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Metal Speciation in Excessively Limed Lakes

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Abstract

The possible existence of the toxic oxyanions of Al ($\text{Al}(\text{OH})_4^-$), As (HAsO_4^{2-}), Cr (CrO_4^{2-}), and Mo (MoO_4^{2-}) was examined in excessively limed lakes. Dialysis (MWCO 1000 D) was performed in the surface and bottom waters of two excessively limed lakes (pH 7.1-7.7) and one acidic lake (pH ~5.4). The dialysed concentrations were compared to equilibrium distribution of species calculated using the speciation program Visual Minteq incorporating the Stockholm Humic Model. Modelling was also performed assuming a higher pH, in order to investigate if the oxyanion concentration rises at higher pH. The metals As, Cr, and Mo in the excessively limed lakes were at large extent present in the dialysable fraction (>79%, >63%, and >92% respectively). They were also calculated to exist mostly as free oxyanions, except for Cr in the bottom waters of the lakes, where it was modelled as Cr(III) complexed to humic substances. The total concentrations of the three metals were low compared to toxicological levels for aquatic organisms. The Al concentrations however, were much higher, but most of the Al was in the non dialysable fraction (51-82%). Aluminium was also modelled as colloids or bound to humic substances, only a small fraction was $\text{Al}(\text{OH})_4^-$. However, according to the program the $\text{Al}(\text{OH})_4^-$ concentration starts to rise above pH 8.0. As toxicological data is scarce on aluminate, it is difficult to state the pH where the aluminate concentration becomes a risk to the environment.

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Introduction

Aim and purpose

The aim of this work was to examine the presence and magnitude of toxic metal species of Al, As, Cr and Mo in excessively limed lakes. To investigate how much of these metals that occurred in the form of inorganic species, in situ dialysis (1000 D) was performed in two excessively limed lakes (pH 7.1-7.7) and one acidic (pH ~5.4) reference lake. Pre-dominance area diagrams of the metals were performed with the program Medusa (Puigdomenech, 2001). Modelling of the metal species was performed using Visual Minteq (Gustafsson, 2007) including the Stockholm Humic Model (Gustafsson, 2001) for modelling of inorganic species, amount adsorbed to humic substances, precipitated phases and adsorption to ferrihydrite. Differences between the field results and the model were evaluated, to investigate if modelling is an effective tool for estimating the dissolved (<1000 D) fraction. The aim was to try to define the pH where the concentration of toxic metal forms constitutes a risk for hazardous effects on the environment, and to suggest a maximum pH that should not be exceeded during liming.

Background

Swedish lakes have been limed since 1976 by the government, to counteract the effects of acidification. One common method of liming is to add an excessive amount of lime into the lake that is the highest one in the lake system. Then the rest of the lakes in the system receive lime in appropriate doses, even if the first lake receives an unnaturally high level of lime. This is a cheap and simple method, since the number of limings can be reduced and it is sometimes easier to obtain access to the first lake rather than to all the other lakes in the system. Dosage is also achieved naturally by the first lake, instead of using a commercial doser. The disadvantages are that the first lake often is subject to an extremely high pH and alkalinity. 10-20% of the limed lakes in Sweden have pH-values above 7 up to 8.5. A third of the limed lakes have maximum alkalinities above 0.5 meq/ L (Persson et al, 2007). Today around 90% of the acidified lakes in Sweden are limed, totalling a number of 7,500 lakes. In addition to that 11% of the water-courses are also limed. Every year around 200,000 tons of lime are distributed in the lakes, to a total cost of 160-170 millions Swedish kronor (Swedish Environmental Protection Agency, 2002).

Possible problems with overlimed lakes are not as fully studied as the problems with acidified lakes. Persson et al (2007) suggest that toxic metal complexes of aluminium, arsenic and chromium could dominate in pH-solutions above 7. Another study shows elevated concentration of molybdenum in limed and/or alkaline streams (Borg et al 2001). It is the oxyanions $\text{Al}(\text{OH})_4^-$, HAsO_4^{2-} , CrO_4^{2-} and MoO_4^{2-} which are the metal species that are soluble and therefore more bioavailable at high pH (Persson et al, 2007 and Gustafsson, 2003).

The metal ions can adsorb to humic substances, to oxides (e.g. iron, manganese and aluminium oxides) and exist as colloids. This makes them less bioavailable and therefore less toxic.

Metals

Aluminium

Aluminium is the third most abundant crustal element, therefore it is highly available in the environment. It is a generally agreed fact that aluminium is not an essential element for any organisms. Instead it is toxic; the most toxic aqueous species are the inorganic monomeric forms. These are the Al hydroxy species, including $\text{Al}(\text{OH})_4^-$, but also complexes formed with F^- , SO_4^{2-} and silicic acid (H_4SiO_4). Aluminium also forms complexes with humic and fulvic acids, but they are considered less toxic to aquatic biota. In the pH-range 6-8, aluminium is mostly precipitated (Poléo and Hytterød, 2003). According to the simple equilibrium modelling program Medusa (Puigdomenech, 2001), the $\text{Al}(\text{OH})_4^-$ concentration starts to rise from pH 8 (Persson et al, 2007). For a predominance area diagram of Al with some of its common ligands, see Figure 1.

Al is greatly toxic to fish in acidic waters; the explanation is that cationic Al species bind to the negatively charged gills. There are however studies that show that AlOH_4^- present in alkaline waters is not as toxic to salmon and rainbow trout as the cationic species (Poléo and Hytterød, 2003).

Aluminium can be toxic to algae under acidic, neutral and alkaline conditions, according to a study by Hörnström et al (1995), where toxic levels were reached at 300 $\mu\text{g/L}$ Al at pH 8.5 for the species *Monoraphidium griffithii*.

More toxicological data about Al are found in Table 1, but only under acidic conditions where the cationic species dominate.

$$[\text{SO}_4^{2-}]_{\text{TOT}} = 21.00 \mu\text{M}$$

$$[\text{F}^-]_{\text{TOT}} = 2.00 \mu\text{M}$$

$$[\text{Al}^{3+}]_{\text{TOT}} = 3.70 \mu\text{M}$$

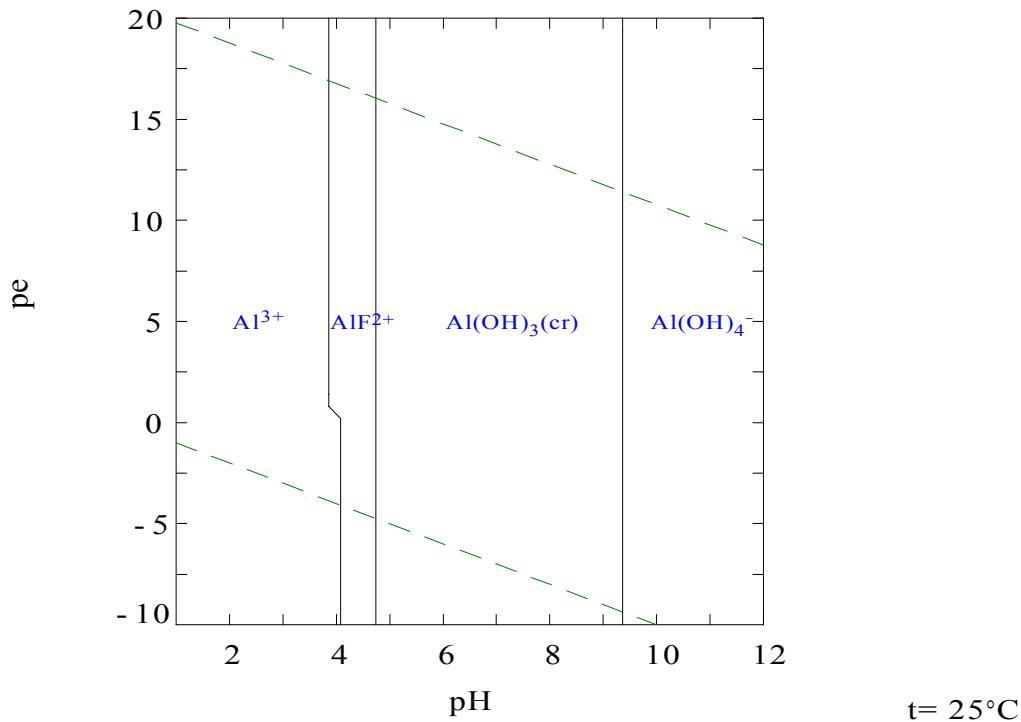


Figure 1. Predominance area diagram for Al (100 $\mu\text{g/L}$) in water with an F^- concentration of 2 μM and a SO_4^{2-} concentration of 21 μM . The concentrations are in the range of the lakes in this study.

Arsenic

Unnatural sources of arsenic to surface waters are pesticides, mining and processing sulphide ores, and burning of fossil fuels (Pierce and Moore, 1982). Arsenic is considered to be an essential element (Jain and Ali, 2002). In oxygenated waters, As(V) species are stable, especially H_2AsO_4^- and HAsO_4^{2-} in the pH of natural waters. At more reducing conditions, As(III) species are more stable, including H_3AsO_3 (Pierce and Moore, 1982). Biologically, As(III) is considered to be more toxic than As(V) (Jain and Ali, 2002). The toxicity of As decreases in the order $\text{H}_3\text{AsO}_3 > \text{H}_3\text{AsO}_4 > \text{CH}_3 - \text{As} - \text{O}_3\text{H}_2 > (\text{CH}_3)_2\text{-As-O}_2\text{H} \geq$ “biological As” (Mushak, 1985). For a predominance area diagram of As in pure water, see Figure 2.

For some toxicity data of both As(III) and As(V), see Table 1.

$$[\text{AsO}_4^{3-}]_{\text{TOT}} = 5.00 \text{ nM}$$

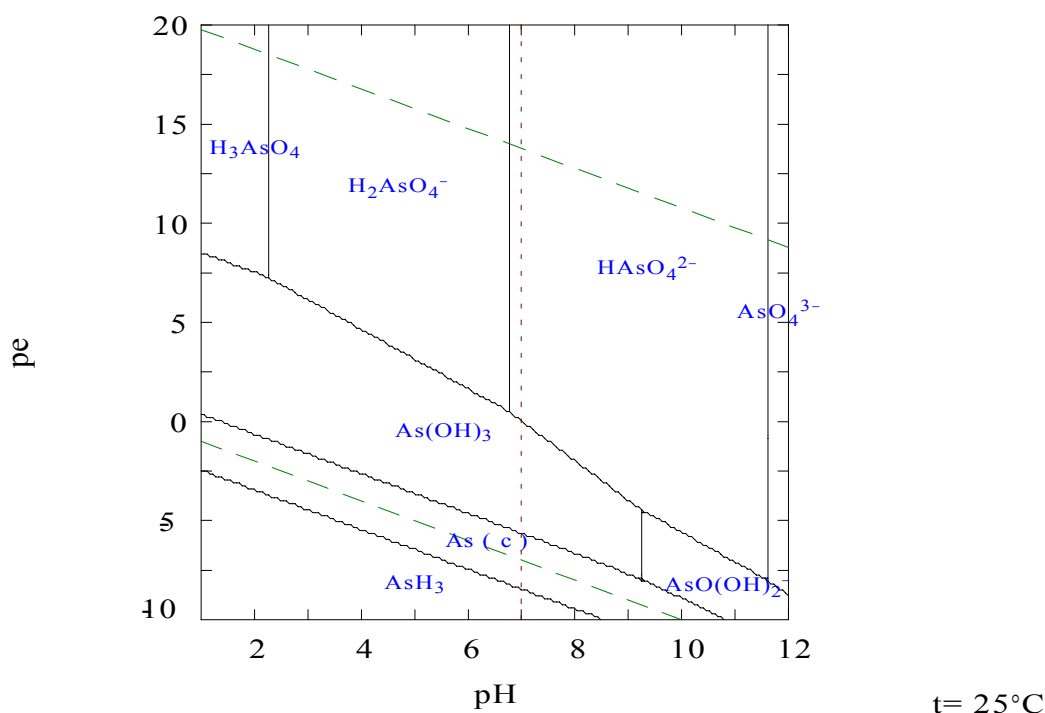


Figure 2. Predominance area diagram for As with a concentration of $0.4 \mu\text{g/L}$ in pure water. The concentration is in the range of the lakes in this study.

Chromium

Hexavalent chromium is used in stainless steel manufacturing, chrome plating, leather tanning, wood treatments, dyes, and pigments (Puzon et al, 2005). Chromium is an essential trace element for humans; it is part of the glucose metabolism. It is also toxic to humans, it can cause tumours, ulcers, and it can induce cancer by alteration of the DNA. Cr exists in two oxidative states in natural waters, (III) and (VI); see the predominance area diagram in Figure 3. Cr(III) is easily sorbed or present in solid forms in the pH-range of natural waters. Since Cr(VI) occurs in the negatively charged aqueous complex of CrO_4^{2-} , it is not easily sorbed and therefore potentially more bioavailable (Peterson et al, 1997). Hexavalent Cr has also been found to be more toxic to microbiota (Peterson et al, 1997), whereas Cr(III) salts are non-toxic and even used as food supplements (Puzon et al, 2005). For toxicity data of both Cr(III) and Cr(VI), see Table 1.

$$[\text{CrO}_4^{2-}]_{\text{TOT}} = 1.90 \text{ nM}$$

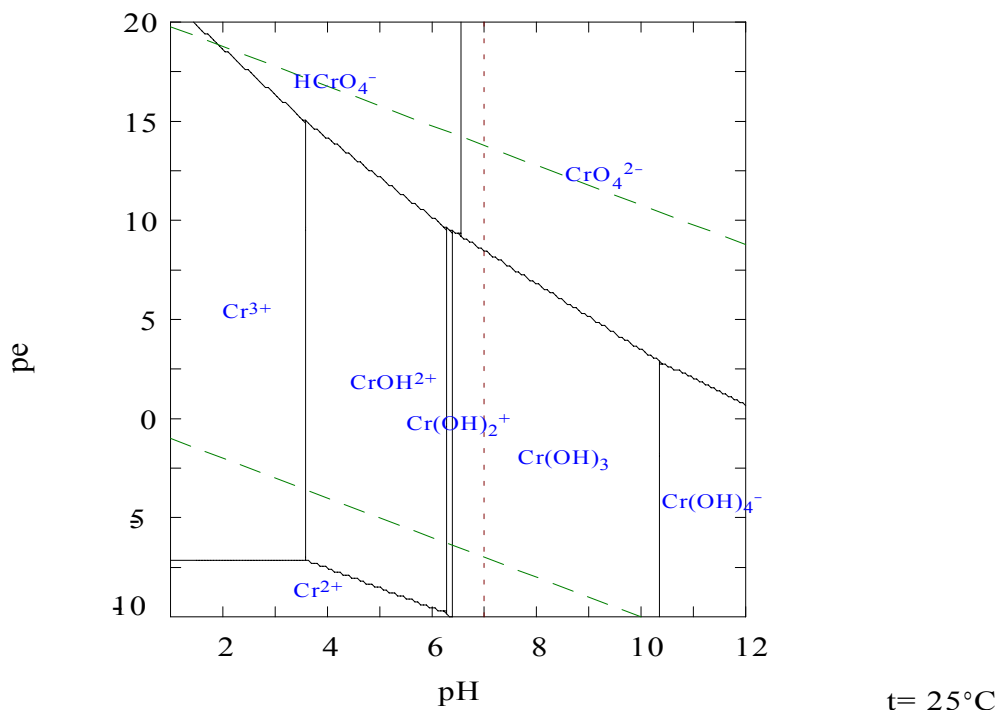


Figure 3. *Predominance area diagram of Cr (concentration 0.1 $\mu\text{g/L}$) in pure water. The concentration is in the range of the lakes in this study.*

Molybdenum

Molybdenum is an essential trace element for humans, but also for animals and plants. In humans and other mammals it exists in metalloflavoproteins, in plants it is necessary to fix atmospheric nitrogen by bacteria as the start of protein synthesis. Since it is common in food, no diets have been found to cause a molybdenum deficiency. The soluble forms of molybdenum are easily absorbed in humans and are generally more toxic to both humans and animals than the solid forms (Vyskočil and Viau, 1999). One test of molybdate toxicity to a tubicid worm is presented in Table 1 (Khangarot, 1991). I have not found any more studies which show toxicity for MoO_4^{2-} to aquatic organisms, therefore some data available on ruminants are included. Ruminants are more sensitive than monogastric animals.

