

# Reduced European emissions of S and N - Effects on air concentrations, deposition and soil water chemistry in Swedish forests

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4	Reduced European emissions of S and N – effects on air
5	concentrations, deposition and soil water chemistry in
6	Swedish forests
7	
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17	Capsule
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19	Reduced European emissions have led to decreased acidic deposition and a slow
20	recovery of soil water but nitrogen deposition remains the same in Swedish forests.
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1	Abstract
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3	Changes in sulphur and nitrogen pollution in Swedish forests have been assessed in
4	relation to European emission reductions, based on measurements in the Swedish
5	Throughfall Monitoring Network. Measurements were analyzed over 20 years with a
6	focus on the 12-year period 1996 to 2008. Air concentrations of SO <sub>2</sub> and NO <sub>2</sub> , have
7	decreased. The SO <sub>4</sub> -deposition has decreased in parallel with the European emission
8	reductions. Soil water SO <sub>4</sub> -concentrations have decreased at most sites but the pH,
9	ANC and inorganic Al-concentrations indicated acidification recovery only at some of
10	the sites. No changes in the bulk deposition of inorganic nitrogen could be
11	demonstrated. Elevated NO <sub>3</sub> -concentrations in the soil water occurred at irregular
12	occasions at some southern sites. Despite considerable air pollution emission
13	reductions in Europe, acidification recovery in Swedish forests soils is slow. Nitrogen
14	deposition to Swedish forests continues at elevated levels that may lead to leaching of
15	nitrate to surface waters.
16	
17	Keywords: Acidification, Nitrogen leaching, Recovery, Forest, Swedish Throughfall
18	Monitoring Network (SWETHRO)
19	
20	
21	Research highlights:
22	• S deposition to Swedish forests has decreased in parallel with European
23	emissions.
24	Soil water pH, ANC and inorganic Al-concentrations indicated a slow
25	recovery.

- The bulk deposition of inorganic nitrogen over Sweden has not decreased.
- Continued N deposition to Swedish forests may cause leaching of N to surface waters

### 1. Introduction

Anthropogenic emissions of sulphur and nitrogen have caused acidification and eutrophication of terrestrial and aquatic ecosystems in Europe (Reuss & Johnson, 1986; Galloway et al., 2004). The emissions have however decreased considerably since 1990 (Nyiri et al., 2009). Over the period 1990-2008, the emission reductions reported by EMEP for the 27 EU member countries were 73, 39 and 22 % for oxidized sulphur, oxidized nitrogen and reduced nitrogen, respectively. The corresponding values for emission reductions for Sweden were 71, 49 and 8 % for oxidized sulphur, oxidized nitrogen and reduced nitrogen, respectively.

The emission reductions have improved the situation to some extent e.g. in streams and lakes in Sweden (Skjelvåle et al., 2001; Fölster & Wilander, 2002). But the recovery is often slow and model simulations show that a full recovery is far away in the future in many regions, where the soils have been depleted of base cations (Sverdrup et al., 2005). Continuous evaluations of effects of the reduced emissions on air pollutant concentrations, on deposition to the forests and on soil and soil water chemistry are necessary in order to assess whether or not the emission reductions are large enough to allow for sufficient ecosystem recovery.

1	The Swedish Throughfall Monitoring (SWETHRO) network started in 1985, with the
2	aim to measure air concentrations, deposition and soil water chemistry in managed
3	forest ecosystems across Sweden. The measurements started in southern Sweden,
4	where the acidification problems were largest, but the network has expanded and
5	today measurements are carried out across the entire country. Evaluation of data for
6	the period 1985-1994 has shown a gradient with the highest S and N deposition in the
7	south-western part of Sweden (Hallgren Larsson et al., 1995). Furthermore, there was
8	a temporal trend with decreasing sulphur deposition during this period.
9	
10	In this article, air concentrations, deposition and soil water chemistry were evaluated
11	with respect to trends over time and geographical gradients for the different
12	monitoring sites within the SWETHRO network. Focus was on the period of October
13	1996 - September 2008, for which continuous time series of measurements are
14	available for more than 50 sites for throughfall and soil water chemistry, covering the
15	entire country. Results are also shown from a few long time series in southern
16	Sweden, starting in the late '80s or early '90s. The changes in air concentrations and
17	deposition to Swedish forests are compared to the reported European emission
18	reductions and discussed in relation to the progress of recovery of soil water
19	chemistry.
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22	2. Materials and methods
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24	2.1 Sites and measurements
25	

1 The SWETHRO network is financed by regional air quality protection associations 2 and local county administrative boards. They decide what to measure and when, in 3 collaboration with the SWETHRO scientists. As a result, the measurements at 4 different monitoring sites cover different time periods. 5 6 The SWETHRO network includes measurements of air concentrations and bulk 7 deposition (BD) in open areas, as well as throughfall deposition (TF) and soil water 8 chemistry inside forest stands (Table 1). In 2008 air concentrations were measured on 9 22 sites, TF in forests on 60 sites, BD on open field on 19 sites and soil water 10 chemistry on 67 sites (Figure 1). Some of the original sites, from 1985, are still 11 operating, resulting in time series of up to 23 years. Monitoring sites are positioned in 12 closed, mature managed forests with no major roads or other pollution sources in the 13 vicinity. Relatively homogenous locations, with regard to topography and tree 14 density, are chosen. The BD as well as the air concentration measurements are 15 positioned in an open area close to the TF sites, preferably with similar topographical 16 properties. Many sites were replaced with new sites, in the vicinity of the old site, due 17 to an ageing forest and subsequent harvests. The new sites were assigned a new 18 identity. 19 20 Air concentrations of SO<sub>2</sub>, NO<sub>2</sub> and NH<sub>3</sub> were measured with diffusion samplers as 21 described in Ferm & Rodhe, (1997). 22 23 During winter, TF was measured in open buckets ( $\emptyset$ =21.4 cm) lined with plastic 24 (polyethylene) bags. During summer polyethylene bottles lined with plastic bags were

used with polyethylene funnels ( $\emptyset$ =15.5 cm) threaded into the lid. The plastic bags

