



**KTH Land and Water
Resources Engineering**

**IRON AND ALUMINIUM SPECIATION IN
SWEDISH FRESHWATERS
IMPLICATIONS FOR GEOCHEMICAL MODELLING**

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*"Gold is for the mistress - silver for the maid -
Copper for the craftsman cunning at his trade."
"Good!" said the Baron, sitting in his hall,
"But Iron - Cold Iron - is master of them all."*

From "Cold Iron", Rudyard Kipling

SUMMARY

Spårmetaller kan vara giftiga i höga koncentrationer. Totalkoncentrationerna av spårmetaller i vatten har oftast inte något samband med biotillgängligheten; den senare styrs till största del av halten fria joner. Andelen fria joner av totalhalten är därför en viktig faktor vid riskbedömningar av naturliga vatten. Ett exempel där riskbedömningar av spårmetaller är viktiga är antropogent försurade vatten. Varje år spenderar svenska staten 208 miljoner kronor på kalkning av antropogent försurade ytvatten. Dock, så minskar den försurande svaveldepositionen och på sikt bör kalkningen kunna upphöra. Ett hjälpmedel för sådana framtidsscenarier och vid riskbedömning av ytvatten är geokemiska modeller. Dessa grundar sig ofta på jämviktsuttryck mellan oorganiska joner, en modell för bindningen till organiska humusämnen och en adsorptionsmodell till (hydr)oxider. Två viktiga faktorer som styr andra metallers speciering är metallerna järn och aluminium. De är vanliga i sura vatten. De kan båda bilda hydroxider och oxider, som i sin tur kan adsorbera andra spårmetaller vilket gör de senare mindre biotillgängliga. Järn och aluminium binder också mycket bra till humusämnen. De kan därmed konkurrera om bindningsplatser med andra metaller, vilket i sin tur gör dessa metaller mer biotillgängliga. Trots mycket forskning är järn och aluminiums kemi i naturliga vatten delvis okänd. Denna studie har som syfte att studera järns och aluminiums former i fem svenska sjöar, för att bättre kunna simulera aluminium och andra metallers speciering i ytvatten. Den förbättrade modellen kan sedan användas för förutsägelser av vattenkemi efter avslutad kalkning i Sverige.

Järn studerades kvalitativt genom att mäta järn(II) och genom "extended X-ray absorption fine structure" (EXAFS) spektroskopi i två näringsfattiga sjöar. Järn och aluminium fraktionerades genom 0,45 µm-filtrering och 1 kDa-cross flow (CF) ultrafiltrering, samt med dialys i ytterligare tre sjöar. Bly och koppars adsorption till syntetisk ferrihydrit studerades med och utan förekomst av fosfor i skakförsök och med EXAFS-spektroskopi. Resultaten visade att järn delvis kunde finnas som järn(II) i syrerika ytvatten. Uppmätta partiklar (> 0,45 µm) i ett prov visade sig innehålla ferrihydrit. Vissa av kolloidproverna (<0,45 µm >1 kDa) innehöll även de delvis en järn(III)(hydr)oxid. Dock var kolloidalt järn(III) framför allt komplexbundet till löst organiskt material (DOM) i monomera komplex. Den monomera komplexbindningen var starkare än vad som tidigare antagits. Komplexkonstanterna för järn(III)-bindning till humusämnen i modellen Stockholm Humic Model (SHM) justerades därefter och järns speciering simulerades. Den starkare komplexbindningen till DOM medförde att järn(III) konkurrerade starkt med aluminium om bindningsplatser enligt modellen. En modell konstruerades med SHM i programmet Visual MINTEQ för att kunna simulera pH, oorganiskt monomert aluminium (Al_i) och andra metaller samtidigt. Först kalibrerades modellen för andelen aktivt löst organiskt material i förhållande till löst organiskt kol (den så kallade ADOM/DOC kvoten) genom att simulera pH via jonbalansen. Den kvot som visade sig ge lägst fel var 1,65. Samma kvot och modelluppsättning användes för att simulera halten Al_i i flera stora dataset. Modellen gav ett tydligt samband med uppmätta Al_i -halter men med vissa modifieringar beroende på analysmetod för Al_i . Modellen kunde även simulera storleksfraktionering av koppar och bly i två sjöar. Därefter användes modellen för att simulera kalkavslut i de 3 043 kalkade sjöarna i Sverige. Modellresultaten visade att man

bör kunna avsluta kalkningen i 30 % av sjöarna, framför allt i Norrland, och även minska kalkningsverksamheten i andra delar av landet.

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LIST OF APPENDED PAPERS AND MY CONTRIBUTIONS

Paper I

Sjöstedt, C., Wällstedt, T., Gustafsson, J.P., and Borg, H. (2009) Speciation of aluminium, arsenic and molybdenum in excessively limed lakes. *Science of the Total Environment*, 407, 5119-5127. Reprinted with permission from Elsevier.

I participated in planning, sampling and experimental work, performed the geochemical modelling and the main part of data analysis and writing.

Paper II

Sjöstedt, C., Gustafsson, J.-P., and Köhler, S.J. (2010) Chemical equilibrium modeling of organic acids, pH, aluminium, and iron in Swedish surface waters. *Environmental Science and Technology*, 44 (22), 8587–8593. Reprinted with permission. Copyright (2010) American Chemical Society.

I performed almost all modelling, data analysis and main part of writing.

Paper III

Sjöstedt, C., Persson, I., Hesterberg, D., Berggren Kleja, D., and Gustafsson, J.P. Iron speciation in soft-water lakes and soils as determined by EXAFS spectroscopy and geochemical modelling. Submitted to *Geochimica et Cosmochimica Acta* 31 January 2012.

I performed most of the field and laboratory work, EXAFS and wavelet interpretations, geochemical modelling and main part of writing.

Paper IV

Sjöstedt, C., Andrén, C, and Gustafsson, J.P. Modelling of pH and inorganic aluminium after termination of liming in 3 000 Swedish lakes. Manuscript.

I performed all the modelling and the major part of data analysis and writing.

Paper V

Tiberg, C., **Sjöstedt, C.**, Persson, I., and Gustafsson, J.P. Phosphate effects on copper(II) and lead(II) sorption to ferrihydrite. Manuscript.

I was involved in EXAFS and wavelet interpretations and contributed to writing.

NOMENCLATURE AND ABBREVIATIONS

ADOM/DOC	Active dissolved organic matter to dissolved organic carbon ratio
Al _i	inorganic monomeric aluminium
CD-MUSIC	The Charge distribution - multi site complexation model
CF(F)	cross-flow (filtration)
Colloids	here defined as species being between 1 kDa and 0.45 μm
DDL	diffuse double layer
DGT	diffusive gradients in thin films
DOC	dissolved organic carbon
DOM	dissolved organic matter
EXAFS	extended X-ray absorption fine structure spectroscopy
FFF	field-flow fractionation
ICP-OES	inductively coupled plasma- optical emission spectroscopy
IR spectroscopy	infrared spectroscopy
NOM	natural organic matter
OC	organic carbon
OM	organic matter
Particles	Here defined as species larger than 0.4(5) μm
PCV	pyrochatechol violet
SHM	The Stockholm humic model
TOC	Total organic carbon
XAS	X-ray absorption spectroscopy

ABSTRACT

Speciation governs transport and toxicity of trace metals and is important to monitor in natural waters. Geochemical models that predict speciation are valuable tools for monitoring. They can be used for risk assessments and future scenarios such as termination of liming. However, there are often large uncertainties concerning the speciation of iron and aluminium in the models, due to the complicated chemistry of these metals. Both are important in governing the speciation of other metals, due to (i) their capacity to form minerals onto which metals can adsorb and (ii) their ability to compete for binding sites to natural organic matter (NOM). Aluminium is also potentially toxic and is therefore closely monitored in acidified freshwaters. In this study different phases of iron in Swedish lakes were characterised. This required a good method for preconcentrating the iron colloids. A new method was developed in this thesis that uses an anion-exchange column to isolate the iron colloids prior to characterisation with extended X-ray absorption fine structure (EXAFS) spectroscopy. Iron was present as ferrihydrite in particles but was also strongly monomerically complexed to NOM in two Swedish lakes. Based on the results an internally consistent process-based geochemical equilibrium model was presented for Swedish freshwaters. The model was validated for pH ($n = 9\ 400$) and inorganic monomeric aluminium (Al_i) ($n = 3\ 400$). The model could simulate pH and Al_i simultaneously, and be used for scenario modelling. In this thesis, modelling scenarios for decreases and complete termination of liming are presented for the 3 000 limed Swedish lakes. The results suggest that liming can be terminated in 30 % of the Swedish lakes and decreased in many other lakes.

Key words: Geochemical equilibrium modelling; pH; adsorption to ferrihydrite; metal-NOM complexation; liming; EXAFS spectroscopy

1. INTRODUCTION

1.1. Rationale for the thesis

Trace metals in the environment are by definition present in small concentrations, but they have a large impact. They can both be essential to life but also toxic at quite low concentrations. They are important to monitor due to their inability to be degraded. They can however be immobilised by *e.g.* sedimentation and become less available to biota. Their low concentrations make them a challenge to study.

Metals have been used by Man since ancient times and they are an important part of the human development. The problems that metals cause are also known to have affected us for a long time. The Roman Empire used large amounts of lead, *e.g.* for water pipes. Even today it is possible to trace the Roman use of lead in the sediments of Swedish waters. Hence, metal pollution is not something new even though it has escalated during the industrial ages. Some examples include the problems caused by acid rain where the low pH of the soil and water cause leaching and elevated concentration of potentially toxic metals such as aluminium; emissions of mercury and lead, arsenic poisoning due to natural

high concentrations. Trace metals can be transported far from the pollution source by air, and by ground and surface water.

Some of the aforementioned problems have caused significant costs in human suffering, biological and economical degradation. Trace metals are taken up by humans through drinking water, food and air. Children and foetuses are especially vulnerable to lead and mercury toxicity. Biologically there is a loss of biodiversity; for example, fish is especially vulnerable to acidity and cationic metals such as aluminium. The Swedish state pays for instance 208 million SEK per year to counteract acidification with liming (Swedish EPA, 2011).

For these reasons, monitoring of the potentially toxic trace metals is of great importance. The good news about these toxicants is that certain forms of them are not available to biota and are also not transported far; instead they are immobilised in the soil and in the sediments. The conditions under which they are immobilised are therefore of considerable interest. The focus of this thesis is to improve the knowledge about how to ensure that the forms of certain potentially toxic metals are in the non-toxic form for biota. Other good news is that acidification is now on the retreat in Europe and North America, due to lower emissions of sulphur and nitrogen (Granier *et al.*, 2011). Therefore it is of interest to know if it is possible to terminate or decrease liming without adverse effects on biota.

1.1.1. Toxicity and speciation of metals

For a long time it was assumed that the total concentration of the toxic metal could be directly linked to toxicity. It was not until the 1970's that some researchers suggested that it could be the free ions that are the most important (Sunda and Guillard, 1976; Morel, 1983). This gave rise to the free ion activity model (FIAM), according to which the free ions are easily taken up by the organisms. As a result they are the most important forms that cause toxicity. On the other hand, if the ions are bound to natural organic matter (NOM) or adsorbed to solids, they are no longer free and therefore less bioavailable. The form of the metal, *i.e.* its speciation, is accordingly of major interest. Later on this has been further developed into the biotic ligand model (BLM) (di Toro *et al.*, 2001; Niyogi and Wood, 2004), in which not only the free ion activity of the toxic metal is important but also the competition of other ions. Both the toxic and the non-toxic ions compete for binding sites on the biotic ligands of the organism that takes up the metal. Therefore not only the free ion concentration of the toxic metal is important, but also the concentration and speciation of other ions surrounding it. The pH value has an intricate relationship to toxicity, since a lower pH generally means larger solubility of metals and consequently more free ions, but at the same time more hydrogen ions which can compete for binding sites on the biotic ligand. This is complicated further when NOM is present, which can bind the toxic metal as well as the competing metal ions. The BLM approach for water quality criteria is now

currently used in regulations in the US for copper (US EPA, 2007), and in the EU BLM:s can be used for deriving quality standards (European Communities, 2011). It is therefore important that it is valid. However, it is only valid if the relationships between all the important factors are known. The FIAM and BLM are only valid for situations where there is equilibrium in the surroundings of the organism. The uptake of ions by biota is then a much slower process than the diffusion in the environment (van Leeuwen *et al.*, 2005). For other situations diffusion may govern biological uptake (van Leeuwen *et al.*, 2005).

Much research has been focused upon determining the speciation of metals and other important molecules in natural water (*e.g.* Alfaro-de La Torre *et al.*, 2000; Gimpel *et al.*, 2003; Sigg *et al.*, 2006). There are many different speciation techniques available, which use different principles for separating the different forms of the metals. There are direct measurements of the free ion, *e.g.* by potentiometry and ion-selective electrodes, but they are selective and usually require high concentrations of the metal. There are methods which separates molecules by size, since the smaller fractions include the more potentially toxic free ions and dissolved inorganic complexes. These methods include various forms of ultrafiltration, dialysis, size-exclusion chromatography and field-flow fractionation (FFF). Another separation technique is by charge: *e.g.* cation- and anion-exchange columns. One challenge is the high detection levels compared to natural concentrations. This can be dealt with by preconcentration of the sample, *e.g.* by using the Donnan membrane technique, by hollow fiber permeation liquid membrane or by cross-flow ultrafiltration. When determining the speciation, *in-situ* techniques are preferable due to possible changes occurring during transport and at the laboratory. However, there are few techniques available for *in-situ* speciation. One *in-situ* device is diffusive gradients in thin films (DGT), but this technique can cause problems with interpretation and is difficult for low-ionic-strength soft-water (Alfaro-de la Torre *et al.*, 2000). Also, qualitative studies of the detailed structure of the species by using large instruments are not possible in the field. All methods have their advantages and limitations including problems with contamination, changes during collection, storage and treatment, and problems with interpretation. One thing they have in common is that they are expensive, work-demanding and time-consuming. They can therefore not be used for *e.g.* monitoring of the 80 000 lakes in Sweden. They are also more or less momentaneous, *i.e.* they reflect the speciation at one particular point of time. To counteract these problems much work has been devoted to producing geochemical models that can:

1. Estimate the free ion concentration and the other species in water if the total concentration is known.
2. Predict what will happen in the future after changes of certain chemical or physical parameters.

Several attempts have been made to evaluate and compare measured species of trace metals in surface water with simulated ones using geochemical models (*e.g.* Gimpel *et al.*, 2003; Lyvén *et al.*, 2003; Unsworth *et al.*, 2006; Vasyukova *et al.*, 2010). The results reported are variable. Some papers report that Cu and Pb are often not correctly modelled (Gimpel *et al.*, 2003; Lyvén *et al.*, 2003; Unsworth *et al.*, 2006). Many of the conclusions focus on the role of iron and aluminium which need to be better assessed to achieve a “good” model (Unsworth *et al.*, 2006). Iron(III) and aluminium(III) can form (hydr)oxides that can adsorb toxic metals reducing their bioavailability. Both metals can also bind to NOM and thereby compete with toxic metals for binding sites (Tipping *et al.*, 2002). This is especially important for soft-water environments such as the Swedish lakes and rivers with a high Fe, Al and dissolved organic carbon (DOC) content, which will affect the other metals strongly. Without knowing the correct forms of iron and aluminium, simulation of other metals becomes more difficult.

1.1.2. Objective and aims of this thesis

The objective of this thesis is to improve the understanding of the speciation of iron and aluminium in surface water. This is important to be able to more accurately assess the speciation of other metals. My more specific aims are:

- To determine if iron is present as a particulate, colloidal or truly dissolved fraction in five Swedish lakes, to determine if it is present as a mineral or an organic colloidal phase, and to characterise the binding mode to dissolved organic matter (DOM) in two Swedish lakes. To be able to characterise the binding mode to DOM, a new method was needed for preconcentrating the iron colloids (Paper I, Paper III)
- To determine if aluminium is present as a particulate, colloidal or truly dissolved fraction; and if it is associated with a mineral or with an organic colloidal/particulate phase in five Swedish lakes. (Paper I, Paper III)
- To determine the speciation of potentially toxic metals in excessively limed lakes by comparing measured and modelled fractions (Paper I)
- To constrain and to test a consistent process-based geochemical model concerning simulation of pH, aluminium, iron, and adsorption of metals to ferrihydrite. The model should be both internally consistent (the same parameters are used when simulating an isolated one-component system as when using the model for the whole system), and geochemically consistent with results obtained earlier. (Paper II and V)
- To use the model to predict what will happen with pH and inorganic monomeric aluminium (Al_1) at changes in lime doses in the 3 043 limed Swedish lakes. (Paper IV)

1.2. Review of previous work

1.2.1. Iron

Iron is the second most abundant metal in the Earth's crust and present in primary minerals such as silicates, oxides, and sulphides. It is an essential element for many different kinds of organisms. It is only toxic at very high concentrations to freshwater species (*e.g.* Khan and Nugegoda, 2007 with references) compared to other metals.

Most of the iron in surface waters originates from the catchment, much less comes from atmospheric deposition (Lydersen *et al.*, 2002). Iron has a complicated chemistry in freshwaters and soils, and can exist in the environment in two oxidation states, iron(II) and iron(III). Iron(II) is the stable form in reducing environments such as low-oxygen sediments, hypolimnetic lake water and ground water. Iron(III) is the stable form in well-oxygenated waters and soils. In oxygenated, circum-neutral pH water the oxidation of iron(II) to iron(III) is fast, whereas in more acid water the oxidation is slower (Davison, 1993). Organic matter and light are known to be able to reduce iron(III) to iron(II) (Miles and Brezonik, 1981). Few studies have measured iron(II) in oxygenated surface water, even though it is not always negligible (Lofts *et al.*, 2008).

Iron(II) is generally present in the free hydrated ion form, since it does not bind strongly to natural organic matter (van Dijk, 1971). At significant concentrations and in the presence of other ions it can precipitate in various mineral forms such as vivianite [$\text{Fe}_3(\text{PO}_4)_2 \cdot 8 \text{H}_2\text{O}$], siderite (FeCO_3) or amorphous iron sulphide (FeS) (Davison, 1993).