Molybdenum intoxication resembles the symptoms of copper deficiency and the symptoms are often but not always helped by treatment of extra copper. For steers, one of the most sensitive mammals, the lethal, oral dose is $3 \text{ mg/kg}^{-1} \text{ day}^{-1}$ (Vyskočil and Viau, 1999). For humans there is a lack of data showing toxicity, no lethal levels are known (Vyskočil and Viau, 1999). The maximum tolerable level has been suggested to 0.6 mg/d by the European Commission in 2002, based on animal studies (Novotny and Turnlund, 2007).

In diluted waters at $\text{pH} > 4.4$ and at relatively high Eh molybdenum exists mainly as fully dissociated MoO_4^{2-} (Gustafsson, 2003), see also the predominance area diagram in Figure 4.

Table 1. Toxicity of the different metals to different aquatic organisms, concentrations in µg/L.

Species	Bacteria ¹	Daphnid ²	Tubicid worm ³	Pulmonate snail ⁴	Toad tadpoles ⁵	Protozoa ⁶	Amphipod ⁷	Fish ⁸	Daphnid ⁹
Latin name	<i>Escherichia coli</i>	<i>Daphnia magna</i>	<i>Tubifex tubifex</i>	<i>Lymnaea luteola</i>	<i>Bufo melanostictus</i>	<i>Tetrahymena pyriformis</i>	<i>Hyalella azteca</i>	<i>Pimephales promelas</i>	<i>Ceriodaphnia dubia</i>
Type of test	MIC	Reproductive Impairment	EC50 (96 h)	LC50 (96 h)	LC50 (96 h)	IC50	LC50 (4 weeks)	LC50 (48 h)	IC50 (1 week)
pH	7.0 (start)	6.5-8.2	7.6 (7.5-7.7)	7.4 (7.2-7.6)	7.4 (7.1-7.6)	Unknown	Unknown	<8.1	<8.1
Al III	54,000	320							
As III			8,870						
As V		550					420		
Cr III	260,000	330				40,000		19,790	3,428
Cr VI	10,400		190	3,880	49,290		38	22,460	37
Mo VI			28,910						

¹ Nies, 1999. Minimal inhibitory concentration (MIC) for the bacteria *Escherichia coli* determined on TRIS-buffered mineral salts medium. Starting pH 7.0, incubation time 2 days at 30 °C. The test with Al had to be acidified to keep the metal ion in solution.

² Biesinger and Christensen, 1972. Chronic (3-week) testing with the endpoint 16% reproductive impairment (number of youth counted) to the daphnid *Daphnia magna* in Lake Superior (USA) water. The pH ranges between 6.5 and 8.2.

³ Khangarot, 1991. EC50 (effective concentration at which 50% immobilization response was recorded) after 96 hours for the freshwater tubicid worm, *Tubifex tubifex*. The mean pH was 7.6, but in order to dissolve sodium arsenite, it had to be boiled in dilute HCl.

⁴ Khangarot, and Ray, 1988. Lethal concentration for 50% of the tested animals (LC50) after 96 hours for the freshwater pulmonate snail, *Lymnaea luteola*. The mean pH-value was 7.4, but it was decreased for the higher concentrations of Cr.

⁵ Khangarot, and Ray, 1987. Lethal concentration for 50% of the tested animals (LC50) after 96 hours for the freshwater toad tadpole *Bufo melanostictus* (Sneider).

⁶ Sauvant et al, 1997. Inhibitory concentration 50% (IC50) for the doubling time of the population of the ciliated protozoa *Tetrahymena pyriformis*.

⁷ Norwood et al, 2006. Lethal concentration for 50% of the tested animals after 4 weeks for the freshwater amphipod *Hyalella azteca*.

⁸ Baral et al, 2005. Lethal concentration for 50% of the tested animals after 1 week for the freshwater fish fathead minnow, *Pimephales promelas*.

⁹ Baral et al, 2005. IC50 is the toxicant concentration at which a 50% reduction in reproduction occurs after 1 week for the daphnid *Ceriodaphnia dubia*.

Mn(II) is oxidised very slowly without catalysts, for 7 years nothing happened in a solution with pH 8.4. Under natural conditions however, both bacteria and particles serve as catalysts and can oxidize Mn(II) much faster, with half lives of days at pH 6.5. Bacteria and particles can also reduce the oxidized forms of Mn (Björkvald, 2007).

When comparing with Fe, Mn(II) is oxidised more slowly than Fe(II). Mn(II)/Mn(IV) also has a higher pe° than Fe(II)/Fe(III) and Mn(II) therefore occurs higher up in the water column than Fe(II) (Davison, 1993).

Mn is not considered to complex to humic material in any relevant amount (Davison, 1993).

Manganese oxides usually have a negative surface charge at pH values above 5, which makes them ideal for adsorbing positive trace metals (Björkvald, 2007).

Humic and fulvic acids

Trace metals can be sorbed to both humic substances and various oxides in natural waters. Organic matter contains *humic substances* (HS), which are polyelectric acids that can adsorb metals, and non-adsorbing material, e.g. organisms, small organic acids and saccharides (Appelo and Postma, 2005, p 344). The humic substances are non-volatile and usually have molecular weights of 500-5000 g (Stumm and Morgan, 1996, p 141). They can be divided into two major groups, *humic acids* and *fulvic acids*. If the humic material is brought to pH= 1 with HCl, some of it will be precipitated. This fraction is called humic acid (HA). The rest which is still in solution is called fulvic acid (FA) (Stumm and Morgan, 1996, p 141). Two main groups of acids are common in humic substances, carboxylic (R-COOH groups) with $pK_a < 5$, and phenolic with $pK_a > 8$ (Appelo and Postma, 2005, p 345). Fulvic acids contain more R-COOH and R-OH groups than humic acids (Stumm and Morgan, 1996, p 141).

Isolation of aquatic humic substances can for example be done with a non-ionic XAD-resin or a weakly basic ion exchanger (Stumm and Morgan, p 141).

By titration with acid or base of humic and fulvic acids, the charge of the acids can be determined. The charge differs at different pH-values. The ionic strength also determines the charge of the acids, but not to a large extent, usually within the measurement error. Since the substances are very heterogeneous they can be difficult to model. One of the difficulties is to model the electrostatic contribution, since the differences in shape and size of the humics complicate the calculations (Appelo and Postma, 2005, pp 344-345).

Metal sorption to oxides and humics

The mechanism of sorption includes two effects: a chemical bond between the ion and the surface atoms, and an electrostatic effect that depends on the surface charge. Adsorption of trace metals to solid surfaces is mainly controlled by specific binding to the variable charge surfaces of oxides, but is also affected by ion-exchange mechanisms. (Appelo and Postma, 2005). Adsorption to humic substances takes place at the deprotonated acid functional groups (Appelo and Postma, 2005).

Al can adsorb both weakly and strongly to humic and fulvic acids (Poléo and Hytterød, 2003). I have not found any data showing aluminium adsorption to oxides, which indicate that it does not occur to any large extent.

As can adsorb to hydrous oxides of iron, aluminium, and manganese, but the adsorption is dependent on pH, redox potential, and species of arsenic (Mushak, 1985). H_3AsO_3 , $H_2AsO_4^-$,

and HAsO_4^- can also adsorb in a small extent to humic substances, even though the two latter are negatively charged (Buschmann et al, 2006).

Cr often occurs adsorbed to manganese oxides and clay material, but not to the same extent to iron oxide and humified organic material according to Covelo (2007). The study is however performed at pH 4.5, which is not so relevant for this study, and the redox state of Cr is unknown.

Iron, aluminium and to some extent, titanium oxides can be important sorbent materials for MoO_4^{2-} . The adsorption of MoO_4^{2-} on two-line ferrihydrite (hydrated ferric oxide, $\text{Fe}(\text{OH})_3$) was tested by Gustafsson (2003), and the study showed that molybdate adsorbs better at lower pH than at higher pH. Phosphate competes with molybdate in adsorption to ferrihydrite (Gustafsson, 2003).

Hypothesis

Due to the possible presence of Al as a colloid in the pH of the excessively limed lakes studied, a low concentration of $\text{Al}(\text{OH})_4^-$ was expected. The As and Cr oxyanions are known to adsorb quite well to different oxides, so they were not expected to be present to a large extent as free ions. The molybdate concentration was expected to be higher in the limed lakes than in the acidic lake, in accordance with the study mentioned above (Borg et al, 2001).

The modelling results were expected to differ from the field values, due to the system not being in equilibrium and the difficulties of setting the correct input model parameters, e.g. binding to humics and sorption to oxides.

A suggestion of a maximum pH that should not be exceeded during liming was pH 8.0, since the aluminate concentration according to the model Medusa starts to rise at this pH. The chromate concentration is also dominant at this pH.

Materials and methods

Characteristics of the lakes

Three different lakes in western Sweden were examined: Lakes Motjärn and Stora Vrångstjärnet situated in Dalsland, and Rotehogstjärnen in Bohuslän (Fig. 5).

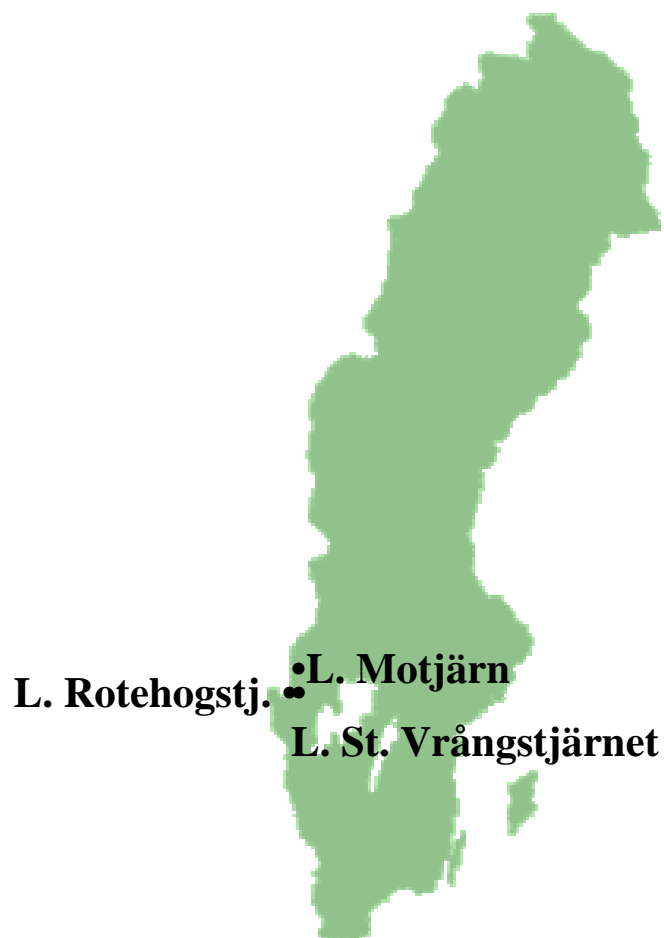


Figure 5. Map of Sweden with the three lakes.

Lakes Motjärn and Stora Vrångstjärnet are excessively limed, whereas the reference lake Rotehogstjärnen has never been limed. Lake Motjärn is 11.3 ha and the maximum depth found was 10 m. Lake St Vrångstjärnet is 9.4 ha and the maximum depth found was 12 m. Lake Rotehogstjärnen is 16.8 ha with a maximum depth of 10 m. All the lakes are oligotrophic and situated in boreal forests. The deepest part in every lake was chosen for the dialysis experiment, to enable placement of the membranes at two different depths with as different conditions as possible. The depths were one meter from the surface and one meter above the bottom of the lakes.

Field work

Oxygen and temperature profiles were measured in the lakes with a *Microprocessor Oximeter, OXI 196*, both at the time of placement and at the gathering of the samples. At the Lake Motjärn the oximeter did not work at the time of the placement, so a temperature profile was made using the *Tamm water sampler* instead.

Water samples were collected with a metal-free *Tamm water sampler* at the same depths as the placement of the membranes. The *Tamm water sampler* was rinsed with lake water before taking the samples. Three different polyethene bottles were used, one for pH, alkalinity, colour, turbidity, conductivity, absorbance, anions and major cations and the remaining two for aluminium fraction and Total Organic Carbon (TOC). One acid washed and acid leached polypropene bottle was used for trace metals. This bottle was kept in a plastic bag in order to

avoid contamination. Before taking the water samples, the bottle was rinsed once with lake water. All bottles were stored in cool boxes upon collection.

The secci depth was also measured at the lakes, at both times. Samples for determination of nutrients were also taken, but due to a heavy work load at the lab, analytical results from another sampling, performed 1-2 days later at approximately the same depths for the monitoring program ISELAW (Integrated Studies of the Effects of Liming Acidified Waters), were used in this study.

Dialysis

Spectra/por® regenerated cellulose dialysis membranes with a molecular weight cutoff (MWCO) of 1 000 Dalton were used for the study. The dialysis membranes were cut in approximately 29.5 cm long pieces and then leached in 1 M HCl for a minimum of 12 hours in order to remove possible metal contaminants from the membranes. Plastic gloves were worn when handling the membranes for all laboratory procedures and in the field. After the acid leaching, the membranes were put in a beaker with Milli-Q water. Then they were sealed by making a knot of the membrane at one end, and rinsed in Milli-Q-water three times. The membranes were filled with Milli-Q water and sealed by making a knot of the membrane in the other end. Nylon strings were tied on the membranes, in order to be able to attach them to the cylinders that were used in the lakes (see below). The membranes were then stored in polypropylene bottles which had been machine-washed, acid washed and acid leached for at least a week, and then rinsed three times in Milli-Q water. The filled membranes were stored in them in Milli-Q water until placement in the lakes. The membranes were stored in a cold storage room at 4° C before departure, and then in a cool box, in order to avoid bacterial growth. Since the membranes are made of cellulose, which is a substrate for bacteria, the membranes could get digested and the pores therefore increase in size (Borg, 1986).

The membranes were attached with the nylon strings, two by two inside Perspex cylinders with holes on the lids. The cylinders were attached to a rope with a float and a sinker at each end. The Perspex cylinders were 20 cm long, so the membranes were placed approximately between the depths 1.1 m - 1.3 m under the surface and 0.9 m - 0.7 m above the bottom, when including the length of the strings. Two cylinders were attached at each depth, with the intention to obtain at least triplet samples.

One storage bottle with two membranes was brought to the field as a blank. Milli-Q water was changed once back at the laboratory. Another membrane was stored in 4° C at the laboratory all the time and was also used as a blank.

The sampling took place in September 2007 and the membranes were left in the lakes for five days to reach equilibrium (Borg, 1986).

The storage bottles were rinsed two times with Milli-Q water at the laboratory and then used again for collecting the membranes. They were rinsed once with the lake water at site and then filled with lake water, from the water depth where the membranes had been placed in the lake. The membranes were brought up from the lake and rinsed with lake water from a spray bottle which was acid washed and leached. The membranes were placed two by two in the storage bottles and then kept in cool boxes until entering the laboratory. After a maximum of three days the membranes were cut open standing in an acid leached graduated glass cylinder. The dialysed water was transferred by an acid leached pipette into an acid washed and leached polypropylene bottle, wrapped in a plastic bag. The volume dialysed was approximately 80 ml. The dialysates were then treated with 150 µL distilled concentrated HNO₃ to keep the metals in a soluble form and then stored for at least two days. Three replicates per lake and depth were analysed with ICP-MS.

The lake water left in the storage bottles was measured directly afterwards for temperature and oxygen with the oxygen meter.

TOC experiment

Since TOC was not originally analysed in the dialysates, a lab experiment was set up to provide a measure of the dialysable fraction of the organic substances in the lakes. Two 5L-cans were leached with 1 M HNO₃ for 12 hours, then rinsed three times with Milli-Q water. Samples were taken at L. Motjärn and L. Stora Vrångstjärnet in October 2007 at 1 m depths and sent by mail to the laboratory. A blank sample was also made, using Milli-Q water. Dialysis membranes with an approximate volume of 120 mL were placed in the cans for 6 days at room temperature, while being stirred by a magnetic stirrer. After that they were emptied like the other membranes and put into TOC-bottles for measuring. Samples from outside the membranes were also measured. Absorbance was measured both inside the membranes and outside. In the blank, the dialysis membrane was sticking up 2 cm above the water surface at the end of the experiment. Since the membranes become very fragile when they dry, it may possibly have been broken.

