Environ. Sci. Technol. 2006, 40, 3494−3500

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

NEIL CORY,*,† ISHI BUFFAM,‡
HJALMAR LAUDON,§
STEPHAN KÖHLER,⊥ AND KEVIN BISHOP†

*Department Environmental Assessment, Swedish University of Agricultural Sciences, Sweden, Department Forest Ecology, Swedish University of Agricultural Sciences, Sweden, Department Ecology and Environmental Science, Umeå University, Sweden, and Department Applied Geosciences, Graz University of Technology, Austria*

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 km$^2$ 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 springflood.

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.

---

* Corresponding author phone: +46 (0)18 673138; fax: +46 (018) 673156; e-mail: Neil.Cory@ma.slu.se.

† Department of Environmental Assessment, Swedish University of Agricultural Sciences.

‡ Department of Forest Ecology, Swedish University of Agricultural Sciences.

§ Umeå University.

⊥ Graz University of Technology.

10.1021/es0523183 CCC: $33.50

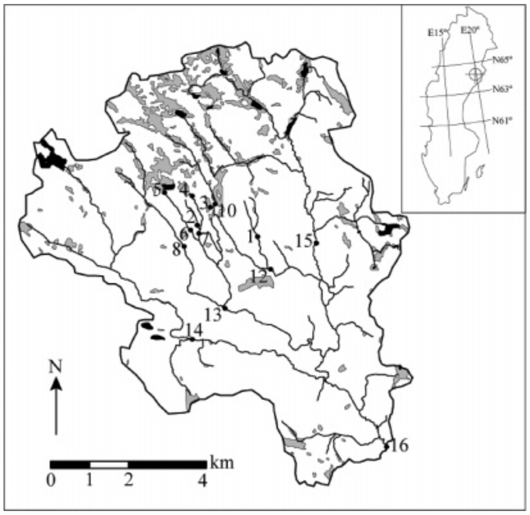


**FIGURE 1. Location of the sampling points throughout the Krycklan catchment. Areas of wetland (gray shading) and lakes (black shading). The inset map shows the location of the catchment in Sweden.**

**Site Description.** The study area is comprised of the upper 68 km$^2$ 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 collection, 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$_{\mathrm{PCH}}$ 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$_{\mathrm{tot}}$) into neutral and anionic (often termed organic aluminum, Al$_{\mathrm{o}}$) and cationic forms (often termed inorganic aluminum, Al$_{\mathrm{i}}$). 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$_{\mathrm{i}}$ was calculated as the difference between Al$_{\mathrm{tot}}$ and Al$_{\mathrm{o}}$. 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$_{\mathrm{tot}}$ and Al$_{\mathrm{o}}$. 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$_{\mathrm{tot}}$ and 8.4% for Al$_{\mathrm{o}}$. These values are based on internal control samples from 2002 to 2004 of standard samples at 1000 $\mu$g·L$^{-1}$ for Al$_{\mathrm{tot}}$ and 550 $\mu$g·L$^{-1}$ for Al$_{\mathrm{o}}$. The error associated with Al$_{\mathrm{i}}$ was calculated with eq 1.

$$\delta Al_i = [(\delta \mathrm{Al}_{\mathrm{tot}})^2 + (\delta \mathrm{Al}_{\mathrm{o}})^2]^{1/2} \tag{1}$$

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 $\mu$g Al per mg DOC. Mineral solubility has been assessed using literature solubility coefficients for common Al minerals. Al$^{3+}$ is calculated from the Al$_{\mathrm{i}}$ 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

