



*Catchment Origins of Al in Freshwaters
with an emphasis on Northern Sweden*

Literature review

by

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1,0 Introduction

Aluminium is the most common metal in the earth's crust (vanLoon and Duffy 2000; Lydersen et al. 2002). Despite its abundance there are still large areas of its cycle in the natural environment which are poorly understood (Gustafsson et al. 2001). One of the leading forces driving Aluminium research, especially with regards to its concentrations in freshwater, is its toxicity to aquatic organisms (Poleo et al. 1997; Herrmann 2001; Stutter et al. 2001; van Hees et al. 2001). Increasing awareness about the detrimental effect of Aluminium has led to intensive research into the factors which control both Aluminium concentrations and speciation in surface waters (Berden et al. 1994).

Acidification is caused by the increased inputs of strong acids to an environment, if that environment is unable to neutralise these inputs, for example due to a low supply of base cations, then an excess of acidity builds up. In the pH range 4.5 – 5.5 Aluminium is a very strong buffer (Driscoll and Postek 1996; Skjellberg 1999; Simonsson 2000), therefore if water in a catchment falls from circum-neutral to lower pH due to acidification many of these excess hydrogen ions will displace Aluminium from the soil. It is the toxic properties of this displaced Aluminium that form the basis of many of the concerns over acidification. In Sweden the addition of base, commonly termed liming, has been used to raise the pH of surface water to reduce the effects of acidification. This has been a large-scale operation, costing over 2 billion crowns (~200 million USD) of government subsidies during the period 1976-2002 (Lydersen et al. 2002). It may seem that this is an area of research which should now be coming to an end as the emissions of sulphur and nitrogen are reduced, however this is now the most critical time for research. Recent advances in the understanding of natural acidity have raised questions about the criteria used for remediation. Lakes and streams are also beginning to return towards natural conditions and it becomes more critical to understand the issues and processes behind acidification so that remediation methods are only applied, or continued to be applied, to areas that truly require them.

As previously discussed, the processes behind Aluminium mobilisation, concentration and speciation, although central to the issue of acidification, are still poorly understood. This information is fundamental to understanding the consequences of acidification since it is often Aluminium and not Hydrogen ions that are the problem for biota. The problems surrounding the study of Aluminium in the natural environment are numerous; it is hard to quantify, it forms a multitude of different complexes both inorganic and organic, it varies with time and depth and also varies with soil type, deposition, pH and temperature (Tipping et al. 1995; Nordstrom and May 1996; Simonsson and Berggren 1998; Lydersen et al. 2002). Also, in natural environments assumptions about equilibrium may not be true and kinetics also need to be considered.

This paper aims to discuss the issues surrounding Aluminium in the natural environment, with an emphasis on Aluminium mobilisation in DOC rich soils of Northern Sweden. In order to fully understand these issues, this paper will first discuss the mechanisms controlling Aluminium solubility, mobility and speciation, and then apply these to the currently poorly understood DOC rich podzol soils.

2.0 Aluminium mobility and solubility

One of the main challenges facing researchers in the field of Aluminium research is that Aluminium can be present in many different forms. The concentrations of these forms are of prime importance when assessing the toxicological impacts of Aluminium. Aluminium in the natural environment can be seen in three main pools: biomass, solid phase soil and solution. Figure 1 shows a schematic depiction of the different forms of Aluminium. In general deposition of Aluminium is a small source, so inputs into the system shown in figure 1 occur by mobilisation and transport of terrestrial Aluminium (Driscoll and Postek 1996). This can be from weathering of primary minerals, or from the dissolution of secondary minerals (Gustafsson et al. 2001), e.g. Gibbsite.

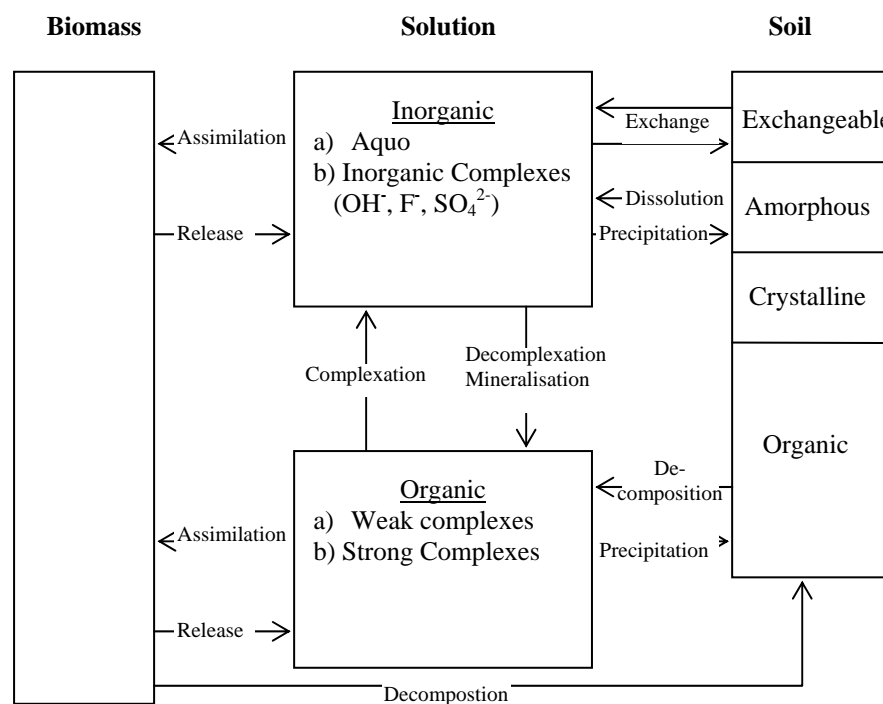
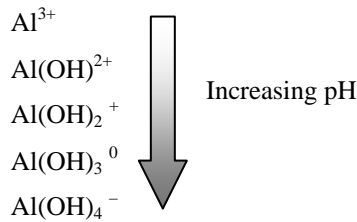


Figure 1 – major pools and transfers of Aluminium in the natural environment. Taken from Driscoll and Postek (1996).

In its ionic form Aluminium is normally notated as Al^{3+} , however Aluminium is a strongly hydrolysing metal (Driscoll and Postek 1996) and reacts with water, abstracting OH^- to form an octahedral hydroxide $\text{Al}(\text{H}_2\text{O})_6^{3+}$. The speciation of Aluminium in soils and freshwaters is an area of active research, and is very much dependent on local variables. As Aluminium has its highest toxicological effects when it is present in the ionic form, speciating Aluminium is a top priority in Aluminium and acidification research.

When looked at from a laboratory point of view, the speciation of Aluminium is dependant on pH and temperature. At low pH values Aluminium is mainly present as ionic Al^{3+} , in the pH range 6,0-8,0 hydrolysis reactions take place with binding of successively more H^+ ions as shown below (Schecher and Driscoll 1987; Andrews et al. 1996; Stumm and Morgan 1996):



In laboratory conditions these reactions are well understood with good thermodynamic and kinetic data (van Hees et al. 2001). If this situation shown above represented the natural environment, then speciating Aluminium would be simple matter of reading values from an Al/pH diagram such as that shown below (Stumm and Morgan 1996).

