

# Recovery of Soil Water, Groundwater, and Streamwater From Acidification at the Swedish Integrated Monitoring Catchments

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**Abstract** Recovery from anthropogenic acidification in streams and lakes is well documented across the northern hemisphere. In this study, we use 1996–2009 data from the four Swedish Integrated Monitoring catchments to evaluate how the declining sulfur deposition has affected sulfate, pH, acid neutralizing capacity, ionic strength, aluminum, and dissolved organic carbon in soil water, groundwater and runoff. Differences in recovery rates between catchments, between recharge and discharge areas and between soil water and groundwater are assessed. At the IM sites, atmospheric deposition is the main human impact. The chemical trends were weakly correlated to the sulfur deposition decline. Other factors, such as marine influence and catchment features, seem to be as important. Except for pH and DOC, soil water and groundwater showed similar trends. Discharge areas acted as buffers, dampening the trends in streamwater. Further monitoring and modeling of these hydraulically active sites should be encouraged.

**Keywords** Recovery from acidification · Sulfur deposition · Soil water · Groundwater · Streamwater · Hydrological compartments

## INTRODUCTION

International actions have successfully diminished sulfur (S) and nitrogen (N) air emissions in North America and Europe. In Sweden, acidifying S deposition has declined by more than 90% since the 1970s, although N deposition has decreased more slowly (Bertills et al. 2007). Between 1990 and 2005, bulk deposition of S and N decreased by 57 and 29%, respectively. In the most heavily polluted southwestern part of Sweden, this corresponds to a reduction from 9 to 3 kg S ha<sup>-1</sup> year<sup>-1</sup> and from 10 to

6 kg N ha<sup>-1</sup> year<sup>-1</sup> (sea salt corrected, Bertills et al. 2007). As a result, it could be expected that ecosystems that had been acidified by earlier and chronic S deposition loading would now be showing signs of recovery, and indeed surface waters throughout the northern hemisphere are doing so (Evans et al. 2001; Skjelkvåle et al. 2005; Stoddard et al. 1999).

In Sweden, both the acid neutralizing capacity (ANC) and pH of 80 reference lakes distributed throughout the country, with a few exceptions, increased during the period 1990–2005, most rapidly in the southwest (Bertills et al. 2007). Furthermore, national forest soil data indicate that the spatial extent of the most acidic soils (B-horizon, low pH and base saturation) decreased throughout the country between 1985 and 1987 and 1999 and 2003, but again most strongly in southwest Sweden, where the spatial proportion of these soils decreased from 48 to 20% (Bertills et al. 2007). However, in spite of a general recovery from acidification, approximately 5% of Swedish lakes larger than 1 ha and 5% of streams (in catchments >2 km<sup>2</sup>) remain classified as acidified. But there are substantial regional differences, with 29% of the lakes in southwest Sweden still being acidified (Bertills et al. 2007). In addition, high concentrations of inorganic aluminum (Al<sub>i</sub>), an indicator of anthropogenic acidification (Lawrence et al. 2007), occur in streams throughout the country, particularly in catchments dominated by Norway spruce (Löfgren et al. 2010a).

S deposition causes an excess input of protons (H<sup>+</sup>) that is partly responsible for the acidification of soils and water. The deposition of neutral salts (e.g., sodium chloride, NaCl) also have the potential to acidify waters by exchanging H<sup>+</sup> with Na<sup>+</sup> ions in the soil. Both sea spray (Hindar 2005) and deicing salt (Löfgren 2001) can have this effect. In addition, excess losses of nitrate (NO<sub>3</sub><sup>-</sup>) due

to nitrification in the soils or imbalanced uptake by the biota of deposited  $\text{NO}_3^-$  and ammonium ( $\text{NH}_4^+$ ) are other acidifying processes (Van Breemen et al. 1984). Hence, the deposition of  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ , and  $\text{NO}_3^-$ , all mineral acid anions, need to be considered in studies concerned with the acidification status of soils and waters.

Several authors have suggested that the observed increase in concentrations of dissolved organic carbon (DOC) in surface waters in Europe, Canada, and the US is due to the mobilization and transport of soil organic carbon (SOC) resulting from the reduction in acid deposition, primarily S (Clark et al. 2010; Evans et al. 2005; Monteith et al. 2007), i.e., it is an anthropogenic acidification recovery response rather than a climate change response. However, based on soil water data from southern Sweden, the postulated causal link between recovery from anthropogenic acidification and increases in surface water DOC has been challenged (Löfgren et al. 2010b; Löfgren and Zetterberg 2011). Instead, the data indicate that climatic drivers, including precipitation, temperature, and changes in hydrological flow patterns, are the most important factors affecting surface water DOC concentrations (Erlandsson et al. 2008; Sarkkola et al. 2009).

Meteorological, hydrological, and chemical conditions have been intensively studied at the four Swedish Integrated Monitoring (IM) catchments since the mid-1990s. All four catchments are located in protected Norway spruce forested areas and form a south-north acid S deposition and climatic gradient. The impact of forest management and land-use change is negligible, thus allowing evaluation of the effects of acid deposition and climatic factors. As described in several contributions in this issue, the recovery from acidification and DOC dynamics in the streams at the four Swedish IM catchments have been simulated using models, including MAGIC (Köhler et al. 2011), INCA-C (Futter et al. 2011), and RIM (Winterdahl et al. 2011). The modeling exercises were primarily intended to test hypotheses regarding factors influencing the dynamics of streamwater DOC concentrations and fluxes. However, little use was made of the observed soil water and groundwater data, and generalizations were made.

In this article, we provide a detailed assessment of the temporal trends in the pH, ANC, ionic strength (IS), aluminum (Al),  $\text{SO}_4^{2-}$  and DOC concentrations in deposition, soil water, groundwater, and streamwater at the four Swedish IM catchments over the period 1996–2009. We focus on the recovery from acidification primarily in soil water and groundwater along the hillslopes. Recovery from acidification is assumed to have occurred if  $\text{SO}_4^{2-}$  concentrations decreased, pH, ANC and DOC concentrations increased, and IS and Al concentrations decreased over the study period. Trends in  $\text{Cl}^-$  concentrations are assumed to be weather induced. We hypothesized that (i) the recovery rates would

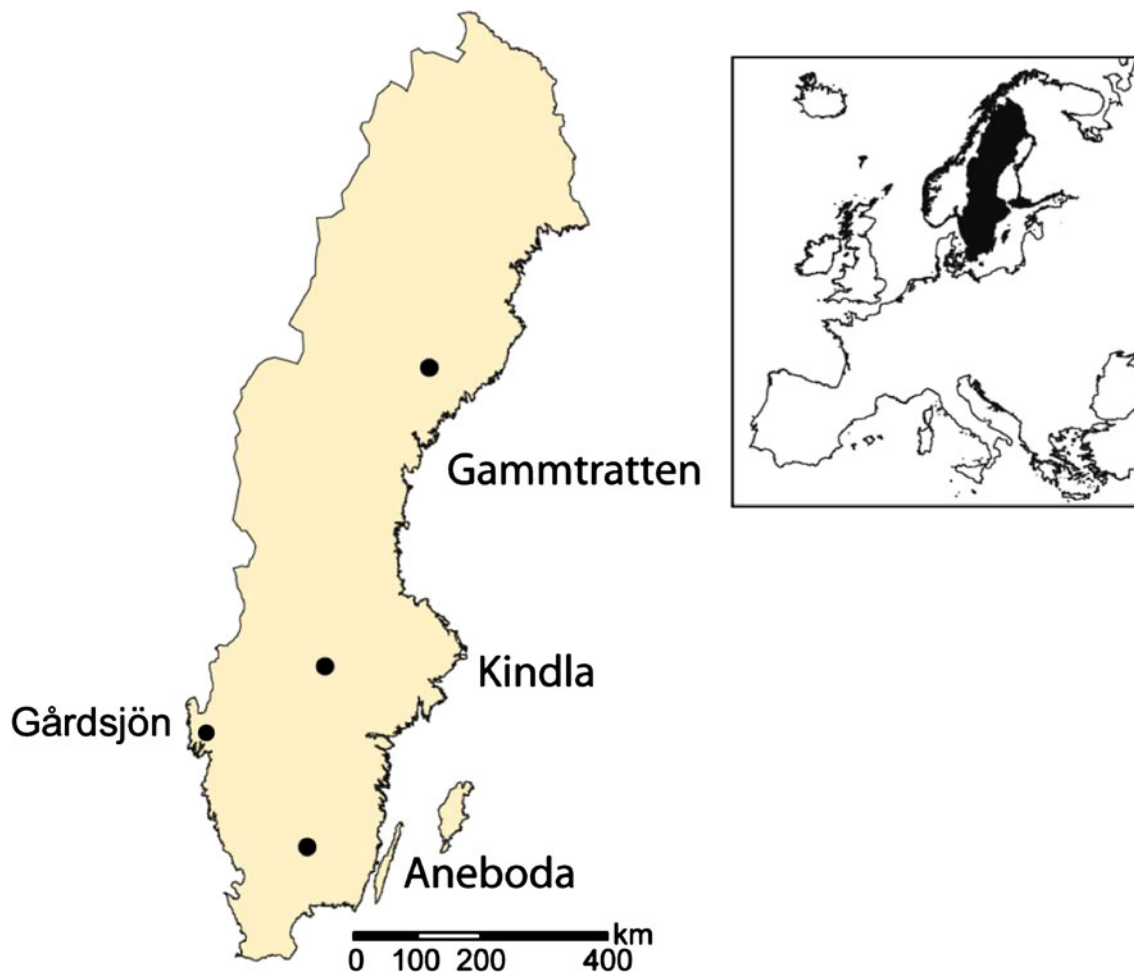
be proportional to the  $\text{SO}_4^{2-}$  deposition reductions, and (ii) recharge areas, because of the more restricted aqueous contact with soils in both time and space, would show greater recovery than discharge areas, and (iii) groundwater would show less recovery than soil water.

## SITE DESCRIPTIONS

The four Swedish IM catchments, Aneboda, Gårdsjön, Kindla, and Gammtratten, are located along a south-north climate and S deposition gradient, at varying distances from the west coast (Fig. 1). They are in natural reserves that have been minimally affected by forestry activities during the last century. The deposition of S, N, and Cl differs widely among the sites and the historical acidification pressure has been much higher in the south, especially at Gårdsjön, than in the north (Westling and Lövblad, 2000). In the late 1980s, S deposition was more than double current loads (Westling and Lövblad, 2000). The long-term (1961–1990) annual mean temperatures, precipitation and duration of snow cover at the sites ranges from 1 to 7°C, 750 to 1000 mm, and 50 to 175 days, respectively (Raab and Vedin, 1995). All sites have granitic bedrock and till is the dominant parent material for soils (Table 1). Organic-rich soils (gleysols, histosols, regosols) dominate in depressions and discharge areas, while podzols dominate the recharge areas. Based on vegetation surveys, moist to wet conditions prevail at 17, 10, 24, and 16% of the catchment area at Aneboda, Gårdsjön, Kindla, and Gammtratten, respectively (Table 1).

The Aneboda catchment is 18.9 ha in area and dominated (73%, Table 1) by Norway spruce (*Picea abies* (L.) Karst.). In January 2005, the area was hit by a severe storm causing substantial damage to the forest, tripling the volume of coarse woody debris. This was followed by a bark beetle infestation, which killed or severely damaged a large proportion of the remaining mature Norway spruce trees. In 2009, approximately 50% of the trees were dead or seriously affected (Ulf Grandin, SLU, unpublished data). The Gårdsjön catchment is the smallest (3.7 ha) and located 10 km inland from the Skagerack Sea coast. Norway spruce is the dominating tree species (65%, Table 1). The January 2005 storm also hit this site, but caused much less direct damage and bark beetle infestation than at Aneboda. The soils are shallow and frequently interrupted by bedrock outcrops in upslope locations.

The Kindla catchment is 20.4 ha in area and dominated by Norway spruce (83%, Table 1). The catchment has steep slopes, with up to 100 m changes in altitude over distances of 400 m. A small mire is situated in the centre of the catchment, while bare rock outcrops are found along the water divide and there are a couple of bedrock ridges inside the catchment. The Gammtratten catchment is



**Fig. 1** Sweden and the location of the four Swedish Integrated Monitoring sites

44.8 ha in area and dominated by Scots pine (*Pinus sylvestris* L.) at higher elevations (13% of area) and Norway spruce elsewhere (70%, Table 1). The area is relatively steep with an elevation range of 135 m. Three small mires are located in the upper reaches.