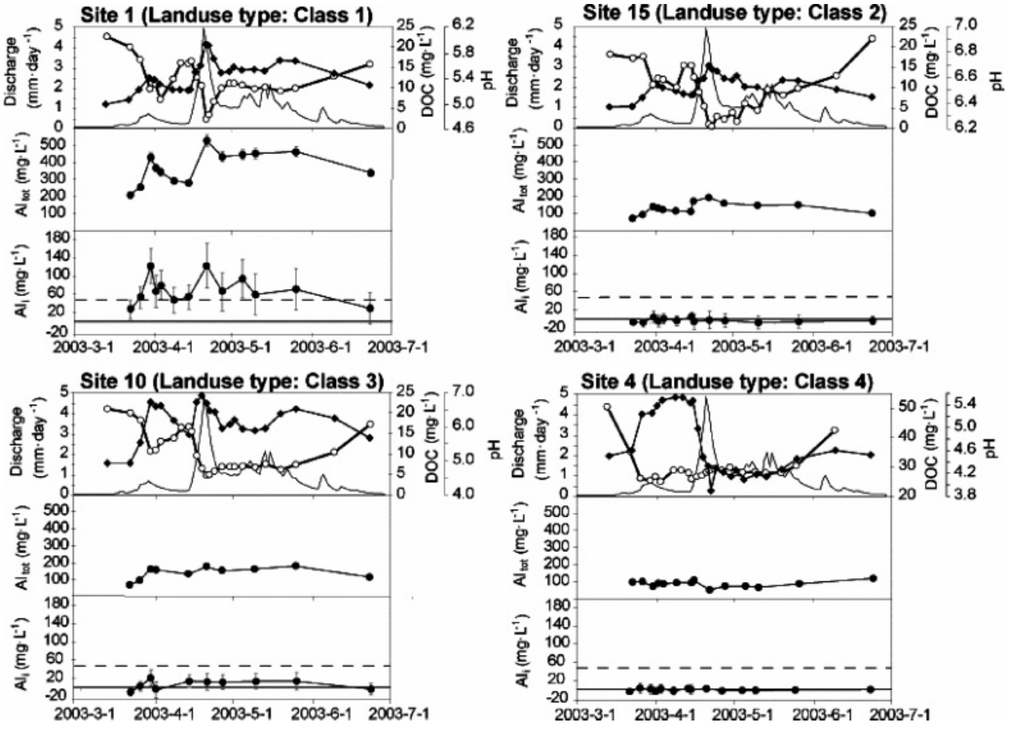


**FIGURE 2. Variations in Al and related parameters during spring flood, showing one example from each of the four landcover groupings ranging from <1% wetland (Class 1) to >40% wetlands (Class 4). The upper panel shows DOC (solid line with black markers) and pH (solid line with white markers), and discharge from a representative site with continuous discharge measurement (solid gray line, no markers). The central panel shows $Al_{tot}$ with analytical uncertainty as error bars. The lower panel shows $Al_i$ with analytical uncertainly 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 smoothes 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.

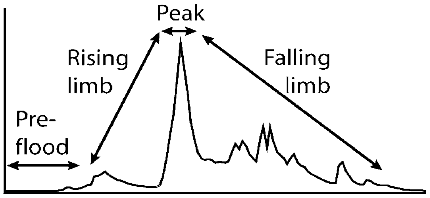
Organically bound Al dominated the speciation at all sites (median 90% SD ± 6). Nonetheless, the concentrations of $Al_i$ were still consistently linked with the concentrations of $Al_{tot}$. Sites with higher percentage of wetlands (classes 3 and 4) had significantly lower $Al_{tot}$ (t-test, $p < 0.001$), 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% ± 5 (SD) for classes 3 and 4, vs 88% ± 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: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: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) |
|---|---|---|---|---|
| **$Al_{tot}$ ($\mu g \cdot L^{-1}$)** | | | | |
| 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 | $98^{(1)}$ | $193^{74-244\ (13)}$ | $56^{(1)}$ | $157^{68-353\ (9)}$ |
| **$Al_i$ ($\mu g \cdot L^{-1}$)** | | | | |
| 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 ($mg \cdot L^{-1}$)** | | | | |
| 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 occassions), Al fractionation from a subset of samples (14 occassions).

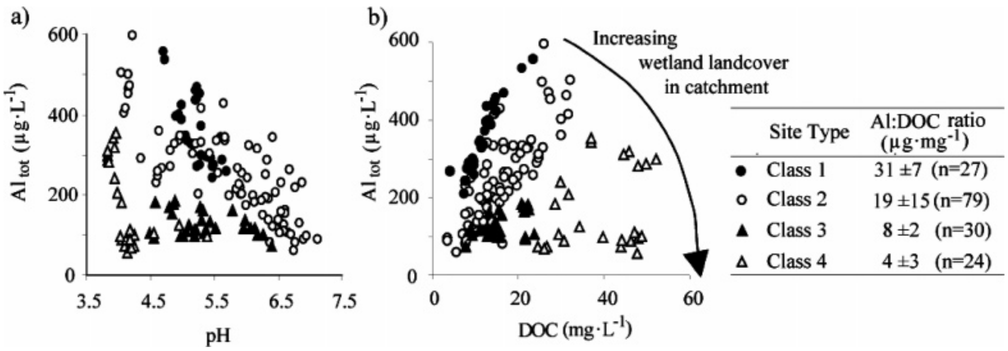


**FIGURE 3. Relationships of Al to DOC and pH for landcover classifications, Class 1 (●), Class 2 (○), Class 3 (▲), and Class 4 (△).**

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 $\mu g \cdot L^{-1}$ 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 $Al^{3+}$ 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.

