



Evolution of soil solution aluminum during transport along a forested boreal hillslope

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[1] Aluminum (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 ($<0.1 \text{ mg}\cdot\text{L}^{-1}$). This is not consistent with a vertically infiltrating acidification front mobilizing Al from across the catchment. As water moves laterally downslope into the peaty soils of the riparian zone (RZ), Al increased along with organic acids and iron. The RZ in this study was thus a net source of Al to soil solution on all 9 sampling occasions where Al was measured, as well as a net source of dissolved organic carbon (DOC) on another 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 toxic stream Al concentrations. Organic carrying capacity was in excess of Al for all samples. Only samples from the deeper mineral soils showed supersaturation; however, none of the samples showed degrees of supersaturation high enough for spontaneous mineral precipitation. A key area for further research is how the RZ can sustain a larger Al pool than upslope mineral soils when the supply of Al from these upslope soils to lateral flux is currently lower than that from 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.

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1. Introduction

[2] 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 *et al.*, 2003, 1998]. However, it is still common to find Al_i 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 and Pettersson, 1996; Laudon *et al.*, 2005] giving a characteristic “acid shock”. This coincides with sensitive stages of life for aquatic organisms [Poleo and Muniz, 1993]. The general explanation of toxic Al levels has been that soil acidification has mobilized Al from catchments into streams [Simonsson, 2000; Skyllberg, 1999]. Recent research on the causes of this acid shock, however, has shown that during the late 1990s, only 5–10% of the pH drop in boreal Swedish streams during snowmelt was due to atmospheric deposition [Laudon and Hemond, 2002]. This raises the question of whether the 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 1990s) is mobilizing Al from the soil, thus increasing Al_{tot} and Al_i in runoff.

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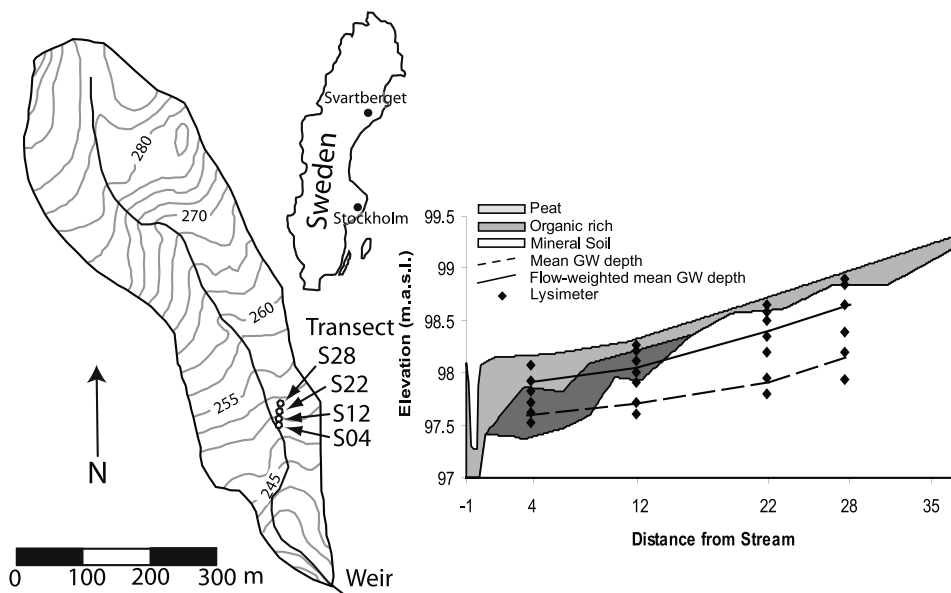


Figure 1. The Västrabäcken catchment in northern Sweden and a cross section of the hillslope transect showing the location of suction lysimeters in relation to the soil organic content and the groundwater level. Note the difference between the mean GW depth and the volume-weighted mean flow path. Most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

[3] Stream water Al must have been derived from 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 in the future. Detailed data on transport through catchments are few, and so far the modeling of Al export in many widely used biogeochemical models is still not mechanistic e.g. MAGIC [Cosby *et al.*, 1985; Sullivan and Cosby, 1995], WITCH [Godderis *et al.*, 2006].

[4] Acid deposition will create an acidification front in the soil profile due to vertical percolation of acidified precipitation [Eriksson *et al.*, 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 and Schofield, 1979; Dickson, 1980; Kirchner and 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 *et al.*, 1991; Stieglitz *et al.*, 2003; Vogt and Muniz, 1997] and north America [Palmer *et al.*, 2005]. This natural accumulation in the RZ has generally been attributed to episodic changes in flowpathways, and co-transport with organic matter.

