NOTICE: this is the author's version of a work that was accepted for publication in Environmental Science and Technology. A definitive version was subsequently published in *Environmental Science and Technology* **44**, 8587-8593, 2010. <http://dx.doi.org/10.1021/es102415r>

Chemical equilibrium modeling of organic acids, pH, aluminum and iron in Swedish surface waters

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A consistent chemical equilibrium model that calculates pH from charge balance constraints and aluminum and iron speciation in the presence of natural organic matter is presented. The model requires input data for total aluminum, iron, organic carbon, fluoride, sulfate and charge balance ANC. The model is calibrated to pH measurements ($n = 322$) by adjusting the fraction of active organic matter only, which results in an error of pH prediction on average below 0.2 pH units. The small systematic discrepancy between the analytical results for the monomeric aluminum

fractionation and the model results is corrected for separately for two different fractionation techniques ($n = 499$), and validated on a large number ($n = 3419$) of geographically widely spread samples all over Sweden. The resulting average error for inorganic monomeric aluminum is around $1\ \mu\text{M}$. In its present form the model is the first internally consistent modeling approach for Sweden and may now be used as a tool for environmental quality management. Soil gibbsite with a $\log K_s$ of 8.29 at 25°C together with a pH dependant loading function that uses molar Al/C ratios describes the amount of aluminum in solution in presence of organic matter if pH is roughly above 6.0.

Validating an equilibrium model for the surface water parameters pH, Al speciation and iron and aluminum particulates using Visual Minteq for 4000 datapoints across Sweden.

Introduction

Geochemical models are important tools for quantifying temporal changes in chemical conditions in soils and surface waters affected by human impact. Examples are risk assessment of metal toxicity, estimation of effects of acid rain on aluminum mobility (1-4) but potentially even when predicting the anticipated changes in sulfate and DOC concentrations in large regions over Northern Europe.

Several programs have been presented that account for geochemical equilibrium conditions, such as ALCHEMI (5), WHAM (6), and Visual Minteq (7). The constants for inorganic complexes are usually well established in those programs, but reactions involving dissolved organic matter (DOM) are more difficult to quantify. Several models exist for the dissociation and metal complexation reactions of macromolecular organic acids, ranging from simple (e.g. 1-3-protic acids; (8, 9)) to more advanced models such as the Stockholm Humic Model (SHM) (10) or Model VI (6).

When equilibrium models are calibrated, attention is often paid to only one parameter such as major ion charge balance (11) or inorganic aluminum fractions (12), or a limited range of landscape elements (13). This approach may result in models that may be element- or site-specific.

The set of equations used to account for organic acids when modeling pH or inorganic aluminum speciation varies from simple triprotic organic acid approaches (8, 13) to complex distribution models such as WHAM (e.g. ref 12)). Previously, calibrated values of organic site density of organic acids in Swedish surface waters differed when modeling pH or aluminum fractions (12, 13). This will lead to inconsistent modeling if both the pH and aluminum data are to be modeled simultaneously. Simultaneous modeling of aluminum chemistry and equilibrium

pH for larger areas has been studied only very rarely (8). Recently the interest in acid rain effects in both North America (2, 3) and Scandinavia (14, 15) has been growing owing to the fact that chemical changes in surface waters are due to a combination of changing sulfate and nitrate concentrations and changing DOC concentrations both of which affect pH and metal mobility. Assessment of environmental quality standards in Sweden need to be based on a quantitative, internally consistent model that has been validated across the whole country.

