

Accessory publication

Assessing WHAM/Model VII against field measurements of free metal ion concentrations: model performance and the role of uncertainty in parameters and inputsStephen Lofts^{A,B} and Edward Tipping^A^ACentre for Ecology and Hydrology, Lancaster Environment Centre, Library Avenue, Bailrigg. Lancaster, LA1 4AP, UK.^BCorresponding author. Email: stlo@ceh.ac.uk**Sources of supporting chemical composition for speciation calculations**

Tables A1 and A2 summarise the sources of supporting chemical compositional data required for speciation modelling of the water samples in this study.

Table A1. Sources of major ion concentrations in datasets

Ticks indicate measured data quoted for all samples. Empty cell indicates concentrations not estimated. Alk, Alkalinity

Datasets	Reference	Na	Mg	Al	K	Ca	Fe ^{II}	Fe ^{III}	Cl	NO ₃	SO ₄	Alk	F
Ni-04, Cu-08, Zn-05, Cd-05, Pb-04	[1]	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓	
Cd-02	[2]	✓	✓	A	✓	✓		B	✓	✓	✓	✓	
Cu-10, Zn-06, Cd-06	[3]	✓	✓	✓	✓	✓		✓	✓	✓	✓	✓	
Ni-01	[4]	✓	✓	✓	✓	✓		✓	✓	✓	✓	B	✓
Cu-01, Zn-01, Cd-01	[5]	✓	✓	✓	✓	✓		✓	C	✓	C	B	✓
Ni-03, Cu-07, Zn-04, Cd-04, Pb-03	[6]	✓	E	D	✓	E		F, G, H, I	J		K	B	✓
Cu-02, Zn-02	[7]	L	E	D	L	E		G, M	L	N	O	✓	
Cu-04, Pb-01	[8]	P	✓	D		✓		Q	P		R	✓	
Co-01	[9]	S	S	D	S	✓		T	S	S	S	✓	
Ni-02, Cu-03, Cd-03, Pb-02	[10]	✓	✓	Q	✓	✓		F, G	✓	✓	✓	✓	
Ni-05	[11]	✓	✓	✓	✓	✓		✓	✓	✓	✓	✓	
Cu-05	[12]	?	✓	D		✓		F	✓	✓	✓	✓	
Zn-03	[13]	?	✓	D		✓		F, U	V		V	✓	

^AHydroxide solubility control assumed for Lake Greifen samples.^BAssumed to be 0.08 μM, based on measurements given in Emmenegger et al.^[14]^BPartial pressure of atmospheric CO₂ set to 36.98 Pa (365 ppm).^CQuoted concentrations for 2002 samples unrealistically low. Quoted concentrations from 2001 samples used.^DHydroxide solubility control assumed.^ECalculated from measured hardness assuming a Mg : Ca ratio of 1 : 9.^FConcentrations in Lake Greifen from Emmenegger et al.^[14]

^GConcentrations in Furtbach stream from mean of all concentrations recorded for the Limmat River by NADUF (National River Monitoring and Survey Programme, <http://www.bafu.admin.ch/hydrologie/01831/01840/index.html?lang=en>), for the month of sampling.

^HConcentrations in the Rhine at Wageningen from mean of all concentrations recorded for the Rhine at the Netherlands–German border by the United Nations Global Environment Monitoring System (GEMSTAT; <http://www.gemstat.org>), for the month of sampling.

^IConcentration in River Wyre from Unsworth et al.^[10]

^JCalculated as $[Cl] = [Na] + [K]$.

^KCalculated from charge balance.

^LFor Furtbach samples, after Kalis et al.^[6] For Glatt samples, from concentration in Lake Greifen after Cao et al.^[2]

^MAssumed to be 0.1 μ M, based on measurements made in Emmenegger et al.^[14]

^NFor Furtbach samples, after Kalis et al.^[6] Not estimated for Glatt samples.

^OFor Furtbach samples, after Kalis et al.^[6] For Glatt samples, from charge balance.

^PCalculated by fitting to charge balance and measured conductivity.

^QFrom Kauppi et al.,^[15] using mean concentration given for northern Finnish lakes.

^RCalculated by assuming that if $[Ca] + [Mg] - 2[HCO_3] > 0$, $[SO_4] = [Ca] + [Mg] - 2[HCO_3]$, otherwise $[SO_4] = 0$.

