	3.3-3.4	2.44	0.02	
HPb_03	29	1.0	5.0	5.3-10.8	3.2-5.7	2.60	0.20	
HPb_05	100	1.0-1.1	3.9-8.0	2.7-10.5	2.3-5.8	2.22	0.29	
HPb_06	22	2.0	4.5	5.9-9.9	3.9-6.1	2.47	0.14	
HPb_07	17	2.3	4.5	4.3-7.1	3.1-4.5	2.47	0.09	
HPb_08	52	1.0	4.0-8.0	3.4-10.3	2.6-5.2	2.20	0.20	
HPb_09	66	2.0	4.0-5.5	4.2-9.3	3.0-5.7	2.46	0.20	
HPb_10	45	1.0	5.5-6.0	4.3-7.7	3.0-4.8	2.06	0.15	
	399					**2.39**	**0.16**	
FPb_01	41	1	4.0-6.0	4.4-6.2	2.8-4.2	2.24	0.11	
FPb_02	2	1	3.5-5.0	5.9-6.2	4.3-4.9	2.06	0.09	
FPb_03	29	1	4.0-5.0	4.4-5.9	3.0-4.2	2.28	0.12	
FPb_04	46	1	4.0-6.0	4.4-6.7	2.5-4.5	2.37	0.24	
FPb_05	20	1	6.4	3.6-6.4	2.7-4.1	1.83	0.10	
FPb_06	16	1	5	4.2-6.0	2.7-3.6	2.48	0.13	
FPb_07	305	2	4.0-5.0	5.0-9.0	3.2-6.1	2.10	0.10	
FPb_08	58	1	4.0-8.0	3.4-10.3	2.6-5.0	2.15	0.26	
FPb_09	51	2.0	4.0-6.0	4.8-9.6	2.9-5.3	2.2	0.23	
FPb_10	45	1.0	5.5-6.0	3.8-6.9	3.0-4.9	1.71	0.12	
	613					**2.14**	**0.15**	

HPb_01 Stevenson, F.J. (1976). Stability constants of Cu^{2+}, Pb^{2+}, and Cd^{2+} complexes with humic acids. Soil Sci. Soc. Am. J. 40, 665-672.
HPb_02 Ibarra JV, Osacar J, Gavilan JM (1979) Acidos humicos de lignitos: II. Complejos con los iones estroncio, plomo, uranilo y torio. Medida de sus constantes de estabilidad. Anales de Quimica 77, 224-229.
HPb_03 Pinheiro JP, Mota AM, Simoes Goncalves ML (1994) Complexation study of humic acids with cadmium(II) and lead(II). Anal. Chim. Acta 284, 525-537.
HPb_05 Christl I, Milne CJ, Kinniburgh DG, Kretzschmar R (2000) Relating ion-binding by fulvic and humic acids to chemical composition and molecular size: II. Metal binding. Environ. Sci. Technol. 35, 2512-2517
HPb_06 Mota AM, Rato A, Brazia C, Simoes Goncalves ML (1996) Competition of Al3+ in complexation of humic matter with Pb2+: a comparative study with other ions. Environ. Sci. technol. 30, 1970-1974.
HPb_07 Pinheiro JP, Mota AM, Benedetti MF (2000) Effect of aluminium competition on lead and cadmium binding to humic acids at variable ionic strength. Environ. Sci. Technol. 34, 5137-5143.
HPb_08 Christl I, Milne CJ, Kinniburgh DG, Kretzschmar R (2000) Relating ion-binding by fulvic and humic acids to chemical composition and molecular size: II. Metal binding. Environ. Sci. Technol. 35, 2512-2517
HPb_09 Christl I, Metzger A, Heidmann I, Kretzschmar R (2005) Effect of Humic and Fulvic Acid Concentrations and Ionic Strength on Copper and Lead Binding Environ. Sci. Technol. 39, 5319-5326
HPb_10 Gondar D, López R, Fiol S, Antelo JM, Arce F (2006) Cadmium, lead, and copper binding to humic acid and fulvic acid extracted from an ombrotrophic peat bog Geoderma 135, 196–203.