Our aim was to test the performance of a process-based geochemical model (Visual MINTEQ using the SHM for organic complexation) that can simulate both pH, inorganic monomeric aluminum, and the particle fraction of Al and Fe in a consistent manner. An important criterion for such a model is that it should be both internally consistent (i.e. same parameter settings for all samples considered) and geochemically consistent with results obtained earlier, therefore only the generic constants in the Visual Minteq was used (see, e.g., (16, 17)). Except for Fe(III) complexation to DOM, the only parameter that was optimized was the fraction of active dissolved organic matter, the so-called ADOM/DOC ratio. This approach is based on prior findings that organic acid site density may be considered to be constant in Sweden when modeling organic acid charge density and pH (18, 9)

Methods

Data Sets. A large number of surface waters were made available either from within the Swedish environmental monitoring program or from synoptic studies throughout the country. In total the different datasets consist of around 5200 samples for pH and 4000 samples for aluminum fractionation. First we used one dataset for optimization of the ADOM/DOC ratio based on pH simulations, with samples from a countrywide lake sampling (“Målsjöar”, this study

$n = 322$). Subsequently the same data was used to analyze the usefulness of the default binding constant for aluminum to predict the measured concentration of inorganic aluminum and to study the outcome of varying that constant by a factor of 2.

When evaluating the modeling of the inorganic monomeric aluminum, we used the datasets Målsjöar and “Forest streams” (14) (Table 1) as calibration of a correction function for the two different Al fractionation methods used (see section linear correction function).

For validation of both the pH calculations and the inorganic monomeric aluminum calculations, samples were used from lakes and streams from two countrywide lake surveys (“Lake1995”, “Lake2000” and “Stream2000” (19)), from lakes and streams from a countrywide sampling program of acidified sites (“IKEU”, this study), from a study of randomly selected sampling sites in the Dalarna region in the middle of Sweden (“Dalarna”, Löfgren pers. comm.), from a study of streams in Northern Sweden (“Krycklan”, (20)), and finally from three intensively monitored smaller catchments (“IM sites”, this study) (Table 1). A smaller subset of the dataset Krycklan also contained data for amounts of particulate aluminum and iron (21).

Chemical Analyses. With the exception of the Krycklan data all measurements of major chemical parameters (base cations, anions, total Al and Fe, TOC, alkalinity and pH) were obtained from one single accredited laboratory, for details see

http://www.ma.slu.se/ShowPage.cfm?OrgenhetSida_ID=11081. For details of the Krycklan methods, see (20). In Krycklan no alkalinity was determined, instead inorganic carbon (IC) was determined using a head space method. For the Målsjöar dataset, Si was not analyzed; therefore for modeling purposes a concentration of 0.1 mM silicic acid was assumed. The modeling results were not sensitive to the exact value of the Si concentration. Total aluminum was determined on

acid-treated samples and either detected by ICP-OES (Al_{tot}) or with pyrochatechol violet ($Al_{acid\ sol.}$).

Aluminum fractionation was performed using a cation exchange column method according to (22) on all datasets. The method determines monomeric, labile inorganic aluminum ($Al_{i\ mon}$) as:

$$Al_{i\ mon} = [Al_{tot\ mon} - Al_{org}] \quad (1)$$

where $Al_{tot\ mon}$ is the total monomeric aluminum and Al_{org} is the non-labile monomeric aluminum that passes through the column.

However, the determination method varied between the datasets (Table 1 and 2). In Målsjöar, Lake1995, Lake2000, Stream2000 and IKEU aluminum was determined spectrophotometrically using pyrochatechol violet (for whole procedure, see ref 23). The datasets Forest streams, Dalarna, Krycklan and IM used ICP-OES as the detection method on unacidified samples for Al_{org} (http://www.ma.slu.se/ShowPage.cfm?OrgenhetSida_ID=11081). Fluoride was mainly determined using ion chromatography, except for Krycklan in the year 2003 where total fluoride was determined using an Orion F-selective electrode after treatment with TISAB buffer.