Chemical analyses

All water chemical analyses were performed using Swedish standard methods. All analyses followed quality control routines, defined in the accreditation of the laboratories (except for the anions and absorbance).

The pH-determination was done in room temperature with a *PHH 93 Reference pH Meter*. The pH electrode was calibrated with pH 4 and 7 buffer solutions. The alkalinity/acidity was measured with a *TIM 865 titration manager*, which titrates with HCl/ NaOH to pH-level 5.4. Conductivity measurements were done at 25° C with a *CDM83 Conductivity meter*. The colour of the water was measured with a *Lovibond Daylight 2000 unit*. Absorbance was measured both filtered (0.45 µm) and unfiltered at 420 nm, with a 5 cm cuvette, using a *Milton Roy spectronic 601* spectrophotometer. The turbidity of the water was measured with a *Hach 2100 N IS Turbidimeter*, at the FNU mode. When comparing the pH, alkalinity, conductivity, temperature and oxygen levels from the first and the second sampling, the results were approximately the same, indicating that there had not been a turn-over in the lakes and that the conditions had been relatively constant through the period of the dialysis. Further analyses were therefore made only on water from the second sampling.

The 250 ml bottles for metal analyses of the lake water, were preserved with 500 µl distilled concentrated HNO₃ and then stored dark and cold for two days. Then they were analysed with ICP-MS (*Thermo X Series 2*) for Ag, Al, As, Cd, Cr, Cu, Fe, In, Mn, Mo, Ni, Pb, U and Zn. Internal standards were Rh and Sc.

The anions fluoride, chloride, nitrate and sulphate were analysed with ion chromatography (IonPac® AS14). Eluent was 3.5 mM Na₂CO₃/ 1.0 mM NaHCO₃ with a flow rate of 1.2 mL/min and the injection volume was 100 µl. Detector was a Suppressed Conductivity at 10 µSFS ASRS®- ULTRA.

The cations Ca²⁺, K⁺, Mg²⁺ and Na⁺ were analysed with atom absorption spectrometry, atomization in flame, using a *Perkin Elmer 3100*, according to the methods SS 028150-2, 52-2, 60-2, 61-2. Caesium chloride was added to the sodium and potassium samples and standards to reduce ionization. Lanthanum chloride was added to the calcium and magnesium samples to reduce interference with P, S, and Al.

The bottles for aluminium fractionation, phosphate and silicon were stored in the dark in 4° C in a cold storage room. The aluminium fractions were analysed by cat ion exchange and determination of the pyrocatechol complex with spectrometry, (*Autoanalyzer Bran & Luebbe AAI*, year model 1990).

The TOC bottles were stored frozen before analysis. They were not preserved, but pretreated with HCl. Then they were analysed by oxidative combustion with a *Shimatzu TOC 5050* with sample injector *ASI-502* at the Department of Environmental Assessment at SLU.

Phosphate, silicon and ammonium-N were analysed at the Department of Environmental Assessment at SLU for the monitoring program ISELAW. The phosphate concentration was measured with a *Bran & Luebbe Autoanalyzer 3*, with the Bran & Luebbe Method No. G-175-96 Rev. 2. The silicon samples were preserved with H₂SO₄ and then analysed on a *Technicon Traacs 800* with the Bran&Luebbe Industrial Method No. 811-86T. The ammonium-N was measured on a *Bran & Luebbe Autoanalyzer 3* with a Fenatmethod according to the Bran & Luebbe Method No G-171-96 Rev. 1.

Models

In this study one program for speciation of metals was used, Visual Minteq (Gustafsson, 2007, <http://www.lwr.kth.se/English/OurSoftware/vminteq/>) with the Stockholm Humic Model (SHM)(Gustafsson, 2001). Other examples of models are the NICA-Donnan model (also included in Visual Minteq) and PHREEQC (Parkhurst and Appelo, 1999, http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/index.html). For PHREEQC a certain model which describes metal adsorption to humic substances called Model V (Tipping and Hurley, 1992) can be used, but since it did not include any of the metals of interest (Al, As, Cr and Mo) in this study it was not used here.

Models for humic substances can be represented either by a continuous distribution of pK_a-values, or a discrete site approach. NICA-Donnan is a continuous model whereas Model V and SHM are discrete site models. The individual sites used in the discrete site models should not be viewed as physically present sites (Gustafsson, 2001). In the Model V and SHM, the almost identical method is used, with eight different discrete sites. Four represent strong, mainly carboxylic acid sites and the other four weaker, mainly phenolic sites (Gustafsson, 2001). Metal binding is assumed to occur to one or two proton binding sites (monodentate or bidentate) in SHM and Model V (Gustafsson, 2001).

Salt dependence of proton binding to HS is also an important parameter in the models. This is described differently by the different models. In Model V, the HS are viewed as impermeable spheres, and the charge is assumed to be localised on the exterior part. In the NICA-Donnan model, on the other hand, the HS is thought to be a separate gel phase in the bulk water phase, where the gel phase is electrically neutral (Gustafsson, 2001).

The SHM uses a third approach, where the bulk of the humic substances is considered to form gels. The gels are described and mainly treated as impermeable spheres, where the electrostatic interactions on the surfaces are modelled using the Basic Stern Model. Some humic molecules are however allowed to have certain groups outside the gel that behave like normal monomeric molecules (Gustafsson, 2001).

I tested the NICA-Donnan model included in Minteq, but the SHM results agreed better with the results of the dialysis, so I chose to continue with the SHM model.

Included in Minteq are different adsorption models. The one used in this study is adsorption to hydrous ferric oxide using the Diffuse Layer Model (HFO with DLM). The database

included in the model is the one made by Dzombak and Morel 1990 for surface complexation of metals to hydrous ferric oxide (ferrihydrite) (Gustafsson, 2007, Help file Visual Minteq).

The metal speciation program called Hydra/Medusa (Puigdomenech, 2001, <http://web.telia.com/~u15651596/>), is good for creating fractions, logarithmic and predominance area diagrams. It does not include any humic model or adsorption model though, but it has been used here to make the predominance area diagrams in the introduction and a logarithmic diagram below.

Visual Minteq assumes that the concentrations mol/L and mol/kg are the same. I made the same assumption when entering concentrations in the program.

In Visual Minteq, the input values used were: total concentrations of metals Ag, Al, As, Ca, Cd, Cr, Cu, Fe, In, K, Mg, Mn, Mo, Na, Ni, Pb, and Zn. U was excluded because of its low concentration (0.03-0.06 µg/L) and difficulties in deciding which redox state it would be set to. Mo was entered as MoO_4^{2-} , as that is the only input species available in Minteq. The function "Specifying redox couples" was chosen for As, Cr, Cu, Fe and Mn. The anions Cl^- , F^- , NO_3^- and SO_4^{2-} were entered. The F^- concentration of L. Stora Vrångstjärnet was below detection limit, so the value entered in the model was the detection limit 0.010 mg/L. When NO_3^- was below detection limit (50 µg/L), none was introduced in the model. Total Si was recalculated and entered as silicic acid, H_4SiO_4 . The measured alkalinity was recalculated as mg HCO_3^- , since the program requires it. For metal concentrations, temperature, pH and alkalinity, the values used were the ones from the day when the dialysis membranes were gathered in the field, since dialysis is much affected by what happens at the end of the dialysis period (Gimpel et al, 2003).

Difficulties arose in determining which pe that should be entered, since it is difficult to measure in natural waters and it is seldom in equilibrium for all elements in the lake at the same time (Stefánsson et al 2005). Setting the pe in the lakes was based on the following principles:

-Oxygen levels. Higher pe at the well oxygenated surfaces than in the almost oxygen-free bottom waters.

-pH. In oxygen-saturated waters pe can be estimated by the formula:

$$\text{pe} = 20.78 + 1/4 \log P_{\text{O}_2} - \text{pH}$$

(Drever, 1988, p 289).

-Probable appearance of hydrogen sulfide in the bottom water of L. Rotehogstjärnen (according to the smell of the water during sampling). This indicates a low pe, SO_4^{2-} is reduced to S^{2-} at pe -1.5 by modelling in Medusa, see Figure 6.

pH=5.33

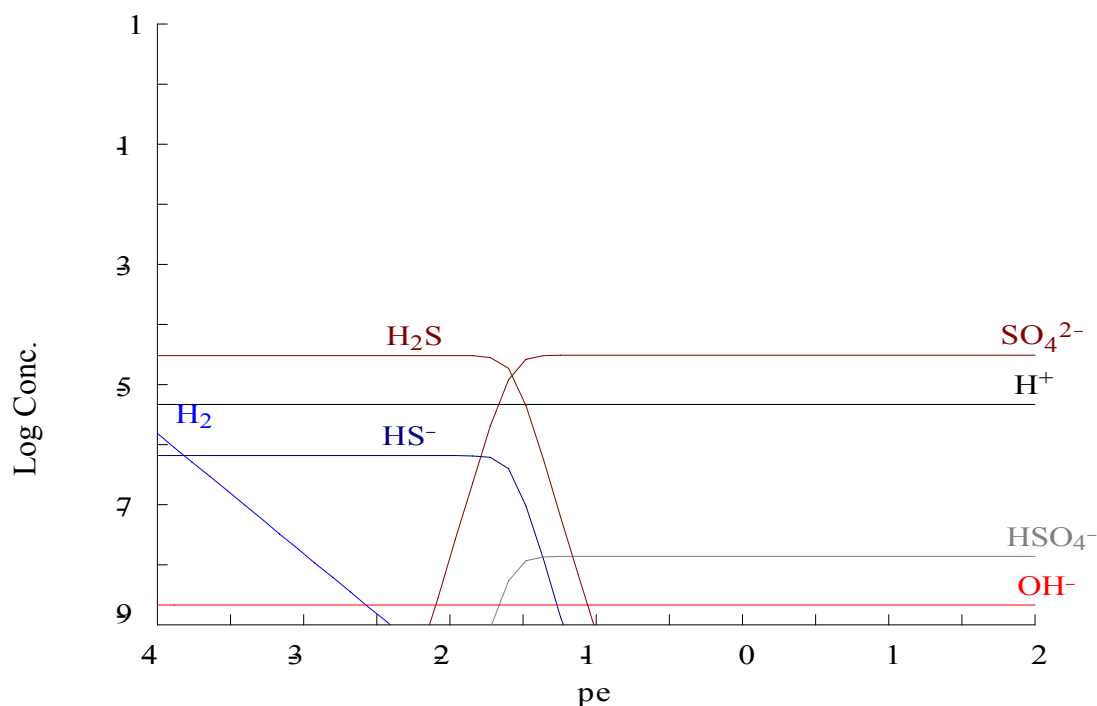
 $[\text{SO}_4^{2-}]_{\text{TOT}} = 31.00 \mu\text{M}$ 

Figure 6. Logarithmic diagram with the total SO_4^{2-} concentration in L. Rotehogstjärnen, and pe on the variable axis.

-Solubility of iron. The assumptions first made are that all Fe that enters the membranes is divalent, aqueous ions and the Fe outside the membrane is solid Fe(III). When entering these assumptions into the Minteq program and choosing the function “pe computed: supply a guess for pe”, the program gave the results of the bottom waters of L. Motjärn to 1, in L. Vrångstjärnet 0.5 and in L. Rotehogstjärnen to 6. The value of L. Rotehogstjärnen is much higher than the pe at which hydrogen sulphide is reduced to H₂S.

-Solubility of manganese. Since dialysis of the surface waters of the limed lakes showed that almost none of the Mn passed the membrane, it indicates a solid phase based on oxidised Mn, either tri- or tetravalent. The other options are that Mn²⁺ should adsorb to humics or a particle, but that is less likely (Davison, 1993). Above pe 11 the Mn-containing mineral birnessite (δ -MnO₂) precipitates in the limed lakes when modelling in Minteq. The mineral birnessite is a naturally occurring Mn-mineral (Davison, 1993).

After these considerations pe was set in well oxygenated surface waters according to the equation $pe = 20.78 + 1/4 \log P_{\text{O}_2} - \text{pH}$. The oxygen pressure was assumed to be 0.2 atm. In L. Motjärn pe was set to 13, in L. Stora Vrångstjärnet to 13.5 and in L. Rotehogstjärnen to 15. In the bottom waters the pe was set to 1 in L. Motjärn and 0.5 in L. Stora Vrångstjärnet based on iron solubility and -1 in L. Rotehogstjärnen based on the appearance of hydrogen sulphide.

Three solids were specified as possible solid phases: Al(OH)₃ (soil), ferrihydrite (aged), and birnessite, see Table 2 for log K values and enthalpies of reaction, as defined by Minteq. Al(OH)₃ (soil) and ferrihydrite (aged) were chosen after personal communication with Jon Petter Gustafsson. The solubility of aluminium is controlled by Al(OH)₃ (soil) in acidic podzolized soils according to Gustafsson et al (2001). For iron, the solubility products for laboratory formed ferrihydrite, “amorphous iron hydroxide”, “hydrated ferric oxide”, etc., vary between log K: 2.5 to 5 (Tipping et al, 2002). Birnessite was chosen since it is considered a possible precipitated Mn-mineral in lakes (Davison, 1993).

Table 2. Log *k* values and enthalpies of reaction for the solubility of the three possible solids, from the database in Minteq.

Solid	Reaction	log <i>k</i>	Δ <i>H_r</i>
Al(OH) ₃ (soil)	Al(OH) ₃ + 3H ⁺ = Al ³⁺ + 3H ₂ O	8.29	-105
MnO ₂ Birnessite	MnO ₂ + 4 H ⁺ + e ⁻¹ = Mn ³⁺ + 2 H ₂ O	18.091	-
Fe(OH) ₃ Ferrihydrite (aged)	Fe(OH) ₃ + 3H ⁺ = Fe ³⁺ + 3H ₂ O	2.69	-100.4

Adsorption to ferrihydrite using the predefined parameter set of “HFO with DLM” was entered at sites where ferrihydrite precipitated. The amount of ferrihydrite was calculated based on the amount of Fe that precipitated and the molecular weight of 89 g (FeO(OH)).

The values for total organic carbon, TOC, were assumed to be the same as dissolved (<45 μm) organic carbon, DOC, since they differ by less than 5% for Fenno-Scandias boreal forest areas according to Temnerud et al (2007). Adsorption to humics was modelled with the default settings for SHM and aqueous speciation: assuming that 100% of the humic substances consist of fulvic acids and 0% is humic acids. The actual value was not determined in this study, the value of 90% fulvics and 10% humic acids is for instance used by Gimpel et al (2003), but the model works best assuming that 100% is fulvic acids. The default settings also say that the ratio of DOM to DOC is 1.4. DOM is considered to consist of 50% of C, but since not the entire DOC is reactive with respect to proton and metal binding, the value of 1.4 is chosen instead of 2. (Gustafsson, 2007, Help file Visual Minteq)

The function “Sweep” in Visual Minteq was used when modelling changes in pH. The input values are the same, except for the pH value which can range.

Results

Field results

Since the conditions were approximately the same regarding pH, alkalinity, temperature and conductivity in the lakes at placement of the membranes and at gathering, only the results from the gathering are shown in the tables below. These were also the values used in the modelling.

Major cation and anion concentrations, pH, alkalinity, TOC content, temperature, oxygen concentration, secci depth, absorbance, colour, and conductivity are shown in Table 3 for all the sites.

Table 3. Chemical characteristics of the three lakes at the 10-11 of September, 2007.