## MATERIALS AND METHODS

Soil water, groundwater, and streamwater (runoff) have been sampled at all four sites as part of the routine IM-program (Table 2). Maps of each of the IM catchments demonstrating the location of the sampling stations are shown in Fig. 2.

### Bulk Deposition on Open Field

Bulk deposition has been collected since 1996 at Aneboda, Gårdsjön (since 1979), Kindla, and Gammtratten (since 1999) on open treeless areas within or adjacent to each catchment (Fig. 2). At each catchment, two collectors with

20 cm diameter funnels were used. During the snow-free period, the open field collectors consisted of a funnel combined with a plastic bottle. Nylon netting (mesh size 2 mm) at the bottom of the funnel prevented contamination of the collected water by forest litter and insects. The water was collected into polythene bags, replaced at each sampling occasion, supported in plastic bottles covered by aluminum foil to keep the contents dark and prevent excessive warming. In winter at Aneboda, Kindla, and Gammtratten, the funnel was replaced by a snow-sack, a tubular polythene bag mounted on PVC plastic rings ( $\varnothing = 19.5$  cm), in order to collect snow. At Gårdsjön, the snow-free equipment was used throughout the year. Water volume was registered and the samples were sent to laboratory in polythene bottles the day of sampling. Deposition fluxes were calculated from the concentrations and water volumes.

### Throughfall

Throughfall has been collected since 1996 at Aneboda, Kindla, and Gammtratten (since 1999) using 10 funnels

**Table 1** Ecosystem characteristics of the four Swedish IM catchments

	Aneboda	Gårdsjön	Kindla	Gammtratten
Location	N 57° 05' E 14° 32'	N 58° 03' E 12° 01'	N 59° 05' E 14° 54'	N 63° 51' E 18° 06'
Area, ha	18.9	3.7	20.4	44.8
Altitude, m above sea level	210–240	114–140	312–415	420–540
Bedrock geology	Granite	Granite	Granite	Granite
Quaternary deposit	Glacial till	Glacial till	Glacial till	Glacial till
Proportion of moist and wet soils, mainly peat <sup>a</sup>	17%	10%	24%	16%
Main tree species <sup>b</sup>				
Spruce	73%	65%	83%	70%
Birch	20%	14%	14%	16%
Pine	3%	17%	2%	13%
Beech	1%	–	–	–
Alnus	2%	–	–	–
Stem volume, m <sup>3</sup> ha <sup>-1</sup>	319	219	244	138
Mean annual temperature, °C	5.8	6.7	4.2	1.2
Temperature sum of degree-days above +5°C, °C	1350	830	1260	970
Snow cover, days	110	50	150	175
Precipitation, mm year <sup>-1</sup>	750 (880)	1000 (1330)	900 (970)	750 (670)
Evapotranspiration, mm year <sup>-1</sup>	470	480	450	370
Runoff, mm year <sup>-1</sup>	280	520	450	380

Long-term average climatic data from 1961 to 1990 (Raab and Vedin 1995) and, within brackets (precipitation), for the study period (1996–2009)

<sup>a</sup> Data based on vegetation community surveys

<sup>b</sup> Data based on the number of trees of a species compared with the total number of trees (circular plots, Fig. 2), breast height diameter > 5 cm

(Ø = 15.5 cm) on poles systematically placed at 20 m intervals along a line, and by identical collectors placed along two lines (six per line) at Gårdsjön (since 1979). The water was collected in the same way as for bulk deposition. In winter, this equipment was replaced by buckets (Ø = 21.4 cm) to collect snowfall. The polythene bags in both types of collectors were replaced at each sampling occasion. Samples are taken monthly throughout the year. The water volumes of each collector was registered, and then combined into a composite sample for each catchment. Deposition fluxes were calculated from the concentrations and water volumes. Detailed analyses of throughfall deposition systematically collected within the circular plots shown in Fig. 2 indicate that the collector lines generally provide representative samples for the respective IM catchments (Swedish IM, unpublished data). However, the representativity of the samples collected at Aneboda following the storm and bark beetle outbreak in 2005 is unclear.

**Total Deposition**

In this assessment, we have used the total deposition values by Köhler et al. (2011) covering the years 1996–2009 for

all IM sites except Gammtratten where the measurements started in 1999. The input of major ions in wet and dry deposition was estimated from bulk deposition and throughfall. Wet deposition was calculated from bulk deposition adjusted for the contribution of dry deposition by subtracting a defined proportion (10 or 25%) of the measured bulk deposition for each ion except Cl<sup>-</sup>, which was estimated from the wet deposition of sodium (Na<sup>+</sup>) normalized by the Cl/Na ratio of sea water. Total deposition was mainly estimated from throughfall. Sodium and SO<sub>4</sub><sup>2-</sup> were assumed to be inert ions not affected by canopy processes such as uptake or leaching and the throughfall data were assumed to represent total deposition. Calcium (Ca<sup>2+</sup>), magnesium (Mg<sup>2+</sup>), and potassium (K<sup>+</sup>) are affected by canopy processes, which were adjusted for by the Na ratio method. Total deposition of Cl<sup>-</sup> was estimated from the total deposition of Na<sup>+</sup>, normalized to the Cl/Na ratio in sea water. The total deposition of NO<sub>3</sub><sup>-</sup> and ammonium (NH<sub>4</sub><sup>+</sup>) was estimated from wet deposition scaled up by a site specific factor varying from south (1.3) to north (1.01). Dry deposition was estimated by subtracting wet deposition from total deposition. For a more detailed description of the methodology see Köhler et al. (2011).

**Table 2** Site and hydrology, sample type, number of collectors, soil type and horizon, and sampling months used for trend test over the period 1996–2009 (divergent time period defined under Sample type) at the Swedish IM catchments

Site and hydrology	Sample type	No. of collectors	Soil	Horizon	Sampling months
<b>Aneboda</b>					
Recharge area	SW	6	Podzol	B-hor	4, 8, 11
Recharge area	GW	1	Podzol	C-hor, 4.2 m	2, 4, 8, 11
Intermediate zone	SW	2	Podzol	B-hor	4, 8, 11
Intermediate zone	GW	1	Podzol	C-hor, 2.1 m	2, 4, 8, 11
Intermediate zone	GW	1	Podzol	C-hor, 3.1 m	2, 4, 8, 11
Discharge area	SW	1	Histosol	Peat, 0.37 m	4, 8, 11
Discharge area	SW	3	Gleysol	Mineral, 0.37 m	4, 8, 11
Discharge area	GW	1	Gleysol	Mineral, 1.0 m	2, 4, 8, 11
Discharge area	GW	1	Gleysol	Mineral, 2.0 m	2, 4, 8, 11
Catchment runoff	Streamwater				1–12
<b>Gårdsjön</b>					
Recharge area	SW	1	Podzol	B-hor, upper, 0.2 m	1, 4, 8
Recharge area	SW	1	Podzol	B-hor, lower, 0.4 m	1, 4, 8
Recharge area	SW	1	Podzol	C-hor, 0.7 m	1, 4, 8
Recharge area	GW	2	Podzol	C-hor, 1.0 m	4, 6, 10
Discharge area	SW	1	Histosol	Peat, 0.2 m	1, 4, 8
Discharge area	SW	1	Histosol	Peat, 0.4 m	1, 4, 8
Discharge area	SW	1	Histosol	Mineral, 0.7 m	1, 4, 8
Discharge area	GW	2	Histosol	Mineral, 1.0 m	4, 6, 10
Catchment runoff	Streamwater				1–12
<b>Kindla</b>					
Recharge area	SW	1	Podzol	E-hor	5, 8, 10
Recharge area	SW	3	Podzol	B-hor	5, 8, 10
Recharge area	GW <sup>a</sup>	1	Podzol	C-hor, 2.4 m	2, 4, 8, 11
Recharge area	GW <sup>a</sup>	1	Podzol	C-hor, 3.4 m	2, 4, 8, 11
Intermediate zone	SW	3	Podzol	E-hor	5, 8, 10
Intermediate zone	SW	3	Podzol	B-hor	5, 8, 10
Intermediate zone	GW <sup>a</sup>	1	Podzol	C-hor, 2.0 m	2, 4, 8, 11
Intermediate zone	GW <sup>a</sup>	1	Podzol	C-hor, 2.9 m	2, 4, 8, 11
Discharge area	SW	3	Histosol	Peat, 0.3 m	5, 8, 10
Discharge area	SW	3	Gleysol	Mineral, 0.5 m	5, 8, 10
Discharge area	GW <sup>a</sup>	1	Histosol	Mineral, 1.1 m	2, 4, 8, 11
Discharge area	GW <sup>a</sup>	1	Histosol	Mineral, 2.0 m	2, 4, 8, 11
Catchment runoff	Streamwater				1–12
<b>Gammtratten</b>					
Recharge area	SW <sup>b</sup>	2	Podzol	E-hor	6, 8, 10
Recharge area	SW <sup>b</sup>	2	Podzol	B-hor	6, 8, 10
Intermediate zone	SW <sup>b</sup>	1	Podzol	B-hor	6, 8, 10
Intermediate zone	GW <sup>c</sup>	1	Podzol	C-hor, 3.2 m	6, 8, 10
Discharge area	SW <sup>b</sup>	3	Histosol	Peat, 0.3 m	6, 8, 10
Discharge area	GW <sup>c</sup>	1	Histosol	Mineral, 1.0 m	6, 8, 10
Discharge area	GW <sup>c</sup>	1	Histosol	Mineral, 1.9 m	6, 8, 10
Catchment runoff	Streamwater <sup>d</sup>				1–12

SW soil water, GW groundwater

<sup>a</sup> 1997–2009<sup>b</sup> 2001–2009<sup>c</sup> 2000–2009<sup>d</sup> 1998–2009<sup>e</sup> 1999–2009

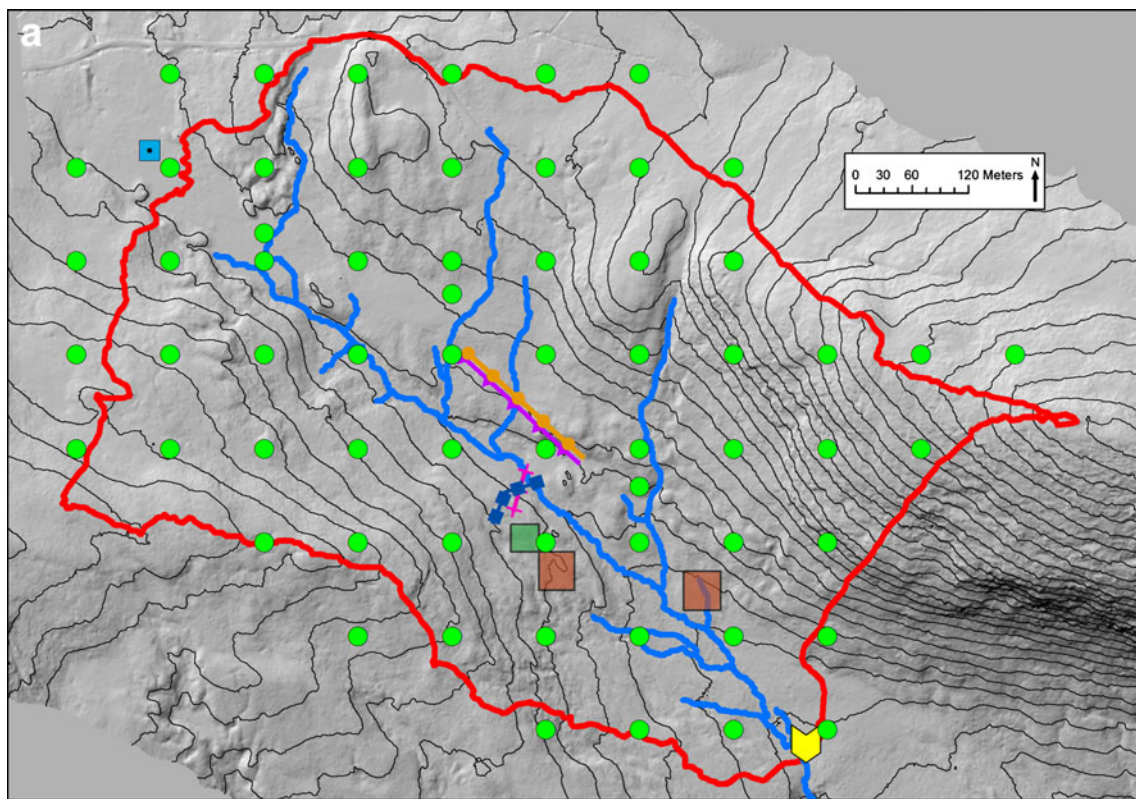


**Soil Water**

At Aneboda, Kindla, and Gammtratten suction lysimeters (P80 ceramic cups, ca. 1 μm pore size) were installed along hillslopes in 1994, 1994, and 1999–2000, respectively. At Aneboda, an additional set of lysimeters was installed in a recharge area close to the intensive soil and vegetation plots (Fig. 2). In recharge areas and intermediate zones (recharge areas at the border to discharge areas), the lysimeters were installed in the mineral soil just below the O-horizon (E-horizon) and in the middle of the B-horizon (Table 2). The E- and B-horizon lysimeters were installed pair-wise (<1 m apart) at <6 m intervals along the hillslope transects at each site. The additional set of lysimeters in Aneboda were grouped in a central flat recharge area at distances <22 m from each pair. In discharge areas (downslope areas with peaty gleysols and histosols), the lysimeters were installed at a depth of 30–50 cm below the soil surface (Table 2). To minimize installation effects (Fölster et al. 2003b), only data from 1996 (2000 at

Gammtratten) has been used in this study. If available, soil water was collected three to four times per year; once after snowmelt (in April, May or June) and after precipitation events in August and in October or November. A suction of –0.3 bar was applied to the lysimeters using a hand pump and the sample collected into a glass vessel located on top of the soil kept in darkness and at ambient air temperature the following day. E-horizon data from Aneboda are not considered here, since there were too few samples.