Modeling Methods. The model was created using the geochemical model program Visual Minteq version 2.61 (7). The equilibrium constants are mostly based on the NIST compilation (24). Aluminum was entered as the total concentration (acid-treated) and was allowed to precipitate when the solubility product for $Al(OH)_3$ ($\log *K_s$ of 8.29 at 25°C) was exceeded. Iron was entered as Fe(III) and was also allowed to precipitate when exceeding the solubility product of ferrihydrite ($Fe(OH)_3$, with $\log *K_s$ of 2.69 at 25°C), but Fe(III) was not allowed to be reduced to Fe(II). The temperature was set to either to the temperature as determined in the field during sampling (1) or temperature = 10°C (2). Equilibrium constants were corrected for temperature

using van't Hoff's equation with values of the enthalpy of reaction taken from the default database of Visual MINTEQ. The field average ($\pm$ stdev) temperature is 7.8 ($\pm$ 4.9) °C and ranged from -1 to 26 °C. Since the aluminum fractionation and pH were determined at room temperature, an intermediate value of 10 degrees was chosen for the final calculations.

Modeling of pH was performed with the measured value for IC (Krycklan) or calculated IC using measured alkalinity or an estimate for pCO₂ (Målsjöar, Lake2000, Forest streams and Dalarna) according to the relationship between dissolved organic carbon and inorganic carbon for open-water seasons in Swedish lakes, suggested by (25):

$$\text{pCO}_2 = (1.079 \cdot \text{TOC} + 2.332) \cdot 10^{-4} \quad (2)$$

where pCO₂ represents the partial pressure of CO₂ in atm and TOC represents total organic carbon in mg L⁻¹. This relationship was also used for samples with no alkalinity.

Modeling of dissolved organic matter was performed using the Stockholm Humic Model (10). The model uses a discrete-site approach for proton- and metal-binding, similar to that of Model VI (6). In principle, the humic substances are treated as impermeable spheres. However, in part these may form gel-like structures. The electrostatic interactions on the surface are modeled using the Basic Stern Model. The radius of the spheres was set to 1.75 nm for humic acid and 0.8 nm for fulvic acid. Metals may form monodentate or bidentate complexes with DOM. All of the “active” dissolved organic matter (i.e. the proton- and metal-binding fraction of DOM) was considered to be fulvic acid (FA). To describe proton and metal binding we used generic parameters for fulvic acid (26) (Table S1 in Supporting Information), with the exception of Fe(III) for which we used optimized parameters for monomeric complexation of Fe(III) to FA, see Supporting Information for details.

When modeling the pH value of the datasets in this study the option called “Calculate pH from mass and charge balance” was used. We used the root mean square error in the modeled pH in the Målsjöar calibration dataset to identify the optimum ADOM/DOC ratio in the range 1.0 to 2.0 using a step size of 0.05.

To predict inorganic monomeric Al according to the Driscoll fractionation procedure ($Al_{i\ mon}$), pH was fixed at the analyzed value in Visual MINTEQ to obtain the sum of the concentrations of Al^{3+} , $Al(OH)^{2+}$, $Al(OH)_2^+$, AlF^{2+} , $Al(F)_2^+$, $AlSO_4^+$, $Al_2(OH)_2^{4+}$, $Al_2(OH)_2CO_3^{2+}$, $Al_3(OH)_4^{5+}$, $AlCl^{2+}$ and $AlH_3SiO_4^{2+}$.

Linear Correction Function. Differences between the modeled and measured aluminum fractions of the two determination methods were evaluated using an iteratively reweighted least squares (IRLS) method for robust regression of weighted linear curve fitting (27). The reasoning why we chose a correction function is discussed further down. We assumed that a linear relationship existed that may describe the difference between the measured and modeled values with an offset and a slope only. According to ref 28 an equation that is described in the Supporting Information can be minimized when establishing the regression curve. This method will favor low concentration values that represented a much larger amount of samples in all datasets when fitting the regression correction function. Prior to this operation we excluded values below a detection limit of 0.5 μM and those with a measured pH above 6 where the speciation method is uncertain (29). Two separate correction functions M^* were then created for the two different determination methods on the Målsjöar and Forest streams datasets, according to their linear relationships, and were then applied to the other datasets.