[5] 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 groundwater a few meters from the stream relate to upslope areas. The RZ of such catch-

ments has been shown to be the proximal source of much stream runoff and its associated chemistry [Bishop *et al.*, 1990a; Hinton *et al.*, 1998]. The upslope areas, however, are more extensive and provide much of the water which comes out of the RZ into the stream.

[6] This study investigates a hillslope in northern Sweden to elucidate 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 modeled, 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 modeled.

2. Site Description and Research Setup

2.1. Site Description

[7] The study hillslope is located on the Västrabäcken stream (Figure 1) that drains a 13 ha subcatchment of the Krycklan 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.

[8] A locally derived glacial till with an average thickness of 10–15 m overlies gneiss bedrock. Soils are predominantly well-developed iron podzols that grade into Gleysols and then humic Gleysols with peat deposits of more than 0.5 m 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 et al., 2003b]. At high flow conditions such as a spring flood it is the superficial, transiently saturated pathways that dominate the lateral transport [Laudon et al., 2004b; Stähli et al., 2001].

[9] 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. The channel was deepened along its entire length upstream of the study site. The impact of forest management in the area is low. The catchment has never been clear cut and the last activity harvesting was in the 1920s when some of the larger trees were removed. Since 1923, the catchment has been part of a research forest.

[10] The soil solution data used in this study were collected from a series of suction lysimeters. These were installed at distances of 4 m, 12 m, 22 m and 28 m 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 6 cm to 90 cm in autumn 1995 (Figure 1). Solid soil samples were taken from each depth of the soil lysimeters during installation. Weekly stream water samples were taken at the weir just above the confluence of Västrabäcken and the main channel. Soil solution from the transect (in total 26 depths with 2–3 replicates of each depth) was analyzed for pH and TOC during 1996–1998 on 22 occasions. Complete soil water anion and cation analyses were performed on up to 9 of these occasions during 1997–1998 with a greater sampling frequency for the riparian lysimeters, S04 and S12 than the upslope S22 and S28 (see Table 1 for sample numbers). Replicate values were averaged for each sample date. The flow situation on these 9 occasions varied from 0.1 to 1.7 mm·day⁻¹. Discharge measurements were made using a 90° thin plate V-notch weir where stage height was recorded continuously with a pressure transducer connected to a Campbell Scientific CR10 data logger. Mean baseflow for the period 1996–1998 was 0.37 mm·day⁻¹ and mean springflood flow 2.8 mm·day⁻¹ with a peakflow of 6.5–8 mm·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.

[11] 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 ha), 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 centimeters 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., 2004b] 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. However, it is accepted that this is a single transect and therefore can not represent the catchment without considerable uncertainty. Therefore, the paper focuses on the changes occurring within the hillslope transect rather than the export from the soil to the stream.

[12] 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 et al., 1990b; Bishop, 1991; Nyberg et al., 2001] for earlier hydrochemical mass-balance studies based on the adequacy of a two-dimensional flow system when considering the flux of buffering capacity [Bishop et al., 1990a], carbon [Bishop et al., 1993, 2004], mercury [Bishop et al., 1995] and lead [Klaminder et al., 2006]. 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., 2003a]. 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].

[13] 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., 2004b].

2.2. Chemical Analysis

[14] For all samples (22 sample dates), both stream water and soil water, were analyzed 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 (pCO₂ = 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 et al., 2002], both in lakes [Köhler et al., 1999] and streams [Ivarsson and

Table 1. Suction Lysimeter Data for All Samples From 1996 to 1998^a

	DOC mg/l	pH ^b	Na mg/l	K mg/l	Mg mg/l	Ca mg/l	Al mg/l ^c	Fe mg/l ^c	SO ₄ mg/l	Cl mg/l
S28 -5	72.48 ± 0.00 (1)	n.d.	n.d.	n.d.	n.d.	n.d.	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)	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	3.89 ± 0.00 (1)	n.d.	1.71 ± 0.00 (1)	0.76 ± 0.00 (1)	0.14 ± 0.00 (1)	0.52 ± 0.00 (1)	≤0.10 ± 0.00 (1)	≤0.03 ± 0.00 (1)	n.d.	n.d.
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)	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	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)	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	1.03 ± 0.27 (2)	6.64 ± 0.21 (2)	1.86 ± 0.13 (3)	0.48 ± 0.08 (3)	0.58 ± 0.03 (3)	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	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)	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	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)	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	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)	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	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)	1.31 ± 0.09 (6)	≤0.10 ± 0.04 (5)	≤0.03 ± 0.00 (3)	3.87 ± 0.16 (6)	0.79 ± 0.12 (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)	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	1.58 ± 1.00 (12)	6.44 ± 0.26 (13)	2.22 ± 0.20 (7)	0.25 ± 0.14 (7)	0.63 ± 0.12 (7)	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	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)	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	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)	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	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)	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	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)	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	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)	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	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)	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	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)	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	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)	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	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)	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	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)	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	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)	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	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)	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	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)	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	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)	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	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)	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	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)	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	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)	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	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)	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	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)	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)

^aMean values, standard deviation and number of samples are shown for each location and depth.^bpH averaged as H⁺ and then converted back to pH.^cQuantification limits: Al 0.10 mg/l, Fe 0.03 mg/l, NH₄ 0.01 mg/l.