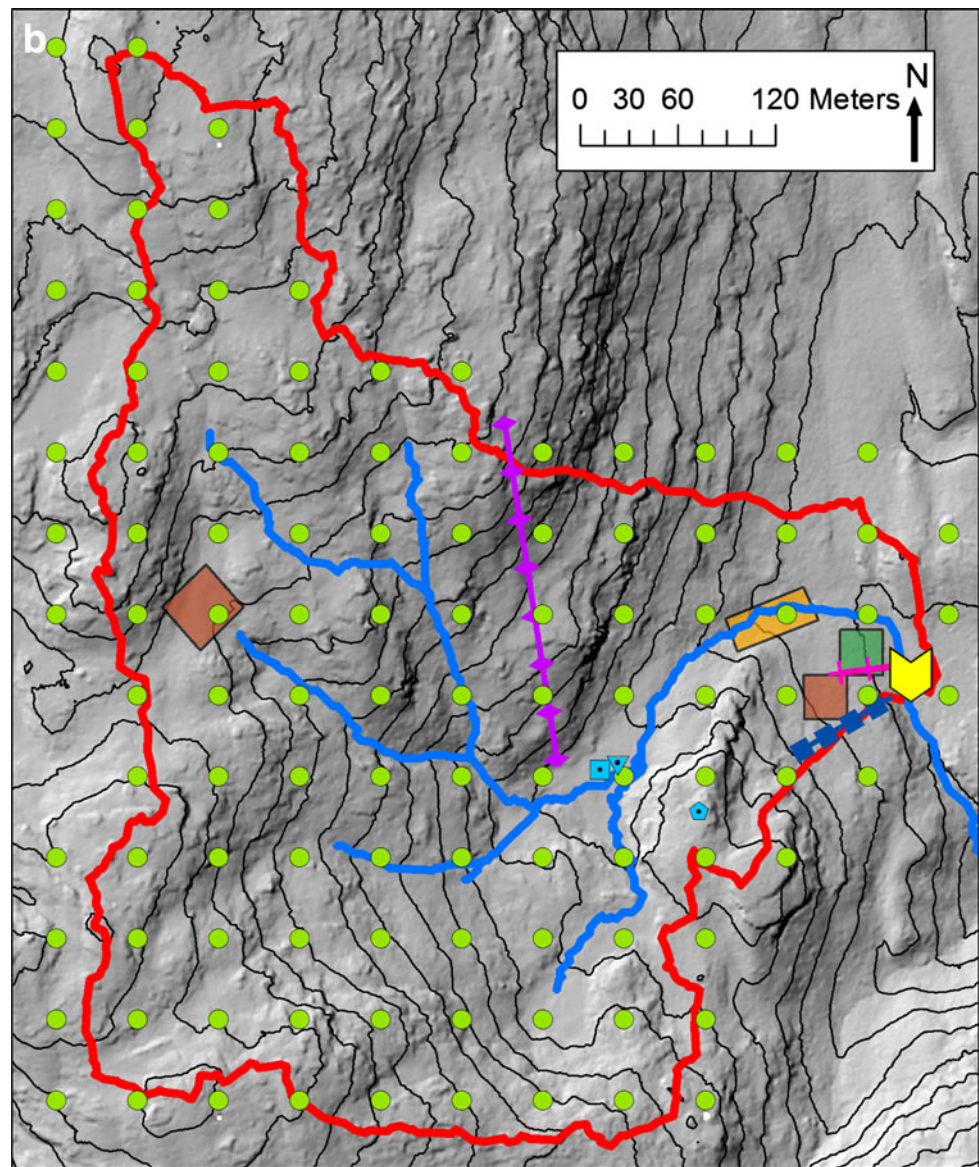
At Gårdsjön, suction lysimeters (Prenart Teflon, ca. 2 μm pore size) were installed in 1979 along two transects (Fig. 2). In both recharge and discharge areas, the lysimeters were installed at 5–10 cm (O-horizon), 20 cm (upper B-horizon), 40 cm (lower B-horizon), and 70 cm (C-horizon) soil depths within a distance of 1.5 m (Table 2). Since soil water from the O-horizon has not been collected at the other IM sites, the O-horizon data from Gårdsjön has not been used in this study. Soil water is collected at non-frozen conditions in winter (mainly January), spring (mainly April), and summer (mainly August).



**Fig. 2** Generalized maps of the **a** Gammtratten, **b** Kindla, **c** Gårdsjön, and **d** Aneboda catchments showing the approximate location of the sampling stations. Red line catchment water divide, blue line stream, light blue squares with black dot bulk deposition and meteorology (outside the map at Aneboda), orange area or line with circles litterfall, purple area, or line with diamonds throughfall, dark green area soil sampling plot, brown area vegetation plot, blue

squares or line with squares groundwater sampling, pink cross or line with cross soil water sampling, green rings circular plots for monitoring tree layer, needle chemistry, algae, and lichen cover on needles, yellow arrow hydrology and water chemistry in catchment outlet. Contours at 2 m (Aneboda and Gårdsjön) or 5 m (Kindla and Gammtratten) intervals (Maps prepared by Ola Langvall and Ivan Clegg, SLU)

Fig. 2 continued



An electric pump system was used to maintain a suction of  $-0.4$  bar during 48 h for the lysimeters included in this study.

### Groundwater

Piezometers were installed at Aneboda, Kindla, and Gammtratten in 1996, 1997, and 2000, respectively. They consisted of a plastic tube ( $\varnothing = 32$  mm) sealed at the bottom and with holes drilled into the lower 0.5 m. In the recharge areas and intermediate zones, one to two piezometers were installed at 2.0–4.2 m soil depth (Table 2). In the discharge areas, two piezometers were installed at ca 1 and 2 m, respectively (Table 2). The piezometers were installed adjacent to the soil water lysimeter pairs (Fig. 1). The groundwater at these sites was sampled according to the Manual for Integrated Monitoring (Internet 2003). The

tubes were first emptied, and then allowed to refill before taking the sample. Filtered ( $0.45 \mu\text{m}$ ) and unfiltered groundwater were collected four times per year; in winter (February or March), after snowmelt (April, May or June), at low groundwater levels (August), and during autumn precipitation events (October or November).

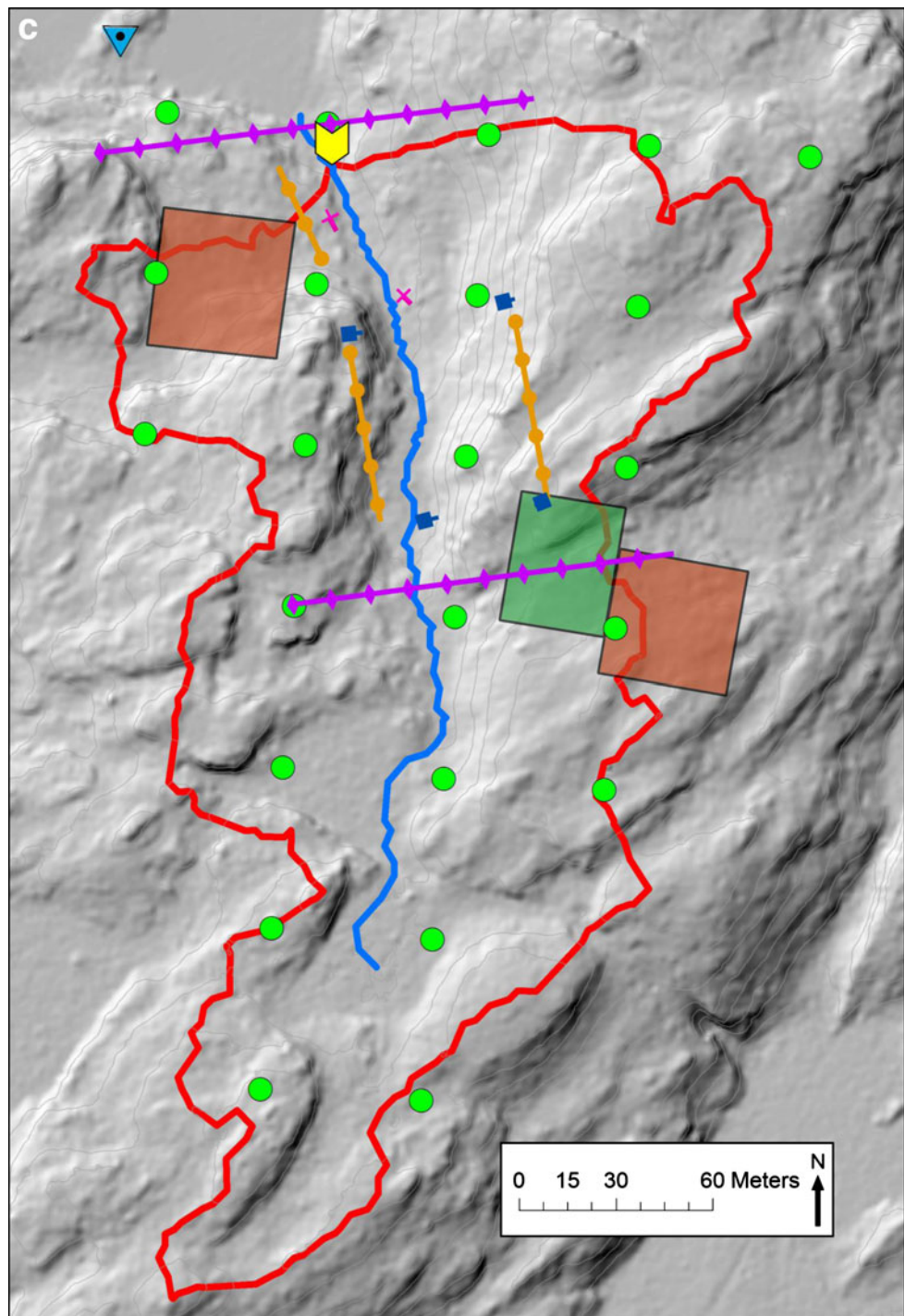
Piezometers at Gårdsjön were installed in 1979 and all with the perforated screen (lower 0.2 m) at 1 m depth below the soil surface (Table 2). Groundwater was sampled during spring (mostly April), summer (mostly June), and autumn (mostly October).

