

**Natural and Anthropogenic Influences
on Aluminium in the Humic Rich
Waters of Northern Sweden**

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Abstract

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The issue of acidification of surface waters has been one of the central environmental problems in Sweden for the last four decades. Aluminium (Al) is critical to the issue of acidification because it is often the combination of depressed pH along with elevated concentrations of Al, and specifically inorganic Aluminium (Al_i), which are implicated in the decline and disappearance of aquatic organisms. In northern Sweden where sulphate deposition has not been as high as in the south, chronic soil acidification has not taken place; instead it is episodic acidification, especially during the spring snow melt that is important. The presence of organic matter complicates the issue of acidification and Al by providing both natural acidity and abundant binding capacity that reduces the inorganic fraction of Al. This thesis addresses the issue of anthropogenic influence in northern Sweden by examining Al solubility, speciation and modelling across spatial and temporal scales that range from a hillslope or episode to a landscape and decades.

At the hillslope scale Al transport and speciation were strongly influenced by the organic phase. No front of Al mobilization was seen in the mineral soil that would be indicative of chronic soil acidification. The superficial, transiently saturated flow pathways in the riparian peats had accumulated a large amount of Al, and were the major source of Al leaving a hillslope transect. At the landscape levels the influence of landcover was important for both concentration and speciation of Al. Areas draining wetlands had lower concentrations of Al than forested sites despite significantly lower pH. This was attributed to source limitation, with wetlands lacking a mineral source of Al. Forested sites showed higher concentrations of total Al and Al_i , especially during snowmelt episodes.

Aluminium speciation was modelled for lake and river samples from Sweden's national survey using the Windermere Humic Aqueous Model (WHAM). The calibration proved robust, and Al_i could be correctly placed in toxicological classes in 89-95% of cases. Combining this modelling work with a tool for the modelling of anthropogenic impact of sulphate deposition during episodes (one-point Boreal Dilution Model, pBDM) allowed us to model Al_i during spring snowmelt in a northern Swedish landscape from 1970-2020. This covers the period of peak anthropogenic sulphate deposition through to the full implementation of current emissions legislation. There was a major reduction in Al_i and an increase in pH from 1970 to 2004, with smaller further improvements by 2020. From a toxicological viewpoint, the number of streams with Al_i concentrations deemed toxic to acid tolerant species reduced from 64% in 1970 to 14% in 2004. This episodic acidification history should be borne in mind when assessing the aquatic biota in boreal regions where the stream chemistry has recovered but the biological recovery may still be ongoing.

Keywords: Aluminium, speciation, acidification, soil, water, DOC, organic matter, transport, ecotoxicology, modelling, WHAM, pBDM.

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Contents

Introduction 7

Background 7

Objectives 8

Methods 9

Site Description 9

The Hillslope scale (Paper I) 11

The Landscape scale (Paper II) 11

Modelling of Aluminium (Papers III and IV) 11

Results and Discussion 13

Aluminium at the Hillslope scale 13

Spatial and temporal variations at the landscape scale 15

Modelling inorganic Aluminium 17

Retroactive and predictive modelling of inorganic Aluminium 19

Conclusions 23

References 24

Acknowledgements 29

Appendix

Papers I – IV

This thesis is based on the following papers, which will be referred to in the text by their respective Roman numerals.

- I.** Cory, N., Laudon, H., Köhler, S., Seibert, J. & Bishop, K. Aluminium from soil to stream in a boreal catchment. *Biogeochemistry* (under review).
- II.** Cory, N., Buffam, I., Laudon, H., Köhler, S. & Bishop, K. 2006. Landscape control of stream water aluminum in a boreal catchment during spring flood. *Environmental Science & Technology* 40, 3494-3500.
- III.** Cory, N., Andrén, C. & Bishop, K. Modelling inorganic Aluminium with WHAM in environmental monitoring. *Applied Geochemistry* (Accepted).
- IV.** Cory, N., Laudon, H., & Bishop, K. Past, present and future concentrations of inorganic Aluminium in a boreal landscape (Manuscript).

Paper II is reproduced with the kind permission of the publisher.

Introduction

Aluminium (Al) is the most common metal in the earth's crust (Lydersen, Löfgren & Arnesen, 2002; vanLoon & Duffy, 2000), yet despite its abundance there are still large areas of its cycle in the natural environment which are poorly understood (Gustafsson *et al.*, 2001). The issue of acidification of surface waters has brought Al research strongly into focus due to the toxicity of certain Al forms at low pH. Al solubility and toxicity, however, are not only dependant of the acidity of a system, but also on the presence of binding ligands. In the boreal zone dissolved organic carbon (DOC) is an important factor controlling both Al transport and toxicity.

Previous work has shown that in the late 1990's there was a modest anthropogenic impact superimposed on the natural spring flood pH decline in N. Sweden (Laudon & Bishop, 1999; Laudon, Westling & Bishop, 2000) It is, however, not low pH that is responsible for fish mortality, but rather high inorganic Al (Al_i) concentrations. It is well documented that soil acidification has mobilized Al from soils to surface waters in S.W. Sweden, S. Norway and Central Europe (Baker *et al.*, 1996; Dickson, 1978; Muniz & Leivestad, 1980) However, there is little information on the extent of soil acidification and concomitant Al mobilization in soils in N. Sweden. In order to improve our understanding of the processes controlling anthropogenic influences on aquatic organisms, we need to describe and quantify both the spatial and temporal patterns of Al in N. Sweden and the boreal zone in general, and how the presence of DOC can affect these. A further hinderance to Al research is the considerable cost and often high analytical uncertainty involved in the analysis of individual Al fractions.

Presented in this thesis are results from several studies examining Al at both the hillslope and landscape scale as well as the application of modelling as a compliment to laboratory analysis. This is then used to model past and future impacts of anthropogenic acidification on surface water Al concentration and speciation. The overall goal is to contribute to a better understanding of the extent to which acid deposition influences Al in the surface waters of N. Sweden.

Background

The issue of surface water acidification has been one of the central environmental problems in Sweden, with remediation through liming costing over 2 billion crowns (~200 million USD) during the period 1976-2002 (Lydersen, Löfgren & Arnesen, 2002). This remediation has been undertaken to buffer the excess acidity from the deposition of anthropogenic sulphate. Al is critical to the issue of acidification because it is often the combination of depressed pH along with elevated concentrations of Al, and specifically Al_i , that are attributed to declines or disappearance of aquatic organisms, principally fish (Brodeur *et al.*, 2001; Poleo

et al., 1997; Ytrestoyl, Finstad & McKinley, 2001) but also invertebrates (Herrmann, 2001).

The concentration and speciation of Al are strongly connected to the acidity of a system. In the pH range 4.5 – 5.5 Al is a strong buffer (Driscoll & Postek, 1996; Simonsson, 2000; Skyllberg, 1999), therefore if water in a catchment falls from circum-neutral to lower pH due to acidification these excess hydrogen ions may displace Al from the soil to surface waters. However, the toxicity of Al is due to a combination of concentration and speciation. In fish, acute effects have been shown through both ionoregulatory and respiratory disturbances (Playle, Goss & Wood, 1989; Poleo, 1995) due to the presence of cationic Al_i. Al is a strongly hydrolysing metal (Driscoll & Postek, 1996) reacting with water to form a hydroxide Al(H₂O)₆³⁺ at pH 4.5 or less. As pH increases successive hydrogen ions are bound reducing the potential toxicity (Schecher & Driscoll, 1987; Stumm & Morgan, 1996).

Both Al solubility and toxicity are also dependant on the presence of binding ligands. In organic rich boreal waters, the dominant ligand is DOC. The organic acids in DOC are another, largely natural, source of acidity in surface waters (Kortelainen & Saukkonen, 1995). By decreasing pH, DOC increases Al solubility and influences the speciation of Al towards more toxic forms. At the same time though, DOC is a ligand that binds a portion of the Al in organic forms that are less toxic (Gensemer & Playle, 1999; Laitinen & Valtonen, 1995). The double-edged nature of organic acidity complicates the issue of distinguishing natural from anthropogenic pH decline and Al toxicity.

In northern boreal climates, spring flood is associated with a characteristic decline in pH (Laudon *et al.*, 2001) and Acid Neutralizing Capacity (ANC) as well as an increase in Al (Paper II) that coincide with sensitive life stages of aquatic organisms (Poleo & Muniz, 1993). Acidified precipitation adds to the pH decline and Al increase (Laudon, *et al.*, 2001). However, there is also a large natural component of pH decline in spring flood due to lower ANC created by dilution with snowmelt, and an increase in organic acids (Laudon, Westling & Bishop, 2000). It is these boreal zones, where episodic rather than chronic acidification are the threat to aquatic organisms (Eshleman *et al.*, 1995), where rapid response to reductions in sulphate deposition can be expected. Studying how Al solubility and speciation behave in these organic rich, episodically acidified, environments is important to understanding the stresses these communities were exposed to earlier, and what these Al stresses will be in the future.

Objectives

This thesis aims to further our understanding of Al solubility and speciation in the boreal environment of northern Sweden, with the goal of quantifying the anthropogenic component of Al_i. In order to understand the effects of anthropogenic sulphate inputs on Al in surface waters one needs to take a holistic

approach, following the Al from mineral soil sources, through transport in the soil, discharge to the stream, and finally scaling up to the landscape level in a long term perspective. This will be done by:

1. Following the evolution of Al chemistry during water transport through the soil to a stream.
2. Describing the spatial pattern of Al in a landscape during a springflood.
3. Modelling Al speciation in surface waters from standard monitoring data.
4. Predicting springflood Al speciation in a landscape during decades when acid deposition has gone from its maximum to levels approaching background.

Methods

The specific projects undertaken can be broadly divided into three areas: hillslope scale; landscape scale; and modelling. At the hillslope scale detailed studies of transect hydrology and soil water chemistry have been undertaken. By coupling the hydrology and chemistry it is possible to examine the integrated soil water chemistry from the time rain enters the soil to when it leaves as stream runoff. At the landscape scale, the spatial and temporal variations in stream water Al are assessed for a 68km² catchment in northern Sweden. Sampling from 16 sites during the springfloods of 2003-2005 covers a range of landscape types from small forested or wetland headwaters to larger mixed downstream sites. Modelling work concentrated on two main areas: modelling of Al fractionation; and retrospective / predictive modelling of the influence of anthropogenic sulphate on Al fractionation. The modelling work utilized two main models, WHAM for Al speciation (Tipping, 1994) and the pBDM for sulphate impact on stream ANC during springflood (Laudon, *et al.*, 2001).

Site Description

Sampling and modelling from Papers I, II and IV are from the upper 68 km² of the Krycklan river catchment (64°14'N, 10°46'E) in northern Sweden (Figure 1). This study site is the basis of a large multi-disciplinary study of the boreal spring flood period (more information at <http://ccrew.sek.slu.se>). The annual mean air temperature is 1° C, with 600 mm annual mean precipitation, of which one third falls as snow. The Krycklan catchment ranges from 130 to 369 meters in elevation. Throughout the catchment, gneissic bedrock is overlain by glacial till varying in thickness up to tens of meters (Ivarsson & Johnsson, 1988). Well-developed iron-podzol soils are common, with organic-rich soils near the channel of smaller streams (Bishop *et al.*, 1994). In the lower reaches of the catchment, larger streams have deeply incised channels carving through fine glaciofluvial sediments, with a substantial riparian floodplain. Brown trout (*Salmo trutta*), Brook trout (*Salvelinus fontinalis*) and Grayling (*Thymallus thymallus*) reside in the larger streams in the region.

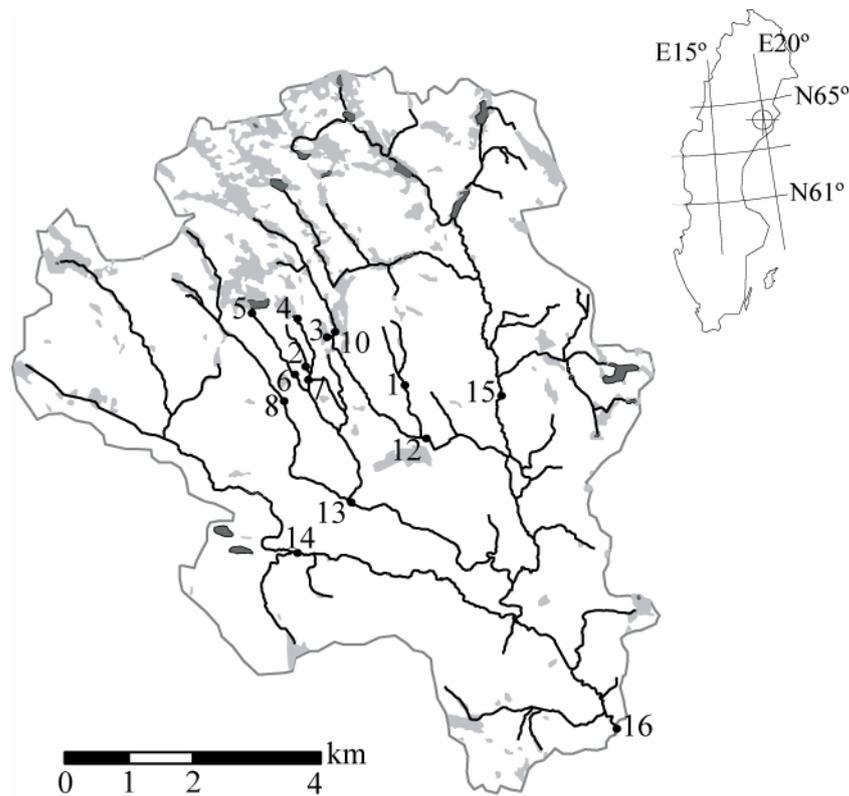


Fig. 1. The Krycklan catchment. Site numbers refer to sampling location for Papers II and IV, the transect for Paper I is located at Site 2. Areas of wetland (■) and lakes (■). The inset map shows the location of the catchment in Sweden.

The upland portions of the catchment are forested primarily with mature Scots Pine (*Pinus sylvestris*) and Norway Spruce (*Picea abies*). The forested landscape is interspersed with patches of sphagnum-dominated peat wetlands, making up 8% of the total area, but with a large percent coverage in some of the smaller subcatchments (Figure 1).

The catchment hydrology is dominated by a characteristic springflood. In northern Sweden the springflood is a critical hydrological period where up to half the annual discharge occurs over a period of three to four weeks during snowmelt (Bishop & Pettersson, 1996; Laudon, Westling & Bishop, 2000). This can lead to a characteristic acid pulse with snowmelt pH depressed by up to 2 pH units (Bishop, Laudon & Köhler, 2000; Laudon, Westling & Bishop, 2000; Laudon, *et al.*, 2001).

The location of sampling points used in Paper III are distributed throughout Sweden, encompassing both rivers and lakes. For more information see Paper III, or Wilander *et al.* (2003; 1998).

The Hillslope scale (Paper I)

Understanding how Al moves through the hillslope in a boreal environment is critical in determining if there is chronic or incipient soil acidification as well as understanding the source of Al entering the stream. Soil solution chemistry from a series of suction lysimeters placed down to a depth of 1m at increasing distances from the stream combined with hydrological data mean it is possible to study the integrated soil solution chemistry of lateral flow from the top meter of soil (Bishop *et al.*, 2004; Stähli *et al.*, 2001). This allows one to look for vertical and lateral fronts of Al likely to be associated with soil acidification (Eriksson, Karlton & Lundmark, 1992) and to study the possible influences of changes in flow pathways during episodes. Chemical analysis included a full charge balance, with the charge from organic acids determined using an empirical triprotic acid model (Köhler *et al.*, 2001). This allows one to relate changes in Al to changes in other factors along the hillslope. Al fractionation based on a cation exchange method (Driscoll, 1984), determined both the concentration and speciation of Al as it moves towards the stream. The solubility of Al was also assessed through the calculation of the organic carrying capacity (Buurman, 1985; Farmer & Lumsdon, 2001) and equilibrium with common mineral phases.

The Landscape scale (Paper II)

To assess the spatial and temporal patterns of stream water Al, a catchment wide survey of a 68km² boreal catchment was undertaken during the hydrologically important springflood period. Stream water grab samples were analysed for major chemical characteristics including Al speciation using cation exchange column method (Driscoll, 1984). By sampling the whole catchment, the landscape influences on Al concentration and speciation can be assessed, along with changes from headwater to downstream areas. Spatial distribution patterns are toxicologically important, since they reveal whether aquatic organisms can avoid less favourable areas (Gray, 1990). Although research specifically on avoidance of Al is limited (Åtland & Barlaup, 1995), increases in Al in low pH areas have been shown to increase avoidance behaviour in fish (Exley, 2000). This study seeks to redress the depth of landscape scale data during springflood in boreal landscapes where Al_i can be a critical limitation for the biota. Spatial data may also help resolve the degree to which Al_i in streams is determined by catchment sources or in-stream processes (*i.e.* how far downstream does the stream “remember” the effect of elevated Al as different waters mix and equilibrate to surface water conditions).

Modelling of Aluminium (Papers III & IV)

There are a number of obstacles within the environmental monitoring of specific Al fractions including prohibitive costs, sample handling and analytical uncertainty of cation exchange in organic rich environments. Modelling Al fractionation opens up several possibilities including the analysis of a larger number of samples, retroactive sampling and as the basis of more advanced

predictive modelling. Using an established mechanistic chemical equilibrium model (WHAM) that encompasses specific and non-specific binding by humic substances (Tipping, 1994) Al fractions can be modelled. In order to create an operational tool applicable in environmental modelling throughout Sweden, WHAM was calibrated using data from the national survey of rivers and lakes from 1995 and 2000 (Wilander, Johnson & Goedkoop, 2003; Wilander, *et al.*, 1998). The calibration process used systematic adjustment of the amount of fulvic acid active in binding cations to reduce the root mean square error between observed and modelled Al_i. The model assumes that humic substances consist of humic acids and fulvic acids (FA). As FA are more mobile they are assumed to make up the majority of dissolved organic matter (Tipping, 2002). WHAM regards FA as hypothetical spherical molecules carrying proton dissociating groups capable of binding metals by specific binding. These binding sites include strong and weak acids with different median pKa values. The non-specific binding occurs through accumulation in the diffuse double layer around the charged surface of the FA. As there is uncertainty in both the analytical data and the modelled data the final results are also assessed by placement in broad toxicological categories.

The second application of Al modelling is to predict the effects of anthropogenic sulphate on stream water concentrations of Al_i. Acidification and its effect on stream water pH and Al have had detrimental effects on aquatic biota in much of Europe and North America (Wright *et al.*, 2005). Acidification has the potential to affect both the concentration and speciation of Al in freshwater environments. Understanding patterns of Al_i in freshwater environments is central to understanding the distribution of acid sensitive fish. Historically sulphate deposition has been far higher than current levels with the peak in deposition in Sweden during the 1970s (Mylona, 1996). Assuming compliance with the 1999 Gothenburg Protocol to the Geneva Convention on Long-Range Transport of Air Pollutants a further reduction of 55% relative to 1990 levels can be expected by 2010 (Warfvinge & Bertills, 1999). To understand why we have the ecological communities in streams and lakes today it is important to understand the stresses these communities were exposed to earlier, and what these Al stresses will be in the future.

By combining an existing tool for prediction of how springflood is influenced by sulphate deposition (pBDM) with a cation binding model (WHAM), the effects of episodic acidification on stream water Al concentration and speciation can be studied. This approach is applied to an intensively studied catchment in northern Sweden from the period of peak sulphate deposition through to the implementation of current emission legislation (1970-2020). Sulphate deposition records and future predictions are combined with observed stream chemistry from 2004 for 15 sites covering a range of landscape characteristics. Through this approach it is possible to see the pressures which the landscape has been exposed to. By forecasting it will also be possible to assess potential gains under different emission control scenarios.

Results and Discussion

Aluminium at the Hillslope scale

The total Al concentrations in soil solution exhibit consistent and distinct profiles along both the vertical and horizontal axes of the transect. In the areas upslope of the riparian zone (~80% of this catchment), water enters the hillslope as precipitation moving vertically down through the mor layer, where Al, H⁺ and DOC concentrations are high. This is a feature of the podzolization process with higher Al concentrations just below the organic horizon (Lundström *et al.*, 2000). In the upslope areas this gives a sharp vertical decline in Al concentration from ca 1000 µg·L⁻¹ at 10cm depth, just beneath the organic mor layer, to less than 100 µg·L⁻¹ from ca 20cm depth and below. Further downslope, entering the organic-rich soils of the riparian zone 4m from the stream, the decline in Al concentration with depth is more gradual, with concentrations above 200 µg·L⁻¹ commonly found down to 70cm depth. In the riparian zone, the highest concentrations of Al are found deeper in the soil profile (at ca 30cm depth), and the peak is much broader (Figure 2). The Al concentrations are also much higher in the riparian zone, compared to upslope plots. This defines the horizontal trend of increasing Al levels from the upslope profiles towards the stream.

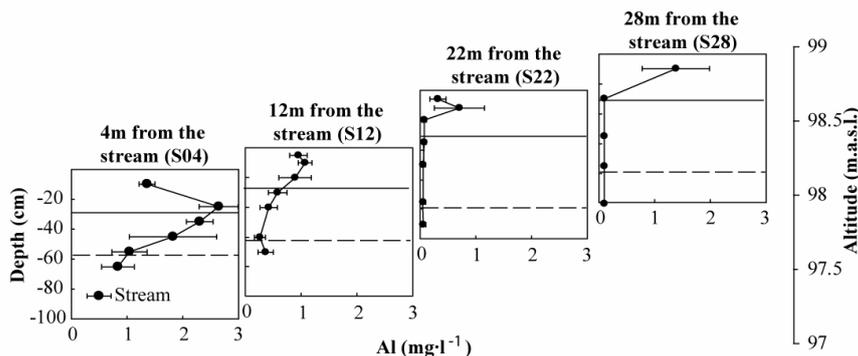


Fig. 2. Total Al during the period 1996-1998. Dashed horizontal reference lines indicate the median groundwater level and solid reference lines the flow-weighted mean groundwater level. The “error bars” on each dot indicate the range of the 9-22 observations.

The hydrology of the transect showed strong patterns in flow pathways during different periods of discharge. During peak flow, the water table is elevated and more of the flow moves laterally at superficial depths due to the higher hydraulic conductivity closer to the soil surface (Bishop, 1991; Laudon *et al.*, 2004; Nyberg *et al.*, 2001). In the upslope areas, these superficial pathways traverse soils with low solution Al concentrations. Nearer the stream, and especially in the riparian zone, more superficial high flow pathways traverse soils with higher solution levels of DOC, H⁺ and Al.

The organic carrying capacity of the DOC was in excess of total Al in all samples. The excess carrying capacity was largest in the O horizon of all four

profiles and in the organic rich peat of the riparian zone. The fraction present as Al^{3+} showed undersaturation with regards to proto-Imogolite and amorphous Gibbsite in all but two of the samples, these were the samples from the deepest samples at 12m and 22m from the stream. No samples showed more than 10 times super saturation of these mineral phases. This implies that an organic phase control of Al may play an important role in solubility and mobilization of Al (Berggren & Mulder, 1995; Simonsson & Berggren, 1998; Skyllberg & Magnusson, 1995).

The observed changes in Al along the transect are related to changes in other constituents that combine to preserve the electro-neutrality of the soil solution. Therefore, changes in the full charge balance as well as changes in DOC may provide clues to the controls on Al transport through the catchment to the stream. A cross-section of the soil and stream water chemistry taken from the transect on June 3rd 1998, represents the evolution of soil solution chemistry as it moves along the transect (Figure 3). The relative changes in soil solution chemistry along the slope are largest for Al and DOC. There is no other apparent counter-ion to explain the changes in Al. The large increase in “unknown” is interpreted as more organic acid dissociation and binding than provided by the organic acid model used.

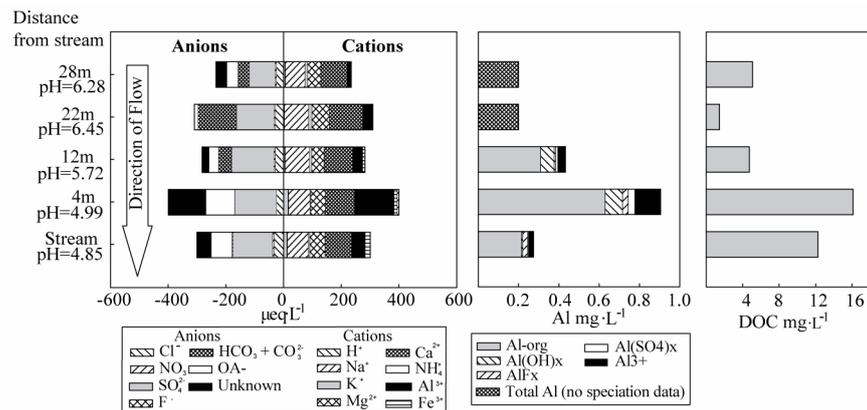


Fig. 3. Snap shot of the vertically integrated soil solution chemistry of soil water on June 3rd, 1998, as it moves downslope towards the stream. The diagram represents how the laterally flowing water (integrated over the depth of the soil profile) evolves downslope, moving from 28m to the stream. The direction of flow is in the downward direction of the large arrow. Left panel - mass balance of the major anions and cations. Central panel - speciated Al. Right panel - DOC.

Another key feature of Al evolution revealed by the transect cross-section is that the organic soils of the riparian zone serve as a source of Al (as well as DOC). This poses a paradox since the mineral source areas of Al in the upslope areas have significantly lower Al solution concentrations than the riparian zone. This implies that the riparian zone Al pool has built up earlier, or is being replenished episodically at peak flow. During episodic flow the superficial flow pathway is about 10 centimetres from organic rich layers. This could provide a source of

organic acids enabling a lateral transport of Al from the up-slope areas to the near stream zone. A portion of the Al moving laterally during episodes could be retained in the riparian zone, bound to the solid phase peat material in the near stream zone. The peat has developed in this near stream zone since the last glaciation (~6000 y.a.). Repeated cycles of episodic lateral flow followed by peat development could lead to the build up of elevated Al concentrations in this organic zone. The Al build up could have been facilitated by the constant creation of new peat, thereby providing new binding sites.

An alternative explanation for the Al that has accumulated in the riparian zone could be a recent change in the hydrology of the transect from the situation which had existed since the last glaciation. Starting in the late 1800's and into the latter half of the 1900's, stream deepening was undertaken extensively in Sweden to improve drainage. It is now difficult to find any headwater streams which have not been subjected to drainage in Sweden (Dahlström, 2005). The channel in this study was deepened over half a meter in the 1920's by ditching. This lowered the flow pathways and therefore may have disturbed the natural cycle of lateral transport and binding in the riparian zone which had occurred for thousands of years. Assuming this ditching effect has occurred, then this widely used practice for improving forest productivity might have permanently changed flow pathways and induced elevated Al concentrations during episodes of high flow in many streams.