Analysis of Modeled Particulate Aluminum. The results from the modeling exercise from the datasets with PCV determination were used to classify the samples along with their elemental ratios [$\mu\text{M Al/mM C}$]. The aim was to distinguish between samples where the program predicted the presence of particulate aluminum and those where all aluminum is calculated to be fully in the solution phase. The molar ratios were plotted as a function of sample pH and samples with the modeled presence of particulate aluminum were marked. The two sample groups separated from each other when using a third degree polynomial that uses pH as the sole input parameter of type:

$$\langle \text{Al/C} \rangle_{crit} = A_0 \text{pH}^3 + A_1 \text{pH}^2 + A_2 \text{pH} + A_3 \quad (3)$$

with $A_0 = -2.435$, $A_1 = 52.68$, $A_2 = -381.9$ and $A_3 = 928.9$.

Results

The ADOM/DOC ratio that gave the best agreement between measured and modeled pH values was 1.65, and this value was then used for the other datasets and in the aluminum modeling. An analysis of sensitivity reveals that varying this factor in the range 1.55 to 1.75 increased the root mean square error in modeled pH in both cases from 0.03 to 0.033 and 0.038 respectively in the pH range 5 to 6.5. Average predicted pH in this range changes from 5.55 to 5.62 and 5.49 respectively as compared to the average measured value of 5.58.

Assuming that DOM consists of 50% carbon by weight, the value of 1.65 implies that 82.5% of the DOM was active as regards to proton and metal binding and the calculated site density is $11.5 \mu\text{M mg}^{-1} \text{ C}$.

The pH values of the calibration dataset Målsjöar (Figure 1a) and the validation datasets (Dalarna, Figure 1b) were reasonably well modeled using Sobek's relationship between CO₂ pressure and TOC (eq 2). The choice for temperature (field or 10°C) and solubility product for Al(OH)₃ and ferrihydrite had minor effects on the pH and the Al_{i,mon} simulations.

The speciation modeling results for aluminum revealed significant and strong linear correlation between analyzed and modeled inorganic aluminum in all datasets (Målsjöar, $r^2=0.87$, $rmse=0.68$ μM , Lake1995, $r^2=0.63$, $rmse=0.63$ μM , Lake2000, $r^2=0.51$, $rmse=0.67$ μM , Streams2000, $r^2=0.35$, $rmse=0.61$ μM , IKEU, $r^2=0.84$, $rmse=0.75$ μM , Forest Streams, $r^2=0.79$, $rmse=0.95$ μM , Dalarna, $r^2=0.87$, $rmse=0.86$ μM , Krycklan $r^2=0.43$, $rmse=0.90$ μM , and IM sites, $r^2=0.68$, $rmse=1.23$ μM). Varying the binding constant of aluminum to organic matter by a factor of two (0.3 log units) in Målsjöar had no significant effect on the offset of the correction function when comparing measured and modeled values but did change the slope by 12% in either direction. The following correction functions were used to correct the validation datasets:

$$Al_{i,mon}^* = a + b * Al_{i,mon} (MOD) \quad (4)$$

With $a = 0.46 \pm 0.09$ and $b = 1.10 \pm 0.04$ for the PCV method and $a = -0.18 \pm 0.13$ and $b = 0.74 \pm 0.04$ for the ICP-OES method (Figure 2, validation datasets in Figure S1 in Supporting Information). Using individual correction functions did improve the precision for both the ICP-OES and the PCV method but we have no reason to believe that the datasets should be treated separately given that all samples were run in the same laboratories.

At pH values above 5, the large majority of analyzed monomeric aluminum is bound to organic carbon in all samples. An analysis of the distribution of the modeled species revealed

that fluoride speciation largely controlled the amount of inorganic aluminum in the pH range 5 to 6.5 with more than 80% of all inorganic aluminum being in either of the fluoride complexes.