Table 1. (continued)

NO ₃ mg/l	NH ₄ mg/l ^c	F mg/l	Si mg/l
n.d.	n.d.	n.d.	n.d.
0.20 ± 0.14 (2)	≤0.01 ± 0.00 (2)	n.d.	3.97 ± 0.00 (1)
0.20 ± 0.14 (2)	≤0.01 ± 0.00 (2)	n.d.	n.d.
0.20 ± 0.14 (2)	≤0.01 ± 0.00 (2)	n.d.	n.d.
0.17 ± 0.12 (3)	0.02 ± 0.01 (3)	0.06 ± 0.00 (1)	n.d.
0.17 ± 0.12 (3)	≤0.01 ± 0.00 (2)	0.08 ± 0.00 (1)	n.d.
0.20 ± 0.00 (1)	≤0.01 ± 0.00 (1)	n.d.	6.24 ± 3.2 (2)
0.18 ± 0.10 (4)	≤0.01 ± 0.00 (3)	0.01 ± 0.00 (1)	6.91 ± 0.00 (1)
0.18 ± 0.10 (4)	≤0.01 ± 0.00 (3)	0.04 ± 0.03 (2)	5.74 ± 0.45 (2)
0.18 ± 0.10 (4)	≤0.01 ± 0.01 (4)	0.04 ± 0.01 (2)	6.93 ± 1.14 (2)
0.13 ± 0.06 (3)	≤0.01 ± 0.00 (2)	0.26 ± 0.01 (3)	8.50 ± 0.39 (2)
0.16 ± 0.09 (5)	≤0.01 ± 0.01 (5)	0.02 ± 0.00 (1)	4.78 ± 1.10 (2)
0.13 ± 0.05 (4)	≤0.01 ± 0.00 (4)	0.04 ± 0.02 (2)	4.81 ± 0.00 (1)
0.18 ± 0.10 (4)	0.02 ± 0.01 (4)	0.06 ± 0.01 (3)	6.33 ± 1.09 (2)
0.16 ± 0.09 (5)	≤0.01 ± 0.00 (5)	0.06 ± 0.01 (3)	6.41 ± 0.51 (2)
0.16 ± 0.09 (5)	≤0.01 ± 0.00 (5)	0.07 ± 0.02 (3)	6.88 ± 0.28 (2)
0.16 ± 0.09 (5)	0.02 ± 0.01 (5)	0.11 ± 0.02 (4)	8.32 ± 0.59 (2)
0.20 ± 0.10 (3)	0.07 ± 0.11 (4)	0.13 ± 0.03 (4)	9.11 ± 0.00 (1)
0.10 ± 0.00 (2)	0.02 ± 0.01 (2)	0.03 ± 0.00 (2)	4.76 ± 0.00 (1)
0.16 ± 0.09 (5)	≤0.01 ± 0.00 (5)	0.03 ± 0.01 (3)	3.41 ± 0.00 (1)
0.18 ± 0.10 (4)	0.02 ± 0.02 (4)	0.07 ± 0.00 (1)	6.96 ± 0.26 (2)
0.33 ± 0.36 (5)	≤0.01 ± 0.01 (4)	0.08 ± 0.02 (4)	7.87 ± 0.46 (3)
0.22 ± 0.16 (6)	≤0.01 ± 0.00 (5)	0.08 ± 0.02 (4)	8.10 ± 0.43 (2)
0.28 ± 0.30 (6)	0.06 ± 0.10 (5)	0.08 ± 0.02 (4)	9.11 ± 0.92 (2)
0.16 ± 0.09 (5)	0.01 ± 0.00 (6)	0.12 ± 0.03 (2)	5.91 ± 0.56 (2)
0.16 ± 0.11 (3)	≤0.01 ± 0.01 (3)	0.06 ± 0.00 (1)	3.97 ± 0.00 (1)
0.16 ± 0.08 (5)	≤0.01 ± 0.00 (6)	0.16 ± 0.09 (3)	7.12 ± 1.11 (2)
0.16 ± 0.08 (5)	0.05 ± 0.09 (6)	0.11 ± 0.04 (4)	7.78 ± 1.06 (2)
0.27 ± 0.29 (6)	0.03 ± 0.03 (6)	0.07 ± 0.02 (5)	8.04 ± 0.22 (3)