While the effect of such hydrological change will vary from site to site, deeper flow paths may have reduced downslope transport of Al from mineral soils. The deeper flow paths might also be expected to change Al and DOC export to the stream during low flow periods, as well as accentuating increases in Al and DOC export during episodes of high flow.

The potential for Al concentrations to be modified during transport through the riparian zone needs to be accounted for in efforts to relate acid deposition to bio-toxic stream Al concentrations in areas such as boreal Sweden where soil acidification has lowered stream pH only marginally. Understanding the controlling mechanisms for Al transport within the soil, during discharge and also in the stream are critical to evaluating human influence on Al due to both atmospheric deposition and physical changes in the terrestrial environment. It appears from this study, that biologically significant levels of Al in the stream do not necessarily imply that acidification has mobilized Al in the soils.

Spatial and Temporal variations at the landscape scale

The spatial and temporal variations seen within a single catchment can be linked to the landcover of the drainage area, and specifically to the percentage of wetland cover. Although the solubility of Al is often linked strongly to pH (Simonsson, 2000; Skyllberg, 1999), the results of this study showed that Al concentration was controlled by source limitation as well as pH. By source limitation we mean that

there must be both a source of Al within the drainage area combined with low pH in order to have elevated Al in the stream.

Sites draining wetland areas were characterised by low pH throughout the springflood, but accompanied by low Al concentrations due to the lack of mineral soils in their drainage areas. This is in agreement with previous work within the study area, with wetland sites showing significantly lower Al than more forested sites (Hruska *et al.*, 2001). The lack of a weathering source for Al in wetlands, and an abundance of solid phase organic binding sites means little Al is mobilized from wetlands into the stream by acidic runoff water (Figure 4). Forested sites showed a characteristic drop in pH and increase in DOC associated with the activation of more superficial, organic rich flow pathways (Bishop, *et al.*, 2004). In the forested sites where the supply of Al is not restricted due to the presence of mineral soils, the decline in pH during spring flood is associated with increased mobilization and transport of Al from the soil (or streambed) to the stream (Figure 4).

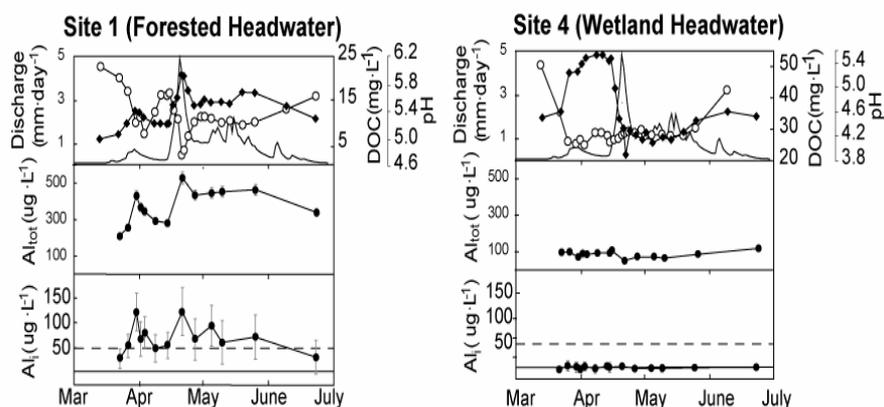


Fig. 4. Variations in Al and related parameters during spring flood. The upper panel shows DOC (solid line with black markers) and pH (solid line with white markers) and discharge from a representative site with continuous discharge measurement (solid grey line, no markers). The central panel shows total Aluminium (Al_{tot}) with analytical uncertainty as error bars. The lower panel shows Al_i with analytical uncertainty as error bars, and a proposed limit for acute Al_i toxicity (Ytrestoyl, Finstad & McKinley, 2001) as shown with a broken grey line.

The solubility of Al in these samples appears to be, as with the wetland sites, dominated by the organic phase. This is reflected in both the excess organic carrying capacity and the undersaturation with respect to commonly formed hydroxylaluminium and hydroxylaluminium silicates. The speciation of Al was dominated by the organically bound fraction at all sites. In the forested catchment sites this could be explained by the flow through the near stream peats just before discharge to the stream (Bishop *et al.*, 1995; Bishop, *et al.*, 2004). The link between Al concentration and flow pathways has also been observed by Palmer *et al.* (2005), where shallow slopes and thicker soils were linked with increased Al_o concentrations. Differences in DOC dynamics between forested and wetland sites were also clearly seen in the Al:DOC ratio which was lower in wetland sites and

higher in forested sites. Similar patterns were also seen by Hruska *et al.* (2001), where the $Al_o:DOC$ ratio (almost analogous with $Al_{tot}:DOC$ due to the dominance of the Al_o fraction) was higher in forested sites than sites draining wetlands. The $Al:DOC$ ratios were relatively stable throughout the spring flood for all sites.

The most biologically relevant data are the concentrations of Al_i , but setting simple toxicity thresholds is difficult because tolerances vary with both the species studied as well as DOC (Herrmann, 2001; Poleo, *et al.*, 1997). Many published studies use Atlantic salmon (*Salmo salar*), which although more sensitive than the species found naturally in the Krycklan streams can help to give a general idea of toxicological limits. Of the 14 streams sampled in this study only three sites (all forest dominated) showed concentrations of Al_i deemed to be acutely toxic (Ytrestoyl, Finstad & McKinley, 2001), with two further sites showing prolonged levels which are deemed chronically toxic (Ytrestoyl, Finstad & McKinley, 2001). The other nine sites in the study catchment remained below the toxicity limits for Atlantic salmon. None of the sites with higher wetland areas exceed these limits, despite pH values between 4 and 5. So despite Al_{tot} concentrations well above $100\mu g \cdot L^{-1}$ in many sites, only a few show toxic levels of Al_i . This suggests that while hazard zones with elevated Al_i may exist, there can also be safe havens where Al_i concentrations are low due to lack of Al weathering sources or the presence of binding ligands. The high levels of DOC, though, result in lower pH which in itself may pose a toxicological issue.

Overall, the importance of landscape in controlling both the spatial distribution and the potential toxicological impact of Al in the catchment is evident. The concentrations of both Al_{tot} and Al_i appear to be governed by the interplay between Al sources, DOC concentration and pH, all of which are linked to the landscape in the drainage areas. This means that the Al chemistry in larger downstream sites, which are important for fish populations, is influenced by the landcover in the headwaters via contributions of runoff and Al to the stream network.

Modelling inorganic Aluminium

Calibration of the mechanistic, equilibrium model WHAM for the modelling of inorganic Al (Al_i) from total Aluminium (Al_{tot}) in the often organic rich surface waters of Sweden opens up a wide range of possibilities. Currently Al speciation is undertaken on only a subset of national lake and stream survey samples. This is partly due to the fact that many samples have a circumneutral pH, and therefore little Al_i . Another reason, though, is the prohibitive cost and analytical uncertainty in organic rich waters. Modelling of Al_i from Al_{tot} can act as a complement to laboratory fractionation, and also allow samples to be retroactively examined.

A preliminary sensitivity analysis identified the critical input variables for WHAM as Al_{tot} , pH, TOC and Fluoride which all gave a deviation in Al_i from the mean sample of 100% or greater. To a less extent Iron, Calcium and Magnesium were also significant in the modelling with variation between 10-100%.

Potassium, Sodium, Chloride, and Sulphate all gave deviation in Al_i from the mean sample of <10%. A further consideration was the use of filtered or unfiltered samples, during episodic conditions elevated levels of particulate bound Al were identified which could influence modelled results.

The calibration procedure identified a systematic variation in optimal calibration when subdivided by pH, with individual calibrations for pH <5, pH 5-6 and pH >6 providing the best results. When assessing modelled Al_i concentrations reasonable success in model calibration of Al_i was achieved in the lake samples from 2000 (Spearman's rho 0.59, n=299), however this was lower in 1995 (Spearman's rho 0.50, n=299) and poor in the river samples from 2000 (Spearman's rho 0.19, n=203) (Figure 5). However, Al_i is normally of interest to environmental monitoring due to its toxic effects at elevated concentrations, meaning it is relevant to consider the error in classifying toxicity, rather than the absolute error. Although Al toxicity varies widely with fish species (Poleo, *et al.*, 1997) boundaries have been proposed for the commonly studied atlantic salmon (*Salmo salar*) (Ytrestoyl, Finstad & McKinley, 2001) and these are in close agreement with guidelines published by the Swedish Environmental Protection Agency (SEPA, 2002). When viewed from this toxicological viewpoint, the modelling had a high success rate in all three data sets with correct placement for 89-95% of the samples into toxicological categories (Al_i : <30 $\mu\text{g}\cdot\text{L}^{-1}$, 30-50 $\mu\text{g}\cdot\text{L}^{-1}$, >50 $\mu\text{g}\cdot\text{L}^{-1}$) (Figure 5).

Calibration is always critical in modelling, and if WHAM is to be used as an environmental monitoring tool it is important that, once calibrated, the model can be applied outside the calibration data. In the absence of a second data set of similar size and spatial distribution on which a validation could be performed, a reduction of the calibration data set allowed the robustness of the modelling to be tested. WHAM was systematically calibrated with a smaller randomly selected fraction of each data set (100%, 75%, 50%, 25% and 5%) and then applied to the remaining data. The results showed a successively decrease in the correlations and, to a lesser extent, increasing error in toxicological classification with decreasing size of the calibration data set. The correlation between modelled and observed Al_i (Spearman rho values) was approximately halved when the calibration set was only 5% of the target data. The ability to model toxicological class was minimally affected in all cases, with a change of $\leq 4\%$ for both rivers and lakes.

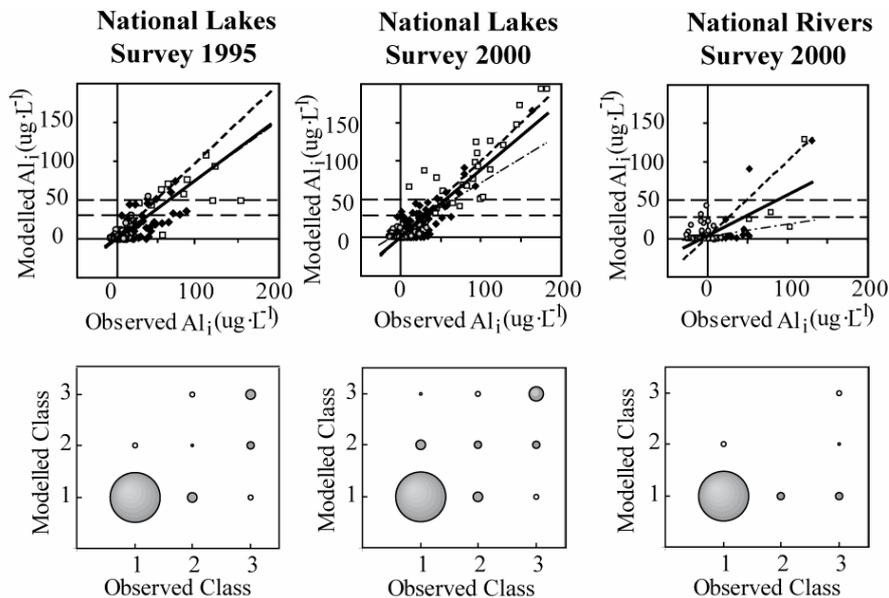


Fig. 5. Modelling of Swedish national lakes and river survey data using WHAM. Top panels show correlations between observed laboratory fractionation and modelled speciation: symbols represent the pH classes used in calibration (pH <5 (white square), pH 5-6 (black diamond), pH >6 (grey circle). The dashed black line is a 1:1 fit. The solid black line is the composite fit using separate pH classes, and the patterned line (dash-dot-dash) is the fit with no pH sub-classes. Horizontal reference lines show $30\mu\text{g}\cdot\text{L}^{-1}$ and $50\mu\text{g}\cdot\text{L}^{-1}$ Al_i . The lower panels show the distribution of samples when assigned a toxicological class (Al_i : Class 1 $<30\mu\text{g}\cdot\text{L}^{-1}$, Class 2 $30\text{-}50\mu\text{g}\cdot\text{L}^{-1}$, Class 3 $>50\mu\text{g}\cdot\text{L}^{-1}$).

The accuracy of modelling Al speciation on a national level using WHAM software depends strongly on both the perspective of the modeller and the intended application of the results. Results of the continuous assessment varied markedly between data sets and were strongly influenced by the distribution of data. Toxicological assessment of the samples into classes achieved good overall results, but accuracy at elevated concentrations was significantly lower, presumably due to the strong bias towards low Al_i samples in the calibration data. Increasing the number of samples with $\text{Al}_i >30\mu\text{g}\cdot\text{L}^{-1}$ in the calibration would help improve the modelling of these samples. The high accuracy of the toxicological assessment is also re-enforced by the skewed distribution of calibration data allowing for a wide margin of error. With an emphasis on improving calibration data, and provided the necessary input data are available, it is possible to calibrate WHAM to model Al_i speciation in surface waters with reasonable accuracy.

Retroactive and predictive modelling of inorganic Aluminium

Sulphate deposition peaked in northern Sweden in the 1970s and had declined by 65% by 1990 (Mylona, 1996). Assuming compliance with the 1999 Gothenburg Protocol to the Geneva Convention on Long-Range Transport of Air Pollutants a further reduction of 55% relative to 1990 levels can be expected by 2010

(Warfvinge & Bertills, 1999). Modelling how these changes in anthropogenic deposition have affected Al_i in surface waters during spring flood will aid in understanding the present and future stresses on aquatic environments in northern Sweden and other boreal regions.

The modelled pH from 1970 based on the pBDM prediction of ANC, combined with the triprotic acid model (Köhler, *et al.*, 2001) and an assumption of unchanged DOC as well as Al_{tot} , predicted lower pH and higher Al_i^{n+} throughout the Krycklan catchment compared to 2004 values. The landscape influence on Al_i is apparent with areas of wetlands showing lower Al_i^{n+} concentrations than forested sites despite having significantly lower pH (Figure 6, Table 1). In 2004, the Al speciation at all sites was dominated by the organic phase with the fraction bound to organic matter >80%. The make up of the remaining Al_i^{n+} fraction is strongly dependant on the pH of the system. During low flow conditions the relatively high pH means that $Al(OH)_x^{n+}$ dominate. During peak flow, principally in the more forested sites, the pH drops and aquo-Al (Al^{3+}) becomes a more dominant fraction.

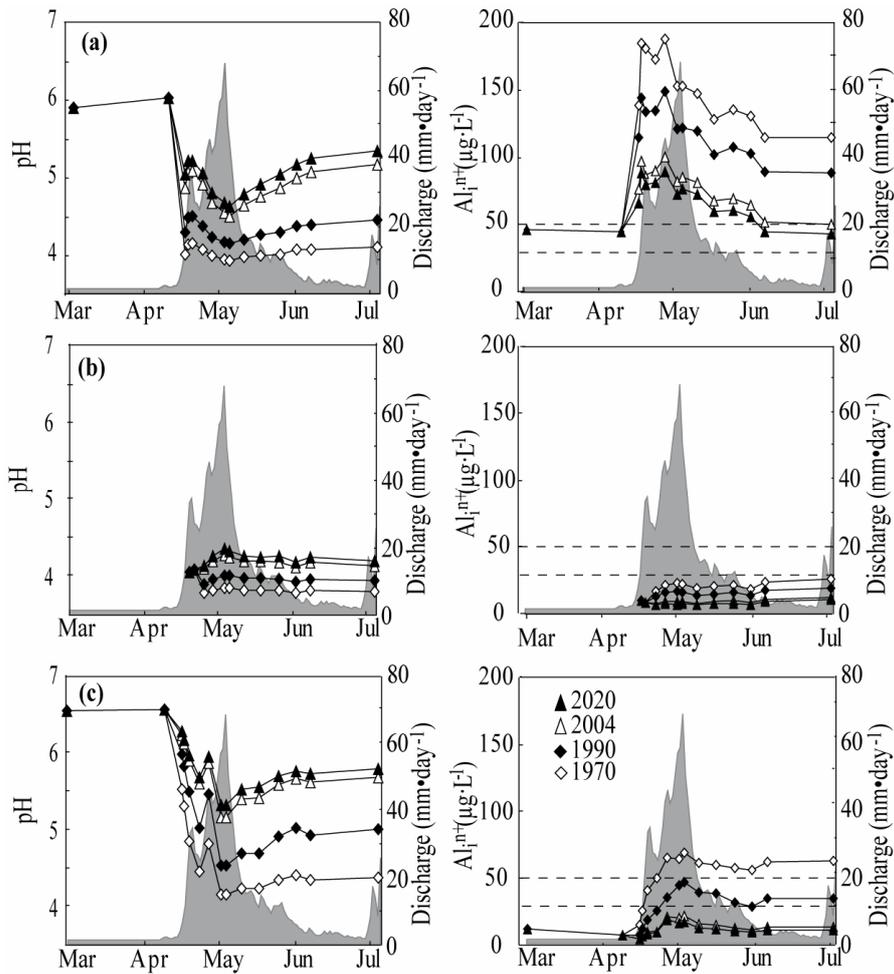


Fig. 6. Response in pH and Al_i^{n+} during spring flood for three characteristic sites in the catchment, (a) Site 2, forested headwater, (b) Site 3, wetland headwater and (c) Site 13, mixed downstream site. Data shown for 1970 (white diamond markers), 1990 (filled diamond markers), 2004 (white triangle markers) and 2020 (filled triangle markers).

The reduction in the inorganic phase from 1970 to 2020, was compensated by an increased fraction in the organic phase with the overall Al_o fraction increasing from $81 \pm 9\%$ in 1970 to $94 \pm 4\%$ by 2020. The speciation of the inorganic phase also changed during the period 1970-2020, due to the increasing pH. The average valency associated with Al_i^{n+} decreased from 1.80 in 1970 to 1.53 by 2020 (Table 1).

Table 1. Al_i^{n+} given as a mean values ($\mu\text{g}\cdot\text{L}^{-1}$) along with standard deviation. The average valency of Al_i^{n+} is given in parentheses.

Al_i^{n+}	Forested Headwaters	Wetland Headwaters	Mixed Downstream
1970	121±47 (2.06)	14±7 (2.04)	41±24 (1.72)
1990	92±37 (1.93)	10±5 (1.98)	26±18 (1.68)
2004	59±25 (1.73)	5±3 (1.89)	4±3 (1.56)
2020	53±23 (1.69)	4±3 (1.87)	12±9 (1.45)

The reductions seen in modelled Al_i^{n+} from 1970-2020, translated into a reduction in the number of samples exceeding toxicological boundaries. The observed and predicted sulphate reductions from 1970 to 2020 resulted in a decline of spring flood sampling occasions exceeding limits for acid tolerant and acid sensitive species from 48% and 40% to 15% and 6% respectively, using SEPA (2002) guidelines for Al ecotoxicology. The landscape variation gives a spatial aspect to the effects of sulphate deposition (Table 2). Forested headwater sites show exceedence in the highest Al_i category for the entire study period, whilst wetland sites show concentrations which never exceed toxicological Al_i limits despite having the lowest pH values. The remaining sites show exceedence of toxicological limits in the period 1970-1990, however for the more recent period and onwards (2004-2020) the majority of sites are below toxicological limits (Table 2).

Table 2. Classification of stream Al_i^{n+} concentrations into toxicological classes

Site Nr	Site Type	Al_i^{n+} (1)			
		1970	1990	2004	2020
1	Forested (> 99% forest)	Black	Black	Black	Black
2		Black	Black	Black	Black
7		Black	Black	Grey	Grey
8		Black	Black	Grey	Grey
12	Forest dominated (>85% forest, <16% wetlands)	Black	Black	Black	Black
13		Black	Black	Black	Black
14		Black	Black	Black	Black
15		Black	Black	Black	Black
16	Significant wetlands (>24% wetlands)	Black	Black	Black	Black
5		Black	Black	Black	Black
6		Black	Black	Black	Black
10		Black	Black	Black	Black
3	Wetlands (>40% wetland)	Black	Black	Black	Black
4		Black	Black	Black	Black

(1) Classification for Al_i^{n+} is shown as:
 White - no toxicity ($<30\mu\text{g}\cdot\text{L}^{-1} Al_i^{n+}$)
 Grey - toxicity to acid sensitive species ($30\text{-}50\mu\text{g}\cdot\text{L}^{-1} Al_i^{n+}$)
 Black - toxicity to acid tolerant species ($>50\mu\text{g}\cdot\text{L}^{-1} Al_i^{n+}$)

Our modelling has focused on the effects of pH upon Al speciation, and has not permitted a change in Al_{tot} (DOC is also assumed to be unchanged) either from an increased flux from the soil in response to higher levels of acid deposition or due to precipitation of Al as pH rises. This assumption is supported by stable Al_{tot} values in one of the monitored site over the last decade (unpublished monitoring data available at www.ma.slu.se), and the lack of an Al “acidification” front in a hillslope transect study on the catchment of stream 7 (Paper I)(Cory *et al.*, in review). However, MAGIC modelling of a severely acidified catchment in the Czech Republic predicted a reduction in Al_{tot} of 38% between 1992 and 2000 (Hruska, Moldan & Kram, 2002). The sensitivity analysis in this study assessed the variation which could be introduced by a higher Al_{tot} concentration during peak sulphate deposition, for example by the effects of soil acidification lowering soil pH and giving rise to larger flux of Al_{tot} from soil to stream (Simonsson, 2000; Skyllberg, 1999). In all cases, an increase in the concentration of Al_{tot} resulted in an increase in predicted Al_i^{n+} . In some sites from 1970 the pH was still low enough for this increase to occur as strong cationic fractions (e.g. Al^{3+}), shown by a higher average valency of Al_i^{n+} . This could be of toxicological importance due to the increased binding strength of di- and tri-valent ions. As sulphate deposition decreased resulting in higher pH values the addition of Al_{tot} resulted in hydrolysis of the Al to give $Al(OH)_x$ species, giving a smaller changes in average valency for Al_i^{n+} . As Al buffering is not explicitly accounted for in the modelling of pH, these results are likely to be an overestimation of the effect on Al_i^{n+} .

When viewed from a broader perspective, the recovery seen here is in line with other research showing a general chemical recovery in Europe (Wright, *et al.*, 2005), albeit more rapid and complete. Wider scale monitoring projects have mostly focused on changes in ANC rather than specifically on Al_i , however

smaller scale monitoring projects have shown significant reductions in Al_i in response to decreased sulphate deposition (Skjelkvåle *et al.*, 2001). Improvement however, is not unilateral, for example research in the Adirondack and Catskill regions of western North America showed little reduction in response to emission control for concentrations of soil and freshwater Al (Chen & Driscoll, 2004). Recent MAGIC modelling work in Norway (Larssen, 2005) notes the large gains made in the last 20 years, and, in line with the results presented in this study, predicts limited further improvement in the coming years under current deposition legislation. Although the general picture of a recovery from acidification is optimistic, a chemical recovery does not necessarily imply a return to pre-industrial biological conditions (Wright, *et al.*, 2005) due to the long term stresses these communities were exposed to earlier. Much of the focus today is on tracking the biological recovery of chronically acidified areas, but it is also important to consider that all areas with springflood conditions are essentially recovering ecosystems. These areas of episodic acidity merit study of how the biota is responding to major improvements in springflood chemistry as they return towards the natural levels of springflood acidity and associated Al dynamics.

Conclusions

By following the Al dynamics from mineral source through to toxicological impacts on aquatic organisms one can have a better understanding of the Al cycle and how anthropogenic activities can affect it. It has been shown in the results presented here that there is no clear acidification front of Al at the hillslope level, indicating that chronic soil acidification is unlikely. Rather, it is water flowing through the organically rich, transiently saturated superficial flow pathways which is important in controlling the mobilization of Al from catchment soils to stream. The riparian zone has been shown to be both an important source and sink of Al, with previous long term build up in the near stream peats which now appear to act as a source of Al to the stream. At the landscape scale, organic matter is also important, with the combination of pH and source limitation being the key factors controlling Al concentration and speciation in the stream. Areas draining wetlands have low concentrations of Al despite high levels of acidity, due to the lack of a mineral source in the drainage area. This gives a large natural spatial variability in Al concentration and toxicity.

The modelling of Al_i is feasible for toxicological classification. Modelling of Al_i was consistent even at the national scale, and this opens possibilities of predicting Al toxicity in a far larger number of sites than previously undertaken. Combining the modelling of Al_i with retroactive and predictive modelling of stream chemistry during spring flood means we can model both past and future stresses to aquatic ecosystems from the impacts of acidification in the boreal zone. Retroactive and predictive modelling of Al_i showed that in northern Sweden Al_i concentrations were ~10 times higher during the period of peak sulphate deposition (1970s). Al_i also had a significantly higher average valency. Assuming continued deposition decline in compliance with current emission control legislation, predicted Al_i by

2020 concentration will exceed toxicological limits only in smaller forested headwaters of northern Sweden. Modelling of this type is critical in understanding the ecological communities we have in streams and lakes today, and in predicting how further controls on anthropogenic emission may affect them in the future.

Key findings

- o No acidification front was seen in a hillslope transect at an intensively studied forest headwater site in northern Sweden. This implies that chronic soil acidification has not mobilized Al, but the eventual effects of incipient acidification on Al export to surface waters need to be considered.
- o The dominant discharge-weighted flow pathways pass through the superficial, transiently saturated organic rich layer at ~30cm depth in the riparian zone.
- o A large build up of Al is seen in the riparian peats, these now act as a source of Al to the stream. But these same soils must be (or have been) sinks at some time in order to accumulate the Al now there.
- o The landscape distribution of Al is strongly dependant on the landcover. Areas with significant wetlands have no mineral source of Al and therefore despite low pH have low concentrations of Al. Forested sites show higher concentrations of Al, especially during springflood when pH is depressed.
- o Concentrations of Al_i can be successfully modelled using the mechanistic chemical equilibrium model WHAM. The modelling of exact concentrations was problematic, but modelling of toxicological classification had a high success rate.
- o Retroactive and predictive modelling of Al_i showed that in northern Sweden Al_i concentrations were ~10 times higher during the period of peak sulphate deposition (1970s). Al_i also had a significantly higher average valency. Assuming continued deposition decline in compliance with current emission control legislation, predicted Al_i by 2020 concentration will exceed toxicological limits only in smaller forested headwaters of northern Sweden.