Our model predictions can be compared to those using the WHAM 6.0 code. For this comparison we used a synthetic sample set with varying fulvic acid concentration (1 - 46 mg L⁻¹), and with a fixed fluoride concentration of 2 μM in the pH range 5.0 to 7.5 in the absence of iron. In these runs we adjusted the WHAM fulvic acid concentration so that the amount of carboxylic and phenolic sites was similar for both models (FA = 1.65*DOC). Total aluminum concentration in the Visual Minteq runs was set to 100 μmol L⁻¹ in all samples and aluminum was allowed to precipitate when the soil gibbsite phase was supersaturated. The same aluminum values were subsequently used for the WHAM 6.0 runs thus preserving the similar Al/C ratios. On average the difference in predicted Al_{i mon} amounted to 7%. Further analysis reveals that this difference is mainly due to the pH region 4.5 to 5.0 where the model calculations may differ systematically up to 15%. From pH 5.5 and above the difference is smaller than 2% in all cases.

The particulate fraction of Al and Fe (defined here as the concentration of unfiltered water subtracted by the 0.45 μm filtered fraction) in Krycklan was evaluated against the modeled fraction of precipitated Al(OH)₃(s) and ferrihydrite, since it is reasonable to assume that the particles consisted of precipitated (hydr)oxide phases. There was a positive linear relationship with high concentrations of particles and modeled precipitation for both Al and Fe (Al r² = 0.95, rmse = 2.8 μM and Fe r² = 0.81, rmse = 6.3 μM) (Figure S2 in the Supporting Information). For Al the offset for the linear relationship is below 0.4 μM. For Fe this offset is much larger (8.2 μM) as many points with higher modeled ferrihydrite occurred compared to the measured particulate Fe.

The molar ratios of Al and TOC [$\mu\text{M Al/mM C}$] were plotted as a function of sample pH and samples with the modeled presence of particulate aluminum were marked (Figure 3a). A test of the function of molar ratios of Al/C against pH for the Krycklan dataset on samples where particulate Al represents at least 50% of the total aluminum, revealed that most of the measured data was above the function (Figure 3b).

Discussion

Modeling pH. The pH simulations indicated no significant bias when using an ADOM/DOC ratio of 1.65 considering all the modeled pH data. The ratio (1.65) is close to the reported range of other authors (1.3 (30); 0.92 (31); 1.22-1.4 (32)). The calculated site density of $11.5 \mu\text{M mg}^{-1}$ C is very close to the value of $10.2 \mu\text{M mg}^{-1}$ C proposed in ref 9. The remaining bias is probably due the fact that the average positive charge contribution of aluminum and iron was not considered in that study. The remaining random error in modeled pH is due to the measurement errors from the 9 different concentrations used as input parameters (31). In order to achieve higher precision when modeling pH the CBALK method is preferable (33).

Modeling Inorganic Aluminum. The main aim of the paper is to deliver a geochemical modeling tool that will allow assessing the quantitative reasons for the presence of inorganic aluminum in Swedish surface waters using data from both analytical techniques that are currently under use in the Swedish environmental surface water program. Analysis of our data set revealed significant differences between our two different methods. Systematic offsets between methods are due to a number of factors such as variation in column size, flow rate, or

253 prefiltration steps which may be partly corrected for using correction functions (34). Absolute
254 differences between modeled and measured can be due to both systematic over- and
255 underestimation of inorganic aluminum which is why these types of methods are often
256 operationally defined. In order to reconcile both methods with our modeled data we were obliged
257 to use correction functions. The linear correction function parameters reveal small but significant
258 offsets of below 0.5 μM for both methods. The PCV method is systematically 10% larger, thus
259 slightly overestimating $\text{Al}_{i, \text{mon}}$, while the ICP-OES method is systematically 25% lower than the
260 modeled $\text{Al}_{i, \text{mon}}$ values. For the PCV method this might be due to the partial dissociation of
261 organic Al complexes in the column. During the ICP-OES method the 40% higher flow rate, 3.8
262 ml per ml exchanger volume as compared to 2.8 in the PCV method, will tend decrease the $\text{Al}_{i, \text{mon}}$
263 fraction due to shorter reaction times. The exact reason for these difference is however
264 unknown.