### Streamwater

Since 1996 (Gammtratten since 1998), streamwater has been sampled biweekly at the inlets to the catchment discharge measurement dams (Fig. 2). The samples were



Fig. 2 continued



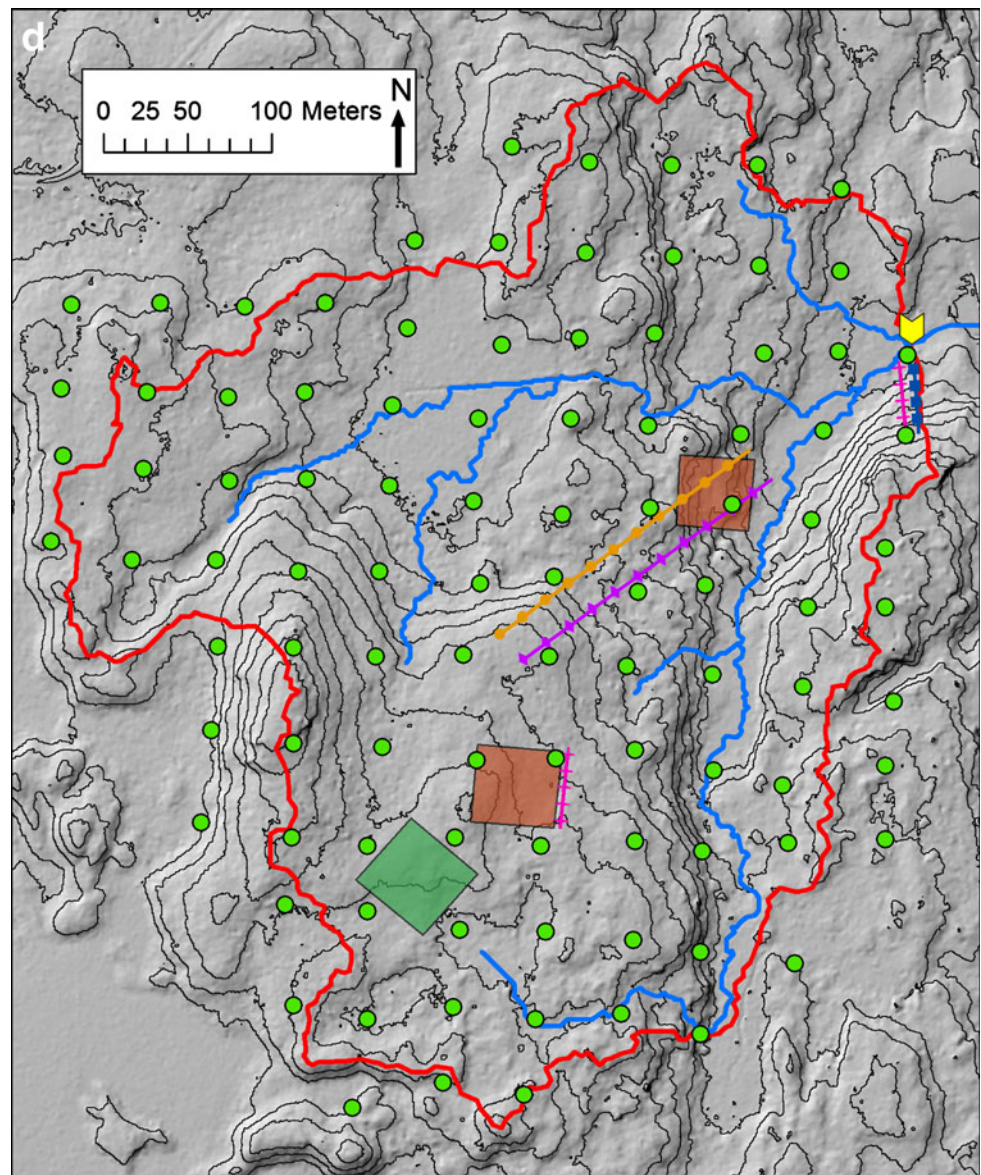
collected just below the water surface in streamwater rinsed polyethylene bottles. The bottles were completely filled, stored dark, and delivered to the laboratory the day after collection. Water chemical data from the Gårdsjön stream are available from 1979. Sporadic data from Aneboda and Kindla are available from 1983 and 1994, respectively. Here, we use data only from 1996 and onwards in order to cover as long sampling period as possible at the three southern sites.

**Water Chemical Analyzes**

The soil water, groundwater, and streamwater from Gårdsjön were analyzed at the Swedish Environmental Research Institute, IVL. Soil water, groundwater, and streamwater samples from Aneboda, Kindla, and Gamtratten were analyzed at the Department of Aquatic Sciences and Assessment, SLU. Both laboratories have been accredited by the Swedish Board for Accreditation



Fig. 2 continued



and Conformity Assessment. The methods (described below) have been applied throughout the study period unless otherwise stated.

At SLU, ambient pH was measured directly after opening the bottle and peristaltically pumping it through an airtight cuvette equipped with a combination pH-electrode adapted for low ionic strength waters (Metrohm 6.0253.100). Alkalinity, occasionally present in deep groundwater and in streamwater at Gammtratten, was determined by titration to pH 5.4 (i.e., when the alkalinity is above zero and it mainly corresponds to bicarbonate). Concentrations of major cations were analyzed in acidified samples (0.5 ml concentrated  $\text{HNO}_3$  per 100 ml sample) by induced coupled plasma with optical emission spectroscopy detector (ICP-OES, Varian Vista Ax Pro) and strong acid anions by ion chromatography (LDC Conducto Monitor III). Total organic carbon (TOC)

concentrations were measured using a Shimadzu TOC 5050 analyzer with ASI-502 sample injector following acidification. Since 1996, TOC concentrations in samples from Gårdsjön were also determined at SLU. Streamwater collected at Gårdsjön was filtered (0.45  $\mu\text{m}$ ), but not at the other three IM sites, before TOC analysis and therefore corresponds directly to DOC. In many Swedish forest streams, including the four IM sites, TOC has been shown to be a good proxy for DOC (Löfgren et al. 2010a). Because of the filtering effects of the lysimeter cups, soil water TOC measurements are considered to be DOC. Groundwater samples were filtered (0.45  $\mu\text{m}$ ) and so the TOC measurements correspond directly to DOC. Hereafter, all TOC measurements are taken to be DOC.

At IVL, pH was measured with a combination pH-electrode adapted for low ionic strength waters (Radiometer).

Concentrations of major cations are determined by ion chromatography (Dionex ICS-1100) and strong acid anions by ion chromatography (Dionex ICS-2000). Total aluminum ( $Al_t$ ) and, if the sample volume was sufficient, non-cationic Al ( $Al_o$ , Driscoll, 1984) were analyzed by AAS (Atomic Absorption Spectroscopy) until 2004 and thereafter by ICP-AES (Inductively Coupled Plasma Atomic Emission Spectroscopy) at SLU. Cationic Al ( $Al_i$ ) was calculated as the difference between  $Al_t$  and  $Al_o$  ( $Al_i = Al_t - Al_o$ ).

Acid neutralizing capacity (ANC,  $\mu\text{eq l}^{-1}$ ) is calculated according to Reuss and Johnson (1986):

$$ANC = Ca^{2+} + Mg^{2+} + K^+ + Na^+ - (SO_4^{2-} + NO_3^- + Cl^-) \quad (1)$$

and ionic strength (IS,  $\text{mmol l}^{-1}$ ) was calculated according to:

$$IS = \frac{1}{2} \sum_i c_i z_i^2 \quad (2)$$

where  $c$  is concentration,  $z$  is ionic charge and  $i$  refers to the ions  $H^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Na^+$ ,  $K^+$ ,  $NH_4^+$ ,  $SO_4^{2-}$ ,  $NO_3^-$ ,  $Cl^-$ ,  $HCO_3^-$ , and  $Al^{n+}$ . The net charge of aluminum ( $n_{Al}^+$ ) in soil water and groundwater was estimated from the relationship between pH and the  $Al_i/Al_t$  ratio ( $r^2 = 0.54$ ,  $P < 0.001$ ) in soil water at 60 sites in southern Sweden (Löfgren and Zetterberg, 2011). Using this method, it was possible to estimate the  $Al^{n+}$  component of the ionic strength for occasions when Al speciation data were lacking. With the differences in pH encountered, the  $n_{Al}^+$  range was 0.1–3 (median 2.2, 5th percentile 1.3, 95th percentile 2.7) at the IM sites. In streamwater,  $n_{Al}^+$  was estimated from the charge balance cation deficit, calculated as the difference between cation and anion concentrations. Besides the ions included in the ionic strength calculations (see above), the concentration of organic anions ( $A^-$ ) was included. Estimated  $A^-$  concentrations were calculated using a triprotic organic acid model calibrated for boreal Swedish surface waters (Hruska et al. 2003). Based on the cation deficit and measured  $Al_i$  concentrations, the median positive net charge,  $n_{Al}^+$ , value for streamwater was 0.1, 1.6, 1.7, and  $\approx 0$  for Aneboda, Gårdsjön, Kindla, and Gammtratten, respectively.

### Statistical Tests

The non-parametric Seasonal Kendall test (Hirsch and Slack, 1984; Loftis et al. 1991) was used for detecting monotonic trends over the study period in the throughfall, soil water, groundwater, and streamwater chemistry time series. For tests of trends for the combined data (Loftis et al. 1991) from all four IM sites, an Excel-program developed by Anders Grimvall, SLU and further extended and modified by Jens

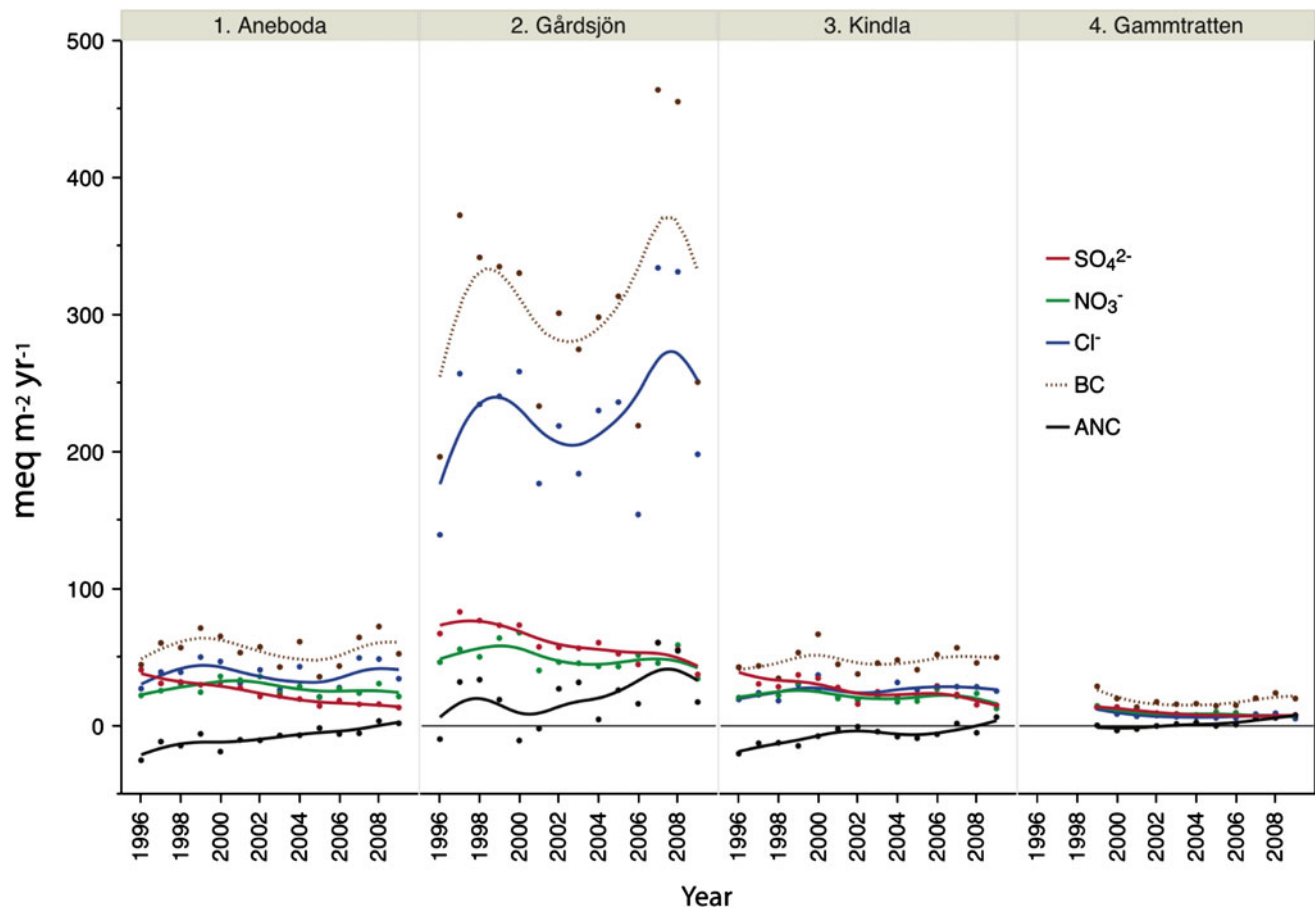
Fölster and Jan Seibert, SLU was used for the calculations (Fölster et al. 2003a). For throughfall and streamwater, monthly (seasons) values were used; for soil water, three seasons were used (spring, summer, and autumn); and for groundwater, four seasons were used (winter, spring, summer, and autumn). The data were first graphically displayed and visually examined to determine whether trends were monotonic or not. Non-monotonic trends were excluded. The trend slope estimate (known as Theil’s or Sen’s slope), which describes the median rate of change in constituent concentrations over the study period, was used to quantify the overall trend (acidification recovery rate). A non-parametric ANOVA (Kruskal–Wallis test, JMP 9.0) followed by a post hoc test (Wilcoxon test for each pair, JMP 9.0) was used to test for differences in soil water recovery rates (Theil slope values) among the four IM sites and between recharge/discharge locations, and for differences between soil water and groundwater.