Iron(III) has a completely different chemistry. It has a very low solubility; it easily precipitates as different secondary oxides and hydroxides. Examples of those are ferrihydrite, goethite [$\alpha\text{-FeO}(\text{OH})$], hematite [$\alpha\text{-Fe}_2\text{O}_3$], lepidocrocite [$\gamma\text{-FeO}(\text{OH})$], etc. The iron(III) (hydr)oxides have some things in common. They can easily adsorb other ions, both anions (due to positively charged surfaces at environmental pH values) and cations that complex specifically to the surfaces. This strong adsorption is due to a high surface area and to a high amount of functional hydroxyl groups with a pH-dependent charge. Another thing that distinguishes iron(III) from iron(II) is that it readily complexes to natural organic matter. These two features make iron(III) omnipresent in particulate and colloidal form in freshwater.

Ferrihydrite is ubiquitous in the environment. It is nano-crystalline and present in particles of sizes between 1 and 7 nm (Cismasu *et al.* 2011), which is smaller than the operationally used cut-off size for particles, 0.45 μm . However, it can also aggregate into larger particles. The exact structure is not known even for laboratory-produced material. Recent research suggests the structure of a single phase with a hexagonal space group $P6_3mc$ and unit cell dimensions of $a = 5.95 \text{ \AA}$ and $c = 9.06 \text{ \AA}$ (Michel *et al.*, 2007) (Fig. 1). The amount of tetrahedrally coordinated iron was later

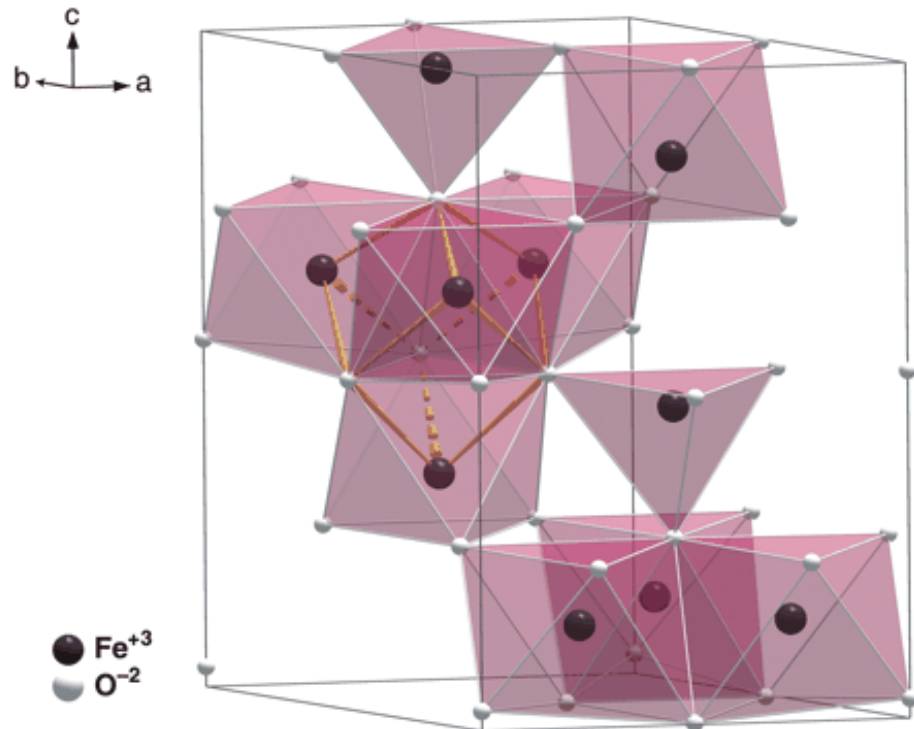
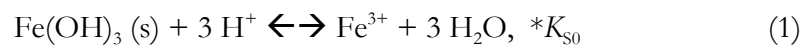


Fig. 1. Polyhedral representation of the hexagonal unit cell for ferrihydrite. The bonded atoms (yellow) define a cubane-like moiety that connects the basic structural motif of the model. From Michel *et al.* (2007). Reprinted with permission from AAAS. Readers may view, browse, and/or download material for temporary copying purposes only, provided these uses are for noncommercial personal purposes. Except as provided by law, this material may not be further reproduced, distributed, transmitted, modified, adapted, performed, displayed, published, or sold in whole or in part, without prior written permission from the publisher.

changed from 20 % to approximately 10 % (the remainder is octahedral iron) due to higher cation vacancies and the composition was adjusted to $(\text{Fe}_{8.2}\text{O}_{8.5}(\text{OH})_{7.4} \cdot 3 \text{H}_2\text{O})$ (Michel *et al.*, 2010). The simpler formula of $\text{Fe}(\text{OH})_3$ is often used when calculating the solubility product. The solubility product is also not well known, but laboratory studies for the reaction



range between a $\log *K_{\text{S}0}$ of 2.5 to 5.0 (Tipping *et al.*, 2002). Lower values are determined for aged materials and higher for freshly formed ferrihydrite (Tipping *et al.*, 2002). The enthalpy of the reaction has been determined to $-100.4 \text{ kJ mol}^{-1}$ by Liu and Millero (1999).

However, the structure of the laboratory-synthesized ferrihydrite can be different from the natural ferrihydrite, which in turn will affect the adsorption capacities and the solubility. Other elements present can substitute for Fe(III) or adsorb to the surface and thereby hinder or affect polymerisation, *e.g.* Al, SiO_4 , or NOM (Cismasu *et al.* 2011; Liu and Hesterberg, 2011). Cismasu *et al.* (2011) examined natural ferrihydrite from acid mine drainage sediments. They found that crystallinity was reduced by adsorbed

Si and by a small amount of NOM. Silica was not believed to chemically substitute into the structure due to the difference in ionic radii between Si^{4+} and Fe^{3+} . They also suspected Al to be chemically substituted which could have caused additional structural disorder.

On the contrary, Liu and Hesterberg (2011) precipitated Fe(III) and Al in mixtures of 0, 20, 50, 75, 100 % Al of Al+Fe(III) at pH 7.5, and they did not find Al to substitute for Fe(III) in the precipitates. Instead they interpreted their results for the 20 and 50 % Al samples to consist of core FeO_6 polyhedra with AlO_6 polyhedra integrated at their surfaces. The 75 % sample was believed to consist of separate Al-hydroxide and Fe-hydroxide phases, possibly aggregated together. Ferrihydrite also decreased in structural order and domain size with increasing Al to Al+Fe(III) ratio.

Iron (hydr)oxides can adsorb humic and fulvic acids (Tipping, 1981). Laboratory experiments show more humics to be adsorbed at lower pH (Tipping, 1981). Schwertmann *et al.* (2005) coprecipitated DOM and ferrihydrite which resulted in 96 mg C/g ferrihydrite, as compared to results from adsorption experiments where only between 3.3 and 24.2 mg C/g was adsorbed. They interpreted this result as evidence for DOM being incorporated in the structure. DOM reduced the crystallinity of ferrihydrite and suppressed lepidocrocite formation.

When iron(III) and soil organic matter (OM) was mixed together in the laboratory smaller ferrihydrite precipitates were formed than with no OM present (Eusterhues *et al.* 2008). The amount of OM that co-precipitated was 170 mg C per g ferrihydrite. However, since sorption depends on the surface area, and smaller precipitates were formed, the amount of C sorbed compared to the surface area was similar as in other experiments (Eusterhues *et al.*, 2008). Neal *et al.* (2008) modelled the humic acid adsorption with an empirical model, in which more humic substances were adsorbed at lower pH to goethite. They then estimated the binding of DOM to iron(III) oxyhydroxides in field river and lake water to be around 5 %. For some sites there was a large temporal variation.

Iron (hydr)oxide formation in three different waters have been studied by Perret *et al.* (2000). Apparently the type of macromolecular natural organic matter (aquagenic vs pedogenic; flexible vs compact) influences the morphology of the iron particles formed in the oxic/anoxic zone.

Not just the structure and morphology but also the solubility product of ferrihydrite can be different in the field compared to in synthetic water. Lofts *et al.* (2008) calculated the solubility constant for dialysed surface water samples and found that the slope of the relationship between Fe^{3+} activity and pH described in (Eq. 1) was lower compared to the stoichiometric value of -3. They suggested possible explanations from the literature such as substitution of

other anions than OH⁻ in the solid phase or pH-dependent variation in the activity of the solid.

The nature of iron(III) complexation to NOM is also not well understood. Previous studies using extended X-ray absorption fine structure (EXAFS) spectroscopy have indicated that iron can complex both in monomeric (Karlsson *et al.*, 2008; van Schaik *et al.*, 2008; Karlsson and Persson, 2010) and in dimeric/trimeric forms (Rose *et al.*, 1998; Vilg -Ritter *et al.*, 1999; Gustafsson *et al.*, 2007; Mikutta and Kretzschmar, 2011) to organic matter. A problem when using EXAFS spectroscopy for studying natural samples is the high detection limit. To study the samples they generally have to be preconcentrated, which could alter the speciation. Complexation constants are also difficult to determine. They have to be determined at low pH since iron(III) binds very strongly at higher pH and to prevent formation of iron(III) (hydr)oxides. A few studies exist; Langford and Khan (1975) studied iron(III) complexation to fulvic acid in a pH range from 1 to 2.5.

The strong complexation of Fe(III) makes it a competitor for binding sites to organic matter for the metals Cu (Tipping *et al.*, 2002; van Schaik *et al.*, 2010), Zn, Cd, Ni, VO²⁺ (Gustafsson *et al.*, 2007) and probably also Pb (Tipping, 2005). This would increase the presence of these metals in their dissolved inorganic form which makes them more bioavailable.

Previous studies of iron and its correlations with DOC and with other trace metals in surface water give a very mixed result depending on origin, type of surface water, season, discharge, etc. Iron was positively correlated to DOC in cloud water, rainfall, throughfall and stemflow, streams, but not to groundwater in the UK (Neal *et al.*, 2008). Increasing iron concentrations in streams and lake have been notified in the UK together with DOC increases, but this was claimed not to be due to complexation of Fe(III) to DOM. Instead they explained it by colloidal stabilization of iron (hydr)oxide particles by organic matter, which would cause them to be more easily transported. Some studies of size fractionation do not show a correlation between iron and DOC, instead iron colloids and DOC colloids were seen as two different pools in circum-neutral boreal Russian rivers, streams, swamps and lakes (Pokrovsky and Schott, 2002; Vasyukova *et al.*, 2010). Aluminium and lead were associated with iron, probably due to co-precipitation according to the authors.

Lyv n *et al.* (2003) studied a pH 6.5 creek water with a DOC concentration of 4 mg L⁻¹ and an iron concentration (< 0.45 µm) of 884 µg L⁻¹. Here iron and DOC were present in two size fractions, where the iron colloids (~ 4 nm) were larger than the DOC colloids (~1.2 nm). An intermediate fraction also existed.

To sum up, iron influences the transport and toxicity of several metals. This is caused either by competition for binding sites to organic matter or by the formation of (hydr)oxides to which

metals can bind. It is however a complex relationship since iron (hydr)oxides also adsorb organic matter.

This study will investigate in what forms iron resides in Swedish lakes, by use of size separation, Fe(II) determination and characterisation by EXAFS spectroscopy. A new method was developed to preconcentrate the colloids for EXAFS spectroscopy using an anion-exchange column. Also, adsorption to ferrihydrite is studied in detail for Cu and Pb by batch experiments and by EXAFS spectroscopy. The results are used to improve geochemical modelling of other metals such as aluminium, copper and lead.

1.2.2. Aluminium

Aluminium is the third most abundant element and the most common metal in the Earth's crust. It is present in granites and gneisses. So far it has not been proved that aluminium is an essential element to any organism. Instead it is toxic at large concentrations, especially to fish, but also to other aquatic organisms *e.g.* invertebrates and plankton (for a review, see *e.g.* Gensemer and Playle, 1999).

The major potentially toxic forms of aluminium are the inorganic cations, especially the free Al^{3+} ion. Two types of toxic mechanisms are suggested for fish; ionoregulatory problems at lower pH due to Al^{3+} displacing Ca^{2+} at tight junctions or interfering with Na, K-ATPase (Gensemer and Playle, 1999). This is similar to the potential toxicity of the H^+ ion and other metal cations. The other mechanism is precipitation and/or polymerisation of Al at the gills causing respiratory problems. This is most severe at pH around 6 (Gensemer and Playle, 1999). High Ca^{2+} , H^+ and DOM counteract the problem with potential Al toxicity for fish in accordance with BLM theory.

Atmospheric inputs of Al to surface waters are probably low (Lydersen *et al.*, 2002). Acidification has caused a larger input of Al to the surface waters from the surrounding soils, especially at areas with low weathering rates in the catchment. Therefore the concentrations of Al are quite high in natural waters in Sweden.

Similarly as for iron(III), aluminium(III) can precipitate as mineral phases and be complexed to DOM, but the details are uncertain. Above pH 6 aluminium solubility is low in both surface waters and soils, and it is controlled by a mineral phase with $\text{Al}(\text{OH})_3$ -type solubility (Tipping, 2005). The actual mineral form that is controlling Al solubility is not confirmed yet. Suggestions in soils are amorphous $\text{Al}(\text{OH})_3$, gibbsite (crystalline $\text{Al}(\text{OH})_3$), and silica-containing (proto)-imogolite or allophane (Gustafsson *et al.*, 2001). The theoretical $\text{Al}(\text{OH})_3$ phase has a higher log solubility product than $\text{Fe}(\text{OH})_3$, at 25° C it is estimated to be: 8.5 in natural waters (Tipping, 2005), 8.77 in lakes in the north-east U.S. (Warby *et al.*, 2008), and 8.29 in moderately acid Bs horizons of podzolised soils (Gustafsson *et al.*, 2001). Temperature has a large effect on the $\text{Al}(\text{OH})_3$ solubility, the colder the higher solubility product. When estimating the solubility of Al in soils, Gustafsson *et al.* (2001) used

the heat of reaction, ΔH_r^0 , determined for gibbsite as $-105.0 \text{ kJ mol}^{-1}$ (Palmer and Wesolowski, 1992) whereas Tipping (2005) used a mid-range value from several studies of -107 kJ mol^{-1} (see Tipping *et al.*, 2002, and references therein). In nature with high NOM concentrations and pH below 6, Al is often undersaturated with respect to $\text{Al}(\text{OH})_3$ and instead controlled by complexation to organic matter (Tipping, 2005; Warby *et al.*, 2008). The complexation of Al to organic acids is important for mitigating Al toxicity. However, aluminium has also been known to compete with other metals for binding sites; *e.g.* with Cu (Tipping *et al.*, 2002; van Schaik *et al.*, 2010), Eu (Susetyo *et al.*, 1990; Bidoglio *et al.*, 1991), Pb (Mota *et al.*, 1996; Pinheiro *et al.*, 2000), and Cd (Pinheiro *et al.*, 2000). Aluminium complexation to organic acids is therefore not only decreasing its own bioavailability, it could also increase the bioavailability of other potentially toxic metals.

Aluminium in boreal surface water has been found to be mainly associated with iron colloids at pH above 6, and not with organic carbon (Pokrovsky and Schott, 2002; Vasyukova *et al.*, 2010). However, for two organic-rich rivers Al was associated with $< 10 \text{ kDa}$ organic complexes (Pokrovsky and Schott, 2002). Aluminium correlated better with organic carbon (OC) than with Fe for water draining granitic rocks compared to basic rocks (Vasyukova *et al.*, 2010). In another study with Swedish creek water (pH 6.5) Al was associated with both iron and organic carbon colloids (Lyvén *et al.*, 2003).

The inorganic complexes of aluminium include the hydroxide-complexes, but aluminium also forms inorganic complexes with in particular F^- but also SO_4^{2-} , and in small amounts SiO_4^- , CO_3^{2-} and Cl^- . According to the FIAM, complexation with fluoride would reduce toxicity of Al due to less Al^{3+} activity. Lowered toxicity has been shown in a study of fish, but not to as much as expected due to the lower Al^{3+} (Wilkinson *et al.*, 1990). This could be due to toxicity of Al-fluoride complexes or that the Al-fluoride complexes are not strong enough to compete with binding sites to the gills (Gensemer and Playle, 1999).

Inorganic monomeric aluminium (Al_i) has often been monitored on a large scale due to its toxicity at high concentrations. Inorganic monomeric aluminium can be analysed with several different methods (Barnes, 1975; Clarke *et al.*, 1992), but the most common one is the cation exchange column method developed by Driscoll (1984). The method retains the inorganic cations, while the anionic or neutral forms of organic and inorganic Al passes through the column. The inorganic monomeric Al is determined indirectly as the difference between total (monomeric) Al and Al in the eluate. Aluminium can be detected in several different ways, *e.g.* by complexation with pyrocatechol violet (PCV) with spectrophotometric detection. Another more inclusive detection method uses detection with inductively coupled plasma-optical emission spectroscopy (ICP-OES). One possible problem for the

Driscoll method could be decomplexation of Al from organic matter when passing through the column, which would overestimate the inorganic monomeric Al (Backes and Tipping, 1987). Another possible artefact is physical retention of particulate/colloidal inorganic Al due to its large size in the column. A problem with all methods is that they generally overestimate soluble, inorganic monomeric Al. This is due to the equilibrium shift that occurs when a chelating agent, complexing agent or a resin is added that releases more Al^{3+} to the system. The increased Al^{3+} is then detected by the complexing agent (Lindsay and Walthall, 1996; Gensemer and Playle, 1999).

Many studies have attempted to model Al_i in surface waters (Schecher and Driscoll, 1988; Driscoll *et al.*, 1994; Cory *et al.*, 2007; Tipping and Carter, 2011). Often it is only inorganic aluminium that has been modelled. Few studies have modelled both pH and Al_i simultaneously (Driscoll *et al.*, 1994), even though pH and Al_i is closely linked.