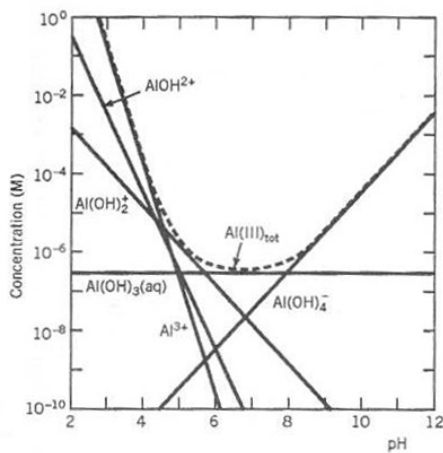


Figure 2 – Hydrolysis of Aluminium, taken from Stumm and Morgan (1996)

However, Aluminium is a type A metal (Ahrlund et al classification, 1958), and therefore also forms strong complexes with Fluoride and phosphorous as well as with OH ions (vanLoon and Duffy 2000). It can also form somewhat weaker complexes with Sulphate and Nitrate (Driscoll and Postek 1996). Therefore the speciation of Aluminium also depends on the concentrations of these ligands.

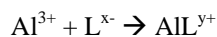
Finally, but most importantly is the impact of organic matter and colloids on the speciation of Aluminium. Aluminium can bind to both dissolved- and solid phase-organic matter. All the previous ligands discussed can be isolated in the lab and specific information about their reactions with Aluminium studied, however organic matter is extremely heterogeneous and this leads to problems in modelling Aluminium-organic binding (Tipping et al. 1991).

If we are to understand Aluminium mobilisation and speciation in the natural environment then it is critical to understand the factors that control Aluminium solubility and form, and to know which factors are integral to this in different natural environment. For example the factors controlling the levels of harmful Al^{3+} in a clear-water perched lake could well be different from those controlling them in waters draining from organic rich marshlands. To understand and finally be able to model this requires an understanding of organic and inorganic

processes coupled with hydrological information about a catchment, for example flow pathways. In the following sections of this paper the theory behind how inorganic and organic molecules bind with Aluminium and their relative importance will be discussed.

2.1 Inorganic Aluminium Complexes

As discussed in the previous section there are many different forms of inorganic Aluminium. All of these forms involve the binding of Aluminium with a single, or succession of ligands.



The ligand shown in the above equation could be OH^- , F^- , SO_4^{2-} or NO_3^- , or a combination of these together. The dominant ligand is the OH^- ion (Andrews et al. 1996), and assuming the solvent involved is water, it is in abundant supply. Fluoride is the most electronegative of the remaining ligands and forms very strong bonds with Aluminium, up to AlF_6^{3-} (Goldberg et al. 1996). The level of Aluminium-Fluoride bonding is usually governed by the concentration of F^- ions. In comparison with the hydrolysis reactions, Fluoride complexes form relatively slowly (minutes to hours), however when considering natural environments this is sufficiently fast to assume an equilibrium (Tipping 2002). The only other ligand which is thought to be significant when studying natural waters is the Sulphate ion, which can form complexes if the concentration of SO_4^{2-} ions is high enough. The Alumino-sulphate complex is not as strong as the OH^- or F^- complexes and it is also very temperature dependant (Driscoll and Postek 1996).

There are well researched thermodynamic data for all of the ligands discussed above (Stumm and Morgan 1996; van Hees et al. 2001), and this means that with knowledge of the free ligand concentration and the total Aluminium concentration it is possible to accurately calculate the concentration of free Al^{3+} .

As the rate of primary weathering is assumed to be a constant, and disregarding organic ligands, the concentration of Al^{3+} in soil water should be controlled by two factors:

- a) pH and temperature controlling the dissolution of secondary minerals
- b) Ligand concentration.

With this known, much of the early research into Aluminium chemistry in freshwaters focused on creating computer models which, given the variables: ligand concentration, pH and temperature, would be able to predict Aluminium speciation in soils and freshwaters. Examples of these kinds of catchment acidification models are MAGIC, Birkenes Model, ILWAS Model and PROFILE. A common feature in many of these models was the central role of Aluminium solubility controlled by a solid phase Aluminium-hydroxide, normally $\text{Al}(\text{OH})_3$ (Gibbsite). The applicability of such models and mineral solubility in general will be discussed in section 2.3.

2.2 Organic Aluminium Complexes

Aluminium forms strong complexes with active sites on both dissolved organic carbon (DOC) and solid organic Matter (SOM). These complexes can be fundamental to the speciation of Aluminium, for example vanHees et al (2001) estimated that total Aluminium measured in surface waters in Sweden can have an organically bound component which ranges from 30 to 75%. However, even the seemingly simple task of an accurate definition of these organic substances still eludes researchers, with the root of the problem being the heterogeneity of organic matter (Tipping et al. 1991). Organic matter is derived from the partial decomposition of living material, and can be loosely classified according to the following definitions:

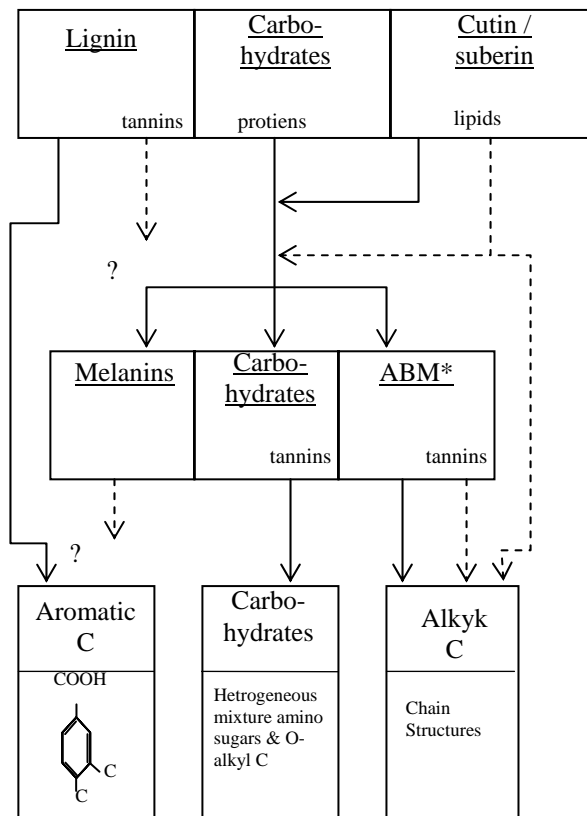


Figure 3 – The breakdown products of organic matter. Adapted from Kögel-Knabner (1992) (* ABM = aliphatic biomacromolecules)

When considering Alumino-organic complexes the key factor is the type and number of active binding sites that are present on the organic molecule, as it is the type, number and co-ordination of these sites that decides the suitability for binding Aluminium (Tipping et al. 1991). In it's most simple form the reaction for an Alumino-organic complex is:



If shown in more detail, the Aluminium ion can complex to organic matter in 5 different ways, as shown below

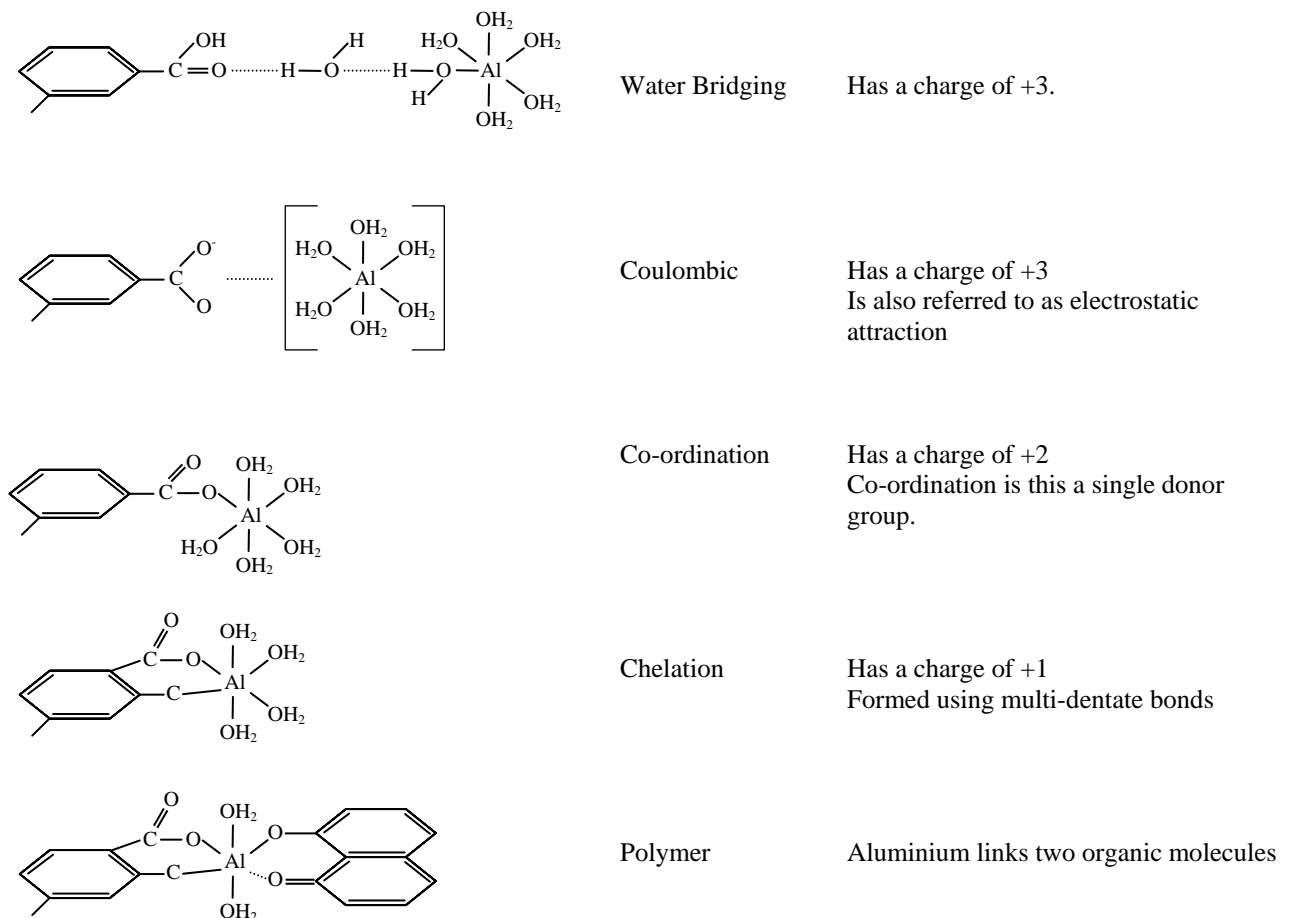


Figure 4 – Possible Alumino-organic complexes (Vance et al. 1996).

The first two binding types generally dominate (water bridging and coulombic), whereas co-ordination and chelation become more important as binding sites become saturated (Vance et al. 1996), Aluminium polymers are an area of active research.

Knowing how the Aluminium ion complexes with organic matter is only half way to being able to say exactly how much Aluminium is bound to organic matter, this is where the definition of organic matter becomes important. As discussed earlier in this section, our knowledge about organic matter is still poor, and therefore it is impossible to say exactly how many, and what type, of active sites an organic molecule has. An organic molecule can contain two main types of organic substance:

- **Biochemical compounds**, which are synthesised by micro-organisms and plants. These are a large groups of temporary substances which are well defined and made up of:
 - a) *Low molecular weight organic acids*
 - e.g. formic acid (HCOOH), acetic acid (CH₂COOH) and citric acid (COH(CH₂COOH)₂COOH)

These form stable complexes with Aluminium, hydroxy acids form stronger complexes than those with single COOH groups. Forest litter generally contains a mix of these acids.

b) *Hydroxamate Siderophores*

These contain the anionic reactive group R-CO-NO⁻ and are produced by micro-organisms and plants. They predominantly bond with Iron, but can also bond with Aluminium.

c) *Sugar Acids*

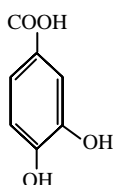
e.g. gluconic-, glucuronic- and galacturonic-acids

This is an important group which can make up 25% of the organic acids, they are common metabolites of micro-organisms.

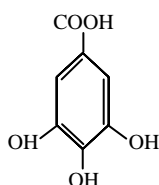
d) *Phenols and Phenolic Acid*

These are thought to be of considerable importance in the binding of Aluminium. They are widely distributed and are synthesised from litter (plant and animal) by micro-organisms. The most important Aluminium bind groups are:

Protocatechuic Acid



Gallic Acid



Caffeic Acid

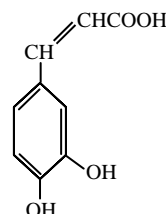


Figure 5 . Phenolic binding sites (Vance et al. 1996).

e) *Polymeric Phenols*

These are phenols which contain more than one aromatic ring, this means that they can form highly stable complexes with Aluminium by building up into larger molecules. They include the flavanoids and tannins.

f) *Other biochemical compounds*

Both proteins and carbohydrates can form complexes with Aluminium, although how important these are is not known.

(Vance et al. 1996)

- **Humic and Fulvic acids**, these are the secondary synthesis products, which can only be loosely defined as yellow/black substances. This second group is far more important in the binding of Aluminium.

Both humic and fulvic acids contain a variety of functional groups including:

- Carboxyl (COOH)
- Phenolic (-OH)
- Enolic (-OH)
- Alcoholic (-OH)
- C = O

Of these the carboxyl groups are most important contributor, and as Fulvic acids contain both a high total acidity and a higher proportion of carboxyl groups, they are generally more important in binding Aluminium.

