



LUND UNIVERSITY

Acidification trends in south Swedish forest soils 1986-2008 : Slow recovery and high sensitivity to sea-salt episodes.

Akselsson, Cecilia; Hultberg, Hans; Karlsson, Per Erik; Pihl Karlsson, Gunilla; Hellsten, Sofie

Published in:
Science of the Total Environment

DOI:
[10.1016/j.scitotenv.2012.11.106](https://doi.org/10.1016/j.scitotenv.2012.11.106)

2013

[Link to publication](#)

Citation for published version (APA):
Akselsson, C., Hultberg, H., Karlsson, P. E., Pihl Karlsson, G., & Hellsten, S. (2013). Acidification trends in south Swedish forest soils 1986-2008 : Slow recovery and high sensitivity to sea-salt episodes. *Science of the Total Environment*, 444, 271-287. <https://doi.org/10.1016/j.scitotenv.2012.11.106>

Total number of authors:
5

General rights

Unless other specific re-use rights are stated the following general rights apply:
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

Read more about Creative commons licenses: <https://creativecommons.org/licenses/>

Take down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

LUND UNIVERSITY

PO Box 117
221 00 Lund
+46 46-222 00 00

1 Title:
2 Acidification trends in south Swedish forest soils 1986-2008 – slow recovery and high
3 sensitivity to sea-salt episodes
4

5 Corresponding author:
6 Akselsson, Cecilia^a
7

8 Co-authors:
9 Hultberg, Hans^b
10 Karlsson, Per Erik^b
11 Pihl Karlsson, Gunilla^b
12 Hellsten, Sofie^b
13

14 ^aDepartment of Physical Geography and Ecosystem Science, Lund University,
15 Sölvegatan 12, SE-223 62 Lund, Sweden.
16 Phone: +46 46 222 86 89
17 Fax: +46 46 222 03 21
18 E-mail: cecilia.akselsson@nateko.lu.se
19

20 ^bIVL Swedish Environmental Research Institute, Box 53021, SE-400 14 Gothenburg,
21 Sweden.
22 E-mails: hans.hultberg@ivl.se, pererik.karlsson@ivl.se, gunilla.pihl.karlsson@ivl.se,
23 sofie.hellsten@ivl.se
24
25

26 Abstract

27

28 Soil water chemistry in forest soils over 20 years was studied at nine sites in southern
29 Sweden. The aim was to investigate the recovery from acidification and the influence of
30 strong sea salt episodes that occur in the region. All sites but one showed signs of
31 recovery from acidification along with the reduced sulphur deposition, but the recovery
32 progress was slow and the soil water was in most cases still highly acidic at the end of the
33 period. In several cases the recovery was delayed by episodes of sea salt deposition,
34 leading to transient acidification. The less marked decrease of sulphur concentrations in
35 soil water than of sulphur deposition, highlighted the importance of sulphur
36 adsorption/desorption in the acidification and recovery process. Nitrogen retention
37 capacity was exceeded on one site, leading to nitrate leaching and extremely low pH.
38 Storm fellings on two sites in the end of the period led to effects similar to those of
39 regeneration fellings. It was concluded that the soils in the region are in an early stage of
40 recovery. The future progress of recovery strongly depends on future nitrogen retention
41 of forest soils and the frequency of sea salt episodes.

42

43 Key words: sulphur, sea salt, acidification, nitrate leaching, soil water chemistry, forest

44

45

46 1. Introduction

47 Acid deposition caused by emissions and long-range transport of acidifying substances,
48 mainly sulphur and nitrogen, has led to acidification of soils and waters in Europe (Reuss
49 and Johnson, 1986). Deposition of sulphur has, however, decreased substantially during
50 the last decades (Nyiri et al., 2009) and many acidified lakes show clear signs of recovery
51 (Evans et al., 2001; Skjelkvåle et al., 2001; Fölster and Wilander, 2002). However, much
52 of the problem with acidified soils and waters persists. Model simulations show that the
53 soil recovers slower than the lakes do (Sverdrup et al., 2005), which is due to the slow
54 replacement, through weathering and deposition, of the base cations that were lost during
55 acidification. Lakes will not fully recover until also soils are recovered. Model runs
56 indicate that lake recovery will soon level off and the lakes will remain substantially
57 more acidified than before industrialization (Sverdrup et al., 2005).

58

59 The recovery processes can be delayed by several climate-related factors (Skjelkvåle et
60 al., 2003). Sea salt episodes increase the net charge in soil solution and lead to increased
61 ion exchange, and in acidic soils it can cause a temporary flush of acidity from the soil to
62 soil water and surface waters (Hindar et al., 1995; Skjelkvåle et al., 2007; Laudon, 2008).
63 Increased temperature can lead to elevated nitrification and leaching of $\text{NO}_3\text{-N}$ (van
64 Breemen et al., 1998; Wright and Jenkins, 2001), with possible implications for the risk
65 of both eutrophication and acidification. Frequency of drought (Aherne et al., 2006;
66 Laudon, 2008) and enhanced organic carbon turnover rate (Skjelkvåle et al., 2007) also
67 has the potential to affect recovery. Intensified forestry, for example in order to increase
68 the production of renewable energy, may also be important. Hultberg and Ferm (2004)

69 considered stem harvesting and found it to be as important as acid rain for the loss of
70 exchangeable calcium from the soil. Akselsson et al. (2007) compared stem harvesting
71 with whole-tree harvesting and concluded that the losses of calcium and potassium are
72 substantially higher at whole-tree harvesting. Aherne et al. (2012) demonstrated that
73 whole-tree harvesting, including foliage removal, has a high potential impact on the soil
74 nutrient status.

75

76 The difference in the course of recovery between soil and surface waters, as well as the
77 different time frames, depends on soil and catchment properties. Increased knowledge
78 about soil water beneath the root zone, i.e. between the solid soil and the surface water,
79 can be a key for a better understanding of the interactions between soil and surface water
80 recovery. Within the “Swedish Throughfall Monitoring Network” (SWETHRO),
81 pollutant air concentrations, deposition and soil water chemistry has been investigated on
82 a large number of forested sites since 1985 (Pihl Karlsson et al., 2011). These time series
83 constitute a unique basis for studies on recovery processes in relation to deposition
84 trends.

85

86 The main aim of this study was to investigate the recovery from acidification in forest
87 soils in southern Sweden, and the influence of strong sea salt episodes that occur in the
88 region. Our hypotheses were that (1) soil water has become less acidified as the
89 acidifying deposition has decreased, but that (2) sea salt episodes can temporarily re-
90 acidify soil water, slowing down the rate of recovery. Long time series of soil water
91 chemistry from nine sites were analyzed, discussed and compared with trends for

92 throughfall deposition of sulphur and chloride. In a few cases the results were analysed in
93 light of other drivers that strongly influence soil water chemistry, such as storm fellings
94 and nitrification due to exceeded soil nitrogen retention capacity.

95

96 2. Materials and methods

97 2.1 The SWETHRO network – measurements and chemical analyses

98 The SWETHRO network (Pihl Karlsson et al., 2011) includes measurements of air
99 concentrations, throughfall deposition and deposition on the open field as well as soil
100 water chemistry in forest soils. In 2008, throughfall in forests was measured on 62 sites
101 and soil water chemistry on 64 sites. The first measurements started in 1985. The sites are
102 located in closed, mature managed forests with no major roads or other pollution sources
103 in the vicinity. The sites are relatively homogenous with regard to topography and stand
104 conditions.

105

106 Throughfall deposition is collected monthly by the turn of each month. During winter,
107 throughfall is measured in open buckets ($\varnothing=21.4$ cm) lined with plastic (polyethylene)
108 bags. During summer, polyethylene bottles are used with polyethylene funnels ($\varnothing=15.5$
109 cm) threaded into the lid and into the plastic bag placed inside the bottle. The plastic bags
110 are replaced at each sampling occasion. Ten throughfall collectors are placed in an L-
111 shaped pattern with five bottles at each side or in some cases in a cross-shaped pattern
112 (30 x 30 m) in a homogeneous part of the forest. The bottles are wrapped with aluminium
113 foil to minimize the effect of heat and sunlight (Ferm, 1993). To prevent contamination
114 by insects and forest litter, a piece of nylon netting (mesh diameter ≈ 1 mm) is attached

115 between the funnel and the bottle. The ten throughfall samples are merged to one
116 composite sample for analysis.

117

118 Soil water is collected three times a year, approximately corresponding to spring, summer
119 and autumn. The sampling dates vary to some extent between the years and sites. 95 % of
120 the spring samples were collected in the period 30 March – 10 May. The corresponding
121 period for summer was 1 July – 10 September and for autumn 20 October – 13
122 December. Soil water samples are taken using suction lysimeters with ceramic cups (P
123 80). The ceramic cups are placed at 50 cm depth in the mineral soil. In general, five
124 lysimeters are installed on each forest site, inside the canopy, close to the throughfall
125 collectors. However, in some cases the number of lysimeters is smaller (three or four), for
126 example due to stoniness. At sampling the lysimeters suck water for two-three days. The
127 water from the lysimeters is combined into one composite sample for analysis.

128

129 The water samples are analysed for pH, alkalinity and conductivity. The samples are then
130 filtrated using a cellulose acetate filter (0.8 μm). A small subsample is preserved with
131 sulphuric acid (H_2SO_4) and analyzed for Kjeldahl-N and $\text{NH}_4\text{-N}$. Another subsample is
132 preserved with nitric acid (HNO_3) for analysis of Fe and Al. The remaining sample
133 volume is used for the remaining analyses. All samples are stored in a fridge before
134 analysis.

135

136 $\text{SO}_4\text{-S}$, $\text{NO}_3\text{-N}$, Cl, Ca, Mg, Na, K, Mn are analysed by Ion Chromatography (IC) using
137 Dionex chromatographs, the anions according to SS-EN ISO 10304-1 and the cations

138 according to SS-EN ISO 14911. NH₄-N is analysed by Flow Injection Analysis (FIA)
139 with spectrophotometric detection according to the modified SS-EN ISO 11732. During
140 the FIA analysis the sample is mixed with sodium hydroxide. Ammonium is then
141 transformed to ammonia, which is separated from the sample by passing it through a
142 membrane. A color indicator takes up ammonia and the sample then passes through a
143 spectrophotometer. The results are calculated from the absorbance at 590 nm. Kjeldahl-N
144 is measured according to Foss-Tecators method AN 52212002-10-24. Fe and Al are
145 measured with ICP-MS according to SS-EN ISO 17294-2:2005. Organic and inorganic
146 Al is separated using ion exchange according to the “Driscoll method” (Driscoll, 1984).
147 The analysis of DOC in soil water is done with NDIR. The DOC analysis leads to a small
148 overestimation of the values since the filter size is 0.8 µm, whereas DOC is normally
149 based on a filter size of 0.45 µm.

150

151 2.2 Study sites

152 Nine sites in southern Sweden from the SWETHRO network were considered (Fig. 1;
153 Table 1-2). The selection criteria were that the start year should be 1990 or earlier, and
154 that the site should still be active in 2008. The prevailing wind direction in this area is
155 from southwest.

156

157 FIG. 1

158

159 TABLE 1, 2

160

161 2.3 Data processing and time series analysis

162 The results from the soil water chemistry analysis were scrutinized, e.g. through the use
163 of charge balance tests (de Vries et al., 2003), and obvious unrealistic data were removed.
164 At some sampling occasions no soil water samples could be obtained due to dry
165 conditions. The time series contained between 51 and 68 data records per site. In all, 14
166 data records were not used due to small water amounts sampled (<50 ml). Information on
167 water volume exists only from 1998 onwards, so possible earlier occasions with small
168 water amounts could not be identified.

169

170 The time series were statistically analyzed using the non-parametric Mann-Kendall and
171 Seasonal-Kendall methodology (Hirsch and Slack, 1984; Mann, 1945). The methods are
172 not sensitive to extreme values or missing values. Mann-Kendall was used for deposition
173 trends, analysing for yearly data. Seasonal Kendall was used on soil water chemistry,
174 analysed for three different seasons.

