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TITLE: Groundwater Al dynamics in boreal hillslopes at three integrated monitoring sites along a sulphur deposition gradient in Sweden

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ABSTRACT

Data from 4 soil water and groundwater transects from 3 small, boreal catchments situated along a south-north sulphur deposition gradient in Sweden were studied to assess whether the soils in the near stream zone can significantly modify the groundwater aluminium (Al) chemistry just before it enters the stream and to what extent different levels of acid deposition influences this. The results show that the groundwater aluminium species composition (Al_t=total, Al_o~organic, Al_i~inorganic) and concentrations reflected the variations in groundwater pH (r^2_{Ali}=0.74) or TOC (r^2_{Alo}=0.93) or a combination of both (r^2_{Alt}=0.89). The highest Al concentrations were recorded in shallow groundwater, creating the prerequisites for large lateral Al-fluxes along the hillslopes during episodes of high flow when superficial flow paths are active. A downhill gradient was also seen, with increasing Al_o and TOC concentrations towards the stream. Reduced Al_i in absolute as well as relative terms but increased Al_t concentrations in the discharge areas, indicate complex reactions favouring Al_o formation and a local input of Al_o from the soils. Results from the transect with the most detailed riparian sampling showed that in the last few meters before lateral flow reaches the stream, the mixing of superficial acid soil/groundwater and well-buffered groundwater that had moved along deeper flow paths increased pH and reduced the Al_i and Al_t concentrations, tangibly. The Al_o concentrations were little affected by this pH increase, but at the soil and stream water interface Al_i formation was favoured due to the low pH and DOC concentrations in the surface water. Hydrological and soil forming processes within the catchments were more important than acid deposition for the Al dynamics along the hillslopes.

Keywords: Aluminium, groundwater, soil water, transect, acidification

1. INTRODUCTION

The surface water concentrations of metals in the boreal zone of Fenno-Scandia surface waters are generally low, and a very limited number of streams and lakes have metal concentrations above or close to levels where biological effects are expected. Only inorganic aluminium (Al_i) seems to be a regional problem for aquatic life, especially gill breeding organisms such as fish and benthic fauna (Lydersen et al., 2002). Acidification of soils and surface waters increases the mobilization of toxic Al_i (Cronan and Schofield, 1979; Kirchner and Lydersen, 1995). The Al_i present in ionic forms in natural water can normally be expected to occur as the free aquo Al^{3+}, hydroxide-, fluoride-, sulphate- and silicate-complexes. In waters of pH > 6, or in waters with high DOC concentrations, the concentrations of these monomers are low, while polymerised Al-hydroxides and Al-organic aggregates of colloidal and subcolloidal size predominate (Driscoll et al., 1980).

Aluminium (Al) in boreal surface waters mainly derives from the soils in surrounding catchments. Hence, in order to understand why toxic Al_i levels can occur in surface waters, naturally or due to anthropogenic acidification, it is necessary to have insight into the processes that influence Al mobilization, retention and migration within the soils. The hydraulic connectivity between recharge and discharge areas creates the prerequisites for a potential redistribution of water soluble substances from upper parts of the catchment, downhill and ultimately into the stream (Bishop et al., 2004).

The soil types evolved since the last glacial period are vertically stratified with respect to their biological activity and chemical composition. In recharge areas, characterized by percolating water in the topsoil during the summer period, podzolization is the most important Al mobilization process. The classical view is that weathering in the E-horizon releases Al (and Fe), which forms complexes with low and high molecular weight organic acids. These complexes migrate further down in the soil profile where they are arrested in the B-horizon (Lundström et al., 2000b). However, many recent studies show (Giesler et al., 2000; Lundström et al., 2000b; Rustad and Cronan, 1995) that the Al output from the O-horizon might be as high as from the eluvial zone. This might be a result of translocation of Al from the E-horizon to the O-horizon due to mineral soil redistribution, capillary rise, root uptake and litterfall or redistribution by roots and mycorrhizal hyphae (op. cit.). In the B-horizon and in other soil types rich in organic matter, pH and organic ligand dependent complexation reactions between Al^{3+} and solid-phase organic matter (SOM) determine the Al solubility (Berggren and

Mulder, 1995; Simonsson, 2000; van Hees et al., 2001). Studies show that >85% of the Al in soil solution from Swedish soils are bound to organic acids in the podzol profile (van Hees and Lundstrom, 2000) and that colloidal organic matter contribute to the vertical translocation of Al through the E-horizon (Riise et al., 2000). In discharge areas, characterized by up-welling groundwater and lateral movements in the topsoil (Bishop et al., 2004; Seibert et al., 2003), different types of organic rich soils dominate e.g. humus podzols, gleysols and histosols.

Many studies have shown a higher concentration of exchangeable Al in the discharge area soils compared with upslope (Mulder et al., 1991; Nörrstrom, 1993). Giesler et al. (2002) concluded that the accumulation of Al in the humus layer of the groundwater discharge areas is most likely linked to groundwater flow pathways, redistributing Al from the mineral soil into the humus layer. Lawrence et al. (1995; 1988), Vogt & Muniz (1997) and Pellerin et al. (2002) put forward similar explanations. The study by Giesler et al. (2002) indicated that it is very unlikely that other processes such as litterfall or bioturbation could explain the Al accumulation.

The accumulation of exchangeable Al in the riparian zone in combination with a positive correlation between Al concentrations and water flow in streams (Kirchner, 2003; Laudon and Bishop, 1999) suggests that processes in the near stream zone have a profound effect on the stream water Al concentrations, similar to that found for TOC. Bishop et al. (1995; 2004) showed how the DOC concentrations in the stream were dependent on the varying depth of the groundwater flow path and the corresponding soil solution chemistry. The strong interaction between Al and DOC in soil and soil solution strengthens this hypothesis.

Important as riparian zone processes are believed to be for Al, and indeed other aspects of water chemistry e.g. nitrogen (Jacks and Norrström, 2004), sulphur (Löfgren et al., 2001) and methylmercury (Bishop et al., 1995), there are still relatively few studies that document the changes of Al related chemistry through the riparian zone. In this study the Al chemistry in soil water and groundwater (Al_t, Al_i and Al_o in relation to pH and TOC) was studied along the hillslopes of 3 small, forested catchments during 2000-2002. These catchments were located along an acid deposition gradient from southern to northern Sweden allowing evaluation of the influence that anthropogenic acid deposition can have on the function of the riparian zone in controlling the Al-flux to streamwater.

The aim of this study was thus to assess whether the soils in the near stream zone can significantly modify the groundwater Al chemistry just before it enters the stream and to what extent the acid deposition gradient influenced this.