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I



The evolution of soil solution Aluminium during transport along a forested boreal hillslope

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Abstract

Aluminium (Al) transfer from soils to surface waters is a crucial determinant of aquatic biodiversity in acidified and/or naturally acid surface waters. Defining how landscapes and acid deposition influence Al export depends on our understanding of the mobilization of Al within catchments. This paper documents the evolution of Al chemistry in water during its transport through a hillslope by using soil water chemistry combined with hydrometric data. Al levels moving laterally from upslope mineral soils were low. This is not consistent with a vertically infiltrating acidification front mobilizing Al from across the catchment. As water moves downslope into the peaty soils of the riparian zone, Al increased along with organic acids and iron. The riparian zone (RZ) on the transect in this study was thus a net source of Al on all 9 sampling occasions where Al was measured, as well as a net source of dissolved organic carbon (DOC) on dozen measurement occasions. The potential for Al concentrations being modified during transport through the RZ needs to be accounted for in efforts to relate acid deposition to bio-toxic stream Al concentrations. Organic carrying capacity was in excess of Al for all samples. None of the samples showed supersaturation with regards to the given mineral phases. Oversaturation was observed for samples from the deeper mineral soils of the upslope areas. A key area for further research is how the RZ can sustain a larger Al pool than upslope mineral soils when the source of the Al in the RZ is presumably the upslope mineral soils that currently output less Al than is found in the RZ. Two possibilities are either episodic downslope transport during periods of high lateral flow, or drainage-induced changes in hydrology that transformed the RZ from an accumulator of Al to a source of Al.

Key words: Aluminium, Soil, Stream, Transect, Transport, Acidification

Introduction

Anthropogenic acidification of soils and surface waters has increased the concentration of inorganic Aluminum (Al_i) in many areas. In Sweden, the degree of acidification and concentrations of Al_i are generally lower in the north than in the south (Wilander, Johnson & Goedkoop, 2003; Wilander *et al.*, 1998). However it is still common to find Al concentrations in excess of limits known to cause toxic effects in aquatic fauna in both the north and south of Sweden (Poleo *et al.*, 1997). This anthropogenic impact is superimposed upon natural Al levels mobilized by podzol formation. The highest Al concentrations in the northern regions are found during spring flood when up to half the annual discharge occurs over a period of three to four weeks (Bishop & Pettersson, 1996; Laudon *et al.*, 2005) giving a characteristic “acid shock”. This coincides with sensitive life stages of aquatic organisms (Poleo & Muniz, 1993). The general explanation of toxic Al levels has been that soil acidification has mobilized Al from catchments into stream (Simonsson, 2000; Skjellberg, 1999). Recent research on the causes of this acid shock, however, has shown that during the late 1990’s, only 5-10% of the pH drop in boreal Swedish streams during snowmelt was due to atmospheric deposition (Laudon & Hemond, 2002). This raises the question of whether the bio-toxic levels of Al_i during spring flood are a natural phenomena or whether they are an effect of incipient acidification. By incipient acidification we mean that even though acid deposition may not be lowering the pH in runoff by more than one or two tenths of a pH unit, the soil acidification which neutralizes anthropogenic acid deposition (ca. 1-2 Kg S/ha/yr since the latter half of the 1990’s) is mobilizing Al from the soil, thus increasing Al_{tot} and Al_i in runoff.

Streamwater Al must have been derived from the surrounding soil. Therefore it is important to understand the relationship between Al in the stream and Al mobilisation in the soil, as well as how acidification has altered that connection. This also provides insight into related questions of how climate and land-use change will affect stream water Al . Detailed data on transport through catchments are few, and so far the modeling of aluminum export in many widely used biogeochemical models is still not mechanistic e.g. MAGIC (Cosby *et al.*, 1985; Sullivan & Cosby, 1995), WITCH (Godderis *et al.*, 2006).

Acid deposition will create an acidification front in the soil profile due to vertical percolation of acidified precipitation (Eriksson, Karlton & Lundmark, 1992). Deeper in the soil, lateral flow can transport Al mobilized by soil acidification downslope to the stream network. In some areas, the export of Al from soils has been explicitly linked to soil acidification (Cronan & Schofield, 1979; Dickson, 1980; Kirchner & Lydersen, 1995). However several studies have found lateral transport and accumulation of Al near the stream in the riparian zone (RZ) of pristine sites both in Europe (Mulder, Pijpers & Christophersen, 1991; Stieglitz *et al.*, 2003; Vogt & Muniz, 1997) and north America (Palmer *et al.*, 2005). This natural accumulation in the riparian zone has generally been attributed to episodic changes in flowpathways, and co-transport with organic matter.

Ideally, one would like to separate the effect of acid deposition from natural processes on the export of Al from catchments to soils. A useful step towards this will be documenting the evolution of Al in soil solution chemistry as it moves through the catchment towards the stream. Of particular interest in boreal till soils will be how the concentrations in shallow ground water a few meters from the stream relate to upslope areas. The near stream zone of such catchments has been shown to be the proximal source of much stream runoff and its associated chemistry (Bishop, Grip & O'Neill, 1990; Hinton, Schiff & English, 1998). The upslope areas, however, are more extensive and provide much of the water which comes out of the RZ into the stream.

This study investigates a hillslope in northern Sweden to see how Al concentration and speciation evolve as water is transported downslope along a two dimensional hillslope transect. To support the interpretation, other dissolved parameters are measured or modelled, and the pattern of extractable Al on the solid phase along the hillslope is reported. A key feature of the analysis is to examine factors which co-vary with Al and its speciation. While many of the parameters studied can be directly measured, organic acid charge and the bicarbonate system charge contributions need to be modelled.

Site description and research setup

Site description

The study hillslope is located on the Västrabäcken stream (figure 1) that drains a 13.3 ha subcatchment of the Svartberget Research Catchment, located ~60 km inland from the Baltic Sea in Northern Sweden (64°14'N, 19°46'E). The elevation in the catchment ranges from 235 to 310 m above sea level. The catchment is mainly covered by Scots pine (*Pinus sylvestris*) in the upper, drier areas and by Norway spruce (*Picea abies*) in the lower areas.

A locally derived glacial till with an average thickness of 10-15m overlays gneissic bedrock. Soils are predominantly well-developed iron podzols that fade into Gleysoils and then humic Gleysols with peat deposits of more than 0.5m in the riparian zone near the stream channel. Due to the glacial till of the area, the soil is less compact near the surface allowing a greater transmission of water in more superficial pathways in a mechanism described as transmissivity feedback (Bishop, 1991; Seibert, Rodhe & Bishop, 2003). At high flow conditions such as a spring flood it is the superficial, transiently saturated pathways that dominate the lateral transport (Laudon *et al.*, 2004; Stähli *et al.*, 2001).

Most headwater streams in Sweden, this study site included, have been deepened in the last century to improve drainage and forest productivity (Dahlström, 2005). Around 1920 Västrabäcken was deepened by *ca* 50 cm which will have lowered the flow pathways, especially in the near stream zone.

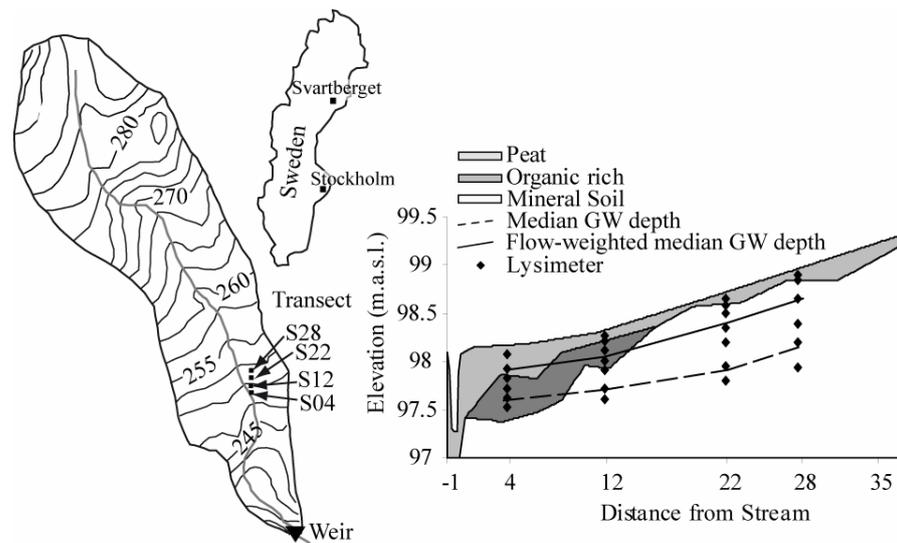


Fig. 1. The Västrabäcken catchment in Northern Sweden and a cross section of the hillslope transect showing the location of suction lysimeters in relation to the soil organic content and the groundwater level. Note the difference between the median GW depth and the volume-weighted mean flow path. Most of the runoff during episodes of high flow moves laterally through the upper transiently saturated zone (Bishop *et al.*, 2004; Laudon, *et al.*, 2004; Stähli, *et al.*, 2001)

The soil solution data used in this study was collected from a series of suction lysimeters. These were installed at distances of 4m, 12m, 22m and 28m from the study stream (S04, S12, S22, S28) along the local topographic fall line to follow the downslope movement of water. The porous ceramic cup lysimeters were installed in triplicate at seven depths from 6cm to 90cm in autumn 1995 (figure 1). Solid soil samples were taken from the vicinity of the soil lysimeters at that time. Weekly stream water samples were taken at the weir just above the confluence of Västrabäcken and the main channel. Soil solution from the transect (some 20 points with 2-3 replicates of each point) was measured for pH and TOC during 1996-1998 on 22 occasions. Complete soil water anion and cation analyses were performed on 9 of these occasions during 1997-1998. The flow situation on these 9 occasions varied from $0.1 \text{ mm}\cdot\text{day}^{-1}$ to $1.7 \text{ mm}\cdot\text{day}^{-1}$. Discharge measurements were made using a 90° thin plate V-notch weir where stage height was recorded with a pressure transducer connected to a Campbell Scientific data logger. Mean baseflow for the period 1996-1998 was $0.37 \text{ mm}\cdot\text{day}^{-1}$ and mean springflood flow $2.8 \text{ mm}\cdot\text{day}^{-1}$ with a peakflow of $6.5\text{-}8 \text{ mm}\cdot\text{day}^{-1}$. Groundwater level was measured manually on a regular basis between 1996 and 1998. A groundwater level-stream discharge relationship was constructed (Nyberg *et al.* 2001). This relationship and daily stream discharge values were used to define the median groundwater level along the transect, and the volume weighted average groundwater level during the 1996-1998 calendar years.

As is common in transect studies, the assumption is made that the soil water sampled on the transect is representative of the catchment area draining to the

stream. The catchment area in this study is small (13.3ha), and the vegetation and soil morphology on the transect are similar to other sites within the catchment. A survey of near stream soil found that the depth of the contact between mineral soil, organic-rich mineral soil and peat soil is within a few centimetres of the median depth for these interfaces measured at 30 transects on the east side of the stream (Bishop, 1994). It is therefore assumed that the transect sampled in this study is a fair representation of the catchment. A stable isotope investigation of water sources and flow pathways (Laudon, *et al.*, 2004) has found that the amount of event and pre-event water leaving the transect during spring flood was similar to that for the entire catchment.

The foundation of the analysis in this paper is that the hydrological system along the study transect is essentially two-dimensional, with a no flow boundary at 1 m depth. In other words, there is no significant flow crossing the bottom of the transect, only rainfall and evapotranspiration cross the upper boundary, and no significant divergence out of or convergence of lateral flow into the transect along the “sides”. These conditions have been established hydrometrically (Bishop, 1994; Bishop, Grip & Piggott, 1990; Bishop, 1991; Nyberg *et al.*, 2001) as the basis for earlier hydrochemical mass-balance studies based on the adequacy of a two-dimensional flow system when considering the flux of buffering capacity (Bishop, Grip & O'Neill, 1990), carbon (Bishop, Lundström & Giesler, 1993; Bishop, *et al.*, 2004), mercury (Bishop *et al.*, 1995) and lead (Klaminder *et al.*, in press). In short, the no-flow condition along the lower boundary is evident from the exponential decline in flow as the water table falls towards the minimum level observed during over a decade of monitoring (always less than a meter from the ground surface within 25 m of the stream) on this and other transects (Seibert *et al.*, 2003). If there was flow across the lower boundary, the water table would continue falling as water “leaked” downwards. Pump tests have also established the rapid decrease in hydrological conductivity of the till soil on this catchment, and the apparent lack of macropore flow in excavated soil pits (Bishop, 1991).

The lack of convergent or divergent flow in or out of the plane of the transect was established prior to the installation of the lysimeters on the transect by mapping the local groundwater table using two parallel transects of groundwater tubes and piezometers 10 and 20 m “upstream” from the transect, and 10 m “downstream” from the study transect. The planar surface of the groundwater table confirmed that the lateral flow paths were parallel to the transect (Bishop, 1994). A unique and successful test of the hydrological balance existing on this hillslope was provided by a stable isotope study of snow, groundwater, soil water and runoff during spring flood 1999 (Laudon, *et al.*, 2004).

Chemical Analysis

For all samples (22 sample dates), both streamwater and soilwater, were analysed for pH and total organic carbon (TOC). Since the partial pressure of CO₂ (pCO₂) will influence pH above 4.5, both the ambient pH and aerated pH of all samples were measured in the laboratory at 25°C. The aeration of the pH samples was

carried out for 20 minutes with compressed standard air ($p\text{CO}_2=380$ ppm). TOC was measured with a Shimadzu TOC-5000 using catalytic combustion. TOC has been shown to be present almost exclusively as dissolved organic carbon (DOC) in these boreal environments (Gadmar, Vogt & Osterhus, 2002), both in streams (Ivarsson & Jansson, 1994) and lakes (Köhler, Hruska & Bishop, 1999) including high flow conditions (Laudon *et al.*, 2001). Therefore, these measurements are referred to as DOC throughout this article. Inorganic anions and cations were analysed on nine of these sample dates using liquid ion chromatography for inorganic anions and atomic absorption spectrophotometry for cations. Following the approach in estimating organic anions described in Köhler *et al.* (2000) measured amounts of base cations ($\text{Cb} = 2[\text{Ca}^{2+}] + 2[\text{Mg}^{2+}] + [\text{Na}^+] + [\text{K}^+]$) and acid anions ($\text{Ca} = 2[\text{SO}_4^{2-}] + [\text{Cl}^-] + [\text{NO}_3^-] + [\text{F}^-]$) were all assumed to be the total dissolved amounts.

A sub-set of the samples was also studied in more detail with regards to Al (Eq. 1) through analysis of the total monomeric aluminium (Al_M) and organic monomeric aluminium (Al_O).

$$\text{Al}_M = \text{Al}_i + \text{Al}_O \quad (1)$$

Total monomeric aluminum, estimated by complexation with pyrocatechol violet (La Zerte *et al.*, 1988; Røgeberg & Henriksen, 1985), includes nonlabile and labile monomeric forms (Driscoll, 1984). Organic monomeric aluminium was separated using an ion exchange method (Driscoll, 1984), column diameter 1cm, height 4cm, flow rate $10\text{mL}\cdot\text{min}^{-1}$. Inorganic monomeric aluminium (Al_i), which includes all cationic forms (Al^{3+} , $\text{Al}(\text{OH})^{2+}$, $\text{Al}(\text{OH})_2^+$, AlF_2^+ , AlF_2^+ , $\text{Al}(\text{SO}_4)^+$), was calculated as the difference between Al_M and Al_O (Eq. 1). From the calculated Al_i , empirically calculated temperature, and measured ion concentrations, the speciation of inorganic aquo-aluminum (Al^{3+}) and the charge of the Al_i fraction were calculated using the chemical equilibrium model Visual MINTEQ 2.15 (Gustafsson, 2005).

A charge balance has been used to help relate changes in Al to changes in other species along the hillslope. Results from laboratory analysis, as discussed earlier, have been used for the major anions and cations. These however, do not measure all the anions, leaving an “anion deficit” ([AD]) due to the influence of the bicarbonate system and organic acids (OA^-). In order to close the charge balance an estimate of the contributions from the bicarbonate system and OA^- was calculated (Eq. 2).

$$[\text{AD}] = \text{Cb} - \text{Ca} - [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] - [\text{OA}^-] \quad (2)$$

The bicarbonate system was approximated using an empirical model as no direct measurements of $p\text{CO}_2$ were available for the period studied. More recent field work in 2001 at the same site with weekly $p\text{CO}_2$ measurements at the same depths as lysimeters in the study give an empirical relationship between $p\text{CO}_2$ and soil temperature (pers. comm. Mats Öquist). This cubic relationships had r^2 values >0.93 at all depths. Comparison of daily soil temperature in 1998 and 2001

showed little variation ($r^2=0.83$, mean diff. 0.4°C); therefore we assume that the temperature to pCO_2 –relationship from 2001 can be used to estimate the pCO_2 levels in 1998 based on continually logged soil temperatures. The deprotonation of the organic acids were modelled using an empirical triprotic acid model (Kohler *et al.*, 2001). Any residual imbalance is attributed to errors in either the analytical analysis or modelling.

A series of soil samples was also taken from the transect and analysed for Al. Organically complexed Al was extracted in duplicate or triplicate samples with 0.5 M CuCl_2 for 2 hours using the method of Jou and Kamprath (1979). Around 500 g of soil samples were collected in the different horizons in the field corresponding to the suction lysimeter depth at each soil observation profile. The soil was homogenized and the water content determined on subsamples. For the organic horizons, 3g of dry soil, and for the mineral horizons 10g of dry soil, were mixed with 100 ml of 0.5 CuCl_2 solution in acid-washed polyethylene bottles. The soil was mixed for two hours and then filtered through Schleicher & Schuell No 3 filters. The recovered amount of solution, between 80 and 90 ml, was weighed and the extraction solutions subsequently analyzed by ICP-OES. Assuming that the residual soil water had the same chemical composition, we recalculated equivalent amounts of Al released in $\text{meq}\cdot\text{g}^{-1}$ after blank subtraction.

Aluminium solubility has been investigated with regard to both an organic phase and possible mineral phases. In order to assess the organic binding, the theoretical carrying capacity of the DOC was first calculated. Various carrying capacities have been reported in the literature, ranging from 1.6mmol Al per gram Carbon (Farmer & Lumsdon, 2001) to 7mmol Al per gram Carbon (Buurman, 1985). Unpublished data from this site indicates carrying capacity to be ~6mmol Al per gram C in the deeper horizons up to ~12mmol Al per gram C in the organic horizons. In this article we have followed the work of Buurman (1985) and used a value of 7mmol Al per gram C in all soil profiles. Mineral solubility has been assessed using literature solubility coefficients for common Al minerals. Due to the limited number of laboratory fractionated Al samples, modelled Al fractionation was undertaken to provide data on individual species (WHAM 6.0 (Tipping, 1994)). The default settings in WHAM were assumed and the model was calibrated to the laboratory Al_i data by varying the amount of FA assumed active, optimized calibration had 100% of FA active i.e. $\text{FA}=2*\text{DOC}$.

Lateral Hydrochemical Transport

The flow pathways along this transect have been previously studied in detail. By combining the principle of transmissivity feedback with Darcy's law, integrated lateral flow contributions from each soil layer can be calculated for a given runoff level (Bishop, *et al.*, 2004; Stähli, *et al.*, 2001) (figure 2). By linearly interpolating concentrations between each lysimeter measurement a full concentration profile was created. Overlaying this concentration on the lateral flow profile profiles makes it possible to calculate the integrated amount and chemical composition of

water moving laterally through the upper meter of soil (Bishop, *et al.*, 1995; Bishop, *et al.*, 2004).

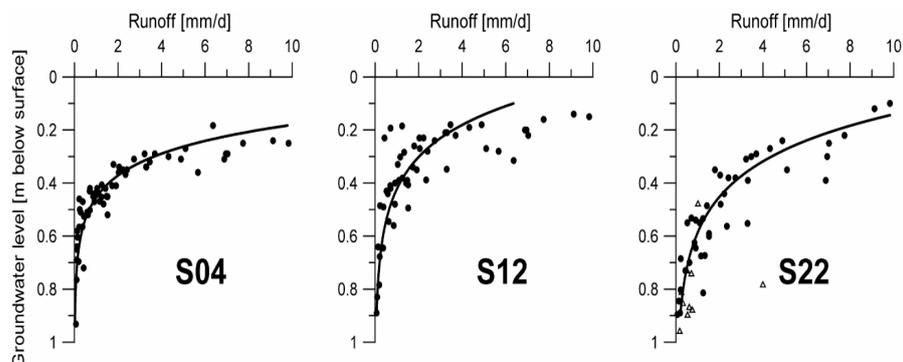


Fig. 2. The relationship between stream discharge and groundwater depth along the study transect. Point data is measured stream discharge (y-axis) and groundwater depth (x-axis). Lines are modelled fits allowing the calculation of a lateral flux from each level in the soil profile. Fewer data points exist for S28, and these are included as triangle symbols on the S22 plot. The same function was used for modelling lateral flow on both S22 and S28.

Results

The total aluminum concentrations in soil solution exhibit consistent and distinct profiles along both the vertical and horizontal axes of the transect with increasing concentrations downslope towards the stream (figure 3). On the upslope plots S22 and S28, there is a sharp vertical decline in Al concentration from ca $1000\mu\text{g}\cdot\text{L}^{-1}$ at 10 cm depth, just beneath the organic mor layer, to less than $100\mu\text{g}\cdot\text{L}^{-1}$ from ca 20 cm depth and below. Further downslope at S12, the decline in Al concentration with depth is more gradual, with concentrations above $200\mu\text{g}\cdot\text{L}^{-1}$ commonly found down to 70 cm depth. At plot S04, adjacent to the stream, the highest concentrations are found deeper in the soil profile (at ca 30 cm depth), and the peak is much broader. The Al concentrations are also much higher at S04, compared to upslope plots. This defines the horizontal trend in increasing Al levels from the upslope profiles towards the stream. These patterns are the average of 9 observations. While there is variability at each sample location (see “whiskers” in figure 3) the same patterns along both the x and y axis were found on each sampling occasion. The trend of increasing Al as one moves downslope is broken at the stream where Al is lower than that observed at S04. The largest variation in Al_{tot} is seen at 45cm depth in the riparian zone (S04) midway between the median groundwater level and the volume-weighted groundwater level. The variation in Al_{tot} is positively correlated to DOC (t-test, $p=0.01$, $n=9$), however from this data it is not possible to say if this increase in DOC is due to lateral inputs or in situ within S04. It is recognized that even though the catchment is small, this is a single transect study, and therefore the possibility of spatial

variation within the catchment precludes a simple definition of riparian zone shallow groundwater chemistry on this transect as the immediate source of stream runoff chemistry from the catchment.

The hydrology of the transect showed strong patterns in flow pathways during different periods of discharge. During low flow conditions, median groundwater levels occurred between 58cm and 79cm. However, as discussed earlier, the spring flood is a critical hydrological period when up to half the annual discharge occurs over a period of three to four weeks (Bishop & Pettersson, 1996; Laudon, Kohler & Buffam, 2004). During this time the ground water levels are more superficial, as reflected by the flow-weighted median groundwater depths of between 26cm and 30cm. Therefore, even though for most of the year the dominant lateral flow pathways are in the mineral soil, a large portion of the lateral flow that becomes discharge occurs in transiently active superficial flow pathways which pass through both upslope mineral soils and organic-rich riparian soils (figures 1 & 3).

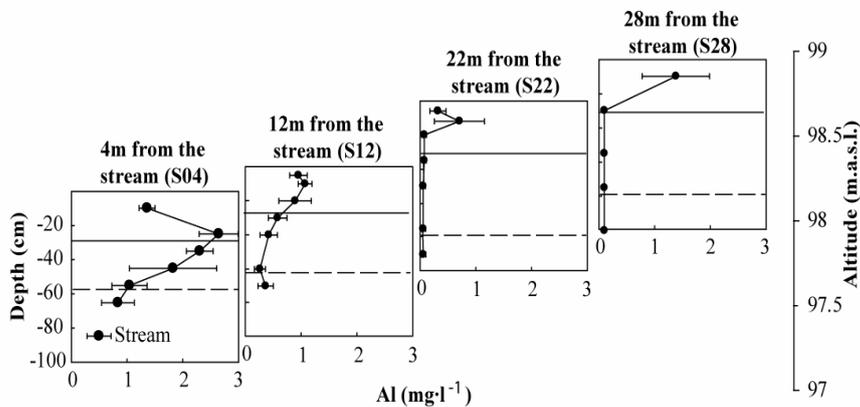


Fig. 3. Total Al during the period 1996-1998. Dashed horizontal reference lines indicate the median groundwater level and solid reference lines the flow-weighted mean groundwater level. The “error bars” on each dot indicate the range of the 9-22 observations.

The organic carrying capacity of the DOC was in excess of total Al in all samples. The excess carrying capacity was largest in the O horizon of all four profiles and in the organic rich peat of the S04 profile. The fraction present as Al³⁺ showed undersaturation with regards to proto-Imogolite and amorphous Gibbsite in all but two of the samples, these were the deepest samples from S12 and S22. No samples showed more than 10 times super saturation of these mineral phases (figure 4).

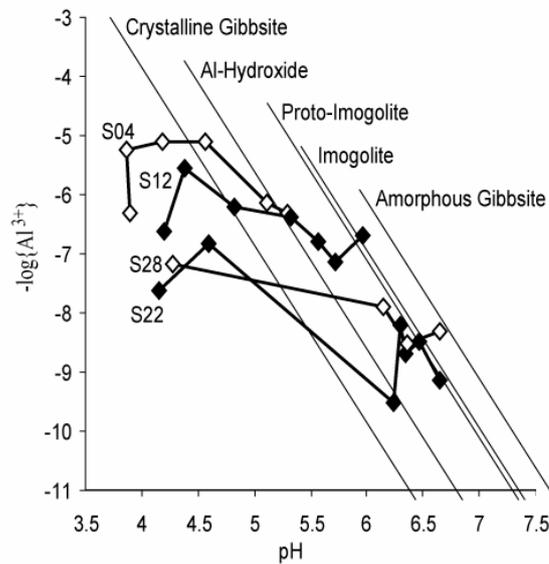


Fig. 4. Controls on Aluminium solubility. Soil profiles show increasing depth from left to right. Solid lines represent the theoretical concentrations at the mean temperature, 6.4°C (n=243, SD=3.15°C) for crystalline Gibbsite, amorphous Gibbsite, and Proto-Imogolite (Gerard, Boudot & Ranger, 2001), the Al-hydroxide proposed by Gustafsson et al (1998) is also shown. Proto-Imogolite is calculated using the mean Si concentration, 514 $\mu\text{mol}\cdot\text{L}^{-1}$ (n=38 SD=120 $\mu\text{mol}\cdot\text{L}^{-1}$). Filled and white markers are used only to help differentiate the profiles.