1 were replaced at each sampling occasion. Ten TF collectors were placed in an L-2 shaped pattern with five bottles at each side or in some cases as a cross-shaped pattern 3 (30 x 30 m) in a homogeneous part of the forest. The bottles were wrapped with 4 aluminium foil to minimize the effect of heat and sunlight (Ferm, 1993). To prevent 5 contamination during summer by insects and forest litter, a piece of nylon netting was 6 attached between the funnel and the bottle. The ten TF samples were merged to one 7 composite sample. 8 9 BD was measured in an open area using a similar type of collectors as was used for 10 TF ( $\emptyset$ =20.3 cm). To prevent contamination, a small funnel with a plastic netting 11 (maze 2 mm) is attached at the bottom of the big funnel. During winter the funnel is 12 replaced by a 1 m long snow sack ( $\emptyset$ =19.5 cm), i.e. a tubular plastic bag mounted on 13 plastic rings. 14 15 Air concentration diffusive samples, as well as samples of TF and BD deposition, 16 were collected monthly throughout the year. 17 18 Soil water samples were obtained using suction lysimeters with ceramic cups (P 80). 19 The ceramic cups were placed at 50 cm depth in the mineral soil. In general, five 20 lysimeters were installed on each forest site, inside the canopy close to the TF 21 collectors. However, in some cases the number of lysimeters could be smaller (three 22 or four) due to difficulties with the stoniness. At sampling the lysimeters were sucking 23 water for two days. The water from the lysimeters was then combined into one 24 composite sample for analysis. Soil water was collected three times a year, to

1 represent the conditions before (Feb-May), during (Jun-Sep) and after the vegetation 2 period (Sep-Dec). 3 4 2.2 Chemical analyses 5 6 When the water samples arrived at the laboratory pH, alkalinity and conductivity were 7 measured directly. The water sample was then filtered using a cellulose acetate filter 8  $(0.8 \,\mu\text{m})$ . A small subsample was preserved with sulphuric acid  $(H_2SO_4)$  to be 9 analyzed for Kjeldahl-N and NH<sub>4</sub>-N. Another subsample was preserved with nitric 10 acid (HNO<sub>3</sub>) for analysis of Fe and Al. The remaining sample volume was not 11 preserved, and used for the remaining analyses. 12 13 SO<sub>4</sub>-S, NO<sub>3</sub>-N, Cl, Ca, Mg, Na, K, Mn were analysed by Ion Chromatography, IC. 14 NH<sub>4</sub>-N was analysed by Flow Injection Analysis (FIA). Kj-N was measured 15 according to Foss-Tecators method AN 52212002-10-24. Fe, total, organic and 16 inorganic aluminium were measured with ICP-MS according to SS-EN ISO 17294-17 2:2005. 18 19 2.3 Time series analysis 20 21 The monthly data for air concentrations and deposition were merged into yearly data 22 based on the hydrological year, October – September. The advantage with using the 23 hydrological year is that the impacts of the precipitation and deposition during the 24 entire winter season can be assigned to a specific year.

1	It was necessary to analyse monitoring data for different time periods adapted to
2	different data coverage for different sites. Time series analysis was done both for the
3	sites with long time series, starting around 1990 or earlier, all situated in southern
4	Sweden, and for sites with time series starting in October 1996. The latter time series
5	covered the whole country and yet the time series was long enough to enable the
6	detection of time trends. As far as possible the same periods have been chosen for air
7	concentrations, deposition and soil water chemistry.
8	
9	The time series were statistically analysed using the non-parametric Mann-Kendall
10	and Seasonal-Kendall methodologies (Mann, 1945; Hirsch & Slack, 1984). Mann-
11	Kendall was used for air concentrations and deposition trends, where annual data
12	were analysed, whereas Seasonal Kendall was used on soil water chemistry, where the
13	data from each sampling occasion (three times a year) were analysed. The changes are
14	referred to as statistically significant when the Mann-Kendall or Seasonal Kendall test
15	results in a p value $\leq 0.05$ .
16	
17	Non-marine S deposition was calculated according to LRTAP (2004). Non-marine
18	$SO_4$ -S = Total $SO_4$ -S - (Cl * 0.0462). Cl was used instead of Na for sea salt
19	corrections since Na deposition measurements were lacking for some sites while Cl
20	deposition was measured at all sites.
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23	3. Results
24	
25	3.1 Air concentrations

1 2 Several of the sites in the SWETHRO network with long-term air pollution 3 concentration measurements were terminated 2006 and several other sites did not start 4 air concentration measurements until the beginning of the 2000s. As a result there 5 were relatively few sites with air concentration measurements covering the entire 6 period 1996/97–2007/08. An example of the geographical distributions of yearly 7 mean air concentrations of SO<sub>2</sub>, NO<sub>2</sub> and NH<sub>3</sub> across Sweden is shown in Figure 2 for 8 the hydrological year 2000/01. The highest concentrations of SO<sub>2</sub> and NO<sub>2</sub> were 9 found around the south and west coast of Sweden and around the Stockholm area 10 (east part of mid-Sweden). The highest NH<sub>3</sub>-concentrations were around the south 11 coast. 12 13 Annual mean air concentrations of SO<sub>2</sub> in mid Sweden during 1996/97-2007/08 have been in the range 0.3-1.6 µg/m<sup>3</sup> (Figure 3 a). The trend analysis of annual SO<sub>2</sub> 14 15 concentrations demonstrated a significant decrease for Sticklinge, one site in mid-16 Sweden, with a decline of 44 % for the whole time period of 12 years, i.e. in the same 17 order as the reported oxidized sulphur emission reductions from EU-27. Sticklinge is 18 positioned near the greater Stockholm region and may to some extent be influenced 19 by local emissions. There were no significant trends for the SO<sub>2</sub> concentrations at the 20 other three sites. Additional information from other air monitoring networks in 21 Sweden show that the SO<sub>2</sub> concentrations in air over Sweden have been decreasing 22 (data not shown, see discussion). 23 24 Annual mean air concentrations of NO<sub>2</sub> in southern and mid Sweden have been between 1 and 12 µg/m<sup>3</sup> during 1996/97–2007/08 (Figure 3 b). There were significant 25