265 A decreased ADOM/DOC ratio (around 1.0 for Målsjöar and Lake2000) was able to generate
266 improved model fits for inorganic aluminum, but this led to considerably poor fits for pH (data
267 not shown). Another way of improving the fit of inorganic aluminum could be to change the
268 aluminum binding constants to DOM. Model runs indicated that the binding constant would
269 require to be changed by more than 1 log unit from -4.2 to -5.6. However, such a low value for
270 the Al-FA binding constant is not consistent with values obtained for pure Al-FA systems (10).

271 The Kindla site was an exception with much lower Al modeled than analyzed. This site has a
272 median TOC of 8.5 is very extreme with regards to pH (median pH 4.6) and aluminum
273 conditions (median $\text{Al}_{i, \text{mon}} = 11 \mu\text{M}$ which only represents the upper 2.5% percentile of all $\text{Al}_{i, \text{mon}}$
274 data studied here) and thus not representative but certainly requires further detailed study
275 which is beyond the scope of this paper.

During the Driscoll aluminum fractionation method the inorganic fraction is determined indirectly by subtraction of the amount that passes through the column (Al_{org}) from the monomeric fraction ($Al_{tot\ mon}$). In our dataset this is manifested by some negative values of $Al_{i\ mon}$ which is why the data treatment required a cutoff at $0.5\mu M$ similar to that of ref 3.

The Particle Fraction in Krycklan. The model predictions for precipitated $Al(OH)_3(s)$ coincided well with the measured concentration of particulate Al for pH values above 5.5, which suggests that the $\log *K_s$ value used was reasonable. It should be noted that the consideration of $Al(OH)_3(s)$ in the model does not necessarily imply that the mineral phase that may control dissolved Al actually has the stoichiometry of Al hydroxide, instead it may be e.g. allophane or imogolite.

The modeled values indicated a larger amount of ferrihydrite in the particulate fraction compared to what was measured, but for a more reliable result a more thorough study of Fe is needed including Fe(II) measurements, smaller filtration sizes and speciation in the field (35).

Implications. The validation datasets all confirm the applicability of the model in various environments. With the exception of one dataset the error margins are on the order of $1\ \mu mol$ aluminum per liter. The model is capable of predicting in which water samples acute fish toxicity ($> 3\ \mu M$) is to be expected and may help to identify environments where further study is necessary. During the phasing out of liming in Sweden, where still more than 5000 lakes and streams are limed today, the occurrence of inorganic monomeric aluminum is one of the major criteria on which further decisions are based. The calibrated SHM for Sweden presented here will, for the first time, allow to combine geochemical speciation of aluminum and concurrent

modeling of pH in combination with other hydrological approaches for use in decision support when selecting vulnerable sites and test the sensitivity of individual parameters such changes in as pCO₂, TOC, sulfate and fluoride.

Our results do not confirm the hypothesis of (2), who claimed that the presence of inorganic aluminum is an unambiguous indication of acidic deposition effects. In both calibration datasets, a Målsjöar and Forest stream, the presence of inorganic aluminum is tightly controlled by the presence of fluoride. As fluoride concentrations vary naturally all over the country the presence of inorganic aluminum may vary too. The comparably good description of the occurrence of particulate aluminum using an empirical pH-dependent equation (equation 3) helps to identify situations where particulate aluminum may actually form. These situations may occur in mixing zones of headwater streams, during recession to baseflow, carbon dioxide degassing or increased photosynthetic activity in lakes.