2. Site Descriptions

Sampling and data collection were undertaken at three integrated monitoring (IM, Lundin et al., 2001) sites in Sweden (Figure 1, Löfgren et al., 2001). The sites are protected areas and almost no forestry activities have been conducted during the last century. The bulk deposition of sulphur and nitrogen exhibits significant gradients between the sites corresponding to a North to South gradient of 2-6 kg S $ha^{-1}\cdot y^{-1}$ and 3-9 kg N $ha^{-1}\cdot y^{-1}$ (Table 1). In the late 1980's, the sulphur deposition was more than twice these levels (Westling and Lövblad, 2000), exhibiting a much higher historical acidification pressure at the southern sites compared with the northern sites.

--- Figure 1 ---

---Table 1 ---

Figure 2 – new figure with individual site maps

Aneboda is a small, forested catchment (19.6 ha) dominated by Norway spruce (*Picea abies*) that is situated in central Småland, southern Sweden. In the stream valley peat soils dominate. Kindla is a similarly sized (19.1 ha), forested catchment dominated by Norway spruce that is situated in Bergslagen, central Sweden. A small mire is situated in the centre of the drainage area. The area is steep, with altitude differences up to 100 m over a distance of 200 m. Gammtratten is a slightly larger, forested catchment (39.6 ha) dominated by Scots pine (*Pinus sylvestris*) in upper parts and by Norway spruce in the central parts. The area is relatively steep, with altitude differences up to 135 m. Three small mires are located close to the water divide. All three sites have granite bedrock and glacial till is the dominant parent material for soils.

3. Methods

The water sampling was integrated into the ordinary IM-program during the years 2000-2002 (Lundin et al., 2001, http://www.environment.fi/default.asp?node=6329&lan=en). If available, soil water (ceramic suction cups P80, 1 μm cut-off) and groundwater (piezometers) were sampled 3-4 times per year after snowmelt (April-May) and precipitation events in August and October-November. The equipment was installed in 1994, but fractionation of the Al species in soil water (see below) started in the year 2000. Regarding groundwater, a special Al fractionation campaign was run during 2001 and 2002. Stream water was sampled biweekly throughout the year. The soil water and groundwater sampling were conducted with closed sampling systems according to Fölster (2000, 2001) originally developed for sampling of unaerated soil water and groundwater for O_2 analysis. Along a hillslope in each catchment, lysimeters and piezometers have been installed at three different distances from the stream (Aneboda: 2m, 25m and 35m; Kindla: 2m, 22m and 43m; Gammtratten: 8m, 30m and 50m). In recharge areas and intermediate zones with podzols, 2-4 lysimeters are installed in each layer in the mineral soil just below the O-horizon (E-horizon) and in the centre of the B-horizon. The piezometers are installed at depths of 1.1-5.0m below the soil surface. In discharge areas, 2-4 lysimeters are installed in the peat approximately 30cm below the soil surface. The piezometers are installed at depths of 1.0-2.0m. At Kindla, the IM-transect was complemented in 1996 by a transect of higher spatial resolution (T3-transect, Folster, 2001). The equipment is installed at distances of 0.2m, 2m, 7m, 28m and 50m from the stream and at soil depths between 0.1-0.4m for the lysimeters and 0.1-1.4m for the piezometers. In the stream bed, piezometers are installed at Gammtratten and on the T3-transect of Kindla at depths of 0.4m and 0.6m. The soil water and groundwater transects are situated close to the stream water sampling sites (Figure 2), but they cannot be considered as representative for the mosaic of hillslope conditions creating the stream water chemistry.

The basic water chemistry were analysed at the Dept. of Aquatic Science and Assessment, Swedish University of Agricultural Sciences (SLU). The analytical methods at the laboratory are accredited by the Swedish Board for Accreditation and Conformity Assessment (SWEDAC) and all analysis follow Swedish standard methods. Ambient pH was analysed in a semi-closed system.. Directly after opening the bottle, the sample was pumped (peristaltic pump) through an airtight cuvette equipped with a combination pH-electrode adapted for low ionic strength waters (Metrohm 6.0253.100). pH at equilibrium with the atmospheric carbon dioxide pressure ($pH_{eq,}$) was determined with the same equipment after bubbling with compressed air (P_{CO2} = 380 ppm). Samples for total organic carbon (TOC) analysis were measured using a Shimatzu TOC 5050 analyzer with ASI-502 sample injector following acidification. Major cation analysis was by ICP-OES (Varian Vista Ax Pro) and strong acid anion by ion chromatography (LDC ConductoMonitor III). The Al samples were collected in separate polythene bottles and the fractionations were performed immediately after filtration on 0.45 µm GFC filters according to a simplified version of Driscoll (1984) using a SWEDAC accredited method at the Swedish Environment Research Institute (IVL, Andrén & Rydin 2009). Total aluminium (Al_t) and the aluminium passing an Amberlite cation exchanger (Al_o) were analysed with AAS, while the cationic Al fraction was calculated as the difference between Al_t and Al_o ($Al_i = Al_t – Al_o$). The Al-fractionation was performed on all water samples with a pH<6 within one day of sampling. The waters buffer capacity (ANC) was calculated according to Reuss & Johnson (1986).

4. RESULTS

Results from the three main transects are shown in table 2 and figure 3.

--- Table 2 ---

--- Figure 3 ---

4.1 Recharge area (22-50m from the stream)

The groundwater chemistry in the soil profiles within the recharge zones indicates that podzolization is an active process at all three sites. The profiles show the highest concentrations of TOC in the E-horizons which decrease with depth; this is more distinct in the profiles from Gammtratten and Aneboda. Gammtratten is characterised by a classic podzol profile even for pH and Al fractions; with increasing pH with depth and elevated Al_t in the E-horizon. This Al_t is dominated by organic complexes and Al_i concentrations are low at all depths. Kindla shows a degree of disruption to the classical podzol profile with low pH values found deep into the soil profile increasing first in the deeper mineral soils. This lower pH results in higher concentrations of Al_t and a greater portion of the inorganic Al_i form. At Aneboda, the same type of pH disruption occurs. The Al_t concentrations at Aneboda do not reduce with depth and this pattern is also seen for the Al_i concentration which remain elevated (>1 $mg \cdot l^{-1}$) even in the deeper mineral soils. The results from soil water in the O/E-horizons indicate that both Al_o and Al_i were mobilised in the humus layer. This is in agreement with the results from three other forested areas in Fenno-Scandia

(Giesler et al., 2000), showing that the Al output from the O-horizon to a large extent (61-108%) could explain the Al output from the eluvial zone.

4.2 Intermediate zone (12-30m from the stream)

Data from the intermediate zone is limited to the groundwater in mineral soils, however a similar pattern to the recharge zone can still be seen. Gammtratten exhibits higher pH and lower concentration of Al_t and Al_i than Kindla and Aneboda. The TOC concentrations in the groundwater are low (<5 mg·l^{-1}) at all the intermediate sites.