decreases for air concentrations of NO2 at all four monitoring sites. The rate of the 1 2 decrease corresponds to a reduction of between 27 and 40 %. Hence, the decrease in 3 NO<sub>2</sub> concentrations over Sweden has been somewhat larger as compared with the 4 averaged emission reductions over Europe. Of the four sites included in the time 5 series, the two sites Farstanäs and Sticklinge, positioned near the greater Stockholm 6 region, may be influenced by local emissions. 7 8 Air concentrations of NH<sub>3</sub> were much lower than NO<sub>2</sub>, and showed a high temporal 9 variability (Figure 3 c). The annual mean NH<sub>3</sub> concentration ranged between the detection limit (0.3 µg/m<sup>3</sup>) and 0.9 µg/m<sup>3</sup>. No statistical trend analysis was made for 10 11 NH<sub>3</sub> concentrations due to the lack of data for some years. 12 13 3.2 Deposition 14 15 3.2.1 Geographical distribution 16 17 The total non-marine S deposition to forests, measured as TF, shows a distinct 18 gradient across Sweden, with the highest values in the southwest and decreasing 19 values towards northeast (Figure 4). The annual S deposition, as a mean value during the hydrological years 2005/06-2007/08, exceeded 5 kg S ha<sup>-1</sup> at several sites in 20 21 southwest Sweden. At the remaining sites in south and mid Sweden, the annual S deposition was 2-5 kg S ha<sup>-1</sup> while in the north the values were below 2 kg S ha<sup>-1</sup>. 22 23 Total deposition of inorganic N to forest, as NH<sub>4</sub>-N and NO<sub>3</sub>-N, is difficult to measure 24

since N is taken up directly to the tree crowns (e.g. Ferm, 1993). Thus open field BD

- 1 was used to assess N deposition (Figure 5). The BD of inorganic N could be assessed
- 2 for fewer sites, as compared to S deposition, but largely followed the same
- 3 geographical pattern as the S deposition. The annual inorganic N BD exceeded 11 kg
- 4 N ha<sup>-1</sup> in southwest Sweden at both the beginning and the end of the 12-year period.
- 5 Most remaining sites in south and mid Sweden had an annual inorganic N deposition
- 6 exceeding 5 kg N ha<sup>-1</sup>. Since dry deposition is not included in the BD measurements,
- 7 the total deposition of inorganic nitrogen to Swedish forests may be considerably
- 8 larger as compared to the values reported here, see the discussion.

# 3.2.2 Trends 1996/97-2007/08

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- 12 Total non-marine S deposition to forests, measured as TF, decreased significantly at
- 13 47 of 52 sites between the two three-year periods 1996/97-1998/99 and 2005/06-
- 14 2007/08 (Figure 4). The largest reductions were found in south-western Sweden,
- where the levels were the highest in the beginning of the period. The non-marine S
- deposition during the two three-year periods 1996/97- 1998/99 and 2005/06-2007/08
- in Sweden has declined between 22% and 67%, which is in the same order of
- magnitude as the 49 % reduction in the European emissions of oxidized sulphur
- during the same period. The open field measurements showed that the S bulk
- deposition decreased significantly at 8 of 14 sites, and the reductions were between 4
- and 8 % (data not shown), hence considerably less changes as compared to TF.

- 23 The BD of inorganic N (NO<sub>3</sub>+NH<sub>4</sub>) increased significantly between 1996/97 and
- 24 2007/08 at two out of 20 sites (Figure 5). There were no significant trends for NO<sub>3</sub>-N
- on the 14 sites with open field measurements (data not shown). There were, however,

1 tendencies towards lowered NO<sub>3</sub>-N deposition on many of the sites. For NH<sub>4</sub>-N two 2 sites showed significant changes, one increase and one decrease, but there was no 3 general trend for the entire country (data not shown). 4 5 Deposition and soil water chemistry is affected not only by antropogenic emissions, 6 but also by sea salt episodes (Hindar et al., 1995; Skjelvåle et al., 2007) and the 7 amount of precipitation. There was, however, not any general time trend neither in 8 amount of precipitation and throughfall nor in the chloride deposition, which is a 9 measure of the sea salt deposition (data not shown). 10 11 3.2.3 Long-term trends 12 13 The changes in S deposition in TF over a longer time period are shown in Figure 6, 14 for four different years with 5-year intervals. Many of the longer time series for S 15 deposition were terminated after 2006. The monitoring sites are not identical for the 16 different years. However, it was considered that the number of monitoring sites were 17 high enough and the changes so large, that this did not influence the overall 18 evaluation of the trends i S deposition. The S deposition to forests has decreased 19 substantially since the early 1990-ies, especially in south-western Sweden (Figure 6), 20 where the deposition was the highest. In the beginning of the 1990s, the S deposition rates were around 20 kg S ha<sup>-1</sup> yr<sup>-1</sup> in southwest Sweden. During 2006/07 the S 21 deposition rates were below 5 kg S ha<sup>-1</sup> yr<sup>-1</sup> except for in the southernmost part of 22

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3.3 Soil water chemistry

Sweden.

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1 2 3.3.1 Geographical distribution 3 4 The sulphur (SO<sub>4</sub>-S) concentrations in soil water were generally higher in the 5 southern part of Sweden than in the northern part, although the variation on a local 6 level was large, especially in the south (Figure 7). For the three acidification 7 indicators pH, ANC (acid neutralizing capacity) and concentrations of inorganic Al 8 there was a distinct gradient with increasing pH and ANC and decreasing 9 concentrations of inorganic Al from the southwest to the north. The pH of soil water 10 was below 4.5 and the ANC was considerably negative on several sites in southern 11 Sweden during 2005/06-2007/08, indicating severe acidification of the soil water 12 (Figures 8 and 10). 13 14 The concentrations of nitrate (NO<sub>3</sub>-N) in soil water were generally very low, in 15 particular in northern Sweden (Figure 11). In the south-western part of Sweden there 16 were several sites with elevated concentrations, e.g. in Arkelstorp where there has 17 been frequent elevated NO<sub>3</sub>-N concentrations during the entire period 1996/97-18 2007/08 (Figure 11). Two of the sites, Vallåsen and Alandsryd, were damaged by a 19 storm incident in January 2005 which led to increased concentrations (Figure 11). In 20 Vallåsen the concentrations were elevated already before the storm, but the 21 concentrations was further increased after the storm. 22 23 3.3.2 Trends 1996/97-2007/08