FPb_01 Saar, R.A. & Weber, J.H. (1980b). Lead(II)-fulvic acid complexes. Conditional stability constants, solubility, and implications for lead(II) mobility. Environ. Sci. Technol. 14, 877-880.
FPb_02 Schnitzer M, Skinner SIM (1967) Organo-metallic interactions in soils. 7. Stability constants of Pb++-, Ni++-, Mn++-, Co++-, Ca++-, and Mg++-fulvic acid complexes. Soil Sci. 103, 247-252.
FPb_03 Saar RA, Weber JH (1980) Comparison of spectrofluorometry and ion-selctive electrode potentiometry for determination of complexes between fulvic acid and heavy-metal ions. Analyt. Chem. 52, 2095-2100.
FPb_04 Saar RA, Weber JH (1980) Lead(II)-fulvic acid complexes. Conditional stability constants, solubility and implications for lead(II) mobility. Environ. Sci. Technol. 14, 877-880.
FPb_05 Turner DR, Varney MS, Whitfield M, Mantoura RFC, Riley JP (1986) Electrochemical studies of copper and lead complexation by fulvic acid. I. Potentiometric measurements and a critical comparison of metal binding models. Geochim. Cosmochim. Acta 50, 289-297.
FPb_06 Lead(II) complexation by fulvic acid: how it differs from fulvic acid complexation of copper (II) and cadmium (II). Geochim. Cosmochim. Acta 44, 1381-1384.
FPb_07 Pinheiro JP, Mota AM, Benedetti MF (1999) Lead and Calcium Binding to Fulvic Acids: Salt Effect and Competition. Environ. Sci. Technol. 33, 3398-3404
FPb_08 Christl I, Milne CJ, Kinniburgh DG, Kretzschmar R (2000) Relating ion-binding by fulvic and humic acids to chemical composition and molecular size: II. Metal binding. Environ. Sci. Technol. 35, 2512-2517
FPb_09 Christl I, Metzger A, Heidmann I, Kretzschmar R (2005) Effect of Humic and Fulvic Acid Concentrations and Ionic Strength on Copper and Lead Binding Environ. Sci. Technol. 39, 5319-5326
FPb_10 Gondar D, López R, Fiol S, Antelo JM, Arce F (2006) Cadmium, lead, and copper binding to humic acid and fulvic acid extracted from an ombrotrophic peat bog Geoderma 135, 196–203.

Pr

Code	n	pI	pH	p[M]	pNu	LKMA	RMSD	Comments
HPr_01	**5**	1.0-2.0	6.0-9.0	10.6-14.0	5.1-5.2	**2.69**	**0.26**	
FPr_01	**5**	1.0-2.0	6.0-9.0	12.2-15.6	5.3-5.8	**2.74**	**0.33**	

HPr_01 Sonke J (2006) Lanthanide-Humic Substances Complexation. II. Calibration of Humic Ion-Binding Model V. Environ. Sci. Technol. 40, 7481-7487.

FPr_01 Sonke J (2006) Lanthanide-Humic Substances Complexation. II. Calibration of Humic Ion-Binding Model V. Environ. Sci. Technol. 40, 7481-7487.

Sc

Code	n	pI	pH	p[M]	pNu	LKMA	RMSD	Comments
HSc_01	**4**	1.0-2.0	7.0-9.0	17.5-20.1	4.6-4.9	**3.61**	**0.11**	

HSc_01 Sonke J (2006) Lanthanide-Humic Substances Complexation. II. Calibration of Humic Ion-Binding Model V. Environ. Sci. Technol. 40, 7481-7487.

Sm

Code	n	pI	pH	p[M]	pNu	LKMA	RMSD	Comments
HSm_01	**5**	1.0-2.0	6.0-9.0	10.9-14.6	5.2-5.3	**2.76**	**0.28**	
FSm_01	**5**	1.0-2.0	6.0-9.0	12.9-16.1	5.5-6.0	**2.81**	**0.31**	

HSm_01 Sonke J (2006) Lanthanide-Humic Substances Complexation. II. Calibration of Humic Ion-Binding Model V. Environ. Sci. Technol. 40, 7481-7487.

FSm_01 Sonke J (2006) Lanthanide-Humic Substances Complexation. II. Calibration of Humic Ion-Binding Model V. Environ. Sci. Technol. 40, 7481-7487.

Sr

Code	n	pI	pH	p[M]	pNu	LKMA	RMSD	Comments
HSr_01	**6**	1.0	5.0	5.1	5.0-5.3	**1.49**	**0.11**	
FSr_01	**5**	1	4.6-8.3	***trace***	***trace***	**1.01**	**0.25**	

HSr_01 Ibarra JV, Osacar J, Gavilan JM (1979) Acidos humicos de lignitos: II. Complejos con los iones estroncio, plomo, uranilo y torio. Medida de sus constantes de estabilidad. Anales de Quimica 77, 224-229.

FSr_01 Nordén, M., Ephraim, J.H. & Allard, B. (1991) Interaction of strontium and europium with an aquatic fulvic acid studied by ultrafiltration and ion exchange techniques. In Humic Substances in the Aquatic and Terrestrial Environments ed B Allard, pp 297-303, Springer, Berlin.

Tb

Code	n	pI	pH	p[M]	pNu	LKMA	RMSD	Comments
HTb_01	**5**	1.0-2.0	6.0-9.0	11.6-15.1	5.3-5.5	**2.86**	**0.33**	
FTb_01	**3**	1.0-1.1	7.1-9.0	14.5-17.1	5.6-6.5	**2.92**	**0.63**	

HTb_01 Sonke J (2006) Lanthanide-Humic Substances Complexation. II. Calibration of Humic Ion-Binding Model V. Environ. Sci. Technol. 40, 7481-7487.