Jansson, 1994] even during high flow conditions [Laudon *et al.*, 2001]. Therefore, these measurements are referred to as DOC throughout this article. Inorganic anions and cations were analyzed on up to nine of these sample dates (higher frequency for S04 and S12, lower for S22 and S28, see Table 1) using liquid ion chromatography for inorganic anions and atomic absorption spectrophotometry for cations. Following the approach in estimating organic anions described in the work of Köhler *et al.* [2000] a charge balance was undertaken. Measured amounts of base cations ($C_b = 2[Ca^{2+}] + 2[Mg^{2+}] + [Na^+] + [K^+]$) and acid anions ($C_a = 2[SO_4^{2-}] + [Cl^-] + [NO_3^-] + [F^-]$) were all assumed to be the total dissolved amounts.

[15] On two occasions samples were also studied in more detail with regards to aluminum (equation (1)) through analysis of the total monomeric aluminum (Al_M) and organic monomeric aluminum (Al_o).

$$Al_M = Al_i + Al_o \quad (1)$$

Total monomeric aluminum, estimated by complexation with pyrocatechol violet [La Zerte *et al.*, 1988; Røgeberg and Henriksen, 1985], includes nonlabile and labile monomeric forms [Driscoll, 1984]. Organic monomeric aluminum was separated using an ion exchange method [Driscoll, 1984], column diameter 1 cm, height 4 cm, flow rate 10 mL·min⁻¹. Inorganic monomeric aluminum (Al_i), which includes all cationic forms (Al^{3+} , $Al(OH)^{2+}$, $Al(OH)_2^+$, AlF^{2+} , AlF_2^+ , $Al(SO_4)^+$), was calculated as the difference between Al_M and Al_o (equation (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].

[16] A charge balance has been used to help relate changes in Al to changes in other aqueous 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 (equation (2)).

$$[AD] = C_b - C_a - [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] - [OA^-] \quad (2)$$

The bicarbonate system was approximated using an empirical model as no direct measurements of pCO₂ were available for the period studied. More recent field work in 2001 at the same site with weekly pCO₂ measurements at the same depths as lysimeters in the study give an empirical relationship between pCO₂ and soil temperature (pers. comm. Mats Öquist). These cubic relationships had r² values >0.93 at all depths. Comparison of daily soil temperature in 1998 and 2001 showed little variation (r² = 0.83, mean diff. 0.4°C); therefore we assume that the temperature to pCO₂ –relationship from 2001 can be used to estimate the pCO₂ levels in 1998 based on continually logged soil temperatures. The deprotonation of the organic acids was modeled using an empirical triprotic acid model [Köhler *et al.*, 2001]. Successful modeling of aerated pH with a mean error below 0.2 pH units using measured chemistry validated this approach (data not shown). OA^- encompasses the pH dependant overall charge arising from the speciation of both Al and organic acids. Any residual imbalance is attributed to errors in either the analytical analysis or systematic errors from the modeling.

[17] A series of soil samples was also taken from the transect and analyzed for Al. Organic matter bound Al was extracted in duplicate or triplicate samples with 0.5 M CuCl₂ 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, 3 g of dry soil, and for the mineral horizons 10 g of dry soil, were mixed with 100 ml of 0.5 CuCl₂ 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 meq·g⁻¹ after blank subtraction.

[18] Aluminum solubility has been investigated with regards 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.