175

176 3. Results and discussions

177 3.1 Throughfall deposition

178 The throughfall deposition of sulphur (S) as sulphate (SO₄-S) decreased substantially on
179 all nine sites over the studied period (p<0.001) (Fig. 2), which can be explained by a
180 decrease in European emissions of oxidized S by 73% between 1990 and 2008 (Nyiri et
181 al., 2009; Pihl Karlsson et al., 2011). Most of this decrease occurred at the end of the
182 1980s and the first half of the 1990s. The reduction was most pronounced at the sites
183 ARK and RYS, where the deposition of the non sea salt SO₄-S was around 20 kg ha⁻¹ y⁻¹

184 in the end of the 1980s and less than $5 \text{ kg ha}^{-1} \text{ y}^{-1}$ in 2005-2008. A likely explanation of
185 the high $\text{SO}_4\text{-S}$ load in ARK and RYS is the high deposition of ammonium nitrogen
186 ($\text{NH}_4\text{-N}$), up to $7\text{-}8 \text{ kg ha}^{-1} \text{ y}^{-1}$ as throughfall, in the beginning of the period (not shown),
187 since rates of dry deposition of SO_2 can be higher in the presence of ammonia (Borrell et
188 al., 1997). The least pronounced reduction appeared in SOS, where the deposition of non
189 sea salt $\text{SO}_4\text{-S}$ was around $10 \text{ kg ha}^{-1} \text{ y}^{-1}$ in the late 1980s and less than $5 \text{ kg ha}^{-1} \text{ y}^{-1}$ in
190 2005-2008. The relatively low levels in the beginning of the period can be explained by
191 the fact that the site was dominated by Scots pine (Table 2), and that the dry deposition in
192 pine forests are generally substantially lower than in spruce forests due to the smaller
193 crowns of pines (Hallgren Larsson et al., 1995). Also SAV had a relatively modest $\text{SO}_4\text{-S}$
194 deposition in the beginning of the period. This site is covered with a Norway spruce
195 forest but it is positioned further north than the other sites (Table 1, Fig. 1), and is thus
196 less exposed to deposition.

197

198 The nitrate nitrogen ($\text{NO}_3\text{-N}$) and ammonium nitrogen ($\text{NH}_4\text{-N}$) deposition in throughfall
199 both decreased significantly on only four of the nine sites (data not shown) although the
200 emissions of $\text{NO}_3\text{-N}$ and $\text{NH}_4\text{-N}$ in Europe decreased by 39 and 22 %, respectively
201 between 1990 and 2008 (Nyiri et al., 2009). However, nitrogen deposition in throughfall
202 is not a quantitative measure of the total N deposition, due to direct uptake in canopy
203 (Harrison et al., 2000; Adriaenssens et al., 2012). Actually, $\text{NO}_3\text{-N}$ deposition increased
204 significantly in one site, KNA, after storm felling in 2005 (Table 1), probably due to the
205 eliminated direct uptake by the canopy.

206

207 FIG. 2

208

209 Deposition of chloride (Cl) is mainly derived from sea salt, which can reach forest areas
210 in high amounts during specific weather conditions. Accordingly, the average chloride
211 deposition decreased with distance from the sea in the main wind direction (Fig. 3). The
212 time series of Cl deposition showed that all sites were affected by sea salt episodes (Fig.
213 4). The deposition was generally elevated between 1989 and 1993 and also after 2005.
214 During the period 1989-1993 there were several sea salt episodes that were clearly
215 evident in the monthly SWETHRO data (not shown), especially in January 1989, March
216 1990 and January 1993. The January 1993 episode has been documented in Hindar et al.
217 (1994, 1995). Since 2005, there have been several storms, for example the storm Gudrun
218 in January 2005 and the storm Per in January 2007, leading to sea salt episodes, although
219 not as marked ones as in the beginning of the time series. Although the general features
220 of the episodes were similar on the sites, their extent differed. The site SOS was one of
221 the sites with the most pronounced peak in the beginning of the 1990s, almost 90 kg ha^{-1}
222 y^{-1} . The Cl episodes in 2005 and beyond were also evident in SOS, but were more
223 pronounced in KNA where the deposition increased from 10-20 to $50 \text{ kg ha}^{-1} \text{ y}^{-1}$. The sea
224 salt episodes in the throughfall data were more pronounced in volume weighted
225 concentrations of chloride than in the deposition (not shown).

226

227 FIG. 3

228

229 FIG. 4

230

231 3.2 Soil water chemistry

232 The soil water chemistry was affected by two main deposition drivers during the studied
233 time period; reduced sulphur load (Fig. 2) and sea salt episodes 1989-1993 as well as
234 after 2005 (Fig. 4). On two sites, ALA and KNA, the two major storm events in 2005 and
235 2007 caused major damage (Table 1), which affected the soil chemistry the last three
236 years of the time series. In ARK the N retention capacity was exceeded during parts of
237 the time series, driving nitrification and $\text{NO}_3\text{-N}$ leaching that in turn affected
238 acidification. The soil chemistry development on the sites is the integrated result of those
239 drivers. The soil water parameters for which time trends are shown (Table 3, Fig. 5-16)
240 and discussed are:

- 241 • Concentrations of sulphur as sulphate ($\text{SO}_4\text{-S}$), which has the most direct link to $\text{SO}_4\text{-S}$
242 S deposition.
- 243 • Concentrations of chloride (Cl) and sodium (Na) as a measure of sea salt influence.
- 244 • Concentrations of the base cations calcium (Ca), magnesium (Mg) and potassium (K)
245 which have a central role in the acidification and recovery process through the ion
246 exchange, and are also important nutrients.
- 247 • pH, acid neutralizing capacity (ANC) and concentrations of inorganic aluminium
248 (Al_i), which are important acidification indicators.
- 249 • Concentrations of inorganic nitrogen as nitrate ($\text{NO}_3\text{-N}$) and ammonium ($\text{NH}_4\text{-N}$), as
250 indicators of exceedance of N retention capacity. If the N retention capacity is
251 exceeded, nitrification and subsequent acidification of soils and eventually surface
252 waters may occur if $\text{NO}_3\text{-N}$ is leached.

253 • Concentrations of dissolved organic carbon (DOC), which is of interest in
254 acidification and recovery studies, as it affects the pH-ANC relationship and also can
255 be affected in the recovery process.

256 In order to separate short-term effects caused by sea salt episodes and storms from long-
257 term trends caused by reduced acid deposition, the soil water trends for base cations,
258 acidification indicators, N and DOC were interpreted in light of the soil water trends for
259 SO₄-S and Cl, along with information about storm events.

260

261 TABLE 3

262

263 3.2.1 SO₄-S concentrations

264 The reduced SO₄-S deposition is reflected in reduced SO₄-S concentrations in eight of the
265 nine sites (Fig. 5, Table 3). The most pronounced decrease occurred in ARK, where the
266 concentration decreased from around 15 to 3 mg l⁻¹. This site also stands out through a
267 large variation on short time-scales, seen in many of the parameters. A possible
268 explanation could be large variations in the hydrological conditions on the site that is
269 situated on a slope (Table 1). The decrease in SO₄-S concentrations was also relatively
270 large in RYS and ALA, from around 10 to 5 mg l⁻¹. On the other sites the concentration
271 decreased from around 5 to 1-3 mg l⁻¹, with KNA as an exception, where the
272 concentration was between 2 and 3 mg l⁻¹ during most of the period. A comparison
273 between the SO₄-S deposition (Fig. 2) and S concentrations in soil solution (Fig. 5) shows
274 that the decrease in SO₄-S concentration in the soil solution was generally lower than the
275 reduction in SO₄-S deposition. The less pronounced effect in soil water can be explained

276 by SO_4^{2-} adsorption/desorption. Eriksson et al. (1992) showed that SO_4^{2-} saturation is
277 often reached in southwestern Sweden, indicating that substantial amounts of SO_4^{2-} are
278 stored in the soil. In the beginning of the time series, it is likely that parts of the SO_4^{2-}
279 input to the soil solution was adsorbed, lowering the concentrations of $\text{SO}_4\text{-S}$ in soil
280 solution. In the end of the period, desorption contributed to the $\text{SO}_4\text{-S}$ input to the soil
281 solution. However, the response varied widely between the sites. The reduced deposition
282 in ARK led to a reduction of $\text{SO}_4\text{-S}$ concentrations in soil water of the same size. In
283 KNA, on the other hand, the reduced $\text{SO}_4\text{-S}$ deposition was not at all reflected in the $\text{SO}_4\text{-S}$
284 concentrations in soil solution. The other sites responded to a varying degree to the
285 reduction in $\text{SO}_4\text{-S}$ deposition. Gustafsson and Jacks (1993) and Gobran and Nilsson
286 (1988) highlighted the importance of organic C as a restricting factor for SO_4^{2-}
287 adsorption. Accordingly, the high DOC concentrations in ARK (Fig. 16) could be part of
288 the explanation to the strong response of reduced $\text{SO}_4\text{-S}$ deposition on $\text{SO}_4\text{-S}$
289 concentrations in soil water.

290

291 3.2.2 Cl and Na concentrations

292 The sea salt episodes (Fig. 4) led to clear signals for Cl and Na in soil water (Fig. 6 and
293 7). The high frequency of sea salt episodes 1989-1993 could be seen in all sites but two,
294 ARK and KLI, where the variation between different measurements was large. The effect
295 was most pronounced in HEN, HJA, RYS, SAV and SOS. The latter is the site with the
296 highest maximum concentrations, the Cl concentration was 59 mg l^{-1} and the Na
297 concentration was 32 mg l^{-1} , but the short-term variation was large. The storms between
298 2005 and 2008 led to less distinct sea salt episodes than in the beginning of the 1990s.

299 The episodes could, however, be seen clearly in ALA, HEN, and KNA. The size of the
300 effect of sea salt episodes on the soil water chemistry cannot be fully explained by the
301 distance to sea in the main wind direction. As an example, RYS, with a long distance to
302 the sea in the southwest direction and relatively low average Cl deposition, is one of the
303 site with the most pronounced peaks of Cl and Na in soil water. A possible explanation to
304 the elevated concentrations in RYS could be occasional southerly winds loaded with sea
305 salt.

306

307 3.2.3 Ca, Mg and K concentrations

308 The concentration of Ca in soil water decreased significantly during the period, except at
309 two of the sites; KNA and ALA (Fig. 8, Table 3). Decreased concentrations of Ca and
310 other positive ions, in parallel with decreases in the acidic input, has also been found in
311 surface water in other studies (Moldan et al., 2004), and is caused by reduced net charge
312 causing reduced release of positive ions from the exchangeable pool. In KNA there was
313 no decrease in $\text{SO}_4\text{-S}$ in soil water, which explains why there was no decrease in Ca. In
314 ALA the soil water chemistry after 2005 was strongly influenced by the storm in January
315 2005, which completely storm-felled the site (Table 1). A similar but weaker effect can
316 be seen in KNA, which was severely damaged in the storms of 2005 and 2007 (Table 1).
317 Storm-felling results, just as normal clear-fellings, in disrupted tree uptake, changed
318 deposition and changed soil physical conditions. Several of the sites, for example HJA
319 and RYS, showed peaks in Ca concentration coinciding with the peak in Cl in the
320 beginning of the period. This is most likely an effect of the increased net charge due to
321 inflow of sea salt, and thus increased release from ion exchange.

322

323 The Mg concentration decreased significantly on seven of the sites (Fig. 9, Table 3). The
324 large-scale decreasing trend can also be explained mainly by the decreased SO₄-S
325 deposition leading to reduced net charge. However, the trends are strengthened by the
326 strong salt episodes in the beginning of the 1990s, due to increased deposition of Mg and
327 increased release of Mg through ion exchange.

328

329 The K concentration showed a significantly decreasing trend on six of the sites (Fig. 10,
330 Table 3). Just like for Ca and Mg, the reduced input of SO₄-S and the sea salt episodes in
331 the beginning of the 1990s can explain the major patterns. ALA had a decreasing trend
332 before 2005, but after storm felling the concentrations increased substantially from below
333 0.5 mg l⁻¹ to more than 4 mg l⁻¹ due to disrupted uptake by the trees. In KNA, where the
334 site was damaged in the storms 2005 and 2007, but not completely storm-felled, there
335 was a smaller increase in K concentrations after the storm. The high concentrations in
336 ARK in the beginning of the period coincide with high concentrations of NH₄-N (Fig.
337 12). The reason for this is not known, but it is probably related to some kind of soil
338 disturbance, possibly due to lysimeter installation.