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1 The concentrations of SO<sub>4</sub>-S in the soil water have decreased significantly on more 2 than half of the sites, and the fraction of sites with decreasing concentration was 3 highest in the southwest (Figure 7). Also, the concentrations of Ca have decreased 4 significantly on many of the sites (data not shown). Chloride concentrations have 5 been higher in the end of the period than in the beginning on eight of the 55 sites (data 6 not shown). 7 8 pH, ANC and concentrations of inorganic aluminium showed reduced acidification on 9 several of the sites in southern Sweden (Figures 8-10). There were also a few 10 examples with a change in the opposite direction. Although there seemed to be a 11 recovery on several of the sites in the worst acidified areas, there were also many sites 12 with no significant change. This showed that the recovery was slow on many sites. 13 14 There were no significant time trends in the NO<sub>3</sub>-N concentrations, except for the 15 increases caused by the storm in January 2005. Elevated concentrations of 16 ammonium in the soil water were rare, but sometimes occurred in connection with the 17 storm incident 2005 (data not shown). 18 19 3.3.3 Long-term trends 20 21 Two 15-year time series for soil water S concentrations in southern Sweden showed 22 somewhat different results (Figure 12). Both sites were affected by a storm in 2005, 23 so data are not shown after 2005. On both sites there was a clear decrease of S 24 concentration in soil water. The rate of the decrease was especially high during the 25 second half of the 1990-ies. The changes in ANC showed different patterns between

1 the sites (Figure 12). In Alandsryd there was no time trend for ANC during the period. 2 At Klippan, on the other hand, there was a clear increase in ANC during the period, from around -0.3 to over -0.15 meqv l<sup>-1</sup>. The increase in ANC indicates recovery from 3 4 acidification. For pH there was no time trend in any of the sites. The analysis of long-5 term trends shows a great variability in the soil water recovery from acidification as a 6 result of the reduced concentrations of SO<sub>4</sub>-S. The long time-trends in southern 7 Sweden are studied more thoroughly and related to deposition development, sea salt 8 episodes and storm damage effects in an on-going study (Akselsson et al., in 9 preparation). 10 11 12 4. Discussion 13 14 The air pollution situation over Sweden, as well as the deposition rates, depends 15 strongly on the weather conditions. However, there were no obvious trends in air 16 temperatures or precipitation during the period 1996/97–2007/08 that might have 17 systematically influenced the air pollution concentration or deposition during this 18 period. This analysis was made for average values across Sweden with yearly and 19 growing season time resolution (data not shown), based on official weather statistics 20 reported by the Swedish Meteorological and Hydrological Institute (SMHI). 21 22 Sweden's location in northern Europe, separated from the continent by the Baltic Sea, 23 in combination with relatively low domestic air pollution emissions, makes air quality 24 over Sweden very sensitive to emission reductions from the European continent and

the UK. European emissions of oxidized sulphur have been estimated to have

1 decreased 73 % between 1990 and 2008 and 49 % between 1997 and 2008 (Nyiri et

2 al., 2009). To what extent can the consequences of these emissions reductions be

3 detected in the context of acidification in Swedish forests?

4 5 Reduced air concentrations of SO<sub>2</sub> could be demonstrated only for one out of four 6 monitoring sites within the SWETHRO network during the 1996/97-2007/08 period. 7 The four sites were positioned in mid-Sweden at approximately the same latitude, 59-8 60 °N (Figure 3). The statistical method used to analyze trends could detect only 9 monotonic trends and there were relatively high SO<sub>2</sub> concentrations during a period 10 2003-2006, which might have been connected with polluted air originating from 11 extensive biomass burning in Russia and neighboring countries (Whitham & Manning 12 (2007). A recent evaluation of air concentrations of gaseous SO<sub>2</sub> measured within the 13 EMEP monitoring stations in southern Sweden indicated that SO<sub>2</sub> concentrations had 14 decreased by 90% since the 1980s until present day on mainland southern Sweden 15 (Sjöberg et al., 2010). Over the period 1997-2008 the corresponding decreases were in 16 the order of 50 % for mainland southern Sweden. A recent analysis by Anttila and 17 Tuovinen (2010) demonstrated significant decreases in air SO<sub>2</sub> concentrations at six 18 out of eight Finnish rural background sites, with yearly decreases in the order of 3-8 19 %. They concluded that the decline of air SO<sub>2</sub> concentrations in Finnish background 20 areas continued also after the year 2000. Corresponding measurements of air  $SO_2$  + 21 SO<sub>4</sub> concentrations at four EMEP stations in Norway also showed a decrease in the 22 order of 50 % during the period 1997-2009 (SPFO, 2010). Hence, overall, is seems 23 likely that the air oxidized sulphur concentrations across the Nordic countries have 24 decreased in parallel with European emission reductions. The strong geographical 25 gradient in the measured air concentrations of SO<sub>2</sub> from southwest towards northeast

supports what has been reported by EMEP (Nyiri et al., 2009), that the most important sources for sulphur deposition in Sweden are long-range transport from continental Europe and from ship emissions in the North sea and the Baltic sea. Sulphur deposition to Swedish forests has declined to the extent expected from European emission reductions, ranging from 22% up to 67% for different sites between the two three-year periods 1996/97-1998/99 and 2005/06-2007/08. The larger changes in TF sulphur deposition to forests, as compared to changes in bulk deposition, indicate that the dry deposition, which decreased substantially between

1985 and 1994 (Hallgren Larsson et al., 1995), has continued to decrease over the

1996/97-2007/08 period.

Sulphur concentrations in the soil water at 50 cm depth at Swedish forest sites showed a considerable variability between nearby monitoring sites due to differences in soil conditions. However, the highest concentrations occurred in the south and south-east part of Sweden but also in mid-Sweden around the Stockholm region and around the lake Mälaren. The soil water acidification parameters pH and ANC were clearly lowest towards the southwest part of Sweden, where the acid deposition has been the highest. The soil water concentrations of S, Ca and inorganic Al are affected by the amount of precipitation and runoff. High flow of water lowers the concentrations due to dilution effects. Since flow varies geographically, with the highest flow in the southwest, differences in concentrations between geographical areas should be interpreted with caution. This effect, however, acts in the opposite direction as compared with the geographical variations in soil water concentrations that was found across Sweden, with higher concentrations in the south.