	L. Motjärn		L. St. Vrångstj.		L. Rotehogstjärnen	
	Surface	Bottom	Surface	Bottom	Surface	Bottom
Depth (m)	1	9	1	11	1	8
pH	7.69	7.16	7.33	7.34	5.54	5.33
Alkalinity (meq/L)	0.63	1.08	0.37	0.91	0.01	0.03
Temperature (C)	14.0	6.2	14	6.7	14.2	7
Oxygen (mg/L)	8.6	0.1	7.8	0.2	7.5	0.1
Cond. (mS/m25)	9.35	13.7	7.02	12.55	4.49	4.90
Secchi depth (m)	3.9		2.9		1.5	
Absorbance	0.091	0.181	0.181	0.160	0.335	0.490
Absorbance filtered	0.078	0.090	0.160	0.108	0.284	0.312
Turbidity	0.47	5.08	0.61	2.24	1.35	6.97
Colour	35	60	60	55	120	140
TOC (mg/L)	7.1	7.1	10.1	7.5	15.5	10.5
Ca (meq/L)	0.675	1.043	0.475	0.546	0.076	0.073
Mg (meq/L)	0.069	0.082	0.052	0.064	0.074	0.070
Na (meq/L)	0.129	0.129	0.145	0.145	0.216	0.208
K (meq/L)	0.010	0.011	0.007	0.010	0.007	0.019
SO4 2- (meq/L)	0.093	0.081	0.090	0.097	0.039	0.092
Cl- (meq/L)	0.145	0.151	0.113	0.183	0.271	0.274
F- (mg/L)	0.052	0.057	< 0.010	0.049	0.047	0.047
NO3- (µg/L)	< 50	< 50	129	951	< 50	< 50
NH4- (µg/L)*	27	310	28	5	12	15
PO4 3- (µg/L)*	3	3	3	6	3	12
Si (mg/L)*	0.37	1.82	1.52	2.43	1.41	3.18

* Samples from 1-2 days later, approximately the same depths.

The charge difference varied between 0.6% and 10.5% in five of the different stations, but in the bottom water of L. Stora Vrångstjärnet the charge difference was -20%. This is an unlikely result, the charge difference ought to give a result with an excess of cations. Since humic substances are negatively charged, they consist of anions with an equal amount of charge as the excessive cations.

The total concentrations of the trace metals and the amount in the dialysable fractions are shown in Table 4. The trace metal concentrations in the dialysable fraction are shown in Table 10 in the Appendix. For all the trace metals, all three dialysed subsamples were similar to each other, with standard deviations within 27% of the sample concentration. The only exceptions were one Zn-sample, (L. Motjärn surface, s. d. 65% of the sample concentration) and one Cd-sample (L. Motjärn bottom, 56%). The dialysis blanks showed mostly concentrations below the detection limit, except for concentrations of Cr, Mo and Zn in some, but not all of the blanks. The contamination values were present either in the field blank or in the laboratory blank, never in both for the same element. When present in the field blank bottle, the contamination was the same in the two membranes. The highest blank concentration of Cr was 32% of the lowest sample concentration. The Mo blank values were close to detection limit, but of the lowest concentrations of the samples the blank values were

Table 4. Total trace metal concentrations in µg/L and the amount dialysable of the total concentration in %.

	Detection limit (µg/L)	L. Motjärn				L. St. Vrångstjärnet				L. Rotehogstjärnen			
		Surface		Bottom		Surface		Bottom		Surface		Bottom	
		Total (µg/L)	% dialysed	Total (µg/L)	% dialysed	Total (µg/L)	% dialysed	Total (µg/L)	% dialysed	Total (µg/L)	% dialysed	Total (µg/L)	% dialysed
Ag	0.0002	0.0007	<29%	0.0004	<50%	0.0007	<29%	0.0008	<25%	0.0006	<33%	0.002	<10%
Al	0.2	36.4	49%	41.0	31%	112	18%	78.1	23%	328.3	25%	478	23%
As	0.010	0.34	85%	0.55	83%	0.35	79%	0.47	96%	0.60	69%	0.53	59%
Cd	0.0005	0.005	40%	0.009	14%	0.010	33%	0.014	37%	0.032	66%	0.040	41%
Cr	0.010	0.08	94%	0.09	196%	0.14	63%	0.11	161%	0.26	57%	0.35	47%
Cu	0.010	0.35	51%	0.17	52%	0.33	35%	0.24	32%	0.46	33%	0.50	18%
Fe	0.5	60	3%	970	63%	79	3%	286	106%	578	4%	2230	50%
In	0.0005	b.d.		b.d.		b.d.		b.d.		0.001	<71%	0.002	<29%
Mn	0.05	10.7	2%	650	90%	11.8	16%	427	107%	50.4	76%	90.5	82%
Mo	0.003	0.05	98%	0.04	114%	0.04	92%	0.05	104%	0.03	84%	0.04	25%
Ni	0.010	0.41	53%	0.40	70%	0.39	41%	0.36	59%	0.96	50%	1.08	64%
Pb	0.0010	0.063	12%	0.110	30%	0.160	2%	0.179	13%	0.593	11%	1.40	7%
U	0.0005	0.030	36%	0.035	49%	0.030	79%	0.043	49%	0.045	18%	0.057	9%
Zn	0.010	0.32	56%	0.85	79%	1.23	40%	1.59	64%	8.09	70%	6.97	73%

b.d.=below detection limit

63 %, since the sample concentration was low. The Zn blank values were at the most 386% of the dialysis sample values, but this is of minor importance since Zn is not in focus in this study.

The oxygen concentrations were higher in the storage bottles, than in the *in situ* bottom waters, see Table 5. For some of the bottles this could be explained by the fact that the storage bottles were not completely full. The surface waters quite contrarily usually contained less oxygen in the bottle than in the lake. This could influence the redox states of the metals, making it more difficult to model and thereby make any conclusions about the real situation in the lakes.

Table 5. The oxygen concentrations (mg/L) in the field compared to the sampling bottles after the dialysis membranes were taken out of them.

	Motjärn		L. St. Vrångstjärnet				L. Rotehogstjärnen					
	Surface	Bottom	Surface	Bottom	Surface	Bottom	Surface	Bottom				
Field value (mg/L)	8.6	0.1	7.3	0.1	7.5	0.1						
Bottle value (mg/L)	8.3	13.0	4.2	4.0	5.2	5.9	3.0	2.7	5.6	5.8	3.3	3.3

Al. The total concentrations were highest in the acidic lake Rotehogstjärnen, but the highest percentage (49%) of dialysable fraction was found in L. Motjärn surface water. The other lakes were usually around 20%.

The result of the aluminium speciation is shown in Table 6. In the inorganic fraction, negatively charged complexes, such as $\text{Al}(\text{OH})_4^-$, are not detected by the cation exchanger, only positively charged complexes.

Table 6. Results of the total aluminium, the aluminium speciation, and the dialysable aluminium in $\mu\text{g/L}$.

	L. Motjärn		L. St. Vrångstjärnet		L. Rotehogstjärnen	
	Surface	Bottom	Surface	Bottom	Surface	Bottom
Total aluminium	36.4	41	112	78.1	328.3	478
Total monomeric Al	14.9	8.4	22.3	11.6	151.0	198.4
Organic monomeric Al	6.9	6.2	18.9	6.6	116.3	148.5
Inorganic monomeric Al	8	2.2	3.4	5.0	34.7	49.9
Dialysable aluminium	17.9	12.6	20.4	18.0	82.7	109

As. The total concentrations were between 0.3 and 0.6 $\mu\text{g/L}$. There was no big difference between surface and bottom water in L. Rotehogstjärnen (<17%), in the other lakes the concentrations were slightly higher in the bottom waters compared to the surface waters (Table 4). The dialysable fraction was $80\% \pm 21\%$ in all lakes and depths.

Cr. The total concentrations were below 0.350 $\mu\text{g/L}$ in all lakes. The acidic lake had the highest concentrations. The concentrations were similar comparing surface and bottom waters. The dialysable fraction was high in the surface waters in the limed lakes (63-94%), but even higher in the bottom waters of the same lakes (161-196%, discussed in the Discussion section). On the contrary in the acidic lake a smaller fraction was dialysable in the bottom water than at the surface.

Mo. Concentrations were below 0.06 µg/L in all lakes, with no major difference between the limed lakes and the acidic lakes. The concentrations of surface and bottom waters were similar. Mo passed to almost 100% through the membrane in the limed lakes; in the bottom waters it exceeded 100%, but probably due to measurement error. In the acidic lake a less portion passed through the membrane, especially at the bottom, where the dialysable fraction was only 25%.

Fe. The total concentrations varied between 59.6 and 2230 µg/L. There was more Fe at the bottom than at the surface in all lakes, ranging between three to 16 times more (L. Motjärn). A few per cent passed through the membrane in the surface waters, in the bottom waters it ranged between 50 and 106%. The last figure is of course unrealistic, but a probable explanation is measurement errors.

Mn. Mn followed the same pattern as Fe, with very low concentrations in the surface compared to the bottom waters, except for L. Rotehogstjärnen, where the difference was just 1.8 times more at the bottom. Here the <1000 D fraction was also only a few percent in the surface waters of the limed lakes, but in the acidic lake it was 76%. In the bottom waters it was 90% and 107% in the limed lakes, and 82% in the acidic lake.

The extra TOC laboration gave the result shown in Table 7. Looking at the blank, the membrane must have leaked some C, but it seemed to be under 1000 D since it was distributed with an equal concentration inside and outside the membrane. Another possible explanation is that there was a hole in the membrane. However, if the assumption is made that the membrane was undamaged, the leaked C must have been under 1000 D and then in the lake experiments it would have been negligible when equilibrating with the whole lake water volume. If these results are correct, it means that 53% and 38% of the humic substances in L. Motjärn and L. Stora Vrångstjärnet respectively could pass the membranes.

Table 7. Results of the TOC experiment. TOC concentrations are shown in mg/L. The blank values were subtracted from the sample values, before calculating the percentages <1000 D.

	TOC (mg/L) dialysable fraction	TOC (mg/L) total	% < 1000 D	Absorbance dialysable fraction	Absorbance total
Blank	1.1	1.0	100	0	0
L. Motjärn	5.0	8.3	53	0.020	0.083
L. St. Vrångstjärnet	4.3	9.4	38	0.025	0.164

Modelling results current situation

As mentioned above it is difficult to set the pe while modelling natural waters, since the elements are often in disequilibrium with each other. The nature of all the elements with two or more redox states, e.g. As, Cr, Fe and Mn changes depending on which pe is set as input. The modelling results are given in Table 9 in the Appendix and Figures 7, 9, 11, 13, 15, and 17. All inorganic fractions are assumed to pass the membrane. The metal fraction adsorbed to DOM, is assumed to be dialysed with the same percentages as the fraction of TOC that was dialysed in the TOC-experiment. For L. Rotehogstjärnen this is not shown, since no experiment was done on its water. The precipitated phases, probably mostly present as colloids, and the adsorbed metals are assumed not to enter the membranes.

Fe. The modelling results are shown in Figure 7 and the dialysed results are shown in Figure 8. In the surface waters most of the Fe is modelled as precipitated ferrihydrite, corresponding well to field data. In the bottom waters Fe is modelled as divalent Fe, mostly in the form of aqueous Fe^{2+} . This is consistent with field data in the limed lakes, but not in L. Rotehogstjärnen, where only 50% is present in the dialysable fraction. A small amount is adsorbed to DOM, but not as much as 50%.

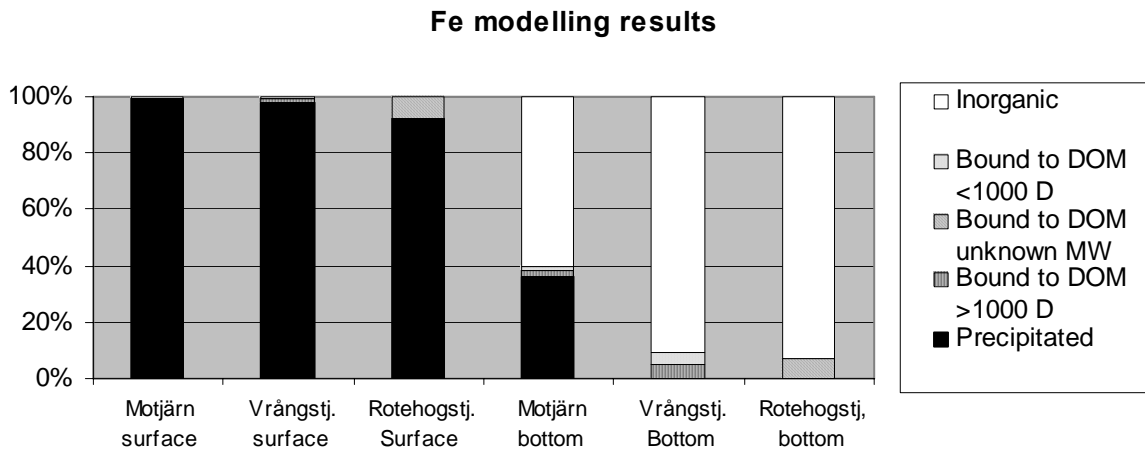


Figure 7. Modelling results for Fe in the different lakes as percentages of the total concentration. The fraction with unknown MW is only present in L. Rotehogstjärnen, since no TOC experiment was performed on its water.

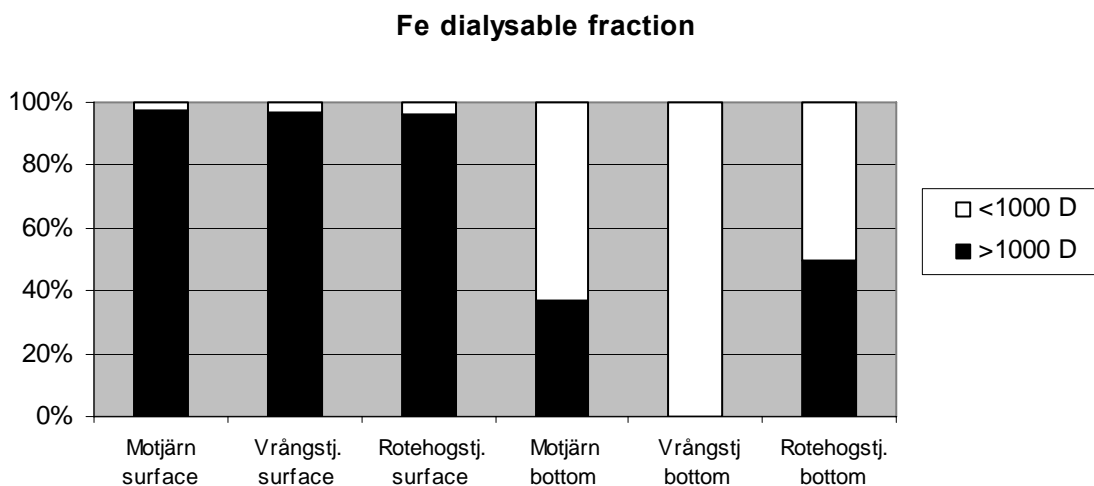


Figure 8. The dialysable fractions (white) of Fe in % of the total concentrations.

Mn. The modelling results are shown in Figure 9 and the dialysed results are shown in Figure 10. Birnessite ($\delta\text{-MnO}_2$) precipitates in the surface waters according to the model. This is consistent with field data in the limed lakes, but not in the acidic lake. In the bottom waters Mn is divalent and mostly present as the aqueous ion Mn^{2+} , which is only to a small extent adsorbed to DOM. This is also consistent with field data.

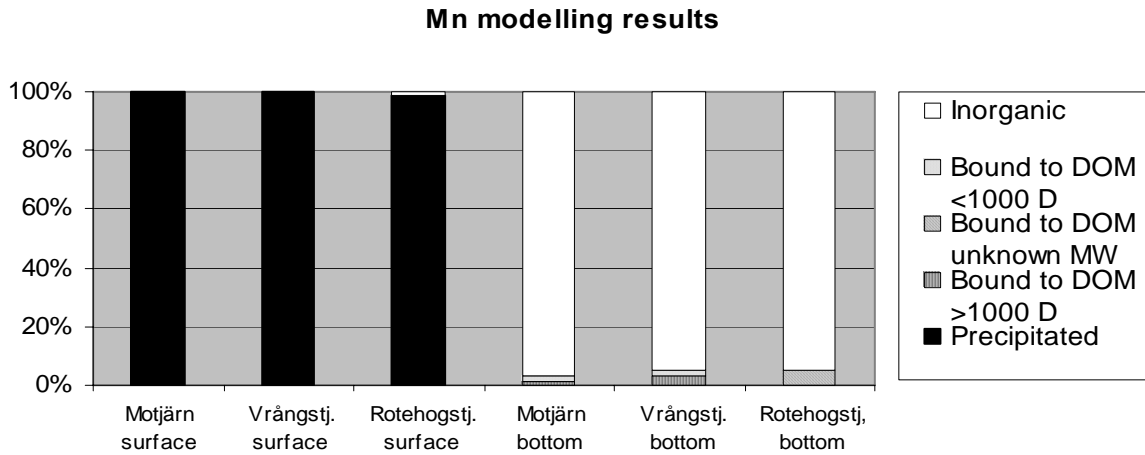


Figure 9. Modelling results for Mn in the different lakes as percentages of the total concentration. The fraction with unknown MW is only present in L. Rotehogstjärnen, since no TOC experiment was performed on its water.