Table 1 – Concentration (cMol[-] kg⁻¹) of oxygen-containing functional groups, from Driscoll and Postek (1996)

	Total Acidity	COOH	Phenolic (OH)	Weakly acidic OH and alcoholic OH	C = O
Humic Acids	560-890	150-570	210-570	20-490	10-560
Fulvic Acids	640-1420	520-1120	30-570	260-950	120-420

Although there is no sound definition and description of humic and fulvic substances, it is known that they contain aromatic rings of the di- or tri-hydroxyphenyl type which are joined by –CH₂–, –O–, –NH–, –N=, or –S–. All humic and fulvic groups contain COOH and OH functional groups, and it is the number and placement of these groups about which so little is known. Possible important bind configurations could be

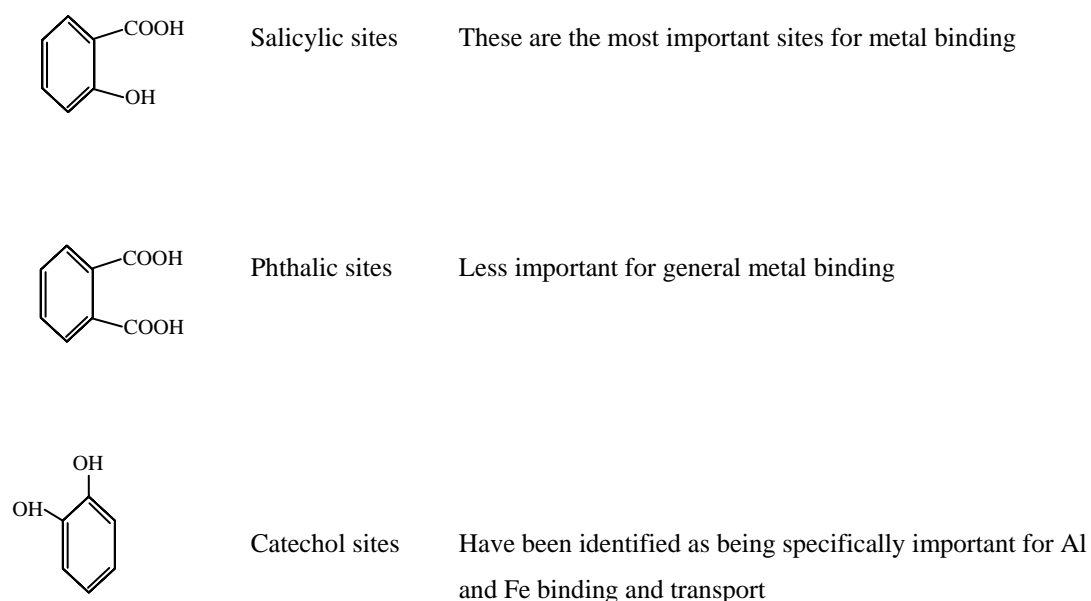


Figure 6 – Humic and Fulvic active sites possibly involved in the binding of metal ions (Vance et al. 1996)

Unfortunately, it is these poorly understood and poorly defined humic and fulvic acids which are the most important in the formation of alumino-organic complexes. There have been numerous studies which have concluded that it is these organic complexes which control the solubility of Aluminium in at least parts of the soil (Skylberg and Magnusson 1995; Simonsson and Berggren 1998; Nissinen et al. 1999; Simonsson 2000; Pellerin et al. 2002). There are currently two schools of thought about the direction of future research into alumino-organic complexes, firstly to continue to improve the definition of humic and fulvic substances leading

towards an accurate chemical speciation, secondly, assuming that it is impossible to accurately define humic and fulvic substances and therefore attempting to generalise them instead.

Understanding the formation of Alumino-organic complexes is central to understanding many of the important issues surrounding Aluminium in the natural environment. For example, Aluminium can bind with DOC and this can act as an effective transport medium for moving Aluminium from the soil to the stream by reducing mineral formation and providing a mobile medium, however equally important may be Aluminium binding to solid phase organic matter therefore retaining it within the soil (Vance et al. 1996). Another aspect of Alumino-organic complexes is that organic matter readily binds with ionic Aluminium, thereby reducing its toxicity, but releasing H^+ ions (Simonsson 2000; Lydersen et al. 2002). Overall interaction between organic substances and Aluminium will therefore effect the chemistry of both the stream (Skylberg and Magnusson 1995) and the soil (Nissinen et al. 1999; Skylberg 1999; Simonsson 2000).

2.3 How and when can these be combined

So far two theories have been proposed for the mechanisms controlling Aluminium solubility:

- inorganic complexes and equilibrium with a mineral phase
- organic complexation

Both of these mechanisms are equally valid in different environments (Driscoll and Postek 1996). Areas with low organic inputs and thick mineral soils may well have Aluminium levels controlled entirely by Aluminium hydrolysis (i.e. equilibrium, with a mineral phase such as Gibbsite). However, areas with thin mineral soils and a thick organic layer could be controlled by equilibrium with organic complexes. Therefore, it is difficult to classify an area into one category, a more representative, and more complex view is that both these mechanisms could be working side-by-side with dominance controlled by many factors such as depth, time, discharge etc. This section will discuss the theory of Aluminium solubility being controlled by both inorganic and organic complexes and how different variables may help define the importance of each mechanism.

Perhaps one of the most obvious theories when studying a podzol soil is that the mechanisms controlling Aluminium solubility changes with depth. The upper O-horizon has high organic matter content and is therefore dominated by organic complexes. The lower B-horizons with lower organic content are controlled by inorganic complexes and hydrolysis (Mulder et al. 1990; Driscoll and Postek 1996; Simonsson and Berggren 1998; van Hees et al. 2001). Another small twist on this theory is that in the O-horizon the mineral solubility is inhibited by organic coatings around the minerals which become less and less with increased depth (Simonsson and Berggren 1998).

Assuming that different horizons can have Aluminium solubility controlled by different mechanisms, then flow pathway and hydrology become important. If the dominant flow pathway is through the o-horizon then organic complexes may be important, if the dominant flow pathway is through the mineral soil then perhaps equilibrium

with a solid mineral phase is the dominant process. A further complication is that in many environments the flowpath way is not static, but changes with discharge, high discharge activates more superficial flow pathways and low discharge is dominated by mineral soil flow (Mulder et al. 1990; Driscoll and Postek 1996; Pellerin et al. 2002).

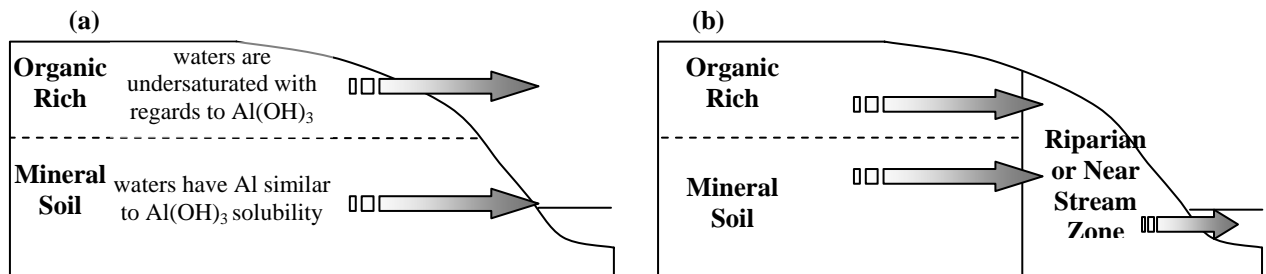


Figure 7 - Al solubility control mechanism varies with depth, (a) as proposed by Driscoll and Postek (1996) and (b) as commonly seen in Northern Sweden.