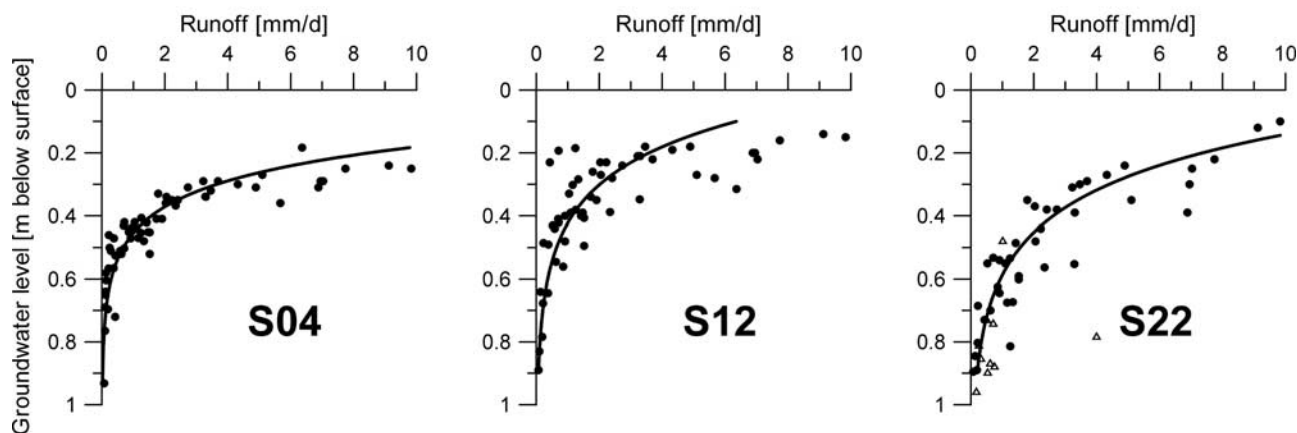


Figure 2. The relationship between stream discharge and groundwater depth along the study transect. Point data is measured stream discharge (y-axis) and groundwater depth (x-axis). Lines are modeled fits allowing the calculation of a lateral flux from each level in the soil profile. Fewer data points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

Various carrying capacities have been reported in the literature, ranging from 1.6 mmol Al per gram C [Farmer and Lumsdon, 2001] to 7 mmol Al per gram C [Buurman, 1985]. Unpublished data from this site indicates carrying capacity to be ~ 6 mmol Al per gram C in the deeper horizons up to ~ 12 mmol Al per gram C in the organic horizons. In this article we have used a value of 12 mmol Al per gram C for the upper 20 cm of the soil profile and 6 mmol per gram C in the remaining soil layers. Mineral solubility has been assessed using literature solubility coefficients for common Al minerals. Due to the limited number of laboratory fractionated Al samples, modeled Al fractionation was undertaken to provide data on organic and inorganic Al fractions (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 Fulvic Acid (FA) assumed active in binding metals. The optimized calibration had 100% of FA active i.e. as FA is 50% carbon, $FA_{active} = 2 \cdot DOC$.

2.3. Lateral Hydrochemical Transport

[19] 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 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, 2004].

3. Results

[20] 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

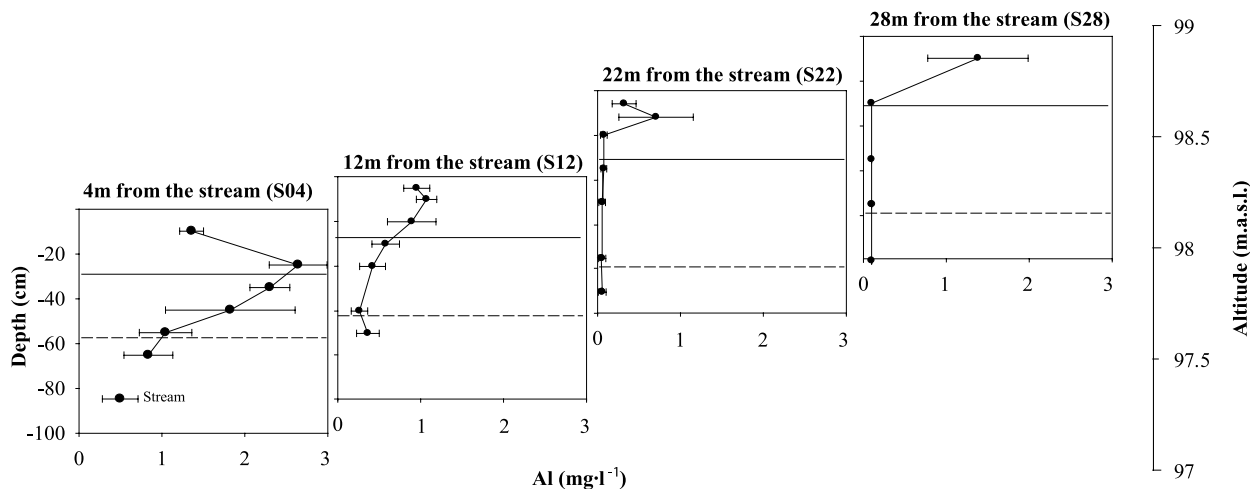


Figure 3. Total Al in soil solution during the period 1996–1998. Dashed horizontal reference lines indicate the median groundwater level and solid reference lines the flow-weighted mean groundwater level. The “whiskers” on each dot indicate the range of the 9–22 observations.