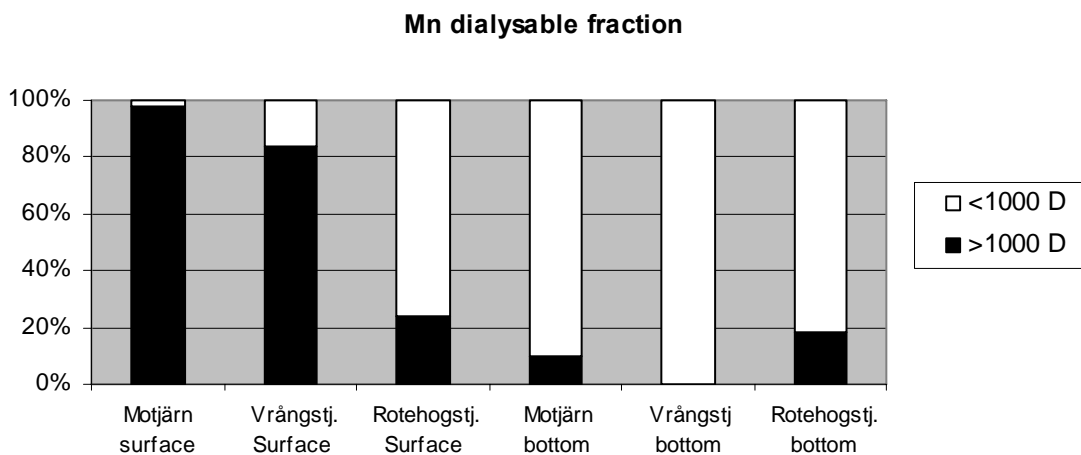


Figure 10. The dialysable fractions (white) of Mn in % of the total concentrations.

Al. The modelling results are shown in Figure 11 and the dialysed results are shown in Figure 12. Al is precipitated to some extent in the limed lakes, but not in L. Rotehogstjärnen. It also adsorbs well to humics. The model fits the data well, except for uncertainties in L. Rotehogstjärnen. Most of the Al in the model is supposed to adsorb to humics in L. Rotehogstjärnen.

Al modelling results

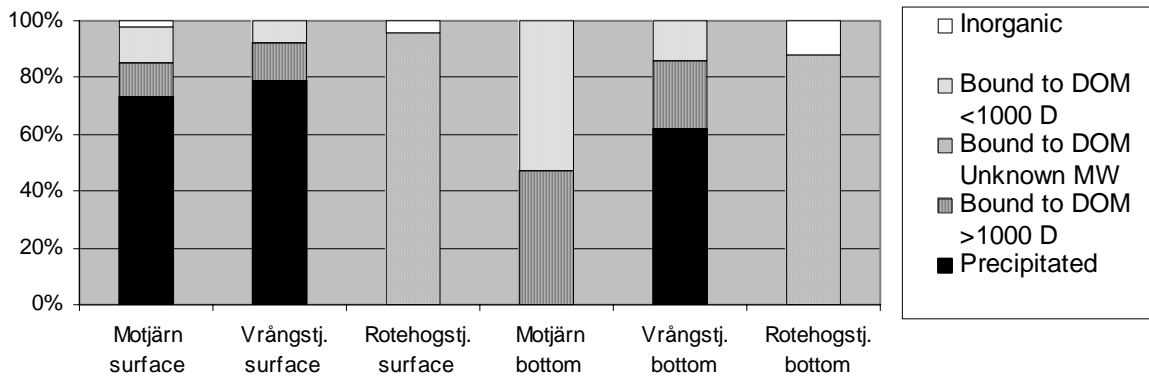


Figure 11. Modelling results for Al in the different lakes as percentages of the total concentration. The fraction with unknown MW is only present in L. Rotehogstjärnen, since no TOC experiment was performed on its water.

Al dialysable fraction

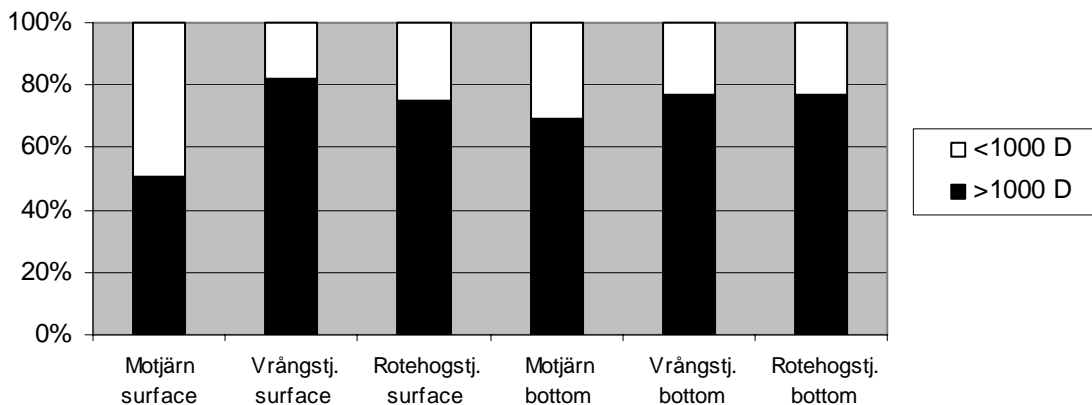


Figure 12. The dialysable fractions (white) of Al in % of the total concentrations.

As. The modelling results are shown in Figure 13 and the dialysed results are shown in Figure 14. As is mostly present as As(V) according to the model, except in the low pe of -1 in the bottom water of L. Rotehogstjärnen, see Table 9. When ferrihydrite has precipitated, arsenate adsorbs very well to it according to the model. Even though As is to a large extent dialysed in L. Motjärn and in the surface water of L. Rotehogstjärnen, the model says most of it should be adsorbed. At the bottom of L. Rotehogstjärnen, no ferrihydrite has precipitated according to the model, so no As can be adsorbed to it. But the dialysable fraction is only ~60%, indicating that probably some of the As is adsorbed. The modelling results in L. St. Vrångstjärnet are in accordance with the field results.

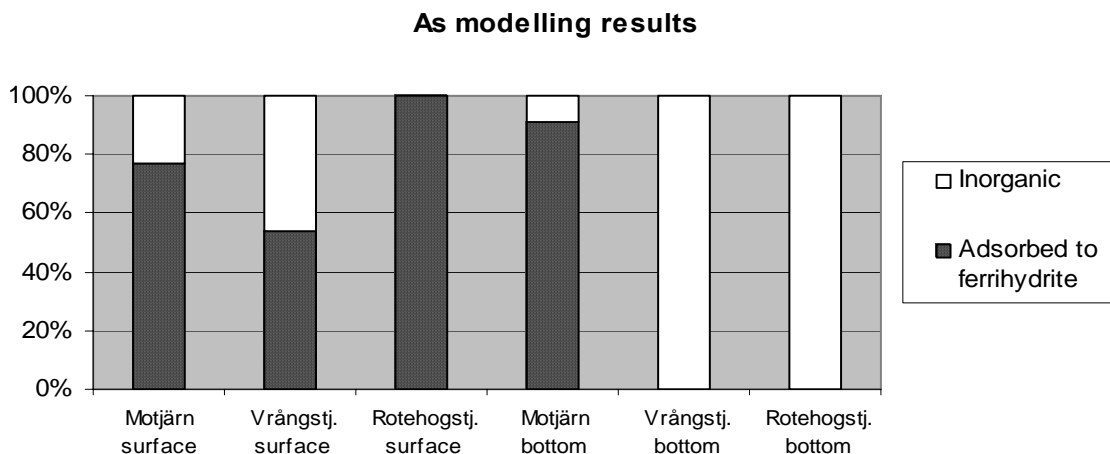


Figure 13. Modelling results for As in the different lakes as percentages of the total concentration.

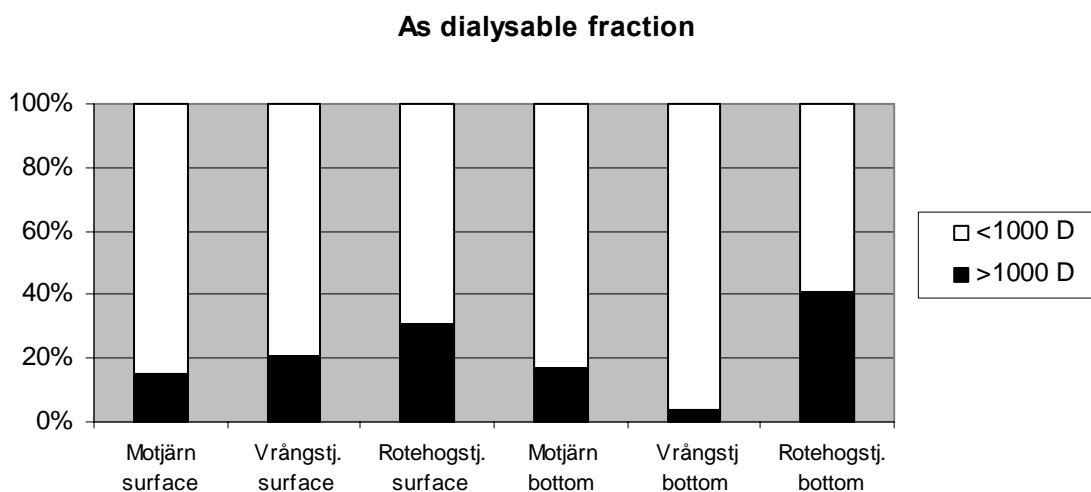


Figure 14. The dialysable fractions (white) of As in % of the total concentrations.

Cr. The modelling results are shown in Figure 15 and the dialysed results are shown in Figure 16. According to the model, chromium is only present as CrO_4^{2-} in the high pe of the surface waters. In the limed lakes all CrO_4^{2-} is present as inorganic complexes that are not adsorbed to ferrihydrite, which fits well with field data. In the acidic lake 47% of the CrO_4^{2-} is adsorbed to ferrihydrite, also in accordance with field data. In the bottom waters of all the lakes Cr is modelled as trivalent Cr bound to DOM. This does not fit well with the field measurements on the bottom waters of the limed lakes, where more than the total concentration was analysed as dialysable fraction. The field data says that 50% of the Cr passes the membrane in the bottom water of L. Rotehogstjärnen. The model results in L. Rotehogstjärnen gives that 98% is bound to DOM, but how valid this result is, is impossible to say without knowing how much of the DOM that passes the membranes.

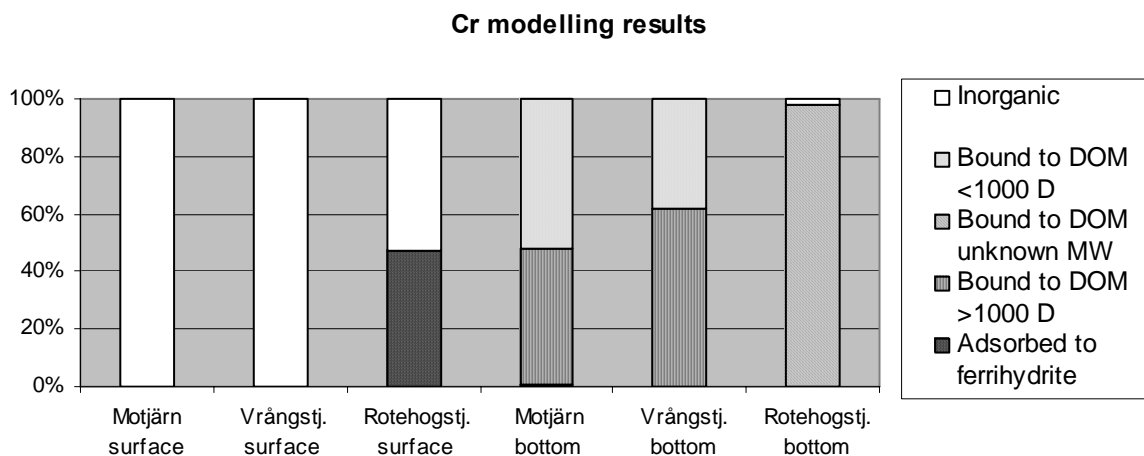


Figure 15. Modelling results for Cr in the different lakes as percentages of the total concentration. The fraction with unknown MW is only present in L. Rotehogstjärnen, since no TOC experiment was performed on its water.

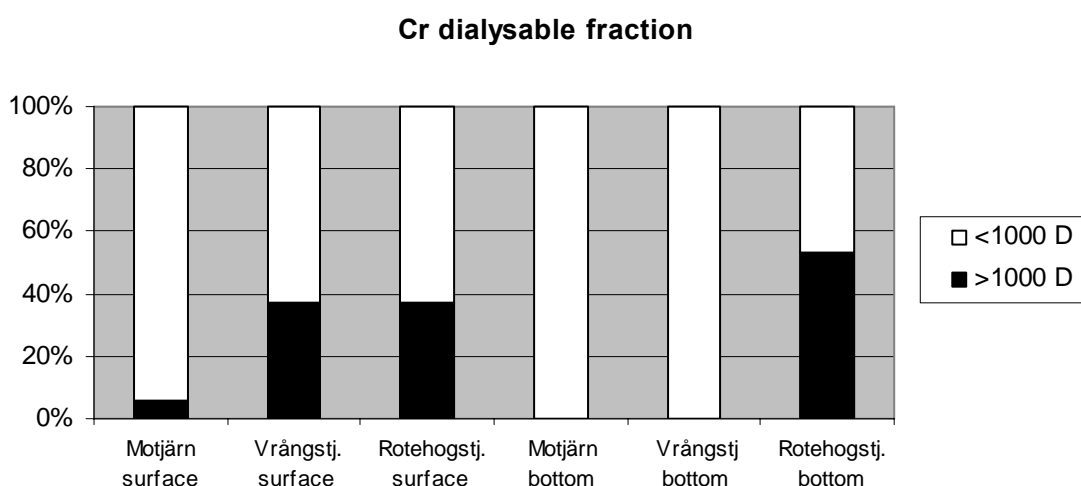


Figure 16. The dialysable fractions (white) of Cr in % of the total concentrations. In the bottom waters of lakes Motjärn and St. Vrångstjärnet the dialysable fractions were more than 100%.

Mo. The modelling results are shown in Figure 17 and the dialysed results are shown in Figure 18. Mo is entered in Minteq as MoO_4^{2-} , no other species are available. When modelling, all the MoO_4^{2-} remains soluble as inorganic species in the limed lakes, which are in accordance with the field data. At the surface of L. Rotehogstjärnen it adsorbs well to ferrihydrite according to the model, but this is contradictory to the fact that most of the fraction is below 1000 D in the actual lake. In the bottom water of L. Rotehogstjärnen no ferrihydrite is precipitated, so no Mo can be adsorbed. This is not consistent with the field data where 75% is > 1000 D. If the pe in the model is raised to 6 (which was suggested during the modelling of pe based on dialysable Fe concentrations) so ferrihydrite precipitates, MoO_4^{2-} would adsorb to a large amount.