4.3 Discharge area (2-8m from the stream)

All three soil profiles show an increasing pH with depth. pH was lowest at Kindla with pH of ~4.5 in the upper horizons; in contrast the soil solution and groundwater was well buffered at Gammtratten and Aneboda with $pH \geq 5$ at all depths. The TOC profiles for Kindla and Aneboda show the greatest concentrations in the upper gley soils whereas Gammtratten showed the highest concentration in the peat layer with rapidly decreasing concentrations with depth.

At Gammtratten the increasing pH and decreasing TOC gave a similar profile to the podzols in the recharge zones, with elevated Al_t in the peat and rapidly decreasing concentrations with depth. The Al_i fraction was low and remained reasonably constant throughout the profile. Concentrations of Al_t for Kindla and Aneboda followed the pattern seen for TOC with maximum concentrations in the upper gley soils. The effect of the lower pH at Kindla was manifested in the Al-fractionation data, where despite lower Al_t concentrations than Aneboda, the Al_i concentrations were greatest at Kindla.

4.4 Near Stream Zone (0.2-2m from the stream)

The more intensively sampled T3 transect from Kindla allows us to examine changes occurring over the last few meters of the hillslope. Data covering the near stream zone (0.2-2m) are shown in table 3 and figure 4.

--- Table 3 ---

Several significant changes occur over the last 2m of the hillslope before discharge to the stream. The pH profile at 2m from the stream and 0.2m from the stream retain the same form but pH increases ~1 pH unit over the whole soil profile. There is a slight reduction in TOC, which was more profound with depth (however, still less than 5 mg·l^{-1}). Both Al_t and Al_i showed reductions over the last 2m for the whole soil profile with ≈0.3 mg·l^{-1} and ≈0.2 mg·l^{-1}, respectively.

--- Figure 4 ---

4.5 Stream water

The stream water exhibited an increasing north-south gradient with respect to the conductivity, chloride (Cl) and sulphate (SO_4) concentrations (Table 4). This reflects the marine influence and the sulphate deposition gradient (Table 1). The two more southerly streams were permanently acidic (pH<5.6). Both Aneboda and Gammtratten maintained a positive acid neutralizing capacity (ANC), mainly due to the buffering of weak organic acids and at Gammtratten occasional occurrence of bicarbonate

(Löfgren, 2004). Aneboda is a humus rich stream with TOC concentrations ≈26 mg TOC·l^{-1}. In boreal Swedish streams, the dissolved organic carbon (DOC) generally constitutes >95% of TOC (Köhler et al., 2000). The streams at Kindla and Gammtratten are less humic (≈8 mg TOC·l^{-1}), but still cannot be considered as clear waters. The Al_t concentrations were in the range of 0.2-0.8 mg·l^{-1}, with Kindla in central Sweden showing the highest values. Al_o was the dominant (>80%) Al-form at Gammtratten and Aneboda, while at Kindla Al_i constituted >50% of Al_t. Among the catchments, the Al_t levels and the Al fractions do not exhibit any correlation with the sulphur deposition or the input of sea salt.

---Table 4---

5. DISCUSSION

Unfortunately, groundwater Al speciation data is only available from two years, yielding a maximum number of observations of 6-8. The number of observations is often less than that due to sampling constraints. At conditions with low groundwater recharge and thereby time consuming sampling, the basic chemistry stipulated by the IM program was prioritized and no samples for Al-fractionation were collected (c.f. Table 2). At some occasions, low groundwater levels prevented sampling of the most shallow soil layers at the T3-transect, Kindla (c.f. Table 3). Occasionally, dry conditions also prevented from soil water sampling (c.f. tables 2 and 3).

Due to the low number of observations the representativity of these data can be disputed. However, time series from lysimeters and piezometers with multiple observations indicate that two to three observations could capture the general features regarding the distribution between Al_o and Al_i as well as the approximate level of Al_t during the study period. As examples on this, Figure 5 shows time series on the Al species at Aneboda in the B-horizon soil water, dominated by Al_i, as well as in soil water and groundwater in the discharge area dominated by Al_o. Additionally, the mean values and standard deviations presented in Tables 2 and 3, strengthen this conclusion.

---Figure 5--- new figure showing time series of the Al species in different media

The soil water and groundwater chemistry exhibited profound vertical gradients in pH, TOC, Al_t, Al_o and Al_i at all sites. With the exception of the intermediate zone along the Kindla transect, pH increased with depth while the other substances decreased with depth. Hence, the groundwater chemistry is very much dependent on the groundwater level. At the three sites, almost 90% of the variation in the average groundwater Al_t concentrations is linearly explained by the pH and TOC concentrations (r^2=0.89, p<0.0001, n=43), Al_o by TOC (r^2=0.93, p<0.0001, n=39) and Al_i by pH (r^2=0.74, p<0.0001, n=38). These results are in agreement with earlier findings showing ion exchange, pH and organic matter to be important for the Al solubility in soils (Tipping et al., 1995; van Hees et al., 2001; van Hees and Lundstrom, 2000). This overall pattern of increasing Al_t accompanied by increasing TOC and decreasing pH was seen in both acidified and pristine sites in other studies (Mulder et al., 1991; Pellerin et al., 2002). Similar observations with an abrupt drop in Al_t accompanied by a rise in pH in the near stream zone have also been observed in these studies.

These results indicate that any process which increases pH or reduces the humus concentrations in groundwater should theoretically reduce the Al concentrations and limit the Al migration. Hence, it is unlikely that quantitatively important amounts of Al could be redistributed from recharge to discharge areas during base flow, since the groundwater flow is low and mainly occurs deep into the soils with high pH, low TOC and thereby low Al-concentrations (e.g. Gammtratten, Table 2). On an annual basis, most of the mobilized Al in the O and E-horizons will be trapped in the B-horizon due to the podzolation process. However, if the groundwater remains acid as found at the Kindla transect, or contains high concentrations of TOC throughout the B-horizon as found on the T3-transect at Kindla, the Al_i and Al_o concentrations might be substantial (Tables 2 and 3) creating a significant Al-flux downhill also at base flow.

During flow events, the main groundwater flow path is close to soil surface over extensive areas of the catchment. This creates the prerequisite for a quantitatively important downhill transport of both Al_i and Al_o rich groundwater due to low pH and high TOC concentrations, respectively (Table 2). At all transects in this study and regardless of lower pH in the discharge areas, the Al_i fraction decreased while the Al_o fraction increased towards the streams (figure 3). This phenomenon is partly explained by the increased TOC concentrations in the groundwater, favouring complexation reactions with Al_i and the formation of Al_o. However, increased Al_t concentrations in the discharge areas indicate a local input of Al_o (Figure 3). This Al_o is likely released from the Al pool in the organic rich soils which generally exhibit excess concentrations of exchangeable Al compared with uphill areas (Cory et al., 2007; Giesler et al., 2002; Mulder et al., 1991).