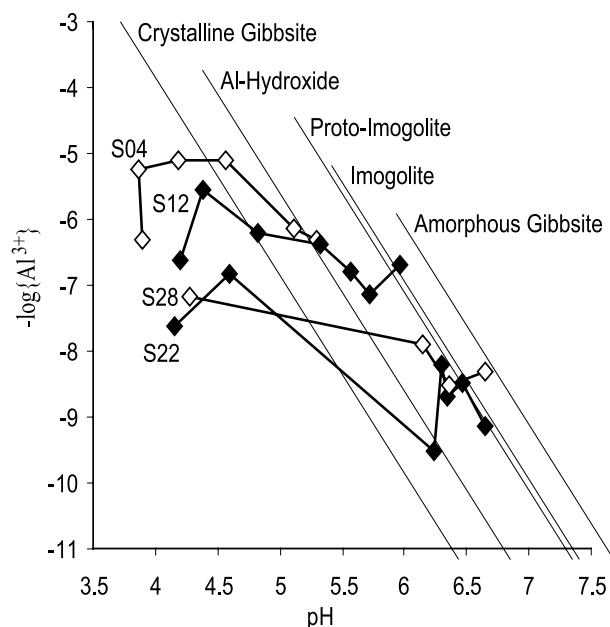


Figure 4. Controls on Al solubility. Soil profiles show increasing depth from left to right. Solid lines represent the theoretical concentrations at the mean temperature, 6.4°C ($n = 243$, $SD = 3.15^\circ\text{C}$) for crystalline gibbsite, amorphous gibbsite, and proto-imogolite [Gerard *et al.*, 2001];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

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.

[21] This defines the horizontal trend of 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 horizontal and vertical 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 45 cm 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, $p = 0.01$, $n = 9$).

[22] 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 ground-

water chemistry on this transect as the immediate source of stream runoff chemistry from the catchment.

[23] The hydrology of the transect varied strongly during different periods of discharge. During low flow conditions, median groundwater levels occurred between 58 cm and 79 cm. 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 and Pettersson, 1996; Laudon *et al.*, 2004a]. During this time the groundwater levels are more superficial, as reflected by the flow-weighted median groundwater depths of between 26 cm and 30 cm. Therefore, even though the dominant lateral flow pathways, most of the year, are in the deeper soils, the large export of water and solutes occurs in transiently active superficial flow pathways which pass through both upslope mineral soils and organic-rich riparian soils (Figures 1 and 3).

[24] 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 Al^{3+} showed undersaturation with regards to proto-Imogolite and amorphous Gibbsite (commonly proposed minerals for the control of Al solubility) in all but two of the samples, these were the deepest samples from S12 and S22, however, no samples showed more than 10 times supersaturation of these mineral phases (Figure 4) implying that conditions for spontaneous precipitation are probably absent.

[25] The observed changes in Al along the transect are related to changes in other constituents that combine to preserve the electroneutrality 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 3 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 what was 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 aluminum (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.

[26] The mean Al concentration 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 go 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

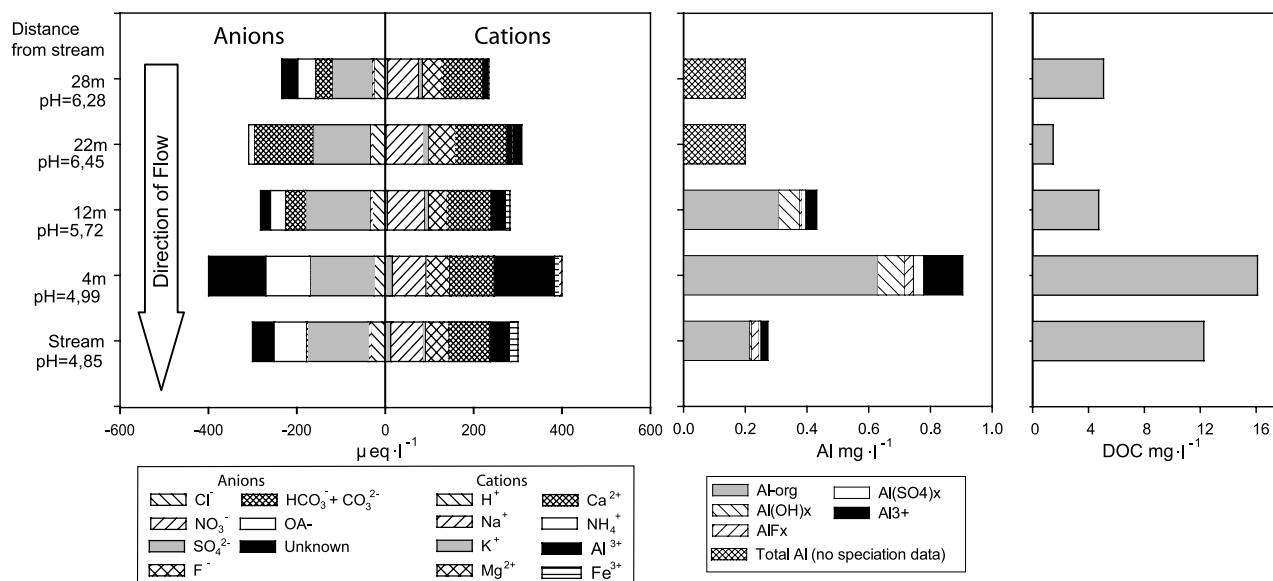


Figure 5. The vertically integrated soil solution chemistry of soil water on June 3, 1998, as it moves downslope towards the stream. The diagram represents how the laterally flowing water (integrated over the depth of the soil profile) evolves downslope, moving from 28 m to the stream. The direction of flow is in the downward direction of the large arrow. (left) Mass balance of the major anions and cations. (middle) Speciated Al. (right) DOC.