1 2 The decreased sulphate concentrations in the soil water on more than half of the 3 monitoring sites across Sweden during 1996/97-2007/08 was on many sites 4 accompanied by reduced Ca concentrations, due to the reduction in anion flow. pH 5 and ANC have increased during the same period at some sites, but clearly less 6 frequent as compared to the number of sites with reduced sulphate concentrations. A 7 significant number of strongly acidified sites remain in south Sweden during the 8 period in 2005/06-2007/08, with a median pH value for the soil water below 4.5 and a 9 strongly negative ANC. Also soil water concentrations of inorganic aluminum have 10 decreased at some sites while it has remained unchanged at quite a number of other 11 sites. Soil water concentrations of inorganic aluminum around or higher than 2 mg l-12 1, an often used limit for aluminium toxicity (e.g. de Vries, 1993), is still common in 13 southern Sweden. Hence, sulphate deposition and sulphate concentrations in the soil 14 water has declined considerably during the 12 year period, but the soil water 15 acidification indicators pH, ANC and inorganic aluminum concentrations show only 16 small signs of recovery. 17 18 On seven sites in the southern half of Sweden there was a significant increased 19 acidity, through decreased pH or ANC or increased concentration of inorganic 20 aluminum. On five of them there was a significant increase in chloride concentrations 21 in soil water, which indicates that the increased acidity can be the temporary effect of

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Cl deposition over time.

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increased concentrations of sea salt in soil water, due to sea salt episodes, although the

sea salt episodes were not strong or frequent enough to lead to significantly increased

1 All sites in the region with the highest sulphur deposition, i.e. southwest Sweden (red 2 area in Figure 13), had negative ANC during the period 2005/06-2007/08. These sites 3 are in the beginning of the recovery process. If the pools of base cations have been 4 depleted to a great extent, it will take a long time before the sites can recover. In the 5 regions with intermediate sulphur deposition (yellow area in Figure 13), many of the 6 sites show a soil water ANC around zero. On these sites the recovery has proceeded 7 further. Most of the sites in northern Sweden, which corresponds to the lowest 8 deposition region, have a positive ANC and high pH, and many of these sites have 9 probably been acidified only to a small extent. The non-linear relation between pH 10 and ANC in soil water may provide some explanation for the lack of pH increase as a 11 response to reduced sulphur concentrations. At highly acidified sites, ANC has to 12 increase considerably before there will be a substantial increase in pH. However, the 13 analysis of the soil water chemistry changes during the time series 1989-2005, 14 demonstrated that also the response of ANC to a reduced sulphate concentration in the 15 soil water can be quite different (Figure 12). These differences are further analysed in 16 a separate study (Akselsson et al., in preparation). 17 18 The sulphate concentrations in soil water have decreased also at ICP Forest level II 19 plots in Norway over the period 1990-2008 (Andreassen et al., 2009). However, most 20 of the decrease occurred during the 1990-ies and in recent years the changes have 21 been small. Also the Norwegian forest plots show a parallel decrease in the soil water 22. calcium concentrations while there were small changes in the soil water pH and 23 inorganic aluminum concentrations (Andreassen et al., 2009). 24

1 European emissions of oxidized and reduced nitrogen have decreased 22 and 8 % 2 between 1997 and 2008, respectively (Nyiri et al., 2009). There was a substantial 3 decline in air NO<sub>2</sub> concentrations at all four monitoring sites in mid-Sweden between 4 1997 and 2008. This decline was even larger than what was expected from the 5 European emission reductions. The decrease in air NO<sub>2</sub> concentrations was consistent 6 with reported decreases in air NO<sub>2</sub> concentrations at the two EMEP monitoring sites 7 Råö, at the west coast of Sweden, and at Vavihill, in southernmost Sweden (Sjöberg 8 et al., 2010). Furthermore, Anttila and Tuovinen (2010) demonstrated significant 9 decreases in air NO<sub>2</sub> concentrations at two out of four Finnish rural background sites 10 during a period 1994-2007. Significant yearly decreases were in the order of 1-2 %. 11 Trends in NH<sub>3</sub> air concentrations have been more difficult to assess due to lower 12 concentrations and higher variability. 13 14 The bulk deposition of inorganic nitrogen over Sweden did not decrease during the 15 1996/97-2007/08 period. The bulk deposition of inorganic N even increased 16 significantly at two out of 20 sites, while there were no statistically significant 17 changes at the remaining sites. The increases were mainly a result of an increasing 18 ammonium bulk deposition. In accordance with the results in this study, the bulk 19 deposition of inorganic nitrogen did not change over time for the Norwegian ICP 20 Forest level II plots over the period 1990-2008 (Andreassen et al., 2009) as well as for 21 two Danish monitoring sites with Norway spruce and beech, respectively, over the 22 period 1986-2005 (Hansen et al., 2006). Fowler et al. (2007) reported that the 23 concentrations of NO<sub>3</sub> in precipitation have increased in remote areas of Europe over 24 the period 1980-2000, even though the emissions from more densely populated part of 25 Europe decreased over the same period. Moreover, a recent report from the UK

1 concluded that the bulk nitrogen deposition over the UK had not, with a few 2 exceptions, changed significantly over a recent twenty-year period (Kernan et al., 3 2010). Thus, due to non-linearity's in atmospheric chemistry (Fowler et al., 2007, 4 Fagerli and Aas, 2008) the reductions in European NOx emissions were not reflected 5 in bulk nitrate deposition to Swedish forests. 6 7 Total deposition of inorganic N to forest as NH<sub>4</sub>-N and NO<sub>3</sub>-N in throughfall, which 8 in theory should include also dry deposition, is difficult to measure due to direct 9 nitrogen uptake by the canopies. A newly developed method to assess nitrogen dry 10 deposition to forests based on the use of surrogate surfaces (Ferm and Hultberg, 1999, 11 Karlsson et al., 2010) indicated that nitrogen dry deposition to forests may be in the 12 order of 40 % of the total deposition in southwest Sweden, while it is considerably 13 lower in the north. The lack of correlations between the trends in air concentrations of 14 NO<sub>2</sub>/NH<sub>3</sub> and the trends in inorganic nitrogen deposition may in part be explained by 15 the fact that the nitrogen dry deposition could not be included in the assessment in the 16 present study. Dry nitrogen deposition should be more strongly connected to air 17 nitrogen concentrations, as compared to the bulk deposition. 18 19 N leaching due to high N input is generally reflected in increased NO<sub>3</sub>-N 20 concentrations in soil water. There was no continuous trend for NO<sub>3</sub>-N concentrations 21 in soil water. Elevated NO<sub>3</sub>-N concentrations in the soil water occurred at irregular 22 occasions, but also after massive fellings caused by a severe storm events, at some

nitrogen stocks in the forest soils in southern Sweden are increasing and are in some areas approaching levels where they are sensitive to disturbances. In accordance with

sites particularly in southern Sweden (Hellsten et al., 2009). This indicated that