339

340 3.2.4 Inorganic N concentrations

341 The concentrations of inorganic N below the root zone are generally low in undisturbed
342 northern forest ecosystems, since they are generally nitrogen limited (Tamm, 1991). This
343 was also the case in eight of the sites (Fig. 11-12). Only in ARK were highly elevated
344 concentrations of both NH₄-N and NO₃-N regularly measured. The site was thinned in

345 1995 (Table 1). However, already at the beginning of the period, the $\text{NH}_4\text{-N}$
346 concentrations were elevated at several sampling occasions, up to 0.7 mg l^{-1} . Around
347 1995 the $\text{NH}_4\text{-N}$ concentrations decreased to a lower level and at the same time the $\text{NO}_3\text{-}$
348 N concentration became elevated. The latter remained elevated in most of the
349 measurements after 1995, up to 9 mg l^{-1} . A possible explanation for these sequential
350 changes in $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ might be that a nitrifier population started to develop when
351 the ammonium concentrations increased, and was fully developed around 1995, leading
352 to reduced $\text{NH}_4\text{-N}$ and increased $\text{NO}_3\text{-N}$. The fact that N is leaching from the site is not
353 surprising, since the N load was high in the beginning of the period, $13 \text{ kg ha}^{-1} \text{ y}^{-1}$ in
354 throughfall as an average for 1988-1990 (not shown). There are also several other
355 SWETHRO sites in the southernmost part of Sweden where elevated $\text{NO}_3\text{-N}$ leaching is
356 common (Akselsson et al., 2010).

357

358 In ALA and KNA $\text{NO}_3\text{-N}$ increased after the storms in 2005 and 2007. Removal of trees
359 through storm felling or clear-cutting, in areas with high historical and present N load,
360 can result in high concentration of $\text{NO}_3\text{-N}$ in soil water (Akselsson et al., 2004). In ALA,
361 completely storm-felled in 2005, the concentration increased to almost 4 mg l^{-1} . In KNA,
362 less damaged by storms, it increased to 2 mg l^{-1} . The peak concentrations have, however,
363 probably not been reached yet. The ammonium concentrations in these two sites were
364 generally very low, both before and after 2005.

365

366 3.2.5 pH, ANC and Ali

367 In the beginning of the period, the sites had generally low ANC, low pH and high
368 concentrations of Ali. ANC increased significantly on seven of the sites, pH increased on
369 five sites and the concentration of Ali decreased on six sites (Table 3; Fig. 13-15). Only
370 at ALA the trend was towards more acidic conditions through slightly increased
371 concentrations of Ali.

372

373 The most acidified sites in the beginning of the time series were the southernmost sites
374 ARK and RYS. ANC was around -0.5 meq l^{-1} , pH around or below 4.5 and the
375 concentration of Ali between 2 and 4 mg l^{-1} (Fig. 13-15). The conditions were still
376 strongly acidic at the end of the period. The ANC increased significantly on both sites but
377 was still negative in the end of the period (between -0.3 and -0.1 meq l^{-1}). In RYS there
378 was a slight but significant increase in pH, whereas there was no trend in ARK, and pH in
379 the end of the period was around 4.5. The concentration of Ali varied substantially during
380 the period and the concentrations tended to be somewhat lower towards the end. The
381 results for the two strongly acidified sites indicate that the overall development was
382 driven by reduced S input driving a slow but significant recovery, but that other factors
383 affected the variation within the period. In RYS, the sea salt episodes in the beginning of
384 the period had a great but transient impact on the acidity as large amounts of Ali was
385 released (Fig. 15), causing a marked dip in ANC (Fig. 14). Also in the nearby site ARK,
386 the pH reduction between 1990 and 1995 may have been an effect of increased sea salt
387 input. After 1995 pH remained below 4.5, which can be explained by the elevated
388 nitrification seen in the elevated $\text{NO}_3\text{-N}$ concentrations in soil water (Fig. 11). This is

389 supported by the fact that the soil water pH increased somewhat after 2005, when the
390 $\text{NO}_3\text{-N}$ concentrations decreased.

391

392 The sites HEN, KLI, SAV and HJA were less acidified than ARK and RYS in the
393 beginning of the period. ANC was between -0.3 and -0.1 meq l^{-1} , pH was between 4.5
394 and 4.8 and the concentrations of Ali were generally elevated (Fig. 13-15). All sites
395 showed signs of recovery, with significantly increased ANC, significantly decreased
396 concentrations of Ali (all sites except HEN) and significantly increased pH in HJA and
397 SAV. In SAV, which is the one that has been least exposed to $\text{SO}_4\text{-S}$ deposition, ANC
398 was slightly positive at the end of the period, pH was around 5 and the concentration of
399 Ali was less than 0.2 mg l^{-1} . In KLI there were no pronounced sea salt episodes, and the
400 increased ANC and decreased concentration of Ali could be explained by reduced $\text{SO}_4\text{-S}$
401 input. Also in HJA, where ANC and pH increased and Ali decreased, reduced $\text{SO}_4\text{-S}$
402 input seemed to be the major driver. However, the trend was strengthened by the sea salt
403 episodes in the beginning of the period as they temporarily lowered pH from around 4.5
404 in 1986 to just above 4 in 1993-1994. After that the pH increased to a level higher than in
405 1986, 4.7-4.9. Correspondingly, there was a peak of Ali in the beginning of the period
406 followed by the subsequent decrease. In SAV and HEN, ANC increased slowly, and it is
407 difficult to separate the effect of reduced acid deposition from the effect of the
408 pronounced sea salt episodes in the beginning of the period. Most likely both factors
409 contributed to the trends.

410

411 In SOS, ANC was around zero in the beginning of the period, pH around 4.5 and the
412 concentration of Ali somewhat below 1 mg l^{-1} . There were significant trends for ANC
413 (increasing), pH (increasing) and Ali (decreasing) during the period. The changes can to a
414 large extent be related to reduced S input, but the trends, especially for ANC, were
415 reinforced by the early sea salt episodes.

416

417 KNA and ALA were storm-damaged in 2005 and 2007, and the later measurements were
418 strongly affected by the changed conditions. The increased input of organic material at a
419 storm-felling, or at a normal clear-felling, may affect the pH positively (Nykqvist and
420 Rosén, 1985; Piirainen et al., 2004). However, increased nitrification and $\text{NO}_3\text{-N}$ leaching
421 during the years after clear-cutting may temporarily counteract this (Akselsson et al.,
422 2004). In ALA, ANC was negative during the whole period, -0.3 meq l^{-1} at the lowest, pH
423 was around 4.7 and the concentration of Ali $1\text{-}2 \text{ mg l}^{-1}$. There were no signs of recovery.
424 On the contrary, there was a significant increase in Ali, which appeared before 2005 and
425 thus cannot be explained by the storm felling. There was no clear effect of the storm-
426 felling, except for a low pH, 4.1, in the last measurement in the period, which can be
427 explained by nitrification and $\text{NO}_3\text{-N}$ leaching following the clearcut (Fig. 11). In KNA,
428 ANC was generally between 0 and -0.2 meq l^{-1} , pH between 4.5 and 4.7 and the
429 concentration of Ali between 0.5 and 1.5 mg l^{-1} . There seemed to be a tendency towards
430 somewhat increased ANC before 2005, but there was no significant trend for the whole
431 period. There was no significant trend for Ali either. For pH there was a weak significant
432 increase, but it was mainly due to a temporary increase in pH after the storm felling. The

433 increased NO₃-N leaching was not as pronounced as in ALA, and it was not reflected in
434 the acidification parameters.

435

436 3.2.6 DOC

437 The concentration of DOC decreased significantly on seven of the sites (Fig. 16), but the
438 changes were relatively small, except for at SAV where there was a large decrease at the
439 start of the measurement period. The sharp decrease at SAV could, however, be an
440 artefact of the lysimeter installation. Decreased DOC concentrations in soil water in
441 forest soils have been reported in studies in Sweden and Norway (Löfgren et al., 2010;
442 Wu et al., 2010). Reduced ionic strength was proposed by Löfgren et al. (2010) as an
443 explanation in soils where the pH increase is small or non-existent.

444

445 FIG. 5-16

446

447 3.3 Acidification status and recovery

448 There were clear signs of recovery from acidification at most of the sites, although sea
449 salt episodes in several cases temporarily interrupted recovery. Signs of recovery, similar
450 to those in southern Sweden but without the episodic effect of sea salt, have been
451 demonstrated in studies from more central parts of Europe. Studies in Norway spruce
452 stands in the northwestern Czech Republic (Oulehle et al., 2006) and in Northern
453 Bavaria, Germany (Alewell et al., 2000), with time series of 7-8 years, showed decreased
454 concentrations of SO₄-S, Ca, Mg and Al_i in soil solution whereas pH remained
455 unchanged. Factors identified as important in controlling recovery were continued high

456 SO₄-S and NO₃-N concentrations in soil solution (Alewell et al., 2000), desorption of
457 previously stored SO₄²⁻ (Oulehle et al., 2006), and reduced Ca deposition (both studies).
458 Similar results were found by Armbruster et al. (2003), who studied two catchments in
459 Germany, one in the southwestern part (11 years time series) and one in the east, close to
460 the border to the Czech Republic (5 years time series). The dominant tree species in the
461 catchments was Norway spruce. The concentrations of SO₄-S decreased and ANC
462 increased in soil solution on both sites. The amount and distribution of stored S was
463 identified as a key factor for controlling recovery. Results from seven sites in Switzerland
464 with time series of 6-8 years (Graf Pannatier et al., 2010) showed a somewhat different
465 picture. There were only a small number of significant trends detected. Five of the seven
466 sites showed no significant trends for SO₄-S at most soil depths and the BC/Al ratio was
467 in most cases stable. It was concluded that the soil solution did not react much to the
468 decreased atmospheric deposition during this period on those specific sites.

469

470 Although most of the nine south-Swedish sites showed signs of recovery, soil water was
471 still highly acidified in most sites in the end of the period, with pH between 4.1 and 4.7
472 on six of the sites and negative ANC on seven of the sites (in two cases ANC was around
473 0). Gustafsson et al. (2001) proposed a number of indicators of soil acidification and one
474 proposal was concentration of Ali in soil water at 60 cm depth in the mineral soil, i.e.
475 approximately the same depth as the lysimeter data in this study. The critical limit was set
476 to 0.4 mg l⁻¹. All sites generally exceeded the limit in the beginning of the period and six
477 of the nine sites still did in the end. The concentration of Ali can also be used for risk
478 assessments for Al toxicity for trees (Schaedle et al., 1989; van Schöll et al., 2004;

479 Álvarez et al., 2005). In a review by Schaedle et al. (1989) different tree species were
480 categorised in three groups, sensitive, intermediate and resistant, depending on the
481 toxicity of Al³⁺ to the trees. Norway spruce (*Picea abies*) was classified as sensitive, with
482 negative growth effects appearing at a concentration of 0.15 mmol l⁻¹ (4 mg l⁻¹).
483 European Beech (*Fagus sylvatica*) was classified as intermediate, with negative growth
484 effects at a concentration of 0.5 mmol l⁻¹ (13 mg l⁻¹). Scots pine (*Pinus sylvestris*) was
485 classified as resistant, with negative growth effects at a concentration of 3-5 mmol l⁻¹ (81-
486 135 mg l⁻¹). A study on Norway spruce and Scots pine by Göransson and Eldhuset (1991)
487 gave higher limits, 0.3 mmol l⁻¹ (8 mg l⁻¹) for Norway spruce and 6 mmol l⁻¹ (162 mg l⁻¹)
488 for Scots pine. The spruce site ARK, with Al³⁺ concentrations between 1 and 8 mg l⁻¹, is
489 the only site where the concentrations are the same order of magnitude as the toxic
490 concentrations of Schaedle et al. (1989) and Göransson and Eldhuset (1991).

491

492 Although the risk for Al toxicity can be considered to be small, the water drained from
493 the soils is substantially acidified, leading to a risk of negative effects in the surface water
494 environment. The slow recovery rate indicates that the soil acidification will persist and
495 runoff water will remain acidified for a long time. The main reason for the slow recovery
496 rate is that a large amount of base cations has leached from the soil during the course of
497 acidification, and the natural processes that can compensate for the losses are slow. The
498 soils are tills that mainly consist of nutrient poor granites and gneisses, with low base
499 cation weathering rates. Base cation input through sea salt deposition can increase base
500 saturation in the soil, but the contribution to recovery is small and at the same time the
501 soil water is temporarily acidified. Several factors can inhibit recovery. Desorption of

502 adsorbed SO_4^{2-} delays recovery to a varying extent on the sites. Increased growth rates of
503 trees and increased biomass harvesting will lead to further losses of base cations, which
504 will inhibit recovery from acidification. It is important to consider these factors in the
505 policy making process regarding sustainable harvesting of forest fuels.