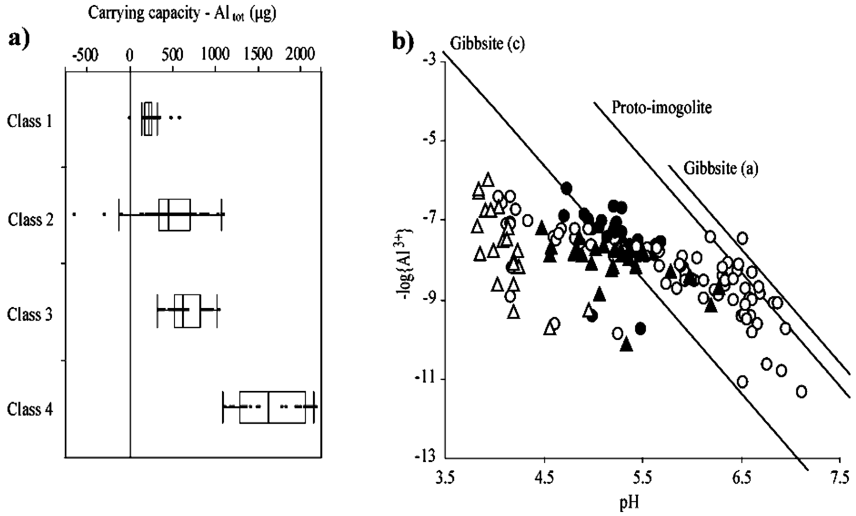


**FIGURE 4. Left panel, excess potential Al organic carrying capacity of DOC ($Al_{tot}$-Carrying capacity), negative values show an exceedance. Right panel, Aluminum mineral solubility, Class 1 (●), Class 2 (○), Class 3 (▲), and Class 4 (△). In the right-hand panel the lines represent the theoretical 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 $\mu mol \cdot L^{-1}$ ($n = 160$, SD = 80 $\mu mol \cdot L^{-1}$).**

However, sites with higher wetland landcover have lower $Al_{tot}$, lower Al: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: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: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 $\mu g \cdot L^{-1}$ of additional $Al_{tot}$ of which 6 $\mu g \cdot L^{-1}$ are $Al_i$. The effect on the class 2 sites is slightly lower with a mean contribution of 22 $\mu g \cdot L^{-1}$ $Al_{tot}$, of which 3 $\mu g \cdot L^{-1}$ 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 been seen at a concentration of 33 $\mu g\cdot L^{-1}$ $Al_i$ (7 day exceedance), and acute effects (24 h exposure) at 56 $\mu g\cdot L^{-1}$ $Al_i$ (*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 ($>56$ $\mu g\cdot L^{-1}$ $Al_i$) that persisted for between 26 and 82 days. Two of the class 2 sites (sites 8 and 14) showed elevated levels ($>33$ $\mu g\cdot L^{-1}$ $Al_i$) 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 $\mu g\cdot L^{-1}$ 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 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

We gratefully acknowledge financial support from the Swedish environmental protection agency and the Swedish research council for environment, agricultural sciences, and spatial planning (FORMAS). Many thanks to Peder Blomkvist, Mattias Sundqvist, Carl-Magnus Mörth, and Johan Temnerud for performing lab analyses and fieldwork.