Acknowledgments

The study was funded by the Swedish Environmental Protection Agency. We thank Cecilia Andrén, Kevin Bishop; Jens Fölster and Stefan Löfgren for the support.

Supporting Information Available

Further information and figures are available free of charge at <http://pubs.acs.org>.

FIGURE 1a. Modeled direct pH in the calibration dataset “Målsjöar” using the equation of Sobek et al. (25) to estimate $p\text{CO}_2$. Mean error in prediction 0.13 pH units.

FIGURE 1b. Modeled direct pH in the validation dataset “Dalarna” using the equation of Sobek et al. (25) to estimate $p\text{CO}_2$. Mean error in prediction 0.18 pH units.

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FIGURE 2a. The corrected inorganic $Al_{i,mon}^*$ versus PCV determined $Al_{i,mon}$ for the calibration dataset “Målsjöar”. Data with pH above 6 are excluded in the analysis and this graph.

FIGURE 2b. The corrected inorganic $Al_{i,mon}^*$ versus ICP_OES determined $Al_{i,mon}$ for the validation dataset “Forest streams”. Data with pH above 6 are excluded in the analysis and this graph.

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FIGURE 3a. Plot of the molar ratios Al/C [$\mu\text{M}/\text{mM}$] as a function of sample pH. Filled circles indicate samples where the SHM predicts the presence of particulate aluminum (Data from the first five sets in Table 1). The red line is equation 3.

FIGURE 3b. Plot of the molar ratios Al/C [$\mu\text{M}/\text{mM}$] as a function of sample pH for samples where particulate aluminum represents at least 50% of the total aluminum in the Krycklan dataset. The red line is equation 3.

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326 **Table 1. General chemical characteristics of the various studied datasets.**

Dataset	Method	[mM] C	[μM] ANC	[μM] Al _{tot}	[μM] Al _{acid sol.}	pH	[μM] F	[μM] Al _{i,mon}	Period	m	n (Ali)
Målsjöar	PCV	1.1 ± 0.7	63 ± 66	9.0 ± 5.2	9.0 ± 4.5	5.3 ± 0.6	3.2 ± 2.3	2.0 ± 1.9	2009	322	322
Lake 1995	PCV	0.8 ± 0.4	320 ± 545	n.a.	4.0 ± 4.7	6.4 ± 0.7	6.0 ± 5.6	0.4 ± 0.9	1995	712	654
Lake 2000	PCV	0.9 ± 0.6	467 ± 630	4.0 ± 4.2	n.a.	6.6 ± 0.7	6.2 ± 5.4	-0.1 ± 1.0	2000	1204	313
Stream 2000	PCV	1.2 ± 0.6	315 ± 220	12 ± 14	n.a.	6.5 ± 0.5	7.3 ± 5.5	-0.1 ± 0.7	2000	216	214
IKEU	PCV	0.8 ± 0.4	108 ± 68	6.0 ± 5.8	12 ± 6.7 ^{&}	6.1 ± 0.6	5.0 ± 2.9	0.9 ± 1.9	1998-2010	1108	1108
Forest streams	ICP-OES	1.6 ± 0.6	85 ± 73	13 ± 5.8	n.a.	4.8 ± 0.5	4.4 ± 2.6	2.1 ± 2.1	2009	177	177
Dalarna	ICP-OES	1.9 ± 0.9	198 ± 99	12 ± 7.9	n.a.	5.8 ± 0.7	6.6 ± 6.7	1.4 ± 1.6	2009	126	126
Krycklan	ICP-OES	1.5 ± 0.7	109 ± 66	9.0 ± 8.2	n.a.	5.4 ± 0.8	5.4 ± 5.1	0.8 ± 1.1	2003-2004	650	347
IM sites	ICP-OES	1.2 ± 1.0	52 ± 59	15 ± 14	14 ± 11	4.9 ± 0.5	5.8 ± 1.2	6.3 ± 5.4	2002-2010	657	657

327 Al_{tot} = Total aluminum HNO₃ digested. Al_{acid sol.} = Aluminum H₂SO₄ digested detected by PCV. Al_{i,mon} = Inorganic monomeric aluminum. PCV=
328 Pyrochatechol violet method.
329 [&] This value is higher than Al_{tot} as a subset of very acidic IKEU samples only had Al_{acid sol} determination.