^SMeasured values where quoted. Remaining value calculated assuming the ratio to Ca to be the mean of that in the other samples.

^TMeasured values where quoted. 0.1 μ M assumed for Lake Lucerne sample.

^U0.1 μ M assumed for Aabach River sample.

^VCalculated from Xue and Sigg^[12] assuming Cl : SO₄ ratio of 1 : 2.

Table A2. Sources of major ion concentrations in dataset Cu-03

Ticks indicate measured data quoted for all samples. Alk, Alkalinity

Sample(s)	Na	Mg	Al	K	Ca	Fe ^{III}	Cl	NO ₃	SO ₄	Alk
Lake Sempach	A	B	C	A	D	C	A	A	A	✓
Lake Sabbia	E	E	C	E	E	C	E	E	E	✓
Lake Inferiore	E	E	C	E	E	C	E	E	E	✓
Lake Zotta	E	E	E	E	E	C	E	E	E	✓
Lake Cristallina	E	E	E	E	E	C	E	E	E	✓
Lake Orta	F	F	F	F	F	F	F	F	F	✓
River Aare, Eichholz/Halenbrucke	G	G	C	G	G	G	G	G	G	✓
River Aare, Brugg	H	H	C	H	H	C	H	H	H	✓
River Birs, Munchenstein	I	I	C	I	I	I	I	I	I	✓
River Glatt, Rheinsfelden/Niederglatt/Rumlang	J	J	C	J	J	C	J	J	J	✓
River Rhine, Reckingen	H	H	C	H	H	C	H	H	H	✓
River Rhine, Village–Neuf	I	I	C	I	I	C	I	I	I	✓
River Thur, Andelfingen	I	I	C	I	I	C	I	I	I	✓

^AFrom log : log regressions between the concentration of this determinand and Ca, at all other sites in this dataset with measured concentrations of this determinand.

^BFrom Xue et al.,^[16] assuming [Mg] : [Ca] is 0.35.

^CAssumed to be 0.1 µM for lake samples, for river samples taken to be the mean of NADUF (National River Monitoring and Survey Programme, <http://www.bafu.admin.ch/hydrologie/01831/01840/index.html?lang=en>) measurements at the site for the month of sampling. Values for Glatt all taken from the single NADUF site on this river. Values for the Aare taken from the other NADUF site on the river.

^DFrom Ramisch et al.^[17]

^EFrom Giovanoli et al.^[18]

^FFrom Calderoni et al.^[19]

^GMean of all concentrations recorded for the Aare at Bern by NADUF for the month of sampling.

^HMean of all concentrations recorded for the sampling location in GEMSTAT (United Nations Global Environment Monitoring System, <http://www.gemstat.org/>) for the month of sampling.

^IMean of all concentrations recorded for the sampling location by NADUF for the month of sampling.

^JMean of all concentrations recorded for the Glatt at Rheinsfelden by NADUF for the month of sampling.

Recalculation of iron(III) solubility using Model VII

Lofts et al.^[20] calculated a solubility expression for Fe^{III} as a function of pH, based on activities of Fe^{III} in natural waters calculated from samples dialysed to remove colloidal Fe^{III} . Because the Fe^{III} activities were calculated using Model VI, it was necessary to recalculate the activities and the solubility expression using Model VII in order to calculate Fe^{III} solubilities for application in WHAM/Model VII. Recalculated activities are shown in Fig. A1 along with the activities calculated using WHAM/Model VI.