23

24

2 nitrogen leaching in a study where four different modeling and monitoring 3 approaches, including SWETHRO, were used to assess the risk of nitrogen leaching 4 (Akselsson et al., 2010). 5 6 Future trends in air concentrations, deposition and soil water chemistry will be 7 affected by direct and indirect effects of climate change. Changed wind and 8 precipitation patterns may affect air concentrations and deposition (Languer et al., 9 2005). Changes in temperature and moisture will affect tree growth (Laubhann et al., 10 2009), weathering, decomposition, and other processes in the forest ecosystems, 11 which will affect soil water chemistry. Adaptation and mitigation of climate change 12 may lead to changed emission patterns of S and N and intensified forestry for 13 production of biofuels and/or increased C sequestration (Beland Lindahl & Westholm, 14 2011). Increased biofuel harvesting may hamper recovery from acidification (Olsson 15 et al., 1993; Joki-Heiskala et al., 2003; Akselsson et al., 2007) and N fertilization 16 leads to build-up of N in the forest soils, which may lead to N saturation and N 17 leaching in areas with high N status (Emmett, 2007; Akselsson et al., 2010). In order 18 to be able to optimize abatement strategies for climate gas emissions, it is important to 19 keep track of the concentrations of pollutants as well as the forest deposition and soil 20 water chemistry trends in the changing climate. 21 22 23 5. Conclusions 24

these results, the southwestern part of Sweden was identified as a risk area for

- 1 Changes over time in sulphur and nitrogen air concentrations, deposition and soil
- 2 water concentrations in forest ecosystems in Sweden as well as in other Nordic
- 3 countries were assessed in relation to European emission reductions for oxidized
- 4 sulphur and oxidized- and reduced nitrogen. The analysis of the time series 1996/97-
- 5 2007/08 gave the following results.

- The SO<sub>2</sub> and NO<sub>2</sub> air concentrations have decreased substantially, whereas there was no trend for NH<sub>3</sub>.
  - Reductions in SO<sub>4</sub> deposition were found for the majority of monitoring sites
    across Sweden, as well as for the other Nordic countries, and the reductions
    were in the same order of magnitude as the European emission reductions.
  - Soil water SO<sub>4</sub> concentrations decreased at most, but not all, monitoring sites
    across Sweden in parallel with the SO<sub>4</sub> deposition reductions. The soil water
    acidification indicators pH, ANC and inorganic Al concentrations indicated
    acidification recovery on some of the sites but there were also many sites with
    no significant change.
  - Despite the substantial decrease in NO<sub>2</sub> air concentrations, no statistically significant decreases in the bulk deposition of inorganic nitrogen deposition could be demonstrated. However, we were not able to include the dry nitrogen deposition in the trend analyses.
  - Elevated NO<sub>3</sub> concentrations in the soil water occurred at irregular occasions, but also after massive fellings caused by severe storm events, at some sites particularly in southern Sweden. This indicated that nitrogen stocks in the forest soils in southern Sweden are increasing and may be approaching saturation.

1	
2	We conclude that, despite considerable air pollution emission reductions in Europe,
3	the recovery from acidification is slow and for many sites far from complete.
4	Furthermore, the relatively high nitrogen deposition to Swedish forests still appears to
5	continue at a constant rate and this level is probably high enough to influence the
6	biodiversity of the forest ground vegetation (c.f. Nordin et al., 2005) as well as to
7	cause increasing nitrogen stocks in the forest ecosystem, resulting in an increasing
8	risk for leakage of nitrate to surface waters. The careful monitoring of Swedish forest
9	ecosystems needs to proceed in order to follow up the trends of recovery and nitrogen
10	leaching.
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12	
13	6. Acknowledgements
13 14	6. Acknowledgements
	6. Acknowledgements  This research has been funded by various regional air quality protection associations,
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14 15	This research has been funded by various regional air quality protection associations,
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<ul><li>14</li><li>15</li><li>16</li><li>17</li></ul>	This research has been funded by various regional air quality protection associations, county administrative boards and the Swedish Environmental Protection Agency. The Swedish Throughfall Monitoring Network (SWERHRO) is run by IVL Swedish
<ul><li>14</li><li>15</li><li>16</li><li>17</li><li>18</li></ul>	This research has been funded by various regional air quality protection associations, county administrative boards and the Swedish Environmental Protection Agency. The Swedish Throughfall Monitoring Network (SWERHRO) is run by IVL Swedish Environmental Research Institute. The work with this publication was funded by the
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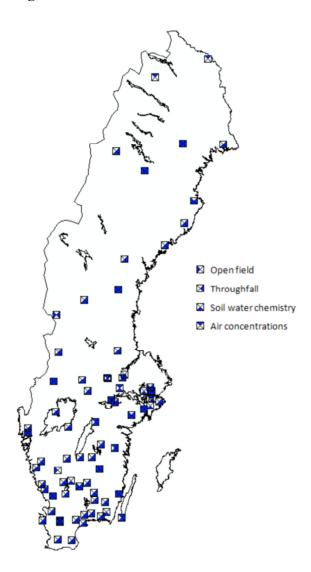
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# 1 Figures



**Figure 1.** Currently operating measurements in the Swedish Throughfall Monitoring

4 Network (SWETHRO) in 2008.

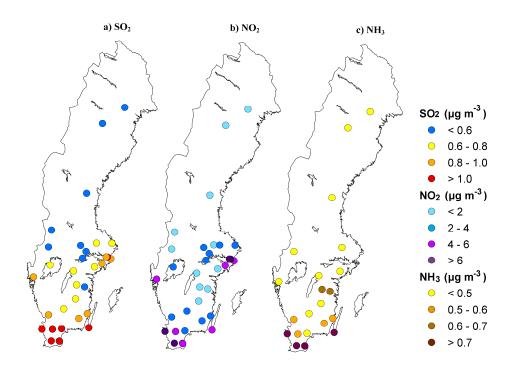
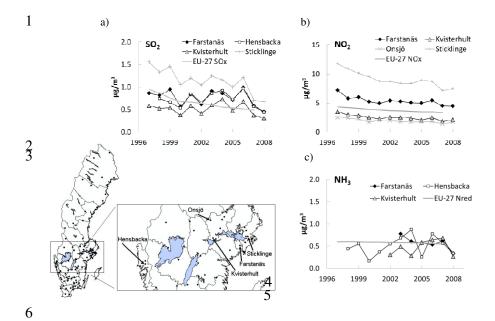