This study will focus on the derivation of a model for predicting both pH and Al_i for Swedish surface waters, using a consistent set of parameters. It is explored how well the model works for simulating Al_i , as determined by the cation-exchange method using either the PCV or the ICP-OES method for detection. Colloidal and particulate forms of Al will be studied to see if they relate to a potential precipitated phase of Al.

1.2.3. Other trace metals

Aluminium is the potentially toxic metal present in the highest concentrations in Swedish surface water compared to potentially toxic levels (Lydersen *et al.*, 2002). However, if aluminium is present together with other metals with lower concentrations it can result in an additive toxic effect (*e.g.* Hutchinson and Sprague, 1986). Therefore, it is important to study the speciation of the total amount of potentially toxic metals, even though they individually may be present in concentrations that are considered non-toxic.

Copper

Copper is an essential element for all organisms, but it is toxic at high concentrations, especially to algae, fungi and vertebrates (Lydersen *et al.*, 2002).

Copper is mainly present in the environment as Cu(I) or Cu(II), but Cu(I) is only stable at highly reducing conditions. Copper (II) readily adsorbs to organic matter. Copper has been showed to be strongly complexed to organic matter in surface waters (Sigg *et al.*, 2006). In the ultrafiltrated waters of Pokrovsky and Schott (2002) copper was not appearing as organic or iron-rich colloids, instead it was mainly in the < 1 kDa fraction (possibly associated with < 1 kDa organic matter or present as dissolved inorganic species). Copper in a Swedish creek was associated with organic colloids, and not with the larger iron colloids (Lyvén *et al.*, 2003).

Copper(II) adsorbs to ferrihydrite, and evidence exists that it forms inner-sphere edge-sharing bidentate complexes (Scheinost *et*

al., 2001). Copper(II) might adsorb more strongly in the presence of other anions, but such systems have rarely been studied.

In this study copper adsorption to ferrihydrite with and without the presence of phosphate was studied both qualitatively using EXAFS spectroscopy and quantitatively using batch experiments. The results have been used to optimise surface complexation constants using the Charge Distribution Multi Site Complexation (CD-MUSIC) model (Hiemstra and van Riemsdijk, 1996). Further, with the new constants Cu has been modelled using a geochemical equilibrium model in two lakes and compared with ultrafiltration fractionation to see if the model captures Cu speciation correctly.

Lead

Lead is naturally present in low concentrations. During the 1970s and 1980s leaded petrol caused widespread pollution of lead to the environment. As the evidence concerning the potential toxicity of lead grew, it was phased out from the use as a petrol additive, and since the 1980s the concentrations have decreased in the environment (Lydersen *et al.*, 2002).

Lead is mainly present as inorganic Pb(II) in the environment, but there are also organic lead compounds from human contamination. Inorganic lead(II) readily adsorbs to iron (hydr)oxides and complexes to organic matter, and is therefore often retained in the soil very strongly. Lead is also often associated with iron and organic matter in natural waters (Fuller *et al.*, 1988; Erel and Morgan, 1992; Lyvén *et al.*, 2003; Wällstedt *et al.*, 2009). Lead has been found to be associated with iron colloids and not with organic colloids in surface water (Pokrovsky and Schott., 2002; Lyvén *et al.*, 2003; Sigg *et al.*, 2006; Vasjukova *et al.*, 2010).

There may be competition between iron(III) and aluminium(III) with lead(II) for complexation to organic matter (see sections 1.2.1 and 1.2.2).

Lead adsorption to ferrihydrite has been studied previously using batch experiments by *e.g.* Swedlund *et al.* (2003) and by Gustafsson *et al.* (2011). X-ray absorption spectroscopy has been used to study the complex qualitatively, and both inner-sphere edge-sharing bidentate complexes (Scheinost *et al.*, 2001; Trivedi *et al.*, 2003) and inner-sphere monodentate complexes have been found (Trivedi *et al.*, 2003). There has been evidence of increased Pb adsorption in the presence of phosphate on iron oxides (Xie and Giammar, 2007).

Therefore, similar as for Cu, lead adsorption to ferrihydrite with and without phosphate was examined in this study and the CD-MUSIC model was constrained. The resulting CD-MUSIC model was used together with a consistent geochemical model for comparison with ultrafiltration fractionation to see if the model captures Pb speciation correctly for two lakes.

1.2.4. Natural organic matter

Natural organic matter (NOM) is a large, heterogeneous group of compounds. It consists of partly degraded plant, animal and microbial residues. Parts of it include smaller organic acids such as citrate, oxalate, alate, acetate and salicylate acids, sugar acids and phenols. They are easily degraded and therefore not present in high amounts. The major part of NOM is called humic substances and they have traditionally been separated into three groups based upon pH solubility: humin, humic acids and fulvic acids. They are important for metals since they can complex them and thereby reduce their bioavailability. It has also been shown that DOM is not toxic in itself to fish (31 mg L⁻¹ DOC, pH 7) (Richards *et al.*, 1999). One problem with humic substances is to find a good way to analyse them (for a review, see *e.g.* Hedges *et al.*, 2000). The origin (*e.g.* from the soil or lake) of the humic and fulvic acids is not considered important for their characteristics.

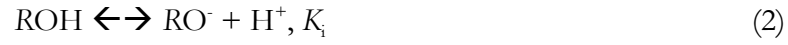
Humic and fulvic acids can be separated through acid and base treatments, and can thereafter be used in titration experiments to determine the complexation constants for H⁺ and metal ions. A question that has been raised is whether the isolation method is destructive so that the results are not representative for field conditions. The complexation constants can later be used in geochemical models. One problem when modelling acid dissociation is the fact that the acids dissociate over a large range of pH values due to the heterogeneity of the compounds. Some patterns do exist. There is a large number of acid groups having pK_a-values between 4 and 6; these are considered to be carboxylic acid groups. For another type of group the pK_a-values range from 8 to 10; these are considered to be phenolic acid groups. The carboxylic acid groups are more involved in complexation of H⁺ and cations at natural pH values than the phenolic groups.

There are different models available for simulating the proton and metal binding properties of humic substances. One of the simplest ones is the equation by Oliver *et al.* (1983), which is an empirical model designed for estimating the organic acidity in acidic waters. Then there are also monoprotic, diprotic and triprotic models (Driscoll *et al.*, 1994; Schecher and Driscoll, 1995; Köhler *et al.*, 2000; Hruška *et al.*, 2003). The most advanced models are the Non-Ideal Competitive Adsorption Donnan (NICA-Donnan) model (Kinniburgh *et al.*, 1999), Model VI (Tipping, 1998) with its precursor Model V (Tipping and Hurley, 1992), and the Stockholm Humic Model (SHM) (Gustafsson, 2001). These last models separate between metals bound specifically to the organic ligand forming complexes and metals accumulated electrostatically due to the negatively charged ligand.

NICA-Donnan is a model based upon a bimodal, continuous distribution of complexation sites, divided into the two different forms of sites: carboxylic and phenolic.

Contrary to the NICA-Donnan model, the Humic binding Model VI is a model based on discrete sites for binding of protons and

metals and their first hydrolysis product. The Stockholm Humic Model (SHM) is based upon the Model VI in this respect. The dissociation reaction is defined as:



where R represents the humic molecule and K_i is an intrinsic dissociation constant, which includes a correction term for electrostatics. There are eight sites divided into two groups. Group A representing strong H^+ binding (numbers 1-4), mainly carboxylic acid groups, and group B with weaker sites (numbers 5-8), mainly phenolic acid groups. Both groups are represented by four sites constants each, which are calculated as

$$i = 1 - 4 : \log K_i = \log K_A - \frac{(2i-5)}{6} \Delta pK_A \quad (3)$$

$$i = 5 - 8 : \log K_i = \log K_B - \frac{(2i-13)}{6} \Delta pK_B \quad (4)$$

where $\log K_A$, $\log K_B$, ΔpK_A and ΔpK_B are needed to define the eight $\log K_i$ values.

The metals can be complexed to the same sites in monodentate and bidentate complexes in the Stockholm Humic Model. The monodentate reaction for Cd^{2+} is defined as:



where the constant K_{Cdm} includes electrostatics. The same K_{Cdm} is used for the eight proton-binding sites, but the heterogeneity of site affinity is accounted for by a heterogeneity parameter, ΔLK_2 , in the expression:

$$\log K_{\text{Cdm},x} = \log K_{\text{Cdm}} + x \cdot \Delta LK_2 \quad ; x = 0, 1, 2 \quad (6)$$

The larger ΔLK_2 , the more heterogeneity, *i.e.* a small amount of sites binds the metal very strongly compared to the majority of sites. Each site is subdivided into three subsites in the generic version of SHM, where x is set to 0 for 90.1 % of the sites, 1 for 9 % and 2 for 0.9 % of the sites.

All models assume that the DOM resembles the isolated humic and fulvic acids. However, generally there can be a fraction of the DOM that is not humic and fulvic acids, *e.g.* cellulose, which does not bind protons or metals. Therefore, there is a need to determine how much of the natural organic matter that consists of humic and fulvic acids, *i.e.* is active in proton and metal binding. Total organic matter is often estimated by determining the organic carbon content and multiplying by two, since organic matter generally consists of approximately 50 % of carbon by weight. The maximum active fraction of dissolved organic matter compared to DOC (the so-called ADOM/DOC ratio) is therefore 2, but in natural waters it is often smaller. Often the ADOM/DOC ratio is

the parameter that is fitted when modelling a data set and different values have been used ranging between 0.6 and 1.98 for surface waters (Bryan *et al.*, 2002: 1.12-1.98; Tipping *et al.*, 2002: 1.2-1.4; Tipping and Carter, 2011: 0.6-1.35). This is quite a large range and it has significant importance for pH modelling and metal speciation. Few have set the fraction to a common value for two separate parameters, *e.g.* pH and a metal complexation reaction (Driscoll *et al.*, 1994).

Recently, an increase of DOC in surface waters in Europe and North America has been detected (*e.g.* Driscoll *et al.*, 2003; Evans *et al.* 2005), but the mechanism is under debate.

1.2.5. Mineral surfaces and surface complexation models

Mineral surfaces are important for the adsorption of trace metals. Iron, aluminium and manganese (hydr)oxides are important surfaces due to their large abundance in natural waters and their high amounts of surface groups available for binding. The most data for metal adsorption exist for the iron (hydr)oxides ferrihydrite and goethite. Dzombak and Morel (1990) were pioneers in establishing a database for adsorption to hydrous ferric oxides and also developed the Diffuse Layer model (which they referred to as the Generalized Two-Layer model).

The Al, Fe and Mn (hydr)oxides have variable charge depending on pH. Ferrihydrite has a point-of-zero charge at between 7.9 and 8.3 meaning that at natural pH a majority of the sites are positively charged (Stachowicz, 2007). This means that it can easily adsorb inorganic anions and organic acids. Ferrihydrite can also adsorb metal cations forming strong surface complexes. Ferrihydrite contains singly-, doubly and triply coordinated oxygen surface groups, but the singly coordinated ones are the most common and therefore probably most important for proton binding.

Modelling of adsorption to (hydr)oxides are generally performed with surface complexation models. They involve surface reactions treated as complexation reactions in which inner-sphere ions are adsorbed to discrete sites on the mineral and a mass-action equation defines the sorption constant K . They also often involve electrostatics due to counter-ion accumulation in the so-called diffuse double layer (DDL). The location of the ion charge in the diffusive double layer is important and will affect the proton co-adsorption and release. With spectroscopic data, obtained by *e.g.* EXAFS- or infrared (IR) spectroscopy, the structure of the surface complexes can be determined. By using such data the description of the sites can become more precise and more realistic. This idea led to the development of the Multi Site Complexation (MUSIC) model (Hiemstra *et al.*, 1989a and b). Additionally, it was suggested that the inner-sphere-adsorbed ions should not be treated as point charges, since they rather have a distributed charge (Hiemstra and van Riemsdijk, 1996). This idea is the key concept in the charge distribution (CD) model (Hiemstra and van Riemsdijk, 1996), which, in combination with the MUSIC model becomes the CD-MUSIC model.

2. MATERIAL AND METHODS

2.1. Site description and sampling

Two different areas, Dalsland and Tyresta, where sampled in this study.

2.1.1. Dalsland - (Paper I)

Three lakes were studied in south-western Sweden, two that were excessively limed, L. Motjärn and L. Stora Vrångstjärnet in Dalsland, and one unlimed reference lake, L. Rotehogstjärnen in Bohuslän. L. Motjärn is 11.3 ha with an average pH of 7.4 and the maximum depth is 10 m. Lake St Vrångstjärnet is 9.4 ha, with an average pH of 7.3, and the maximum depth is 12 m. Lake Rotehogstjärnen is 16.8 ha, with an average pH of 5.3, and with a maximum depth of 10 m (ISELAW, 2007, <http://info1.ma.slu.se/IKEU>). All the lakes are oligotrophic and situated in boreal forests. The lakes were sampled in September 2007. The lake water chemistry was studied with *in-situ* dialysis and geochemical modelling.

2.1.2. Tyresta – (Paper III and Paper IV)

Tyresta National Park is located 20 km SE Stockholm, Sweden. It is a boreal forest landscape with thin soil and slowly weathering bedrock, mainly gneissic-granite (Wällstedt *et al.*, 2009). Four lakes present in this area have been monitored since 1977. The lakes are all oligotrophic and dimictic. Two of them, the previously limed L. Trehörningen and the unlimed L. Årsjön, were sampled in this study and characterised in detail with regards to water chemistry. Lake Trehörningen was also modelled for termination of liming in Paper IV using data from monitoring (see Wällstedt *et al.*, 2009 for details). One of the other two lakes, L. Långsjön (limed until 1995), was modelled for termination of liming in Paper IV, also using monitoring data.

Lake Trehörningen was sampled in March 2008, October 2008, April 2009, January 2010, and March 2011 whereas L. Årsjön was sampled the same occasions except the first one. Water was taken from the surface (0.2 m depth) directly into 10-L HDPE containers that had been acid leached and rinsed with deionised (Milli-Q) water. The water was further filtrated and run on an anion column as described in sections 2.2.2 to 2.2.3 and in the generalised scheme (Fig. 2). General water chemistry and Fe(II) concentration was also determined.

2.2. Laboratory methods

2.2.1. Dialysis – (Paper I)

Dialysis is a method that separates molecules based upon size. In this work a 1 kDa pore size was used to separate small molecules, mainly inorganic ions and small organic acids, from colloids and particles. Spectra/por® regenerated cellulose (Spectrumlabs) dialysis bags were placed *in-situ* at the surface and the bottom of the Dalsland lakes and left for five days to equilibrate. For more details, see Material and Methods section in Paper I.

2.2.2. In-line prefiltration – (Paper III)

In-line prefiltration was performed with a Geotech 142 mm polycarbonate (or acrylic) filter holder and with 0.45 μm polyvinylidene filters. In-line filtration was used to be able to collect the particles and characterise them using Fe K-edge EXAFS spectroscopy. Samples from Tyresta were filtrated immediately upon returning to the lab, starting 3-8 hours after sampling and finishing within additional 3 hours.

2.2.3. Cross-flow ultrafiltration – (Paper III)

In cross-flow filtration (CFF) (also called tangential flow filtration) the water flows fast over a filter and back to a container. Molecules smaller than the pore size passes through the filter into a container (the permeate) while larger molecules flows over the filter and concentrates into a retentate. In this study two 1 kDa regenerated cellulose membranes (Pellicon2, Millipore), a Pellicon cassette acrylic filter holder, and a Millipore Masterflex I/P Easyload peristaltic pump were used. The CF-ultrafiltration generally started within 30 hours after sampling on the pre-filtered water, generally it took 2.5-3 hours to filtrate 10 litres. Approximately 10-20 litres of water were ultrafiltrated with a concentration factor of 20, resulting in a retentate of approximately half a litre. The retentate

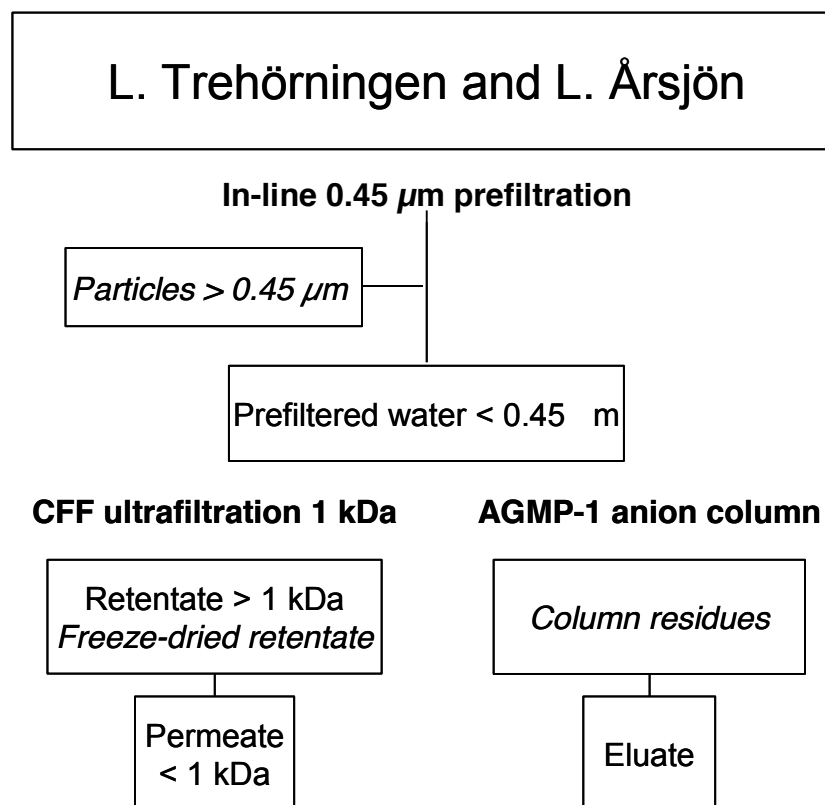


Fig. 2. General chart of filtration and preparation of the water from L. Trehörningen and L. Årsjön. Text in bold refers to the techniques used. Text in italics refers to the samples measured by EXAFS spectroscopy. Water chemistry was characterised for samples in normal font.

was analysed for water chemistry and afterwards freeze-dried. The freeze-dried retentate was characterised by Fe *K*-edge EXAFS spectroscopy. The permeate was analysed for water chemistry and cation exchange Al fractionation (Driscoll, 1984).