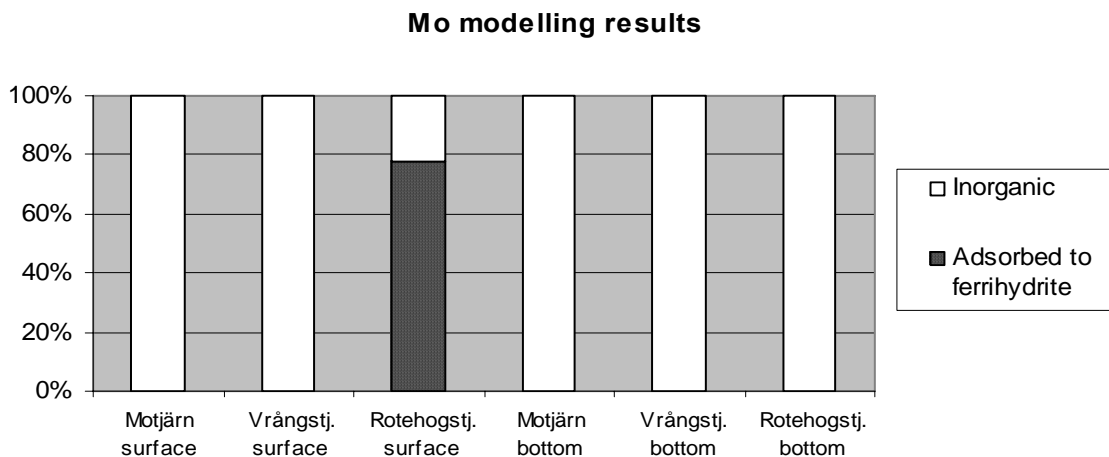


Figure 17. Modelling results for Mo in the different lakes as percentages of the total concentration.

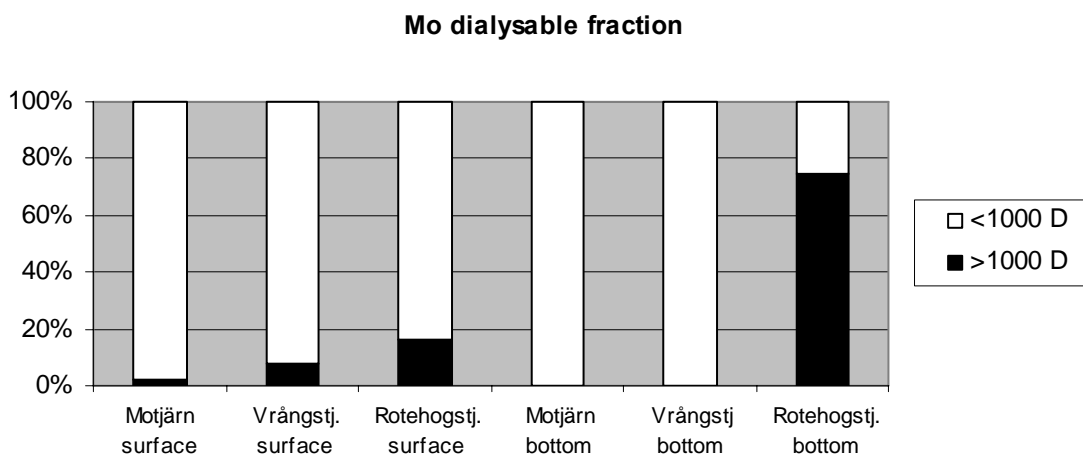


Figure 18. The dialysable fractions (white) of Mo in % of the total concentrations.

Discussion

Sampling and analytical methods

There are many problems associated with measuring trace metals and their speciation in the environment. Problems arise during sampling and storage. Speciation can change due to adsorption on container walls and microbial activity that can change the oxidation state but also aggregate small colloids into bigger particles (Gimpel et al, 2003). It is possible that this could have happened in this study.

Contamination is also a problem, even though it here seems to be a small problem, viewing the results of the blanks. When high blank values occurred, they were always from the same bottle, indicating a contamination during preparation or storage time. Since the three replicates came from two different bottles, there is a possibility that at least one of the replicates was not contaminated. The Cr-concentrations might have been affected by contamination, since at the most the dialysis blanks contained 32% of the concentration in the samples. The blank values for Mo were low, so they should not matter so much. The Zn blank

values were high compared to the contents in the dialysis samples, but since no blanks were done for the total concentrations, it is hard to know if they were contaminated. If they were contaminated and the concentrations were overestimated, it probably would not have a large impact on the modelling results of the metals discussed in this study.

The storage of the membranes after dialysis for over two or three days was not an ideal solution, it is better to shorten the storage time if possible. The oxidation state may have changed in the samples, because of higher oxygen levels in the storage bottles than at the bottom of the lakes. This may have been prevented by shorter storage and full and air-tight bottles, but since there was a difference in dialysable fractions between surface and bottom regarding many of the metals and lakes, the impact may not have been so large considering the metal speciation.

The cases with higher concentrations of Cr in the dialysable fraction than the total concentrations are difficult to explain. It always happened at the bottom of the limed lakes, suggesting it had to do with changes in pe. When the oxic membranes were placed in the anoxic environment in the lakes, Fe^{2+} and/or Mn^{2+} may have entered and precipitated rapidly in the membranes. Cr may have adsorbed to the iron/manganese hydroxide and more Cr would have entered the membrane. When the water in the membrane became anoxic from the lake, the iron/manganese hydroxide may not have been dissolved until the HNO_3 was added before ICP analysis. This could explain the higher Cr concentrations in the dialysis membranes, and the slightly higher concentrations of Fe and Mn (106-107%) at the bottom of L. St. Vrångstjärnet. The results could also be due to contamination (see results for the blanks above), but if the blank concentration is subtracted from the dialysis samples, the dialysable fractions are still 171% (L. Motjärn bottom) and 140% (Lake St. Vrångstjärnet bottom) of the total concentration. There would also be a large coincidence, if only the six subsamples of the bottom waters of the limed lakes and none of the others were contaminated so much.

The result with the charge balance being -20% in the bottom water of L. Stora Vrångstjärnet, was probably due to measurement errors.

If the amount of organic anions makes up a large fraction of the total amount of anions, there may be a larger proportion of inorganic anions in the dialysis membrane than in the total fractions. This is explained by the fact that large organic anions cannot enter the membrane, and are therefore left on the outside (LaZerte, 1984). This might have happened in the more humic lake Rotehogstjärnen. To find out if this happened, anions in the dialysis membranes should have been measured.

Total metal concentrations

Aluminium

The total metal concentration of Al was highest in the acidic lake (478 $\mu\text{g/L}$). The concentration for the acidic lake is quite high, compared to the concentration in most Swedish lakes according to Riksinventeringen 2005, where the 95 percentile for 611 Swedish lakes is 359.5 $\mu\text{g/L}$, even though concentrations up to 978 $\mu\text{g/L}$ exists (data can be found at [http://info1.ma.slu.se/ri/www_ri.acgi\\$Project?ID=2005KS](http://info1.ma.slu.se/ri/www_ri.acgi$Project?ID=2005KS)). Al is not classified by the Swedish Environmental Protection Agency, see information below.

Arsenic and Chromium

The Swedish Environmental Protection Agency (1991) classifies surface water based on biological effects at different metal concentrations. The classifications for As and Cr are shown in Table 8. Arsenic was present in the three lakes of this study in concentrations below

or just above the level for class 1: Very low concentrations. Chromium was also present mostly in Class 1, or just above. For Class 1, none or only very small risks exist for biological effects. For Class 2, there are small risks for biological effects. The majority of the lakes in this class have been exposed to point sources and/or long range transport pollution. Usually no measurable effects can be shown in this class. For class 3, which for As and Cr appear at concentrations above 5 µg/L, effects can be found. Class 4 and 5 elevates the risk for effects. For class 5 the survival of aqueous organisms is reduced even after short exposal.

Table 8. *Classification of As and Cr in surface waters by the Swedish Environmental Protection Agency. (1991)*

Class	Name	As (µg/L)	Cr (µg/L)
1	Very low concentrations	≤ 0.4	≤ 0.3
2	Low concentrations	0.4-5	0.3- 5
3	Moderate high concentrations	5-15	5-15
4	High concentrations	15-75	15-75
5	Very high concentrations	>75	>75

The concentrations of As and Cr in 116 lakes all over Sweden never exceed the values of 1.1 µg/L (As) and 2 µg/L (Cr) (Riksinventeringen, 2005). They are classified as Class 2-lakes, according to the Swedish Environmental Protection Agency.

Molybdenum

There was no difference between the limed lakes and the acidic lakes. Borg et al (2001) found a positive correlation between high Mo concentrations and pH in streams, but the spread was quite large, ranging from no difference up to 0.4 µg/L Mo between alkaline and acidic streams. The small difference in this study (<0.021 µg/L) could be a coincidence, since only three lakes were studied.

Mo is not present in the classification of surface waters by the Swedish Environmental Protection Agency.

TOC experiment

There would have been more exact results, if the TOC had been measured in the dialysis membranes placed in the lake. Now the conditions were not the same, which may have had an impact. In the laboratory experiment the Milli-Q water in the membrane diluted the sample water in the can, but the Milli-Q water was only ~2% of the total water, so it is not a large dilution. The proportions of the amount dialysable should also be the same, irrespective of the amount of Milli-Q water.

In a study of DOC in Lake Geneva with a 1000 D TFF (tangential flow filtration) membrane, 42-64% of the total DOC passed the membrane (Guéguen et al, 2002). Albéric et al (2000) did ultrafiltration with a 1000 D membrane on water from an oligotrophic meromictic, 92 m deep lake in France. They found that ~ 35% of the total DOC passed the membrane. From a more similar lake, the limed L. Stensjön south of Stockholm, Sweden, approximately 20% of the TOC passes a 1000 D TFF membrane (unpublished results). LaZerte (1984) has done tests with 1000 MWCO dialysis in acidified catchments in Ontario, with a short equilibrium time of 24 hours, where 6-12% of the organic material entered the membranes. During a longer time period, more organic material enters the membranes according to him.

Even though these lakes are different from the ones in this study and the analysing method is different, it still shows that the results of the TOC experiment in this study give reasonable results.

Modelling method

Modelling results are no better than the data that is put into the model.

Since humic substances are so heterogeneous, they are difficult to model. The using, of the default value with 100% of the humics consisting of fulvic acids, was probably a good approximation. Unsworth et al (2006) calculated labile concentrations of Cd, Cu, Ni and Pb with the NICA-Donnan model in Visual Minteq, and the differences were small between using 100% fulvic acids and using 90% fulvic and 10% humic acids.

The values for DOC entered in the model are based on the TOC-values measured. In reality the DOC-values are probably a little lower, but only less than 5% for Fenno-Scandias boreal forest areas according to Temnerud et al (2007). This may have overpredicted the amount of metals bound to DOC by the model, to a small extent.

Which solubility products that are used is also important when determining how much solids/colloids that forms. For Al, Fe and Mn there is a wide range of constants used in natural waters.

Modelling adsorption to oxides is not complete with adsorption only to ferrihydrite. As mentioned above the metals can adsorb also to other oxides, e.g. aluminium and manganese oxides, which are not included here. According to the modelling, Al and Mn oxides were formed, at least in the limed lakes.

The setting of pe is also important, since it decides the amount and solubility of species of metals with two or more redox states. The redox states of Fe and Mn also determine other metals, since Fe and Mn form oxides in higher redox states where the metals can adsorb. The modelling results in this study are based on the fact that all the elements are in equilibrium with the pe introduced in the model, which is not a realistic assumption. The redox potentials in natural waters are usually mixed potentials, where all the different redox elements are in disequilibrium with each other. The difference can be up to 16 pe-units (1000 mV) in ground water (Lindberg and Runnels, 1984).

Stefánsson et al (2005) have shown that ground water has not reached redox equilibrium even after 25,000 years. In dilute natural waters they claim that measuring Eh-values with a Pt-electrode has limited meaning. Instead they suggest that every element and its redox states must be measured separately.

The modelling results in this study were often in accordance with the dialysed results. Iron was modelled in accordance with field data, but considering that the pe-values entered for the bottom water of the limed lakes were based on the solubility of iron, this is not surprising. In the bottom water of the acidic lake the modelling was worse for Fe, as shown from the dialysis results where 50% of the Fe should be precipitated or bound to DOM. Considering the high concentration of total Fe, some of it may in reality be precipitated. According to Davison iron oxides can coexist with sulphides in anoxic water columns (1993). If some of the iron was precipitated, this means that Cr and Mo could have adsorbed to it and that the model results presented here could be wrong for them as well. Manganese was well modelled, except for at the surface of L. Rotehogstjärnen. Aluminium was quite well modelled. Arsenic was predicted by the model to adsorb too much to ferrihydrite, exposing the difficulties of modelling adsorption. Chromium was modelled well, except in the bottom waters of the limed lakes, as discussed above. Similar to As, molybdenum was calculated to adsorb too much to ferrihydrite at the surface of L. Rotehogstjärnen. In the bottom water of L. Rotehogstjärnen,

not much is dialysed, indicating that much of the Mo is adsorbed. The modelling results for Mo would have been better at this location, if the assumption was made that some iron hydroxide had precipitated on where Mo could adsorb.

In another study Unsworth et al (2006) modelled Cd, Cu, Ni and Pb with Model VI in WHAM 6 and the NICA-Donnan model in Visual Minteq, and compared the results with measurements with DGT, GIME, HF-PLM and DMT. They found that labile concentrations (i.e. inorganic and organic metal complexes) were fairly well predicted by the two models. Gimpel et al (2003) modelled total dissolved concentrations of Cu, Fe, Mn, and Zn with WHAM 1 and compared with measured values by DGT in one acidic and five circumneutral lakes. There was good agreement in the acidic lake, where the metals were modelled and measured mainly as inorganic species. In the circumneutral lakes, only the Mn was in agreement with the model, estimated to be largely present as uncomplexed Mn^{2+} ions. The modelling of Cu, Fe and Zn were more difficult because of complexing to humic substances and precipitation of Fe colloids.

Concentrations in higher pH and toxicity

Using the Sweep function in Minteq, concentrations in higher pH can be modelled, as shown in the diagrams below. Since the pe is not altered when changing the pH, the model results should be interpreted with caution. The adsorption surface of ferrihydrite does not change either, which should also be accounted for.

Al. (Fig. 19 and 20) Most of the aluminium is precipitated at pH 8, but then it gets more soluble again, since $Al(OH)_4^-$ starts to increase in concentration. Below pH 8 most of the dissolved Al is bound to humics according to the model. At pH 10 all of the aluminium is in the form of $Al(OH)_4^-$. There is no difference between surface and bottom waters, therefore the bottom waters are not shown here. The difference in the diagrams of the surface waters is only visual (Fig. 19-20), the same amount of Al is soluble at pH 9, approximately 16 $\mu g/L$ Al. Very low concentrations of $Al(OH)_4^-$ exist in the pH of the lakes in this study. In a lake with pH above 8 and high aluminium concentration, there may be a problem with high $Al(OH)_4^-$ concentrations, but since toxicological data on aluminate is rare, it is difficult to suggest any maximum pH-values that should not be exceeded.

Al Motjörn surface pe 13

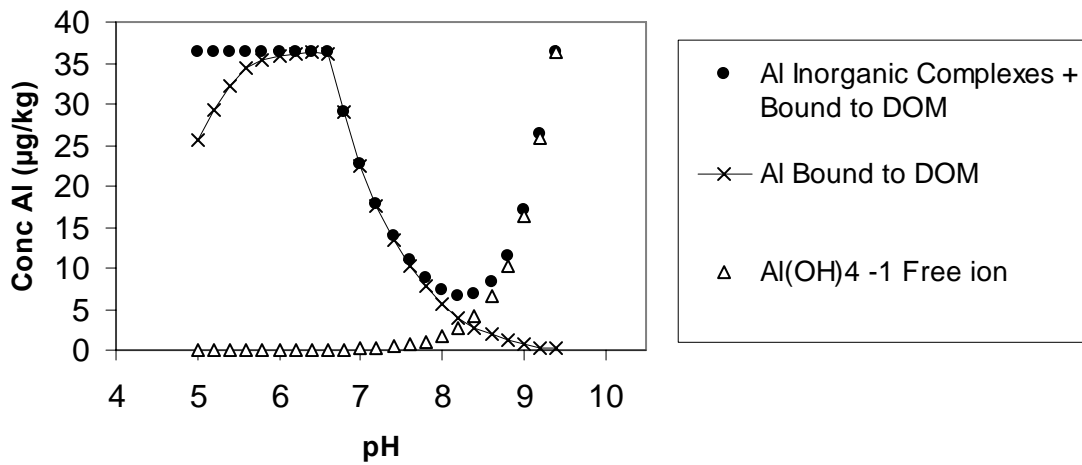


Figure 19. Modelling predictions for Al when pH is varied between 5.0 and 9.4 at the surface of L. Motjörn, pe 13. The “Al Inorganic complexes” fraction shows all complexes with inorganic ligands, including the free ion of $Al(OH)_4^-$. This fraction is shown here added with the fraction of Al bound to DOM.