Another theory proposed is that acidification could lead to a change in the mechanism controlling Aluminium solubility and speciation. There are two sources of Aluminium in a soil, weathering of primary minerals and inflow from adjacent horizons, Aluminium is removed by leaching. Solid phase minerals may well control Aluminium solubility, however if there is a continued input of strong acids due to acidification then leaching of Aluminium will be greater than the inputs and this pool of $\text{Al}(\text{OH})_3$ will slowly be depleted. If this happens the solubility of Aluminium in the soil may move from equilibrium with a solid mineral phase to equilibrium with organic complexes (Berggren and Mulder 1995; Gustafsson et al. 2001). This is shown in the figure below.

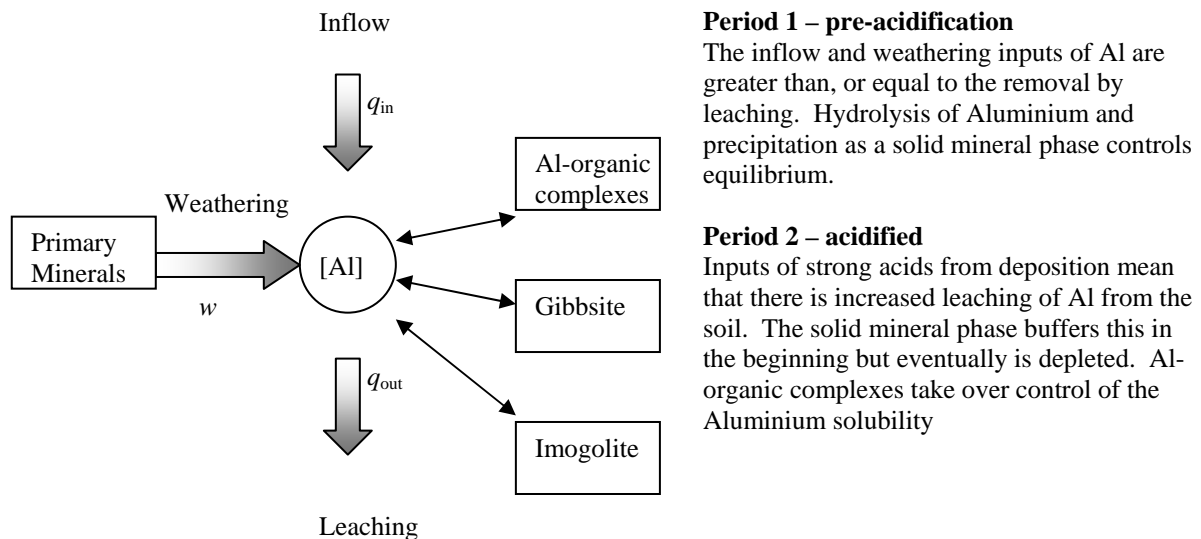


Figure 8 – Acidification controlled Al solubility (Gustafsson et al. 2001)

The stage of acidification within a soil with regards to which mechanisms dominates has been discussed by Gustafsson et al (2001) and Berggren and Mulder (1995). They find that soils with a pH of less than pH~4.1

generally have Aluminium speciation controlled by organic complexes, and soil with pH greater than pH~4.1 are controlled by a solid phase mineral solubility.

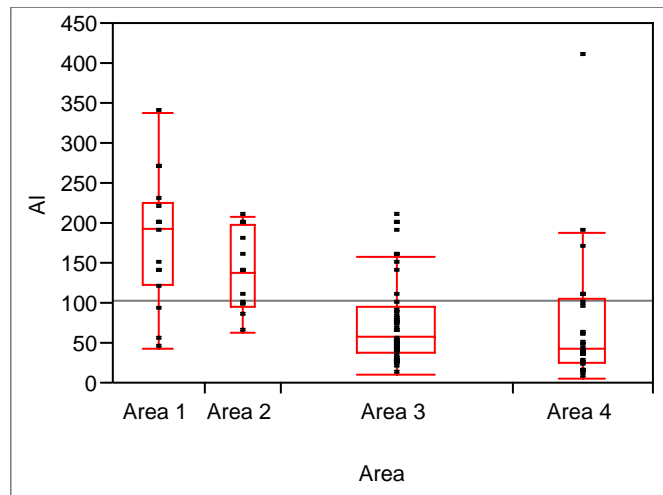
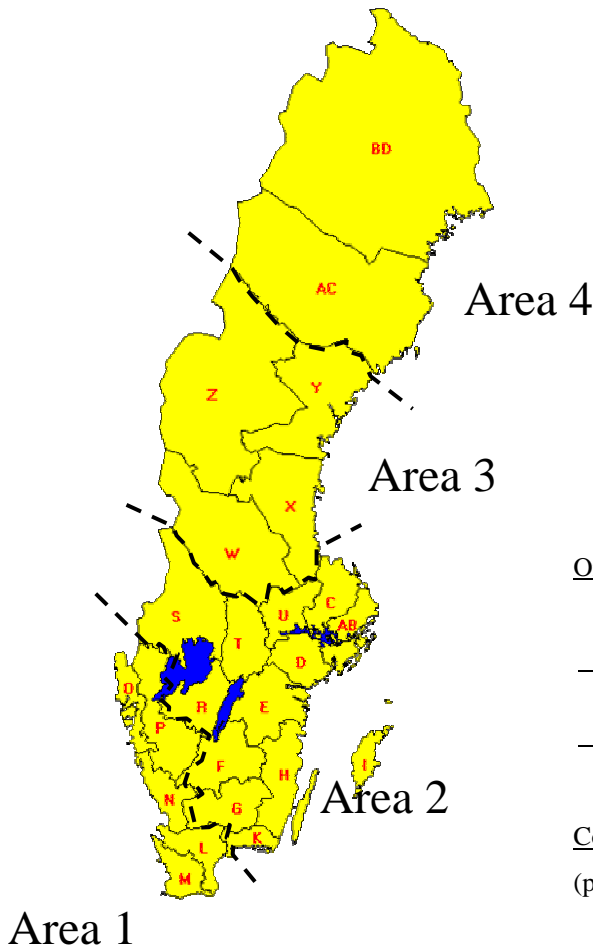
The final objective with combining these mechanisms for the control of Aluminium solubility and speciation has to be the creation of a model which can successfully calculate today's Aluminium in streams and soils and also be used to predict possible future scenarios. As the development of this field has evolved there have been numerous models presented, below is a brief summary of the more significant models and how they predict Aluminium.

Table 2 – Common models used for prediction of Aluminium.