2.2.4. Ferrozine method – (Paper III)

The first step in the method described in Viollier *et al.* (2000) was used to determine iron(II) in the lake water in the field in Tyresta and for some of the treated water. Ferrozine forms a purple complex with iron(II) with a maximum absorbance at 562 nm. Iron(III) also forms a complex with ferrozine but it absorbs much less at this wavelength and it can be compensated for. The samples were first pre-filtered with 0.2 μm syringes and then ferrozine was added and the complex formed was immediately detected with a spectrophotometer. The samples were also measured without ferrozine addition to see the contribution to the absorption from organic matter, and these results were deducted from the samples. Total Fe concentration in the water was determined by ICP and finally the iron(III) and iron(II) concentration could be calculated.

2.3. New method for concentrating of iron species – Anion-exchange column

To be able to study the Fe speciation with EXAFS spectroscopy, a concentration method was needed. In addition to freeze-dried retentates from CF ultrafiltration (see section 2.2.3) a new method was developed in Paper III using a column with AGMP-1 anion exchange resin (Bio-rad, 100-200 mesh). The AGMP-1 resin consists of strongly basic trimethylammonium groups with a macro-porous structure composed of a styrene divinylbenzene copolymer. It adsorbs the negatively charged organic material due to charge-based separation. The volume of the resin was 3 ml placed in a 5 ml glass column and the water was pumped with a flow rate of 1 ml min^{-1} . The residues collected on top of the column were analysed by EXAFS spectroscopy. The eluate was monitored for pH, total iron, DOC or absorbance. A test was also performed determining iron(II) prior and after passing the column.

2.4. EXAFS spectroscopy – (Paper III and Paper V)

2.4.1. General

X-ray absorption spectroscopy (XAS) is a technique that uses X-rays to characterise the structure around a specific element, for example coordination atoms and bond lengths. The experiments are performed at large synchrotrons where charged particles are accelerated into a booster ring which emits X-rays. From that ring X-rays can be withdrawn in a so-called beamline, where the experiments are performed. As for the commonplace use of X-rays in medicine, heavier elements, such as Ca, more easily absorb the X-rays compared to softer elements, such as C and O. Element-specific energies are used for exciting an electron from an inner-electron shell of the atom studied out to continuum (Kelly *et al.*, 2008). Extra energy causes the electron to move in a wave that is scattered to other neighbouring atoms. The scattering gives rise

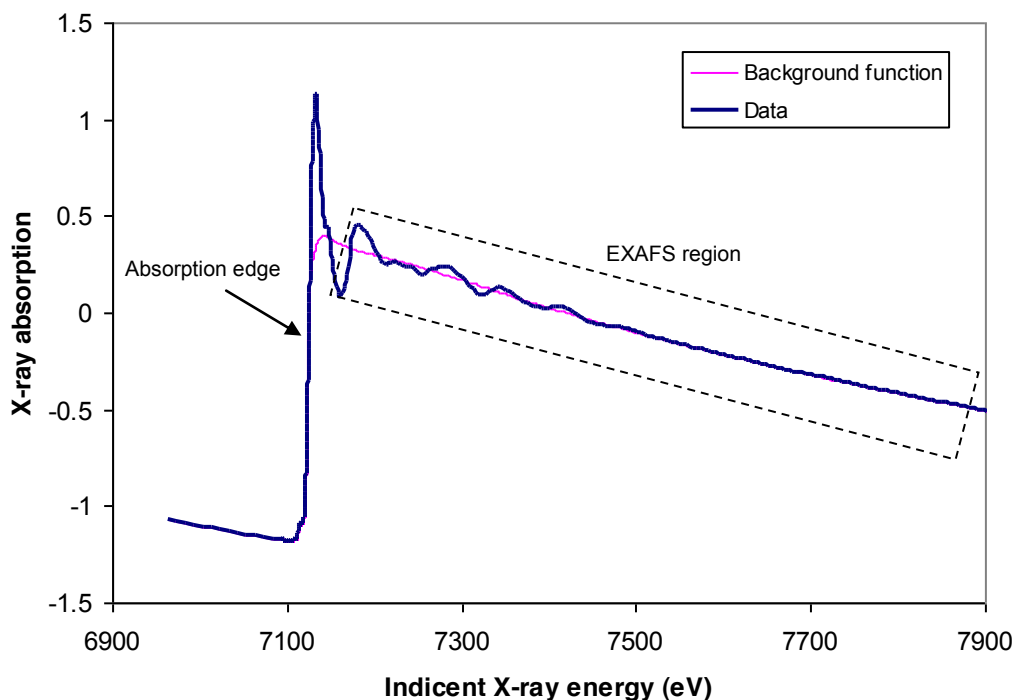


Fig. 3. An example of an iron *K*-edge X-ray absorption spectrum (= hematite) with the absorption edge and the EXAFS region noted. The background function (pink) is subtracted from the recorded spectrum to receive the EXAFS spectrum. eV = electronvolts

to a certain absorption spectrum whenever the waves are in phase or out of phase (Fig. 3). At certain energies the wave is in phase due to a certain distance to and to the atomic weight of the neighbouring atom. The spectrum can therefore be used to determine the type and the coordination of neighbouring atoms, including the bond length. In Extended X-ray Absorption fine structure (EXAFS) spectroscopy uses, the spectrum recorded at energies above the absorption edge is analysed (Fig. 3).

The iron *K*-edge EXAFS experiments were performed at MAX-Lab (MAX II), Lund University at beamline I-811. Samples (all from Tyresta) included particles collected from the in-line prefiltration, colloids from the anion-exchange column, and colloids from freeze-dried retentates. In April 2009 soil samples from the Oe horizon surrounding L. Trehörningen were also included. To improve EXAFS spectra soil subsamples were treated with additions of 15 mmol kg⁻¹ soil Fe(NO₃)₃ and pH was adjusted to 2.6 and 4.0 with HCl and NaOH respectively.

The structure of the lead and copper surface complexes on ferrihydrite was examined at beamline 4-1 at the Stanford Synchrotron Radiation Lightsource (SSRL), Stanford, California. Details are presented in Paper V.

2.4.2. EXAFS Data Analysis

The resulting absorption spectrum has to be treated by first increasing the resolution by drawing a so-called spline/background

function in the middle of the absorption spectrum (Fig. 3). Later the background function is subtracted from the absorption spectrum resulting in an EXAFS spectrum. This spectrum is fitted with a model representing a possible phase or a mixture present in the samples. Sometimes different models fit equally well. EXAFS spectroscopy is often regarded as a method that can falsify a hypothesis, not verify it.

EXAFS data treatment and modelling of the spectra were performed using the Athena/Artemis program package (Ravel and Newville, 2005) which incorporate the FEFF code (Rehr and Albers, 2000) and Atoms (Ravel, 2001). Wavelet transform (WT) analysis of EXAFS spectra can be used to differentiate between heavy and light backscatters for higher coordination shells (Karlsson *et al.*, 2008). The Morlet wavelet transform incorporated in the Igor Pro script (Wavelet2.ipf) developed by Chukalina (2010) was used. The k^3 -weighted EXAFS spectra were used with a frequency of 8 (the κ parameter) for a high resolution plots for the second shell (2-4 Å), while the half width of the Gaussian envelope (σ) was set to 1.

For more details, the reader is referred to paper III and paper V.

2.5. Geochemical modelling – (Paper I, II, III, IV, V)

2.5.1. Data sets for modelling – (Paper II and IV)

Large data sets with measured surface water chemistry from various parts all over Sweden were used to constrain a geochemical model to be able to simulate pH and Al_i simultaneously (Paper II). In total the different datasets consisted of 5 172 samples for pH and 3 918 samples for aluminium fractionation. First one data set was used for optimisation of the ADOM/DOC ratio based on pH simulations, with samples from a countrywide lake sampling of unlimed lakes (“Målsjöar” $n = 322$). The ADOM/DOC ratio was optimised using different values and the pH value was modelled from charge balance. Subsequently the same data was used to analyse the usefulness of the default binding constant for aluminium to predict the measured concentration of inorganic aluminium and to study the outcome of varying that constant by a factor of 2.

When evaluating the modelling of the inorganic monomeric aluminium, data sets with two methods for determining Al_i were used, the PCV-method ($n = 2\ 611$) and the ICP-OES method ($n = 1307$) (section 1.2.2 and Table 1). Due to the different results for the two methods, the data sets Målsjöar and “Forest streams” (Löfgren *et al.*, 2010) were used as calibration data sets of a correction function (see section 3.5.2).

One data set consisting of a group of northern streams, “Krycklan” (Buffam *et al.*, 2007; Björkvald *et al.*, 2008), had determined concentrations for both unfiltered and 0.4 μm -filtered Al and Fe. Measured chemistry using unfiltered concentrations was modelled for precipitated $Al(OH)_3$ (Table 1) and ferrihydrite, and

the modelled precipitates were compared to determined Al and Fe particles (unfiltered minus filtered concentrations).

The dataset Målsjöar was part a larger national survey of 1 807 unlimed lakes and the 3 043 limed lakes in Sweden (Fölster *et al.*, 2011a), sampled both in autumn 2007 and spring 2008. These lakes were simulated for pH as a test of the model. The 3 043 limed lakes were also simulated for lower concentrations of Ca and Mg, as estimated for termination of liming (Paper IV).

2.5.2. Modelling methods

There are several different geochemical models developed for metal speciation, like PHREEQC (Parkhurst and Appelo, 1999), WHAM (Tipping, 1994), Visual MINTEQ (Gustafsson, 2012), ALCHEMI (Schecher and Driscoll, 1995), MINEQL+ (www.mineql.com) etc. The equations governing inorganic speciation are generally the same or similar in the models.

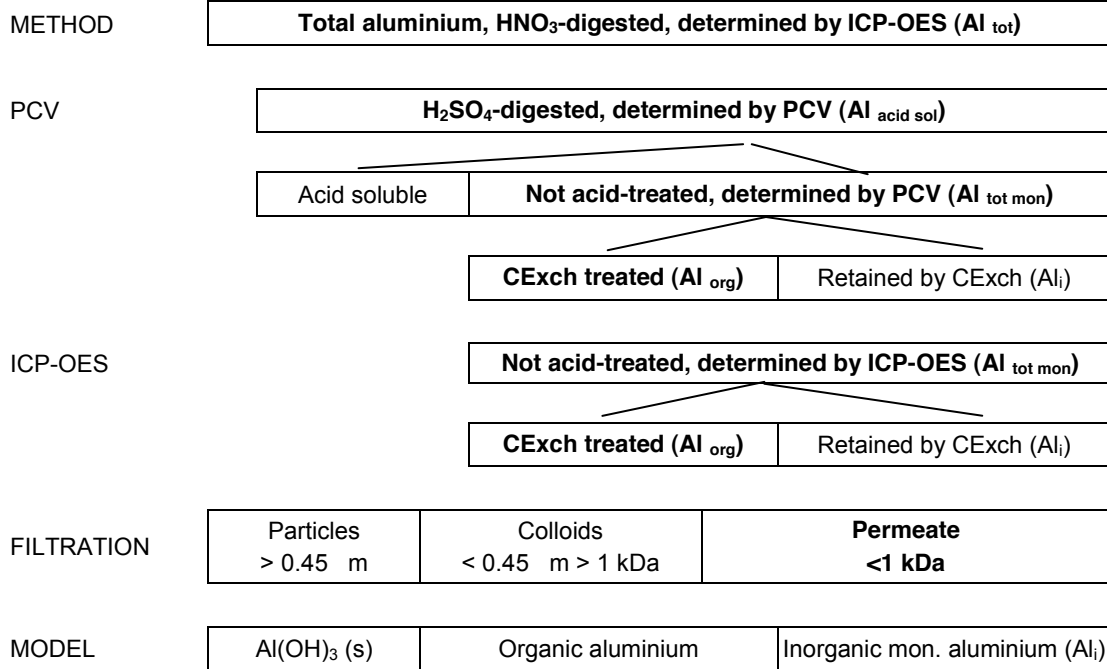
The geochemical program Visual MINTEQ (versions 2.53, 2.60 and 3.0) (Gustafsson, 2012) was used for the geochemical modelling. For inorganic complexes, the thermodynamic default database was used, which is mostly based on the NIST compilation (Smith *et al.*, 2003). Total concentrations of analysed cations and anions were used in the modelling, unless otherwise stated.

Total iron(II) and iron(III) as determined by the ferrozine method and ICP-(MS or OES) were entered, either estimated (Paper I) or determined using the ferrozine method (Paper III). For the simulations in paper II and IV no measurements of iron(II) were available, so instead all iron was considered to be iron(III).

If the solubility product was exceeded, the minerals Al(OH)₃, ferrihydrite and for paper I birnessite (MnO₂) were allowed to precipitate. Different log *K_{s0} were tested for Al(OH)₃ (around 8.29) and ferrihydrite (between 2.69 and 3.8) in paper II. For birnessite the log *K_{s0} value of 18.091 was chosen (Smith *et al.*, 2003).

The temperature can affect the solubility products Al(OH)₃ and ferrihydrite significantly. The field temperatures for the Tyresta lakes ranged from -0.7 to 12.9 °C, but the pH determination and aluminium fractionation was performed at room temperature. Filtration was performed on semi-cold water, in room temperature but with cold water from the field or from the cold storage room (4 °C). For the simulations in Paper I and Paper III the measured field temperature was used. For the data in paper II the field temperature averaged 7.8 °C and ranged between -1 to 26 °C. For the data in paper IV the average field temperature was 11.7 °C and ranged from -1.8 to 24.4 °C. However, since pH, Al_i fractionations and filtration were performed at room temperature an intermediate value of 10 °C was chosen for paper II and IV.

Table 1. Simplified sketch of aluminium fractionation methods and aluminium models used. Bold text refers to measured data, normal formatting to fractions calculated by difference. CExch = cation exchange. PCV = Pyrochatechol violet Al_i = Inorganic monomeric aluminium



For dissolved inorganic carbon (IC), measured IC or alkalinity can be used. However, when measured alkalinity values were used it occasionally gave erroneous results at high pH values. Instead the relationship for pCO_2 suggested by Sobek *et al.* (2003) was tested:

$$pCO_2 = (1.079 \cdot DOC + 2.332) \cdot 10^{-4} \quad (7)$$

where pCO_2 represents the partial pressure of CO_2 in atm, and DOC represents dissolved organic carbon in $mg\ L^{-1}$. This relationship for pCO_2 was used in paper II, III, and IV.

Dissolved organic matter was modelled with the Stockholm Humic Model, with default values for acid-base and metal-binding parameters. In Fennoscandia little of the total organic carbon (TOC) analysed in surface waters has been found to be present as particles larger than 0.45 μ m (less than 5 %, Temnerud *et al.*, 2007), therefore it was assumed that all analysed unfiltered organic carbon is dissolved organic carbon (DOC). The previous default value of the active DOM to DOC ratio, 1.4, (derived from the data of Bryan *et al.*, 2002) was used for the Dalsland lakes (Paper I). For Paper II this figure was fitted for the pH simulations for the calibration dataset "Målsjöar" and determined to be 1.65. This figure was then used throughout in Paper III and IV. Active DOM could be humic or fulvic acid, but it was assumed here that all of it was fulvic acid. Originally SHM contained the dimeric constants of

Fe(III) complexation to DOM (Gustafsson *et al.*, 2007). Later on these were changed in this study to monomeric constants and fitted for two data sets of mor layers Risbergshöjden Oe and Korsmossen Oe (Gustafsson *et al.*, 2007) (procedure described in the appendix of paper II). Complexation constants of Pb to fulvic acids was also changed according to Gustafsson *et al.* (2011), and was used for the modelling of Pb in L. Trehörningen and L. Årsjön.

Adsorption to ferrihydrite was estimated using the CD-MUSIC model (Hiemstra and van Riemsdijk, 1996). The model calculated the amount of adsorbing ferrihydrite that was precipitated from the total dissolved iron concentration, using the approach described by Wällstedt *et al.* (2010). New constants for Cu and Pb adsorption to ferrihydrite were developed in Paper V. Complexation constants for Al³⁺ adsorption to ferrihydrite was developed in Edkymish (2009), and was only used for modelling Al in the Tyresta lakes.

2.5.3. Modelling scenarios for termination of liming – (Paper IV)

To model termination of liming for the 3 043 limed Swedish lakes, background steady-state concentrations of Ca and Mg not affected by liming were needed. The method used to estimate these values was based upon the Ca to Mg ratio in unlimed reference lakes upstream or within 20 km of the limed lakes. This method relies on the assumption that Ca and Mg have similar chemical properties and therefore co-vary in time and space (Fölster and Wilander, 2005; Göransson *et al.*, 2006). During liming the Ca to Mg ratio is increased, as the liming agent has a higher Ca to Mg ratio than lake water. Therefore to calculate the steady-state Ca concentration for the unlimed state, the Ca to Mg ratio has to be adjusted in the limed lake to reach the ratio of the reference lake. Thus for lakes subject to liming, this principle can be used to estimate concentrations of Ca after termination of liming (Fölster *et al.*, 2011b):

$$[\text{Ca}^{2+}]_{\text{unlimed}} = [\text{Mg}^{2+}]_{\text{meas}} \cdot \left(\frac{[\text{Ca}^{2+}]}{[\text{Mg}^{2+}]} \right)_{\text{ref}} \quad (8)$$

where $[\text{Ca}^{2+}]_{\text{unlimed}}$ is the projected steady-state concentration of Ca after termination of liming, $[\text{Mg}^{2+}]_{\text{meas}}$ is the measured concentrations (in the limed lake) and $([\text{Ca}^{2+}]/[\text{Mg}^{2+}])_{\text{ref}}$ is the ratio of Ca to Mg in nearby unlimed reference lakes. Detailed calculations with adjustments for added Mg in the liming agent are described in Paper IV.