The observed changes in Al along the transect are related to changes in other constituents that combine to preserve the electro-neutrality of the soil solution. Therefore it is important to study changes in the full charge balance as well as changes in DOC. A cross-section of the soil and stream water chemistry taken from the transect on 3rd June 1998, represents the evolution of soil solution chemistry as it moves along the transect (figure 5). The flow for this date (0.7 $\text{mm}\cdot\text{day}^{-1}$) was typical of baseflow, and the chemical patterns are typical of that which is seen on the nine sampling occasions when Al was measured. The figure shows the vertically integrated lateral flow at each site on the transect, with the transect represented vertically. The figure contains four key elements, the integrated solution pH (on y axis); a mass balance of the major anions and cations (left panel); speciated aluminium (central panel) and finally DOC (right panel). Combining all these factors in a single figure allows one to observe the pattern of Al evolution along flow paths through the catchment in a more complete context.

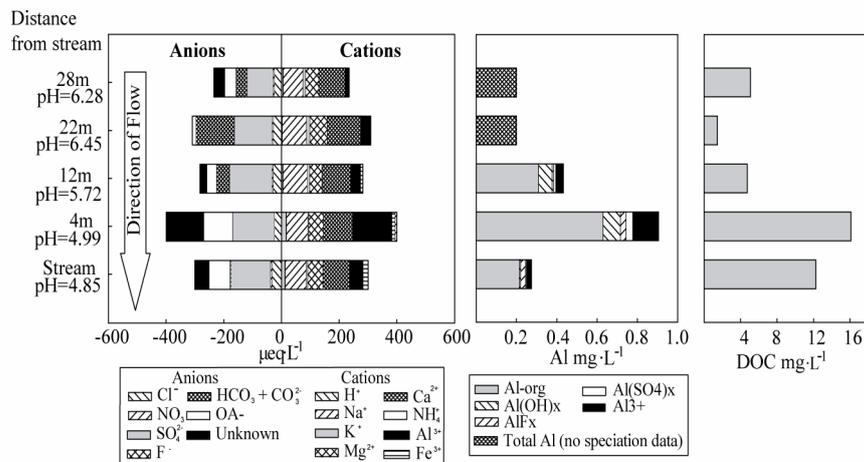


Fig. 5. Snap shot of the vertically integrated soil solution chemistry of soil water on June 3rd, 1998, as it moves downslope towards the stream. The diagram represents how the laterally flowing water (integrated over the depth of the soil profile) evolves downslope, moving from 28m to the stream. The direction of flow is in the downward direction of the large arrow. Left panel - mass balance of the major anions and cations. Central panel - speciated Al. Right panel - DOC.

The mean Al concentrations of laterally flowing groundwater was ca 200 $\mu\text{g}\cdot\text{L}^{-1}$ at the sites furthest upslope from the stream. The concentration increases downslope to over 900 $\mu\text{g}\cdot\text{L}^{-1}$, at S04, 4 m from the stream (figure 5). The riparian site also contains the highest fraction of aquo-aluminum (over 100 $\mu\text{g}\cdot\text{L}^{-1}$ of Al^{3+} , which is 14% of the Al_{tot} concentration). DOC shows a similar pattern with concentrations increasing from the lowest values upslope (< 5 $\text{mg}\cdot\text{L}^{-1}$) to the highest level (16 $\text{mg}\cdot\text{L}^{-1}$) in the riparian zone. These changes in DOC along the transect are reflected in the contribution to charge from the organic acids that increase from 33 $\mu\text{eq}\cdot\text{L}^{-1}$ or 13% of the total negative charge at S22, to 72 $\mu\text{eq}\cdot\text{L}^{-1}$ or 29% of the negative charge 4 m from the stream. Also, as expected, the charge contribution from carbonate is greatest in the upslope mineral soils, and declines considerably as water moves into the near stream zone. This results from the declining pH that shifts the bicarbonate equilibrium to CO_2 . Stream concentrations of Al_{tot} and Al^{3+} are less than half of those seen in the riparian zone, whereas the DOC concentration of the laterally flowing water showed a smaller decline. Many of the other chemical parameters have similar values in this riparian zone and the catchment runoff.

The results of the soil extraction data reveal that the concentrations seen in the soil water reflect the pattern of Al in the solid phase of the surrounding soils (figure 6). The observed solid phase extractable Al concentrations correlate to those in soil water (linear correlation, $r^2=0.83$). DOC concentrations also follow the trends in the solid and dissolved phase Al.

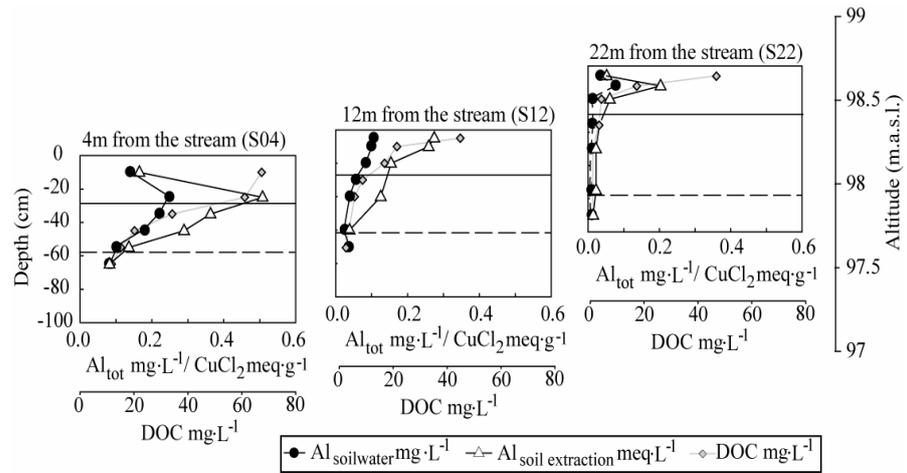


Figure 6 – CuCl_2 extractable Al in soil samples at depths corresponding to the suction lysimeters. CuCl_2 extractable Al (triangle symbols), mean soil water Al_{tot} (filled circles) and mean soil water DOC (grey diamonds). Dashed horizontal reference lines indicate the median groundwater level and solid reference lines the flow-weighted average groundwater level.

Table 1. *Suction Lysimeter data for all samples from 1996-1998. Mean values, standard deviation and number of samples is shown for each location and depth.*

	DOC mg·L ⁻¹	pH ²	Na mg·L ⁻¹	K mg·L ⁻¹	Mg mg·L ⁻¹
S28 -5	72.48 ±0.00 (1)	n.d.	n.d.	n.d.	n.d.
S28 -10	60.69 ±9.74 (3)	4.27 ±0.02 (3)	1.05 ±0.37 (4)	2.58 ±0.68 (4)	0.26 ±0.04 (4)
S28 -30	3.89 ±0.00 (1)	n.d.	1.71 ±0.00 (1)	0.76 ±0.00 (1)	0.14 ±0.00 (1)
S28 -55	1.87 ±0.00 (1)	6.15 ±0.15 (4)	1.71 ±0.08 (3)	0.41 ±0.05 (3)	0.50 ±0.05 (3)
S28 -75	2.64 ±1.76 (3)	6.36 ±0.24 (4)	1.88 ±0.13 (3)	0.36 ±0.03 (3)	0.59 ±0.01 (3)
S28 -100	1.03 ±0.27 (2)	6.64 ±0.21 (2)	1.86 ±0.13 (3)	0.48 ±0.08 (3)	0.58 ±0.03 (3)
S22 -6	47.56 ±12.99 (7)	4.18 ±0.11 (6)	1.40 ±0.00 (3)	0.66 ±0.38 (3)	0.32 ±0.22 (3)
S22 -12	19.32 ±8.44 (11)	4.69 ±0.18 (10)	1.84 ±0.30 (4)	0.57 ±0.06 (4)	0.24 ±0.07 (4)
S22 -20	4.97 ±2.20 (10)	6.28 ±0.19 (10)	1.60 ±0.04 (5)	0.46 ±0.06 (5)	0.38 ±0.04 (5)
S22 -35	4.04 ±7.27 (11)	6.36 ±0.27 (11)	1.82 ±0.15 (6)	0.27 ±0.05 (6)	0.37 ±0.05 (6)
S22 -50	1.78 ±1.13 (12)	6.30 ±0.22 (12)	2.10 ±0.33 (7)	0.12 ±0.02 (7)	0.54 ±0.11 (7)
S22 -75	1.58 ±1.00 (12)	6.44 ±0.26 (13)	2.22 ±0.20 (7)	0.25 ±0.14 (7)	0.63 ±0.12 (7)
S22 -90	2.03 ±1.09 (14)	6.63 ±0.32 (16)	2.29 ±0.10 (6)	1.09 ±0.07 (6)	0.99 ±0.06 (6)
S12 -5	46.16 ±14.94 (12)	4.19 ±0.20 (13)	1.50 ±0.16 (6)	0.17 ±0.07 (6)	0.43 ±0.04 (6)
S12 -10	22.63 ±8.63 (11)	4.40 ±0.09 (13)	1.71 ±0.03 (5)	0.07 ±0.04 (5)	0.40 ±0.05 (5)
S12 -20	18.00 ±4.14 (18)	4.79 ±0.10 (16)	1.75 ±0.06 (8)	0.07 ±0.03 (8)	0.40 ±0.05 (8)
S12 -30	9.96 ±2.83 (19)	5.27 ±0.25 (16)	1.91 ±0.13 (9)	0.11 ±0.01 (9)	0.50 ±0.05 (9)
S12 -40	7.10 ±1.45 (18)	5.57 ±0.32 (15)	2.06 ±0.10 (8)	0.15 ±0.02 (8)	0.58 ±0.04 (8)
S12 -60	4.91 ±1.28 (14)	5.75 ±0.33 (15)	2.20 ±0.10 (9)	0.35 ±0.06 (9)	0.63 ±0.03 (9)
S12 -70	4.00 ±0.95 (12)	5.83 ±0.27 (11)	2.25 ±0.24 (6)	0.53 ±0.13 (6)	0.61 ±0.20 (6)
S04 -10	67.38 ±18.63 (12)	3.95 ±0.24 (11)	0.44 ±0.09 (5)	0.59 ±0.62 (5)	0.24 ±0.05 (5)
S04 -25	61.16 ±16.75 (17)	3.85 ±0.29 (17)	0.63 ±0.19 (6)	0.22 ±0.14 (6)	0.17 ±0.04 (6)
S04 -35	34.19 ±8.46 (16)	4.11 ±0.21 (18)	1.74 ±0.20 (7)	0.17 ±0.07 (7)	0.33 ±0.06 (7)
S04 -45	19.37 ±7.95 (20)	4.49 ±0.19 (19)	1.92 ±0.16 (9)	0.11 ±0.04 (9)	0.47 ±0.07 (9)
S04 -55	14.97 ±3.88 (20)	5.07 ±0.19 (18)	1.99 ±0.14 (9)	0.15 ±0.01 (9)	0.66 ±0.06 (9)
S04 -65	11.56 ±3.18 (20)	5.21 ±0.25 (19)	2.08 ±0.15 (9)	0.19 ±0.03 (9)	0.76 ±0.06 (9)
Stream	15.44 ±6.66 (12)	4.99 ±0.54 (10)	2.02 ±0.56 (7)	0.20 ±0.13 (7)	0.81 ±0.29 (7)
Integrated S28	5.20 ±3.99 (3)	6.30 ±0.25 (5)	1.51 ±0.63 (4)	1.19 ±1.59 (4)	0.48 ±0.16 (4)
Integrated S22	4.71 ±8.15 (17)	6.52 ±0.30 (16)	2.19 ±0.18 (8)	0.46 ±0.28 (8)	0.70 ±0.15 (8)
Integrated S12	5.56 ±2.02 (19)	5.71 ±0.35 (17)	2.20 ±0.13 (9)	0.37 ±0.14 (9)	0.62 ±0.05 (9)
Integrated S04	15.58 ±6.48 (19)	4.90 ±0.37 (18)	1.97 ±0.19 (9)	0.16 ±0.03 (9)	0.64 ±0.13 (9)

Table 1. *Cont.../*

	Ca mg·L ⁻¹	A mg·L ⁻¹	Fe mg·L ⁻¹	SO4 mg·L ⁻¹	Cl mg·L ⁻¹
S28 -5	n.d.	n.d.	n.d.	n.d.	n.d.
S28 -10	1.01 ±0.13 (4)	1.39 ±0.61 (4)	0.71 ±0.55 (4)	2.52 ±2.14 (2)	1.07 ±0.44 (2)
S28 -30	0.52 ±0.00 (1)	≤0.10 ±0.00 (1)	≤0.03 ±0.00 (1)	n.d.	n.d.
S28 -55	1.92 ±0.07 (3)	≤0.10 ±0.00 (3)	≤0.03 ±0.00 (3)	4.68 ±0.02 (2)	0.84 ±0.04 (2)
S28 -75	1.91 ±0.04 (3)	≤0.10 ±0.00 (3)	≤0.03 ±0.00 (3)	4.49 ±0.18 (3)	0.99 ±0.05 (3)
S28 -100	1.77 ±0.10 (3)	≤0.10 ±0.00 (3)	≤0.03 ±0.00 (3)	4.06 ±0.17 (3)	0.92 ±0.11 (3)
S22 -6	1.13 ±0.71 (3)	0.32 ±0.14 (3)	2.33 ±1.95 (3)	1.47 ±0.17 (2)	0.41 ±0.01 (2)
S22 -12	0.76 ±0.15 (4)	0.71 ±0.45 (4)	0.41 ±0.18 (4)	2.99 ±1.86 (4)	0.94 ±0.36 (4)
S22 -20	1.75 ±0.15 (5)	≤0.10 ±0.04 (4)	0.04 ±0.04 (5)	4.67 ±0.56 (6)	0.57 ±0.20 (6)
S22 -35	1.31 ±0.09 (6)	≤0.10 ±0.03 (5)	≤0.03 ±0.00 (3)	3.87 ±0.16 (6)	0.79 ±0.12 (6)
S22 -50	1.69 ±0.38 (7)	≤0.10 ±0.04 (7)	≤0.03 ±0.01 (6)	5.33 ±0.53 (6)	0.98 ±0.25 (6)
S22 -75	1.92 ±0.40 (7)	≤0.10 ±0.04 (5)	≤0.03 ±0.01 (3)	5.62 ±0.47 (6)	1.10 ±0.18 (6)
S22 -90	3.37 ±0.12 (6)	≤0.10 ±0.05 (4)	≤0.03 ±0.02 (4)	6.95 ±0.44 (6)	1.09 ±0.05 (6)
S12 -5	1.07 ±0.06 (6)	0.95 ±0.16 (6)	1.03 ±0.22 (6)	2.65 ±1.33 (6)	0.80 ±0.35 (6)
S12 -10	1.04 ±0.08 (5)	1.07 ±0.12 (5)	0.77 ±0.24 (5)	3.44 ±0.75 (5)	0.69 ±0.25 (5)
S12 -20	1.39 ±0.16 (8)	0.89 ±0.29 (8)	0.50 ±0.48 (8)	4.48 ±1.44 (8)	0.80 ±0.28 (8)
S12 -30	1.93 ±0.17 (9)	0.58 ±0.17 (9)	0.26 ±0.32 (9)	6.08 ±1.26 (9)	0.96 ±0.21 (9)
S12 -40	2.29 ±0.16 (8)	0.42 ±0.15 (8)	0.18 ±0.17 (8)	6.84 ±0.97 (8)	1.01 ±0.10 (8)
S12 -60	2.54 ±0.12 (9)	0.26 ±0.10 (9)	0.16 ±0.11 (9)	7.55 ±0.93 (9)	0.98 ±0.14 (9)
S12 -70	2.42 ±0.87 (6)	0.36 ±0.14 (6)	0.23 ±0.20 (6)	7.55 ±1.79 (6)	0.94 ±0.07 (6)
S04 -10	1.57 ±0.22 (5)	1.35 ±0.14 (5)	1.49 ±0.28 (5)	1.29 ±1.40 (2)	0.45 ±0.40 (4)
S04 -25	0.72 ±0.23 (6)	2.63 ±0.35 (6)	1.48 ±1.34 (6)	2.09 ±1.33 (6)	0.72 ±0.39 (6)
S04 -35	1.13 ±0.21 (7)	2.29 ±0.24 (7)	1.10 ±1.21 (7)	5.27 ±2.76 (7)	1.01 ±0.13 (7)
S04 -45	1.58 ±0.28 (9)	1.82 ±0.78 (9)	0.97 ±1.08 (9)	6.03 ±2.69 (8)	0.96 ±0.08 (8)
S04 -55	2.22 ±0.21 (9)	1.04 ±0.32 (9)	0.53 ±0.51 (9)	6.41 ±1.55 (9)	0.95 ±0.06 (9)
S04 -65	2.51 ±0.22 (9)	0.83 ±0.29 (9)	0.41 ±0.35 (9)	7.18 ±0.89 (9)	0.95 ±0.05 (9)
Stream	2.29 ±0.75 (7)	0.54 ±0.22 (7)	0.45 ±0.18 (7)	6.81 ±3.38 (7)	0.98 ±0.23 (7)
Integrated S28	1.66 ±0.44 (4)	0.19 ±0.19 (4)	0.40 ±0.75 (4)	4.44 ±0.13 (3)	0.95 ±0.04 (3)
Integrated S22	2.26 ±0.60 (8)	≤0.10 ±0.03 (8)	0.09 ±0.19 (8)	5.97 ±0.63 (7)	1.06 ±0.14 (7)
Integrated S12	2.48 ±0.24 (9)	0.30 ±0.09 (9)	0.23 ±0.18 (9)	7.42 ±1.03 (9)	0.99 ±0.07 (9)
Integrated S04	2.14 ±0.43 (9)	1.16 ±0.32 (9)	0.66 ±0.70 (9)	6.27 ±1.62 (9)	0.93 ±0.05 (9)

¹Quantification limits: Al 0.10mg/l, Fe 0.03mg/l, NH4 0.01mg/l

²pH averaged as H+ and then converted back to pH

Table 1. *Cont.../*

		NO3 mg·L ⁻¹	NH4 mg·L ⁻¹	F mg·L ⁻¹	Si mg·L ⁻¹		
S28	-5	n.d.	n.d.	n.d.	n.d.		
S28	-10	0.20 ±0.14 (2)	≤0.01	±0.00 (2)	n.d.	3.97	±0.00 (1)
S28	-30	n.d.	n.d.	n.d.	n.d.		
S28	-55	0.20 ±0.14 (2)	≤0.01	±0.00 (2)	n.d.	n.d.	
S28	-75	0.17 ±0.12 (3)	0.02	±0.01 (3)	0.06 ±0.00 (1)	n.d.	
S28	-100	0.17 ±0.12 (3)	≤0.01	±0.00 (2)	0.08 ±0.00 (1)	n.d.	
S22	-6	0.20 ±0.00 (1)	≤0.01	±0.00 (1)	n.d.	6.24	±3.2 (2)
S22	-12	0.18 ±0.10 (4)	≤0.01	±0.00 (3)	0.01 ±0.00 (1)	6.91	±0.00 (1)
S22	-20	0.15 ±0.10 (4)	≤0.01	±0.00 (3)	0.02 ±0.02 (2)	5.75	±0.00 (1)
S22	-35	0.18 ±0.10 (4)	≤0.01	±0.00 (3)	0.04 ±0.03 (2)	5.74	±0.45 (2)
S22	-50	0.18 ±0.10 (4)	≤0.01	±0.01 (4)	0.04 ±0.01 (2)	6.93	±1.14 (2)
S22	-75	0.20 ±0.10 (3)	≤0.01	±0.01 (4)	0.07 ±0.03 (2)	6.89	±0.76 (2)
S22	-90	0.13 ±0.06 (3)	≤0.01	±0.00 (2)	0.26 ±0.01 (3)	8.50	±0.39 (2)
S12	-5	0.16 ±0.09 (5)	≤0.01	±0.01 (5)	0.02 ±0.00 (1)	4.78	±1.10 (2)
S12	-10	0.13 ±0.05 (4)	≤0.01	±0.00 (4)	0.04 ±0.02 (2)	4.81	±0.00 (1)
S12	-20	0.18 ±0.10 (4)	0.02	±0.01 (4)	0.06 ±0.01 (3)	6.33	±1.09 (2)
S12	-30	0.16 ±0.09 (5)	≤0.01	±0.00 (5)	0.06 ±0.01 (3)	6.41	±0.51 (2)
S12	-40	0.16 ±0.09 (5)	≤0.01	±0.00 (5)	0.07 ±0.02 (3)	6.88	±0.28 (2)
S12	-60	0.16 ±0.09 (5)	0.02	±0.01 (5)	0.11 ±0.02 (4)	8.32	±0.59 (2)
S12	-70	0.20 ±0.10 (3)	0.07	±0.11 (4)	0.13 ±0.03 (4)	9.11	±0.00 (1)
S04	-10	0.10 ±0.00 (2)	0.02	±0.01 (2)	0.03 ±0.00 (2)	4.76	±0.00 (1)
S04	-25	0.16 ±0.09 (5)	≤0.01	±0.00 (5)	0.03 ±0.01 (3)	3.41	±0.00 (1)
S04	-35	0.18 ±0.10 (4)	0.02	±0.02 (4)	0.07 ±0.00 (1)	6.96	±0.26 (2)
S04	-45	0.33 ±0.36 (5)	≤0.01	±0.01 (4)	0.08 ±0.02 (4)	7.87	±0.46 (3)
S04	-55	0.22 ±0.16 (6)	≤0.01	±0.00 (5)	0.08 ±0.02 (4)	8.10	±0.43 (2)
S04	-65	0.28 ±0.30 (6)	0.06	±0.10 (5)	0.08 ±0.02 (4)	9.11	±0.92 (2)
Stream		0.16 ±0.09 (5)	0.01	±0.00 (6)	0.12 ±0.03 (2)	5.91	±0.56 (2)
Integrated S28		0.16 ±0.11 (3)	≤0.01	±0.01 (3)	0.06 ±0.00 (1)	3.97	±0.00 (1)
Integrated S22		0.16 ±0.08 (5)	≤0.01	±0.00 (6)	0.16 ±0.09 (3)	7.12	±1.11 (2)
Integrated S12		0.16 ±0.08 (5)	0.05	±0.09 (6)	0.11 ±0.04 (4)	7.78	±1.06 (2)
Integrated S04		0.27 ±0.29 (6)	0.03	±0.03 (6)	0.07 ±0.02 (5)	8.04	±0.22 (3)

The data in Figure 5 shows detailed results from a single sampling date. However, the transect has been sampled on 9-22 occasions during both spring and summer, over a two year period (Table 2). To visualize these patterns in the downslope evolution of Al and related parameters, pH, Fe and Al_{tot} soil solution data have been grouped and normalized with respect to the near stream zone concentrations (S04) (figure 7). This helps in indicating whether different ions are increasing or decreasing as the water moves down the transect into the RZ and then onwards to the stream. Al_{tot} is reasonably stable in the upslope areas, increasing markedly in the RZ with a sharp drop again in the stream. Iron shows a similar, although less extreme, pattern to Al_{tot}. The pH decreases towards the RZ and then shows a slight increase in the stream samples. DOC is lower in the

upslope areas than in the RZ, and then has relatively similar values in the stream as found in the RZ.

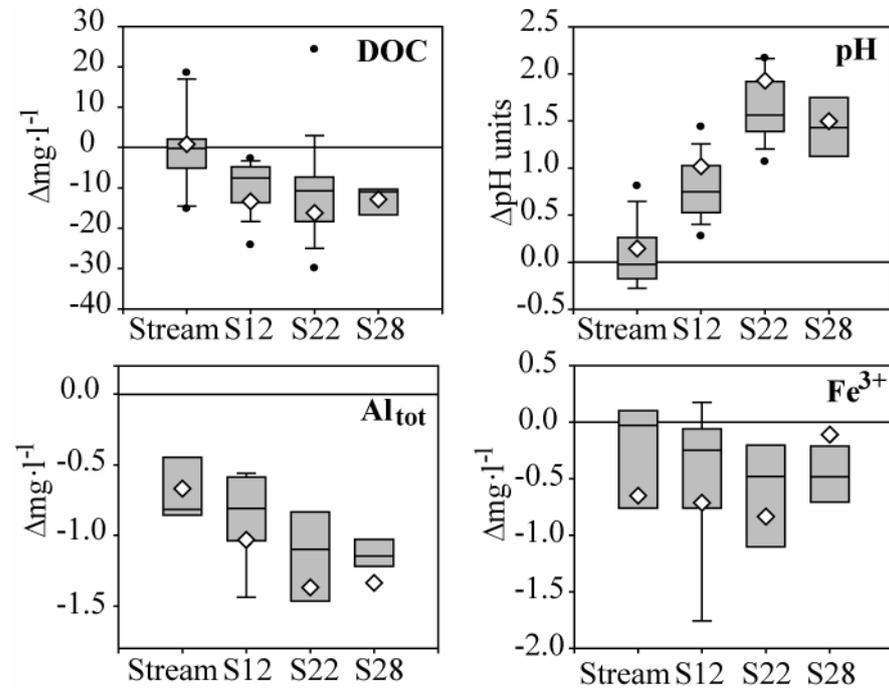


Fig. 7. Relative difference in Al and related chemical parameters between the near stream zone (S04) and each sample site. The direction of lateral flow is from right (S28) to left (S12), and then into the stream. Box plots show the data for the whole sample period, 1996-1998 with 9 sampling occasions for cations and 22 occasions for pH and DOC. The concentrations used to create this diagram are the vertically integrated mean values of laterally flowing soil water on different sampling occasions. The upper and lower limits of the box represent the 25th and 75th percentiles, while the whiskers represent the 10th and 90th percentiles. The line dividing the box is the 50th percentile (median). Diamond symbols show the flow weighted averages of these data. Positive values indicate concentrations higher than S04 (and vice-versa).

Discussion

In the areas upslope of the peat soils in the riparian zone (~80% of this catchment), water enters the hillslope as precipitation moving vertically down through the mor layer, where Al_{tot}, H⁺ and DOC concentrations are high. This is a feature of the podzolization process with higher Al concentrations just below the organic horizon (Lundstrom *et al.*, 2000). This water continues vertically downward into the underlying mineral soil where adsorption reactions to solid phases reduces soil water concentration. Upon reaching the water table with these low DOC, H⁺ and Al concentrations, water begins moving laterally downslope towards the stream. Most of the time, the lateral flow is occurring at more than half a meter depth

below the soil surface where the median water table is located. As the water moves into the organic rich soils of the RZ, Al_{tot} , DOC and H^+ concentrations increase. This is the most common situation in terms of duration (figure 7). During peak flow, the depth of vertical infiltration is less, because the groundwater level is higher. More of the flow moves laterally at a more superficial depth, because of higher hydraulic conductivity closer to the soil surface (Laudon, *et al.*, 2004; Nyberg, *et al.*, 2001). In the upslope areas, these superficial pathways traverse low Al areas. At 12m, and especially 4m from the stream, more superficial high flow pathways traverse soils with higher levels of DOC, H^+ and Al. Thus the downslope increase in the RZ is even more accentuated along the more superficial flow pathways (figure 7) with Al reaching the highest values in the organic rich peat adjacent to the stream.