	Al- release	Al-OH species	Inorganic Al- Species	Organic species	Ref
Birkenes	☑				(Christophersen et al. 1982)
PROFILE	☑	☑			(Sverdrup 1990)
STEADQL	☑	☑	☑	☑	(Furrer et al. 1990)
ILAW	☑	☑	☑	☑	(Gherini et al. 1985)
MAGIC	☑	☑	☑	☑	(Cosby et al. 1985)

Aluminium in Sweden

Acidification has been, and still is, a major environmental issue in Sweden, due to both a high input of anthropogenic acids and a generally low natural buffering capacity. The detrimental effects of acidification are dominated by mobilized Aluminium and therefore the distribution and factors controlling Aluminium in Swedish soils and freshwaters are of great interest. The connection between acidified soils and acidified fresh water has been well established in highly impacted areas in the South, but it is not clear if that pattern is also present in the North of the country. One interesting pattern in Aluminium distribution is that acid lakes in the northern half of Sweden have statistically lower levels of Aluminium than acid lakes in the southern half of Sweden. This is based on the total Aluminium levels (inorganic and organic) and is therefore is not just due to speciation differences.



One-way ANOVA

Source	DF	Sum of Squares	Mean Square	F ratio	Prob > F
Area	3	157890,97	52630,2	11,1178	<0,001
Error	89	421314,05	4733,9		
C. Total	2	579204,92			

Comparison of all pairs using Tukey-Kraner HSD

(positive values show pairs are significantly different (alpha=0,05))

	Area 1	Area 2	Area 3	Area 4
Area 1	-63,6903	-33,4856	47,6629	44,9007
Area 2	-33,4856	-70,6580	9,6597	7,2271
Area 3	47,6629	9,6597	-40,2813	-44,4211
Area 4	44,9007	7,2271	-44,4211	-52,0029

Figure 9 - Statistical analysis of Aluminium data (Al_NAD (ug/l)) from the National Lakes Survey 1995 (Riksinventering 95). Acid lakes are classified according to Naturvårdsverket guidelines, here the most acid class is used (class 5, lakes with pH <5,6). Statistical analysis have been undertaken using JMP 4.0.0.

The lakes in the figure above are all classified as “very acid”, yet there are marked differences in the amount of Aluminium which is present in the lakes. It should be noted however that the survey data is from summer, low flow conditions and northern areas have the lowest pH values and highest Aluminium concentrations during the spring flood. However, that the Aluminium concentrations observed are still significantly lower in Northern Sweden could be due to four possibilities:

1. Aluminium is not being transported in the soil; therefore it cannot be transferred to the lakes.
2. Aluminium is mobilized in the soil but is removed before it leaves the soil, e.g. in the near stream zone.
3. Aluminium is mobilized in the soil but is removed by in-stream or in-lake processes.
4. A combination of all three, with the significance of each depending on local conditions.

It is well known that Aluminium is mobilized and transported in northern Swedish soils, as shown by the podzolization process which has been occurring for the last 9000-13000 years throughout Sweden. The classical ‘bleached’ eluvial horizon and dark illuvial horizon of a podzol are due to the transport of principally iron, but also Aluminium down through the soil column with organic acids leached from foliage and litter (Driscoll and Postek 1996; Simonsson 2000; van Hees et al. 2001). Therefore this is not an issue of if Aluminium can be mobilized in Northern Swedish soils, but which processes are involved and if there is subsequent transportation down slope. In many areas of Southern Sweden inputs of anthropogenic strong acids (principally Sulphate) have increased Aluminium transport to the stream by lowering the pH and providing mobile anions. It is not clear what the dominant transport mechanisms are in Northern Swedish areas which have received significantly lower anthropogenic inputs.

Looking at data from a northern Swedish soil transect (figure 10) the high Aluminium levels in the illuvial horizon can clearly be seen. Another important observation is that Aluminium levels increase when moving towards the stream, with the near stream zone (4m) showing up to ten times the Aluminium found further up the hillslope. Also shown in the figure is the Aluminium level in the stream, and this shows a significantly lower Aluminium level than the near stream zone. This evidence seems to indicate that Aluminium is being mobilized in the soil and moving downslope towards the stream but that a process, or combination of processes, is either stopping or removing the Aluminium in the near stream zone, or at the stream/near stream zone interface. A key issue is the process behind the mobilisation, which could be completely natural or due to incipient acidification. This discontinuity is of significant importance as it is often assumed that stream water is a reflection of soil water, a deviation from this would mean that this ‘memory’ effect might not always occur.

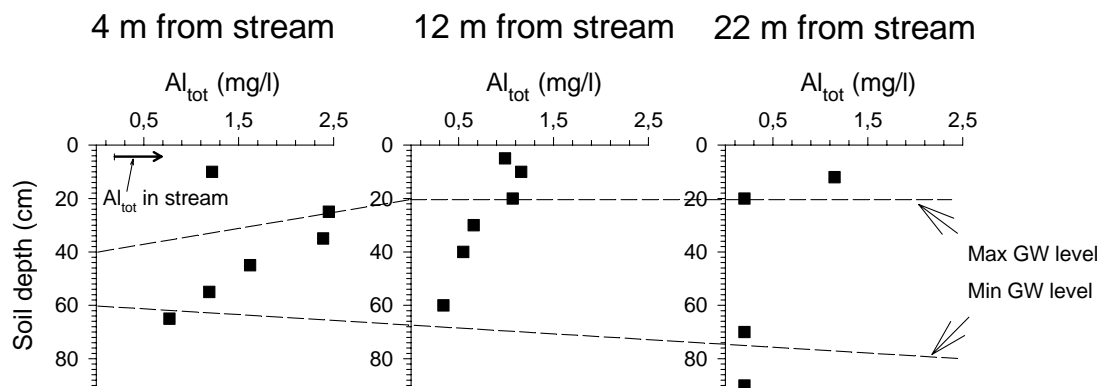


Figure 10 – Total Aluminium measured at S-transect, Vindelns Research Catchment, Northern Sweden.

This near stream zone build up of Aluminium has also been observed by a number of other research groups including Pellerin et al (2002), Mulder et al (1990; 1991), and Vogt and Muniz (1997). Between them, they have suggested a number of theories which could be responsible for this sudden change in Al at the riparian/stream interface.

1. De-gassing of CO₂.

Within the soil increased CO₂ levels lower the pH by causing disassociation of H₂CO₃. A lower pH will cause a change in speciation of the inorganic Aluminium in the soil increasing the proportion of the mobile Al³⁺ fraction. When soil enters the stream the CO₂ level re-equilibrate with atmospheric concentrations causing degassing of CO₂, a rise in pH, and subsequent precipitation of Al(OH)₃ (Driscoll and Postek 1996; Pellerin et al. 2002).

2. Soil water mixing

The near stream zone could be a mixing site for upper and lower flow pathways. The mixing of acidic, Al-rich shallow water with higher pH baseflow could lower pH and decrease Aluminium solubility (Pellerin et al. 2002).