## 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.

## Literature Cited

(1) Poleo, A. B. S.; Ostbye, K.; Oxnevad, S. A.; Andersen, R. A.; Heibo, E.; Vollestad, L. A. Toxicity of acid aluminium-rich water to seven freshwater fish species: A comparative laboratory study. *Environ. Pollut.* **1997**, *96*, 129−139.
(2) Skyllberg, U. pH and solubility of aluminium in acidic forest soils: a consequence of reactions between organic acidity and aluminium alkalinity. *Eur. J. Soil Sci.* **1999**, *50*, 95−106.
(3) Simonsson, M. Interactions of aluminium and fulvic acid in moderately acid solutions: stoichiometry of the H+/Al3+ exchange. *Eur. J. Soil Sci.* **2000**, *51*, 655−666.
(4) Kortelainen, P.; Saukkonen, S. Organic vs minerogenic acidity in headwater streams in Finland. *Water Air Soil Pollut.* **1995**, *85*, 559−564.
(5) Gensemer, R. W.; Playle, R. C. The bioavailability and toxicity of aluminum in aquatic environments. *Crit. Rev. Environ. Sci. Technol.* **1999**, *29*, 315−450.
(6) Laudon, H.; Westling, O.; Lofgren, S.; Bishop, K. Modeling preindustrial ANC and pH during the spring flood in northern Sweden. *Biogeochemistry.* **2001**, *54*, 171−195.
(7) Poleo, A. B. S.; Muniz, I. P. The effect of aluminium in soft water at low pH and different temperatures on mortality, ventilation frequency and water balance in smoltifying Atlantic salmon, Salmo salar. *Environ. Biol. Fishes.* **1993**, *36*, 193−203.
(8) Laudon, H.; Westling, O.; Bishop, K. Cause of pH decline in stream water during spring melt runoff in northern Sweden. *Can. J. Fish. Aquat. Sci.* **2000**, *57*, 1888−1900.
(9) Gray, R. H. Fish behaviour and environmental assessment. *Environ. Toxicol. Chem.* **1990**, *9*, 53−67.
(10) Åtland, A.; Barlaup, B. T. Avoidance of Toxic Mixing Zones by Atlantic Salmon (Salmo-Salar L) and Brown Trout (Salmo-Trutta L) in the Limed River Audna, Southern Norway. *Environ. Pollut.* **1995**, *90*, 203−208.
(11) Gunn, J. M.; Noakes, D. L. G. Avoidance of low pH and elevated Al concentrations by brook charr (*Salvelinus fontinalis*) alevins in laboratory tests. *Water Air Soil Pollut.* **1986**, *30*, 497−503.
(12) Exley, C. Avoidance of Aluminum by Rainbow Trout. *Environ. Toxicol. Chem.* **2000**, *19*, 933−939.
(13) Rosseland, B. O.; Blakar, I. A.; Bulger, A.; Kroglund, F.; Kvellstad, A.; Lydersen, E.; Oughton, D. H.; Salbu, B.; Staurnes, M.; Vogt, R. The mixing zone between limed and acidic river waters: complex aluminium chemistry and extreme toxicity for salmonids. *Environ. Pollut.* **1992**, *78*, 3−8.
(14) Palmer, S. M.; Wellington, B. I.; Johnson, C. E.; Driscoll, C. T. Landscape influences on aluminium and dissolved organic carbon in streams draining the Hubbard Brook valley, New Hampshire, USA. *Hydrol. Process.* **2005**, *19*, 1751−1769.
(15) Pettersson, C.; Bishop, K. Seasonal variations of total organic carbon, iron, and aluminium on the Svartberget catchment in northern Sweden. *Environ. Int.* **1996**, *22*, 541−549.
(16) Temnerud, J.; Bishop, K. Spatial variation of streamwater chemistry in two Swedish boreal catchments: Implications of environmental assessment. *Environ. Sci. Technol.* **2005**, *39*, 1463−1469.
(17) Ivarsson, H.; Johnsson *Stratigraphy of the Quaternary deposits in the Nyänges drainage area within the Svartbergets forest experimental area and a general geomorphological description of the Vindeln region.* (Swedish with English summary); Swedish University of Agricultural Sciences: Uppsala, 1988.
(18) Nyberg, L.; Stahli, M.; Mellander, P. E.; Bishop, K. H. Soil frost effects on soil water and runoff dynamics along a boreal forest transect: 1. Field investigations. *Hydrol. Process.* **2001**, *15*, 909−926.
(19) Bishop, K.; Pettersson, C.; Allard, B.; Lee, Y.-H. Identification of the riparian sources of aquatic dissolved organic carbon. *Environ. Int.* **1994**, *20*, 11−19.
(20) Köhler, S.; Hruska, J.; Bishop, K. Influence of organic acid site density on pH modeling of Swedish lakes. *Can. J. Fish. Aquat. Sci.* **1999**, *56*, 1461−1470.
(21) Ivarsson, H.; Jansson, M. Regional Variation of Dissolved Organic-Matter in Running Waters in Central Northern Sweden. *Hydrobiologia* **1994**, *286*, 37−51.
(22) Driscoll, C. T. A procedure for the fractionation of aqueous aluminum in dilute acidic water. *Int. J. Environ. Anal. Chem.* **1984**, *16*, 267−284.
(23) Rodriguez-Rosa, R.; Sanz-Medel, A.; Cannata, J. Determinación de aluminio en liquidos biológicos de enfermos de riñón por espectrometria de emisión atómica de plasma generado por inducción (ICP). *Quim. Anal.* **1986**, *5*, 150−163.
(24) Farmer, V. C.; Lumsdon, D. G. Interactions of fulvic acid with aluminium and a proto-imogolite sol: the contribution of E-horizon eluates to podzolization. *Eur. J. Soil Sci.* **2001**, *52*, 177−188.
(25) Gustafsson, J. P. Visual MINTEQ ver 2.40; Royal institute of technology: Stockholm. http://www.lwr.kth.se/english/OurSoftware/vminteq/index.htm, 2005.
(26) Ytrestoyl, T.; Finstad, B.; McKinley, R. S. Swimming performance and blood chemistry in Atlantic salmon spawners exposed to acid river water with elevated aluminium concentrations. *J. Fish Biol.* **2001**, *58*, 1025−1038.
(27) Gerard, F.; Boudot, J.-P.; Ranger, J. Consideration on the occurrence of the Al13 polycation in natural soil solutions and surface waters. *Appl. Geochem.* **2001**, *16*, 513−529.