Stream water Al_{tot} concentrations are significantly lower than those in the RZ examined in this study. Many other constituents are more consistent between the RZ and those found in the stream. A discontinuity between the RZ and the stream is therefore implied. However, the RZ sampled is only one of many contributing to the stream and so spatial variability in the hillslope could also explain this anomaly.

It is interesting to note that stream Al concentrations are similar to those observed in the upslope mineral soil. The simplest explanation of this Al pattern is macro-pore or overland flow which could transfer water with the upslope mineral soil chemical signature to the stream. However other chemical and hydrological data contradict this theory. The hydrology and flow pathways of this transect have been well established using both hydrometric information and stable isotope tracers (Bishop, 1991; Bishop, *et al.*, 2004; Laudon, *et al.*, 2004; Seibert, Rodhe & Bishop, 2003). Significant macro-pore flow was not found, but rather matrix flow based on a transmissivity feedback mechanism (Bishop, 1991; Laudon, *et al.*, 2004; Stähli, *et al.*, 2001) where the majority of water passes through the RZ before entering the stream. Another line of evidence arguing for matrix flow passage through the RZ comes from the behavior of other chemical parameters contributing to the charge balance. Table 2 summarizes the results for changes in solution chemistry moving from the upslope podzol to the RZ and then from the RZ to the stream. These results demonstrate that Al showed a major charge deviation when moving along the transect. The other chemical parameters are more conservative as they leave the RZ and retain the 'signature' of the RZ to a much greater degree. The major changes in charge contribution from the RZ (4m) to the stream are associated with Al, Fe and organic acids. Other constituents, including SO_4 , Ca, and DOC do not have upslope concentrations similar to those seen in the stream, which would be expected if bypass flow were indeed an important runoff generation process on this catchment.

Table 2. Change in charge contribution ($\mu\text{eq}\cdot\text{L}^{-1}$) for water moving from 22m to 4m from the stream, and then from 4m to the stream. Values are from the integrated lateral flux, and therefore reflect the total volume of water moving. The different sampling occasions ($n= 9$ to 23) are flow weighted averages of all samples dates with sufficient data. Categories correspond to no change -- ($\pm 0-25 \mu\text{eq}\cdot\text{L}^{-1}$), minor change $\uparrow\downarrow$ ($\pm 25-50 \mu\text{eq}\cdot\text{L}^{-1}$) and major change $\hat{\uparrow}\hat{\downarrow}$ ($\pm > 50 \mu\text{eq}\cdot\text{L}^{-1}$) in the charge balance.

S22 to S04		S04 to Stream	
Change	Factor	Change	Factor
$\hat{\uparrow}$	$\text{Al}^{3+} \text{OA}^- \text{Fe}^{3+}$	$\hat{\uparrow}$	
\uparrow	SO_4^{2-}	\uparrow	
--	$\text{H}^+ \text{Ca}^{2+} \text{Mg}^{2+} \text{Na}^+ \text{K}^+ \text{NH}_4^+$ $\text{Cl}^- \text{NO}_3^- \text{F}^-$	--	$\text{H}^+ \text{Ca}^{2+} \text{Mg}^{2+} \text{Na}^+ \text{K}^+ \text{NH}_4^+ \text{Cl}^-$ $\text{NO}_3^- \text{F}^- \text{SO}_4^{2-} \text{HCO}_3^-$
\downarrow	HCO_3^-	\downarrow	$\text{OA}^- \text{Fe}^{3+}$
$\hat{\downarrow}$		$\hat{\downarrow}$	Al^{3+}

The increase in soil water Al from upslope to the RZ, and the patterns with depth in the soil profiles are consistent with the pattern of solid phase soil Al (figure 6). This indicates that in the short term, changes in the soil water Al, as water passes through the transect, reflect equilibration with the solid phase Al of the transect. In a longer-term perspective, the solid phase Al is influenced by the flow of water and its dissolved constituents. Between 28 and 22 meters from the stream the soil water chemistry and solid phase soil Al are reasonably stable. The solid phase Al pool increases in the organic-rich RZ soils, relative to the upslope soils. Nearer the stream, these thicker organic deposits function as a rapid Al-exchanger buffer for the soil water.

The mosses making up the RZ peats grow without direct contact with the mineral soils, suggesting that the Al build up in the RZ is allochthonous. This external source of Al is presumably the B-horizon upslope. As the hydrological connection between the extensive, upslope mor layer and the RZ goes via the mineral soils of the B and C horizons with much lower Al levels, lateral movement of Al from the mineral soil is implied.

It is not known if the accumulated Al in the RZ results from long-term podzol development since the last glaciation and/or more recent factors that may have increased Al mobilization from the mineral soil. One factor which could mobilize extra Al would be the input of anthropogenic sulfate providing mobile anions for Al transport. However the patterns of Al in the hillslope do not indicate that there is an acidification front moving vertically downwards in the soil profile, mobilizing Al that is then flushed laterally to the stream in shallow groundwater. There is a superficial zone of high Al in the mor layer of the upslope soils, but the hydrological pathways linking this surface layer to the stream traverse deeper mineral soils where Al concentrations were lower in both soil solution and the solid phase (soil solution, however, has not been sampled at peak flow). Furthermore, the major anions seen in association with increased Al are organic acids and this would seem to indicate a natural process rather than an anthropogenic influence. Associations of elevated Al with organic acids have been

observed in other studies. In a study in North America, Pellerin et al (2002) noted Al mobilization by organic acids resulting in a natural lateral transport of Al which subsequently accumulated in the near stream zone. Similar observations have been made in Norway by Vogt and Muniz (1997). Mulder et al (1991) also noted the importance of organic acids in the transport of Al laterally in the hillslope but emphasized that organic Al complexes would not lead to toxic levels of Al_i in streams.

The solubility of Al in these samples shows a complex pattern. The RZ and associated organic soils have often been attributed to an organic phase control of Al (Berggren & Mulder, 1995; Simonsson & Berggren, 1998; Skyllberg & Magnusson, 1995). In the data presented here the organic carrying capacity is in excess of Al for all samples implying an organic phase control. Control by organic exchanger sites is also supported by the close correlation of the solid and soil solution phases (figure 6). Two thirds of the samples are oversaturated with regards to crystalline Gibbsite, but the precipitation of this phase is energetically hindered in the presence of small amounts of silica (Nagy (1995) and refs therein). Of the more kinetically favorable mineral phases there was oversaturation with regards to the soil Gibbsite proposed by Gustafsson et al (1998) in the deeper samples from S12-S28. Only a small fraction of the samples showed oversaturation with regards to Imogolite phases or amorphous Gibbsite, none of the samples showed supersaturation of 10 times or more. The deeper samples from S04 and S12 appear to be close to equilibrium with the Al-hydroxide proposed by Gustafsson et al (1998), whereas the samples from the mineral soils of S22 and S28 are close to equilibrium with an Imogolite phase.

A paradox which exists is that the source areas of Al in the upslope areas have significantly lower Al concentrations than the RZ and this implies that the RZ Al pool has built up earlier, or is being replenished episodically at peak flow. No clear lateral Al transport front is seen along the most common, median flow pathway. The more superficial, flow weighted average pathway however does move closer to the elevated Al concentrations in the mor layer. It is thus conceivable that the hydrologically important springflood episodes provide a short but intensive transport of Al from the upslope to the near stream zone. During spring flood the main, superficial flow pathway is about 10 centimeters from organic rich layers. This could provide a source of organic acids enabling a lateral transport of Al from the up-slope areas to the near stream zone. For this to work, a portion of the Al moving laterally would need to be retained in the RZ, bound to the solid phase peat material in the near stream zone. The peat has developed in this near stream zone since the last glaciation (~6000 i.e.). Repeated cycles of episodic lateral flow followed by peat development could lead to the build up of elevated Al concentrations in this organic zone. The Al build up could have been facilitated by the constant creation of new peat, thereby providing new binding sites. However most Al export from the RZ occurs during the episodes and this period would also need to be the time of Al build-up in the RZ.

An alternative explanation for the Al that has accumulated in the RZ could be a recent change in the hydrology of the transect from the situation which had existed

since the last glaciation. Starting in the late 1800's and into the latter half of the 1900's, channel ditching was undertaken extensively in Sweden to improve drainage. It is now difficult to find any headwater streams which have not been subjected to drainage in Sweden (Dahlström, 2005). The channel in this study was deepened over half a meter in the 1920's by ditching. This lowered the flow pathways and therefore may have disturbed the natural cycle of lateral transport and binding in the RZ which had occurred for thousands of years. Before ditching, flow pathways were more superficial, making it more likely that at peak flow, and possibly even base flow, that superficial lateral flows with high DOC concentrations could transport Al from the upslope areas downslope into the RZ. There, Al and DOC-rich water would intersect accumulating peat which would also have organic-rich pore water, but less Al since the peat does not have its own local source of Al. In this situation, Al could bind to the new, Al-poor solid phase organic matter, building up a store of Al in the RZ. The ditching lowered the upslope lateral flow pathways into horizons with less Al and DOC in soil solution. This would result in the laterally flowing water from upslope transporting Al and DOC at lower concentrations to the RZ. This laterally flowing water subsequently passes through the RZ equilibrating with the elevated pool of Al previously accumulated there. This could yield the situation seen in the study reported here, where the RZ is functioning as a source of Al to water as it moves downslope through the catchment. Assuming this ditching effect has occurred, then this widely used practice for improving productivity might have permanently changed flow pathways and thus induced elevated aluminum concentrations in many streams.

Conclusions

Following Al concentrations along the flow paths through a catchment revealed large downslope increases in the Al, Fe and DOC concentrations when lateral flow through mineral soil entered the organic rich soils of the RZ. Elevated Al was associated with organic acids, and there was no source of Al movement from upslope soils in an "acidification front". Both of these circumstances imply that processes other than anthropogenic deposition are responsible for Al moving through the catchment to the stream on the sampling occasions (The flow pathways, however, are strongly influenced by the ditching of the catchment). The RZ on the transect in this study had higher concentrations of Al than the upslope mineral soils, making the RZ a net source of Al along the hydrological flow paths. This occurred despite the fact that the organic soils of the RZ must have accumulated the Al now present from lateral transport originating upslope. Since mineral soils are the ultimate source of Al that can be transported from catchments to streams, the Al in the RZ accumulated there either by episodes not observed in our study, or during the original flow regime that existed for thousands of years until ditching some 80 years ago. The potential for Al concentrations being modified during transport through the RZ needs to be accounted for in efforts to relate acid deposition to bio-toxic stream Al concentrations in areas such as boreal Sweden where soil acidification has lowered stream pH only marginally.

Understanding the controlling mechanisms for Al transport within the soil, during discharge and also in the stream are critical to evaluating human influence on Al. It appears from this study, that biologically significant levels of Al in the stream do not necessarily imply that acidification has mobilized Al in the soils.

Acknowledgements

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II



Landscape Control of Stream Water Aluminum in a Boreal Catchment during Spring Flood

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Inorganic aluminum (Al) concentrations are critical for defining the biological effects of acidification. The landscape's role in controlling the spatial variability of Al and its speciation has received only limited attention. We analyzed the speciation of stream Al at 14 sites within a 68 km² boreal catchment during spring snowmelt, a period of episodic acidity. Three factors that influenced Al at these sites were landscape type (specifically the proportion of wetland areas), stream pH, and dissolved organic carbon (DOC). Forested catchment sites underlain by mineral soils had higher total Al concentrations and greater inorganic Al proportions than catchments with larger wetland areas, despite significantly higher pH. We suggest that this difference results from source limitation of Al in the peat wetlands. The control of Al solubility was dominated by organic complexes, with the organic carrying capacity exceeding Al in the majority of samples. When assessing the inorganic phase, only four percent of the samples were oversaturated with regards to commonly forming secondary Al minerals, with no samples showing supersaturation higher than 10 times with respect to any given solid phase. Inorganic Al rarely exceeded biological thresholds, except for short periods during peak flow in forested areas, despite two-thirds of the streams having minimum pH values below 4.9. Streams with a high percentage of wetland area were associated with lower Al:DOC ratios. The Al:DOC ratios were quite stable in each stream before, during, and after snowmelt, with the exception of isolated spikes in the Al:DOC ratio associated with particulate Al at a downstream site during high flow.

Introduction

The toxic effects of aluminum (Al) on fauna and flora are central to the acidification issue with the adverse effects of elevated Al in freshwaters shown in many studies (e.g., ref

1). The toxicity of Al is dependent on the form it takes, and this is determined by a combination of pH and the presence of ligands, e.g., fluoride and dissolved organic carbon (DOC). Acid deposition can increase the levels of Al transported from soils to surface waters by Al buffering of increased acidity in the soil (2, 3). The organic acids in DOC are another, largely natural source of acidity in surface waters (4) that also affect the lateral transport capacity of Al. By decreasing pH, DOC increases Al solubility and influences the speciation of Al toward more toxic forms. At the same time though, DOC is a ligand that binds a portion of the Al in organic forms that are less toxic (5). The double-edged nature of organic acidity, together with the influence of anthropogenic acidification make it difficult to separate natural from anthropogenic influence on Al, especially during events of high flow.

In northern boreal climates, spring flood is associated with a characteristic decline in pH (6) and acid neutralizing capacity (ANC), as well as an increase in Al that coincides with sensitive life stages of aquatic organisms (7). Acidified precipitation adds to the pH decline and Al increase (6). However, there is also a large natural component of pH decline in spring flood due to lower ANC created by dilution with snowmelt, and an increase in organic acids (8).

The potential for fish to relocate to avoid less favorable areas may play an important role in the fishery status for a region (9). Research focusing specifically on the avoidance of Al is limited (10) due to the problems in differentiating the effects of low pH from those of high Al (e.g., ref 11). However, in low pH conditions, increases in Al have been shown to increase avoidance behavior in fish (12). This suggests that spatial patterns in stream Al are relevant to the issue of Al toxicity during spring flood.

The dynamics of stream chemistry during episodes at discrete sites in boreal streams have been the focus of a number of studies, but the chemical conditions for aquatic ecosystems are not likely to be well defined by the situation at any single point. There can be a great variability in surface water chemistry across a landscape, and the channel network connects these, often very different, chemical environments. With regards to Al toxicity, mixing zones at junctions where waters of different acidity levels meet have received some attention (e.g., ref 13). Downstream patterns of Al transport have also been investigated (14). However, landscape-scale investigations linking stream Al chemistry to catchment characteristics remain few. Recent work by Palmer et al. (14) on the spatial patterns of Al and DOC distribution in a temperate forested catchment in New Hampshire, U.S.A. found links at the landscape-scale between elevation and Al with more elevated sites having higher Al. However, this study was undertaken under low flow conditions, while the highest levels of Al concentrations are often seen during high flow (15). Lack of episode data on the spatial patterns of Al speciation at a catchment scale is a barrier to understanding and predicting the effects of anthropogenic acidification in relation to natural processes.

This study seeks to redress that shortcoming in a boreal landscape where inorganic aluminum (Al_i) can be a critical limitation for the biota, especially during the spring flood with its characteristic decline in pH. The high degree of spatial variability in streamwater chemistry in this type of landscape has been noted in a nearby catchment (16). This study will look for patterns in landscape controls on Al, specifically in the landcover and co-variation of water chemistry parameters that could be of use in predicting where and when Al will restrict the habitat of acid-sensitive aquatic biota.

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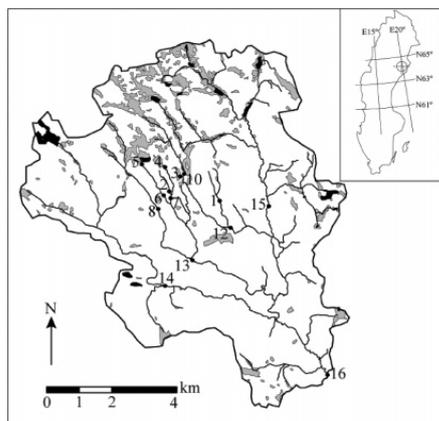


FIGURE 1. Location of the sampling points throughout the Krycklan catchment. Areas of wetland (gray shading) and lakes (black shading). The inset map shows the location of the catchment in Sweden.

Site Description. The study area is comprised of the upper 68 km² of the Krycklan river catchment in northern Sweden (Figure 1). Annual mean air temperature is 1 °C, with 600 mm annual mean precipitation, of which one-third falls as snow.

The Krycklan catchment ranges from 130 to 369 m in elevation. Throughout the catchment, gneissic bedrock is overlain by glacial till, varying in thickness up to tens of meters (17). Subsurface pathways dominate streamflow delivery in forested sites, with overland flow rare due to high infiltration capacity of the till soils (18). Well-developed iron-podzol soils are common, with organic-rich soils near the channel of smaller streams (19). In the lower reaches of the catchment, larger streams have deeply incised channels carving through fine sediments, with a substantial riparian flood plain. Brown trout (*Salmo trutta*), Brook trout (*Salvelinus fontinalis*), and Grayling (*Thymallus thymallus*) reside in the larger streams in the region.

The upland portions of the catchment are forested primarily with mature Scots Pine (*Pinus sylvestris*) and Norway Spruce (*Picea abies*). The forested landscape is interspersed with patches of sphagnum-dominated peat wetlands, making up 8% of the total area, but with a large percent coverage in some of the smaller subcatchments.

The 14 intensively studied subcatchments reported here (nr. 1-16, excluding sites 9 and 11 where Al sampling was not conducted) span a wide range of areas and percent coverage of wetland and forest, the two major landcover types in the region (Figure 1, Supporting Information Table S1). While most of the catchments (9 of 14) are independent of one another, many of the larger streams receive some flow from other study sites upstream (Figure 1). This overlap is a result of the effort to represent a range of stream orders within the same catchment.

Materials and Methods

Field Sampling. Discharge was measured continuously at site 7 using a 90° V-notch weir in a heated damhouse. The water sampling strategy was based on grab samples taken at 14 stream sites approximately every second day during the 5-week period encompassing the 2003 spring flood, with less intensive sampling (approximately weekly) at low flow conditions prior to and after the snowmelt period. Water samples were collected in acid-washed 250 mL high-density polyethylene bottles, with multiples rinses. Following col-

lection, water samples were kept dark and cool until they were subsampled for chemical analyses. Samples were not filtered.

Chemical Analyses. pH was measured using a low conductivity Ross 8102 combination electrode (Thermo-Orion). Samples for total organic carbon (TOC) analysis were frozen until analysis. TOC was measured using a Shimadzu TOC-V_{PCH} analyzer after acidification and sparging to remove inorganic carbon. TOC is at least 95% DOC in these boreal environments, both in lakes (20), and streams (21), including episodic conditions (6). Therefore, these measurements are referred to as DOC throughout this article. pH and DOC were measured on all sampling occasions ($n = 25$).

On 14 of the sampling occasions Al fractionation was also undertaken. Al fractionation divided total Al (Al_{tot}) into neutral and anionic (often termed organic aluminum, Al_o) and cationic forms (often termed inorganic aluminum, Al_i). Sampling is based on the cation exchange method of Driscoll (22), with an exchange column directly coupled to an ICP-OES (Varian Vista AX), without acid addition. The column had a length 140 mm, diameter 5 mm, and flow 4 mL·min⁻¹·mL⁻¹ Amberlite (IR-120 Plus, 99% Na form, 1% H form, Sigma-Aldrich). The instrument setup followed Rodriguez-Rosa et al. (23). The Al_i was calculated as the difference between Al_{tot} and Al_o . It is recognized that an ICP determination rather than spectrophotometric determination (22) may increase interference from colloidal and particulate Al in both the determination of Al_{tot} and Al_o . This problem is reduced by not acidifying the samples prior to analysis. The issue of particulate interference in this catchment is localized to a region of finer sediments in the downstream areas (unpublished data) and will be discussed in detail in a separate article.

Analytical uncertainty at a 95% confidence level is 6.4% for the determination of Al_{tot} and 8.4% for Al_o . These values are based on internal control samples from 2002 to 2004 of standard samples at 1000 μg·L⁻¹ for Al_{tot} and 550 μg·L⁻¹ for Al_o . The error associated with Al_i was calculated with eq 1.

$$\delta Al_i = [(\delta Al_{tot})^2 + (\delta Al_o)^2]^{1/2} \quad (1)$$

Aluminum solubility has been investigated with regard to both an organic phase and possible mineral phases. To assess the organic binding, the theoretical carrying capacity of the DOC was calculated. Following the work of Farmer and Lumsdon (24) precipitation begins as the molar DOC:Al ratio falls below 50, which is taken as the limiting ratio in natural waters. This gives a potential carrying capacity for DOC of 45 μg Al per mg DOC. Mineral solubility has been assessed using literature solubility coefficients for common Al minerals. Al^{3+} is calculated from the Al_i and ligand concentrations (Visual Minteq v.2.40, ref 25).

Supporting Information Available

Landcover Analysis. The 14 sites were subdivided into both spatial and temporal categories. Spatial division was performed using a hierarchical clustering analysis of the landcover information (SAS JMP client software, SAS Institute Inc.). Significant differences were identified between the percentages of forest and wetland coverage (Table S1), and 4 separate spatial groups were defined: Class 1, <1% wetland ($n = 2$); Class 2, 5–16% wetland ($n = 7$); Class 3, 25–36% wetland ($n = 3$); Class 4, >40% wetland ($n = 2$). Temporally, the data were divided into four periods: pre-flood, rising limb, peak flood, and falling limb.

Results

The snowmelt spring flood at Krycklan in 2003 had two distinct phases. The first was a small rise in flow at the end

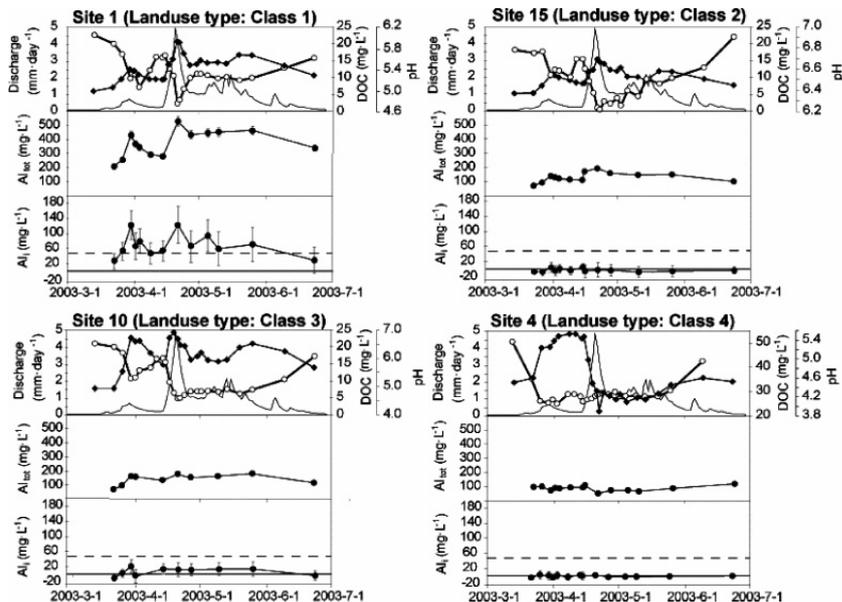


FIGURE 2. Variations in Al and related parameters during spring flood, showing one example from each of the four landcover groupings ranging from <1% wetland (Class 1) to >40% wetlands (Class 4). The upper panel shows DOC (solid line with black markers) and pH (solid line with white markers), and discharge from a representative site with continuous discharge measurement (solid gray line, no markers). The central panel shows Al_o with analytical uncertainty as error bars. The lower panel shows Al_i with analytical uncertainty as error bars, and a proposed limit for acute Al_i toxicity (26) as shown with a broken gray line.

of March, resulting from a short warm spell. After an intervening period of cold weather, the main spring flood occurred in mid- to late-April, peaking on April 21st, with flow remaining elevated above baseflow levels until the start of June. The general chemical dynamics of the spring flood depended greatly on the landcover of the drainage area (Figure 2, Table 1). The sites with <40% wetland (classes 1–3) showed an increase in DOC (range: 0–19 $mg\cdot L^{-1}$ increase, mean 10.5) and, in all but one case, a decrease in pH (range: -1.69 to +0.12 pH units, mean -0.9) during the spring flood. Of the two class 4 sites (>40% wetland), one showed a decrease in pH (site 4, -1.4 pH units), while the other site was frozen during baseflow conditions. The DOC in the class 4 sites increased during the rising limb but fell during peak flow (-4.4 and -16.7 $mg\cdot L^{-1}$, for sites 3 and 4, respectively).

Al_{tot} also varied with landcover (Figure 2, Table 1). Class 1 sites with minimal wetlands had high Al_{tot} that increased at high flow, whereas sites with higher wetland percentages (classes 3 and 4) showed significantly lower concentrations of Al_{tot} (t-test, $p < 0.001$) in combination with slight decreases during peak flow at some sites. The upstream sites generally showed a more peaked response in Al_{tot} than the downstream sites where the mixing of waters from different tributaries smooths the variation. Three spikes of Al_{tot} at the catchment outlet (site 16) during peak flood and an early summer rain event are an exception to this pattern. The concentrations observed in these spikes (max 1123 $\mu g\cdot L^{-1}$) are far above those seen in tributary streams on the same day (mean 332 $\mu g\cdot L^{-1}$, max 413 $\mu g\cdot L^{-1}$). These spikes were not accompanied by similar increases in Al_i but rather were identified as increased Al_o . In larger downstream sites the finer bottom sediment could lead to significant suspended sediment. We propose that particulate or colloidal bound Al is responsible for the observed spikes, which due to its neutral charge would pass through the cation exchange column and be attributed to Al_o . This issue of particulate interference was investigated

more fully in the following year's spring flood and is being described in a separate article.

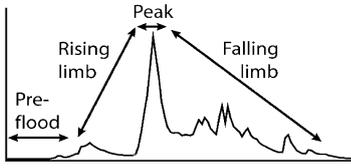
Organically bound Al dominated the speciation at all sites (median 90% SD ± 6). Nonetheless, the concentrations of Al_i were still consistently linked with the concentrations of Al_{tot} . Sites with higher percentage of wetlands (classes 3 and 4) had significantly lower Al_{tot} (t-test, $p < 0.001$), higher DOC concentrations (t-test, $p < 0.05$), and a higher Al_o/Al_{tot} (t-test, $p < 0.05$) as compared to classes 1 and 2. Al_o/Al_{tot} was $93\% \pm 5$ (SD) for classes 3 and 4, vs $88\% \pm 7$ (SD) for classes 1 and 2. This gives class 1 and 2 sites a mean of 12% Al_i and class 3 and 4 sites 7% Al_i as a % of Al_{tot} .