506

507 Acid soils are, as shown in this study, sensitive to sea salt episodes. Hindar et al. (1995)
508 showed that a sea salt episode in January 1993 in the coastal area of southwestern
509 Norway led to an acidifying effect over two years. Evans et al. (2001) showed that there
510 are no simple relationship between site acidity and the relative extent to which Ca, Ali
511 and H is exchanged at a sea salt episode. In this study, the most common ion to be
512 exchanged was Ali, but there are also clear signs of exchange of other ions (e.g. in HJA,
513 where Ca and H were exchanged as well). The production and transport of sea salt is
514 depending on several climate related factors, namely wind speed, atmospheric stability,
515 wind friction velocity, sea surface and air temperatures, present and prior rain or snow
516 and the amount and nature of surface-active materials in the near-surface ocean waters
517 (Lewis and Schwartz, 2004). The effect of climate change on sea salt episodes is unclear,
518 but there will certainly be episodes also in the future, and it will lead to acidification
519 episodes in surface waters as long as the soils are acidic. Although there are large
520 uncertainties in the future wind climate, there are indications of increased risk for critical
521 wind speeds from southern wind directions in the region (Blennow and Olofsson, 2008),
522 and if the frequency and strength of sea salt episodes would increase, recovery of surface
523 waters would be substantially delayed. As recovery progresses, sea salt episodes will

524 have a less marked acidifying effect (Wright, 2008), but on the sites in this study it can be
525 expected to have effects for a long time to come.

526

527 If the critical wind speeds from southern wind directions do increase in the future, it can
528 increase the risk for storm-fellings. Changes to ground frost from warming and reduced
529 snow cover can likewise increase the risk, as the “anchoring” of trees is affected. Storm-
530 fellings can have about the same effect on NO₃-N leaching and soil acidification as
531 normal clear-fellings. A difference is, however, that storm-fellings can affect a large part
532 of the landscape at the same time, which increases the risk of effects on surface waters.
533 Increased nitrification during some years after clear-cutting leads to increased NO₃-N
534 leaching (Akselsson et al., 2004) and may lower pH temporarily. The effect on pH is
535 counteracted by the increased input of organic material that stimulates decomposition and
536 has a positive effect on pH (Nykqvist and Rosén, 1985; Piirainen et al., 2004). The net
537 effect on pH depends on site-specific factors, for example the N status of the soil. For
538 example, in KNA there was a pH increase after the storm-felling whereas ALA showed
539 no clear effects except from the most recent pH measurement which showed a very low
540 pH, probably due to nitrification and the subsequent NO₃-N leaching. The clearcut effect
541 on NO₃-N leaching often last 5-6 years with a peak after a couple of years (Futter et al.,
542 2010), thus effects can be expected over the next few years.

543

544 One of the sites, ARK, showed chronically elevated NO₃-N concentrations in soil water,
545 indicating N saturation. Since the nitrification process is acidifying if the NO₃-N is
546 leached, this also leads to acidification. There are several other sites with chronically

547 elevated NO₃-N concentrations in southern Sweden (Akselsson et al., 2010). A warmer
548 and wetter climate may push more ecosystems towards N saturation (van Breemen et al.,
549 1998; Wright and Jenkins, 2001), causing a risk of increased eutrophication and
550 acidification. Continued monitoring of NO₃-N concentrations in forest in these regions is
551 crucial since it is the most robust indicator of exceeded N retention capacity, which may
552 affect eutrophication of lakes and oceans, acidification of soils and waters and
553 concentrations of NO₃-N in ground water (Galloway et al., 2003).

554

555

556

557 4. Conclusions

558 The data presented in this study emphasizes the importance of long time series for
559 interpreting recovery trends in a changing climate. The following specific main
560 conclusions are drawn:

- 561 • All sites but one showed signs of recovery from acidification along with the reduced
562 deposition, in accordance with our first hypothesis. The recovery progress was,
563 however, slow, and the soil water was still highly acidic in the end of the period at
564 most of the sites. Six of the nine sites still had a negative ANC and a concentration of
565 Ali exceeding 0.4 mg l⁻¹. The low ANC, the elevated concentrations of Ali and the
566 fact that only a few of the sites showed increases in pH indicates that the sites are
567 generally in an early stage of recovery from acidification.
- 568 • Sea salt episodes caused strong but transient acidification episodes in soil water, in
569 accordance with our second hypothesis. On some of the sites where sea salt episodes

570 led to a marked acidification peak in the beginning of the period, it was difficult to
571 evaluate the relative importance of reduced SO₄-S deposition and “recovery” from sea
572 salt episodes for the trends in pH, ANC and Ali in soil water. Sea salt episodes can be
573 expected to continue to appear and will cause transient acidification episodes for soil
574 water and surface water in southwestern Sweden as long as the soils are acidic.

575 • For most of the sites the SO₄-S concentration in soil water did not decrease to the
576 same extent as the SO₄-S deposition, which highlights the importance of desorption of
577 previously adsorbed SO₄²⁻. The response differed widely between the sites, which
578 could partly be explained by differences in DOC concentrations.

579 • One of the sites showed persistently elevated concentrations of NO₃-N, indicating that
580 the N retention capacity is exceeded on the site. The high NO₃-N concentrations
581 coincided with very low pH. The results from the site highlight the importance of N
582 retention in counteracting eutrophication and acidification.

583 • The two storm-felled sites showed substantially increased NO₃-N concentrations,
584 similar to the effects of clear-cutting. The initial effect on pH differed between the
585 sites, but the time period was too short to allow general conclusions to be drawn. If a
586 large part of a landscape is storm-felled in the regions where deposition of SO₄-S and
587 inorganic N has been high, there is a risk of episodes of N-leaching and surface water
588 acidification.

589

590 Role of the funding source

591 The nine sites in this study are part of the SWETHRO Network run by IVL Swedish

592 Environmental Research Institute and financed by regional air quality protection

593 associations, county administrative boards and the Swedish Environmental Protection
594 Agency. The monitoring setup, sampling and chemical analysis methodologies has been
595 designed by IVL Swedish Environmental Research Institute, in consultation with the
596 financiers. The present study was financed by the Swedish Environmental Protection
597 Agency. The data analysis has been made solely by the authors.

598

599 References

- 600 Adriaenssens S, Hansen K, Staelens J, Wuyts K, de Schrijver A, Baeten L et al.
601 Throughfall deposition and canopy exchange processes along a vertical gradient within
602 the canopy of beech (*Fagus sylvatica* L.) and Norway spruce (*Picea abies* (L.) Karst).
603 *Science of the Total Environment* 2012;420:168–182.
- 604 Aherne J, Larssen T, Cosby BJ, Dillon PJ, 2006. Climate variability and forecasting
605 surface water recovery from acidification: Modelling drought-induced sulphate release
606 from wetlands. *Science of the Total Environment* 2006;365:186-199.
- 607 Aherne J, Posch M, Forsius M, Lehtonen A, Härkönen K. Impacts of forest biomass
608 removal on soil nutrient status under climate change: a catchment-based modelling study
609 for Finland. *Biogeochemistry* 2012; 107:471-488.
- 610 Akselsson C, Belyazid S, Hellsten S, Klarqvist M, Pihl-Karlsson G, Karlsson PE et al.
611 Assessing the risk of N leaching from forest soils across a steep N deposition gradient in
612 Sweden. *Environmental Pollution* 2010;158:3588-3595.
- 613 Akselsson C, Westling O, Örlander G. Regional mapping of nitrogen leaching from
614 clearcuts in southern Sweden. *Forest Ecology and Management* 2004;202:235-243.

615 Akselsson C, Westling O, Sverdrup H, Holmqvist J, Thelin G, Uggla E et al. Impact of
616 harvest intensity on long-term base cation budgets in Swedish forest soils. *Water, Air,
617 and Soil Pollution :Focus* 2007;7:201-210.

618 Alewell C, Manderscheid B, Gerstberger P, Matzner E. E atmospheric deposition on soil
619 solution chemistry and elemental contents of spruce needles in NE-Bavaria, Germany.
620 *Journal of plant nutrition and soil science* 2000;163:509-516.

621 Álvarez E, Fernández-Marcos M L, Monterroso C, Fernández-Sanjurjo M J. Application
622 of aluminium toxicity indices to soils under various forest species. *Forest Ecology and
623 Management* 2004;211:227–239.

624 Armbruster M, Abiy M, Feger K-H. The biogeochemistry of two forested catchments in
625 the Black Forest and the eastern Ore Mountains (Germany). *Biogeochemistry*
626 2003;65:341-368.

627 Blennow K, Olofsson E. The probability of wind damage in forestry under a changed
628 wind climate. *Climate change* 2008;87:347–360.

629 Borrell P, Builtjes P, Grennfelt P, Hov Ø, van Aalst R, Fowler D et al. Photo-oxidants,
630 acidification and tools: policy applications of EUROTRAC results. *Transport and
631 Chemical Transformation of Pollutants in the Troposphere*, Vol. 10; 1997.

632 De Vries W, Reinds GJ, Vel E. Intensive monitoring of forest ecosystems in Europe 2:
633 Atmospheric deposition and its impact on soil solution chemistry. *Forest Ecology and
634 Management* 2003;174:97-115.

635 Driscoll C T. A Procedure for the Fractionation of Aqueous Aluminium in Dilute Acidic
636 Waters. *International Journal of Environmental Analytical Chemistry* 1984;16:267-283.

637 Eriksson E, Karlton E, Lundmark JE. Acidification of Swedish forest soils. *Ambio*
638 1992;21:150-154.

639 Evans CD, Cullen JM, Alewell C, Kopáček J, Marchetto A, Moldan F, Prechtel A,
640 Rogora M, Veselý J, Wright R. Recovery from acidification in European surface waters.
641 *Hydrology and Earth System Sciences* 2001;5(3):283–297.

642 Evans C, Monteith D, Harriman, R. Long-term variability in the deposition of marine
643 ions at west coast sites in the UK Acid Waters Monitoring Network: impacts on surface
644 water chemistry and significance for trend determination. *The Science of the Total*
645 *Environment* 2001;265,115-129.

646 Ferm M. Throughfall measurements of nitrogen and sulphur compounds. *International*
647 *Journal of Analytical Chemistry* 1993;50:29-43.

648 Fölster J, Wilander A. Recovery from acidification in Swedish forest streams.
649 *Environmental Pollution* 2002;117:379-389.

650 Futter M, Ring E, Högbom L, Entenmann S, Bishop K. Consequences of NO₃-N leaching
651 following stem-only harvesting of Swedish forest soils are dependent on spatial scale.
652 *Environmental Pollution* 2010;158:3552-3559.

653 Galloway JN, Aber JA, Erisman JW, Seitzinger SP, Howarth RW, Cowling EB, Cosby J.
654 The nitrogen cascade. *Bioscience* 2003;53(4):341-356.

655 Gobran GR, Nilsson SI. Effects of forest floor leachate on sulfate retention in a spodosol
656 soil. *Journal of Environmental Quality* 1988;17:235-239.

657 Graf Pannatier E, Thimonier A, Schmitt M, Walthert L, Waldner P. A decade of
658 monitoring at Swiss long-term forest ecosystem research (LWF) sites: can we observe

659 trends in atmospheric acid deposition and in soil solution acidity? Environmental
660 monitoring and assessment 2011;174:3-30.

661 Göransson A, Eldhuset T D. 1991. Effects of aluminium on growth and nutrient uptake
662 of small *Picea abies* and *Pinus sylvestris* plants. *Trees* 1991;5:136-142.

663 Gustafsson JP, Jacks G. Sulphur status in some Swedish podzols as influenced by acidic
664 deposition and extractable organic carbon. *Environmental Pollution* 1993;81:185-191.

665 Gustafsson JP, Karlton E, Lundström U, Westling O. Urvalskriterier för bedömning av
666 markförsurning. Temaserie Markförsurning och motåtgärder. Swedish Forest Agency.
667 Report 2001;11D (In Swedish).

668 Hallgren Larsson E, Knulst J, Malm G, Westling O. Deposition of acidifying compounds
669 in Sweden. *Water, Air and Soil Pollution* 1995;85:2271-2276.

670 Harrison A F, Schulze E-D, Gebauer G, Bruckner G. Canopy uptake and utilization of
671 atmospheric pollutant nitrogen. In: Schulze E-D, editor. *Carbon and Nitrogen Cycling in*
672 *European Forest Ecosystems*. Berlin Heidelberg: Springer-Verlag; 2000. p. 171-188.

673 Hindar A, Henriksen A, Kaste Ø, Tørseth K. Extreme acidification in small catchments in
674 southwestern Norway associated with a sea salt episode. *Water, Air and Soil Pollution*
675 1995;85:547-552.

676 Hindar A, Henriksen A, Tørseth K, Semb A. Acid water and fish death. *Nature*
677 1994;372:327-328.

678 Hirsch RM, Slack JR. A nonparametric trend test for seasonal data with serial
679 dependence. *Water Resource Research* 1984;20:727-732.