FTb_01 Sonke J (2006) Lanthanide-Humic Substances Complexation. II. Calibration of Humic Ion-Binding Model V. Environ. Sci. Technol. 40, 7481-7487.

Th

Code	n	pI	pH	p[M]	pNu	LKMA	RMSD	Comments
HTh_01	5	1.0	3.5	7.3-7.6	4.0-4.4	3.16	0.20	
HTh_02	6	1.0	4.0			3.65	0.12	trace, but outputs not sensitive to assumptions
	11					**3.41**	**0.16**	

HTh_01 Ibarra JV, Osacar J, Gavilan JM (1979) Acidos humicos de lignitos: II. Complejos con los iones estroncio, plomo, uranilo y torio. Medida de sus constantes de estabilidad. Anales de Quimica 77, 224-229.
HTh_02 Nash, K.L. & Choppin, G.R. (1980). Interaction of humic and fulvic acids with Th(IV). J. Inorg. Nucl. Chem. 42, 1045-1050.

Tm

Code	n	pI	pH	p[M]	pNu	LKMA	RMSD	Comments
HTm_01	**5**	1.0-2.0	6.0-9.0	12.8-16.6	5.3-5.9	**3.09**	**0.45**	
FTm_01	**4**	1.0-1.1	6.0-9.0	14.6-18.2	6.0-7.2	**3.07**	**0.52**	

HTm_01 Sonke J (2006) Lanthanide-Humic Substances Complexation. II. Calibration of Humic Ion-Binding Model V. Environ. Sci. Technol. 40, 7481-7487.

FTm_01 Sonke J (2006) Lanthanide-Humic Substances Complexation. II. Calibration of Humic Ion-Binding Model V. Environ. Sci. Technol. 40, 7481-7487.

UO2

Code	n	pI	pH	p[M]	pNu	LKMA	RMSD	Comments
HUO2_01	8	2.0	4.5	6.9-7.9	4.9-5.4	2.29	0.06	
HUO2_02				trace	trace			not used (trace)
HUO2_03	19	1.6-2.8	2.0-3.4	2.4-4.1	3.3-5.3	2.69	0.34	
HUO2_04	36	1.0	4.0	5.0-7.2	3.3-4.1	2.95	0.06	
HUO2_05	450	0.5-1.7	5.0-10.1	10.3-18.1	4.1-7.1	2.64	0.78	
	513					**2.64**	**0.31**	
FUO2_01	72	0.7-2.3	5.0-5.7	7.2-8.8	4.7-5.5	2.02	0.34	
FUO2_02	120	0.7-2.0	3.5-5.9	6.8-8.7	4.4-5.6	2.09	0.46	
FUO2_03	259	0.5-1.7	4.9-10.3	9.7-19.0	4.6-7.4	2.56	0.56	
FUO2_04	34	1	5.0-9.9	12.4-18.9	5.8-6.9	2.43	0.34	
	485					**2.28**	**0.43**	

HUO2_01 Giesy JP, Geiger RA, Kevern NR (1986) UO2(2+)-humate interactions in softa, acid, humate-rich waters. J. Environ. Radioact. 4, 39-64.
HUO2_02 Shanbhag PM, Choppin GR (1981) Binding of uranyl by humic acid. J. Inorg. Nucl. Chem. 43, 3369-3372.
HUO2_03 Borovec Z, Kribek B, Tolar V (1979) Sorption of uranyl by humic acids. Chem. Geol. 27, 39-46.
HUO2_04 Czerwinski, K.R., Buckau, G., Scherbaum, F. & Kim, J.I. (1994). Complexation of the uranyl ion with aquatic humic acid. Radiochim. Acta 65, 111-119.
HUO2_05 Glaus MA, Hummel W, Van Loon LR (1997) PSI Bericht, 97-13: Experimental determination and modelling of trace metal-humate interactions: a pragmatic approach for applications in groundwater. Paul Scherrer Institute, Villigen, Switzerland.

FUO2_01 Higgo, J.J.W., Kinniburgh, D.G., Smith, B. & Tipping, E. (1993). Complexation of Co2+, Ni2+, UO22+ and Ca2+ by humic substances in groundwaters. Radiochim. Acta 61, 91-103.
FUO2_02 Higgo, J.J.W., Kinniburgh, D.G., Smith, B. & Tipping, E. (1993). Complexation of Co2+, Ni2+, UO22+ and Ca2+ by humic substances in groundwaters. Radiochim. Acta 61, 91-103.
FUO2_03 Glaus MA, Hummel W, Van Loon LR (1997) PSI Bericht, 97-13: Experimental determination and modelling of trace metal-humate interactions: a pragmatic approach for applications in groundwater. Paul Scherrer Institute, Villigen, Switzerland.
FUO2_04 Glaus MA, Hummel W, Van Loon LR (1997) PSI Bericht, 97-13: Experimental determination and modelling of trace metal-humate interactions: a pragmatic approach for applications in groundwater. Paul Scherrer Institute, Villigen, Switzerland.