3. Changes in DOC and NO₃⁻

Organic Aluminium losses could be due to a fall in DOC levels from the near stream zone to the stream, and immobilization of NO₃⁻ in the near stream zone could lead to a fall in inorganic Aluminium ((Driscoll and Postek 1996)

How these mechanisms fit with the conditions found in Northern Sweden is unknown, clearly a better understanding of the mobilization, transport and removal processes of Aluminium in northern Swedish soils is needed, and this is an area addressed in the doctoral plan for Neil Cory (Cory 2002). A key question must also be: is this build-up of Aluminium at the near stream zone a natural phenomenon, or is it a chronic effect of

anthropogenic influences? A continuation of this line of thought is, how long have these removal processes been active?, what are their capacities for Aluminium removal?, and what might occur if this is exceeded?

Larger scale issues

It is important to keep these issues in context, and although understanding Aluminium dynamics at a hillslope scale is important, the key reason behind the research is the toxicological effects of Aluminium on freshwater biota, and this means also looking at the larger scale. Studies of Aluminium impacts on fish have found that it is not just the Aluminium concentrations and form in lakes which is important, but also the variation in headwaters. For example fish are able to tolerate high inorganic Aluminium levels in a lake if there are “safe-havens” in some of the supplying headwaters (Hesthagen and Jonsson 1998). On a catchment scale there is also the issue of “acid surges” caused by spring melts or rainfall events and how these affect catchment Aluminium dynamics. From a catchment scale we can move up to the regional, national and international levels. How do the factors controlling Aluminium vary with deposition, geology, landuse and climate? Therefore the field of Aluminium in organic rich soils is not just isolated to individual locations but must also be considered in the larger context, these are all issues which are addressed in the doctorate plan for Neil Cory (Cory 2002).

Conclusions

The central issue of environmental research into Aluminium is that despite the toxicological importance of the element, there are relatively few known and universally applicable mechanisms controlling its mobility and toxicology. An important factor hindering research is both the cost and difficulty in speciating and measuring Aluminium. This has meant that there are relatively few extensive datasets for Aluminium, and these form the basis of the classical evolution of scientific theory: observation, empirical models, theoretical models.

The doctoral plan for Neil Cory highlights several key areas where existing data sets could be complimented with new sampling to help better understand the behaviour of Aluminium in boreal environments. These are show below in order of spatial scale:

1. Hillslope scale – Data from a single hillslope collected over a long temporal scale at a site in the Vindelån Research Catchment in Northern Sweden is to be used to describe local Aluminium dynamics and identify the factors which may control Aluminium solubility in boreal environments.
2. Catchment scale - Data collected at Vindelån Research Catchment is to be used to examine how Aluminium varies with increasing stream order. Variation at catchment scale can be an important factor governing Aluminium toxicology to fish higher order streams and lakes.
3. Regional Scale – Combining datasets from the localised surveys with data from the national lakes surveys regional patterns can be examined. This will help to understand the links between Aluminium dynamics and variation in deposition, geology and organic matter.

4. International Scale – combining studies from areas in Sweden with those in the Czech Republic it will be possible to see if unilateral mechanisms control Aluminium solubility, or if localised factors are more important.

In the past much of the research involving Aluminium in larger scale environmental issues such as acidification has been restricted to measuring total Aluminium content. In boreal environments where the presents of organic matter is extremely important it is vital that research also involves full speciation of Aluminium samples. Also work with Aluminium toxicology in fish has shown that certain fractions of Aluminium are far more toxic than others. Bearing these two factors in mind it is therefore important that Aluminium speciation plays a central role in any research.