680 Hultberg H, Ferm M. Temporal changes and fluxes of sulphur and calcium in wet and dry
681 deposition, internal circulation as well as in run-off and soil in a forest at Gårdsjön,
682 Sweden. *Biogeochemistry* 2004;68:355–363.

683 Langner J, Persson C, Robertson L, Ullerstig A. Air pollution assessment study using the
684 MATCH Modelling System. Application to sulphur and nitrogen compounds over
685 Sweden 1994. Swedish Meteorological and Hydrological Institute, Report no. 69,
686 Norrköping, Sweden; 1996.

687 Laudon H. Recovery from episodic acidification delayed by drought and high sea salt
688 deposition. *Hydrology and Earth System Sciences* 2008;12:363-370.

689 Lewis ER, Schwartz SE. Sea Salt Aerosol Production: Mechanisms, Methods,
690 Measurements and Models: A Critical Review. Geophysical monograph series 152; 2004.

691 Löfgren S, Gustafsson JP, Bringmark L. Decreasing DOC trends in soil solution along
692 the hillslopes at two IM sites in southern Sweden — Geochemical modeling of organic
693 matter solubility during acidification recovery. *Science of the total environment*
694 2010;409:201-210.

695 Mann HB. Non-parametric tests against trend. *Econometrica* 1945;13:245-259.

696 Moldan F, Skeffington R, Mörth CM, Torssander P, Hultberg H, Munthe J. Results from
697 the Covered Catchment Experiment at Gårdsjön, Sweden, after Ten Years of Clean
698 Precipitation Treatment. *Water, Air and Soil Pollution* 2004;154:371-384.

699 Nyiri A, Gauss M, Klein H. Transboundary Air Pollution by Main Pollutants (S, N, O₃)
700 and PM. MSC-W Data Note 1;2009.

701 Nykvist N, Rosén K. Effects of clear-felling and slash removal on the acidity of northern
702 coniferous soils. *Forest Ecology and Management* 1985;11:157-169.

703 Oulehle F, Hofmeister J, Cudlín P, Hruška J. The effect of reduced atmospheric
704 deposition on soil and soil solution chemistry at a site subjected to long-term
705 acidification, Načetín, Czech Republic. *Science of the Total Environment* 2006;370:532-
706 544.

707 Pihl Karlsson G, Akselsson C, Hellsten S, Karlsson PE. Reduced European emissions of
708 S and N – Effects on air concentrations, deposition and soil water chemistry in Swedish
709 forests. *Environmental Pollution* 2011;159:3571-3582.

710 Piirainen S, Finér L, Mannerkoski H, Starr M. Effects of forest clear-cutting on the
711 sulphur, phosphorus and base cations fluxes through podzolic soil horizons.
712 *Biogeochemistry* 2004;69:405-424.

713 Reuss JO, Johnson DW. Acid Deposition and the Acidification of Soils and Waters.
714 *Ecological Studies* 1986;59:119-123.

715 Schaedle M, Thornton F C, Raynal D J, Tepper H B. Response of tree seedlings to
716 aluminium. *Tree Physiology* 1989;5:337-356.

717 Skjelkvåle B, Borg H, Hindar A, Wilander A. Large scale patterns of chemical recovery
718 in lakes in Norway and Sweden: Importance of seasalt episodes and changes in dissolved
719 organic carbon. *Applied Geochemistry* 2007;22:1174-1180.

720 Skjelkvåle B, Evans C, Larssen T, Hindar A, Raddum G. Recovery from acidification in
721 European surface waters: A view to the future. *Ambio* 2003;32(3):170-175.

722 Skjelkvåle B, Mannio J, Wilander A, Andersen T. Recovery from acidification of lakes in
723 Finland, Norway and Sweden 1990–1999. *Hydrology and Earth System Sciences* 2001;5
724 (3):327–337.

725 Sverdrup H, Martinson L, Alveteg M, Moldan F, Kronnäs V, Munthe J. Modeling
726 recovery of Swedish Ecosystems from Acidification. *Ambio* 2005;34(1):25-31.

727 Tamm C. Nitrogen in terrestrial ecosystems. *Ecological Studies* 1991;81. Berlin :
728 Springer Verlag.

729 van Breemen N, Jenkins A, Wright R, Beerling D, Arp W, Berendse F. et al. Impacts of
730 Elevated Carbon Dioxide and Temperature on a Boreal Forest Ecosystem (CLIMEX
731 Project). *Ecosystems* 1998;1:345–351.

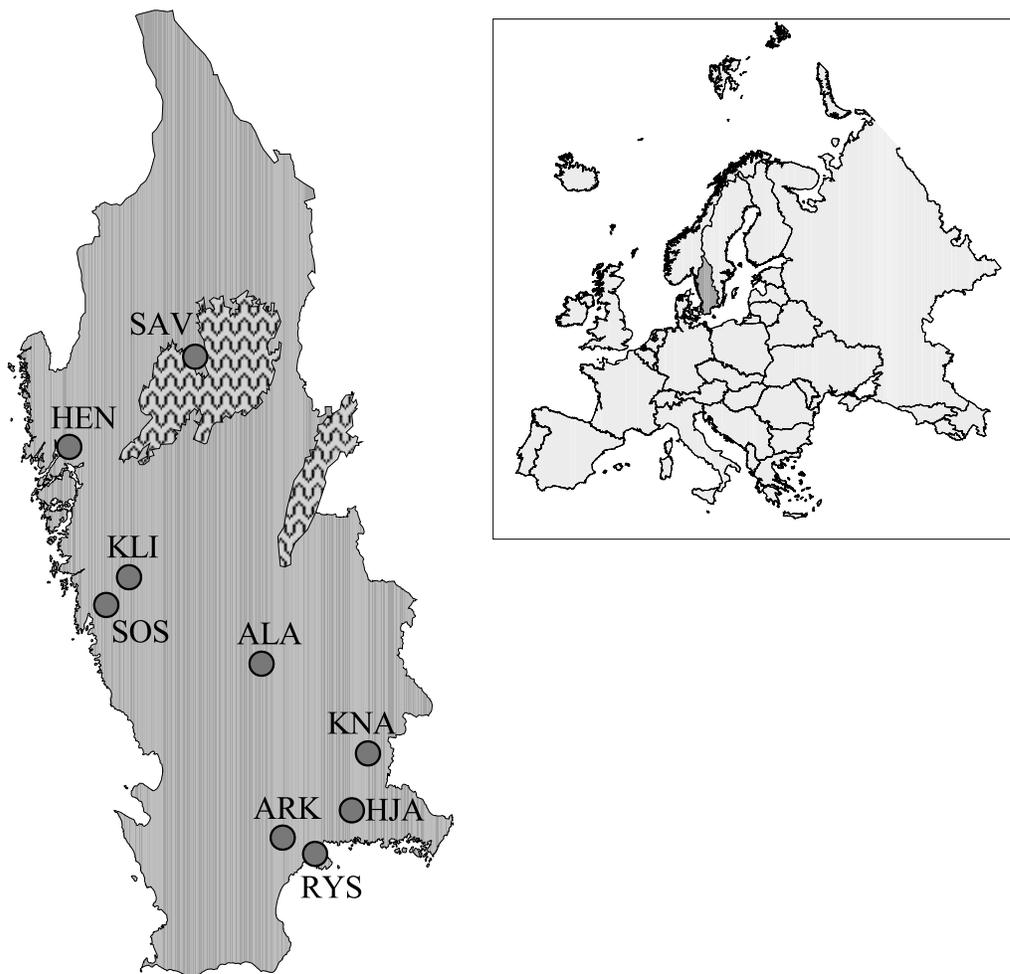
732 van Schöll L, Keltjens W G, Hoffland E, van Breemen N. Aluminium concentration
733 versus the base cation to aluminium ratio as predictors for aluminium toxicity in *Pinus*
734 *sylvestris* and *Picea abies* seedlings. *Forest Ecology and Management* 2004;195:301–309.

735 Wright R. The decreasing importance of acidification episodes with recovery from
736 acidification: an analysis of the 30-year record from Birkenes, Norway. *Hydrology and*
737 *Earth System Sciences* 2008;12:353-362.

738 Wright R, Jenkins, A. Climate change as a confounding factor in reversibility of
739 acidification: RAIN and CLIMEX projects. *Hydrology and Earth System Sciences*
740 2001;5(3):477-486.

741 Wu YJ, Clarke N, Mulder, J. Dissolved organic carbon concentrations in throughfall and
742 soil waters at level II monitoring plots in Norway: short- and long-term variations. *Water,*
743 *Air and Soil Pollution* 2010;205:273–88.

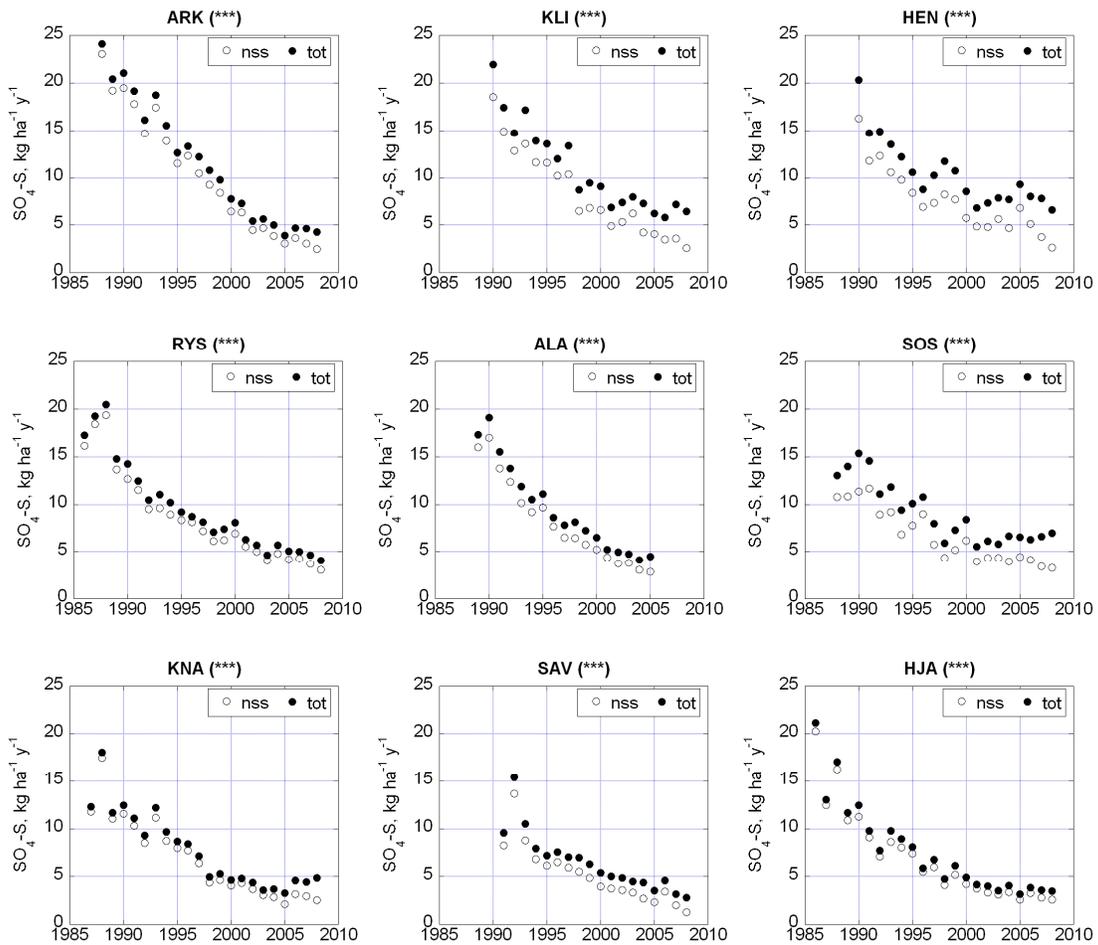
744
745
746
747
748



750

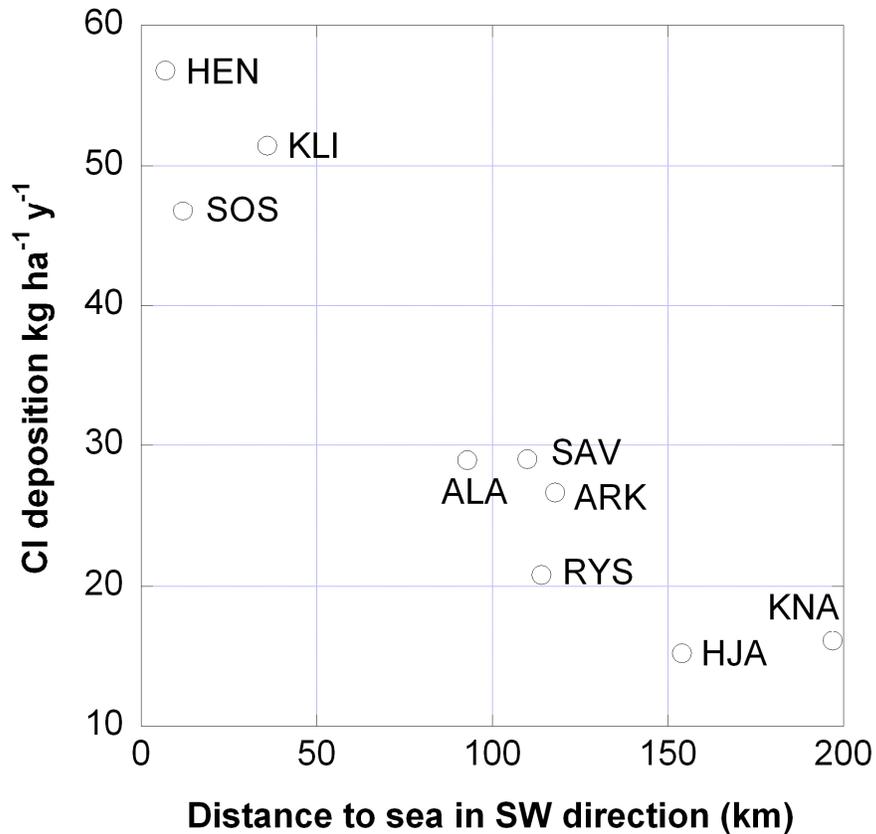
751 Fig. 1. Nine sites with data over long time periods (18-22 years) in southern Sweden.