The limed lakes were predicted for pH and Al_i at “unlimed” conditions using these values of Ca and Mg concentrations and the model described in Paper II. Model predictions of what would happen if liming was decreased in a step-wise manner was also performed, with progressively lower and lower concentrations of Ca and Mg. The concentrations of added Ca and Mg from lime were decreased from 100 % (determined levels at the present

situation) down to 75 %, 50 %, 25 % and 0 % (calculated “unlimed” concentrations).

To get evidence for the applicability of the model, six lakes with monitored termination of liming were studied in the same way as for the large data set. The month when the Ca and Mg concentrations would reach these ratios were calculated based upon lake retention time. A comparison was then made between the predicted and the analysed values of pH and Al_i for that month.

3. RESULTS

3.1. Iron: size fractionation and characterisation

Iron was mostly present in the colloidal (>1 kDa, <0.45 μm) and particulate fractions (>0.45 μm), for both Lake Trehörningen and Lake Årsjön as well as for the surface water of L. Motjärn, L. St. Vrångstjärnet and L. Rotehogstjärnen (Fig. 4-13). The colloidal fraction was often the largest compared to the particle fraction in the Tyresta lakes. Iron(II) was determined to be present in the surface water of L. Trehörningen and Årsjön, sometimes as high as 34 % of total iron (Fig. 5; Table 1 in Paper III). The percentage of iron(II) could not be correlated to any of the parameters pH or TOC (data not shown). It was also evident that the ratio of iron(II) to total iron could both increase and decrease rapidly in the samples at the laboratory, where light was shown to increase the fraction of iron(II) (data not shown).

Total iron was correlated to OC in the L. Trehörningen and L. Årsjön fractionation, especially for the smaller fractions (Fig. 14a). For example, the L. Trehörningen October 2008 sample contained a large amount of iron particles (566 μg L⁻¹), but very little OC particles (0.1 mg L⁻¹) (Table 1 in Paper III).

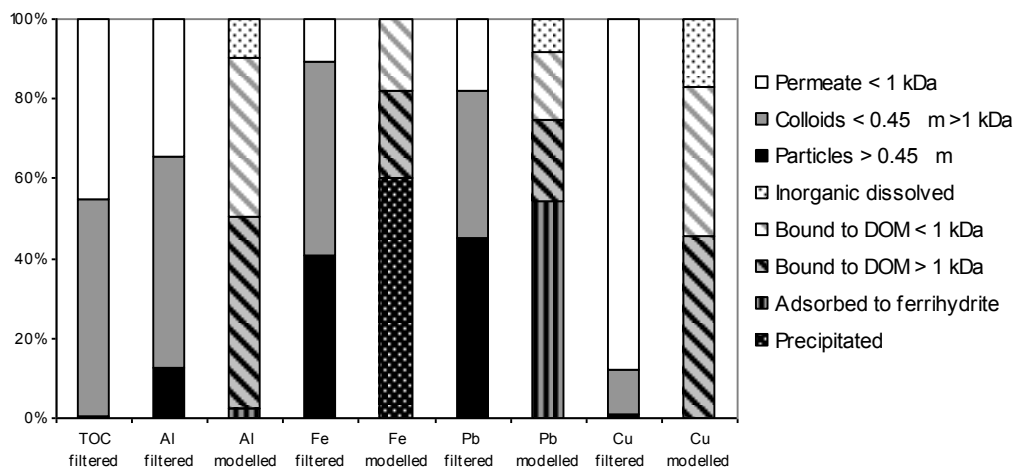


Fig. 4. Size fractionation using pre-filtration and ultrafiltration compared to modelled metal speciation in L. Trehörningen from the October 2008 sampling. Chemistry of bulk water: pH 5.23, TOC 20.5 mg L⁻¹, Al 680 μg L⁻¹, Fe 1 380 μg L⁻¹, Pb 1.3 μg L⁻¹ and Cu 0.49 μg L⁻¹.

The EXAFS results of iron showed mainly iron(III) in all samples, as judged by the typical Fe-O distance of 2.0 Å. The L. Trehörningen particle sample in October 2008 had a distinct resemblance to ferrihydrite, but with a higher Debye-Waller factor for Fe-O in the first coordination shell and fewer coordinated iron and oxygen atoms in higher shells (Table 4 and Fig. 2 in Paper III). The two techniques for preconcentration of the colloids gave slightly different results. The anion-exchange column samples showed iron(III) with Fe···C distances between 2.77 and 2.85 Å (Table 4 in paper III), interpreted as iron complexed in monomeric complexes to NOM. In contrast, the freeze-dried retentate samples showed either a mixture of this monomeric complexation and an iron (hydr)oxide phase, or one or the other of those two phases. Three samples were analysed using both preconcentration methods. In one case both methods gave consistent results, but for two occasions the retentates showed a higher amount of polymeric iron. Generally the EXAFS results showed a predominance of iron(III) complexed to organic matter in the colloids of the two lakes.

The soil samples contained either iron(III) complexed monomerically to organic matter, or a mixture of this phase and of an iron (hydr)oxide phase. The iron (hydr)oxide phase was too low in concentration to be identified.

The obtained results, showing that monomeric complexation of Fe(III) to DOM was the predominating complexation mechanism, motivated a change of the Fe(III) complexation in the SHM model from the generic dimeric constants to new monomeric ones. The new complexation constants were optimised as described in the Methods section and in the Appendix of Paper II and are presented in Table 2. The monomeric constants resulted in a stronger complexation to organic matter. When iron speciation was simulated for L. Trehörningen and L. Årsjön iron(III) was

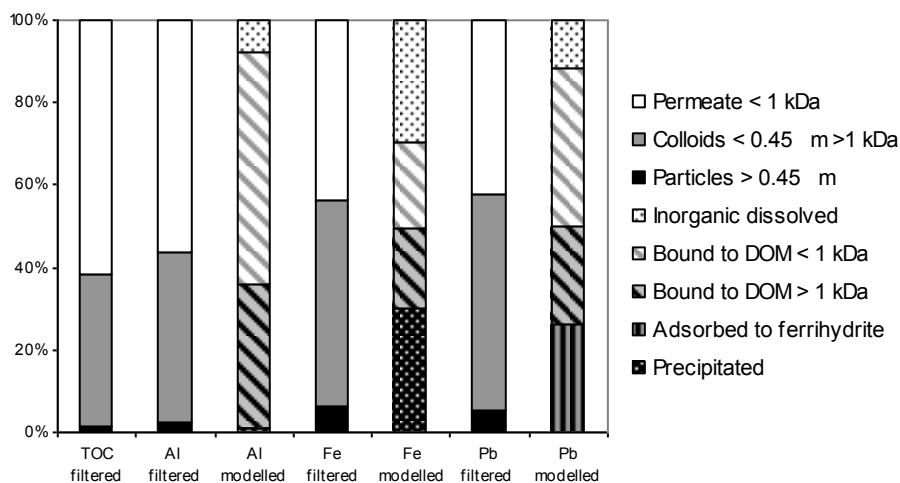


Fig. 5. Size fractionation using pre-filtration and ultrafiltration compared to modelled metal speciation in L. Trehörningen in the April 2009 sampling. Chemistry of bulk water: pH 5.25, TOC 20.9 mg L⁻¹, Al 666 μg L⁻¹, Fe 1 096 μg L⁻¹ where 34 % was Fe(II), and Pb 1.1 μg L⁻¹.

generally found to complex to organic matter instead of precipitating as ferrihydrite (Fig. 4-10). This was also in accordance with the EXAFS results. The geochemical modelling also showed ferrihydrite in approximately the same amount as Fe particles (Fig. 4-10). This was further studied in the Krycklan data set, see section 3.5.3.

3.2. Aluminium: size fractionation and modelling in the five lakes

Aluminium was not present in the particulate fraction of L. Trehörningen and L. Årsjön, other than in very small amounts (< 13 % of total aluminium). Instead it was present in the colloidal fraction (between 28 and 56 %) or in the permeate (between 34 and 69 %). In the excessively limed lakes, Al was present mainly in the colloidal/ particle fraction (between 51 and 82 %) compared to the dialysed fraction (Fig. 11 and 12). In the acid L. Rotehogstjärnen aluminium was also present mainly in the colloidal fraction (75 %) (Fig. 13).

Aluminium, organic carbon and total iron were strongly correlated to each other in the L. Trehörningen and L. Årsjön fractions (Fig. 14a and b; Fig. 15a).

For the two excessively limed lakes, most of the Al was simulated to be precipitated $\text{Al}(\text{OH})_3$, in accordance with the dialysis (Fig. 11 and 12). In contrast, the geochemical model suggested that no aluminium was precipitated as $\text{Al}(\text{OH})_3$ in the Tyresta lakes (Fig. 4-10) and in L. Rotehogstjärnen (Fig. 13), probably due to the low pH (below 5.6) and low temperatures. This was consistent with the low amount of particles. The small amount of particles that existed was present with a positive relationship to iron particles, but in a smaller fraction of total Al (Fig. 4-9). They could be modelled with adsorption to ferrihydrite, albeit in a smaller fraction than measured (Fig. 4-9).

Much of the Al was modelled to be complexed to organic matter, for all the samples from L. Trehörningen (Fig. 4-6), L. Årsjön (Fig. 7-10) and L. Rotehogstjärnen (Fig. 13).

3.3. The speciation of As and Mo in Dalsland – (Paper I).

Arsenic was present in the < 1 kDa fraction in around 80 % of total arsenic in the excessively limed lakes and at 69 % in the acid L. Rotehogstjärnen (Fig. 11-13). Molybdenum was mainly present in the < 1 kDa fraction (Fig. 11-13). Arsenic, and also to some extent molybdenum, were influenced of the modelled speciation of

Table 2. Initial generic complexation constants of iron(III) to fulvic acid (dimeric, tridentate; Gustafsson et al., 2007) and the new constants for monomeric, bidentate complexation in the SHM.

Dimeric complex			New constants for monomeric complex		
Complex	log K	ΔLK_2	Complex	log K	ΔLK_2
$(\text{FA})_3\text{Fe}_2\text{O}^+$	-5.15	1.8 ^a / 1.5 ^b	$(\text{FA})_2\text{FeOH}$	-4.6	1.7
			$(\text{FA})_2\text{Fe}^+$	-1.68	1.7

^a 1.8 = fitted for soil organic matter, ^b 1.5 = fitted for humic acids (see Gustafsson et al., 2007 for details)

iron, since they both can adsorb to ferrihydrite. Arsenic adsorption to ferrihydrite was generally exaggerated by the model. The modelling of molybdenum generally predicted low adsorption to ferrihydrite and low organic complexation, which coincided with the measured concentrations (Fig. 11-13).

3.4. Copper(II) and lead(II) adsorption to ferrihydrite, as influenced by phosphate – (Paper V)

The adsorption of copper(II) and lead(II) to ferrihydrite was significantly increased in the presence of phosphate (Fig. 16 and 17). This was especially true for lower pH and more for Pb than for Cu. For copper(II) a possible picture of the system was constructed using the EXAFS results and the batch experiments in combination with CD-MUSIC modelling. In the absence of phosphate copper was bound in a bidentate edge-sharing complex to ferrihydrite. However, in the presence of phosphate copper was likely bound partly in a ternary complex with phosphate where Cu was monodentately bound to one iron octahedron and at the same time coordinated to one phosphate. The phosphate was in turn complexed to another iron octahedron. The constants in the CD-MUSIC model were changed accordingly and could thereafter describe the system well (Fig. 16).

For Pb the results were the same as for Cu without phosphate present, *i.e.* it formed a bidentate edge-sharing complex. However, in the presence of phosphate the results were a bit more ambiguous. The data could be interpreted in two ways, and both are equally likely. Either it was similar as for Cu, but with a smaller angle than 180° for the monodentate binding to ferrihydrite. The other option is also a ternary complex, but where Pb(II) is bound bidentately to two corner-sharing iron octahedrons and the phosphate ion interacts only with Pb(II) and not with the surface. The constants in the CD-MUSIC model were adjusted according

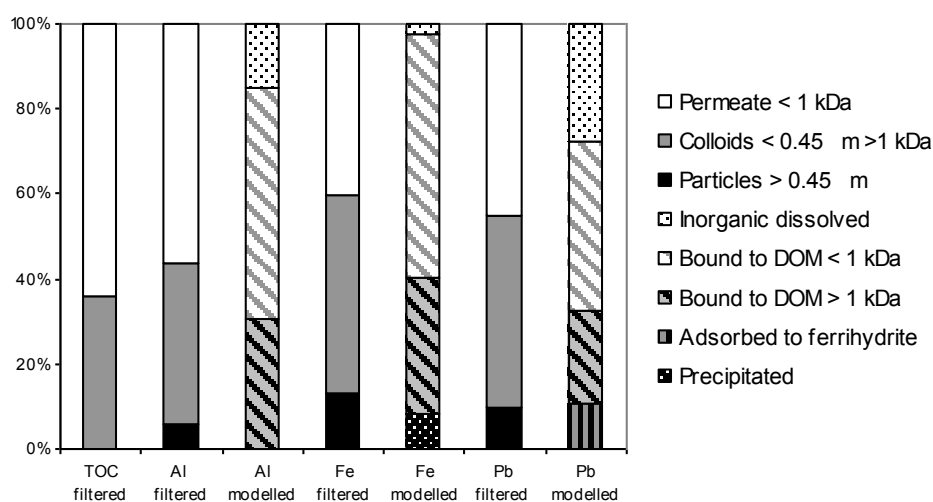


Fig. 6. Size fractionation using pre-filtration and ultrafiltration compared to modelled metal speciation in *L. Trehörningen* in the January 2010 sampling. Chemistry of bulk water: pH 4.88, TOC 22.7 mg L⁻¹, Al 668 μg L⁻¹, Fe 1 270 μg L⁻¹ where 2 % Fe(II), and Pb 1.3 μg L⁻¹.

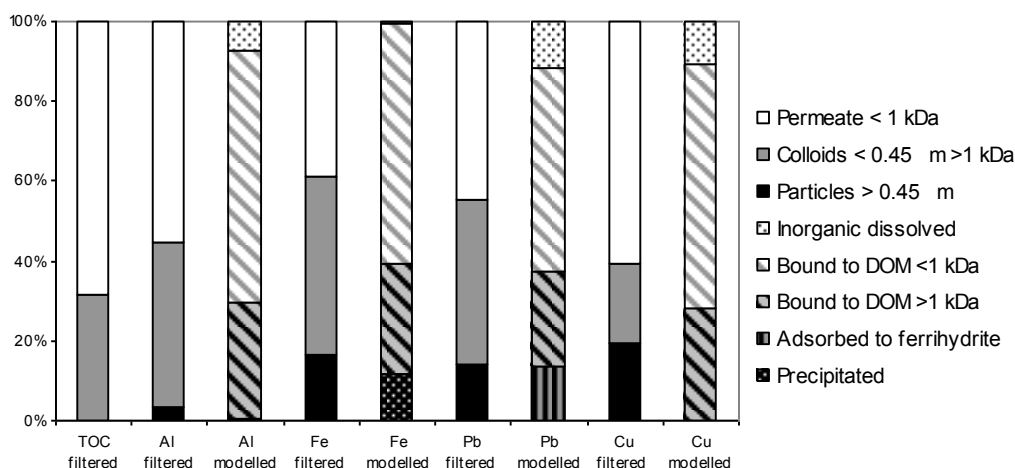


Fig. 7. Size fractionation using pre-filtration and ultrafiltration compared to modelled metal speciation in *L. Årsjön* in the October 2008 sampling. Chemistry of bulk water: pH 5.61, TOC 10.2 mg L⁻¹, Al 184 μg L⁻¹, Fe 304 μg L⁻¹, Pb 0.28 μg L⁻¹ and Cu 0.53 μg L⁻¹.

to the first alternative, and it fitted the data well (Fig. 17). However, the adjusted CD-MUSIC model parameters were in agreement also with what would be expected for the second alternative complex.

3.5. A consistent geochemical model – (Paper II and Paper IV)

A consistent geochemical model for Swedish surface water was derived based upon the results above. The new monomeric constants for Fe(III)-DOM complexation (see section 3.1) were used throughout. The new constants for copper and lead sorption to ferrihydrite were used in section 3.5.4.

3.5.1. Modelling pH

The only factor that was varied in the calibration of the model was the fraction of active dissolved organic matter to DOC. This was calibrated to be ADOM/DOC = 1.65 when simulating pH from the charge balance for the calibration data set of the unlimed reference lakes (Fig. 18a). Assuming that DOM consists of 50 % carbon by weight, the value of 1.65 implies that 82.5 % of the DOM was active with regards to proton and metal binding and the calculated site density is 11.5 μM mg⁻¹ C. The model was validated for a large number ($n = 4\ 850$) of lakes and rivers in Sweden in Paper II (Fig. 18b) and 4 528 lakes in paper IV (Fig. 19a and b) with a mean error of 0.2 pH units. The choice of temperature and solubility constant for Al(OH)₃ and ferrihydrite had minor effects on the pH and Al_i simulations.

3.5.2. Modelling inorganic monomeric aluminium

Al_i was simulated with a strong positive relationship for the two calibration data sets for the detection methods PCV and ICP-OES (Fig. 20a and b). They differed however slightly from the modelling so a correction function was included in the modelling:

$$Al_i^* = a + b \cdot Al_{i(\text{MOD})} \quad (9)$$

where Al_i^* is the new corrected concentrations in $\mu\text{g L}^{-1}$ Al and $Al_{i(\text{MOD})}$ is the geochemically modelled concentrations of inorganic monomeric Al and $a = 12.4$ and $b = 1.10$ for the PCV method and $a = -4.9$ and $b = 0.74$ for the ICP-OES method (Fig. 20c and d).

After that Al_i was validated on a number of datasets, and the mean error was $30 \mu\text{g L}^{-1}$ for the PCV-method ($n = 2\,289$) and $33 \mu\text{g L}^{-1}$ for the ICP-OES method ($n = 1\,130$) (Paper II). Samples with pH values above 6 were excluded from the graphs and in calculations, due to possible artefacts such as particulate/colloidal inorganic Al retained in the column.