## RESULTS

### Deposition Levels and Trends

Annual total deposition of  $SO_4^{2-}$  has significantly ( $P < 0.05$ ) declined over the study period at all catchments (Table 4), although starting from widely differing levels (Fig. 3). Compared with the present deposition, the decline was  $\geq 50\%$  at all catchments. In absolute terms, the decreases were approximately 15, 25, 15, and 5  $\text{meq m}^{-2}$  over the investigation period at Aneboda, Gårdsjön, Kindla, and Gammtratten, respectively. For  $NO_3^-$  and  $Cl^-$ , there was no monotonic trend in total deposition and large inter-annual variations were observed for  $Cl^-$ , especially at Gårdsjön where the inputs were high both at the beginning and end of the study period (Fig. 3). This temporal pattern for  $Cl^-$  was also observed, to some extent, at Aneboda. Nitrate total deposition peaked around the year 2000 at all catchments. Regardless of strong acid anion, the total deposition gradients decline in the order Gårdsjön  $>>$  Aneboda  $\geq$  Kindla  $>$  Gammtratten. At the end of the time series (2006–2009), the median  $SO_4^{2-}$ ,  $Cl^-$ , and  $NO_3^-$  deposition levels varied in the ranges 7–55, 8–331, and 7–45  $\text{meq m}^{-2} \text{ year}^{-1}$  (Gammtratten and Gårdsjön data), respectively. The inputs of strong acid anions, potentially causing soil acidification (Reuss and Johnson 1986), are extremely high at Gårdsjön compared with the other sites, especially Gammtratten.

However, the total deposition of BC almost balanced (range 20–455  $\text{meq m}^{-2} \text{ year}^{-1}$ , median deposition 2006–2009, Gammtratten and Gårdsjön data) the strong acid anion inputs and positive ANC occurred at all catchments at the end of the time series (Fig. 3). Except for Gårdsjön,



**Fig. 3** Total deposition ( $\text{meq m}^{-2} \text{ year}^{-1}$ ) of sulfate ( $\text{SO}_4^{2-}$ ), nitrate ( $\text{NO}_3^-$ ), chloride ( $\text{Cl}^-$ ), base cations (BC), and acid neutralizing capacity (ANC) at the Swedish Integrated Monitoring sites. Data from Köhler et al. (2011)

which did not show a monotonic trend, total deposition ANC had increased by 1.5, 1.3, and 1.0  $\text{meq m}^{-2} \text{ year}^{-1}$  (Table 4) at Aneboda, Kindla, and Gammtratten, respectively. At the end of the time series (2006–2009), the median ANC deposition levels were, respectively, 1.4, 54, 1.3, and 5.3  $\text{meq m}^{-2} \text{ year}^{-1}$  at the catchments. The measurements show increased pH in throughfall at the catchments during the investigation period (Fig. 4). The increases were 0.03, 0.04, 0.03, and 0.01 pH-units  $\text{year}^{-1}$  for the catchments arranged in the same south-north order as for ANC. During the last 3 years of the time series, median pH varied between 4.9 and 5.1, with Gårdsjön and Aneboda showing the lowest and highest pH, respectively.

#### Soil Water, Groundwater, and Streamwater Acidification Levels and Trends

The concentrations of the acidity-related parameters, including DOC, in soil water, groundwater, and streamwater over the study period are described for each IM site in Table 3. Mean  $\text{SO}_4^{2-}$  concentrations across all aqua

media ranged between 100 and 200  $\mu\text{eq SO}_4^{2-} \text{ l}^{-1}$  at the three southern sites, except for the intermediate zone at Aneboda, where concentrations were much higher (300–900  $\mu\text{eq SO}_4^{2-} \text{ l}^{-1}$ ). Compared with the other IM sites, the mean  $\text{SO}_4^{2-}$  concentrations at Gammtratten were low, generally below 50  $\mu\text{eq SO}_4^{2-} \text{ l}^{-1}$ . Gammtratten was the most well-buffered site, with generally positive ANC values and  $\text{pH} > 5$  in most cases. The ANC at the three southern sites was generally negative and  $\text{pH} < 5$ , except in the deep groundwater (>2 m depth) and soil water in the Aneboda discharge area. Water samples from Gammtratten also had the lowest ionic strength, generally being less than half those found in the other catchments. Total aluminum concentrations varied considerably between the aqueous media and there were no clear differences among the sites, except that  $\text{Al}_t$  concentrations in groundwater and runoff were lower at Gammtratten than at the other sites. Based on ANC of the streamwater, acid buffering in the IM sites increases in the order Gårdsjön  $\approx$  Kindla < Aneboda < Gammtratten, while the ionic strength order is Gammtratten < Kindla < Aneboda < Gårdsjön. The streamwater chemistry also indicates that particularly Aneboda is affected by

**Table 3** Water chemistry (mean ± standard deviation) in soil water (SW), groundwater (GW), and streamwater at Aneboda and Gårdsjön during 1996–2009

Hydrology/soil	Code	$n_{\text{min-max}}$	pH	$\text{Al}_t \mu\text{g l}^{-1}$	$\text{SO}_4^{2-} \mu\text{eq l}^{-1}$	$\text{DOC mg/l}^{-1}$	$\text{ANC } \mu\text{eq l}^{-1}$	$\text{IS mmol l}^{-1}$
<b>Aneboda</b>								
Recharge area								
SW, B-hor	7101	28–33	4.97 ± 0.34	400 ± 160	79 ± 26	6.1 ± 5.2	−29 ± 35	0.30 ± 0.08
SW, B-hor	7102	35–42	4.61 ± 0.13	1278 ± 426	220 ± 79	6.6 ± 5.4	−144 ± 59	0.80 ± 0.28
SW, B-hor	7103	14–31	4.74 ± 0.16	742 ± 243	135 ± 49	8.4 ± 6.3	−90 ± 33	0.48 ± 0.15
SW, B-hor	7107	34–39	4.81 ± 0.19	868 ± 416	121 ± 58	4.8 ± 2.9	−79 ± 53	0.45 ± 0.20
SW, B-hor	7109	21–31	4.66 ± 0.08	1114 ± 244	133 ± 50	5.7 ± 1.9	−92 ± 29	0.56 ± 0.19
SW, B-hor	7113	18–26	4.90 ± 0.48	1040 ± 389	141 ± 76	7.7 ± 4.1	−82 ± 65	0.53 ± 0.25
GW, 4.2 m	12	32–54	5.51 ± 0.50	1294 ± 595	522 ± 159	3.9 ± 1.2	112 ± 240	1.51 ± 0.34
Intermediate zone								
SW, B-hor	7104	14–26	4.64 ± 0.40	2838 ± 1239	434 ± 184	8.4 ± 9.2	−284 ± 97	2.09 ± 0.55
SW, B-hor	7105	20–27	4.37 ± 0.07	5455 ± 928	954 ± 121	14.8 ± 23.6	−614 ± 113	3.60 ± 0.48
GW, 2.1 m	21	21–54	5.26 ± 0.63	1050 ± 655	411 ± 407	3 ± 1.3	−19 ± 198	1.02 ± 0.17
GW, 3.2 m	22	47–56	5.01 ± 0.37	1050 ± 1090	277 ± 61	3 ± 3.4	18 ± 240	0.86 ± 0.29
Discharge area								
SW, Peat	7202	26–35	5.06 ± 0.25	637 ± 232	156 ± 218	25.1 ± 8.7	77 ± 63	0.88 ± 0.65
SW, Peat	7204	28–36	5.05 ± 0.45	939 ± 341	286 ± 79	5.5 ± 4.9	−21 ± 115	1.21 ± 0.30
SW, Peat	7205	22–37	5.42 ± 0.28	414 ± 161	209 ± 100	10.2 ± 9.5	27 ± 58	0.96 ± 0.34
SW, Peat	7206	28–35	5.14 ± 0.29	563 ± 136	197 ± 97	8.8 ± 4	−12 ± 106	0.96 ± 0.26
GW, 1.0 m	31	46–56	5.43 ± 0.22	1590 ± 1165	101 ± 116	32.6 ± 15.5	221 ± 89	0.73 ± 0.18
GW, 2.0 m	32	45–56	5.99 ± 0.27	551 ± 607	69 ± 64	15.2 ± 9.7	495 ± 175	0.83 ± 0.18
Streamwater	7900	221–313	4.51 ± 0.12	527 ± 287	145 ± 68	23.5 ± 13.4	78 ± 54	0.84 ± 0.17
<b>Gårdsjön</b>								
Recharge area								
SW, 20 cm	LY1_20	28–35	4.56 ± 0.16	1653 ± 331	151 ± 55	3.2 ± 2.7	−59 ± 80	0.86 ± 0.29
SW, 40 cm	LY1_40	26–34	4.64 ± 0.14	1667 ± 405	181 ± 68	3.2 ± 2.5	−74 ± 79	0.81 ± 0.25
SW, 70 cm	LY1_70	32–36	4.99 ± 0.29	719 ± 379	205 ± 58	3.0 ± 2.2	−26 ± 67	0.76 ± 0.17
GW, 1 m	GW4	33–39	4.72 ± 0.14	680 ± 230	155 ± 64	9.5 ± 26.1	−17 ± 80	1.00 ± 0.21
GW, 1 m	GW9	23–32	4.62 ± 0.12	1280 ± 440	181 ± 51	7.4 ± 1.3	−49 ± 63	1.08 ± 0.17
Discharge area								
SW, 20 cm	LY2_20	26–31	4.76 ± 0.18	825 ± 244	153 ± 39	2.2 ± 1.5	−48 ± 67	0.66 ± 0.16
SW, 40 cm	LY2_40	23–31	4.75 ± 0.13	863 ± 187	150 ± 45	3.6 ± 3.0	−44 ± 63	0.63 ± 0.13
SW, 70 cm	LY2_70	19–30	4.87 ± 0.14	741 ± 214	156 ± 44	2.1 ± 2.2	−43 ± 76	0.67 ± 0.17
GW, 1 m	GW5	32–41	4.44 ± 0.18	950 ± 340	131 ± 80	14.2 ± 6.6	0 ± 69	0.97 ± 0.27
GW, 1 m	GW8	30–37	4.54 ± 0.24	1030 ± 310	167 ± 86	12.1 ± 8.5	−26 ± 70	1.12 ± 0.26
Streamwater	F1	223–278	4.29 ± 0.10	755 ± 206	138 ± 86	12.6 ± 4.8	−17 ± 56	1.02 ± 0.33
<b>Kindla</b>								
Recharge area								
SW, E-hor	6004	38–44	4.28 ± 0.11	1367 ± 331	129 ± 52	19.6 ± 9.0	−53 ± 65	0.62 ± 0.16
SW, B-hor	6104	28–37	4.78 ± 0.14	1076 ± 302	138 ± 50	7.9 ± 6.0	−72 ± 38	0.49 ± 0.15
SW, B-hor	6105	32–37	4.48 ± 0.41	1251 ± 425	137 ± 48	11.7 ± 11.6	−105 ± 174	0.57 ± 0.22
SW, B-hor	6106	33–40	4.79 ± 0.10	1097 ± 217	125 ± 40	7.1 ± 7.2	−74 ± 29	0.46 ± 0.12
GW, 2.4 m	11	41–52	4.72 ± 0.28	1096 ± 416	142 ± 43	4.4 ± 2.5	−52 ± 52	0.37 ± 0.09
GW, 3.4 m	12	43–52	5.23 ± 0.34	598 ± 771	154 ± 14	1.6 ± 0.6	34 ± 98	0.39 ± 0.09
Intermediate zone								
SW, E-hor	6001	37–41	4.41 ± 0.14	1217 ± 225	142 ± 52	11.7 ± 9.2	−84 ± 38	0.56 ± 0.15
SW, E-hor	6002	36–40	4.60 ± 0.09	1266 ± 188	151 ± 55	7.8 ± 3.6	−76 ± 30	0.57 ± 0.16