752



753
 754 Fig. 2. Total (tot) and non sea salt (nss) throughfall deposition of $\text{SO}_4\text{-S}$. Significance
 755 level (Mann-Kendall) is given within brackets in the case of a significant trend, where
 756 one, two and three stars corresponds to $p < 0.05$, $p < 0.01$ and $p < 0.001$.

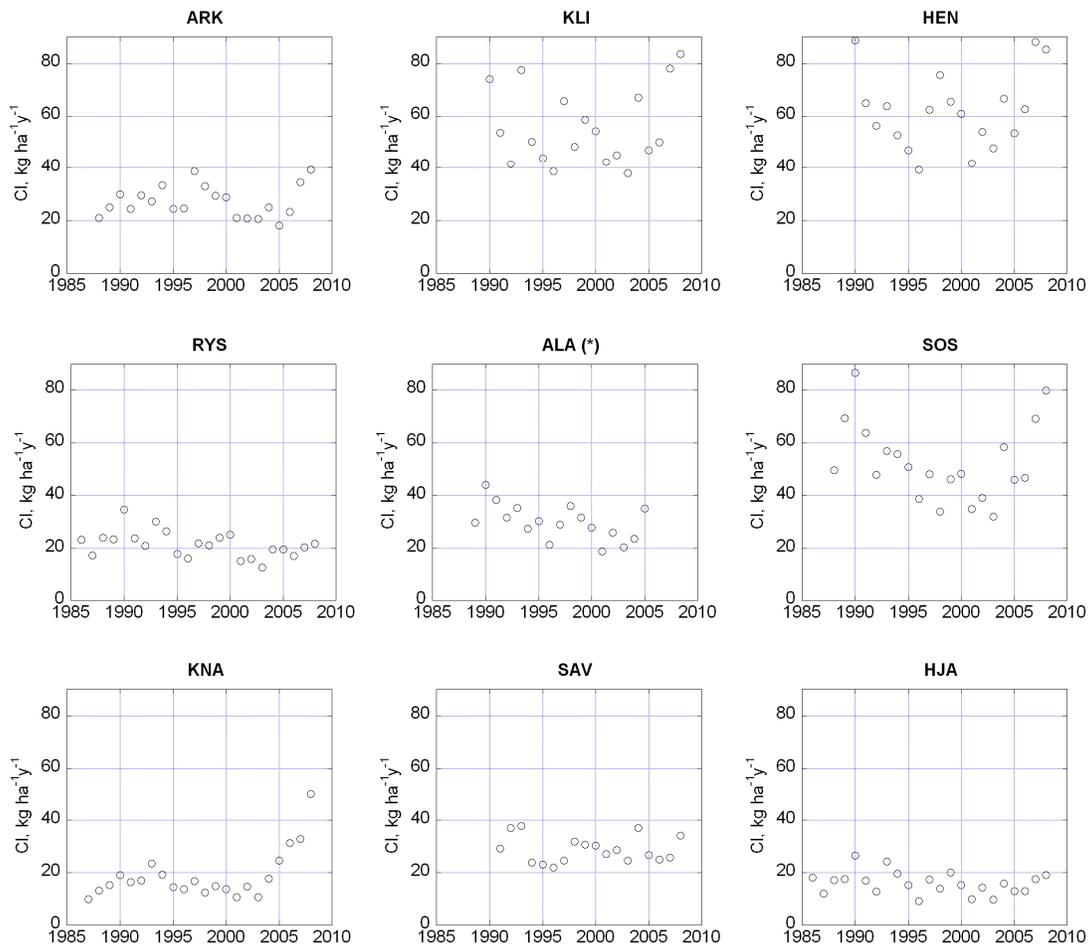
757



758

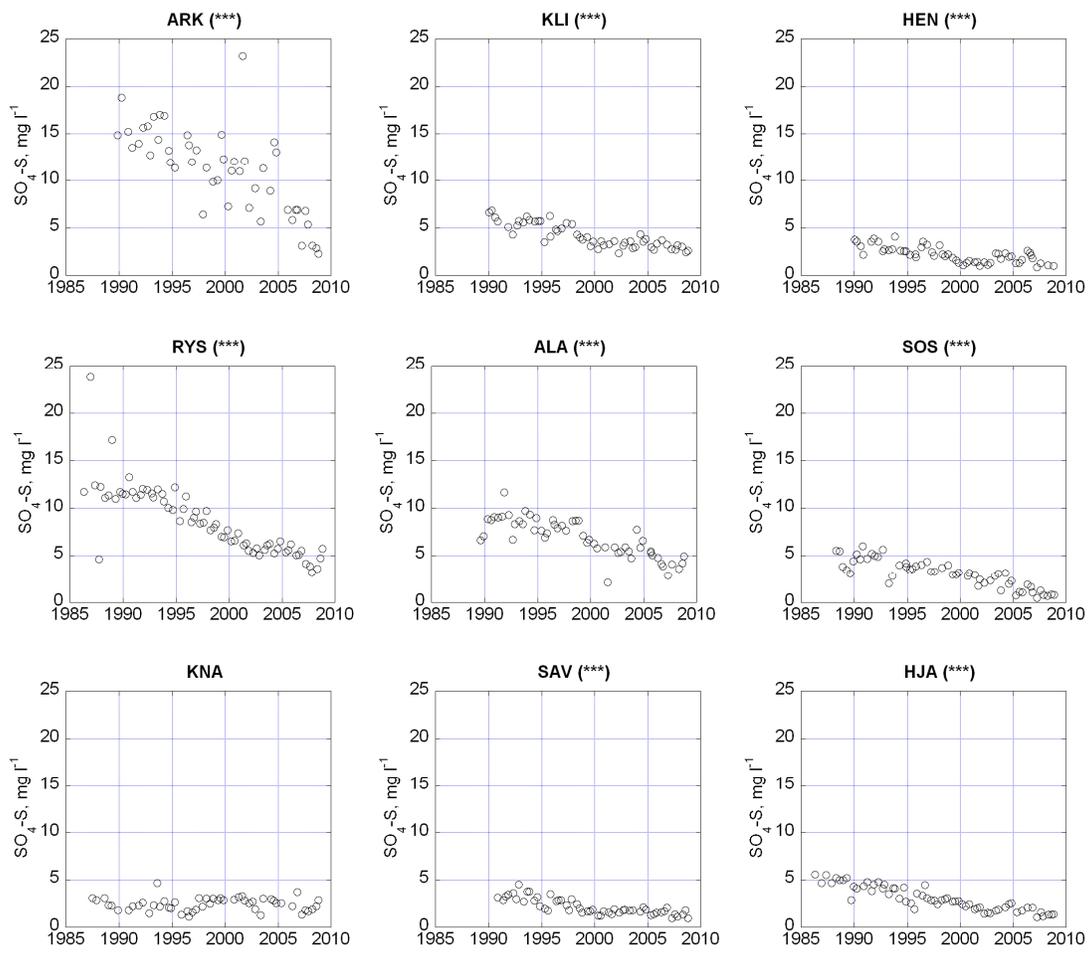
759 Fig. 3. Average chloride deposition (1991-2005) as a function of distance to sea in the
 760 southwest direction for the nine sites. For RYS, the winds from SW touches the coastline
 761 along the east coast, but the sea salt influence from there was assumed to be minor due to
 762 the short path over sea, and thus the distance to the SW coast was used.

763



764
 765 Fig. 4. Throughfall deposition of Cl. Significance level (Mann-Kendall) is given within
 766 brackets in the case of a significant trend, where one, two and three stars corresponds to
 767 $p < 0.05$, $p < 0.01$ and $p < 0.001$.