VO(II)

Code	n	pI	pH	p[M]	pNu	LKMA	RMSD	Comments
FVO_01	**12**	1.4	5	5.2-7.3	2.8-3.8	**2.51**	**0.11**	

FVO_01 Templeton, G.D. & Chasteen, N.D. (1980). Vanadium-fulvic acid chemistry: Conformational and binding studies by electron spin probe techniques. Geochim. Cosmochim. Acta 44, 741-752.

Y

Code	n	pI	pH	p[M]	pNu	LKMA	RMSD	Comments
HY_01	**5**	1.0-2.0	6.0-8.9	11.3-15.1	5.1-5.4	**2.84**	**0.34**	
FY_01	**3**	1.0-1.1	6.0-9.0	14.7-18.3	6.0-7.6	**2.93**	**0.44**	

HY_01 Sonke J (2006) Lanthanide-Humic Substances Complexation. II. Calibration of Humic Ion-Binding Model V. Environ. Sci. Technol. 40, 7481-7487.

FY_01 Sonke J (2006) Lanthanide-Humic Substances Complexation. II. Calibration of Humic Ion-Binding Model V. Environ. Sci. Technol. 40, 7481-7487.

Yb

Code	n	pI	pH	p[M]	pNu	LKMA	RMSD	Comments
HYb_01	**4**	1.0-2.0	7.0-9.0	14.4-1.7	5.4-6.0	**3.12**	**0.43**	
FYb_01	**5**	1.0-2.0	6.0-9.0	14.7-18.3	6.0-7.6	**3.05**	**0.51**	

HYb_01 Sonke J (2006) Lanthanide-Humic Substances Complexation. II. Calibration of Humic Ion-Binding Model V. Environ. Sci. Technol. 40, 7481-7487.

FYb_01 Sonke J (2006) Lanthanide-Humic Substances Complexation. II. Calibration of Humic Ion-Binding Model V. Environ. Sci. Technol. 40, 7481-7487.

Zn

Code	n	pI	pH	p[M]	pNu	LKMA	RMSD	Comments
HZn_01	15	1.0	3.6-7.0	5.0-6.3	3.6-4.7	1.91	0.19	
HZn_02								not used
HZn_03	28	1.0	4.0-7.0	3.5-7.5	3.1-5.8	1.83	0.11	
	43					**1.87**	**0.15**	
FZn_01	2	1	3.5-5.0	5.4-5.5	4.6-5.3	1.62	0.04	
FZn_02	7	1	4.2-6.9	4.4-4.7	2.9-3.5	2.03	0.03	
FZn_03	19	1	3.4-6.5	trace	trace	1.49	0.26	
FZn_04		1	3.9-9.2	trace	trace	~2.01		Trace - too dependent upon adjustment factor
	28					**1.71**	**0.11**	

HZn_01 Randhawa, N.S. & Broadbent, F.E. (1965). Soil organic matter-metal complexes: 6. Stability constants of zinc-humic acid complexes at different pH values. Soil Sci. 99, 362-366.
HZn_02 Oste LA, Temminghoff EJM, Lexmond TM, Van Riemsdijk WH (2002) Measuring and Modeling Zinc and Cadmium Binding by Humic Acid Anal. Chem. 74, 856-862
HZn_03 Companys E, Puy J, Galceran J (2007) Humic acid complexation to Zn and Cd determined with the new electroanalytical technique AGNES. Environ. Chem. 2007, 4, 347–354.

FZn_01 Schnitzer M, Skinner SIM (1966) Organo-metallic interactions in soils. 5. Stability constants of Cu++-, Fe++- and Zn++-fulvic acid complexes. Soil Sci. 102, 361-365.
FZn_02 Wilson, D.E. & Kinney, P. (1977). Effects of polymeric charge variations on the proton-metal ion equilibria of humic materials. Limnol. Oceanogr. 22, 281-289.
FZn_03 Ephraim, J.H., Marinsky, J.A. & Cramer, S.J. (1989b). Complex-forming properties of natural organic acids. Fulvic acid complexes with cobalt, zinc and europium. Talanta 36, 437-443.
FZn_04 Ephraim JH (1992) Heterogeneity as a concept in the interpretation of metal ion binding by humic substances. The binding of zinc by an aquatic fulvic acid. Anal. Chim. Acta 267, 39-45.