In the time perspective of podzol formation (centuries to millenia, Lundström et al., 2000a), the accumulated Al-flux during base and intermediate flow might be of importance for explaining the observed Al accumulation in the soils in the near stream zones (Giesler et al., 2002; Mulder et al., 1991; Pellerin et al., 2002). Generally, the recharge area has a much larger geographical extension compared with the discharge area, concentrating the Al-flux through the surface soils in the near stream zone. At least the Al_i fraction of this flux should get trapped in the discharge area due to ion exchange in the organic soil matrix (Cory et al., 2007). It has previously been proposed that a rise in pH leads to reduced Al solubility and therefore a build up of aluminium in the near stream zone. This pH rise has been attributed to both degassing of CO_2 over pressure (Driscoll and Postek, 1996), and mixing of well buffered upwelling groundwater with acidic superficial flow in the discharge area (Pellerin et al., 2002).

The results from the 0.2m and 2m sites at the T3 transect in Kindla indicate that important geochemical processes occur within the last few meters from the stream bank (Table 3), giving some further insight into the processes behind this Al-accumulation in the soils. At T3, the groundwater pH increased by ~1 pH unit in the upper meter of the soils, while the TOC concentrations remained more or less constant. The most probable explanation for this pH increase is a mixing between shallow acid and a more buffered deep groundwater in the extreme near stream zone. At 0.2m from the stream, ANC and base cation concentrations (BC) were much higher compared with at 2m from the stream (Table 5). This conclusion is corroborated by increased ANC, BC and pH with groundwater depth in the near stream zone. The effects of degassing of CO_2 seem to be negligible compared with the BC and ANC input, as indicated by the groundwater pH measured in a closed system at ambient P_{CO2} compared with the pH measured at equilibrium with the atmospheric P_{CO2} (380 ppm). The groundwater at 0.2 m from the stream was still CO_2 supersaturated causing a pH drop of more than 1.2 pH-units lower than at equilibrium with the atmosphere (Table 5).

---Table 5---

The pH increase in the stream bank affected the Al-chemistry markedly by reducing the Al_i groundwater concentrations from >0.34 $mg \cdot Al_i \cdot l^{-1}$ to <0.13 $mg \cdot Al_i \cdot l^{-1}$, while the Al_o concentrations only decreased slightly (<0.06 $mg \cdot Al_o \cdot l^{-1}$). This caused a drop in the Al_t concentrations with approximately 0.3 mg $Al_t \cdot l^{-1}$. The more or less constant levels of TOC and Al_o at 0.2m and 2m from the stream (Figure 4) indicate that Al_i was captured in the soils rather than complex bound to aquatic humus substances. Soil studies (data not shown) at the T3 transect indicate that the amount of exchangeable Al (1 M non-buffered NH_4Cl) in the upper 40 cm of the soils increase from 4.1, 9.6 and 9.6 eq m^{-2} at 6.6m, 2.8m respective 0.6m from the stream. Hence, mixing of shallow, acid and deep, more buffered groundwater has the potential to reduce the toxic inorganic Al_i fraction to very low levels due to soil adsorption within the distance of 2-3m from the stream. Due to the IM sampling strategy, with a greater distance between the riparian sampling site and the stream, the presence or absence of a similar process at the other transects cannot be confirmed.

There was little effect on the Al_o concentrations from this pH increase in the near stream zone, however, at the soil and stream water interface Al_i formation is favoured due to the low pH and TOC concentrations in the surface water (Table 4). Hence an inflow of Al_o to the stream, for example during a high flow episode, has the potential to generate elevated concentrations of Al_i in the stream water.

The three catchments in this study have been subjected to very different anthropogenic acid deposition (Table 1). The groundwater chemistry regarding pH does not reflect this acidification gradient. However for Al_t and Al_i there are indications of insufficient Al precipitation in the B-horizon resulting in elevated Al concentrations in the C-horizons at both Aneboda and Kindla. This might indicate an influence of anthropogenic acidification at these more affected sites. However, these elevated Al_t and Al_i concentration in the C-horizon at Aneboda occur in reasonably well buffered conditions (pH≈5.5) which suggest that other factors such as ionic strength and thereby the ion exchange properties of the soils (Vogt and Muniz, 1997) may also play a role. Hence, besides atmospheric deposition, the higher input of marine salts in southern Sweden may be of importance (Table 1).

6. CONCLUSIONS

This study shows that the groundwater Al species composition and concentrations were determined by the variations in groundwater pH and TOC. The highest Al concentrations were recorded in shallow groundwater, creating the prerequisites for large lateral Al-fluxes along the hillslopes during flow events. A downhill gradient was also observed, with increasing Al_o and TOC concentrations towards the stream.

Reduced Al_i but increased Al_t concentrations in the discharge areas indicate complexation reactions favouring Al_o formation and a local input of Al_o from the soils as responsible for this pattern. The extreme near stream zone (within a few meters), showed that the mixing of shallow, acid and deep, buffered groundwater increased pH and reduced the Al_i and Al_t concentrations, tangibly. The Al_o concentrations were less affected by this pH increase. At the soil and stream water interface Al_i formation was favoured due to the low pH and TOC concentrations in the surface water. Hydrological and soil forming processes within the catchments were more important than acid deposition for the Al dynamics. The subsidiary effect of acid deposition was most probably larger in the past when the sulphur deposition was higher.

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Table 1. Geographical, climatic and deposition characteristics for the catchments. Average annual chloride (Cl-dep), sulphur (S-dep) and nitrogen (N-dep = NH_4-N + NO_x-N) bulk deposition during the period 2000- 2002. Altitude is above mean sea level, Temperaturess. are annual means, Temp.sum. are day-degrees above +5 °C, P is precipitation, E – evapotranspiration and R – runoff (Raab and Vedin, 1995).

Catchment	Aneboda	Kindla	Gammtratten
Location	N 57° 05' E 14° 32'	N 59° 45' E 14° 54'	N 63° 51' E 18° 06'
Area, ha	19.6	19.1	44.8
Altitude, m	210-240	312-415	4120-5450
Temp. °C	5.8	4.2	1.2
Temp.sum °C	1350	1260	970
Snow cover, days	110	150	175
P, mm	750	900	750
E, mm	470	450	370
R, mm	280	450	380
Cl-dep., kg Cl $ha^{-1} \cdot y^{-1}$	15.3	3.9	1.4
S-dep., kg S $ha^{-1} \cdot y^{-1}$	5.3	3.5	1.9
N-dep, kg N $ha^{-1} \cdot y^{-1}$	9.0	5.2	2.7

Table 2. Concentrations (mg·l^{-1}, mean value, standard deviation) and number of observations (n) of total aAluminium (Al_t), organic aAluminium (Al_o) inorganic aAluminium (Al_i), total organic carbon (TOC), and pH in soil water (SW) and groundwater (GW) at the IM sampling sites at Aneboda, Kindla and Gammtratten. ΔD is distance from stream.