Table 3 continued

Hydrology/soil	Code	$n_{\min\text{-max}}$	pH	$\text{Al}_t \mu\text{g l}^{-1}$	$\text{SO}_4^{2-} \mu\text{eq l}^{-1}$	$\text{DOC mg/l}^{-1}$	$\text{ANC } \mu\text{eq l}^{-1}$	$\text{IS mmol l}^{-1}$
SW, E-hor	6003	37–43	4.59 ± 0.07	1142 ± 220	138 ± 46	7.6 ± 3.6	−81 ± 32	0.52 ± 0.15
SW, B-hor	6101	41–45	4.62 ± 0.10	1213 ± 213	154 ± 38	6.6 ± 5.0	−91 ± 37	0.57 ± 0.11
SW, B-hor	6102	23–32	4.68 ± 0.14	1172 ± 215	181 ± 39	5.9 ± 5.2	−100 ± 30	0.63 ± 0.12
SW, B-hor	6103	41–44	4.74 ± 0.09	1035 ± 239	136 ± 38	6.3 ± 15.7	−76 ± 30	0.48 ± 0.12
GW, 2.0 m	21	44–52	4.88 ± 0.14	1343 ± 1777	159 ± 11	1.7 ± 0.6	−43 ± 32	0.41 ± 0.14
GW, 2.9 m	22	43–52	5.14 ± 0.30	874 ± 1282	149 ± 15	1.8 ± 1.4	12 ± 37	0.40 ± 0.09
Discharge area								
SW, Peat	6201	43–47	4.47 ± 0.09	830 ± 110	126 ± 40	9.9 ± 2.0	−36 ± 20	0.49 ± 0.12
SW, Peat	6202	33–46	4.92 ± 0.34	938 ± 201	104 ± 109	12.3 ± 2.4	−6 ± 45	0.47 ± 0.30
SW, Peat	6203	41–45	4.57 ± 0.17	729 ± 153	101 ± 120	18.8 ± 3.3	20 ± 36	0.47 ± 0.35
SW, Peat	6204	22–33	4.64 ± 0.28	803 ± 289	146 ± 37	11.8 ± 3.5	−52 ± 23	0.56 ± 0.13
SW, Peat	6205	37–43	4.89 ± 0.15	866 ± 182	133 ± 31	7.4 ± 3.2	−28 ± 18	0.48 ± 0.10
SW, Peat	6206	39–43	4.62 ± 0.11	1187 ± 267	132 ± 34	9.9 ± 3.8	−57 ± 28	0.51 ± 0.11
GW, 1.1 m	31	42–52	5.09 ± 0.65	801 ± 830	119 ± 32	11.3 ± 5.6	87 ± 118	0.41 ± 0.13
GW, 2.0 m	32	43–52	5.84 ± 0.29	174 ± 347	127 ± 11	1.5 ± 1.0	249 ± 127	0.50 ± 0.13
Streamwater	6901	233–328	4.60 ± 0.14	659 ± 153	111 ± 37	8.2 ± 3.6	−18 ± 29	0.41 ± 0.08
Gammtratten								
Recharge area								
SW, E-hor	8005	9–15	4.18 ± 0.14	1570 ± 442	32 ± 21	34.4 ± 6.9	47 ± 25	0.44 ± 0.10
SW, E-hor	8009	10–16	4.16 ± 0.17	1258 ± 479	31 ± 21	45.6 ± 19.4	99 ± 37	0.38 ± 0.12
SW, B-hor	8104	22–24	4.98 ± 0.31	70 ± 21	36 ± 3	4.5 ± 4.1	−1 ± 14	0.12 ± 0.02
SW, B-hor	8106	18–20	5.20 ± 0.15	159 ± 32	26 ± 6	3.6 ± 3.2	−2 ± 14	0.09 ± 0.02
Intermediate zone								
SW, B-hor	8101	21–23	5.62 ± 0.19	139 ± 50	32 ± 11	4.8 ± 3.4	21 ± 11	0.13 ± 0.02
GW, 3.2 m	22	24–30	5.96 ± 0.19	1109 ± 3906	41 ± 5	3.6 ± 2	117 ± 38	0.23 ± 0.11
Discharge area								
SW, Peat	8201	23–25	5.61 ± 0.19	233 ± 202	42 ± 12	9.8 ± 9.1	88 ± 39	0.22 ± 0.05
SW, Peat	8202	23–25	5.81 ± 0.16	95 ± 190	42 ± 19	4.3 ± 4.3	99 ± 24	0.22 ± 0.07
SW, Peat	8203	17–25	5.11 ± 0.24	583 ± 285	15 ± 22	25.5 ± 14.5	84 ± 44	0.18 ± 0.11
GW, 1.1 m	31	24–30	5.36 ± 0.22	339 ± 697	43 ± 15	3.5 ± 1.9	60 ± 26	0.16 ± 0.03
GW, 1.9 m	32	25–30	5.98 ± 0.24	56 ± 71	53 ± 4	2.3 ± 2.4	113 ± 42	0.22 ± 0.03
Streamwater	8900	208–282	5.64 ± 0.3	220 ± 87	43 ± 11	8.4 ± 4.0	91 ± 23	0.32 ± 0.06

hydraulically active organic-rich soils, with two to three times higher DOC concentrations ( $24 \text{ mg l}^{-1}$ ) compared with the other sites, where concentrations are fairly similar at around  $8\text{--}13 \text{ mg l}^{-1}$ .

Seasonal Kendall test results indicate that soil water  $\text{SO}_4^{2-}$  concentrations significantly declined over the study period at all of the IM catchments (Table 4). These trends were paralleled by significant increases in soil water ANC and pH at all sites except Gammtratten, where the reduction in the  $\text{SO}_4^{2-}$  deposition rate was minor and the initial total  $\text{SO}_4^{2-}$  deposition level low relative to the other sites (Fig. 3). Indeed, other than soil water  $\text{SO}_4^{2-}$  concentrations, the acid-related parameters at Gammtratten changed little over the study period in any of aqueous media except for streamwater, where significant increases in ANC and pH were detected (Table 4). Significant reductions in the

ionic strength of soil water and streamwater were detected at Aneboda and Kindla, but not at Gårdsjön (Table 4). Reductions in  $\text{Al}_t$  concentrations in streamwater were detected at both Gårdsjön and Kindla, as well as in groundwater (Gårdsjön) and soil water (Kindla). Significant trends in soil water DOC concentrations were detected only at Gårdsjön and Kindla, and the trends were negative. However, significant increases in DOC concentrations were detected in groundwater at Gårdsjön and in streamwater at Kindla (Table 4).

Based on soil water data from all the four IM sites (Table 4), the trends (Theils slope) of acidity-related parameters were statistically different ( $P < 0.05$ , Wilcoxon test for all pairs, data not shown) between Gammtratten and the other sites for all parameters except DOC. The recovery rates were lower at Gammtratten compared with

**Table 4** Theil slope (single value) or quartile distance (25-percentile to 75-percentile) Theil slope values and probability (*P*) for statistically significant trends over the period 1996–2009 for some acidity-related parameters in total deposition (throughfall for pH), soil water, groundwater, and streamwater at the Swedish IM catchments

Parameter	Source	Aneboda		Gårdsjön		Kindla		Gammtratten	
		Slope	<i>P</i>	Slope	<i>P</i>	Slope	<i>P</i>	Slope	<i>P</i>
SO <sub>4</sub> <sup>2-</sup> meq m <sup>-2</sup> year <sup>-1</sup>	Total deposition	-1.9	***	-2.2	**	-1.6	**	-0.7	**
NO <sub>3</sub> <sup>-</sup> meq m <sup>-2</sup> year <sup>-1</sup>	Total deposition	nm		nm		nm		nm	
Cl <sup>-</sup> meq m <sup>-2</sup> year <sup>-1</sup>	Total deposition	nm		nm		nm		nm	
BC meq m <sup>-2</sup> year <sup>-1</sup>	Total deposition	nm		nm		nm		nm	
ANC meq m <sup>-2</sup> year <sup>-1</sup>	Total deposition	1.5	***	nm		1.3	**	1.0	**
pH year <sup>-1</sup>	Throughfall	0.03	***	0.04	***	0.03	***	0.01	*
pH year <sup>-1</sup>	Soil water	0.01 to 0.04	**	0.01 to 0.03	*	0.01 to 0.02	***	-0.03 to 0.01	ns
	Groundwater	-0.08 to -0.01	**	-0.02 to 0.01	ns	-0.05 to 0.02	**	-0.01 to 0.03	<sup>a</sup>
	Streamwater	0.013	**	0.007	ns	0.015	***	0.014	*
Al <sub>t</sub> µg l <sup>-1</sup> year <sup>-1</sup>	Soil water	-58 to -3	ns	-39 to -13	ns	-35 to -15	***	-14 to 7	ns
	Groundwater	-7 to 74	ns	-78 to -32	**	-37 to 41	ns	-0.6 to 0.5	<sup>a</sup>
	Streamwater	0.7	ns	-30	***	-19	**	-1.3	ns
SO <sub>4</sub> <sup>2-</sup> µeq l <sup>-1</sup> year <sup>-1</sup>	Soil water	-13 to -4.4	***	-9.9 to -4.7	**	-8.4 to -6.7	***	-1.6 to -0.1	**
	Groundwater	-13 to -0.9	**	-13 to 8.9	**	4.7 to 0.1	ns	-2.9 to -0.8	<sup>a</sup>
	Streamwater	-7.3	***	-7.8	**	-6.8	***	-2.0	**
DOC mg l <sup>-1</sup> year <sup>-1</sup>	Soil water	-0.2 to -0.1	ns	-0.2 to 0	**	-0.2 to 0	*	-1.2 to 0.1	ns
	Groundwater	<0.1 to 1.1	ns	<0.1 to 1.1	**	-0.1 to <0.1	ns	-0.2 to 0.1	<sup>a</sup>
	Streamwater	0.2	ns	0.1	ns	0.2	***	<0.1	ns
ANC µeq l <sup>-1</sup> year <sup>-1</sup>	Soil water	1.7 to 9.5	***	4.1 to 6.7	*	4.6 to 6.3	***	-1.9 to 1.0	ns
	Groundwater	-18 to 4.4	**	3.9 to 7.6	**	-5.9 to 7.0	**	-4.5 to 0.9	<sup>a</sup>
	Streamwater	3.6	**	2.2	ns	4.7	***	1.9	**
IS mmol l <sup>-1</sup> year <sup>-1</sup>	Soil water	-0.034 to -0.008	***	-0.009 to -0.002	ns	-0.021 to -0.018	***	-0.003 to 0.001	ns
	Groundwater	-0.029 to -0.007	***	-0.025 to 0.001	ns	-0.008 to -0.001	<sup>a</sup>	-0.002 to -0.001	<sup>a</sup>
	Streamwater	-0.013	***	-0.008	ns	-0.010	***	<0.001	ns

1998–2009 for Gammtratten

ns non-significant, nm non-monotonic

<sup>a</sup> Too few observations for statistically reliable results

\* *P* < 0.05, \*\* *P* < 0.01, \*\*\* *P* < 0.001

at the other sites. In addition, the ionic strength was statistically different at Kindla and Gårdsjön, with the former catchment showing a somewhat greater reduction rate.