(28) Hruska, J.; Laudon, H.; Johnson, C. E.; Köhler, S.; Bishop, K. Acid/base character of organic acids in a boreal stream during snowmelt. *Water Resour. Res.* **2001**, *37*, 1043−1056.
(29) Nagy, K. L. Dissolution and precipitation kinetics of sheet silicates. In *Chemical weathering rates of silicate minerals;* White, A. F., Brantley, S. L., Eds.; Mineralogical Society of America: Washington, D. C., **1995**; Vol. 31, p 173.233.
(30) Berggren, D.; Mulder, J. The Role of Organic-Matter in Controlling Aluminum Solubility in Acidic Mineral Soil Horizons. *Geochim. Cosmochim. Acta* **1995**, *59*, 4167−4180.
(31) Berggren Kleja, D.; Standring, W.; Oughton, D. H.; Gustafsson, J.-P.; Fifield, K.; Fraser, A. R. Assessment of isotopically exchangeable Al in soil materials using 26Al tracer. *Geochim. Cosmochim. Acta* **2005**, *69*, 5263−5277.
(32) Bishop, K.; Seibert, J.; Köhler, S.; Laudon, H. Resolving the Double Paradox of rapidly mobilized old water with highly variable reponses in runoff chemistry. *Hydrol. Process.* **2004**, *18*, 185−189.
(33) Bishop, K.; Lee, Y. H.; Pettersson, C.; Allard, B. Terrestrial sources of Methylmercury in surface waters: The importance of the riparian zone on the Svartberget catchment. *Water Air Soil Pollut.* **1995**, *80*, 435−444.
(34) Schiff, S. R.; Aravena, E.; Mewhinney, R.; Elgood, B.; Warner, P.; Dillon, P. J.; Trumbore, S. Precambrian shield wetlands: Hydrologic control of the sources and export of dissolved organic matter. *Clim. Change* **1998**, *40*, 167−188.
(35) Bishop, K. H.; Laudon, H.; Köhler, S. Separating the natural and anthropogenic components of spring flood pH decline: A method for areas that are not chronically acidified. *Water Resour. Res.* **2000**, *36*, 1873−1884.
(36) Laudon, H.; Hemond, H. F. Recovery of streams from episodic acidification in northern Sweden. *Environ. Sci. Technol.* **2002**, *36*, 921−928.
(37) Herrmann, J. Aluminium is harmful to benthic invertebrates in acidified waters, but at what threshold(s)? *Water Air Soil Pollut.* **2001**, *130*, 837−842.
(38) SEPA *Kalkning av sjöar och vattendrag* (in swedish, English translation. Liming of lakes and rivers); Swedish Environmental Protection Agency: Stockholm, 2002.
(39) Stumm, W.; Morgan, J. J. *Aquatic Chemistry*, 3rd ed.; John Wiley & Sons: New York, 1996.
(40) Singh, S. S. The solubility product of gibbsite at 15, 25 and 25 °C. *Soil Science Society of America Proceedings;* Soil Science Society of America: Madison, WI, 1974, *38*, 415−417.
(41) Lumsdon, D. G.; Farmer, V. C. Solubility characteristics of proto-imogolite soils: how silicic acid can de-toxify aluminium solutions. *Eur. J. Soil Sci.* **1995**, *46*, 179−186.

*Received for review November 17, 2005. Revised manuscript received March 20, 2006. Accepted March 23, 2006.*

ES0523183