3.5.3. Modelling aluminium and iron particles

For the Krycklan data set the largest concentrations of particulate Al and Fe were present above pH 5.5 (data not shown). Modelled $Al(OH)_3$ was compared to measured Al in particles in Krycklan for pH values above 5.5. There was a good correlation (Fig. 21a).

Precipitated ferrihydrite was also compared with measured particles in Krycklan. Here there was also a significant relationship, but with more ferrihydrite modelled than in measured particles (Fig. 21b). With a higher \log^*K_{s0} of 3.8 too little ferrihydrite was precipitated, which is not likely. Different temperatures also influenced the results. A higher temperature than 10°C resulted in more $Al(OH)_3$ and ferrihydrite precipitating.

3.5.4. Modelling copper and lead fractionation

Copper had a size fractionation that differed a lot between samplings with no clear pattern to either iron or OC (data not shown). There were some problems with contamination of Cu during pre-filtration and ultrafiltration, therefore only uncontaminated fractionation samples are presented (Fig. 4, 7, and 9). Copper was present in the particulate fraction with a maximum

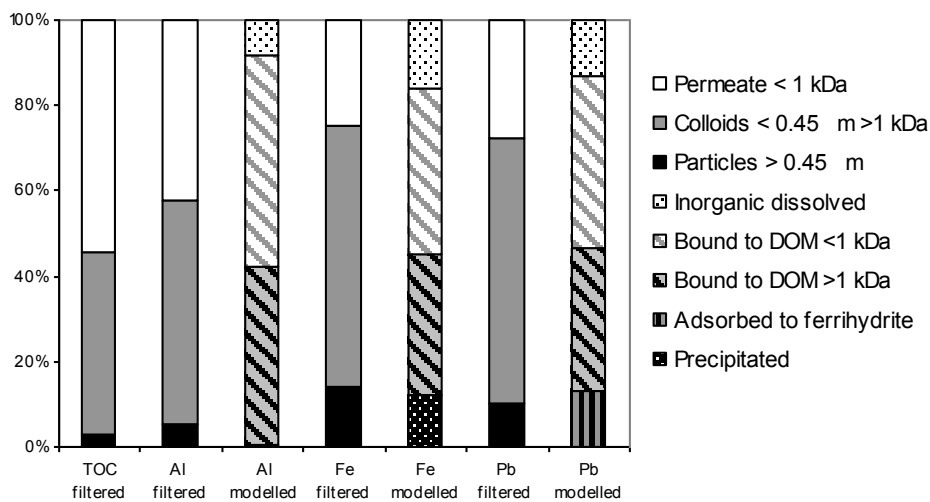


Fig. 8. Size fractionation using pre-filtration and ultrafiltration compared to modelled metal speciation in *L. Årsjön* in the April 2009 sampling. Chemistry of bulk water: pH 5.53, TOC 10.5 mg L^{-1} , Al $217 \mu\text{g L}^{-1}$, Fe $379 \mu\text{g L}^{-1}$ where 18 % was Fe(II), and Pb $0.40 \mu\text{g L}^{-1}$.

of 20 %. It was also not adsorbed to ferrihydrite, according to the model. Instead most of it was complexed to DOM (between 74 and 90 %). Cu was also modelled well when simulating the amount present in the of < 1 kDa fraction for L. Årsjön in October 2008 and January 2010 (Fig. 7 and 9), but it was too low simulated for the L. Trehörningen October 2008 sample (Fig. 4).

For lead the simulated speciation was closely related to iron speciation; if ferrihydrite precipitated, Pb was modelled to adsorb to it in similar percentages (Fig. 4-9). The low concentrations of phosphate (generally < 0.1 μM) in these lakes had a small impact on the adsorption to ferrihydrite according to the new model; modelled adsorption was increased by a maximum of five percentage units when including phosphate as a species. The major part of Pb was generally modelled to be complexed to DOM (Fig. 4-9). The modelling results were generally in agreement with the ultrafiltration results, although with a larger fraction of < 1 kDa modelled than measured (Fig. 4-9). Lead followed closely the size fractionation of iron in the L. Trehörningen and L. Årsjön water (Fig. 15b). Lead was also correlated to the OC size fractionation (data not shown).

3.6. Predicted changes in lake chemistry at terminated liming – (Paper IV)

The model setup was first tested for the six monitored lakes with terminated liming. For the initial limed situation, there was a very good correspondence between simulated and analysed pH (mean error 0.07 pH units, $n = 6$) (Table A1 in Paper IV). Unfortunately there was just one lake with analysis results for Al_i available before liming was discontinued. The calculated Ca and Mg concentrations generally agreed with measured concentrations for the 75, 50, 25 and 0 % lime effect for lakes limed on the lake surface for the previous 10 years (Fig. 1a and b in Paper IV). More importantly,

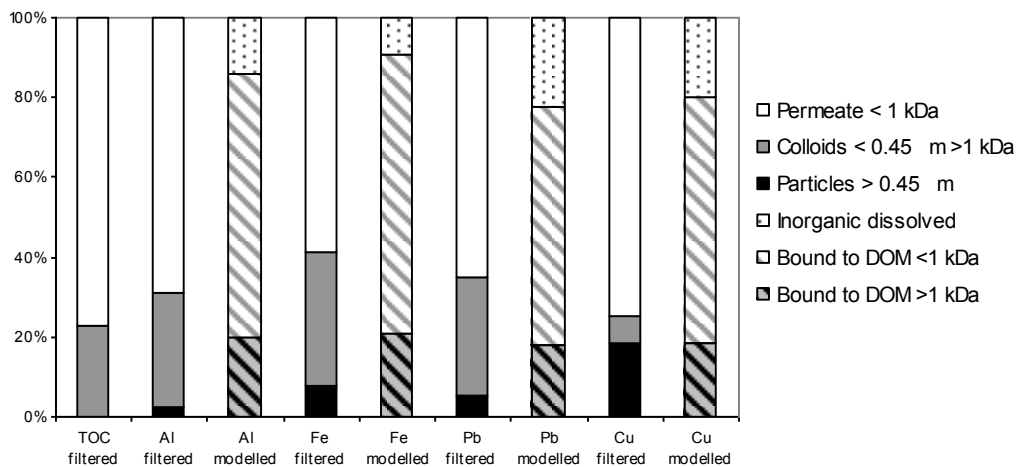


Fig. 9. Size fractionation using pre-filtration and ultrafiltration compared to modelled metal speciation in L. Årsjön in the January 2010 sampling. Chemistry of bulk water: pH 5.26, TOC 10.3 mg L^{-1} , Al $182 \text{ } \mu\text{g L}^{-1}$, Fe $335 \text{ } \mu\text{g L}^{-1}$ where 11 % was Fe(II), Pb $0.35 \text{ } \mu\text{g L}^{-1}$ and Cu $0.87 \text{ } \mu\text{g L}^{-1}$.

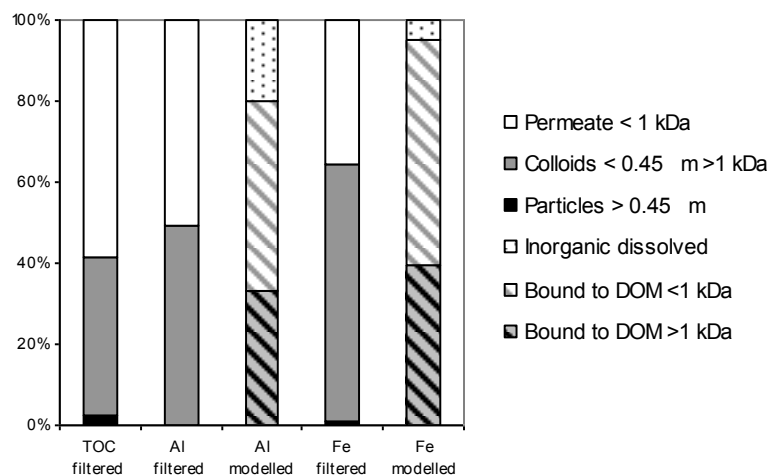


Fig. 10. Size fractionation using pre-filtration and ultra-filtration compared to modelled metal speciation in *L. Årsjön* in March 2011. Chemistry of bulk water: pH 5.18, TOC 11.8 mg L⁻¹, Al 223 μg L⁻¹, and Fe 414 μg L⁻¹ where 5 % was Fe(II).

pH and Al_i were simulated very well (mean error 0.19 pH units, $n = 8$; mean error Al_i 10.6 μg L⁻¹) (Fig. 22a and b; Table A1 in Paper IV). However, for lakes with recent upstream liming; too low Ca and Mg concentrations were calculated (Fig. 1a and b and Table A1 in Paper IV). This is not surprising since the influent water probably had a higher Ca to Mg ratio than the unlimed reference value. Consequently, the model occasionally predicted too low pH and too high Al_i (mean error 0.66 pH units, $n = 11$; mean error Al_i 20.5 μg L⁻¹, $n = 8$) (Fig. 22a and b, Table A1 in Paper IV).

When the 3 043 limed Swedish lakes were simulated with the calculated “unlimed” concentrations of Ca and Mg (*i.e.*, the steady-state concentrations after complete termination of liming), pH was lowered with, on average, 0.92 units compared to the simulated original situation. For 39 % of the lakes, the pH was calculated to be below 5.6. Al_i was increased with on average 17.9 μg L⁻¹ up to 31.1 μg L⁻¹. Thirty-four per cent of the lakes had Al_i concentrations above 30 μg L⁻¹. However, forty per cent of the lakes maintained a pH above 6.0, which is above the policy aims for liming in Sweden. If only the samples from the same lakes taken in the fall 2007 were modelled, still 30 % of the lakes were predicted to have a pH above 6.0 after terminated liming.

When liming was modelled to decrease to 75 % and 50 % of the current level, there were small effects on pH and Al_i compared to the limed situation (Table 3 and Fig. 3b and c in Paper IV). Only a few per cent of the lakes were predicted to have a pH below 5.6 and an Al_i above 30 μg L⁻¹.

The decrease in pH and the associated increase in Al_i were very different for different lakes, as the range of individual pH and Al_i changes was 3 pH units and 450 μg L⁻¹ Al_i, respectively. There was

a clear geographical pattern, with lower pH and higher Al_i in lakes in south-western Sweden (Fig. 23 a and b), corresponding largely to historical and present sulphur deposition patterns (Fig. 24 a and b).

4. DISCUSSION

4.1. Iron speciation

Iron(II) could be present in relatively large concentrations in the surface water of the Tyresta lakes, even though the water was fully oxygenated. This was probably due to high amount of humic material and the acid pH which can help in keeping Fe(II) in high steady-state concentrations (Miles and Brezonik, 1981). The geochemical model was not able to predict the concentration of iron(II) from available environmental monitoring data. This could mean that it would be advisable to determine Fe(II) if geochemical modelling is to be performed, which was also concluded by Lofts *et al.* (2008).

According to the EXAFS results, iron was present as monomeric complexes to DOM and /or an iron (hydr)oxides in the two Tyresta lakes. Other authors have also found monomeric complexation of iron(III) to NOM (Karlsson *et al.*, 2008; van Schaik *et al.*, 2008 and Karlsson and Persson, 2010). The results suggested a stronger complexation than previously suggested from chemical equilibrium modelling. This means that iron(III) could compete strongly with other metals. The new monomeric constants made Fe(III) a strong competitor with Al(III), which resulted in a larger concentration of Al_i than was previously modelled. This was in accordance with the determined Al_i concentrations. None of the samples with organically complexed iron(III) present showed any evidence for di- or trimerically complexed iron(III), as reported by Rose *et al.* (1998) and Vilgér-Ritter *et al.* (1999), later supported by Gustafsson *et al.* (2007) and

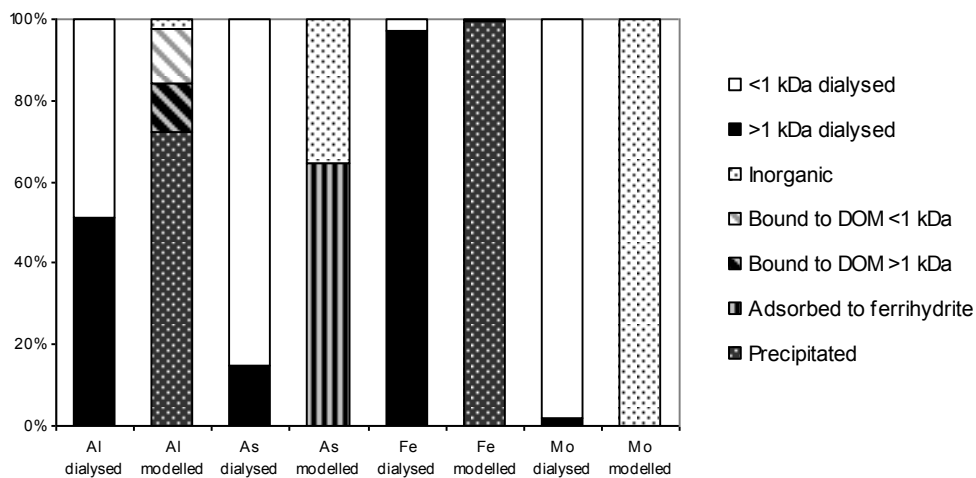


Fig. 11. The dialysable (white) and the non-dialysable (black) fractions of the metals in % of the total concentrations and modelled speciation in the surface water of *L. Motjärn*. Chemistry of bulk water: pH 7.69, TOC 7.1 mg L^{-1} , Al $36.4 \text{ } \mu\text{g L}^{-1}$, As $0.34 \text{ } \mu\text{g L}^{-1}$, Fe $60 \text{ } \mu\text{g L}^{-1}$, and Mo $0.05 \text{ } \mu\text{g L}^{-1}$.

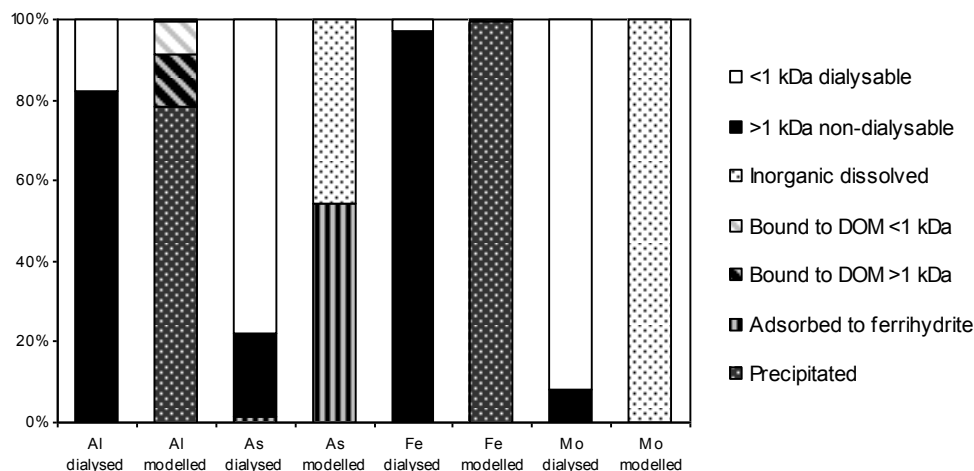


Fig. 12. The dialysable (white) and the non-dialysable (black) fractions of the metals in % of the total concentrations and modelled speciation in the surface water of *L. St. Vrångstjärnet*. Chemistry of bulk water: pH 7.33, TOC 10.1 mg L⁻¹, Al 112 µg L⁻¹, As 0.35 µg L⁻¹, Fe 79 µg L⁻¹, and Mo 0.04 µg L⁻¹.

by Mikutta and Kretzschmar (2011). It is still not clear which chemical conditions that favour different binding modes. Differences in pH, DOM and iron concentrations may be possible determinants.

Ferrihydrite seemed to be the predominant iron phase in *L. Trehörningen* particles, but it did not completely resemble laboratory phases of ferrihydrite. This could be due to substitution of other elements into the structure or adsorption of DOM which could change the size and structure. Another possibility is that pure ferrihydrite was mixed with *e.g.* iron(III) complexed to DOM, since the EXAFS results show an average of all iron present in the sample. As carbon is lighter than iron it is more difficult to detect

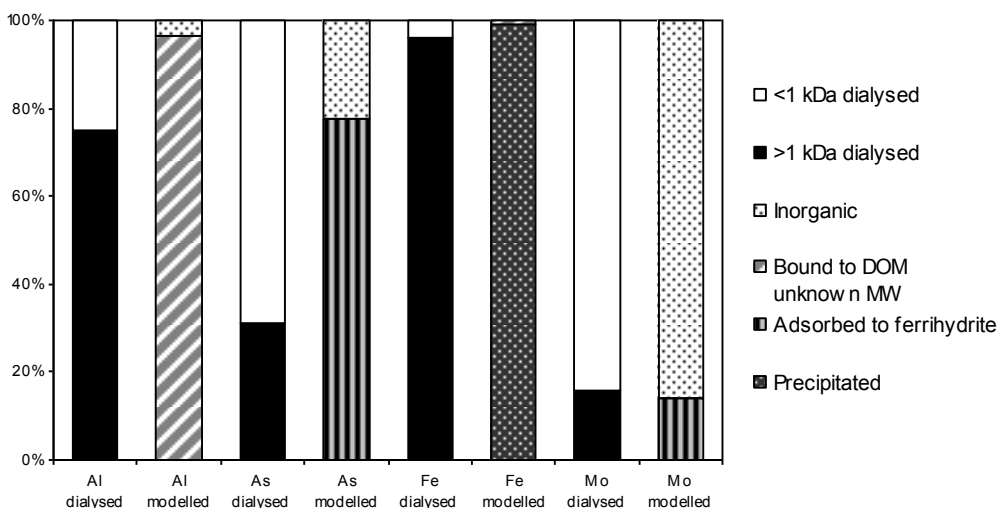


Fig. 13. The dialysable (white) and the non-dialysable (black) fractions of the metals in % of the total concentrations and modelled speciation in the surface water of *L. Rotehogstjärnen*. Chemistry of bulk water: pH 5.54, TOC 15.5 mg L⁻¹, Al 328.3 µg L⁻¹, As 0.60 µg L⁻¹, Fe 578 µg L⁻¹, and Mo 0.03 µg L⁻¹.

iron(III) complexation to DOM; it is masked in the presence of sufficient amounts of polymerised iron.