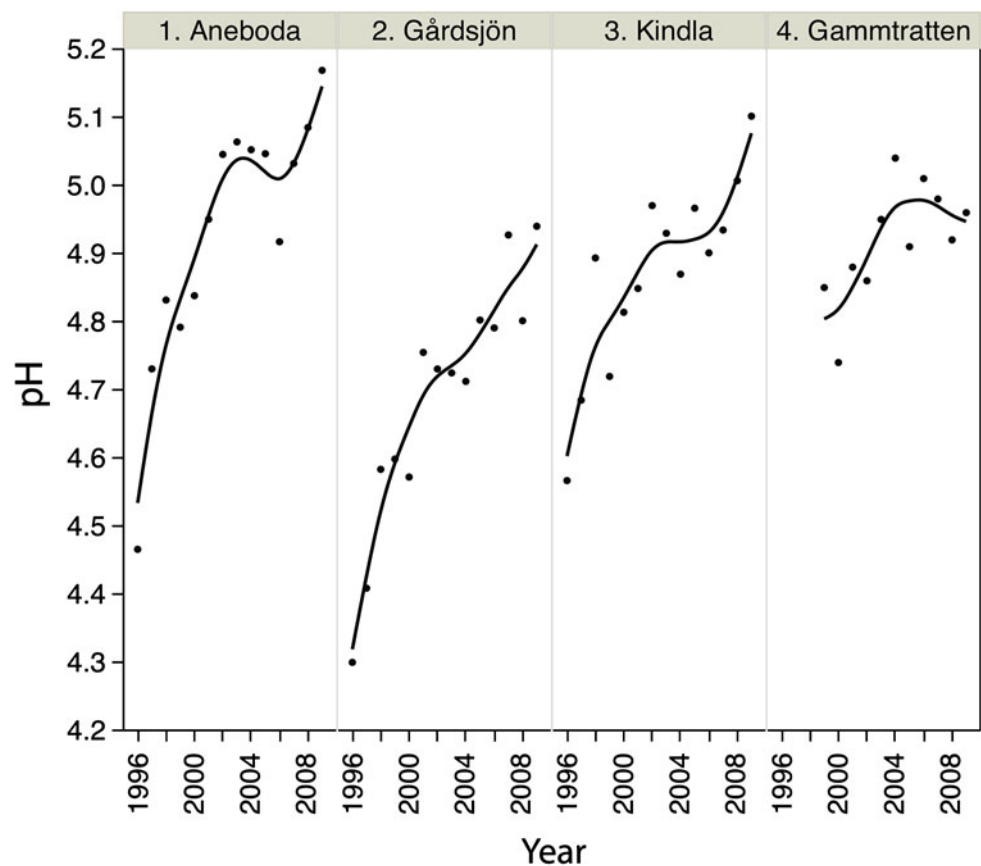
### Differences Between Recharge and Discharge Areas

Testing for differences between recharge and discharge areas was restricted to soil water as there were too few cases (piezometers) for an assessment of groundwater. There were also too few lysimeters in intermediate zones to include in the test. For recharge areas, the test of differences among sites (Kruskal–Wallis test) was performed only on SO<sub>4</sub><sup>2-</sup>, pH and DOC trends (Theil slope, non-significant trends included) due to too few observations (*n*<sub>lys</sub> ≤ 2) of ANC, Al<sub>t</sub>, and IS at Gammtratten. For the recharge areas, significant differences among catchments

were indicated for SO<sub>4</sub><sup>2-</sup> and pH, and for SO<sub>4</sub><sup>2-</sup>, ANC and IS for the discharge areas. Based on these variables, the post hoc test (Wilcoxon test for each pair) showed that the SO<sub>4</sub><sup>2-</sup> concentration decline was significantly (*P* < 0.05) smaller at Gammtratten in both recharge and discharge areas compared with at Aneboda and Kindla and that this difference was very close to significance (*P* = 0.052 for both hydrological locations) at Gårdsjön as well. For the recharge areas, the test indicated significantly greater pH increase rates at Aneboda compared with at Kindla and Gammtratten, while DOC showed no differences among sites. For the discharge areas, the post hoc test showed no significant differences among sites for either ANC or IS.

The above assessments are based on few observations per site and hydrological location (*n*<sub>lys</sub> = 3–6, Table 2). They also include Gammtratten, exposed to low SO<sub>4</sub><sup>2-</sup>

**Fig. 4** pH in throughfall at the Swedish Integrated Monitoring sites



**Table 5** Quartile distance (25-percentile to 75-percentile) for Theil slope estimates (Slope), and Wilcoxon test probabilities (*P*) for statistically significant different slopes between soil water from recharge and discharge areas at the Swedish IM catchments excluding Gammtratten

Parameter	Slope recharge area	Slope discharge area	<i>P</i>
SO <sub>4</sub> <sup>2-</sup> μeq l <sup>-1</sup> year <sup>-1</sup>	-11 to -7.6	-8.1 to -5.0	*
pH-unit year <sup>-1</sup>	0.01 to 0.04	<0.01 to 0.03	ns
ANC μeq l <sup>-1</sup> year <sup>-1</sup>	4.2 to 9.1	2.6 to 6.2	*
IS mmol l <sup>-1</sup> year <sup>-1</sup>	-0.032 to -0.014	-0.019 to -0.060	ns
Al <sub>t</sub> μg l <sup>-1</sup> year <sup>-1</sup>	-62 to -13	-28 to -2.6	*
DOC mg l <sup>-1</sup> year <sup>-1</sup>	-0.23 to -0.09	-0.25 to 0.04	ns

ns non-significant

\* *P* < 0.05

deposition (Fig. 3), limited SO<sub>4</sub><sup>2-</sup> deposition levels (Table 4), and a shorter investigation period (Table 2) compared with the other sites. A complementing assessment, restricted to Aneboda, Gårdsjön, and Kindla, was therefore applied to composite data from the recharge and discharge areas (*n*<sub>lys</sub> = 13 for each hydrological location). Use of composite data for the three southern IM catchments is justified as their SO<sub>4</sub><sup>2-</sup> deposition trends were similar and their recovery rates for all parameters, except IS, were in the same ranges (Table 4, see above). The statistical analyses indicated that the trends for SO<sub>4</sub><sup>2-</sup>, ANC, and Al<sub>t</sub> were greater (i.e., recovery rates more rapid)

for soil water (lysimeters) in the recharge areas than in the discharge areas (by 2.5, 2, and 34 μg l<sup>-1</sup> year<sup>-1</sup>, respectively), but there were no significant differences in recovery rates of pH, IS, and DOC concentrations between these hydrological areas (Table 5).

#### Differences Between Soil Water and Groundwater

Because of the limited groundwater data differences between soil water and groundwater were tested using the combined data from the three southern catchments and excluding the intermediate zones. Significant (*P* < 0.05)

**Table 6** Quartile distance (25-percentile to 75-percentile) for Theil slope (Slope) and Wilcoxon test probabilities (*P*) for statistically significant different slopes between soil water (recharge and discharge areas) and groundwater at the Swedish IM catchments excluding Gammtratten

Parameter	Slope soil water	Slope groundwater	<i>P</i>
SO <sub>4</sub> <sup>2-</sup> μeq l <sup>-1</sup> year <sup>-1</sup>	-9.8 to -6.1	-11 to -3.1	ns
pH-unit year <sup>-1</sup>	0.01 to 0.03	-0.03 to 0.01	***
ANC μeq l <sup>-1</sup> year <sup>-1</sup>	3.3 to 6.8	-0.6 to 7.6	ns
IS mmol l <sup>-1</sup> year <sup>-1</sup>	-0.023 to -0.013	-0.034 to -0.005	ns
Al <sub>i</sub> μg l <sup>-1</sup> year <sup>-1</sup>	-9 to -5	-40 to 20	ns
DOC mg l <sup>-1</sup> year <sup>-1</sup>	-0.2 to 0	>-0.1 to 0.3	**

ns non-significant

\* *P* < 0.05, \*\* *P* < 0.01, \*\*\* *P* < 0.001

differences in Theil slope estimates between soil water and groundwater were observed only for pH and DOC concentrations (Table 6). The median values indicate that pH in soil water had increased by 0.02 units year<sup>-1</sup> over the study period, but decreased by 0.02 units year<sup>-1</sup> in groundwater. Similarly, concentrations of DOC in soil water decreased by approximately 0.2 mg l<sup>-1</sup> year<sup>-1</sup> while they slightly increased (0.05 mg l<sup>-1</sup> year<sup>-1</sup>) in groundwater. There were no significant differences in recovery rates of SO<sub>4</sub><sup>2-</sup>, ANC, IS, and Al<sub>i</sub> between soil water and groundwater at the three southern IM sites.

## DISCUSSION

There have been several studies on the effects of reductions in S deposition on soil water chemistry (Hruska et al. 2009; Löfgren and Zetterberg 2011; Vanguelova et al. 2010; Wu et al. 2010) and surface water (Fölster et al. 2003a; Skjelkvåle et al. 2005; Stoddard et al. 1999), but few that deal with both and with the effects on groundwater. In this study, we have assessed the effect of declining S deposition on a hydrological continuum of soil water and groundwater from recharge and discharge areas, and streamwater in four forested catchments over the period 1996–2009. The four catchments form a deposition gradient. Since S deposition peaked in the early 1980s, our study covers the second half of a 30-year period of successively declining S deposition.

### Effects of S Deposition Decline at Each of the Sites

At Gammtratten, the most northern of the catchments, SO<sub>4</sub><sup>2-</sup> deposition levels were the lowest (Fig. 3), but still showed a significant decline over the study period. Soil water, groundwater, and streamwater showed well-buffered conditions (ANC > 0 μeq l<sup>-1</sup>), relatively high pH (>5),

and low ionic strength (<0.32 mmol l<sup>-1</sup>, Table 3). Throughout the study period, bicarbonate was frequently detected in both groundwater and streamwater (data not shown, Löfgren and Cory, 2010). SO<sub>4</sub><sup>2-</sup> concentrations in soil water and streamwater declined over the study period accompanied by increases in ANC and pH in runoff (Table 4). However, the changes in SO<sub>4</sub><sup>2-</sup> concentrations and ANC (but not pH) in soil water and groundwater were much lower, generally twofold to tenfold lower than those observed at the three southern catchments. Stream water ANC increased almost double as fast at Aneboda and Kindla, while it was at similar rate at Gårdsjön.

Other studies have shown that S deposition in northern Sweden has mainly caused only episodic acidification in streamwater (during snowmelt), and the seasonally large variations in ANC and pH are primarily attributable to base cation dilution in combination with increased DOC concentrations (Bishop et al. 2000; Laudon et al. 2004). In this study, Seasonal Kendal tests of the Gammtratten data showed that a significant (*P* < 0.05) increase in streamwater ANC occurred during late winter (March and April) and summer (June and August) and in pH in June, but no such trends were observed in May, the main snowmelt period. Neither BC (data not shown) nor DOC showed any significant trends for any month, while SO<sub>4</sub><sup>2-</sup> decreased except during the summer months June–August.

The present and historically low S deposition levels at Gammtratten, in combination with the observed acidity trends in the examined aqueous media indicate that the S deposition only marginally affected the acidity status during the study period and that the catchment has been only slightly affected by anthropogenic acidification. In addition, the observed recovery trends for SO<sub>4</sub><sup>2-</sup>, the assumed most important acidification recovery driver, were much lower compared with at Aneboda, Gårdsjön, and Kindla (Table 4). Therefore, the soil water, groundwater, and streamwater results from Gammtratten are not discussed further.

Inorganic N deposition at the IM catchments was almost completely retained within soils and living biomass or lost to the atmosphere. The median NO<sub>3</sub><sup>-</sup> plus NH<sub>4</sub><sup>+</sup> deposition was 50, 93, 38, and 17 meq m<sup>-2</sup> year<sup>-1</sup> at Aneboda, Gårdsjön, Kindla, and Gammtratten, respectively, of which NO<sub>3</sub><sup>-</sup> (Fig. 3) constituted 51–54%. At most sampling stations NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> concentrations were close to the analytical detection limits (data not shown). Not even the storm felling in 2005 and the following bark beetle outbreak at Aneboda caused any tangible effects on the inorganic N concentrations. In streamwater, the maximum NO<sub>3</sub><sup>-</sup> concentrations increased by <8 μeq NO<sub>3</sub><sup>-</sup> l<sup>-1</sup>, while no change in NH<sub>4</sub><sup>+</sup> was detected at all (data not shown). In soil water, the effects were even weaker. During the investigation period, the inorganic N compounds did



not significantly influence the acidity status of soils and waters at the IM catchments, thus they are not discussed further. The same holds true for the storm felling at Aneboda, which had negligible impact on the acidity status.

The changes in soil water concentrations of  $\text{SO}_4^{2-}$ , pH, ANC, and  $\text{Al}_t$  were similar at Aneboda, Gårdsjön, and Kindla (Table 4) and no significant differences ( $P < 0.05$ ) in these parameters among these three sites were observed. A greater reduction in  $\text{SO}_4^{2-}$  concentrations at Gårdsjön than at Aneboda and Kindla was expected since the  $\text{SO}_4^{2-}$  deposition declined by 1.9, 2.2, and 1.6  $\text{meq m}^{-2} \text{ year}^{-1}$ , respectively. However, this pattern was not observed in either soil water or streamwater (Table 4). Possibly the desorption of  $\text{SO}_4^{2-}$  from the mineral soil might be delaying the recovery from acidification (Borken et al. 2011). Data from Gårdsjön indicate that this process is fairly rapid (months) in O- and E-horizons, but it takes years in the B-horizon (Giesler et al. 1996). Other data from Gårdsjön, Aneboda, and Kindla indicate that organically bound S is mineralized and oxidized in humus and peat, which affects the  $\text{SO}_4^{2-}$  concentrations in the mineral soils (Giesler et al. 2005; Löfgren et al. 2001; Mörth et al. 1999). The high  $\text{SO}_4^{2-}$  concentrations in soil water from the intermediate zone at Aneboda and increasing  $\text{SO}_4^{2-}$  concentrations in groundwater at some locations in the Gårdsjön and Kindla catchments (Table 4) indicate that these processes have the potential to mask the effects of changes in  $\text{SO}_4^{2-}$  deposition.