In brown water sites with high Al_o such as those studied here, the calculation of Al_i as the difference between Al_{tot} and Al_o means the analytical error for Al_i can be large. The problem is most obvious in the class 1 sites where the highest Al_{tot} and Al_o values occurred (cf. error bars in Figure 2). This is a problem that is less pronounced in systems with lower DOC (and, therefore, lower Al_o) which were dealt with by many earlier investigations.

Despite the analytical uncertainty in Al_i , strong patterns related to landcover emerged (Table 1). Only the class 1 sites showed mean increases in Al_i of more than 15 $\mu g\cdot L^{-1}$ during snowmelt. The class 2 sites showed increases in Al_i associated with the peaks in discharge in only 2 of the 7 sites, with no change in the mean value. The two groups with more wetland cover (classes 3 and 4) showed small increases in Al_i during snowmelt; however, the absolute values for these sites are low enough to be of little toxicological importance ($< 20 \mu g\cdot L^{-1}$). The Al_i and Al_{tot} concentrations on the falling limb did not return to winter baseflow values, indicating either that summer baseflow had not been reached in this time series of data, or that there is a residual effect of the spring flood remaining in the summer flow.

The Al_i :DOC ratios for sites with more wetland (classes 3 and 4) were also lower than those of sites with more forest cover (classes 1 and 2) (Figure 3b). Although the Al_i :DOC

TABLE 1. Aluminum, pH, and DOC during the Main Spring Flood Peak^a



	pre-flood (0.1–0.2 mm/day)	rising (0.2–0.77 mm/day)	peak (0.6–4.9 mm/day)	falling (3.3–0.1 mm/day)
Al_{tot} (μg·L⁻¹)				
Class 1	227 ^{211–242} (2)	313 ^{259–436} (13)	546 ^{535–557} (2)	403 ^{268–469} (10)
Class 2	213 ^{60–595} (5)	239 ^{80–502} (37)	285 ^{185–360} (7)	289 ^{88–854} (29)
Class 3	94 ^{73–115} (2)	124 ^{100–170} (13)	154 ^{105–181} (3)	127 ^{94–184} (12)
Class 4	98 ⁽¹⁾	193 ^{74–244} (13)	56 ⁽¹⁾	157 ^{68–353} (9)
Al_i (μg·L⁻¹)				
Class 1	42 ^{30–53} (2)	75 ^{51–125} (13)	106 ^{85–126} (2)	66 ^{33–97} (10)
Class 2	28 ^{0–115} (5)	28 ^{–1–125} (37)	28 ^{5–49} (7)	27 ^{0–122} (29)
Class 3	3 ^{–7–13} (2)	11 ^{–2–24} (13)	17 ^{14–20} (3)	10 ^{–1–17} (12)
Class 4	–0.3 ⁽¹⁾	14 ^{0–45} (13)	5 ⁽¹⁾	5 ^{–1–20} (9)
Al_o %				
Class 1	82% ^{78–86%} (2)	76% ^{70–83%} (13)	81% ^{76–85%} (2)	84% ^{78–90%} (10)
Class 2	92% ^{81–99%} (5)	90% ^{75–101%} (37)	90% ^{83–97%} (7)	92% ^{82–100%} (29)
Class 3	99% ^{89–109%} (2)	91% ^{85–101%} (13)	89% ^{88–91%} (3)	93% ^{88–101%} (12)
Class 4	100% ⁽¹⁾	94% ^{86–100%} (13)	91% ⁽¹⁾	97% ^{92–100%} (9)
TOC (mg·L⁻¹)				
Class 1	7.1 ^{6.1–7.8} (3)	10.1 ^{8.3–12.8} (16)	18.1 ^{12.6–23.6} (16)	14.0 ^{9.8–18.4} (22)
Class 2	9.5 ^{2.9–28.4} (14)	16.2 ^{6.5–32.2} (53)	19.9 ^{12.1–30.3} (32)	15.0 ^{5.6–26.5} (88)
Class 3	9.7 ^{6.2–14.9} (6)	15.1 ^{9.3–22.5} (23)	19.9 ^{15.4–24.1} (12)	16.7 ^{11.1–21.7} (33)
Class 4	32.3 ^{31.5–33.1} (2)	45.1 ^{30.8–49.8} (16)	34.5 ^{21.4–47.4} (8)	30.7 ^{24.7–39.6} (22)
pH				
Class 1	5.81 ^{5.47–6.06} (3)	5.38 ^{5.06–5.69} (16)	4.98 ^{4.71–5.41} (8)	5.16 ^{4.88–5.62} (22)
Class 2	6.27 ^{4.14–7.00} (14)	5.90 ^{4.04–6.89} (53)	5.48 ^{4.14–6.65} (32)	5.72 ^{4.50–7.12} (88)
Class 3	6.14 ^{5.50–6.53} (6)	5.65 ^{5.07–6.28} (23)	4.91 ^{4.48–5.62} (12)	5.03 ^{4.54–6.14} (33)
Class 4	5.54 ^{5.38–5.69} (2)	4.04 ^{3.82–4.56} (16)	4.03 ^{3.83–4.96} (8)	4.15 ^{3.95–4.96} (22)

^a Mean values for each site classification are shown along with the range and the number of samples involved. pH and DOC from all samples (25 occasions), Al fractionation from a subset of samples (14 occasions).

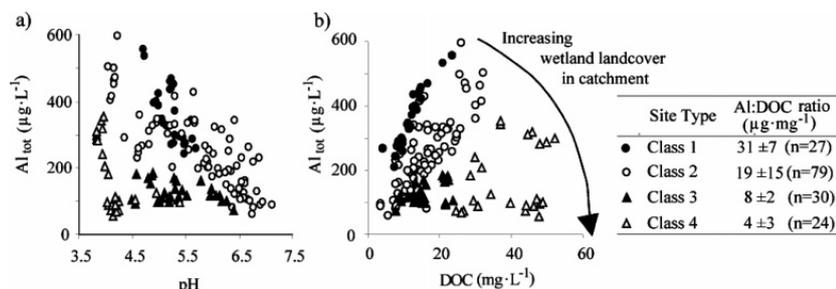


FIGURE 3. Relationships of Al to DOC and pH for landcover classifications, Class 1 (●), Class 2 (○), Class 3 (▲), and Class 4 (△).

ratios varied spatially, particularly with landcover, they remained relatively constant throughout the spring flood, varying only within a factor of 2 for any given sampling site. The only exceptions to this were at the outlet site (nr. 16) following peak flow when the three sampling occasions with Al_{tot} spikes over 600 μg·L⁻¹ also had Al:DOC ratios that increased by up to a factor of 5. The ratios in these three samples (62, 79, and 122) were several times higher, and significantly different from the Al:DOC ratio of all the other sites and dates (t-test, *p* < 0.0001). These samples are excluded from Figure 3.

The solubility of aluminum appears to be dominated at all sites by organic control, shown through the excess of carrying capacity of the DOC once all aluminum has been accounted for (Figure 4a). Classes 3 and 4, due to their higher

DOC concentrations, showed significantly higher carrying capacity than the class 1 and 2 sites (T-test, *p* = 0.0001). The carrying capacity was exceeded by Al_{tot} on four occasions, three during the falling limb at Site 16 (class 2), which coincided with the extreme Al:DOC ratios discussed above, and one sample during the falling limb at site 2 (class 1), all other samples had more potential carrying capacity than Al_{tot}. The fraction present as Al³⁺ showed undersaturation with regards to proto-imogolite and amorphous gibbsite in 96% of the samples (Figure 4b). No samples showed more than 10 times super saturation of these mineral phases.

Discussion

The class 4 sites often had lower pH than the class 1 sites, which might suggest increased Al solubility and mobility.

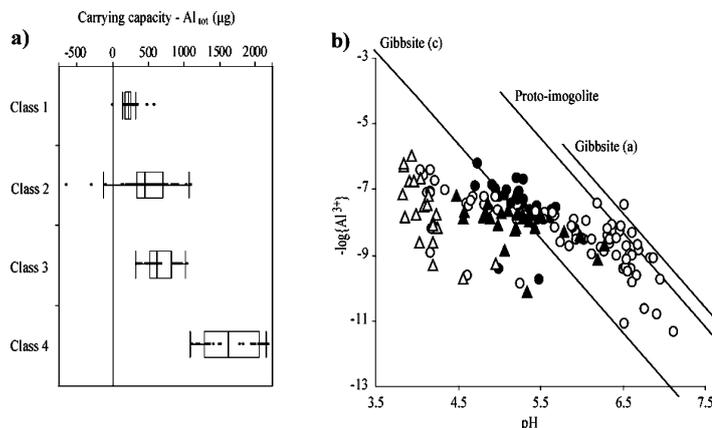


FIGURE 4. Left panel, excess potential Al organic carrying capacity of DOC (Al_{tot} -Carrying capacity), negative values show an exceedance. Right panel, Aluminum mineral solubility, Class 1 (●), Class 2 (○), Class 3 (▲), and Class 4 (△). In the right-hand panel the lines represent the theoretical concentrations at 2 °C (mean temperature, $n = 160$, $SD = 3.3$ °C) for crystalline Gibbsite (39), amorphous Gibbsite (40), and Proto-Imogolite (41). Proto-Imogolite is calculated using the mean Si concentration, $186 \mu\text{mol}\cdot\text{L}^{-1}$ ($n = 160$, $SD = 80 \mu\text{mol}\cdot\text{L}^{-1}$).

However, sites with higher wetland landcover have lower Al_{tot} , lower Al_i :DOC, and in some cases, even decreases in Al_{tot} during spring flood. This is in agreement with previous work within several headwater subcatchments (sites 2, 4, and 7) within the Krycklan catchment studied here (28). The major source of Al to surface waters in boreal environments is from the mobilization of Al from secondary phase minerals and sorption sites following initial weathering of the mineral soils during the podzolization process. In wetland areas, organic material accumulates without the potential to generate Al by weathering. Aluminum source limitation thus appears to be a key factor in explaining the observed landscape patterns at Krycklan. This again shows similar patterns to previous work within the study area, with wetland sites showing significantly lower Al than more forested sites (28). The lack of a weathering source for Al in wetlands, and an abundance of solid-phase organic binding sites, means little Al is mobilized from wetlands into the stream by acidic runoff water.

In the forested sites with little wetland cover, where the supply of Al is not as restricted, the decline in pH during spring flood is associated with increased mobilization and transport of Al from the soil (or streambed) to the stream. The solubility of Al in these samples appears to be dominated by the organic phase, reflected in both the excess organic carrying capacity and the undersaturation with respect to commonly forming hydroxyaluminum and hydroxyaluminum silicates (Figure 4). The precipitation of crystalline gibbsite is energetically hindered in the presence of small amounts of silica (Nagy, ref 29 and refs therein). Aluminum solubility in organic rich soils may be controlled by both organic exchanger sites (30) and imogolite (24) depending on pH. Despite much research in recent years, the question as to which extent imogolite phases participate in Al solubility has not been unambiguously answered (e.g., ref 31). Due to the uncertainty in pAl^{3+} at some sites, we cannot rule out that imogolite type minerals might control solubility at least in some of the class 2 sites. Other factors, however, such as binding by ligands, including organic substances, must play a significant role in Al mobilization, e.g., ref 30.

The speciation of Al was dominated by the organically bound fraction at all sites. In the forested catchment sites this could be explained by the flow through the near stream peats just before discharge to the stream (32, 33). The link between Al concentration and flow pathways was also observed by Palmer et al. (14), where shallow slopes and

thicker soils were linked with increased Al_o concentrations. The higher Al_{tot} concentrations in the forested sites mean that, although the Al_o fraction is almost 90%, the concentrations of Al_i will be higher at the forested sites than in the more acid wetland sites. In classes 1–3, increased DOC and decreased pH during spring flood were coupled to increased Al_o and Al_{tot} , while Al_o/Al_{tot} decreased. As a consequence the relative contribution of Al_i to Al_{tot} increased. This means that at peak flow, the forested sites with higher Al_{tot} also have higher concentrations of Al_i .

Patterns of declining pH and increasing DOC during the period of increased spring flow in forested catchments are hypothesized to be due to changes in flow pathways as proposed by Bishop et al. (32). In these catchments, increased flow gave rise to lower ANC and higher DOC, thereby depressing pH. In wetland catchments the more homogeneous nature of the soil profile means increased flow is unlikely to activate new DOC sources. Dilution by snowmelt may even result in decreased DOC (34), and this can cause pH to rise during peak flow (6), as seen at both class 4 (wetland) sites.

Differences in DOC dynamics between forested and wetland sites were also clearly seen in the Al_i :DOC ratio which was lower in class 3 and 4 sites and higher in class 1 and 2 sites. Similar patterns were also seen by Hruska et al. (28), where the Al_o :DOC ratio (almost analogous with Al_{tot} :DOC due to the dominance of the Al_o fraction) was higher in sites covered by forest than sites draining wetlands. The Al_i :DOC ratios were relatively stable throughout the spring flood for all sites.

The flux of Al from the mineral soil and the temporal variation in the Al_o/Al_{tot} at a particular site is dependent, among other factors, upon pH (2, 3). Previous work in northern Sweden has shown that, while spring snowmelt pH is sensitive to sulfur deposition, natural factors (dilution and organic acidity) are currently the dominant drivers of the spring flood pH decline (6, 28). Since sulfate deposition has declined in the early 1990s, the anthropogenic component of the pH decline during spring flood is rarely greater than 0.2 pH units (35, 36). Using the linear relationships between pH and Al_{tot} (Figure 3a) along with the mean Al_o/Al_{tot} , we estimated the impact of this anthropogenic component. For class 1 sites an additional 0.2 pH unit drop would give an average of $48 \mu\text{g}\cdot\text{L}^{-1}$ of additional Al_{tot} , of which $6 \mu\text{g}\cdot\text{L}^{-1}$ are Al_i . The effect on the class 2 sites is slightly lower with a mean contribution of $22 \mu\text{g}\cdot\text{L}^{-1}$ Al_{tot} , of which $3 \mu\text{g}\cdot\text{L}^{-1}$ are Al_i . Class

3 and 4 sites show little or no change since pH and Al were not well correlated. These estimates indicate that the anthropogenic impact on Al_{tot} , and especially Al_i is currently small in this catchment, but it has the potential to increase on the class 1 and class 2 sites if the human influence on the pH increased.

The most biologically relevant data are the concentrations of Al_i , but setting simple toxicity thresholds is difficult because tolerances vary with both the species studied and DOC levels (1, 37). Many published studies use Atlantic salmon (*Salmo salar*), which, although more sensitive than the species found naturally in the Krycklan streams, can help to give a general idea of toxicological limits. For example, chronic effects of Al_i can be seen at a concentration of $33 \mu\text{g}\cdot\text{L}^{-1}$ Al_i (7 day exceedance), and acute effects (24 h exposure) at $56 \mu\text{g}\cdot\text{L}^{-1}$ Al_i (26). These limits are in close agreement with those proposed by the Swedish EPA (38). Of the 14 streams sampled in this study, the two headwater class 1 sites (sites 1 and 2) and the smallest class 2 site (site 7, 50 ha) showed high levels ($>56 \mu\text{g}\cdot\text{L}^{-1}$ Al_i) that persisted for between 26 and 82 days. Two of the class 2 sites (sites 8 and 14) showed elevated levels ($>33 \mu\text{g}\cdot\text{L}^{-1}$ Al_i) that persisted for between 13 and 41 days. The other nine sites in the study catchment remained below the toxicity limits for Atlantic salmon. None of the sites with higher wetland areas exceed these limits, despite pH values between 4 and 5. So despite Al_{tot} concentrations well above $100 \mu\text{g}\cdot\text{L}^{-1}$ in many sites, only a few show toxic levels of Al_i . This suggests that, while hazard zones with elevated Al_i may exist, there can also be safe havens where Al_i concentrations are low due to lack of Al weathering sources or the presence of binding ligands. The high levels of DOC, though, result in lower pH, which in itself poses a toxicological issue.

Overall, the importance of landscape in controlling both the spatial distribution and the potential toxicological impact of Al in the catchment is evident. The concentrations of both Al_{tot} and Al_i appear to be governed by the interplay between Al sources, DOC concentration, and pH, all of which are linked to the landscape in the drainage areas. Establishing Al dynamics and toxicity without taking into account all three factors is not feasible in these organic-rich boreal streams. This also means that the Al chemistry in larger downstream sites, which are important for fish populations, is influenced by the landcover in the headwaters via contributions of runoff and Al to the stream network.

Acknowledgments

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Supporting Information Available

Description of drainage basin for each sample location. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Additional Material for web edition

Table 1. Description of drainage basin for each sample location.

Site No.	Name	Stream Order	Area (km ²)	% water	% forest	% wetland	% arable	(km)	Statistical grouping ¹
1	Risbäcken	1	0.66	0	99	1	0	2.0	Class 1
2	Västrabäcken	1	0.13	0	100	0	0	0.94	Class 1
7	Kalkkälsbäcken	2	0.50	0	85	15	0	2.0	Class 2
8	Fulbäcken	2	2.5	0	89	11	0	4.8	Class 2
12	Nymyrbäcken	3	5.4	0	84	16	0.3	8.7	Class 2
13	Långbäcken	3	7.2	0.6	89	10	0.4	15.4	Class 2
15	Övre Krycklan	4	19.9	1.7	83	14	1.0	25.9	Class 2
14	Åhedbäcken	3	13.6	0.6	90	5	3.9	13.3	Class 2
16	Krycklan	4	67.8	0.7	88	8	3.0	94.3	Class 2
5	Stortjärnen Outlet	1	0.85	4.7	59	36	0	0.02	Class 3
6	Stortjärnbäcken	1	1.3	3.1	73	24	0	1.4	Class 3
10	Stormyrbäcken	2	2.9	0	74	26	0	2.9	Class 3
3	Lillmyrbäcken	1	0.03	0	20	80	0	0.01	Class 4
4	Kalkkälsmyren	1	0.19	0	60	40	0	0.03	Class 4

¹ Statistical grouping based on hierarchical clustering analysis of landcover data and drainage area (JMP 4.0).



III



Modelling inorganic Aluminium with WHAM in environmental monitoring

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Abstract

Due to the varying toxicity of different Aluminium (Al) species, information about Al concentration and speciation is important when assessing water quality. Modelling Al speciation can support operational monitoring programmes where Al speciation is not measured directly. Modelling also makes it possible to retroactively speciate older samples where laboratory fractionation was not undertaken. Organic-rich waters are a particular challenge for both laboratory analysis and modelling. This paper presents the modelling of Al speciation in Swedish surface waters using the Windermere Humic Acid Model (WHAM). The model was calibrated with data from operational monitoring, the Swedish national survey of lakes and rivers, and covers a broad spectrum of physical and chemical conditions. Calibration was undertaken by varying the amount of DOC active in binding Al. A sensitivity analysis identified the minimum parameters required as model input variables primarily to be total Al, organic carbon, pH, and secondly fluoride, iron, calcium and magnesium.

The observed and modelled Al_i had no significant differences (Spearman rank, $p < 0.01$), however lake samples modelled better than rivers. Samples were placed in the correct toxicological category in 89-95% of the cases. The importance of the size of the calibration data set was assessed, and reducing the calibration data set resulted in poorer correlations, but had little impact on the toxicological placement. Overall, the modelling gave satisfactory results from samples covering a broad spectrum of physical and chemical conditions. This indicates the potential the value of WHAM as a tool in operational monitoring of surface waters.

Key words: Inorganic Aluminium, Modelling, WHAM, toxic, Speciation, Fractionation

Introduction

A central issue in research on acidic systems is increased levels of potentially toxic inorganic Aluminium (Al_i). Al_i toxicity, particularly in fish, has been shown in many studies (Gensemer & Playle, 1999; Rosseland *et al.*, 1992). In organic rich waters, organic carbon can act as a ligand, potentially reducing Al_i toxicity (Laitinen & Valtonen, 1995). Therefore in order to assess the environmental impact on boreal waters where total organic carbon (TOC) values over $5 \text{ mg}\cdot\text{L}^{-1}$ are common, it is critical to know both Aluminium (Al) concentrations and speciation. Although there are a number of established analytical methods for determining Al fractions (Wickstrom *et al.*, 2000), routine measurement is not normally undertaken as part of general environmental monitoring. A complement to laboratory analysis of Al fractionation is modelling speciation (when necessary input data is available) using software such as the Windermere Humic Acid Model (WHAM v. 6.0, (Tipping, 1994)). WHAM is a mechanistic, equilibrium model designed to model ion speciation including the binding of Al to organic matter. Modelling also allows older data, where laboratory fractionation was not undertaken, to be speciated retroactively thereby providing valuable reference material. Computer modelled Al speciation estimates all Al-complexes based on the total stream chemistry rather than just fractionating into organic and inorganic components. This allows one to examine links between specific Al species to both landscape origin and potential toxicological effects.

Previous work with WHAM, which has mainly focused on soil water, has shown success in replicating laboratory batch titrations involving Al in organic soil (de Wit, Kotowski & Mulder, 1999; Tipping *et al.*, 1995), however in a study by de Wit *et al.* (2001)(2001) where WHAM was used to model field data the results were poor. It would be of interest to know if WHAM modelling of Al_i could provide satisfactory results in surface waters on a large scale. Therefore, in this study WHAM modelling of Al_i is undertaken on data from the Swedish national survey of rivers and lakes from 1995 and 2000. These data span a wide range of physio-chemical conditions.

Materials and Methods

Data from the Swedish national lakes and river surveys in 1995 and 2000 was used in this experiment. The national survey is designed to give a spatially representative picture of the chemical and biological status of Swedish surface waters based on 3000-4500 samples chosen in a stratified random sampling design. Stratification was made by county and lake size and based on the Swedish lake register. Lakes size favoured larger more scarce lakes relative to smaller lakes. The geographical stratification based on counties aimed at emphasizing the southern, more acidified lakes. Rivers selection was from two stratified groups ($15\text{-}50 \text{ km}^2$ and $50\text{-}250 \text{ km}^2$) based up the Swedish Meteorological and Hydrological Institute register. The two most recent surveys, conducted in autumn

of 1995 and 2000, are used in this study (Table 1). All water samples underwent a comprehensive chemical analysis that included major constituents, nutrients and selected metals (Wilander, Johnson & Goedkoop, 2003; Wilander *et al.*, 1998). A subgroup of the samples were analysed for Al fractions using the cation exchange method (Driscoll, 1984), see Andrén (1995) for a full description. These samples were randomly selected, but excluded neutral and alkaline water where Al fractionation was of less interest.

Organic carbon was measured as TOC. It has been shown that in these boreal environments TOC is present almost exclusively as dissolved organic carbon (DOC) both in streams (Laudon *et al.*, 2001), and lakes (Köhler, Hruska & Bishop, 1999). The WHAM model requires an input of DOC, for this modelling it was assumed that TOC equals DOC.

Table 1. *Distribution of samples used in this study. Values given as mean and standard deviation*

	Objects sampled (¹)	Used in study (²)	pH	TOC (mg·L ⁻¹)	Al _{tot} (µg·L ⁻¹)	Al _o (ug·L ⁻¹)	Al _i (µg·L ⁻¹)	ANC (µmol·L ⁻¹)
1995 Lakes	4112	315	6.20 ±0.6	10.58 ±5.5	134 ±134	42 ±43	12 ±25	114 ±77
Rivers	708	0 ⁽³⁾	6.50 ±0.3	11.27 ±5.9		41 ±40	8 ±25	211 ±240
2000 Lakes	3465	315	5.96 ±0.7	14.07 ±7.0	175 ±121	86 ±75	15 ±33	113 ±70
Rivers	726	213	6.45 ±0.5	14.29 ±6.9	318 ±378	74 ±72	1 ±20	202 ±138

¹Number of samples in original national lakes and river surveys

²Only samples which were present in both years and with Al_{tot} and Al-fractionation data

³In 1995 no Al_{tot} measurements were made, therefore these samples could not be used.

Both rivers and lakes show a distinct difference in the two surveys with samples from 2000 having significantly higher TOC, total Aluminium (Al_{tot}) and organic Aluminium (Al_o) than the 1995 samples. These conditions reflect the extreme weather conditions of autumn 2000 with heavy rainfall and flooding in many parts of Sweden. This autumn highflow caused the water table to rise, activating more superficial, organic rich flow pathways.

The results of the laboratory-based Al fractionations from the national survey data were used to calibrate the WHAM modelling. The mechanistic chemical equilibrium model WHAM encompasses specific and non-specific binding by humic substances. The model assumes that humic substances consist of humic acids and fulvic acids (FA). FA are more mobile and they are assumed to make up the majority of dissolved organic matter (Tipping, 2002). WHAM regards FA as hypothetical spherical molecules carrying proton dissociating groups capable of binding metals by specific binding. These binding sites include strong and weak acids with different median pKa values. The non-specific binding occurs through accumulation in the diffuse double layer around the charged surface of the FA. Calibration was undertaken by systematically varying the active fraction of FA and recording the subsequent Al speciation. The optimal modelling of Al_i was

obtained by minimising the root of mean squared error (RMSE) between the measured and calculated Al_i .

Calibrations were performed individually on the three data sets (Table 1). The data sets were also subdivided into pH categories to see if there were variations between acid and neutral waters. During each calibration 5% of the points were removed, based on RMSE, to smooth the effects of extreme values.

A sensitivity analysis was undertaken to identify the chemical parameters important in controlling Al speciation and in particular Al_i . Identifying these parameters helps to ascertain dominant ligands in Al binding, and also singles out the minimum chemical analysis required to model Al speciation. The sensitivity analysis was run by creating a mean sample and then systematically varying each chemical variable to the minimum and maximum observed values. The observed deviation in modelled Al_i for extreme values compared to the mean sample could then be used as an indicator of the variable's significance. Not tested in the sensitivity analysis are synergistic effects when two variables change simultaneously.

The modelled Al_i results in this study have been evaluated statistically in two ways, both as continuous data and as categorical data. For continuous data the results of the modelling are correlated linearly to the laboratory results. As the data was not normally distributed the overall significance of the modelling was assessed by rank correlation (Spearman) with the null hypothesis that there was significant difference between the modelled and observed Al_i concentrations ($p < 0.01$). Further, Spearman rank coefficients (ρ) were used to evaluate the goodness of fit between modelled and observed Al_i concentrations.