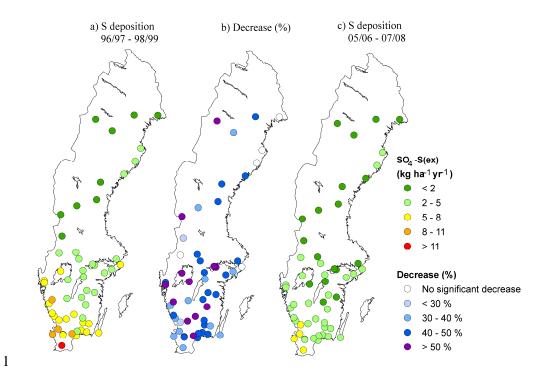
Figure 2. Mean air concentrations at rural monitoring sites in Sweden of a) SO<sub>2</sub>, b)

3 NO2 and c) NH3 ( $\mu g \ m^{-3}$ ) during the hydrological year 2000/01.



respectively, as reported by EMEP (Nyiri et al., 2009).

**Figure 3.** Trends for air concentrations of SO<sub>2</sub> (a), NO<sub>2</sub> (b) and NH<sub>3</sub> (c), measured within the Swedish Throughfall Monitoring Network (SWETHRO) 1996/97 – 2007/08. The grey, solid line represents the time course, in relative units, for the yearly emissions from EU member states (EU-27) for SO<sub>x</sub>, NO<sub>x</sub> and N<sub>red</sub>,



- 2 **Figure 4.** Non-marine S deposition to forest (throughfall) during two time periods,
- 3 1996/97-1998/99 and 2005/06-2007/08. a) The average S deposition during 1996/97-
- 4 1998/99, b) Decrease (%) between the two time periods, c) The average S deposition
- 5 during 2005/06-2007/08,

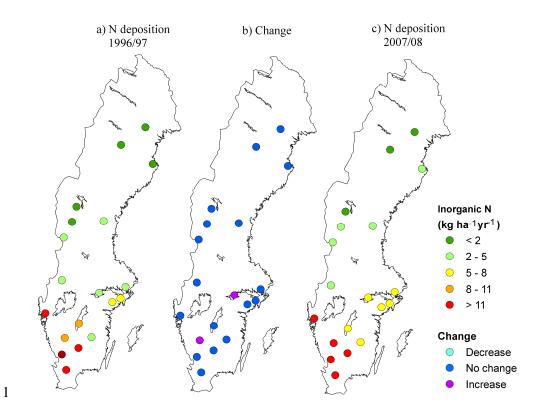
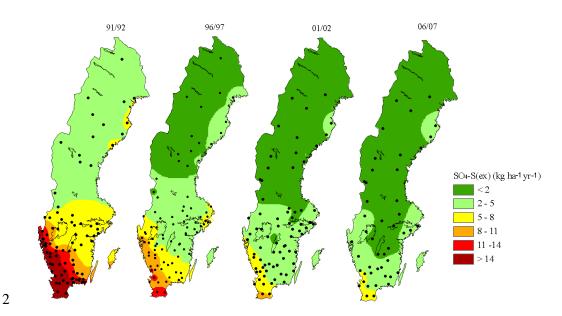


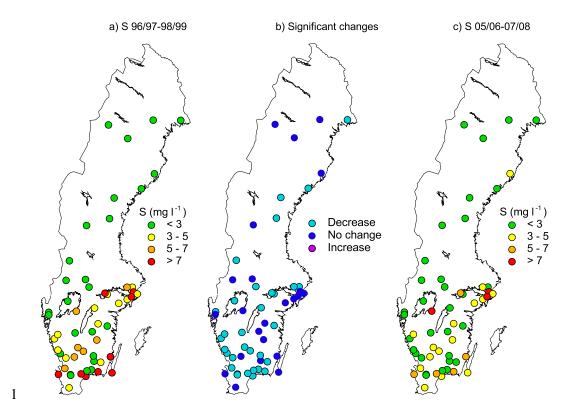
Figure 5. Deposition of inorganic nitrogen (NO<sub>3</sub>+NH<sub>4</sub>) 1996/97 & 2007/08, open

- 3 field (bulk) measurements. a) N deposition 1996/97, b) Significant changes (increase
- 4 or decrease), c) N deposition 2007/08.



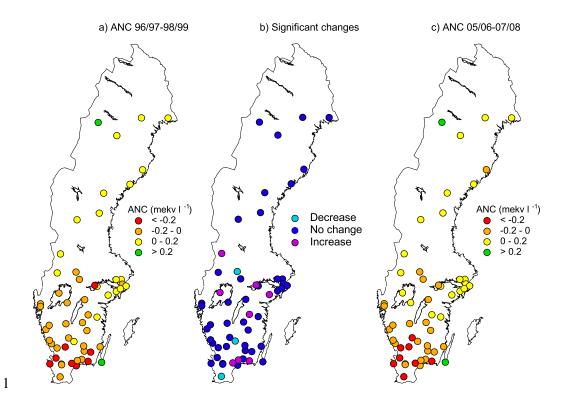
3 **Figure 6.** Deposition of non-marine S in throughfall (kg S ha<sup>-1</sup> yr<sup>-1</sup>) interpolated with

- 4 the Inverse distance weighted (IDW) method, based on the SWETHRO sites: a)
- 5 1991/92, b) 1996/97, c) 2001/02, d) 2006/07. The black dots show active monitoring
- 6 sites during the different time periods. Yearly mean values were calculated for
- 7 hydrological years, October September.



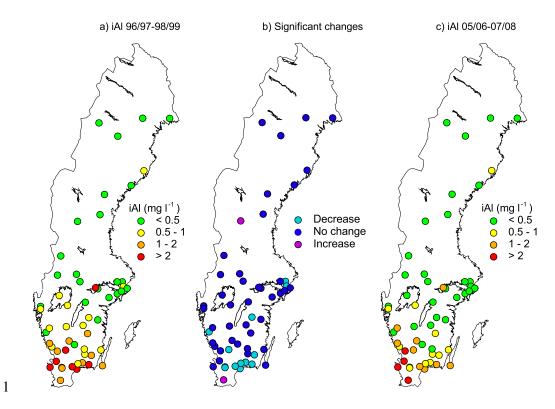
2 **Figure 7.** Sulphur (SO<sub>4</sub> -S) concentration in soil water sampled at 50 cm depth in

- 3 1996/97-1998/99 (median value), mg  $\Gamma^1$  (a), significant changes from 1996/97 to
- 4 2007/08 (b) and sulphur concentrations 2005/06-2007/08 (median value) (c).