Sampling site	ΔD m	Al_t µg·l^{-1}	Al_o µg·l^{-1}	Al_i µg·l^{-1}	n	TOC mg·l^{-1}	n	pH	n
<u>ANEBODA</u>									
SW, recharge area, E-hor	35	1668 ± 182	948 ± 330	720 ± 478	4	41.9 ± 26.7	12	4.73 ± 1.04	10
SW, recharge area, B-hor	35	1407 ± 468	146 ± 66	1261 ± 461	26	6.1 ± 4.4	35	4.66 ± 0.10	35
GW, recharge area, 4.2m	35	1330 ± 390	152 ± 75	1178 ± 384	3	4.3 ± 1.3	10	5.45 ± 0.32	11
GW, intermediate zone, 2.1m	25	812 ± 279	38 ± 8	775 ± 271	2	2.6 ± 0.5	7	5.14 ± 0.37	7
GW, intermediate zone, 3.2m	25	864 ± 289	96 ± 64	768 ± 305	5	3.4 ± 3.6	12	5.10 ± 0.35	12
SW, discharge area, peat	2	932 ± 397	718 ± 440	214 ± 298	29	22.3 ± 21.5	46	5.00 ± 0.28	46
GW, discharge area, 1.0m	2	725 ± 557	1678 ± 598	47 ± 50	5	29.4 ± 14.4	12	5.53 ± 0.11	11
GW, discharge area, 2.0m	2	314 ± 79	304 ± 81	10 ± 9	3	10.5 ± 5.6	12	5.91 ± 0.44	12
<u>KINDLA</u>									
SW, recharge area, E-hor	43	1324 ± 193	391 ± 110	932 ± 195	19	7.9 ± 1.7	19	4.50 ± 0.12	20
SW, recharge area, B-hor	43	1364 ± 240	229 ± 65	1136 ± 214	20	5.0 ± 3.4	21	4.67 ± 0.08	22
GW, recharge area, 2.4m	43	983 ± 442	216 ± 56	766 ± 474	5	4.5 ± 1.6	11	4.75 ± 0.17	12
GW, recharge area, 3.4m	43	320 ± 68	36 ± 7	284 ± 64	6	1.6 ± 0.6	12	5.35 ± 0.37	12
GW, intermediate zone, 2.0m	22	546 ± 187	51 ± 17	504 ± 172	6	2.4 ± 2.7	12	5.12 ± 0.30	11
GW, intermediate zone, 2.9m	22	942 ± 242	42 ± 16	891 ± 251	6	1.9 ± 0.9	12	5.03 ± 0.38	12
SW, discharge area, peat	2	820 ± 149	518 ± 114	302 ± 171	18	13.5 ± 5.3	20	4.55 ± 0.14	20
GW, discharge area, 1.1m	2	830 ± 184	560 ± 188	270 ± 66	6	15.8 ± 5.2	9	4.57 ± 0.74	9
GW, discharge area, 2.0m	2	57 ± 7	26 ± 9	31 ± 8	6	1.4 ± 0.5	12	5.91 ± 0.06	11
<u>GAMMTRATTEN</u>									
SW, recharge area, E-hor	50	815 ± 269	704 ± 204	111 ± 92	6	26.3 ± 8.2	7	4.37 ± 0.14	6
SW, recharge area, B-hor	50	062 ± 6	24 ± 12	37 ± 15	14	4.8 ± 4.6	20	5.18 ± 0.18	20
GW, recharge area, 5.0m	50	043 ± 6	39 ± 11	4 ± 6	2	2. ± 1.0	2	5.97 ± 0.24	2
GW, intermediate zone, 2.0m	30	103 ± 49	39 ± 6	64 ± 42	2	2.5 ± 1.3	3	5.73 ± 0.24	3
GW, intermediate zone, 3.2m	30	88 ± 29	42 ± 7	46 ± 35	3	2.6 ± 1.0	8	5.84 ± 0.08	7
SW, discharge area, peat	8	591 ± 316	508 ± 257	84 ± 67	9	27.0 ± 17.0	17	5.24 ± 0.34	18
GW, discharge area, 1.1m	8	155 ± 40	90 ± 12	65 ± 42	4	5.0 ± 2.4	7	5.47 ± 0.32	6
GW, discharge area, 1.9m	8	92 ± 91	36 ± 20	56 ± 75	4	2.0 ± 0.8	6	6.11 ± 0.43	7
GW, stream bottom, 0.4m	0	278 ± 173	260 ± 182	19 ± 9	2	5.8 ± 2.8	3	6.72 ± 0.17	3

Table 3. Distance to the stream in meters (ΔD), concentrations ($mg\cdot l^{-1}$, mean value, standard deviation) and number of observations (n) of total aAluminium (Al_t), organic aAluminium (Al_o) inorganic Aaluminium (Al_i), total organic carbon (TOC), and pH in soil water (SW) and groundwater (GW) at T3-transect, Kindla (Folster, 2001). n.d.= no data (no sample due to dry conditions)data, ΔD is distance from stream.

Sampling sites	ΔD m	Al_t $\mu g\cdot l^{-1}$	Al_o $\mu g\cdot l^{-1}$	Al_i $\mu g\cdot l^{-1}$	n	TOC $mg\cdot l^{-1}$	n	pH	n
SW, discharge area, 0.1m	2	1574 ± 418	928 ± 220	646 ± 302	4	21.1 ± 4.1	3	4.04 ± 0.19	4
GW, discharge area, 0.2m	2	1292 ± 65	954 ± 125	338 ± 100	3	20.2 ± 8.9	2	4.30 ± 0.04	2
GW, discharge area, 0.6m	2	988 ± 17	607 ± 24	381 ± 31	3	15.1 ± 4.2	3	4.78 ± 0.06	4
GW, discharge area, 1.0m	2	1169 ± 124	963 ± 143	205 ± 71	5	16.6 ± 4.0	6	5.12 ± 0.08	6
GW, discharge area, 1.35m	2	403 ± 83	369 ± 88	33 ± 38	5	8.5 ± 3.7	6	5.51 ± 0.15	6
GW, discharge area, 0.1m	0.2	1022 ± 138	895 ± 152	127 ± 55	5	20.5 ± 4.4	6	5.05 ± 0.09	6
GW, discharge area, 0.5m	0.2	625 ± 43	554 ± 41	71 ± 38	5	12.6 ± 3.7	6	5.44 ± 0.12	6
GW, discharge area, 0.9m	0.2	349 ± 55	328 ± 65	21 ± 12	4	11.1 ± 3.4	5	5.82 ± 0.12	5
GW, discharge area, 1.2m	0.2	n.d	n.d	n.d	n.d	6.1 ± 3.2	6	6.33 ± 0.10	6
GW, stream bottom, 0.6m	0	222 ± 43	169 ± 34	53 ± 9	2	6.2 ± 2.9	6	6.34 ± 0.09	6

Table 4. Stream water concentrations (mean value±standard deviation) and number of observations (n) of pH, conductivity at 25°C (Cond_{25}), acid neutralizing capacity (ANC), sum of base cations (BC), sulphate (SO_4), total organic carbon (TOC), total aAluminium (Al_t), organic aAluminium (Al_o) and inorganic aAluminium (Al_i) for the period 2000 to 2002 at Aneboda, Kindla and Gammtratten.