However, Al_i is of interest due to its toxicological effects, therefore, arguably a more relevant method is to assess the model's ability to categorize a sample into the correct toxicological class. The Swedish Environmental Protection Agency has defined three toxicological classes for Al_i : no toxicological effect ($< 30 \mu\text{g/l}$), effects on sensitive species ($30\text{--}50 \mu\text{g/l}$) and effects on tolerant species ($> 50 \mu\text{g/l}$) (SEPA 2002). Both the correct placement and the number of major placement errors (more than one class) have been used in a more lenient categorical assessment of the modelling.

Calibration is always critical in modelling, and if WHAM is to be used as an environmental monitoring tool it is important that, once calibrated, the model can be applied outside the calibration data. In the absence of a second data set of similar size and spatial distribution on which a validation could be performed, a reduction of the calibration basis allowed the robustness of the modelling to be tested. WHAM was systematically calibrated with a smaller randomly selected fraction of each data set (100%, 75%, 50%, 25% and 5%) and then applied to the remaining data. In each case the simulations were repeated ten times and mean values and standard deviations of the performance were evaluated.

All statistical analyses were performed using SPSS (version 11.5).

Results

The sensitivity analysis isolated the input variables important in the modelling process. Of greatest importance were Al_{tot} , pH, DOC and fluoride (F) which all gave a deviation in Al_i from the mean sample of 100% or greater. To a less extent iron (Fe), calcium (Ca) and magnesium (Mg) were also significant in the modelling with variation between 10-100%. Potassium, sodium, chloride, and sulphate all gave deviation in Al_i from the mean sample of <10%.

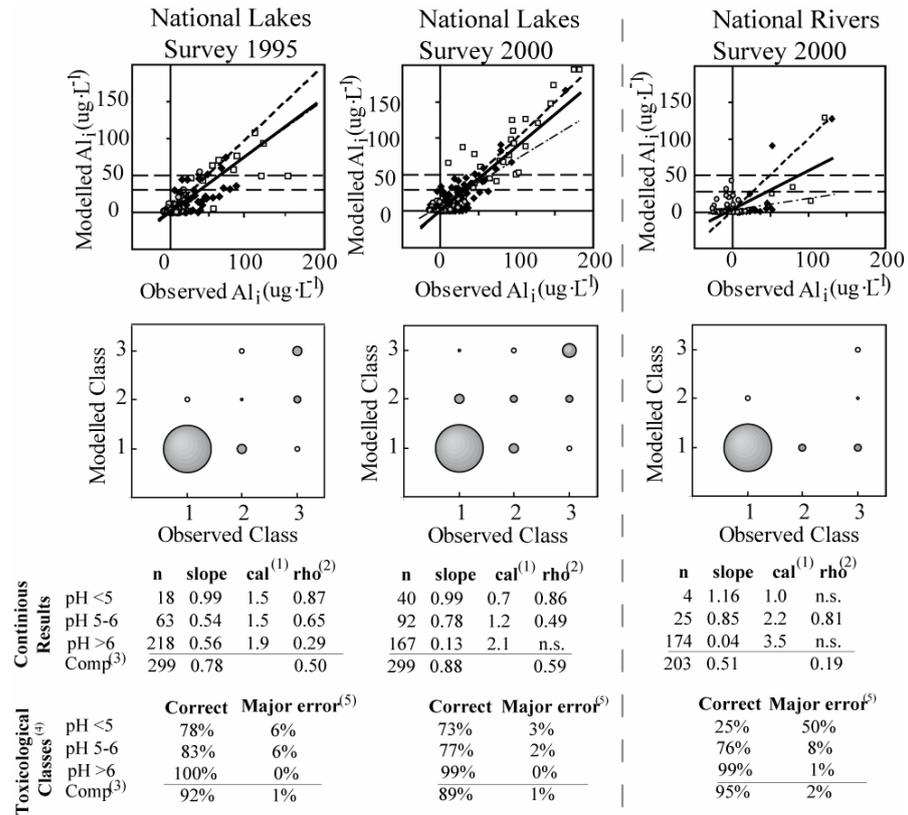
When assessing the continuous results, all three data groups had significant correlation between the observed and modelled Al_i concentrations (Spearman rank, $p < 0.01$). Therefore, the null hypothesis that there are significant differences between observed and modelled data can be rejected. When the data was subdivided in groups based on pH (<5, 5-6, >6) the observed fit was better for all three data sets (Figure 1, top panel), therefore all results given from here on are data from the composite pH class calibration.

The lake samples showed clearer correlations between modelled and observed Al_i than rivers (rho 0.50, $n=299$, and rho 0.59, $n=299$, compared with rho 0.19, $n=203$). Although all data sets were skewed towards low Al_i concentrations, the lake samples also showed more normal distribution than the rivers, with 2000 having a more normal distribution than 1995.

The categorical toxicological analysis (Figure 1 central panel) showed that the majority of the samples contained low (<30 μ g/l) Al_i concentrations. Correct classification was high ($\geq 89\%$) and major errors low ($\leq 2\%$) in both rivers and lakes, for both survey years.

The calibration showed a consistent trend with higher pH samples requiring more of the Al to be organically bound. Although the three data sets showed a similar trend in the level of organic binding (calibration factor), they did not give similar values for each pH category (Figure 1 lower panel).

The study examining the effect of calibration size showed decreasing fit in correlations and, to a lesser extent, increasing error in toxicological classification with decreasing size of the calibration data set. The correlation between modelled and observed Al_i was most effected with Spearman rho values approximately halving when the calibration set was only 5% of the target data. The ability to model toxicological class was minimally affected in all cases, with a change of $\leq 4\%$ for both rivers and lakes.



- (1) Calibration results shown as the DOC multiplication factor to give FA.
(2) Spearman's rho, all values given have a significance ≤ 0.01 . Non-significant values are marked n.s.
(3) Composite result using the individual pH dependant calibrations
(4) Toxicological classes for Al_i based on Swedish Environmental Protection Agency guidelines.
Class 1: <30ug/l, Class 2: 30-50ug/l, Class 3: >50ug/l.
(5) If the classification is wrong by more than one class, i.e. Class 1 modelled as Class 3 or visa versa.

Fig. 1. Modelling of Swedish national lakes and river survey data using WHAM. Top panels shows correlations between observed laboratory fractionation and modelled speciation: symbols represent the pH classes used in calibration (pH <5 (white square), pH 5-6 (black diamond), pH >6 (grey circle). The dashed black line is a 1:1 fit. The solid black line is the fit from using the composite pH classes, and the patterned line (dash-dot-dash) the fit with no sub classes. Horizontal reference lines show 30 $\mu\text{g}\cdot\text{L}^{-1}$ and 50 $\mu\text{g}\cdot\text{L}^{-1}$ Al_i. The central panels show the distribution of samples when assigned a toxicological class, see footnote. The bottom panel shows the optimal calibration factors and numerical representation of the results in different pH classes.

Discussion

The sensitivity analysis identified the dominant ligands binding Al (DOC and F), and also assists in defining the minimum requirements for modelling. Based on variables causing most distortion in the modelling, the minimum parameters required as model input variables are Al_{tot} , DOC, pH, F, Fe, Ca and Mg.

When examined as continuous data, reasonable success in model calibration of Al_i was achieved in the lake samples from 2000 (ρ 0.59, $n=299$), however this was lower in 1995 (ρ 0.50, $n=299$) and poor in the river samples (ρ 0.19, $n=203$). However, as discussed above, Al_i is normally of interest to environmental monitoring due to its toxic effects at elevated concentrations; when viewed from this toxicological viewpoint with categorical data the modelling had a high success rate in all three data sets with correct placement for 89-95% of the samples (Figure 1).

Both the rank correlations and the toxicological classifications were influenced strongly by the data used. The data is representative of the monitored freshwater environments in Sweden and has not been selected to provide an even distribution of data. The data is strongly skewed towards low Al_i concentrations (Table 1 and Figure 1). This results in correlations controlled by a minority of higher Al_i points when the data are considered as a whole. This is particularly true for the results from the river samples where the majority of the observed values are low (close to detection limit). With regards to toxicological categories, the dominance of low Al_i values means that even large percentage errors in the modelling will have little effect on the categorization.

The optimal calibration values for each data set showed consistent trends of higher pH samples requiring more of the Al to be organically bound. In order to accommodate this, the level of active fulvic acid (calibration factor) increased with increasing pH. Although the calibrations showed similar trends in the pH dependence of this parameter, there was still significant variation between the data sets. Spatially, the samples cover all of Sweden, representing a wide range of physical and chemical characteristics, and temporally the samples were taken five years apart, with large differences in hydrological conditions during sampling (high flow in autumn 2000). With these considerations it is not unexpected to see a similar pattern in calibration, but accompanied by significant variation

The aim of this study was to test the applicability of WHAM modelling of Al_i on a national scale. If this kind of modelling is to have a practical application then it needs to be used outside of the calibration data. By reducing the calibration size and then modelling on the remaining data we have tested the robustness of the model. As expected, reductions in calibrations size in relation to target size resulted in a deterioration of the results. The results are subject to similar problems from skewed data resulting in the large decrease in the continuous statistical results and only minor changes in toxicological result when reducing the size of the calibration data set. From this toxicological view it can be seen that even when

the calibration set is only 5% the size of the target set, the modelling is still has a reasonable success rate (between 87-93% correct classification). It can be concluded that extrapolating the calibrations to large-scale data sets is feasible provided the calibration data is representative.

The modelling is not seen as a replacement of laboratory analysis, rather, it allows estimates for many more samples than could normally be budgeted for provided that the basic monitoring data is available. It also opens up opportunities to study origin and effects of specific Al species.

Conclusions

The accuracy of modelling of Al speciation on a national level using WHAM software depends strongly on both the perspective of the modeller and the intended application of the results. Results of the continuous assessment varied markedly between data sets and were strongly influenced by the distribution of data. Toxicological assessment of the samples into classes achieved good overall results, but accuracy at elevated concentrations was significantly lower, presumably due to the strong bias towards low Al_i samples in the calibration data. Increasing the number of samples with Al_i > 30µg·L⁻¹ in the calibration would help improve the modelling of these samples. The high accuracy of the toxicological assessment is also re-enforced by the skewed distribution of calibration data allowing for a wide margin of error. Work with varied calibration data size showed that the model was robust and implies the possibility of the application of this type of modelling outside of the calibration data. With an emphasis on improving calibration data, and provided the necessary input data are available it is possible to calibrate WHAM to model Al_i speciation in surface waters with a reasonable accuracy. This provides both the potential to gain Al speciation data for older samples and to supplement laboratory analysis in new sampling rendering a detailed speciation of the occurring Al-complexes.

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IV



Past, present and future concentrations of inorganic Aluminium in a boreal landscape

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Abstract

By combining an existing tool for the modelling of anthropogenic impact of sulphate deposition during episodes (One-point Boreal Dilution Model, pBDM) with an organic acid and cation binding model (Windermere Humic Aqueous Model, WHAM), the effects of episodic acidification on stream water Aluminium (Al) concentration and speciation have been investigated over the course of half a century. This approach has been applied to an intensively studied catchment in northern Sweden from the period of peak sulphate deposition through to the implementation of current emission legislation (1970-2020). Sulphate deposition records and future predictions are combined with observed stream chemistry from 2004 for 15 sites covering a range of landscape characteristics. The results suggest that inorganic Aluminium concentrations (Al_i^{n+}) were significantly higher in 1970 than at present, and that the average valency of Al_i^{n+} was also significantly higher. The largest reductions in Al_i^{n+} concentrations were seen during the period 1970-2004. From a toxicological view point emission control legislation has reduced the number of streams exceeding limits for acid sensitive and acid tolerant species from 86% and 64% to 36% and 14% respectively for the period 1970-2020. Although this recovery from episodic acidification is positive, a chemical recovery does not necessarily imply a return to pre-industrial conditions due to the long term stresses these communities were exposed to earlier. This episodic acidification history should be borne in mind when assessing biodiversity status in boreal regions such as Sweden.

Key words: Acidification, Recovery; Inorganic Aluminium, Episodic

Introduction

Acidification and its effect on stream water pH and Aluminium (Al) have had detrimental effects on aquatic biota in much of Europe and North America (Wright *et al.*, 2005). Acidification has the potential to affect both the concentration and speciation of Al in freshwater environments. Reduced pH has been associated with an increased flux of Al from soil to stream (Simonsson, 2000; Skjellberg, 1999), and lower pH moves the speciation of Al from neutral to more toxic cationic forms (Stumm & Morgan, 1996). The toxic effects to aquatic organisms from elevated inorganic Aluminium (Al_i^{n+}) associated with low pH are well documented e.g. Poleo *et al.* (1997), Ytre-Stoyl *et al.* (2001). Although separating the effects of low pH from elevated Al_i^{n+} on aquatic organisms is complicated (Gunn & Noakes, 1986), avoidance behaviour by fish in areas of elevated Al_i^{n+} has been shown (Exley, 2000). Understanding patterns of Al_i^{n+} in freshwater environments is central to understanding the distribution of acid sensitive fish.

Due to the effects of anthropogenic sulphate deposition, large areas of Europe and North America have been affected by acidification. Historically sulphate deposition has been far higher than current levels with the peak in deposition in Sweden during the 1970s (Mylona, 1996). It has been shown that the 65% reduction in sulphate emissions since the 1970s have resulted in a 75% areal reduction in seriously acidified surface waters in northern Sweden (Laudon & Bishop, 2002). Assuming compliance with the 1999 Gothenburg Protocol to the Geneva Convention on Long-Range Transport of Air Pollutants, a further reduction of 55% relative to 1990 levels can be expected by 2010 (Warfvinge & Bertills, 1999). To understand the ecological community structure of streams and lakes today it is important to understand the previous stresses these communities have been exposed to and what these Aluminium stresses will be in the future.

In Sweden, the most severe effects from acidification, including soil acidification, have been seen in the south. However, further north beyond the perimeter of this chronically affected zone, the principle effects of acid deposition have been on spring snowmelt episodes. Currently pH and Al levels are not limiting during low flow in most areas of this landscape, but during spring flood, acidity and Al increase. This brings more areas into potentially toxic conditions. In northern Sweden when up to half of the annual discharge occurs over a two to three week period during snowmelt pH can be depressed by 2 pH units (Bishop, Laudon & Köhler, 2000; Laudon, Westling & Bishop, 2000; Laudon *et al.*, 2001). This increase in acidity can be attributed to both natural (Jansson & Ivarsson, 1994; Laudon & Bishop, 1999; Laudon *et al.*, 2005b) and anthropogenic (Eshleman *et al.*, 1995; Jacks, Olofsson & Werme, 1986) factors. It is these areas outside the zone of chronic acidification, where the most rapid response to reductions in sulphate depositions has been seen (Laudon & Bishop, 2002). Recent advances have made it possible to differentiate between the natural and anthropogenic components of springflood ANC decline. It has also been shown that at current deposition levels between 0.1-0.3 pH units of the spring flood pH decline can be attributed to the effects of acid deposition (Laudon, Westling &

Bishop, 2000), with the remaining decline due to natural factors. This recovery has been seen in observational records, but such records are few (Laudon & Hemond, 2002).

It has been demonstrated that the anthropogenic decline in acid neutralizing capacity (ANC) is directly correlated to SO_4^{2-} in the snowpack (Laudon & Bishop, 2002). This allows one to model the recovery in ANC from sulphate deposition data, and also examine how widespread episodic acidification has been during the peak of sulphate deposition in the 1970s. However, it is the concentration of Al_i^{n+} rather than the anthropogenic impact on ANC that is directly linked to toxicological impacts in fish through ionoregulatory and respiratory disturbances (Playle, Goss & Wood, 1989; Poleo, 1995). Therefore, understanding how anthropogenic sulphate deposition has / will affect Al_i^{n+} concentrations in streams is more toxicologically relevant than ANC decline.

Recent work on Al at the landscape scale has shown that Al_i^{n+} and acidity have a large spatial variability from stream to stream in the boreal landscape (Paper II). Al_i^{n+} is not simple a function of pH, but is also related to Al sources in the catchment. Most acid wetlands have low concentrations of Al_i^{n+} because of the lack of mineral sources in their drainage area. Streams draining forested area, with less extreme pH minima have higher Al_i^{n+} related to the larger source of Al from the mineral soils (Paper II). In this landscape dissolved organic matter (DOC) is a key source of natural acidity and also complexes 80-90% of Al_{tot} . This results in Al_i^{n+} concentrations being controlled by three main factors: Al source, DOC and pH.

The heterogeneous nature of DOC has complicated attempts at modelling Al speciation (Tipping, Woof & Harley, 1991). However advances in modelling of cation binding to organic matter (Tipping, 1994) have allowed the successful modelling of Al speciation in organic rich freshwater environments (Paper III). In this paper we combine the ability to model Al speciation with the ability to reconstruct ANC depression caused by acid deposition from Sulphate deposition records to model Al_i^{n+} in a landscape perspective using the intensively studied Krycklan catchment in northern Sweden. To do this we combined an existing tool for the modeling of anthropogenic impact of sulphate deposition during episodes (One-point Boreal Dilution Model, pBDM) with the organic acid and cation binding model (Windermere Humic Aqueous Model, WHAM). Through this approach it will be possible to see the pressures which the landscape has been exposed to and by forecasting it will also be possible to assess potential gains in emission control scenarios.

Materials and methods

Site description

The data used in this study are from the upper 68 km² of the Krycklan river catchment in northern Sweden where 14 streams have been monitored for 2 years (Figure 1). This study site is the subject of a large multi-disciplinary study of the boreal spring flood period (see <http://ccrew.sek.slu.se> for more information). The annual mean air temperature is 1° C, with 600 mm annual mean precipitation, of which one third falls as snow.

The Krycklan catchment ranges from 130 to 369 meters in elevation. Throughout the catchment, gneissic bedrock is overlain by glacial till varying in thickness up to tens of meters (Ivarsson & Johnsson, 1988). Well-developed iron-podzol soils are common, with organic-rich soils near the channel of smaller streams (Bishop *et al.*, 1994). In the lower reaches of the catchment, larger streams have deeply incised channels carving through fine glaciofluvial sediments, with a substantial riparian floodplain. Brown trout (*Salmo trutta*), Brook trout (*Salvelinus fontinalis*) and Grayling (*Thymallus thymallus*) reside in the larger streams in the region.

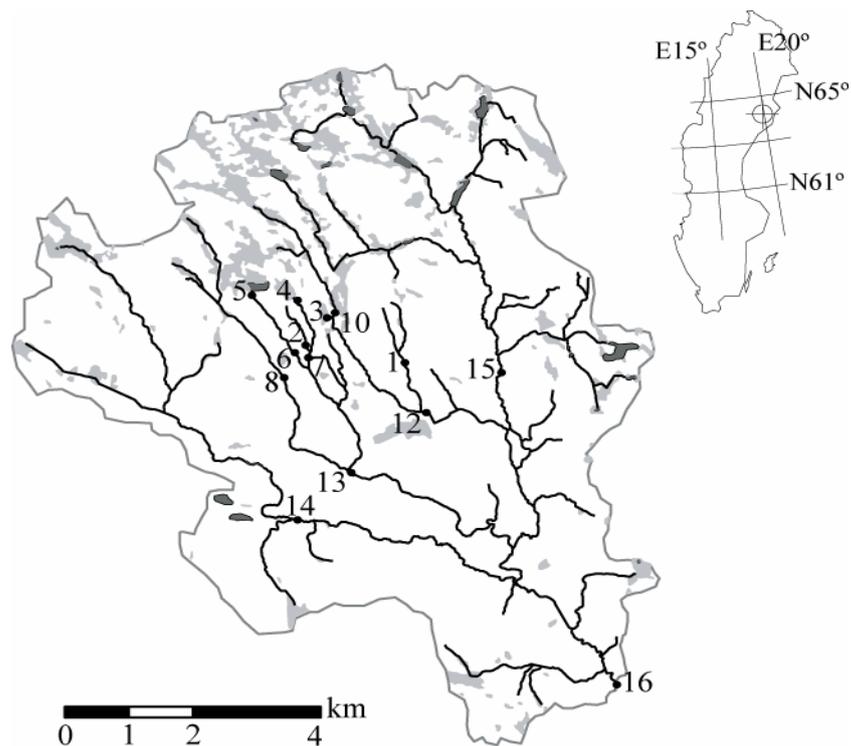


Fig. 1. Location of the sampling points throughout the Krycklan catchment. Areas of wetland (■) and lakes (●). The inset map shows the location of the catchment in Sweden.

The upland portions of the catchment are forested primarily with mature Scots Pine (*Pinus sylvestris*) and Norway Spruce (*Picea abies*). The forested landscape is interspersed with patches of sphagnum-dominated peat wetlands, making up 8% of the total area, but with a large percent coverage in some of the smaller subcatchments.

The 14 intensively studied subcatchments reported here (nr. 1-16, excluding 9 and 11 where Al sampling was not conducted) span a wide range of areas and percent coverage of wetland and forest, the two major landcover types in the region. Refer to Paper II for more info on the stream catchments and their contemporary chemistry. While most of the catchments (9 of 14) are independent of one another, many of the larger streams receive some flow from other study sites upstream (Figure 1). This overlap is a result of the effort to represent a range of stream orders within the same catchment. Sampling was approximately every second day during the 5-week period encompassing the spring flood, with less intensive sampling (approximately weekly) at low flow conditions prior to and after the snow melt period.

Modelling approach

In order to model Al_i^{n+} both retrospectively and into to future deposition scenarios a combination of models and data has been used, as shown in Figure 2. The core of the approach lies in a two-step combination of two pre-existing models, the one-point Boreal Dilution Model (pBDM) (Laudon & Bishop, 2002; Laudon *et al.*, 2005a) to model stream ANC concentrations from Sulphate deposition data, and the Windermere Humic Aqueous Model (WHAM) (Tipping, 1994) to model Al speciation. pH is modeled within the pBDM using the triprotic acid model presented by Köhler *et al.* (2001). The DOC and Al_{tot} values are assumed to be unchanged from the 2004 values. Firstly the pBDM is used along with historical and predicted SO_4^{2-} deposition data to calculate stream ANC and pH for the years 1970, 1990, 2004 and 2020 on each of the 14 streams. This is then used, in combination observed stream chemistry data from 2004, in WHAM to model the Al speciation.

A central assumption of this approach is that the winter deposition of sulphate can be directly related to the anthropogenic impact on the subsequent year's springflood ANC (ΔANC_{poll}) (Laudon, *et al.*, 2005a). This change in ANC can affect both pH and Al_i^{n+} . It is also assumed that soil acidification has not taken place in the north of Sweden (Eriksson, Karlton & Lundmark, 1992), and that the flux of Al from soil to stream has not been affected. Previous work at the hillslope scale has shown no vertical front for Al mobilisation Paper I which could be associated with soil acidification. The effect of a possible increase in Al_{tot} will be explored later in the paper. A further assumption is that long term DOC dynamics have remained constant with no systematic change over the period 1970-2020. Below is a more detailed discussion of the individual components in this approach.

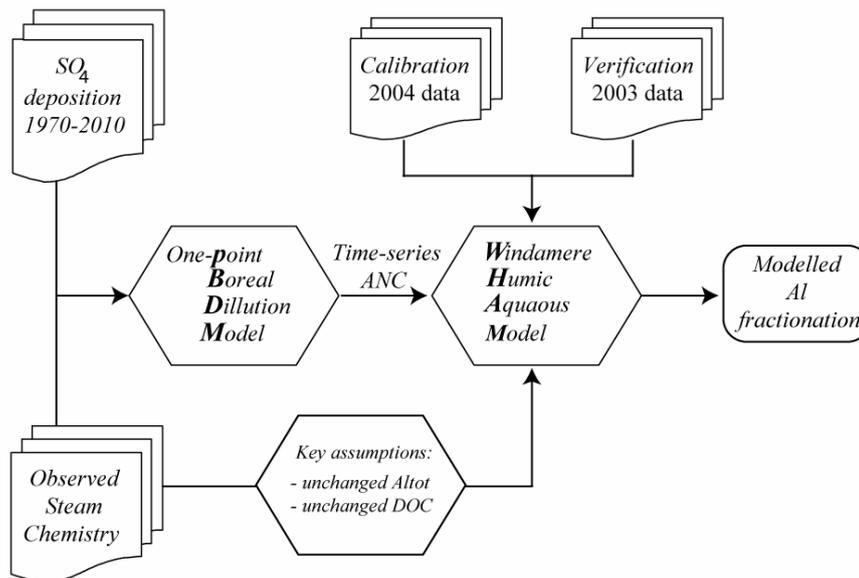


Fig. 2. Schematic representation of the modelling approach used

Stream data

Discharge was measured continuously at a central site using a 90° V-notch weir in a heated damhouse. The water sampling strategy was based on grab samples taken at 14 stream sites approximately every second day during the 5-week period encompassing the 2003 and 2004 spring floods, with less intensive sampling (approximately weekly) at low flow conditions prior to and after the snow melt period (Figure 3).

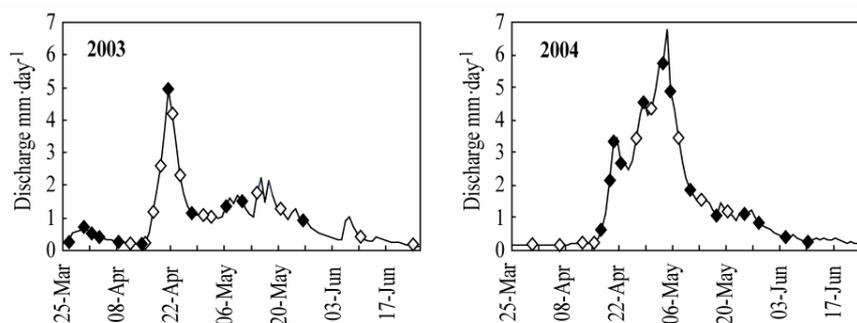


Fig. 3. Discharge from 2003 and 2004 using site 7 as an example of the 14 stream locations. The markers indicate when stream samples were taken. Filled markers represent dates when Al speciation was performed.

All samples were analyzed for major anions and cations as well as pH (low conductivity Ross 8102 combination electrode, ThermoOrion) and total organic carbon (TOC) (Shimadzu TOC-V_{PCH} analyzer). TOC is at least 95% DOC in these

boreal environments, both in lakes (Köhler, Hruska & Bishop, 1999), and streams (Ivarsson & Jansson, 1994), including high flow conditions (Laudon, *et al.*, 2001). Therefore these measurements are referred to as DOC throughout this article. Samples for major cation analyses (K, Mg, Na, Ca) were preserved with ultrapure HNO₃ (1% v/v) and stored until elemental analysis by ICP-OES (Varian Vista Ax Pro). Samples for strong acid anions (SO₄²⁻ and Cl⁻) were stored at 6° C until analysis by ion chromatography (Dionex DX.300 or DX-320). The typical precision in anion and cation analyses based on measurements of certified standards was better than 2%.