The solubility constant of ferrihydrite of $\log^*K_{s0} = 2.69$ seemed to fit the data in Tyresta, Dalsland and Krycklan. For Krycklan there was a higher amount of modelled ferrihydrite than measured particles (Fig. 21b), but this could be explained by presence of colloidal ferrihydrite smaller than $0.4 \mu\text{m}$. The discrepancies for Krycklan could also be attributed to dissolved iron(II) not considered in the model. The choice of temperature influenced the simulation results regarding how much of the minerals that precipitated.

4.2. The anion exchange column method

The new method developed in this study for concentrating of iron species prior to EXAFS spectroscopy, *i.e.* by use of a column with

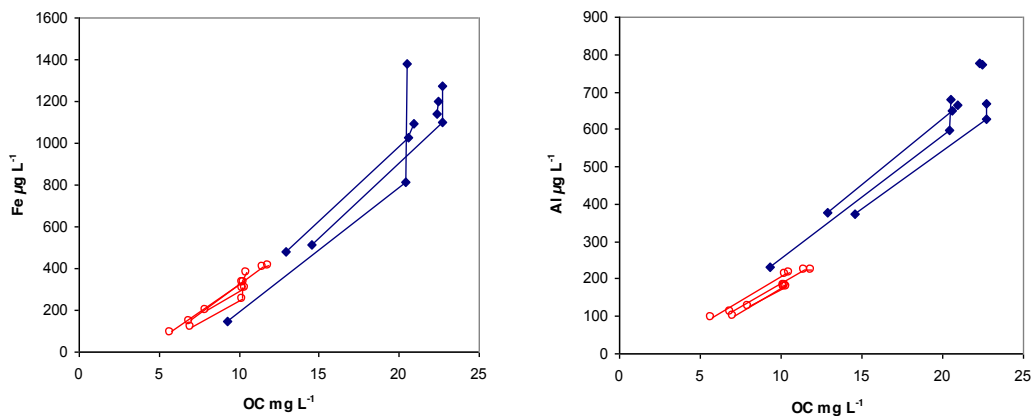


Fig. 14a and b. Variations of iron (a) and aluminum (b) versus organic carbon concentrations in the different filtrates (symbols): Total concentrations, pre-filtered ($> 0.45 \mu\text{m}$) and permeate ($< 1 \text{kDa}$) at the same sampling connected by lines for *L. Trehörningen* (blue diamonds) and *L. Årsjön* (red circles).

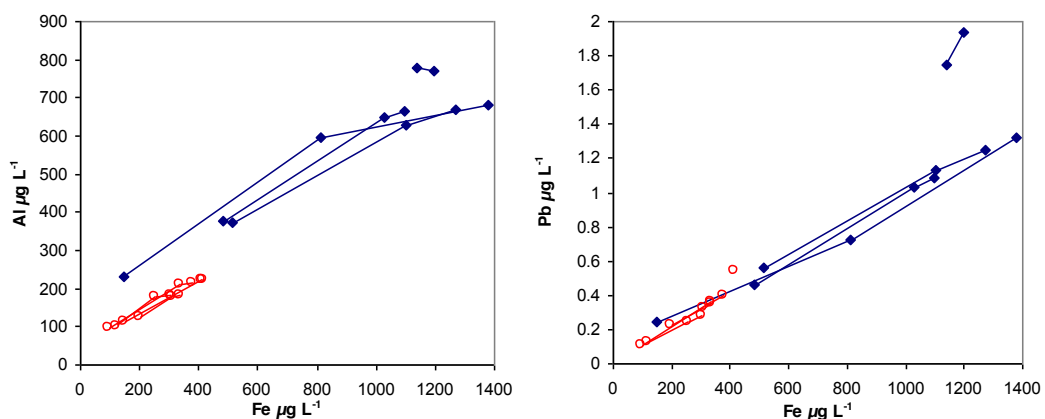


Fig. 15a and b. Variations of aluminium (a) and lead (b) versus iron concentrations in the different filtrates (symbols): Total concentrations, pre-filtered ($> 0.45 \mu\text{m}$) and permeate ($< 1 \text{kDa}$) at the same sampling connected by lines for *Lake Trehörningen* (blue diamonds) and *L. Årsjön* (red circles).

the anion-exchange resin AGMP-1, proved to be a good method for isolating negatively charged iron species. It had a higher recovery than the freeze-dried retentate and it did not require changes in temperature and pressure compared to natural conditions. This would imply that it more closely resembles the speciation in the lake. From the results of this study it seems that the preparation of the freeze-dried retentates may have caused precipitation of an iron (hydr)oxide in some cases, implying that the anion-exchange column method is a better technique for preconcentrating the species. The results also showed that it was important that the isolation was performed in the dark, since in the presence of light some of the iron(III) was reduced to iron(II) in the tubing feeding the column; as a result iron passed through the column as a free ion (Fe^{2+}).

Generally, rapid oxidation/reduction reactions of iron constitute an uncertainty when characterising iron speciation. Therefore it is important to determine Fe(II) in the field as was done in this study. For samples subject to isolation and characterization using EXAFS spectroscopy, it is important to avoid speciation changes as much as possible by storing the samples in the dark and at 5 °C.

4.3. Aluminium speciation

In Visual MINTEQ simulations, consideration of $\text{Al}(\text{OH})_3$ precipitation with a $\log *K_{s0} = 8.29$ (9.27 at 10 °C) seemed to work for Krycklan and in the Dalsland lakes for pH values above 5.5. For the Krycklan data set there was a strong relationship between measured Al in particles and simulated levels of precipitated

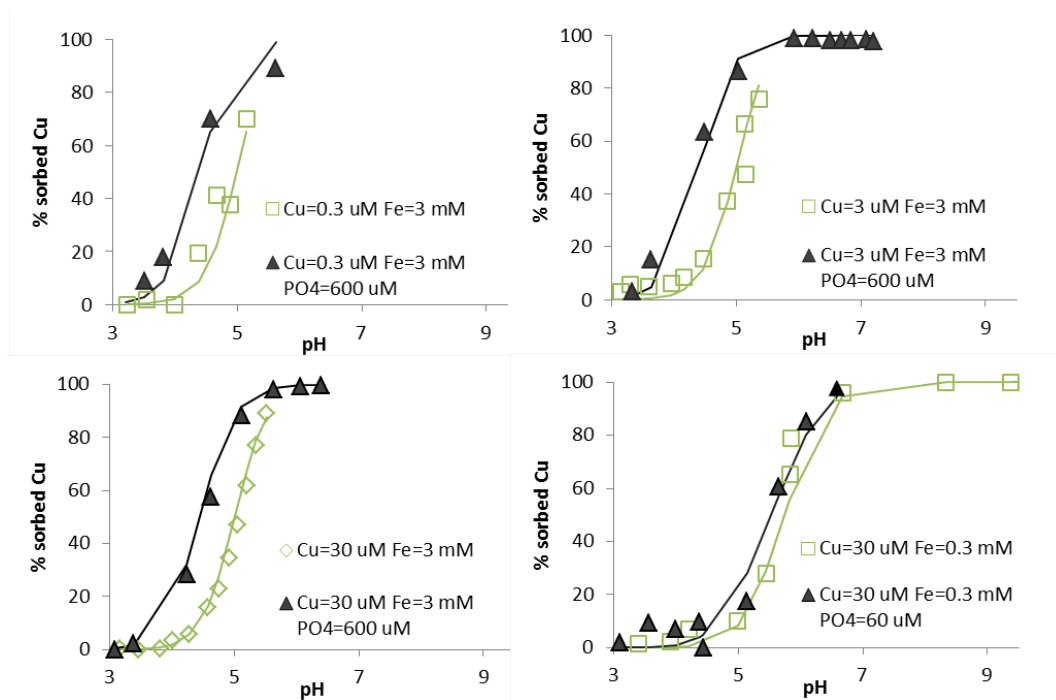


Fig. 16. Results from adsorption batch experiments with copper and ferrihydrite (symbols) and geochemical modelling with Visual MINTEQ (lines), with addition of phosphate (black triangles) and without addition of phosphate (green squares).

$\text{Al}(\text{OH})_3$. Below approximately pH 5.5 Al was undersaturated with respect to $\text{Al}(\text{OH})_3$. The results are similar to those of Tipping (2005), in which a solubility control by $\text{Al}(\text{OH})_3$ with $\log *K_{s0} = 9.5$ at 10 °C could be used for surface waters at pH above 5.8. However, from the results it cannot be concluded if the mineral was truly $\text{Al}(\text{OH})_3$ or if Si was included, due to an excessive amount of Si present. Another possibility not tested in Paper I and II was adsorption of aluminium onto an iron (hydr)oxide. This may be a possible explanation to the Al present in the particles of the water from L. Trehörningen and L. Årsjön (Fig. 4-9). Here pH was too low for precipitated $\text{Al}(\text{OH})_3$ to be stable according to the model. This was also the case for many of the samples of the larger data sets. Undersaturation of $\text{Al}(\text{OH})_3$ has been found previously by Tipping (2005) and Warby *et al.* (2008).

The modelling and size fractionation results mainly indicated Al to be associated with organic colloids, which is in agreement with a study of Norwegian acid streams, where 45-70 % of the total Al was above 10 kDa and probably was organic colloids (Teien *et al.*, 2007).

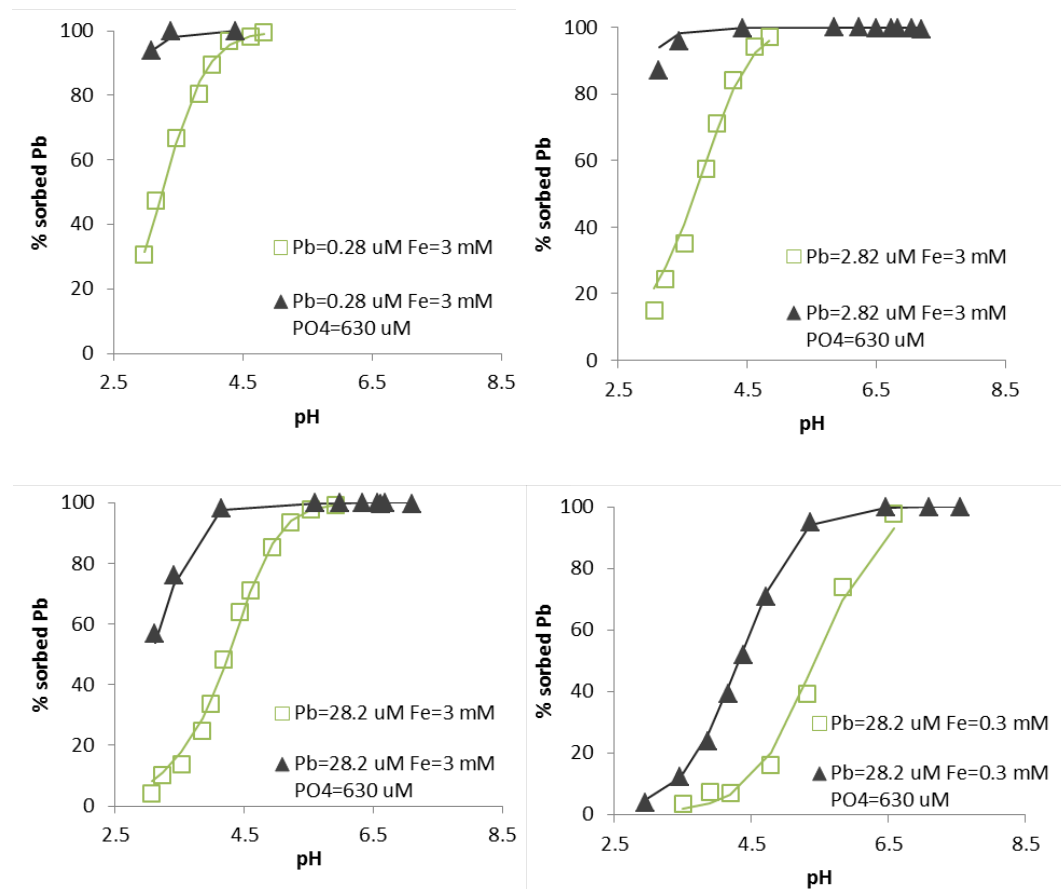


Fig. 17. Results from adsorption batch experiments with lead and ferrihydrite (symbols) and geochemical modelling with Visual MINTEQ (lines), with addition of phosphate (black triangles) and without addition of phosphate (green squares).

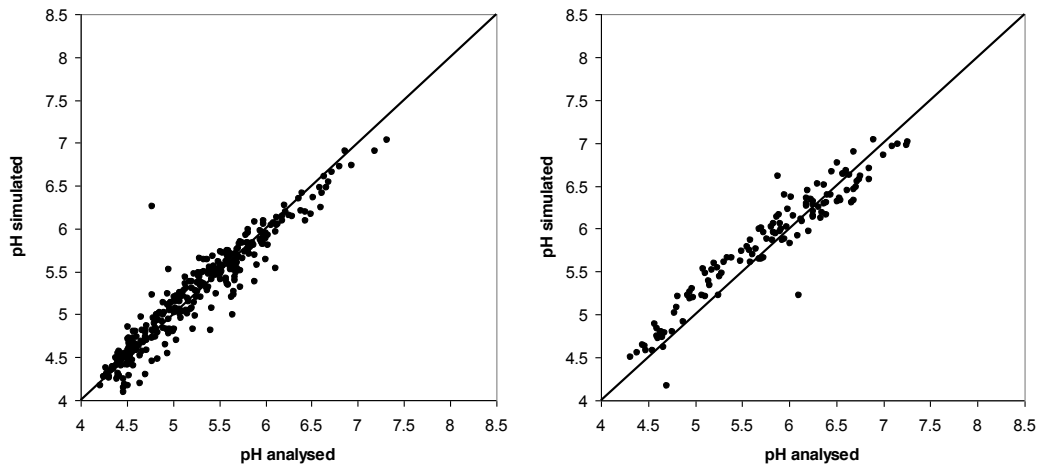


Fig. 18 a) Simulated pH in the calibration data set “Målsjöar” $n = 322$, $rmse = 0.19$ pH units.
 b) Simulated pH in the validation data set “Dalarna” $n = 126$, $rmse = 0.23$ pH units.

4.3.1. Aluminium fractionation

The two detection methods of Al_i , PCV and ICP-OES, gave slightly different results as judged by the two calibration data sets (Fig. 20a and b). The methods are operationally defined and differ in flow rate (3.8 (ICP-OES) and 2.8 (PCV) mL per mL exchanger volume) and it is therefore not strange that they do not completely coincide with each other and with the model. Therefore a correction equation was introduced (Eq. 8, Fig. 20c and d).

For the data sets in paper II the PCV method generally showed low concentrations of Al_i at pH values above 6, which is expected. This has not generally been the case for the ICP-OES method, which might include retained polymeric Al at high pH values (Andrén and Rydin, 2009). At lower pH and high DOC there may

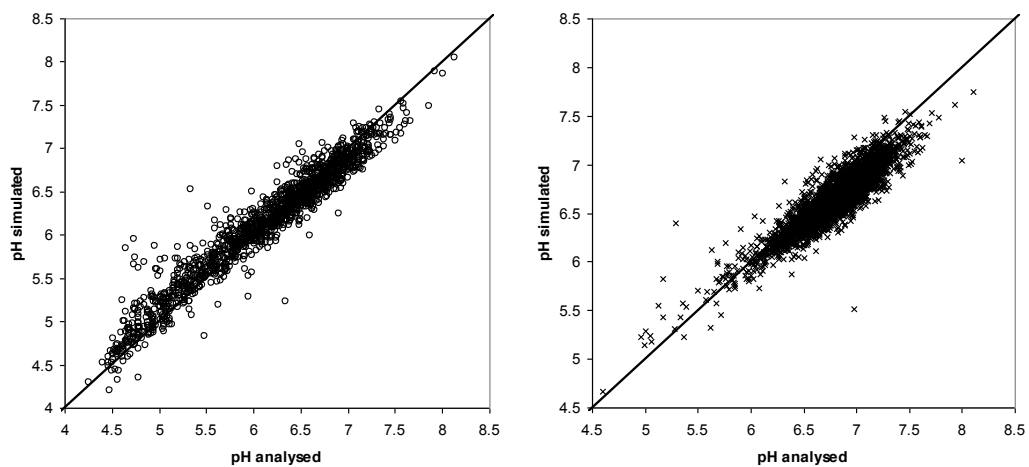


Fig. 19 a) Simulated pH in the validation data set of the unlimed reference lakes spring 2008. $n = 1485$, $rmse = 0.20$ pH units.
 b) Simulated pH in the validation data set of the limed lakes spring 2008. $n = 3043$, $rmse = 0.20$ pH units.

be partial dissociation of Al complexed to DOC for both methods, erroneously detecting a larger concentration of Al_i (Backes and Tipping, 1987; Teien *et al.*, 2007).