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 declined relatively less. Many of the other chemical parameters have similar values in this riparian zone and the catchment runoff.

[27] 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.

[28] The data in Figure 5 show detailed results from a single sampling date. However, the transect has been

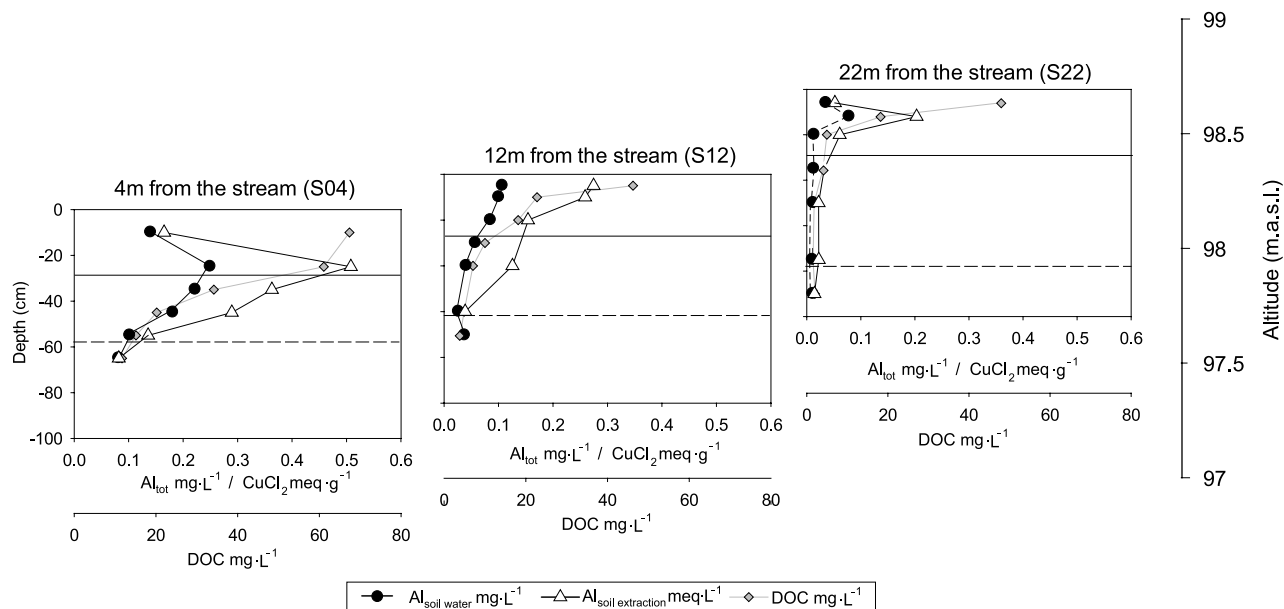


Figure 6. CuCl_2 -extractable Al in soil samples at depths corresponding to the suction lysimeters. CuCl_2 extractable Al (triangles), mean soil water Al_{tot} (solid circles) and mean soil water DOC (grey diamonds). Dashed horizontal reference lines indicate the median groundwater level and solid reference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