On a subset of the sampling occasions Al fractionation was undertaken. Al fractionation divided total Al (Al_{tot}) into neutral and anionic (often termed organic aluminum, Al_o) and cationic forms (Al_i^{nt}, often termed inorganic aluminum). The analysis is based on the cation exchange method of Driscoll (1984), with an exchange column directly coupled to an ICP-OES (Varian Vista AX), without acid addition. Analytical uncertainty at a 95% confidence level is 6.4% for the determination of Al_{tot} and 8.4% for Al_o. See Paper II for a more detailed description of the Al fractionation procedure.

Sulphate deposition data

Sulphate deposition peaked in northern Sweden in the 1970s and had declined by 65% by 1990 (Mylona, 1996). Assuming compliance with the 1999 Gothenburg Protocol to the Geneva Convention on Long-Range Transport of Air Pollutants a further reduction of 55% relative to 1990 levels can be expected by 2010 (Warfvinge & Bertills, 1999). Estimates of sulphate deposition in northern Sweden were created by scaling national deposition data to actual field site observations since 1983 at Vindeln's experimental research park, located within the Krycklan catchment (Figure 4).

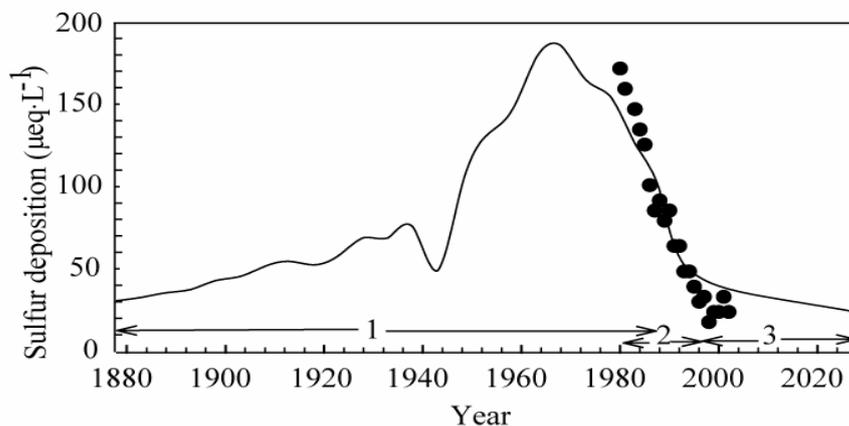


Fig. 4. Measured (dots) and estimated sulphate deposition (solid line) at the field site. Past, present and future deposition was compiled from (1) historical estimate of deposition in Sweden 1880-1991 (Mylona, 1996), (2) EMEP prediction for northern Sweden (Warfvinge & Bertills, 1999) as well as (3) approximation based on the implementation of the 1999 Gothenburg Protocol.

One-point Boreal dilution model

The pBDM (Laudon & Bishop, 2002) is an evolution from the original BDM (Bishop, Laudon & Köhler, 2000; Laudon, 2000) which was developed to distinguish the natural and anthropogenic contributions to the reduction in ANC seen during spring flood episodes. This approach is based on an empirical correlation between anthropogenic contribution to the decline in ANC ($\Delta\text{ANC}_{\text{poll}}$) and winter sulphate deposition (Laudon & Hemond, 2002; Laudon, *et al.*, 2005a). The pBDM has been used to predict both regional episodic acidification in Scandinavia (Laudon & Bishop, 2002) as well as to both hindcast and forecast episodic acidification in a chronically affected site in the Czech Republic (Laudon, *et al.*, 2005a). In this application the pBDM is used to calculate springflood ANC, from historical and future sulphate deposition in the 14 study streams. The pH is calculated from ANC, DOC and pCO₂ within the pBDM using the triprotic acid model presented by Köhler *et al.* (2001).

Windermere Humic Aqueous Model

Windermere Humic Aqueous Model (WHAM) is a mechanistic chemical equilibrium model that encompasses specific and non-specific binding by humic substances (Tipping, 1994). In this application WHAM is used to model Al speciation. This makes it possible to convert the pBDM ΔANC and pH to Al_i^{pH} (with the assumption that Al_{tot} and DOC has been unaffected by land-use, acid deposition or climate). The model assumes that humic substances consist of humic acids and fulvic acids (FA). As FA are more mobile they are assumed to make up the majority of dissolved organic matter (Tipping, 2002). WHAM regards FA as hypothetical spherical molecules carrying proton dissociating groups capable of binding metals by specific binding. These binding sites include strong and weak acids with different median pKa values. The non-specific binding occurs through accumulation in the diffuse double layer around the charged surface of the FA. WHAM has previously been shown to give reasonable results when modeling Al_i^{pH} in Swedish surface waters. (Paper III) In this application, the ΔANC modeled with pBDM for 1970, 1990, 2004 and 2020 is assumed due to anthropogenic factors superimposed upon the natural springflood ANC decline. This, along with the remaining stream chemistry observed in 2004, make up the model inputs for WHAM.

Following previous work in Swedish waters, (Paper III) samples were divided into pH classes. Due to the heterogeneous nature of organic matter the modelling of Al-organic binding is problematic (Tipping, Woolf & Harley, 1991) and therefore a calibration of the WHAM model was undertaken. The WHAM model was calibrated against the 2004 data and then the robustness of the calibration was tested through application to the data from 2003 (table 1). The best fit of the modeled data was achieved using subdivision based on pH, for a more detailed description of the calibration process used see (Paper III).

Table 1. Calibration and verification of the WHAM model

		Calibration (2004 data)	Verification (2003 data)
Spearman's Rho		0.54	0.73
Significance level		0.0000	0.0001
N		208	153
Toxicological classification ¹	Correct	78%	82%
	Minor error ²	15%	12%
	Major error ³	7%	7%

¹ Placement into toxicological classes based on concentration of Al_i^{n+} :

Class 1 <30 μ g/l; Class 2 30-50 μ g/l; Class 3 >50 μ g/l

² Minor error defined as a mis-classification by one class

³ Major error defined as a mis-classification by two classes.

Central to this modelling approach is that Al_{tot} and DOC remain unchanged during the 50 year time span, and that changes in Al_i^{n+} are due to changes in the speciation of Al related to pH. To test the effect of this assumption about Al_{tot} , a sensitivity analysis was also run using systematic increases in the concentrations of Al_{tot} (0-100% increase). This range is based on the spatial pH to Al_{tot} relationship seen for this catchment (Paper II), where spatial variation in the pH range 4-6 for all but the two mire headwaters gave a variation in Al_{tot} from 203-391 μ g·L⁻¹, that is to say an approximate 100% change.

Results

The observed pH from 2004 varied significantly both spatially and temporally as discussed in more detail by Buffam *et al.* (in review) and Paper II. In the headwater sites with forest cover the mean pH was 5.22±0.46 (n=29), however, during the peak flow, acidity increased significantly with pH dropping to 4.52. For headwater wetland sites the pH was significantly lower than the forested sites, mean 4.39±0.34 (n=27), and remained more stable throughout the springflood. The larger, mixed, downstream sites showed a more varied response in pH, mean 5.56±0.65 (n=164), with the peak flow, like the forested headwater sites, showing an increase in acidity (minimum, pH 4.48).

The changes in runoff ANC are due to the reduction in sulphate deposition, and are therefore uniform over the catchment. The modelled anthropogenic reductions in springflood ANC used were -90 μ eq·L⁻¹, -45 μ eq·L⁻¹, and +10 μ eq·L⁻¹ for 1970, 1990 and 2020 respectively.

The modelled pH from 1970 based on the triprotic acid model (Köhler, *et al.*, 2001), predicted lower pH throughout the catchment compared to 2004 values. Forested headwater sites had a mean pH of 4.40±0.68 (n=29) with a minimum of 3.94. Wetland sites demonstrated a smaller effect, with mean 1970 modelled pH at 4.00±0.42 (n=27), whilst the larger downstream sites showed a response similar to the headwater forested sites with a mean pH of 4.76±0.87 (n=164), minimum 3.93. The changes in pH for each modelled year are summarised in Table 2. The largest changes occurred during the period 1970-1990,

Table 2. Modelled changes in pH calculated using the triprotic acid model (Köhler, et al., 2001), given as a mean difference and standard deviation from modelled 2004 values

ΔpH	Forested Headwaters	Wetland Headwaters	Mixed Downstream
1970	-0.82±0.38	-0.39±0.19	-0.80±0.40
1990	-0.50±0.23	-0.24±0.12	-0.42±0.23
2004			
2020	0.12±0.05	0.07±0.03	0.09±0.05

The observed Al_{tot} and Al speciation from 2004 has been discussed in detail in Paper II. The landscape influence on $\text{Al}_i^{\text{n+}}$ is an important factor with areas of wetlands showing lower $\text{Al}_i^{\text{n+}}$ concentrations than forested sites despite having significantly lower pH. The Al speciation at all sites is dominated by the organic phase with the fraction bound to organic matter >80%. The make up of the remaining $\text{Al}_i^{\text{n+}}$ fraction is strongly dependant on the pH of the system. During low flow conditions the relatively high pH means that $\text{Al}(\text{OH})_x^{\text{n+}}$ dominate. During peak flow, principally in the more forested sites, the pH drops and aquo-Al (Al^{3+}) becomes a more dominant fraction.

Table 3. $\text{Al}_i^{\text{n+}}$ given as a mean values ($\mu\text{g}\cdot\text{L}^{-1}$) along with standard deviation. Average valency of $\text{Al}_i^{\text{n+}}$ is given in parentheses.

$\text{Al}_i^{\text{n+}}$	Forested Headwaters	Wetland Headwaters	Mixed Downstream
1970	121±47 (2.06)	14±7 (2.04)	41±24 (1.72)
1990	92±37 (1.93)	10±5 (1.98)	26±18 (1.68)
2004	59±25 (1.73)	5±3 (1.89)	4±3 (1.56)
2020	53±23 (1.69)	4±3 (1.87)	12±9 (1.45)

The increase in pH from 1970 to 2020 resulted in a change in the Al speciation, with $\text{Al}_i^{\text{n+}}$ showing reduction in both mean values and in the more toxicologically important maximum values seen during peak springflood (Figure 5, Table 3). The modelled data from 1970 showed significantly higher $\text{Al}_i^{\text{n+}}$ than 2004 values, $48\pm40\mu\text{g}\cdot\text{L}^{-1}$ and $19\pm21\mu\text{g}\cdot\text{L}^{-1}$ respectively. Assuming compliance to emission controls, the modelled $\text{Al}_i^{\text{n+}}$ will continue to decrease slightly with concentrations by 2020 being $16\pm18\mu\text{g}\cdot\text{L}^{-1}$. All sites showed a general increase in pH and reduction in $\text{Al}_i^{\text{n+}}$, however, this pattern was superimposed upon the Al dynamics associated with each site. As discussed in Paper II the Al dynamic of each site are strongly influenced by the landcover in the catchment, specifically the abundance of wetlands. This gives a large spatial variation in the observed $\text{Al}_i^{\text{n+}}$ concentration dynamics during spring flood (Figure 6).

The reduction in the inorganic phase from 1970 to 2020, was compensated by an increased fraction in the organic phase with the overall Al_o fraction increasing from $81\pm9\%$ in 1970 to $94\pm4\%$ by 2020. For headwater forested sites this fraction was slightly lower (73-88% from 1970 to 2020), and for wetland headwaters slightly higher (90-97% from 1970-1990). The speciation of the organic phase also changed during the period 1970-2020, due to the increasing pH. The average valency associated with $\text{Al}_i^{\text{n+}}$ decreased from 1.80 in 1970 to 1.53 by 2020 (Table 3).

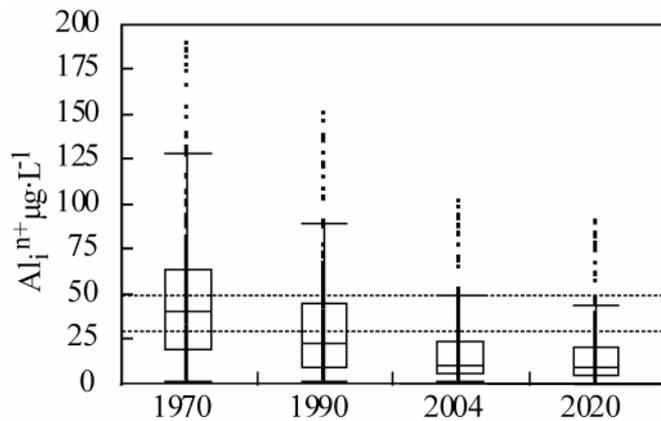


Fig. 5. Modelled changes in Al_i^{n+} from 1970 to 2020. Box plots show median and 10th and 90th percentiles. Horizontal reference lines show proposed toxicological limits (SEPA, 2002; Ytrestoyl, Finstad & McKinley, 2001).

The reductions seen in modelled Al_i^{n+} from 1970-2020 (Figure 5), translated into a reduction in the number of samples exceeding toxicological boundaries. Although Al toxicity varies widely with fish species (Poleo, *et al.*, 1997) boundaries have been proposed for the commonly studied atlantic salmon (*Salmo salar*) (Ytrestoyl, Finstad & McKinley, 2001) and these are in close agreement with guidelines published by the Swedish EPA (SEPA, 2002). Following this work, the observed and predicted sulphate reductions from 1970 to 2020 resulted in a decline of spring flood sampling occasions exceeding limits for acid tolerant and acid sensitive species from 48% and 40% to 15% and 6% respectively (Table 3). The landscape variation gives a spatial aspect to the effects of sulphate deposition (Table 4). Forested headwater sites (sites 1 and 2) show exceedence in the highest Al_i^{n+} category for the entire study period, whilst wetland sites (3 and 4) show concentrations which never exceed toxicological Al_i^{n+} limits despite having the lowest pH values. The remaining sites show exceedence of toxicological limits in the period 1970-1990, however for the more recent period and forecasting (2004-2020) the majority of sites are below toxicological limits.

Table 4. Classification of streams into toxicological classes.

Site Nr	Site Type ¹	Al _i ⁿ⁺ (1)			
		1970	1990	2004	2020
1	Forested (> 99% forest)	Black	Black	Black	Black
2		Black	Black	Black	Black
7		Black	Black	Grey	Grey
8		Black	Black	Grey	Grey
12	Forest dominated (>85% forest, <16% wetlands)	Black	Black	Black	Black
13		Black	Black	Black	Black
14		Black	Black	Black	Black
15	Significant wetlands (>24% wetlands)	Black	Black	Black	Black
16		Black	Black	Black	Black
5		Black	Black	Black	Black
6		Black	Black	Black	Black
10	Wetlands (>40% wetland)	Black	Black	Black	Black
3		Black	Black	Black	Black
4		Black	Black	Black	Black

(1) Classification for Al_iⁿ⁺ is shown as:
 White - no toxicity (<30ug/l Al_iⁿ⁺)
 Grey - toxicity to acid sensitive species (30-50ug/l Al_iⁿ⁺)
 Black - toxicity to acid tolerant species (>50ug/l Al_iⁿ⁺)

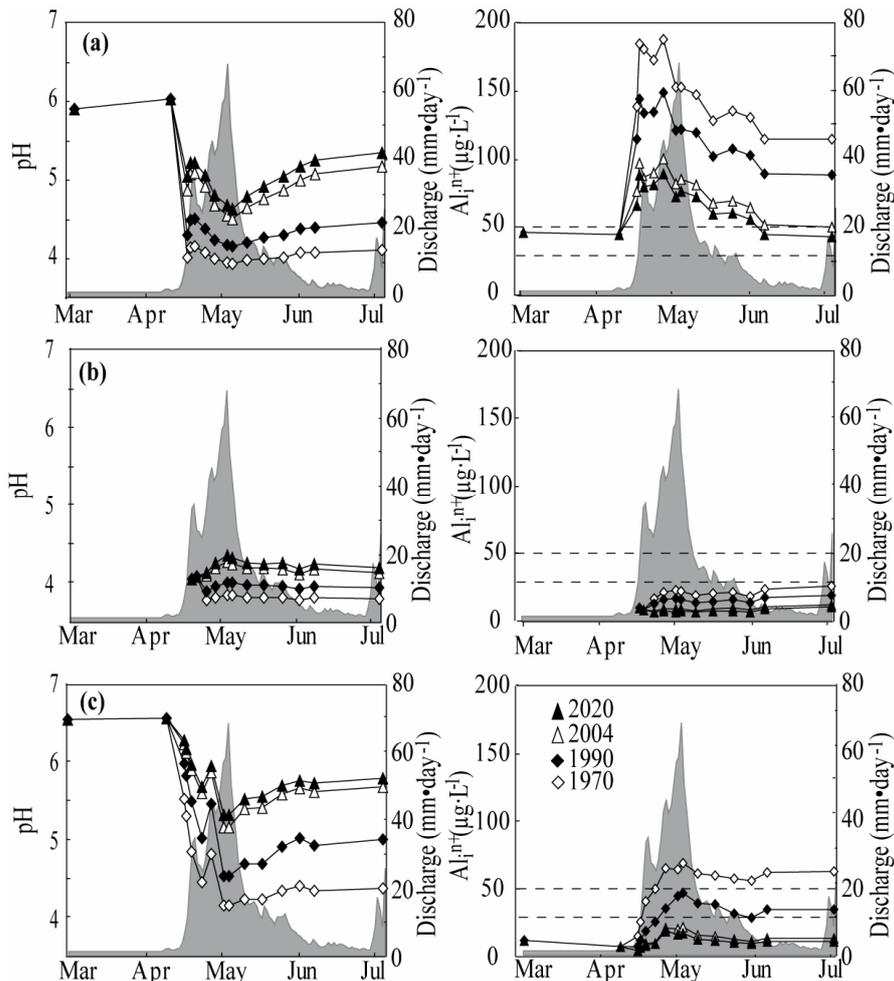


Fig. 6. Response in pH and Al_i^{n+} during spring flood for three characteristic sites in the catchment, (a) Site 2, forested headwater, (b) Site 3, wetland headwater and (c) Site 13, mixed downstream site. Data shown for 1970 (white diamond markers), 1990 (filled diamond markers), 2004 (white triangle markers) and 2020 (filled triangle markers).

Uncertainty Analysis

The modelling is based on several key assumptions, the most critical of which is that the flux of Al_{tot} from soil to stream has not changed during the study period. We tested the sensitivity of the modelling to this assumption. A potential increase in the flux of Al_{tot} entering the stream showed that in all years an increase in Al_{tot} resulted in an increase Al_i^{n+} . For the 1970 data, where pH was significantly lower, this increase was seen in the higher charge cationic Al fractions, shown by the higher average valency (Table 5). In subsequent years, where pH was higher, the increase in Al_i^{n+} was seen predominantly in the $Al(OH)_x^{n+}$, giving a smaller change in average valency (Table 5). It is the strongly positively charged Al forms, especially Al^{3+} , that are commonly associated with fish toxicity.

Table 5. Sensitivity analysis of the effect of a change in the concentration of Al_{tot} . Values shown are modelled Al_i^{n+} ($\mu g \cdot L^{-1}$) followed by the standard deviation. Average valency of Al_i^{n+} is given in parentheses.

	Original Al	+20% Al_{tot}	+50% Al_{tot}	+100% Al_{tot}
1970	48±40 (1.80)	58±50 (1.85)	75±70 (1.92)	108±112 (2.03)
1990	33±31 (1.68)	40±40 (1.73)	53±56 (1.80)	80±93 (1.90)
2004	19±21 (1.56)	24±26 (1.59)	33±38 (1.64)	53±68 (1.73)
2020	16±19 (1.53)	21±24 (1.56)	29±34 (1.61)	48±62 (1.69)

Discussion

Modelled changes in Al_i^{n+}

Although present day deposition levels are considerably lower than during the 1970s, the current biota can not be considered background due to the stresses the landscape has been exposed to earlier. Relative to current values, pH was approximately 0.8 pH units lower in 1970. Al_i^{n+} concentrations in 1970 were between twice and three times the current levels, and the average valency of the Al_i^{n+} was also significantly higher in 1970.

Between 1970 and 1990 Δ pH from 2004 levels approximately halved, from 0.8 to ~0.4 pH units resulting in a significant reduction in the concentration of Al_i^{n+} (Table 3, Figure 5) and drop in average valency from 1.80 to 1.68. Forecast modelling from 2004 to 2020 shows a slight improvement in pH (~0.1pH units) accompanied by a small decrease in Al_i^{n+} and average valency.

Our modelling has focused on the effects of pH upon Al speciation and has not permitted a change in Al_{tot} either from an increased flux from the soil or due to precipitation of Al as pH rises. This is supported by stable Al_{tot} values in one of the monitored site over the last decade (unpublished data), and the lack of an Al “acidification” front in a hillslope transect study on the catchment of stream 7 (Paper I). However, MAGIC modelling of a severely acidified catchment in the Czech Republic showed a predicted reduction in Al_{tot} of 38% between 1992 and 2000 (Hruska, Moldan & Kram, 2002). The sensitivity analysis in this study assessed the variation which could be introduced by an increase in Al_{tot} , for example by the effects of soil acidification lowering soil pH and giving rise to a larger flux of A_{tot} from soil to stream (Simonsson, 2000; Skyllberg, 1999). In all cases, an increase in the concentration of Al_{tot} resulted in an increase in predicted Al_i^{n+} . In some sites from 1970 the pH was still low enough for this increase to occur as strong cationic fractions (e.g. Al^{3+}), shown by the large increase in average valency of Al_i^{n+} . This could be of toxicological importance due to the increased binding strength of di- and tri-valent ions. As sulphate deposition decreased resulting in higher pH values the addition of Al_{tot} resulted in hydrolysis of the Al to give $Al(OH)_x^{n+}$ species, giving a smaller increase in average valency for Al_i^{n+} . As Al buffering is not explicitly accounted for in the modelling of pH, these results are likely to be an overestimation of the effect on Al_i^{n+} . However, the

significance of Al buffering is more important in well buffered waters, over pH 6.5. In organic rich waters (TOC 20ppm, pH <6) the difference due to Al buffering has been previously calculated to be 0.05 pH units or less (Köhler & Bishop, 2005)

The overall pattern of decreasing Al_i^{n+} in conjunction with increasing pH is superimposed upon strong natural spatial variations (Figure 6). The dominant landcover in the catchment is forest, growing on well developed podzol soils, however 8% of the catchment is covered by wetland, which can make up significant portions of some of the upstream sites. These wetland sites, despite lower pH than the forested sites, have no mineral source of Al and subsequently lower Al_i^{n+} than the forested sites (Cory *et al.*, 2006; Hruska *et al.*, 2001). However, in these wetland sites the low pH in itself can be restrictive to aquatic biota.

Connection to deposition reductions

The increase in pH seen in connection with reductions in sulphate deposition (Laudon & Bishop, 2002; Laudon & Hemond, 2002) are also mirrored in the concentrations of stream water Al_i^{n+} when assuming unchanged Al_{tot} and DOC. This reduction in Al_i^{n+} is due to a change in Al speciation rather than changes in the total concentration of Al. This is a feature of the rapid response to sulphate deposition in episodically acidified streams where soil is not acidified strongly. The lack of evidence for chronic soil acidification in the north of Sweden (Eriksson, Karlton & Lundmark, 1992; Kram *et al.*, 2001), and therefore changes in the flux of Al from soil to stream, means that environments such as this with episodic acidification are able to react quickly to changes in sulphate deposition. While this study shows the rapidity of recovery it also underlines how serious acidification of springflood episodes was when sulphate deposition was higher.

Toxicological impacts

Inorganic Aluminium is of interest in relation to sulphate deposition due to its toxic effect on aquatic species, particularly in fish (Gensemer & Playle, 1999; Rosseland *et al.*, 2001). Defining specific toxicological boundaries for aquatic organisms has been difficult due to large variations for different species (Poleo, *et al.*, 1997) and the effects of binding ligands, in particular organic matter (Laitinen & Valtonen, 1995). However in Sweden broad guidelines have been adopted (SEPA, 2002), which are in agreement with published work (Ytrestoyl, Finstad & McKinley, 2001).

From a toxicological viewpoint, the changes in sulphate deposition mean that we move from a system with approximately half the samples in the landscape during spring flood were classed as toxic to acid sensitive species and a over a third of samples toxic to acid tolerant species during the 1970s, to 15% or less of the samples falling in these classes by 2020, assuming full compliance with the CLRTAP 1999 protocol. Two thirds of these remaining samples, including all

exceedence for acid tolerant species, are from the two forested headwater catchments. These small forested headwater sites have been previously shown to have elevated concentrations of Al_{tot} and Al_i^{n+} due to the combination of low pH and a mineral soil source of Al (Paper II). The sites with higher wetland cover (3-5) show no predicted toxicity from Al_i^{n+} over the study period, but can not be seen to be 'safe-havens' due to their low pH resulting from the contributions of organic acidity.

The wider picture

When viewed from a broader perspective, the recovery seen here is in line with other research showing a general chemical recovery in Europe (Wright, *et al.*, 2005). Wider scale projects have mostly focused on changes in ANC rather than specifically on Al_i , however smaller scale projects have shown significant reductions in Al_i in response to decreased sulphate deposition (Skjelkvåle *et al.*, 2001). Improvement however, is not unilateral, for example research in the Adirondack and Catskill regions of western North America showed little reduction in response to emission control for concentrations of soil and freshwater Al (Chen & Driscoll, 2004). Recent MAGIC modelling work in Norway (Larssen, 2005) notes the large gains made in the last 20 years, and, in line with the results presented in this study, predicts limited further improvement in the coming years under current deposition legislation. Although the general picture of a recovery from acidification is generally optimistic, a chemical recovery does not necessarily imply a return to pre-industrial biological conditions (Wright, *et al.*, 2005) due to the long term stresses these communities were exposed to earlier. Much of the focus today is on tracking the biological recovery of chronically acidified areas, but it is also important to consider that all areas with springflood conditions are essentially recovering ecosystems. These areas of episodic acidity merit study of how the biota are responding to major improvements in springflood chemistry as they return towards the natural levels of springflood acidity and associated Al dynamics.

Conclusions

Modelling of inorganic Aluminium (Al_i^{n+}) during the period 1970-2020 showed that in 1970 the levels were significantly higher than observed in 2004. Acute toxicity during the peak of sulphate deposition was widespread during springflood in the Krycklan basin. Today, deposition reductions have reduced Al toxicity to a few forested headwaters. By 2020 only small changes are expected. In northern boreal zones like this catchment, where chronic soil acidification is not seen, it is a change in Al speciation towards a larger organically bound fraction in connection with a rise in pH which causes the decreases seen. The natural spatial variation due to landcover is a significant driver for Al_i^{n+} differences between these sites. Full implementation of the 1999 CLRTAP protocol is predicted to reduce the

number of samples exceeding toxicological boundaries in this study to 15% or less, and restricted to small forested headwaters.

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