Al Rotehogstjärnen surface pe 15

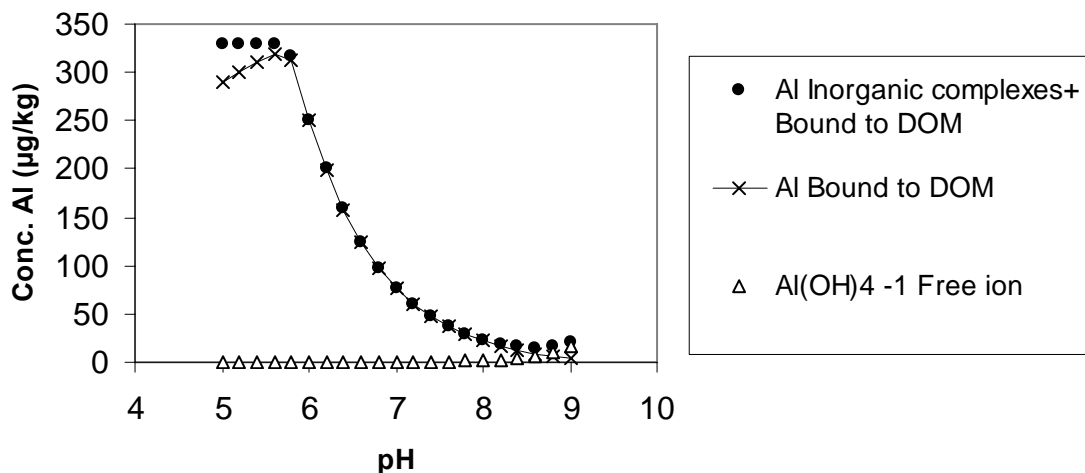


Figure 20. Modelling predictions for Al when pH is varied between 5.0 and 9.0 at the surface of L. Rotehogstjärnen, pe 15. The “Al Inorganic complexes” fraction shows all complexes with inorganic ligands, including the free ion of $Al(OH)_4^-$. This fraction is shown here added with the fraction of Al bound to DOM.

As. In the surface waters arsenate, As(V), sorption to ferrihydrite reaches a peak at pH 7, according to the model (Fig. 21). Above that, arsenate adsorption decreases until pH 8, where approximately half is sorbed and the rest is soluble. This is consistent with an article by Pierce and Moore (1982), where arsenate adsorbs less in more alkaline solutions, but as mentioned above the model overestimates the amount of As(V) adsorbed in L. Motjörn and the surface water of L. Rotehogstjärnen.

As Motjärn surface pe 13

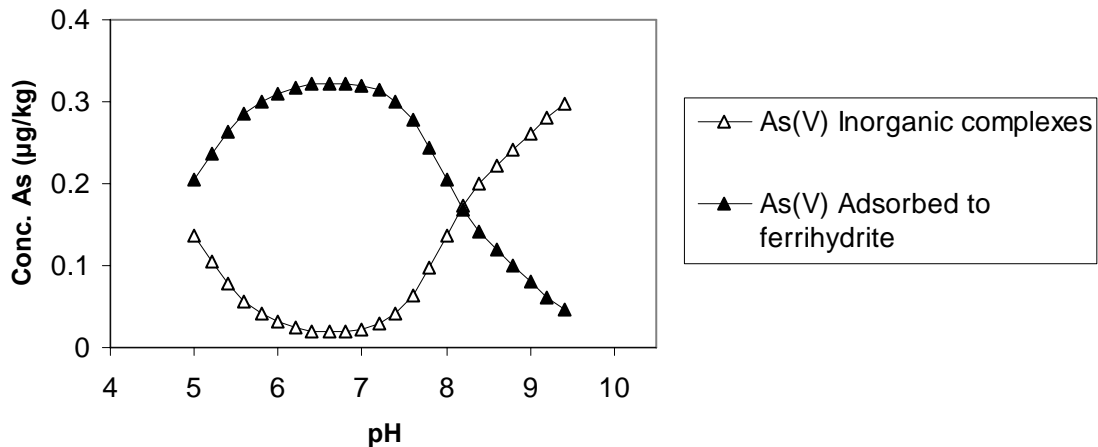


Figure 21. Modelling predictions for As when pH is varied between 5.0 and 9.4 at the surface of L. Motjärn, pe 1. The “As(V) Inorganic complexes” fraction shows all inorganic complexes in solution. The rest of the As(V) inorganic complexes is adsorbed to ferrihydrite.

In the bottom water the model results are similar for L. Motjärn, except that inorganic complexes of arsenite, As(III), dominates at pH-values below 6.0, depending on which pe is chosen (Fig. 22).

As Motjärn bottom pe 1

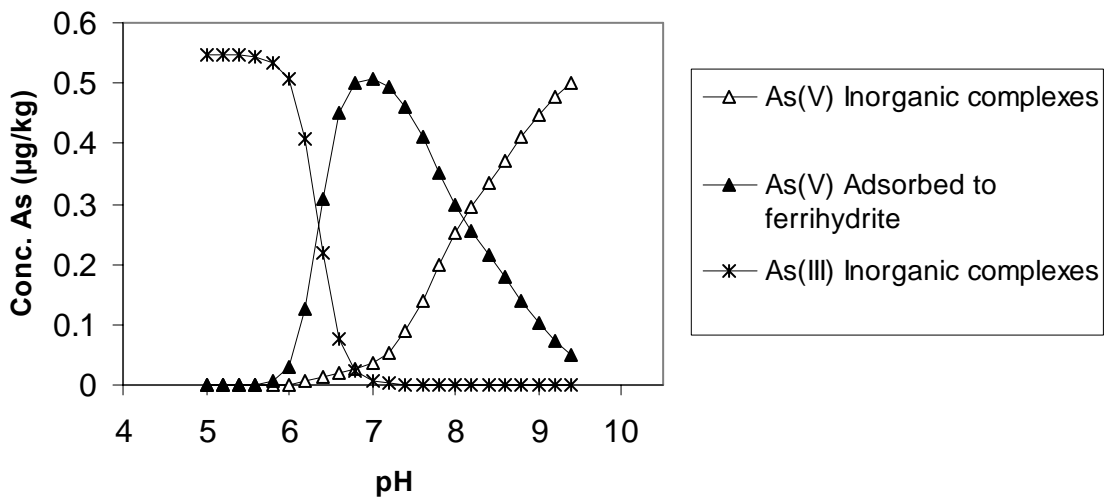


Figure 22. Modelling predictions for As when pH is varied between 5.0 and 9.4 at the bottom of L. Motjärn, pe 1. The As(V) and the As(III) “Inorganic complexes” fractions show all inorganic complexes in solution. The rest of the As(V) inorganic complexes is adsorbed to ferrihydrite.

In the other two lakes, no ferrihydrite has precipitated according to the model, so arsenic is not adsorbed. H_3AsO_3 is dominant in the low pe of L. Rotehogstjärnen (Fig. 23). Arsenite,

As(III), does not adsorb to ferrihydrite according to the model under any conditions tested here, even though Pierce and Moore (1982) claim that it does in their study.

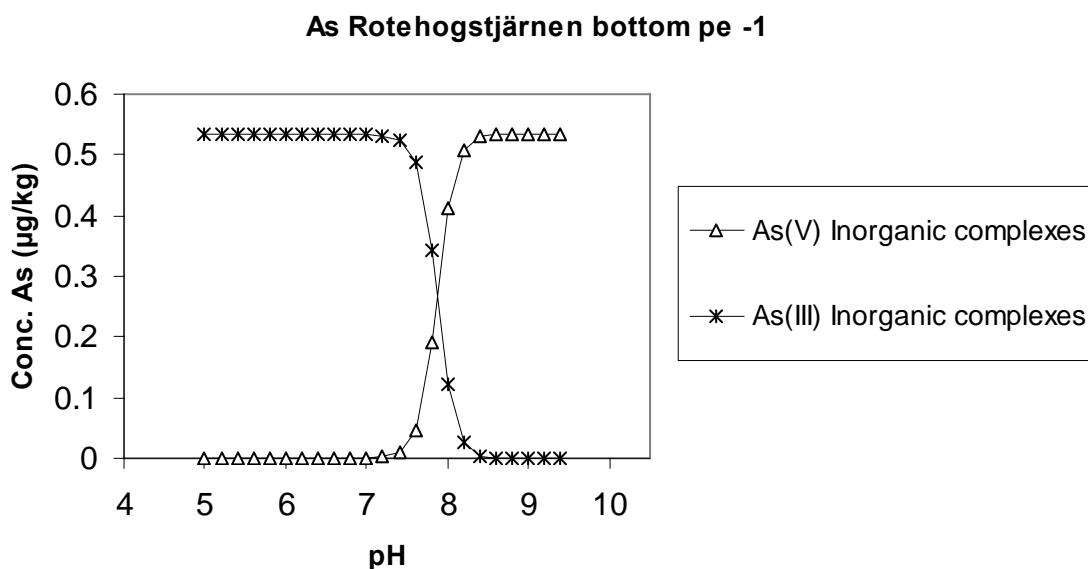


Figure 23. Modelling predictions for As when pH is varied between 5.0 and 9.4 at the bottom of L. Rotehogstjärnen, pe -1. The As(V) and As(III) “Inorganic complexes” fractions show all inorganic complexes in solution. No ferrihydrite exists to where As can adsorb.

As shown by the model and the high amount of the dialysable fraction, arsenic probably exists in toxic forms in all the lakes, including the acidic lake. The total concentration of As is however so low, so it does not reach toxic levels in these lakes. There is a possibility of toxic levels in other lakes, even though the data from Riksinventeringen did not show any lakes with concentrations above 1.1 µg/L.

If the total concentrations are close to the toxic concentrations to *Hyalella azteca* of 420 µg/L (As(V)) (Norwood et al, 2006), precautions should be taken.

Cr. CrO₄²⁻ gets increasingly dominant over Cr(III) at pH above 5 in the L. Motjärn surface water at pe 13 (Fig, 24). At pe 15 in L. Rotehogstjärnen, there is no Cr(III), only Cr(VI) exists, even at low pH-values (Fig. 25). Here CrO₄²⁻ adsorbs to ferrihydrite at the lower pH-values. At pH above 8 the free CrO₄²⁻ ion reaches maxima, above 90% of the total Cr concentration, the rest is inorganic complexes. In the bottom waters Cr(III) dominates independent of the pH-value and is complexed to humic substances (Fig. 26). This is however not consistent with the field data, as mentioned in the Results section and discussed above.

Since it was difficult to measure and model Cr, it is hard to know if there were a high fraction of Cr(VI) in these lakes. It seems possible though, both in the acidic and in the limed lakes. However, the total concentrations of Cr were fairly low in all three lakes, compared to the value of 37 µg/L Cr(VI) which was toxic to *Ceriodaphnia dubia* (Baral et al, 2006). The toxic value is however much closer to the maximum value of 2µg/L found in Swedish lakes (Riksinventeringen, 2005), so Cr may be a risk to the environment in other lakes.

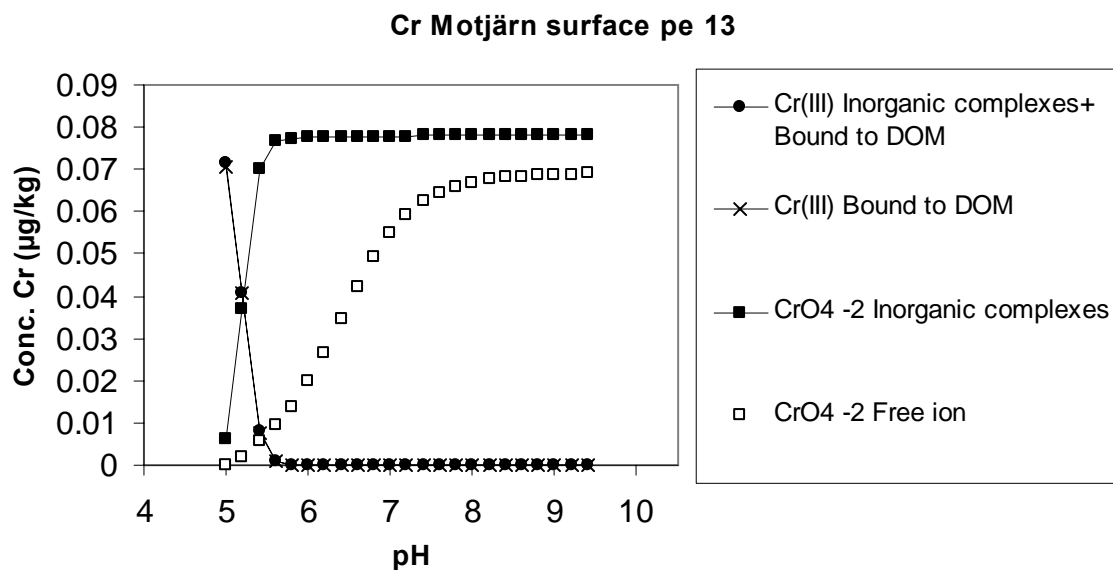


Figure 24. Modelling predictions for Cr when pH is varied between 5.0 and 9.4 at the surface of L. Motjärn, pe 13. The “ CrO_4^{2-} Inorganic complexes” fraction shows all complexes with inorganic ligands in solution, including the free ion of CrO_4^{2-} . The “Cr(III) Inorganic complexes” fraction is shown here added with the fraction of Cr(III) bound to DOM.

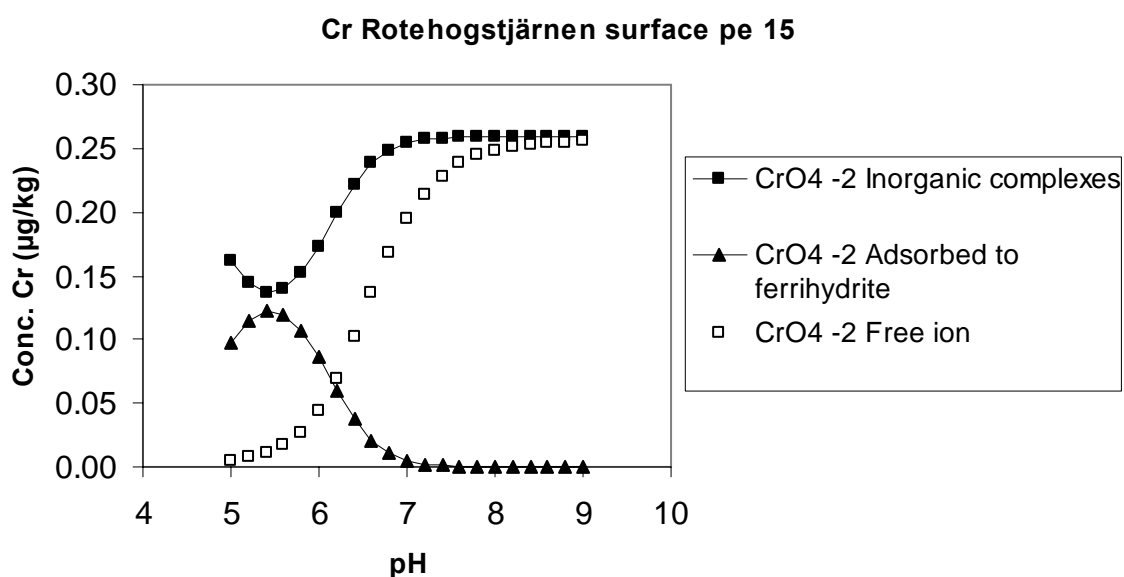


Figure 25. Modelling predictions for Cr when pH is varied between 5.0 and 9.0 at the surface of L. Rotehogstjärnen, pe 15. The “ CrO_4^{2-} Inorganic complexes” fraction shows all complexes with inorganic ligands in solution, including the free ion of CrO_4^{2-} . The rest of the CrO_4^{2-} is adsorbed to ferrihydrite.