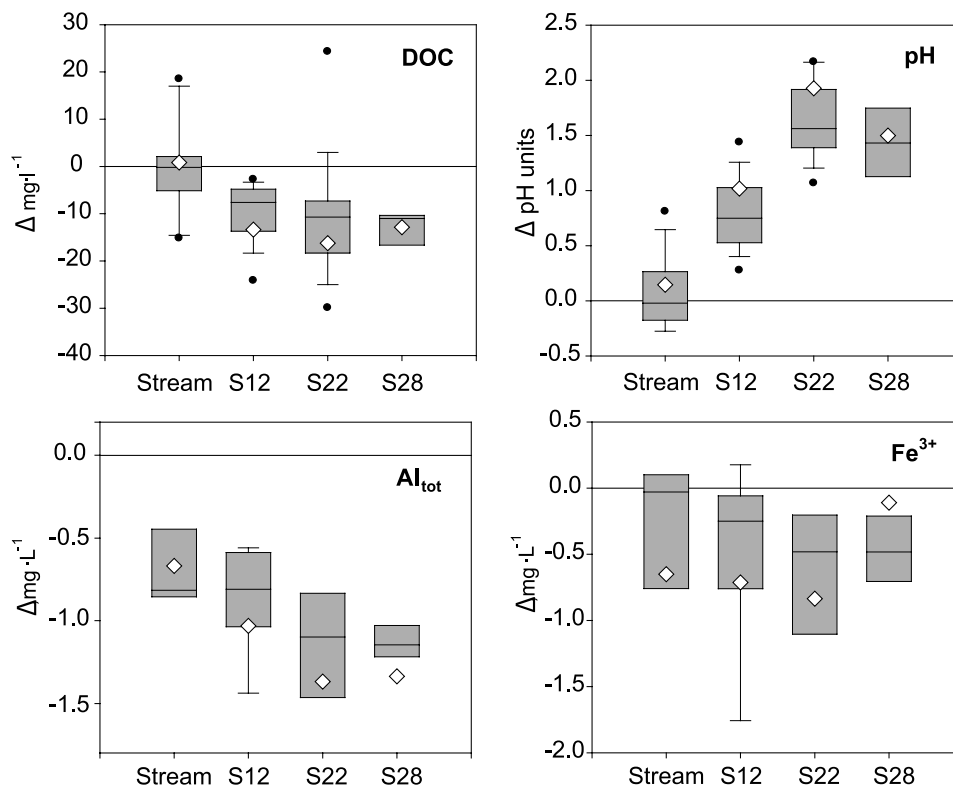


Figure 7. Relative difference in Al and related chemical parameters between the near stream zone (S04) and each sample site. The direction of lateral flow is from right (S28) to left (S12), and then into the stream. Box plots show the data for the whole sample period, 1996–1998 with 9 sampling occasions 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). Diamonds show the flow weighted averages of these data. Positive values indicate concentrations higher than S04 (and vice versa).

sampled on repeated occasions during both spring and summer, over a two year period. 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 ion concentrations are increasing or decreasing as the water moves down the transect into the RZ and then onwards to the stream. Total aluminum is reasonably stable in the upslope areas, increasing markedly in the RZ with a sharp drop again in the stream. Iron shows a similar pattern to Al_{tot}, although less extreme. 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.

4. Discussion

[29] In the areas upslope of the peat soils in the RZ (~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 aluminum concentrations just below the organic horizon [Lundström *et al.*, 2000]. This water continues vertically downward into the underlying mineral soil where adsorption reactions to solid phases reduce soil water concentration. Upon reaching the water table with these low DOC, H⁺ and Al concentrations, water begins moving laterally downslope towards the stream. During most of the year, 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.*, 2004b; Nyberg *et al.*, 2001]. In the upslope areas, these superficial pathways traverse low Al areas. At 12 m, and especially 4 m from the stream, more superficial high flow pathways traverse soils yielding 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.

[30] Stream water Al_{tot} concentrations are significantly lower than those in the RZ examined in this study, whereas many of the other constituents are more similar between this RZ and those found in the stream. A discontinuity between the RZ and the stream is therefore implied. This is consistent with other studies of Al in the hillslope [e.g., *Pellerin et al.*, 2002]. 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.

[31] 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 m 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-exchange buffer for the soil water.

[32] The mosses making up the RZ peats grow without direct contact with the mineral soils, suggesting that the Al buildup in the RZ is allochthonous. The 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.

[33] 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 which 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.

[34] 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 and Mulder*, 1995; *Simonsson and Berggren*, 1998; *Skyllberg and 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 exchange 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 references therein]. Of the more kinetically favorable mineral phases oversaturation with regards to the soil gibbsite proposed by *Gustafsson et al.* [1998] was observed in the deeper samples from S12–S28. Only a small fraction of the samples showed oversaturation with regards to imogolite phases or amorphous gibbsite. 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.

[35] A paradox which exists is that the source areas of Al in the upslope areas have significantly lower Al concentrations than the RZ. This implies that the RZ Al pool 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.

[36] Recent work has shown elevated stream water Al at this site and other forest sites within the surrounding 67 km² during spring flood episodes [*Cory et al.*, 2006]. 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 y.a.). Repeated cycles of episodic lateral flow followed by peat development could lead to the buildup of elevated Al concentrations in this organic zone. The Al buildup 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 buildup in the RZ.

[37] 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 1800s and into the first half of the 1900s, channel ditching was undertaken extensively in Sweden to improve drainage. It is now difficult to find any headwater streams which have not been drained in Sweden [*Dahlström*, 2005]. The channel in this study was deepened over half a meter in the 1920s 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.

[38] 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.

[39] The ditching then 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; this widely used practice for improving forest productivity might have permanently changed flow pathways and thus changed Al dynamics in many areas.

5. Conclusions

[40] 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.

[41] The RZ 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.

[42] The potential for Al concentrations being modified during transport through the RZ needs to be accounted for in efforts to relate acid deposition to 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, as in others, that biologically significant levels of Al in the stream do not necessarily imply that acidification has mobilized Al in the soils.

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