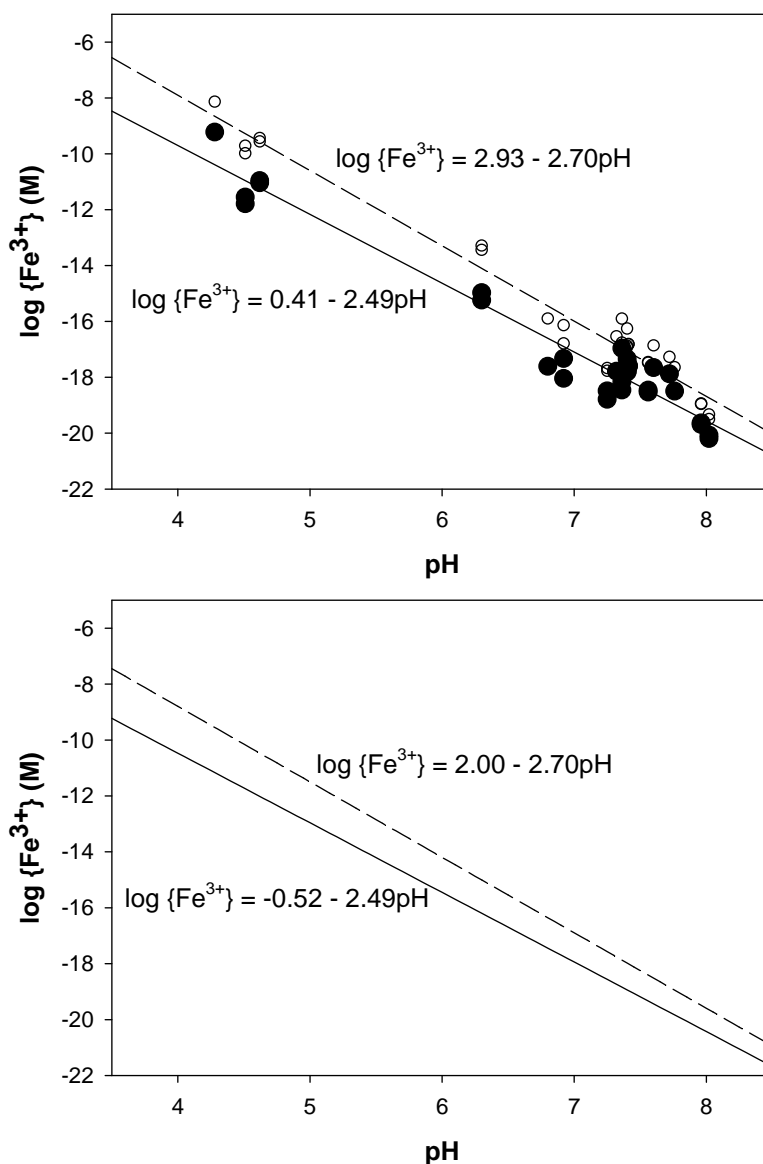


Fig. A1. Top pane: Fe^{III} activities in natural samples dialysates at 283 K calculated using Model VII (filled circles) and values from Lofts et al.^[20] calculated using Model VI (open circles). Regression of Model VII-calculated activities versus pH (solid line) and of Model VI-calculated values against pH (dashed line). Bottom pane: Relationships between Fe^{III} activity and pH at 298 K, assuming the enthalpy change of $\text{Fe}^{\text{III}}(\text{OH})_{3(\text{s})}$ solubility of Liu and Millero.^[21] Solid line: relationship derived using Model VII; dashed line: relationship derived using Model VI.

Comparing Fe^{III} activities calculated using Model VI and Model VII clearly shows that the latter predicts stronger binding of Fe^{III} to humics, and that the increase in predicted binding strength becomes larger at lower pH, giving a somewhat smaller slope of $\log a_{\text{Fe}^{\text{III}}}$ activity against pH. As was done previously, it is possible to generalise the activity–pH–temperature relationship, assuming the enthalpy change for $\text{Fe}(\text{OH})_3$ precipitation of Liu and Millero^[21]:

$$\log \{\text{Fe}^{3+}\} = -18.15 - 2.49\text{pH} + 5253/T \quad (\text{A1})$$

where T is the temperature in Kelvin. Alternatively, the activity can be expressed in terms of a solid phase solubility:

$$K_{\text{so}} = \{\text{Fe}^{3+}\} \cdot \{\text{H}^+\}^{-2.49} \text{ or } \log K_{\text{so}} = \log \{\text{Fe}^{3+}\} + 2.49 \text{ pH} \quad (\text{A2})$$

$$\log K_{\text{so}} = -18.15 - 5253/T \quad (\text{A3})$$

At $T = 298 \text{ K}$, $\log K_{\text{so}} = -0.51$. The root mean squared error in the regression of $\log a_{\text{Fe}^{3+}}$ against pH at 283K was 0.68; this was used (rounded up to 0.7) as the standard deviation of the sampling distribution of $\log K_{\text{so}}$ for calculation of uncertainty in WHAM/Model VII.

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