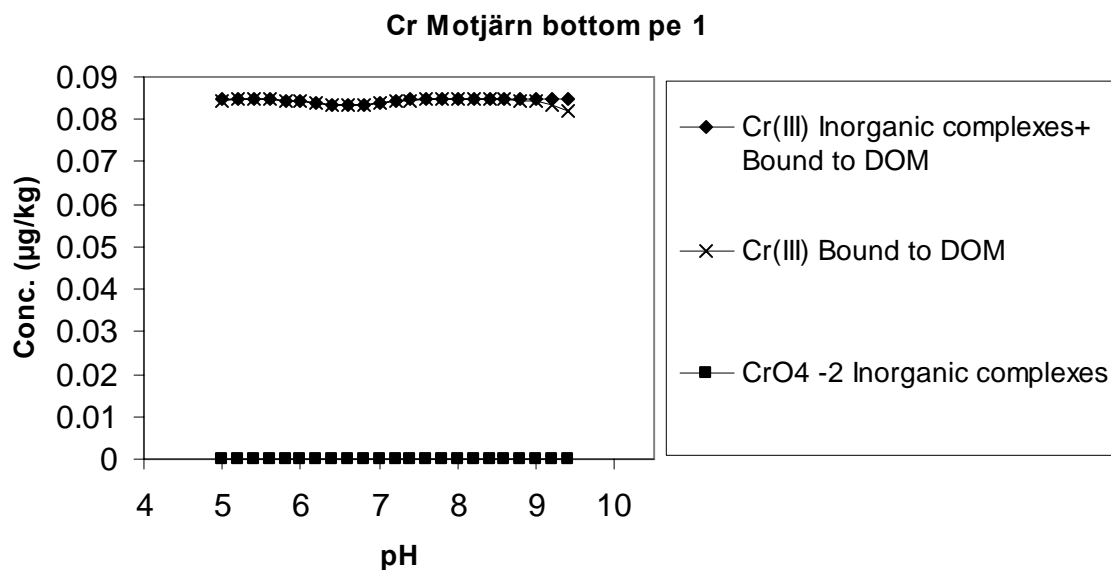


Figure 26. Modelling predictions for Cr when pH is varied between 5.0 and 9.4 at the bottom of L. Motjärn, pe 1. The “Cr(III) Inorganic complexes” fraction shows all complexes with inorganic ligands in solution, it is shown here added with the fraction of Cr(III) bound to DOM.

Mo. There is little change as the pH increases, MoO_4^{2-} is still soluble (Fig. 27). At lower pH, starting at pH 6, more MoO_4^{2-} is adsorbed, in agreement with Gustafsson (2003) as mentioned above. This is especially evident in L. Rotehogstjärnen, possibly due to the large adsorption surface of modelled ferrihydrite there (Fig. 28). There is no difference between surface and bottom waters, except that in L. Stora Vrångstjärnet and L. Rotehogstjärnen no ferrihydrite exists according to the model, so no MoO_4^{2-} can adsorb there.

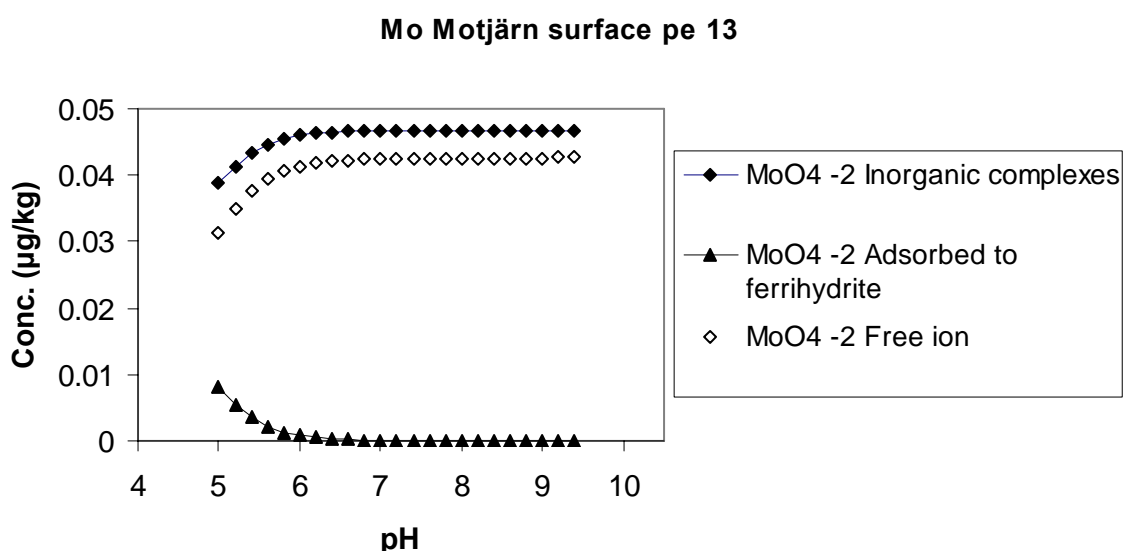


Figure 27. Modelling predictions for Mo when pH is varied between 5.0 and 9.4 at the surface of L. Motjärn, pe 13. The “ MoO_4^{2-} Inorganic complexes” fraction shows all complexes with inorganic ligands in solution, including the free ion of MoO_4^{2-} . The rest of the MoO_4^{2-} is adsorbed to ferrihydrite.

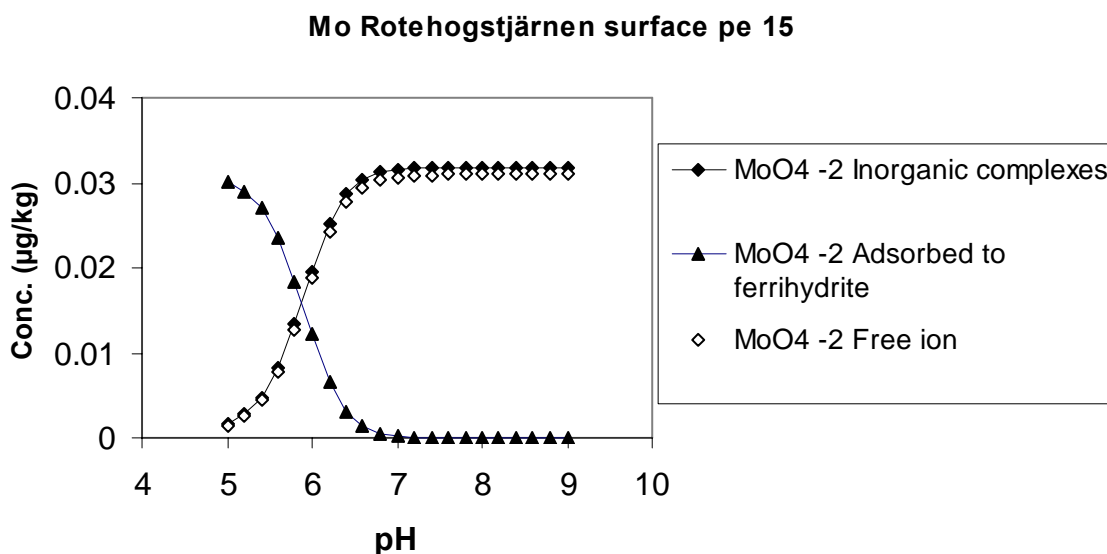


Figure 28. Modelling predictions for Mo when pH is varied between 5.0 and 9.0 at the surface of *L. Rotehogstjärnen*, pe 15. The “ MoO_4^{2-} Inorganic complexes” fraction shows all complexes with inorganic ligands in solution, including the free ion of MoO_4^{2-} . The rest of the MoO_4^{2-} is adsorbed to ferrihydrite.

Molybdenum is present at low concentrations in the lakes of this study, and even though it is very soluble it should not pose a serious threat. The only data found on Mo-toxicity to an aquatic organism show toxic levels at 29 mg/L, several orders of magnitude higher than the concentration in the lakes. The maximum concentration of Mo was 0.4 µg/L in a small selection of Swedish streams (Borg et al, 2001), but higher concentrations are of course possible. More toxicological data is required, but since Mo is an essential element it seems to be more beneficial than toxic in low concentrations.

Suggested improvements and future studies

Redox measurements of every metal of interest would have given more accurate results and better testing of the model. This has been done for Fe(II) in surface and ground waters by Stefánsson et al (2005). More knowledge about the humic substances, e.g. amount fulvic acid/humic acid, size, charge etc. would be good to really evaluate how well the model works. Modelling the dialysable fraction to see if it is in equilibrium would also give valuable information about how well the model works.

Developing new models on humic substances and adsorption would be valuable.

More toxicological data of both lethal and sublethal effects is required, especially on aluminate ions since aluminium exists in high concentrations in natural waters. Most studies focus on metals in acidic solutions or neutral solutions, few are done in pH above 8.

Conclusions

The model predicted the dissolved fractions of Al, Fe and Mn (in the current situation) reasonably well. For As and Mo it overpredicted adsorption to ferrihydrite, but for Mo this only occurred in the acidic lake. Cr was either measured wrongly at the bottom of the limed lakes, which is not likely, or modelled wrongly.

The concentration of $\text{Al}(\text{OH})_4^-$ starts to rise at pH 8 according to Minteq, which makes it a potential threat, but only to a small number of lakes. According to Riksinventeringen (2005), the 95% percentile for pH was 7.69, so few lakes have pH-values above 8. Among the metals with toxic oxyanions, Al is the one with the highest concentration. Al has proven to be toxic to algae at high pH-values (Hörnström et al, 1995), but also relatively non-toxic to certain fish (Poleo and Hytterød, 2003). More toxicological investigations are needed, in order to fully state how toxic aluminate is.

Arsenic seems to exist as inorganic complexes of both As(V) and As(III) to a large percent in all the lakes, including the acidic one, more than the model predicts it to. This could be alarming, if it was not for the fact that the total As concentration is so low in these lakes.

Cr was present in the dialysable fraction to a large extent in all lakes, especially in the limed lakes, and could presumably be present as the toxic CrO_4^{2-} ion. The total concentration was however relatively low in the lakes, but it could be a problem in other lakes in Sweden according to Riksinventeringen (2005).

Mo also seems to exist in low total concentrations, compared to the toxicological data that exist. It is probably present as inorganic species, which adsorbs to ferrihydrite at low pH-values.

Regarding these lakes, a pH of 8.0 is probably safe from an environmental perspective for the metals in this study. At pH 8.5, there could be toxic levels of Al for algae, when comparing with the study of Hörnström et al (1995). In lakes with high concentration of Al, As and Cr, extra caution should be used when liming.

Acknowledgements

The study was financially supported by the Swedish Environmental Protection Agency. I thank my supervisors Teresia Wällstedt, Gunnar Svensson and Hans Borg for all the support. I also thank everyone who has performed and explained the chemical analyses; Jörgen Ek, Klara Hajnal, Karin Holm, Anne-Marie Johansson, Carina Johansson, Malin Söderman and the staff at the Department of Environmental Assessment at SLU. I thank Jon Petter Gustafsson and Magnus Mörth for explaining the models.

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Appendix

Table 9. Model predictions for the different metals in percent of the total concentration. The amount bound to DOM above and below 1000 D is calculated from the amount of TOC that was dialysed in the TOC experiment.

	Al	As III	As V	Cr III	Cr IV	Fe II	Fe III	Mn II	Mn IV	Mo
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L. Motjärn surface pe 13

Inorganic	2		23		100					100
Bound DOM <1000 D	13						0.5			
Bound DOM >1000 D	12						0.5			
Adsorbed to ferrihydrite			77							
Precipitated	73						99		100	

L. Motjärn bottom pe 1

Inorganic			9			60		97		100
Bound to DOM <1000 D	40			52		2		2		
Bound to DOM >1000 D	36			47		2		1		
Adsorbed to ferrihydrite			91	1						
Precipitated	24						36			

L. St. Vrångstj. surface pe 13.5

Inorganic			46		100					100
Bound to DOM <1000 D	8						1			
Bound to DOM >1000 D	13						1			
Adsorbed to ferrihydrite			54							
Precipitated	79						98		100	

L. St. Vrångstj. bottom pe 0.5

Inorganic		9	91			91		95		100
Bound to DOM <1000 D	14			38		4		2		
Bound to DOM >1000 D	24			62		5		3		
Adsorbed to ferrihydrite										
Precipitated	62									

L. Rotehogstj. surface pe 15

Inorganic	4				53			1		22
Bound to DOM	96						8			
Adsorbed to ferrihydrite			100		47					78
Precipitated							92		99	

L. Rotehogstj. bottom pe -1

Inorganic	12	100		2		93		95		100
Bound to DOM	88			98		7		5		
Adsorbed to ferrihydrite										
Precipitated										

Table 10. Trace metal concentrations in the dialysed fractions and blanks. Mean (minimum and maximum) values in µg/L.

	Detection limit	Dialysed blanks	L. Motjärn		L. Vrångstjärnet		L. Rotehogstjärnen	
			Surface	Bottom	Surface	Bottom	Surface	Bottom
Ag	0.0002	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
Al	0.2	b.d.	17.9 (17.8-18.0)	12.6 (12.4-12.8)	20.4 (20.3-20.6)	18.0 (17.4-18.6)	82.7 (81.1-84.0)	109 (106-112)
As	0.010	b.d.	0.29 (0.29-0.30)	0.46 (0.45-0.46)	0.27 (0.27-0.28)	0.46 (0.44-0.47)	0.41 (0.40-0.42)	0.32 (0.31-0.32)
Cd	0.0005	b.d.	0.002 (0.002-0.003)	0.001 (0.001-0.002)	0.003 (0.003-0.004)	0.005 (0.005-0.005)	0.021 (0.021-0.022)	0.016 (0.015-0.018)
Cr	0.010		0.07 (0.07-0.07)	0.17 (0.16-0.17)	0.09 (0.09-0.09)	0.17 (0.15-0.18)	0.15 (0.14-0.15)	0.16 (0.16-0.17)
Cu	0.010	(b.d.-0.02)*	0.18 (0.17-0.19)	0.09 (0.08-0.09)	0.12 (0.11-0.12)	0.08 (0.07-0.09)	0.15 (0.14-0.16)	0.09 (0.08-0.10)
Fe	0.5	b.d.	2 (2-2)	607 (578-624)	2 (2-3)	303 (265-331)	22 (22-22)	1116 (1067-1201)
In	0.0005	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.
Mn	0.05	b.d.	0.2 (0.2-0.2)	583 (580-586)	1.9 (1.8-2.1)	455 (434-467)	38 (38-39)	74 (74-75)
Mo	0.003		0.05 (0.04-0.05)	0.05 (0.04-0.06)	0.04 (0.03-0.04)	0.06 (0.05-0.06)	0.03 (0.02-0.03)	0.01 (0.01-0.01)
Ni	0.010	(b.d.-0.005)*	0.22 (0.22-0.22)	0.28 (0.28-0.28)	0.16 (0.16-0.17)	0.21 (0.21-0.22)	0.48 (0.48-0.49)	0.69 (0.69-0.70)
Pb	0.0010	b.d.		0.033 (n.d.-0.008) (0.027-0.036)	0.003 (0.002-0.003)	0.023 (0.020-0.029)	0.066 (0.065-0.066)	0.096 (0.092-0.100)
U	0.0005	b.d.	0.011 (0.011-0.011)	0.017 (0.017-0.017)	0.002 (0.002-0.002)	0.021 (0.021-0.021)	0.008 (0.008-0.008)	0.005 (0.005-0.005)
Zn	0.010	(b.d.-0.25)**	0.18 (0.07-0.29)	0.67 (0.58-0.77)	0.49 (0.48-0.50)	1.02 (1.00-1.04)	5.64 (5.53-5.74)	5.12 (4.96-5.42)

b.d. = below detection limit

* =Contamination in two blanks from the same bottle, but not in the other bottle.

**=Contamination in one blank, but not in the other bottle.