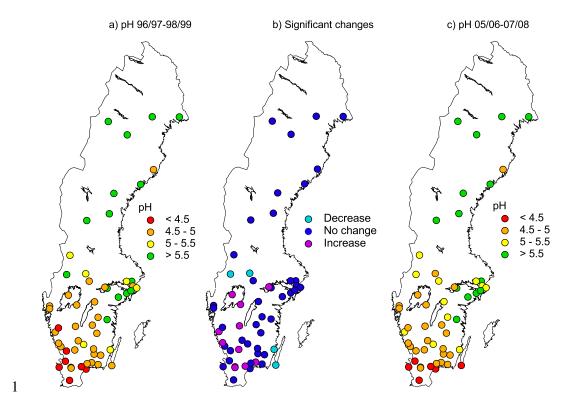
2 **Figure 8.** ANC (Acid Neutralizing Capacity) in soil water sampled at 50 cm depth in

- 3 1996/97-1998/99 (median value) (a), significant changes from 1996/97 to 2007/08 (b)
- 4 and ANC 2005/06-2007/08 (median value) (c). Note that the scale is reversed
- 5 compared to Figur 7 and 9.



2 **Figure 9.** Inorganic aluminium concentration in soil water sampled at 50 cm depth in

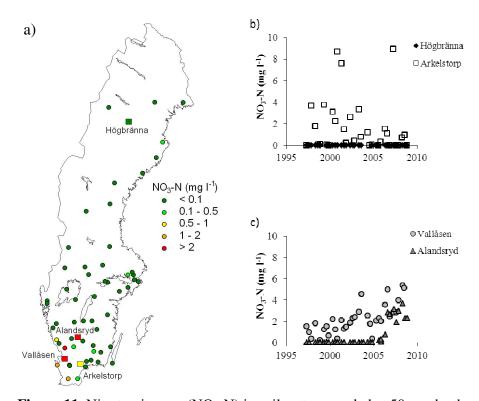
- 3 1996/97-1998/99 (median value), mg  $\Gamma^1$  (a), significant changes from 1996/97 to
- 4 2007/08 (b) and inorganic aluminium concentration 2005/06-2007/08 (median value)
- 5 (c).



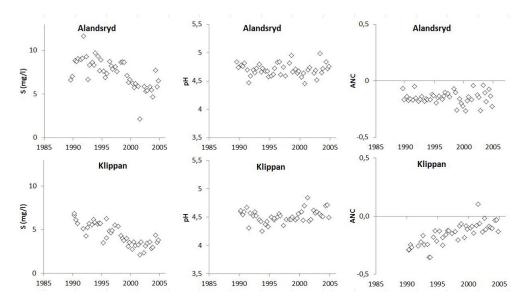
2 **Figure 10.** pH in soil water sampled at 50 cm depth in 1996/97-1998/99 (median

- 3 value), mg l<sup>-1</sup> (a), significant changes from 1996/97 to 2007/08 (b) and inorganic
- 4 aluminium concentration 2005/06-2007/08 (median value) (c). Note that the scale is
- 5 reversed compared to Figur 7 and 9.



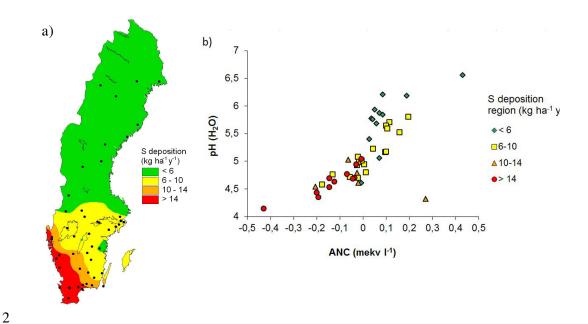


2 **Figure 11.** Nitrate-nitrogen (NO<sub>3</sub>-N) in soil water sampled at 50 cm depth on 60 3 active sites (a). Values are shown as the median from measurements 2005/06 – 4 2007/08, three measurements per year. The squares in the map highlights the four 5 sites for which time series from 1996/97 to 2007/08 are shown (b and c). The time 6 series for Högbränna and Arkelstorp illustrates the difference between north and south 7 Sweden, respectively (b). The time series for Vallåsen and Alandsryd illustrates the 8 effect of a storm incident in January 2005 causing increased nitrate concentrations in 9 soil water (c).



2 Figure 12. S concentration, pH and ANC in soil water sampled at 50 cm depth at

- 3 Alandsryd (August 1989 to December 2004) and Klippan in southern Sweden
- 4 (January 1990 November 2004).



**Figure 13.** A. The historic SO<sub>4</sub>-S deposition, represented by values from 1991/92, used to distinguish different S deposition regions. B. The ANC-pH relation in soil water in the different S deposition regions. The ANC-pH-relation is built on the median of data from autumn 2005 to summer 2008. Sites where soil chemistry in recent years have been strongly affected by storms (seven sites) were excluded.

# 1 Tables

- 2 Table 1. Parameters measured within the Swedish Throughfall Monitoring
- 3 (SWETHRO) Network.

	4
4	-

Parameters	Air conc.	Deposition	Soil water
Sulphur dioxide (SO <sub>2</sub> )	X		
Nitrogen dioxide (NO <sub>2</sub> )	X		
Ammonium (NH <sub>3</sub> )	X		
Ozone (O <sub>3</sub> )	X		
pH		X	X
Alkalinity		X	X
Sulphur (SO <sub>4</sub> -S)		X	X
Nitrate (NO <sub>3</sub> -N)		X	X
Ammonium (NH <sub>4</sub> -N)		X	X
Chloride (Cl)		X	X
Calcium (Ca)		X	X
Magnesium (Mg)		X	X
Sodium (Na)		X	X
Potassium (K)		X	X
Manganese (Mn)		X	X
Kjeldahl nitrogen, Kj-N		X	
Conductivity		X	
Organic aluminium			X
Iron (Fe)			X
Inorganic aluminium			X
Total aluminium			X