768



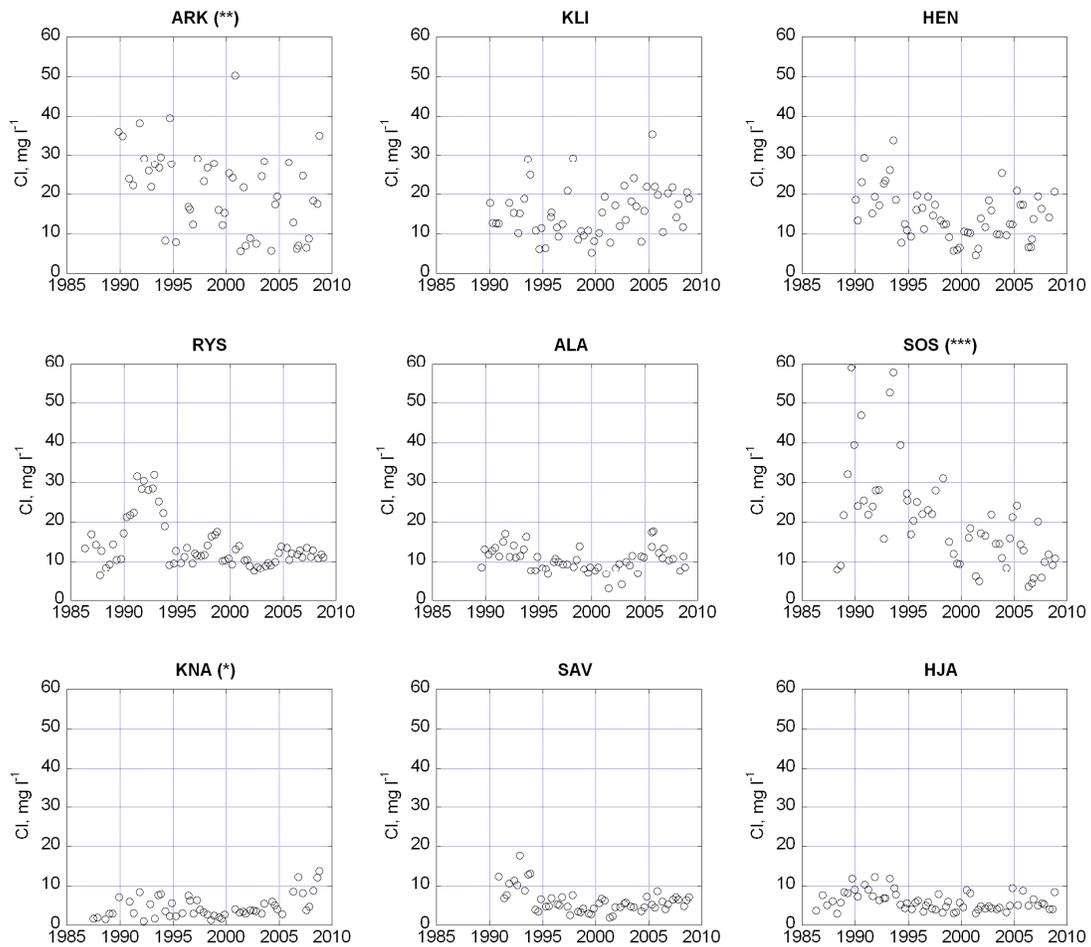
769

770 Fig. 5. Sulphur ($\text{SO}_4\text{-S}$) concentration (mg l^{-1}) in soil water. Significance level (Seasonal-

771 Kendall) is given within brackets in the case of a significant trend, where one, two and

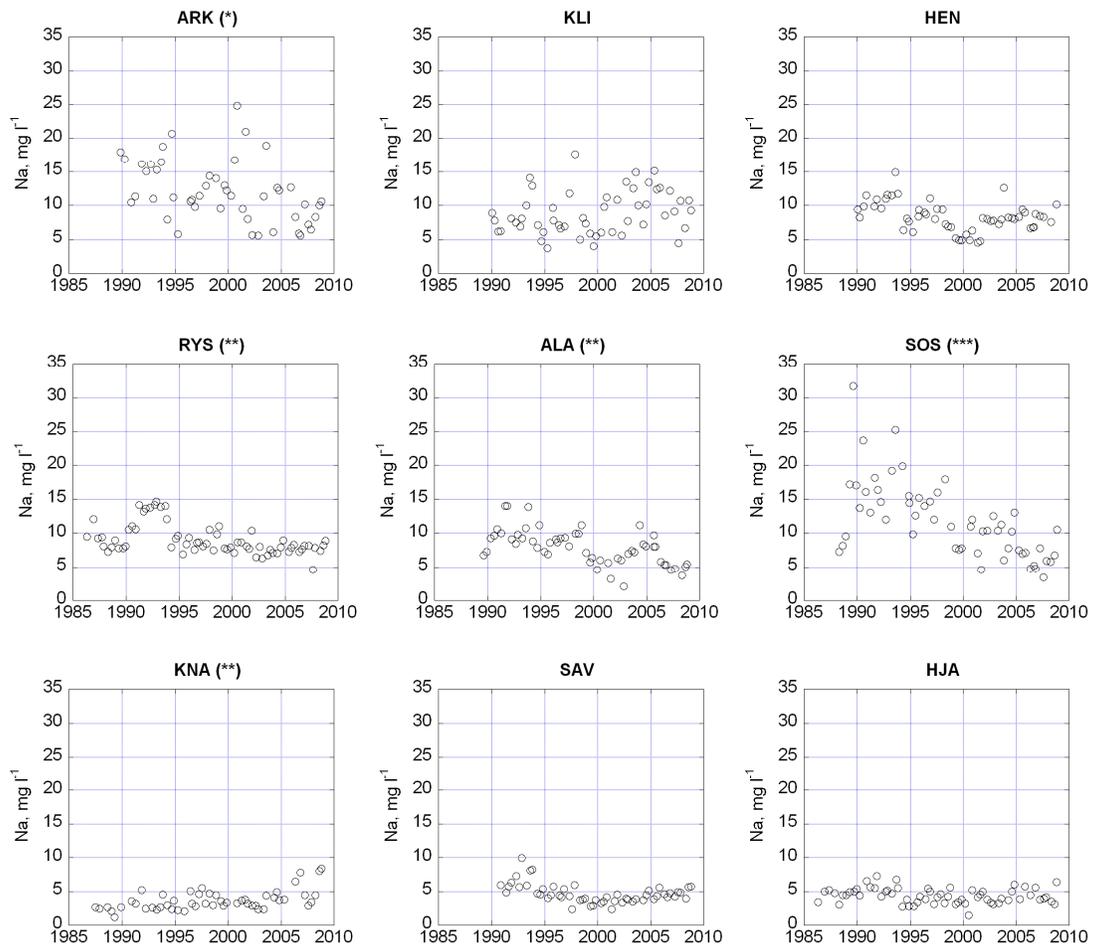
772 three stars corresponds to $p < 0.05$, $p < 0.01$ and $p < 0.001$.

773



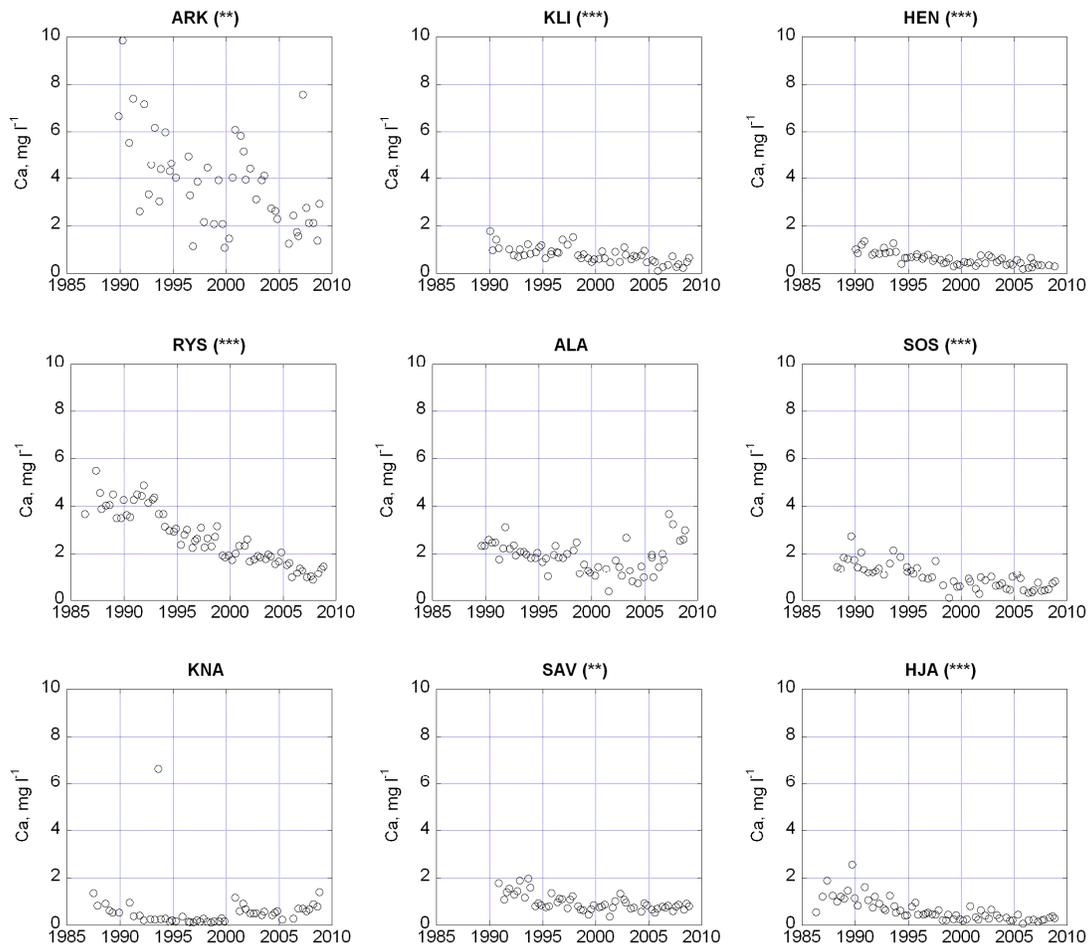
774
 775 Fig. 6. Chloride (Cl) concentration (mg l^{-1}) in soil water. Significance level (Seasonal-
 776 Kendall) is given within brackets in the case of a significant trend, where one, two and
 777 three stars corresponds to $p < 0.05$, $p < 0.01$ and $p < 0.001$.

778



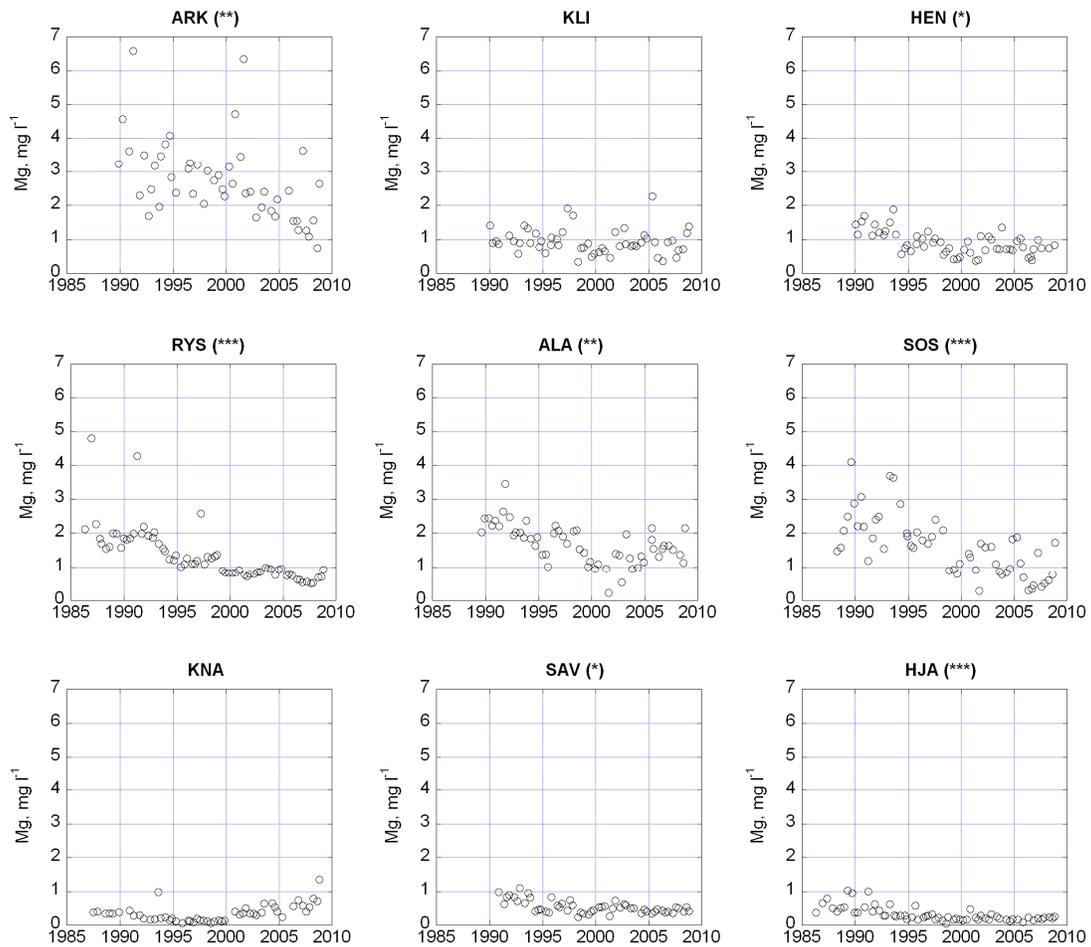
779
 780 Fig. 7. Sodium (Na) concentration (mg l^{-1}) in soil water. Significance level (Seasonal-
 781 Kendall) is given within brackets in the case of a significant trend, where one, two and
 782 three stars corresponds to $p < 0.05$, $p < 0.01$ and $p < 0.001$.

783



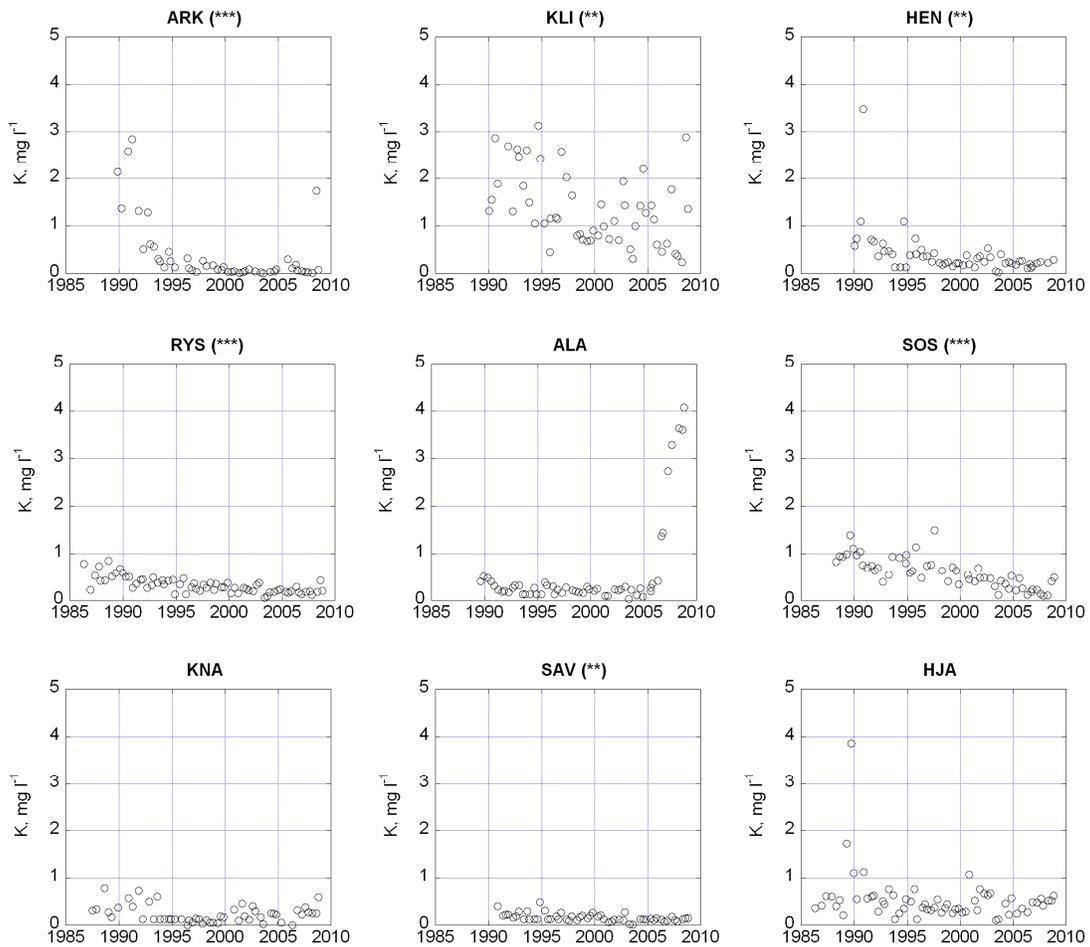
784
 785 Fig. 8. Calcium (Ca) concentration (mg l^{-1}) in soil water. Significance level (Seasonal-
 786 Kendall) is given within brackets in the case of a significant trend, where one, two and
 787 three stars corresponds to $p < 0.05$, $p < 0.01$ and $p < 0.001$.