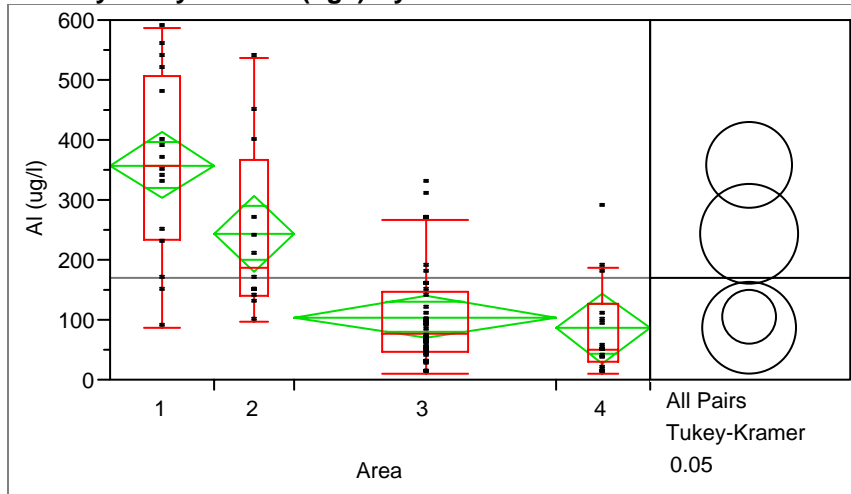
References

- Andrews, J. E., P. Brimblecombe, T. D. Jickells and P. S. Liss (1996). *An introduction to environmental chemistry*, Blackwell Science.
- Berden, M., N. Clarke, L. G. Danielsson and A. Sparen (1994). Aluminum Speciation - Variations Caused by the Choice of Analytical Method and by Sample Storage. *Water Air and Soil Pollution* **72**(1-4): 213-233.
- Berggren, D. and J. Mulder (1995). The Role of Organic-Matter in Controlling Aluminum Solubility in Acidic Mineral Soil Horizons. *Geochimica Et Cosmochimica Acta* **59**(20): 4167-4180.
- Christophersen, N., H. M. Seip and R. F. Wright (1982). A model for streamwater chemistry at Birkenes, Norway. *Water Resources Research* **18**: 977.
- Cory, N. (2002). Doctorate plan for Neil Cory, Department for Environmental Assessment, SLU, Uppsala, Sweden.
- Cosby, B. J., G. M. Hornberger, J. N. Galloway and R. F. Wright (1985). Modeling the effects of acid deposition: assessment of a lumped parameter soil model of soil water and steamwater chemistry. *Water Resources Research* **21**: 51-.
- Driscoll, C. T. and K. M. Postek (1996). The chemistry of Aluminium in surface waters. *The environmental chemistry of Aluminium*, 2nd. G. Sposito, Lewis Publishers: 363-418.
- Furrer, G., P. Sollins and J. C. Westall (1990). The study of soil chemistry through quasi-steady-state models. II. Acidity of soil solution. *Geochimica Et Cosmochimica Acta* **54**: 2363-.
- Gherini, S. A., L. Mok, R. J. M. Hudson, G. F. Davis, S. W. Chen and R. A. Goldstein (1985). The ILWAS model: formulation and application. *Water Air and Soil Pollution* **26**: 425-.
- Goldberg, S., J. A. Davis and J. D. Hem (1996). The surface chemistry of Aluminium oxides and hydroxides. *The environmental chemistry of Aluminium*, 2nd Edition. G. Sposito, Lewis Publishers: 271-332.
- Gustafsson, J. P., D. Berggren, M. Simonsson, M. Zysset and J. Mulder (2001). Aluminium solubility mechanisms in moderately acid Bs horizons of podzolized soils. *European Journal of Soil Science* **52**(4): 655-665.
- Herrmann, J. (2001). Aluminium is harmful to benthic invertebrates in acidified waters, but at what threshold(s)? *Water Air and Soil Pollution* **130**(1-4): 837-842.
- Hesthagen, T. and B. Jonsson (1998). The relative abundance of brown trout in acidic softwater lakes in relation to water quality in tributary streams. *Journal of Fish Biology* **52**(2): 419-429.
- Kögel-Knabner, I. (1992). *Forest soil organic matter: structure and formation*.
- Lydersen, E., S. Löfgren and R. T. Arnesen (2002). Metals in Scandinavian surface waters: Effects of acidification, liming, and potential reacidification. *Critical reviews in environmental science and technology* **23**(2&3): 73-295.
- Mulder, J., N. Christophersen, M. Hauhs, R. D. Vogt, S. Andersen and D. O. Andersen (1990). Water-Flow Paths and Hydrochemical Controls in the Birkenes Catchment as Inferred from a Rainstorm High in Seasalts. *Water Resources Research* **26**(4): 611-622.
- Mulder, J., M. Pijpers and N. Christophersen (1991). Water-Flow Paths and the Spatial-Distribution of Soils and Exchangeable Cations in an Acid-Rain Impacted and a Pristine Catchment in Norway. *Water Resources Research* **27**(11): 2919-2928.
- Nissinen, A., H. Iivesniemi and N. Tanskanen (1999). Equilibria of weak acids and organic Al complexes explain activity of H⁺ and Al³⁺ in a salt extract of exchangeable cations. *European Journal of Soil Science* **50**(4): 675-686.
- Nordstrom, D. K. and H. M. May (1996). Aqueous equilibrium data for mononuclear Aluminium species. *The environmental chemistry of Aluminium*, 2nd Edition. G. Sposito, Lewis Publishers: 39-81.
- Pellerin, B. A., I. J. Fernandez, S. A. Norton and J. S. Kahl (2002). Soil aluminum distribution in the near-stream zone at the Bear Brook Watershed in Maine. *Water Air and Soil Pollution* **134**(1-4): 189-204.
- Poleo, A. B. S., K. Ostbye, S. A. Oxnevad, R. A. Andersen, E. Heibo and L. A. Vollestad (1997). Toxicity of acid Aluminium-rich water to seven freshwater fish species: A comparative laboratory study. *Environmental Pollution* **96**(2): 129-139.
- Schecher, W. O. and C. T. Driscoll (1987). An evaluation of uncertainty associated with Aluminium equilibrium calculations. *Water Resources Research* **23**(4): 525-534.
- Simonsson, M. (2000). Interactions of Aluminium and fulvic acid in moderately acid solutions: stoichiometry of the H⁺/Al³⁺ exchange. *European Journal of Soil Science* **51**(4): 655-666.
- Simonsson, M. and D. Berggren (1998). Aluminium solubility related to secondary solid phases in upper B horizons with spodic characteristics. *European Journal of Soil Science* **49**(2): 317-326.
- Skyllberg, U. (1999). pH and solubility of Aluminium in acidic forest soils: a consequence of reactions between organic acidity and Aluminium alkalinity. *European Journal of Soil Science* **50**(1): 95-106.

- Skyllberg, U. and T. Magnusson (1995). Cations adsorbed to soil organic matter - A regulatory factor for the release of organic carbon and hydrogen ions from soils to waters. *Water Air and Soil Pollution* **85**(3): 1095-1100.
- Stumm, W. and J. J. Morgan (1996). *Aquatic Chemistry*, 3rd Edition.
- Stutter, M., R. Smart, M. Cresser and S. Langan (2001). Catchment characteristics controlling the mobilization and potential toxicity of Aluminium fractions in the catchment of the River Dee, northeast Scotland. *Science of the Total Environment* **281**(1-3): 121-139.
- Sverdrup, J. D. (1990). *The kinetics of base cation release due to chemical weathering*, Lund University Press.
- Tipping, E. (2002). *Cation binding by humic substances*, Cambridge University Press.
- Tipping, E., D. Berggren, J. Mulder and C. Woof (1995). Modeling the Solid-Solution Distributions of Protons, Aluminum, Base Cations and Humic Substances in Acid Soils. *European Journal of Soil Science* **46**(1): 77-94.
- Tipping, E., C. Woof and M. A. Harley (1991). Humic substances in acid surface waters; modelling Aluminium binding, contribution to ionic charge-balance and control of pH. *Water Research* **25**(4): 425-435.
- van Hees, P., U. Lundstrom, R. Danielsson and L. Nyberg (2001). Controlling mechanisms of Aluminium in soil solution - an evaluation of 180 podzolic forest soils. *Chemosphere* **45**(6-7): 1091-1101.
- van Hees, P. A. W., E. Tipping and U. S. Lundstrom (2001). Aluminium speciation in forest soil solution - modelling the contribution of low molecular weight organic acids. *Science of the Total Environment* **278**(1-3): 215-229.
- Vance, G. F., F. J. Stevenson and F. J. Sikora (1996). Environmental chemistry of Aluminium-organic complexes. *The environmental chemistry of Aluminium*, 2nd Edition. G. Sposito, Lewis Publishers: 169-220.
- vanLoon, G. W. and S. J. Duffy (2000). *Environmental chemistry*, Oxford University Press.
- Vogt, R. D. and I. P. Muniz (1997). Soil and stream water chemistry in a pristine and boggy site in mid-Norway. *Hydrobiologia* **348**: 19-38.

Appendix 1 – Statistical analysis of data in figure 9

Oneway Analysis of AI (ug/l) By Area



**Oneway Anova
Summary of Fit**

Rsquare	0.490824
Adj Rsquare	0.47124
Root Mean Square Error	109.5776
Mean of Response	172.8902
Observations (or Sum Wgts)	82

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Area	3	902808.6	300936	25.0629	<.0001
Error	78	936565.4	12007		
C. Total	81	1839374.0			

Means for Oneway Anova

Level	Number	Mean	Std Error	Lower 95%	Upper 95%
1	16	359.813	27.394	305.27	414.35
2	12	245.750	31.632	182.77	308.73
3	40	106.025	17.326	71.53	140.52
4	14	87.857	29.286	29.55	146.16

Std Error uses a pooled estimate of error variance

Means Comparisons

Dif=Mean[i]-Mean[j]	1	2	3	4
1	0.000	114.063	253.787	271.955
2	-114.063	0.000	139.725	157.893
3	-253.787	-139.725	0.000	18.168
4	-271.955	-157.893	-18.168	0.000

Alpha=0.05

Comparisons for all pairs using Tukey-Kramer HSD

Abs(Dif)-LSD	1	2	3	4
1	-101.708	4.205	168.693	166.678
2	4.205	-117.442	45.040	44.723
3	168.693	45.040	-64.326	-71.163
4	166.678	44.723	-71.163	-108.730

Positive values show pairs of means that are significantly different.