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332 **Table 2. Simplified sketch of aluminum fractionation methods and aluminum models used^a.**

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334 ^a Bold text refers to measured data, normal formatting to fractions calculated by difference. CE_{exh} = cation exchange.

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Chemical equilibrium modeling of organic acids, pH, aluminum and iron in Swedish surface waters

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Environmental Science & Technology

September 20, 2010

26 pages, 3 figures, 2 tables

Supporting Information available:

Iron binding parameters to fulvic acids

The Visual Minteq parameters were optimized for two data sets for mor layers, Korsmossen O_e and Risbergshöjden O_e. These data sets have earlier been described and optimized by (36), who optimized Fe(III) binding parameters based on the observation that a dimeric Fe(III)-organic species may form. However, later results consistently show that monomeric Fe(III)-organic complexes seem to dominate in acid organic soils and waters ((37), (38), Sjöstedt et al., in prep.) Therefore the data were reinterpreted using monomeric Fe(III)-organic complexes in the model. The optimized Fe(III) complexation constants were $\log K = -4.6$ for FeOH^{2+} binding to FA, and $\log K = -1.68$ for Fe^{3+} binding to FA, and a ΔLK_2 value of 1.7 for both complexes. See also Table S1.

Equation for minimizing the correction function $\text{Al}_{i, \text{mon}}^*$

The correction function $\text{Al}_{i, \text{mon}}^* = a + b^* \text{Al}_{i, \text{mon}} (\text{MOD})$ was minimized using the following equation:

$$S_{biweight} = \sum_{i=1}^n \rho(r_i)$$

$$\rho(r_i) = \left(\frac{B^2}{2} \right) \left(1 - \left(1 - \left(\frac{r_i}{B} \right)^2 \right)^2 \right); |r_i| \leq B$$

$$\rho(r_i) = \left(\frac{B^2}{2} \right) ; |r_i| \leq B \text{ where } r = \left(\frac{R}{\sigma} \right)$$

R is the residual, σ is a measure of the error such as $1.5 \times \text{median}(\text{LeastSquare}_{\text{residuals}})$. B is a tuning constant usually between 1 and 4.

Lower values will increase the importance of low values in the regression curve.

Table S1. Metal complexation constants to dissolved fulvic acid in the Stockholm Humic Model		
Complex	log <i>K</i>	ΔLK_2
FA ₂ AlOH	-9.3	1
FA ₂ Al ⁺	-4.2	1
FA ₂ FeOH	-4.6 ^a	1.7 ^a
FA ₂ Fe ⁺	-1.68 ^a	1.7 ^a
FaCa ⁺	-2.4	0.3
FA ₂ Ca	-11.3	0.3
FAMg ⁺	-2.5	0.3
FA=fulvic acid		
^a These constants were not the generic constants, instead they were calibrated using the Korsmossen and Risbergshöjden datasets described above.

FIGURE S1a. The corrected inorganic $Al_{i,mon}^*$ versus PCV determined $Al_{i,mon}$ for all validation data. Mean error is 1.1 μM .

FIGURE S1b. The corrected inorganic $Al_{i,mon}^*$ versus ICP-OES determined $Al_{i,mon}$ for all validation data. Triangles are all from site Kindla. Mean error = 0.96 μM after excluding site Kindla.

FIGURE S2a. Amount of predicted Al in form of gibbsite against the amount of particulate aluminum for all samples with pH above 5.5.

FIGURE S2b. Amount of predicted Fe in form of ferrihydrite against the amount of particulate iron for all samples with pH above 5.5.