	Aneboda	Kindla	Gammtratten
nN	64	76	71
n Al_t	56	66	51
n Al_i	56	66	51
pH	4.51 ± 0.16	4.57 ± 0.16	5.62 ± 0.30
Cond_{25}, $mS \cdot m^{-1}$	5.94 ± 0.54	3.21 ± 0.36	1.72 ± 0.25
ANC, $mEq \cdot l^{-1}$	0.084 ± 0.071	-0.017 ± 0.027	0.087 ± 0.023
BC, $mEq \cdot l^{-1}$	0.419 ± 0.045	0.150 ± 0.022	0.151 ± 0.029
SO_4, $mEq \cdot l^{-1}$	0.144 ± 0.065	0.112 ± 0.027	0.044 ± 0.010
Cl, $mEq \cdot l^{-1}$	0.188 ± 0.018	0.054 ± 0.010	0.018 ± 0.004
TOC, $mg \cdot l^{-1}$	26.0 ± 18.6	8.8 ± 5.2	8.4 ± 4.2
Al_t, $\mu g \cdot l^{-1}$	587 ± 373	771 ± 190	232 ± 82
Al_o, $\mu g \cdot l^{-1}$	488 ± 365	366 ± 200	216 ± 78
Al_i, $\mu g \cdot l^{-1}$	99 ± 37	406 ± 129	16 ± 17

*$Al_t \neq Al_i + Al_o$ due to different number of observations

Table 5. Groundwater level (GW) and distance to the stream in meters (ΔD), number of observations (n) and concentrations ($mEq \cdot l^{-1}$, mean value, standard deviation) of acid neutralizing capacity (ANC), base cations (BC), ambient pH (pH) and pH at equilibrium with the atmospheric pCO_2 pressure (pH_{Eq}, pCO_2=0.380 ppm) at transect T3, Kindla.

GW m	ΔD m	n	ANC $mEq \cdot l^{-1}$	BC $mEq \cdot l^{-1}$	pH	pH_{eq}
0.1	0.2	6	0.062 ± 0.013	0.139 ± 0.019	5.05 ± 0.09	6.50 ± 0.16
0.5	0.2	6	0.158 ± 0.013	0.230 ± 0.009	5.44 ± 0.12	6.86 ± 0.09
0.9	0.2	5	0.283 ± 0.024	0.363 ± 0.035	5.82 ± 0.12	7.08 ± 0.11
0.2	2	2	0 ± 0.012	0.121 ± 0.021	4.30 ± 0.04	5.41 ± 0.01
0.6	2	4	0.029 ± 0.003	0.152 ± 0.005	4.78 ± 0.06	6.16 ± *
1.0	2	6	0.060 ± 0.020	0.172 ± 0.012	5.12 ± 0.08	6.07 ± 0.23
0.6	Streambed	6	0.665 ± 0.024	0.756 ± 0.031	6.34 ± 0.09	7.39 ± 0.10
	Stream	76	–0.017 ± 0.027	0.150 ± 0.022	4.58 ± 0.16	n.d.

* n=1

Figure legends

Figure 1. Location of the sites in Sweden and overview map of Europe.

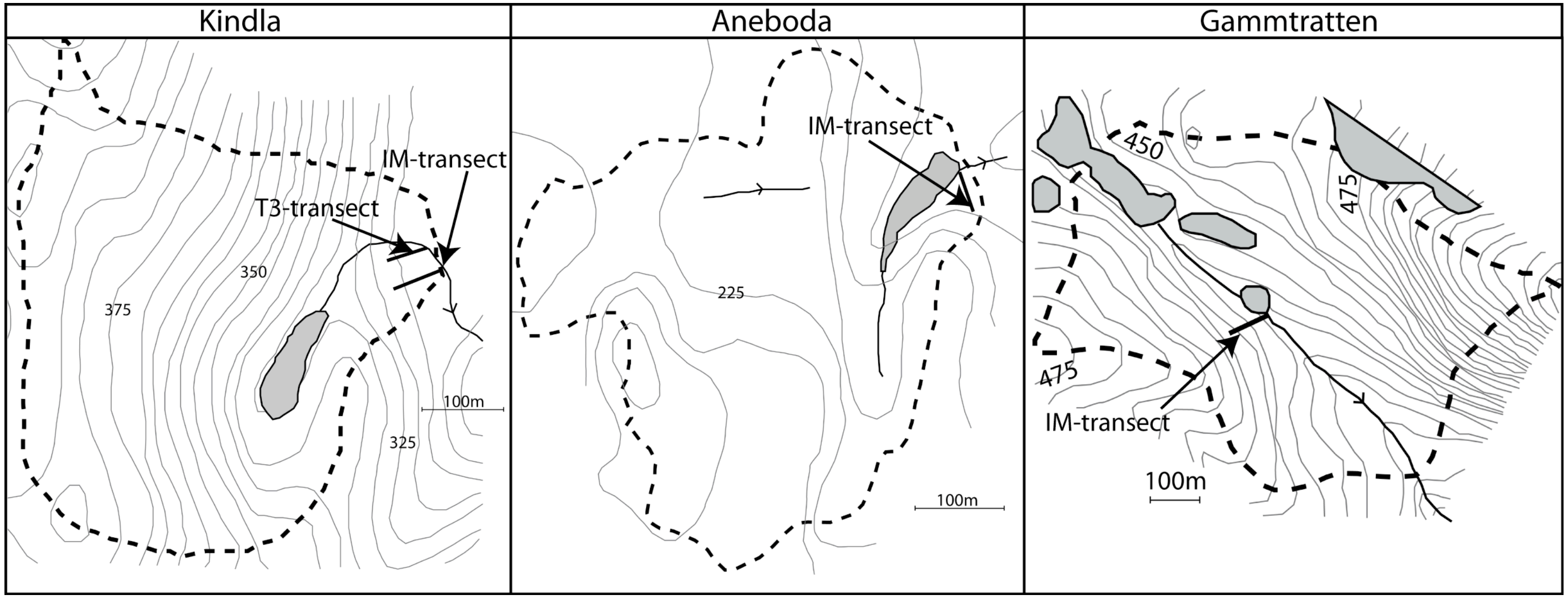
Figure 2. Site maps of the three study areas. Lefthand panel – Kinlda, central panel Aneboda, righthand panel – Gammtratten. Transects marked with arrows and labels, mire areas shown in grey, watershed shown with a brokenline.