Due to its divalent charge, changes in the  $\text{SO}_4^{2-}$  concentration strongly affect the ionic strength of waters in which it is present (cf. Eq. 2). Therefore, it was somewhat surprising that the ionic strength declined more rapidly in soil water at Kindla than at the other two sites (Table 4). However, increases in  $\text{Cl}^-$  deposition (and the balancing cations mainly  $\text{Na}^+$  and  $\text{Mg}^{2+}$ , data not shown) at Gårdsjön and to a lesser degree also at Aneboda occurred at the end of the study period (Fig. 3), which to some extent compensated for the decreased  $\text{SO}_4^{2-}$  concentrations. At Gårdsjön, the mean  $\text{Cl}^-$  concentrations were in the range 400–500  $\mu\text{eq l}^{-1}$  in all aqueous media, while at Aneboda they increased from the recharge areas ( $\approx 100 \mu\text{eq l}^{-1}$ ) toward the stream (200–300  $\mu\text{eq l}^{-1}$ , Table 3), indicating the presence of an unknown local  $\text{Cl}^-$  source (see Köhler et al. 2011). At Kindla, the mean  $\text{Cl}^-$  concentrations were in the range 50–80  $\mu\text{eq l}^{-1}$  in all aqueous media.

ANC in streamwater was also affected by the  $\text{Cl}^-$  input, compensating for lower  $\text{SO}_4^{2-}$  concentrations (cf. Eq. 1). Streamwater at both Aneboda and Kindla showed significant declines in ionic strength and increases in ANC coupled to the decreased  $\text{SO}_4^{2-}$  concentrations (Table 4). The generally low ANC ( $< 0 \mu\text{eq l}^{-1}$ ) and pH ( $< 5.5$ ) in soil water and streamwater (Table 3) indicate that weak organic acids and/or aluminum oxyhydroxides are the most

important buffer systems at all three of the sites. The small increases in pH over the study period at Aneboda and Kindla (0.1–0.5 units) are therefore consistent with expectations. Rapid changes in pH occur mainly when bicarbonate is present ( $\text{ANC} > 0$  and  $\text{pH} > 5.4$ ) (Ågren et al. 2010). At Gårdsjön, significant pH increases were only detected in soil water ( $< 0.4$  units, Table 4).

The  $\text{Al}_t$  concentrations decreased in streamwater at both Gårdsjön and Kindla, indicating increased coagulation (adsorption and/or precipitation) with time in the soils. No such trends were found at Aneboda (Table 4), probably because most of the Al was organically bound ( $\text{DOC} \approx 23 \text{ mg l}^{-1}$ ,  $n_{\text{Al}}^+ \approx 0.1$ ). Recently, the Al dynamics at Aneboda, Kindla, and Gammtratten were evaluated (Löfgren and Cory, 2010) and it was shown that the Al species composition and  $\text{Al}_t$  levels were strongly related to the pH and DOC concentrations in groundwater. In addition, the  $\text{Al}_t$  concentrations were reduced in the near-stream zone ( $< 2 \text{ m}$ ) at Kindla due to mixing with well-buffered deep groundwater. In this study, the observed decreased  $\text{Al}_t$  concentrations at Gårdsjön and Kindla are probably explained by increased pH in soil water and groundwater (significant in groundwater only at Kindla, Table 4). Unfortunately, the IM piezometers are installed too far from the streams to capture processes in the near-stream zone (Löfgren and Cory 2010).

Positive trends in DOC concentrations were found in streamwater at each IM catchment, but the trend was only significantly at Kindla (Table 4). However, DOC concentrations in soil water had not increased, as might have been expected, but showed either negative or non-significant trends (Table 4). DOC concentrations in soil water in southern Sweden and Norway have also been shown to be either decreasing or remaining fairly constant, especially in soil water from or below the B-horizon (Löfgren and Zetterberg, 2011; Wu et al. 2010). Based on data from Aneboda and Kindla, it has been shown that soil water DOC concentrations are strongly influenced by pH, IS, and Al dynamics (Löfgren et al. 2010b).

An increase in DOC concentrations in soil waters that has been linked to increases in surface water DOC concentrations has been detected in the UK (Vangelova et al. 2010), Czech Republic (Hruska et al. 2009), and Germany (Borken et al. 2011). However, in these studies, the positive trends were only found for soil water from the organic topsoil, either at 10 cm or just below the forest floor. Their results indicate that a positive relationship between soil water and streamwater DOC concentrations is restricted to organic soils with shallow groundwater flow paths. These conditions are met in peatlands and near-stream zones. Although no significant difference in soil water DOC concentrations between recharge and discharge areas was found in this study (Table 5), model simulations based

on the Swedish IM data indicate that processes in the riparian zones can explain 36–63% of the streamwater DOC dynamics (Winterdahl et al. 2011), and that runoff and temperature were the main drivers (Futter et al. 2011; Winterdahl et al. 2011) except for at Gårdsjön where the Cl<sup>-</sup> deposition was important (Futter et al. 2011).

**Differences Between Recharge and Discharge Areas**

Significantly greater ( $P < 0.05$ , Kruskal–Wallis test) trend slope estimates (recovery rates) in soil water SO<sub>4</sub><sup>2-</sup>, ANC, and Al<sub>t</sub> concentrations were found for recharge areas compared with discharge areas (Table 5). Over the study period, the median differences between these two hydrological compartments were 35 µeq SO<sub>4</sub><sup>2-</sup> l<sup>-1</sup>, 28 µeq ANC l<sup>-1</sup>, and 475 µg Al<sub>t</sub> l<sup>-1</sup>. Discharge areas have lateral or upward groundwater flow paths, and are located adjacent to the stream and rich in organic matter. Near-stream (riparian zone) dampening effects on acidity-related water variables have been previously demonstrated (Lawrence et al. 1988; Löfgren and Cory, 2010; Pellerin et al. 2002), and our results indicate that these effects can extinguish much of the acidification recovery effects generated in recharge areas. The buffering capacity of soils in discharge areas appears to be related to their high organic matter contents, high cation exchange capacity (CEC), and accumulation of aluminum (Giesler et al. 2000; Löfgren and Cory, 2010). The discharge areas probably delayed and buffered the acidification during the historical period of increasing and high SO<sub>4</sub><sup>2-</sup> deposition loading.

The difficulty in this study, as with others, in linking soil water and groundwater chemistry to streamwater chemistry is the lack of knowledge about the hydraulic flow paths between the recharge areas, discharge areas, and streams, and the spatial representativeness of the soil water and groundwater sampling. Streamwater chemistry reflects the integrated effect of the entire terrestrial area of the catchment and in-stream processes, and is therefore difficult to relate to any particular set of soil water and groundwater sampling points. However, our results indicate that soil water and groundwater chemistry in the upper meter of the riparian soils satisfactorily resembles both the concentrations (Table 7) and temporal trends in streamwater (Tables 5, 8), while soil water from upslope do not. Thus, soil water in recharge areas appears to act independently,

**Table 7** Median concentrations in soil water (SW), groundwater (GW) and streamwater at the Swedish IM catchments excluding Gammtratten

*rech* recharge area, *disch* discharge area  
<sup>a</sup> ≤1 m soil depth

Hydrological compartment	pH	Alt µg l <sup>-1</sup>	SO4 µeq l <sup>-1</sup>	DOC mg l <sup>-1</sup>	ANC µeq l <sup>-1</sup>	IS mmol l <sup>-1</sup>
SW, rech	4.70	1080	143	4.3	-66	0.59
SW, disch	4.93	700	166	5.0	-2	0.74
GW, rech	4.83	479	165	3.6	-10	0.76
GW, disch <sup>a</sup>	4.71	290	114	14.2	52	0.75
Streamwater	4.48	630	119	11.6	5	0.77

**Table 8** Range for Theil slope estimates (Slope) for streamwater at the Swedish IM catchments excluding Gammtratten

Parameter	Slope streamwater
SO <sub>4</sub> <sup>2-</sup> µeq l <sup>-1</sup> year <sup>-1</sup>	-7.8 to -6.8
pH-unit year <sup>-1</sup>	0.007 to 0.013
ANC µeq l <sup>-1</sup> year <sup>-1</sup>	2.2 to 4.7
IS mmol l <sup>-1</sup> year <sup>-1</sup>	-0.013 to -0.008
Al <sub>t</sub> µg l <sup>-1</sup> year <sup>-1</sup>	-30 to <1
DOC mg l <sup>-1</sup> year <sup>-1</sup>	0.1 to 0.2

with no significant impact on the streamwater chemistry in a decadal perspective. Model simulations of streamwater chemistry based on lumped data from hydraulically different compartments of the catchment may thus be flawed. Further discussion of this issue is presented in this volume by Futter et al. (2011), Köhler et al. (2011), and Winterdahl et al. (2011).

**Differences Between Soil Water and Groundwater**

There was no significant difference in the trend slope estimates for SO<sub>4</sub><sup>2-</sup>, ANC, IS, and Al<sub>t</sub> between soil water and groundwater for the three southern IM sites (Table 6). This indicates that these variables are determined by common hydrological and soil chemical processes regardless of the aqueous medium. However, the trends for pH and DOC significantly differed; while pH increased and DOC decreased in soil water, the opposite occurred in groundwater. In groundwater, the simultaneous reductions in pH and SO<sub>4</sub><sup>2-</sup> concentrations should theoretically increase DOC coagulation and reduce the DOC concentrations due to reductions in DOC net charge (Tipping and Woof 1990) and/or the competition between SO<sub>4</sub><sup>2-</sup> and DOC on minerogenic surfaces in mineral soils (Borken et al. 2011; Karlton et al. 2000). Previous analyses of soil water data from Aneboda and Kindla have shown that the relationship between DOC concentrations, pH, IS, and Al<sub>t</sub> are complex and that IS and Al<sub>t</sub> changes can counteract the effects of pH increases (Löfgren et al. 2010b). Hence, the reason for the observed changes in groundwater DOC concentrations remains unclear. Many of the groundwater samples, except those from Gårdsjön, frequently had bicarbonate (data not shown, Löfgren and Cory 2010).

Besides increased organic acidity, the observed reductions in groundwater pH may, therefore, be due to increased CO<sub>2</sub> partial pressure related to the mineralization of DOC.

## CONCLUSIONS

A general reduction in total SO<sub>4</sub><sup>2-</sup> deposition between 1996 and 2009 was observed at the four Swedish IM sites (range 5–25 meq m<sup>-2</sup>). This reduction is the prerequisite for recovery from acidification of the soil–water ecosystem and it was reflected in reduced SO<sub>4</sub><sup>2-</sup> concentrations in soil water, groundwater, and streamwater. In contrast, changes in rates of deposition of inorganic N were minor and had negligible effects on the acidity-related variables considered in this study.

At Gårdsjön, the high input of Cl<sup>-</sup> via sea spray effectively masked the effects of decreased SO<sub>4</sub><sup>2-</sup> deposition, and except for SO<sub>4</sub><sup>2-</sup>, few trends were found among the studied chemical variables. The most obvious acidification recovery effect at this site was a decline in groundwater and streamwater Al<sub>t</sub>, while pH, ANC, IS, and DOC remained fairly unchanged. The most pronounced acidification recovery effects were found at Kindla. ANC and pH increased while Al<sub>t</sub> and IS decreased. Kindla was the only site where streamwater DOC concentrations increased significantly. Except for Al<sub>t</sub> and DOC, the response at Aneboda was similar to that at Kindla. Few recovery effects were detected at Gammtratten, due to low S deposition inputs, both historical and present. Hence, the acidity-related water chemical trends in soil water, groundwater and runoff at the Swedish IM sites were to some extent correlated to the SO<sub>4</sub><sup>2-</sup> deposition gradient, but other factors, such as marine influence and individual catchment characteristics, were at least as important.

Excluding the non-acidified Gammtratten site, soil water in recharge areas showed a greater response to the reduced SO<sub>4</sub><sup>2-</sup> deposition than the discharge (riparian) areas. The organic-rich soils in the riparian zone seemed to have buffered some of the acidification recovery effects observed in the recharge areas. The concentrations and recovery trends in streamwater were more similar to those found in soil water and groundwater in the riparian zones. These findings highlight the need for well-planned and executed studies of hydraulically active and organic-rich sites in catchment studies.

**Acknowledgments** The Swedish Integrated Monitoring program has been funded by the Swedish Environmental Protection Agency. This study would not have been possible without the efforts of all the people who collected and analyzed samples from the IM sites, and those who maintained the data archive. The authors thank Associate Professor Stephan Köhler, SLU, and Therese Zetterberg, IVL for the total deposition data and, together with Associate Professor Martyn

Futter, SLU, for valuable scientific discussions during the preparation of this paper. The authors also thank Ola Langvall, SLU, and Ivan Clegg, SLU for preparing the catchment maps.

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