4.4. Methods for studying trace metal speciation

Dialysis has its advantages due to its *in-situ* speciation, its low contamination and its less disruptive method of separation compared to cross-flow filtration. However, it could not be used for preconcentrating samples for EXAFS spectroscopy. With cross-flow filtration possible artefacts include a higher contamination risk, adsorption to the filters, aggregation or destroying of colloids. The anion-exchange column method solved some of these problems, see section 4.2. However, trace metal speciation is more or less sensitive to temperature changes, changes in redox conditions, light etc and there is always an uncertainty when transferring results determined at the laboratory

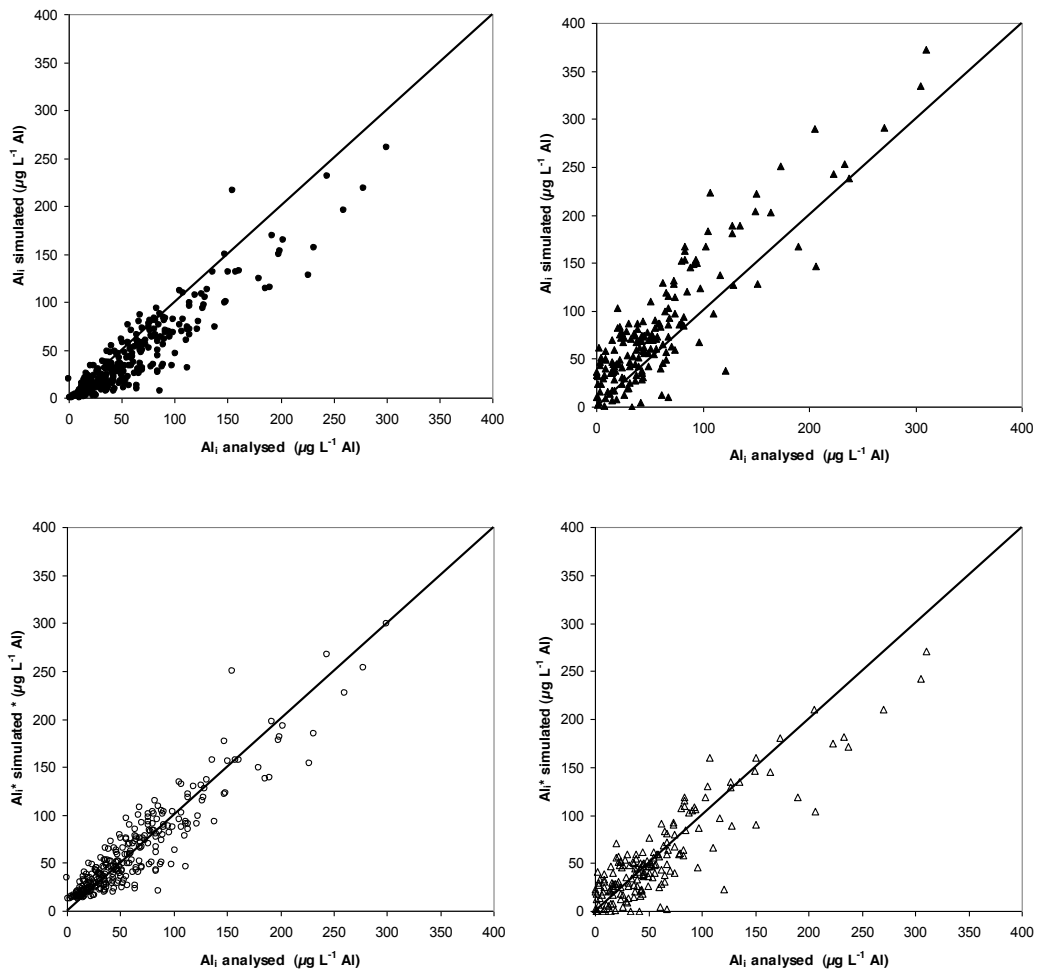


Fig. 20. a) Simulated Al_i versus PCV-determined Al_i for the calibration data set “Målsjöar”, $rmse = 26 \mu g L^{-1} Al$. b) Simulated Al_i versus ICP-OES-determined Al_i for the data set “Forest streams”, $rmse = 38 \mu g L^{-1} Al$. c) The corrected simulated Al_i^* using Eq. 9 versus PCV determined Al_i for the calibration data set “Målsjöar” $rmse = 18 \mu g L^{-1} Al$. d) The corrected simulated Al_i^* using Eq. 9. versus ICP-OES determined Al_i for the data set “Forest streams”, $rmse = 26 \mu g L^{-1} Al$. Data with pH values above 6 are excluded from the analysis and this graph.

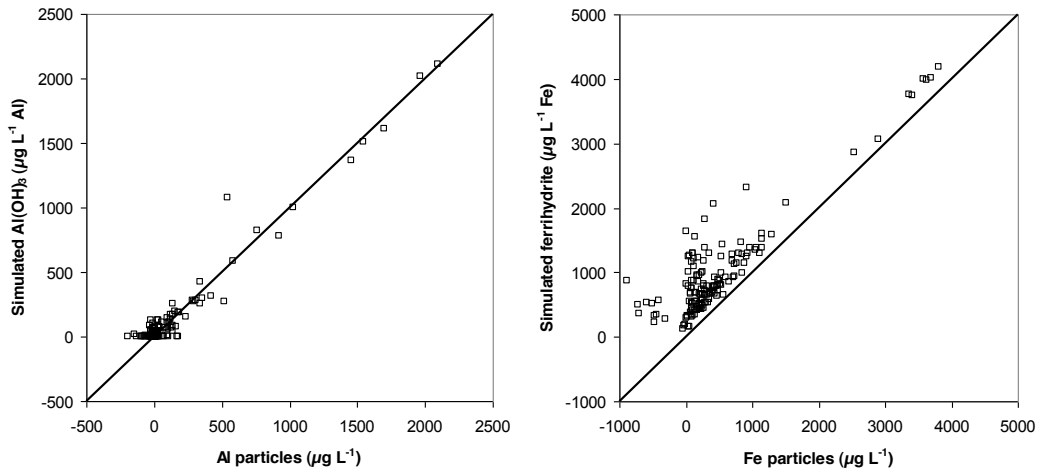


Fig. 21. a) Amount of simulated Al in the form of $Al(OH)_3$ (s) against the amount of particulate ($> 0.4 \mu m$) aluminium for all samples with pH above 5.5 in the data set Krycklan. b) Amount of simulated Fe in the form of ferrihydrite against the amount of particulate ($> 0.4 \mu m$) iron for all samples with pH above 5.5 in the data set Krycklan.

to the field. Due to inherent differences in the techniques it is always an advantage to use several methods simultaneously and to compare the results (Sigg *et al.*, 2006).

4.5. Geochemical equilibrium modelling – is it possible to simulate pH and metal speciation in lakes?

The pH simulations indicated no significant bias when using an ADOM/DOC ratio of 1.65 considering all the modelled pH data. The ratio (1.65) is close to the reported range of other authors (Bryan *et al.*, 2002: 1.12-1.98; Tipping *et al.*, 2002: 1.2-1.4; Tipping and Carter, 2011: 0.6-1.35). The calculated site density of $11.5 \mu M mg^{-1} C$ is very close to the value of $10.2 \mu M mg^{-1} C$ proposed by

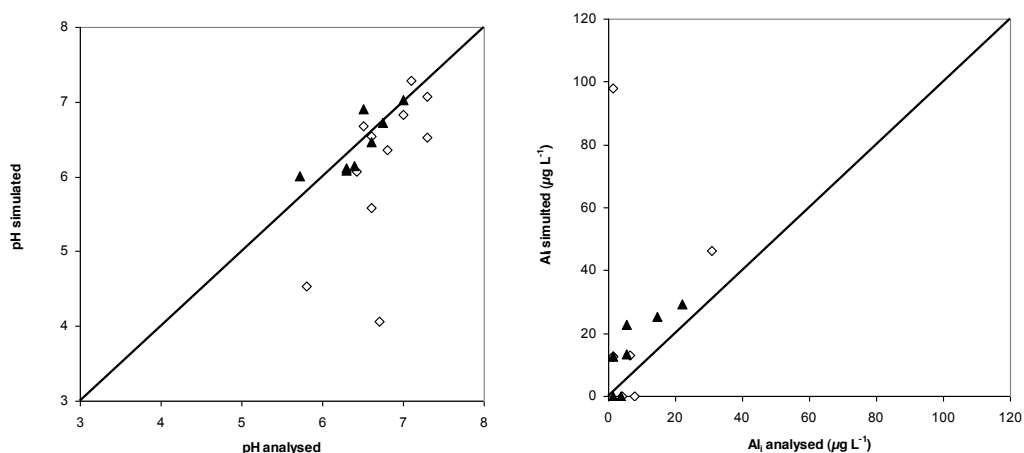


Fig. 22. Results of simulations at 75, 50, 25 and 0 % lime effect for the six lakes with monitored termination of liming. Filled triangles: Lakes limed directly at the lake surface for the previous 10 years. Open diamonds: Lakes that were also limed upstream for the previous 10 years.

a) Comparison of simulated pH versus analysed pH.
 b) Comparison of simulated Al_i versus analysed Al_i .

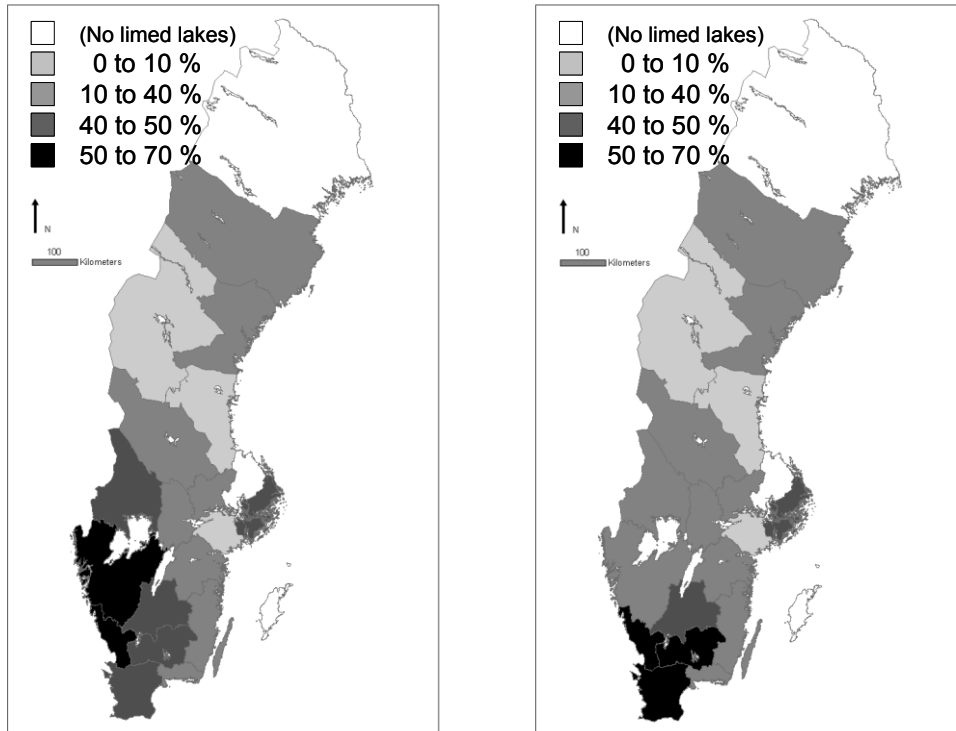


Fig. 23 a) Percentages of limed lakes in the counties that have predicted pH values below 5.6 for the no-lime scenario. b) Percentages of limed lakes in the counties that have predicted Al_i above $30 \mu\text{g L}^{-1}$ for the no-lime scenario.

Hruška *et al.* (2003). The remaining random error in modelled pH is due to the measurement errors from the 9 different concentrations used as input parameters (Tipping *et al.*, 1991). In order to achieve higher precision when modelling pH other methods can be used (Köhler *et al.*, 2000). However, for this study it was important with a more advanced model to be able to model pH and metal speciation simultaneously.

Simulated Al_i concentrations were generally in good agreement with measured values, with some difference in the determination methods, as discussed in section 4.3. The uncertainty is higher for Al_i than for pH, both in the fractionation and in the modelling, so therefore it is better to use pH as the calibration endpoint when calibrating the ADOM/DOC ratio. It was also important to use the same value for the ADOM/DOC ratio when modelling pH and Al_i . If not, competition effects and changes in parameters *e.g.* pH would have become erroneously predicted when some parameters were changed, such as Ca and Mg.

The model worked well for molybdenum in the Dalsland lakes. On the other hand, in the excessively limed lakes too strong adsorption of arsenic to ferrihydrite was predicted. Nevertheless, the general picture (strong arsenic adsorption to ferrihydrite) is probably true due to the high correlation between arsenic and iron detected in Swedish streams (Wällstedt *et al.*, 2010).

Copper and lead were generally simulated well in the Tyresta lakes. Lead was predicted to adsorb more strongly to ferrihydrite than

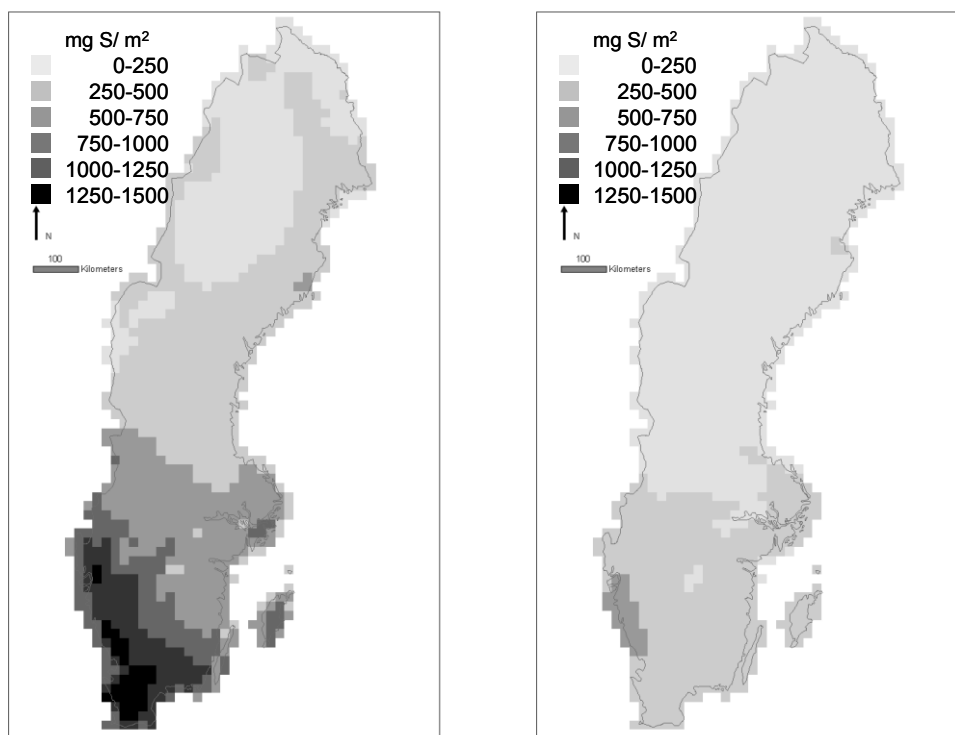


Fig. 24 a) Total sulphur deposition 1998 (SMHI, 2012) in Sweden. b) Total sulphur deposition 2009 (SMHI, 2012).

copper, as expected from the constants derived from the batch experiments in Paper V. Lead has previously been shown a strong relationship with iron in the Tyresta lakes (Wällstedt *et al.*, 2009). The strong adsorption of lead, enhanced in presence of phosphate, could explain the strong relationship between lead and iron found in natural waters (Fuller *et al.*, 1988; Erel and Morgan, 1992). However, complexation to DOM was important as well according to the model and lead was also correlated to DOC in this study as well as for other studies (Fuller *et al.*, 1988).

4.6. The model as a tool for determining the extent of liming – is it possible to predict the future?

The model worked well as a tool to predict changes attributed to change of lime dose in the six monitored previously limed lakes, especially for the three lakes limed directly in the lake. The modelling results of all limed lakes in Sweden indicated that it would be possible to terminate liming in 30 % of the lakes. This was especially true for the lakes in the inland areas of the northern half of Sweden where almost all liming activities can be terminated. In the coastal areas of northern Sweden liming can be terminated in about 50 % of the lakes. The sulphur deposition has decreased to a low level in northern Sweden (Fig. 24b) so it is not surprising that the lakes are recovering from acidification. Also for the rest of the lakes (in southern Sweden) it would be possible to reduce liming. However, downscaling to a specific lake may not work for the data in this study. More measurements of the water chemistry have to be performed for specific lakes before termination of liming. Changes of certain parameters, *e.g.* TOC may change in the

future, which is not considered by the model. Also, the choice and validity of the reference lakes are critical for the model performance. However, the overall picture is probably true due to the consistency of the results and of the sulphur deposition patterns, and due also to the consistency of the results for the unlimed reference lakes and of the six monitored previously limed lakes. This would mean that the liming budget in Sweden of 208 million SEK can be significantly reduced.

4.7. Conclusions

- Iron was characterised in two acidic, oligotrophic and humic lakes. Iron(II) was occasionally present in high concentrations. Iron(III) was found to be mainly complexed in monomeric complexes to organic matter but also precipitated as an (hydr)oxide, likely ferrihydrite. Iron(III) complexation was indicated to be strong, and could therefore be a strong competitor with metals for binding sites to DOM.
- Aluminium solubility is likely controlled by a theoretical $\text{Al}(\text{OH})_3$ phase at higher pH in Swedish surface waters, but at lower pH aluminium is undersaturated and instead controlled by complexation to DOM. Therefore, for monitoring purposes total aluminium needs to be determined in order to be able to model Al_i correctly.
- Phosphate increased the adsorption of copper(II) and lead(II) to ferrihydrite significantly, by forming ternary complexes with the metals. The effect was higher for lead.
- A geochemical equilibrium model was tested and evaluated for freshwater all over Sweden. The model used one value for the active DOM/DOC ratio of 1.65 and it required determined values of total aluminium, iron, organic carbon, fluoride, sulphate, and charge balance from major cations and anions in order to simulate pH, Al_i , $\text{Al}(\text{OH})_3$ and ferrihydrite simultaneously with reasonable modelling errors. Trace metals such as Mo, As, Cu and Pb could also be simulated.
- The model could be used for predicting water chemistry after termination of liming and to assess the amount of dissolved inorganic fractions of different metals. The results suggested that liming can be terminated in 30 % of the currently limed lakes in Sweden and that liming can be decreased in many of the other lakes.
- Future studies should focus on comparing modelled Al_i with toxicity data of natural waters, to see if the model is a valuable tool in predicting toxicity.

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