Figure 3. Profiles for soil water (E-, B- and peat horizons) and groundwater (C-horizon, Upper and Lower Gley horizons) concentrations of pH, TOC, Al_t and Al_i in recharge (left), intermediate (centre) and discharge (right) areas at Aneboda (filled marker, solid line), Kindla (white markers, solid line) and Gammtratten (white marker, dashed line). Exact distances from the stream soil depth are shown in table 2. Error bars = standard error.

Figure 4. Profiles for soil water (white markers) and groundwater (filled markers) concentrations of pH, TOC, Al_t and Al_i at the Kindla T3 transect at 2m (dashed line) and 0.2 (solid line) from the stream. Error bars = standard error.

Figure 5. Concentrations of Al_t, Al_o and Al_i at Aneboda in soil water in the B-horizon (top panel, lysimeter 7107) and in the peat (central panel, lysimeter 7202) and in groundwater at 1.0m soil depth in the discharge area (lower panel, piezometer 7700:31).

Figure 1


Kindla
Aneboda
Gammtratten
IM-transect
T3-transect
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350
325
100m
IM-transect
225
100m
450
475
475
IM-transect
100m

Figure 2

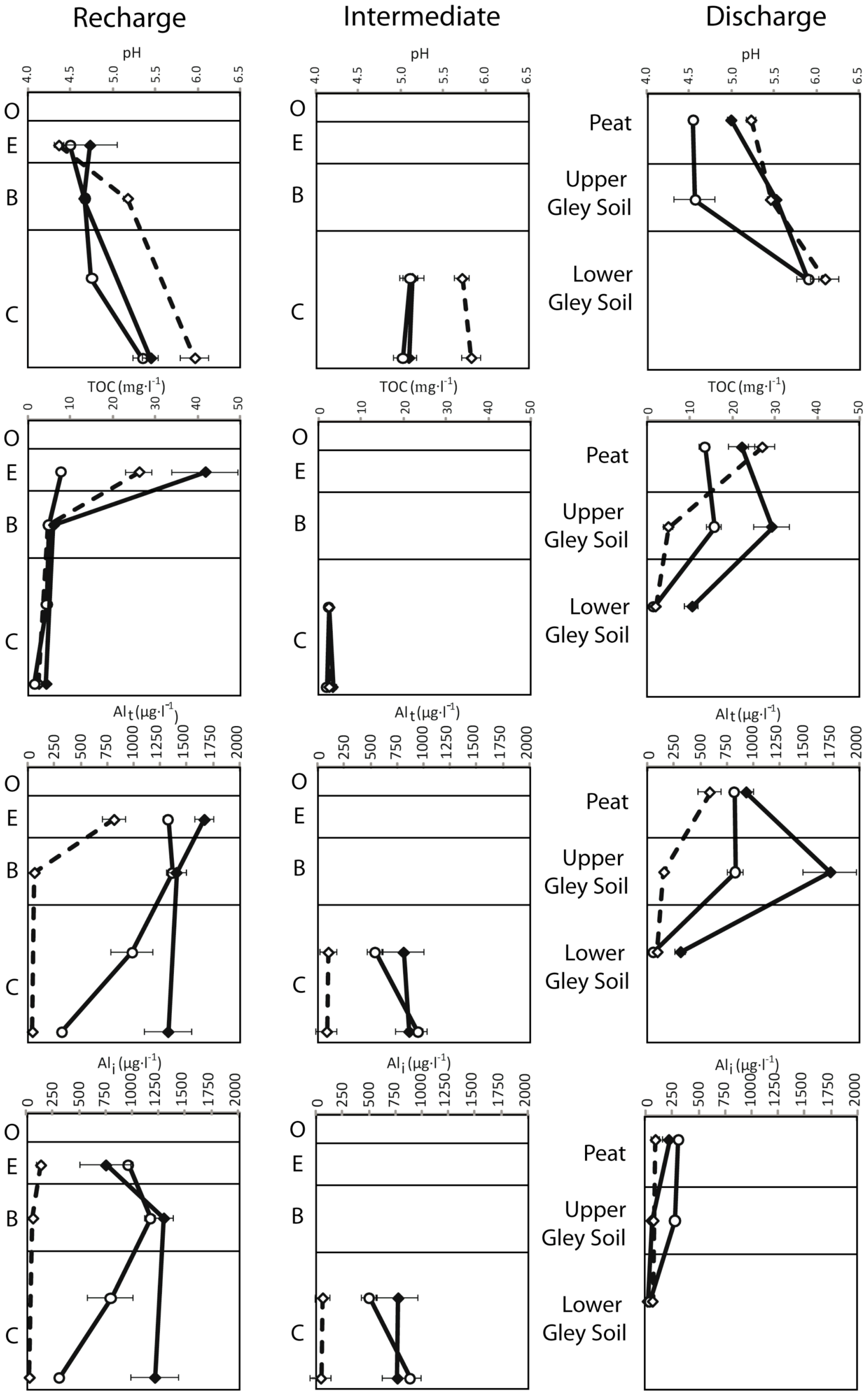
Recharge
Intermediate
Discharge
pH
4.0
4.5
5.0
5.5
6.0
6.5
TOC (mg·l-1)
0
10
20
30
40
50
Alt (µg·l-1)
Ali (µg·l-1)
0
250
500
750
1000
1250
1500
1750
2000
O
E
B
C
Peat
Upper Gley Soil
Lower Gley Soil

Figure 3

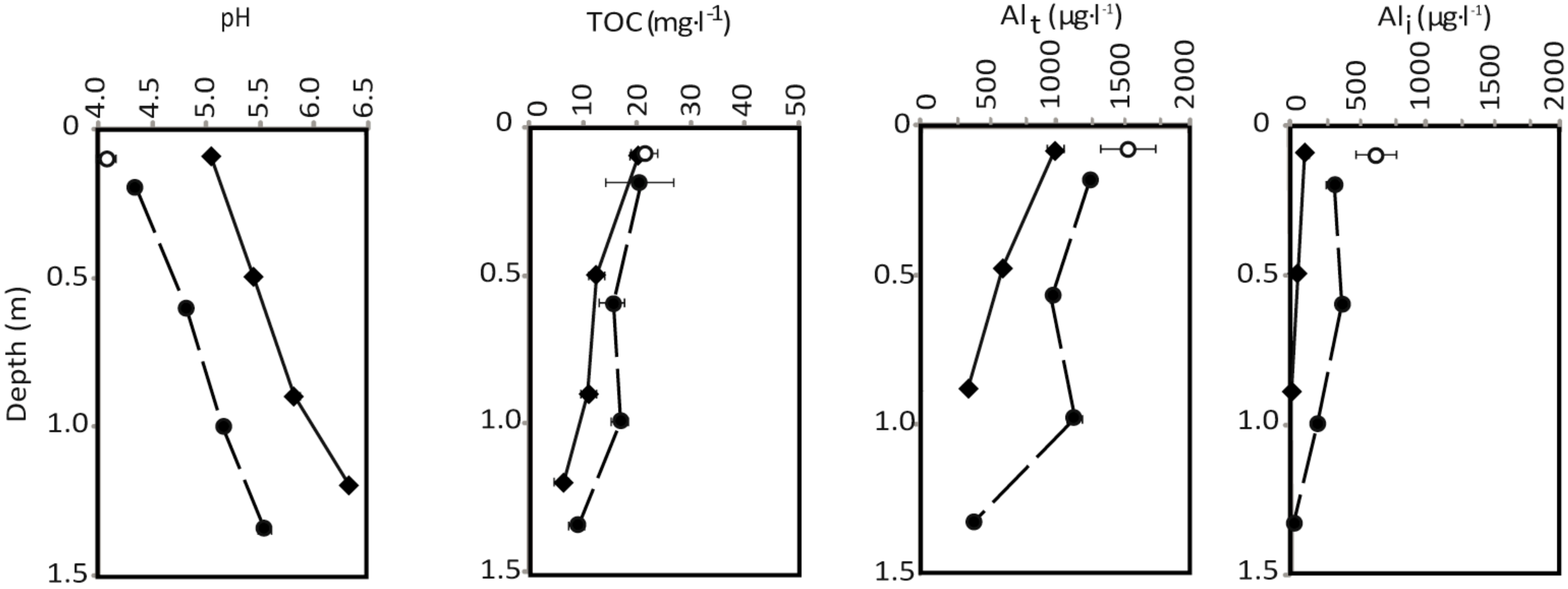
pH
4.0
4.5
5.0
5.5
6.0
6.5
TOC (mg·l-1)
0
10
20
30
40
50
Al t (µg·l-1)
0
500
1000
1500
2000
Al i (µg·l-1)
0
500
1000
1500
2000
Depth (m)
0
0.5
1.0
1.5

Figure 4

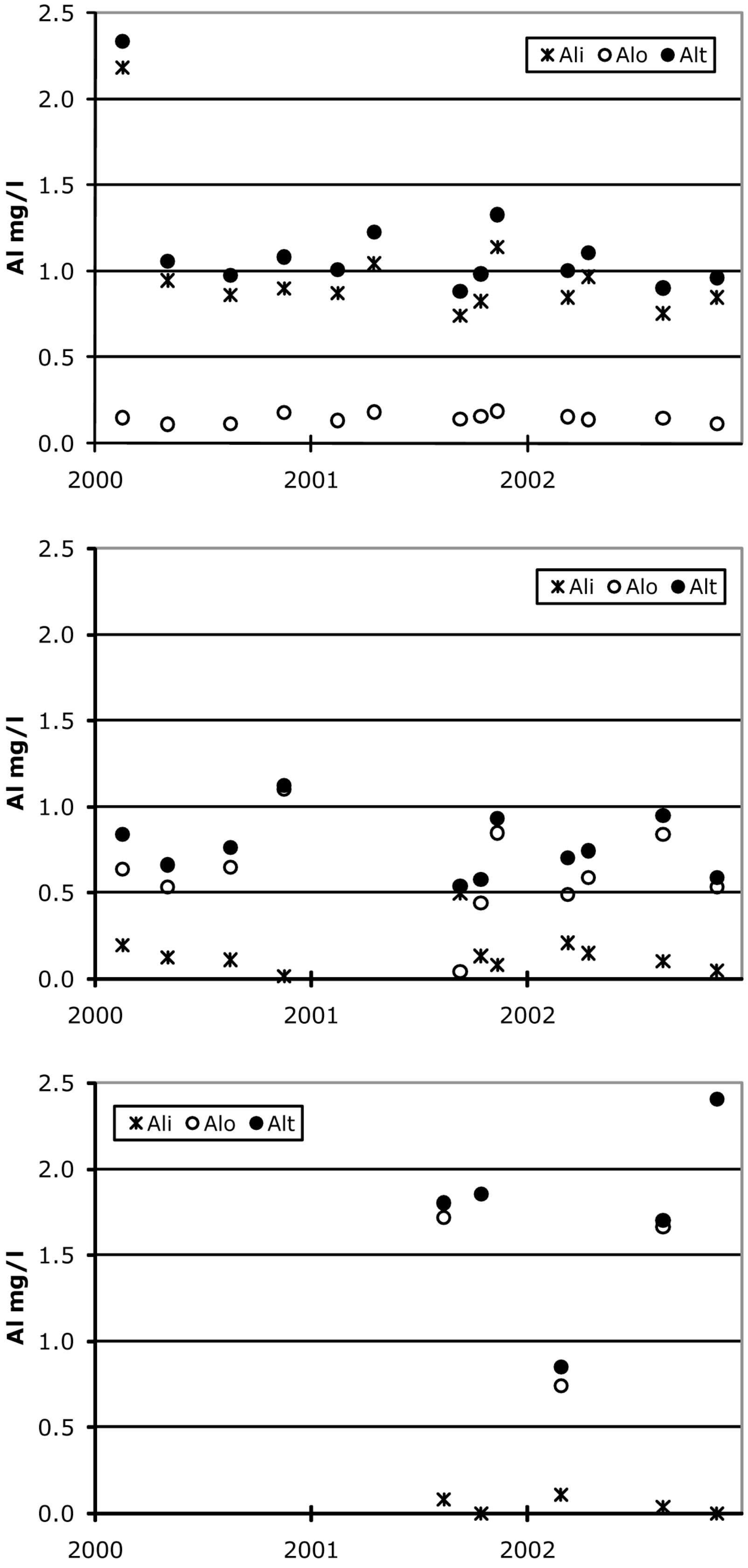
2.5
2.0
1.5
1.0
0.5
0.0
Al mg/l
2000
2001
2002
Ali
Alo
Alt
2.5
2.0
1.5
1.0
0.5
0.0
Al mg/l
2000
2001
2002
Ali
Alo
Alt
2.5
2.0
1.5
1.0
0.5
0.0
Al mg/l
2000
2001
2002
Ali
Alo
Alt

Figure 5