788



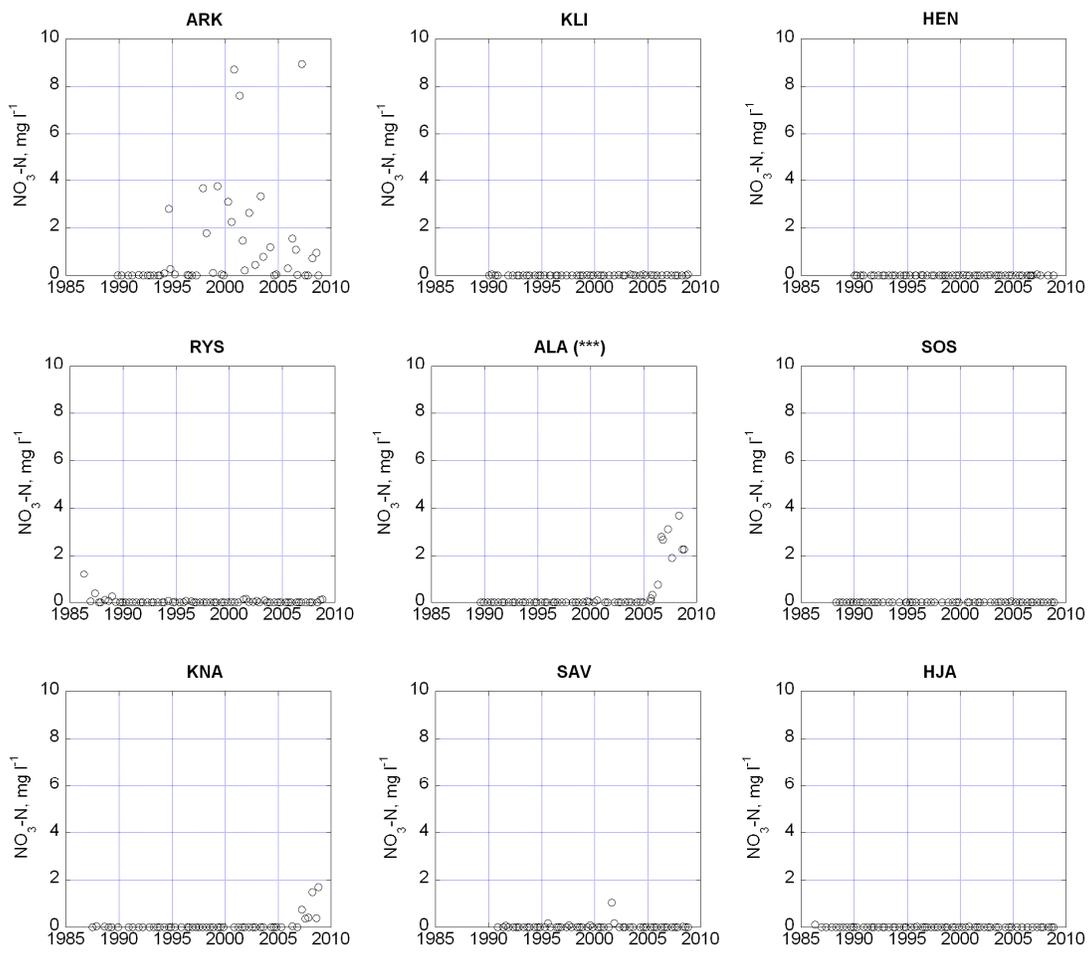
789
 790 Fig. 9. Magnesium (Mg) concentration (mg l⁻¹) in soil water. Significance level
 791 (Seasonal-Kendall) is given within brackets in the case of a significant trend, where one,
 792 two and three stars corresponds to p<0.05, p<0.01 and p<0.001.

793



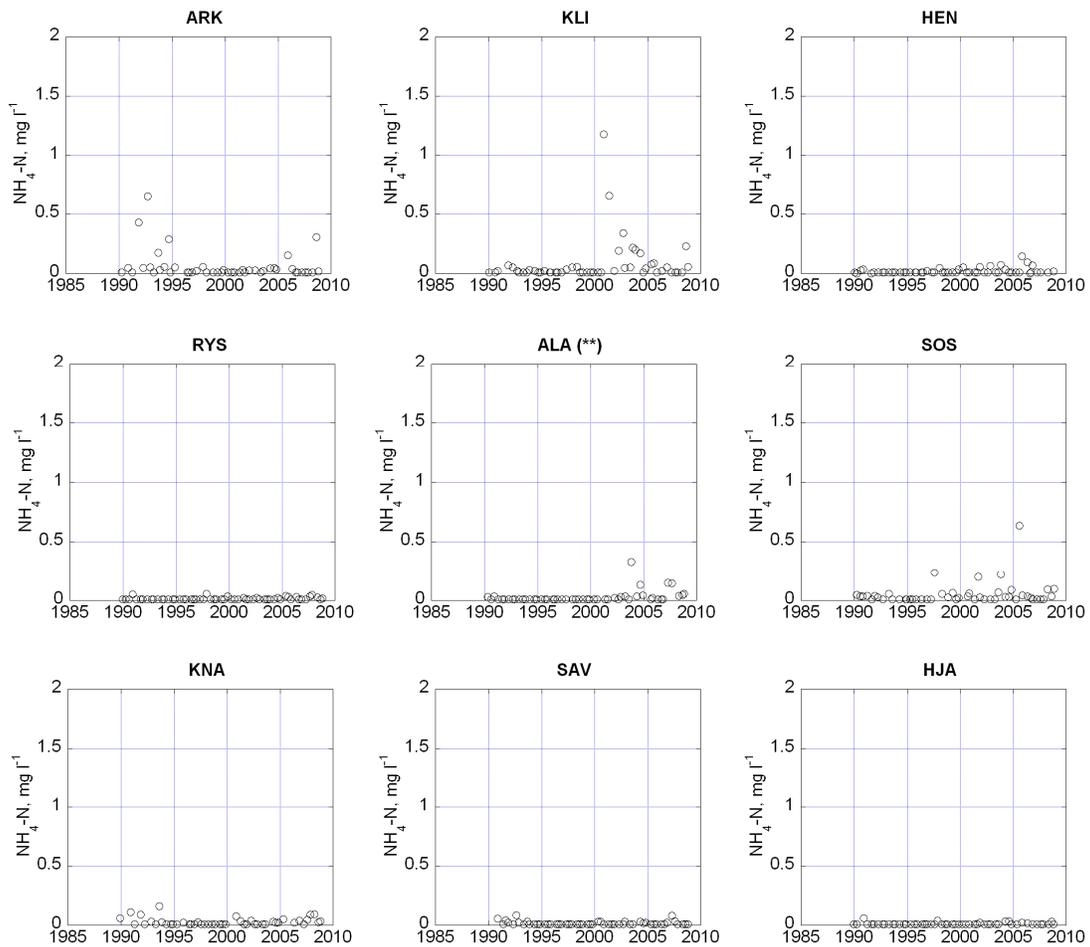
794
 795 Fig. 10. Potassium (K) concentration (mg l^{-1}) in soil water. Significance level (Seasonal-
 796 Kendall) is given within brackets in the case of a significant trend, where one, two and
 797 three stars corresponds to $p < 0.05$, $p < 0.01$ and $p < 0.001$.

798



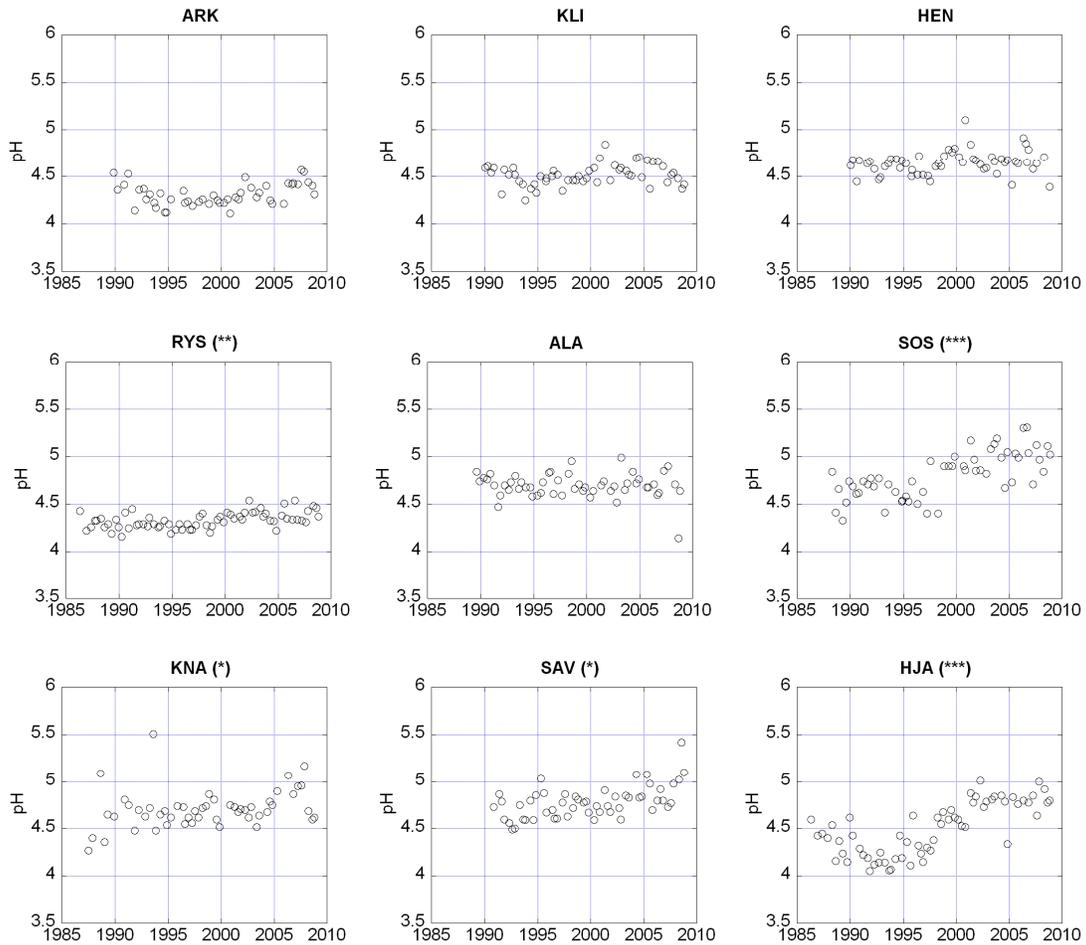
799
 800 Fig. 11. Nitrate nitrogen ($\text{NO}_3\text{-N}$) in soil water (mg l^{-1}). Significance level (Seasonal-
 801 Kendall) is given within brackets in the case of a significant trend, where one, two and
 802 three stars corresponds to $p < 0.05$, $p < 0.01$ and $p < 0.001$.

803



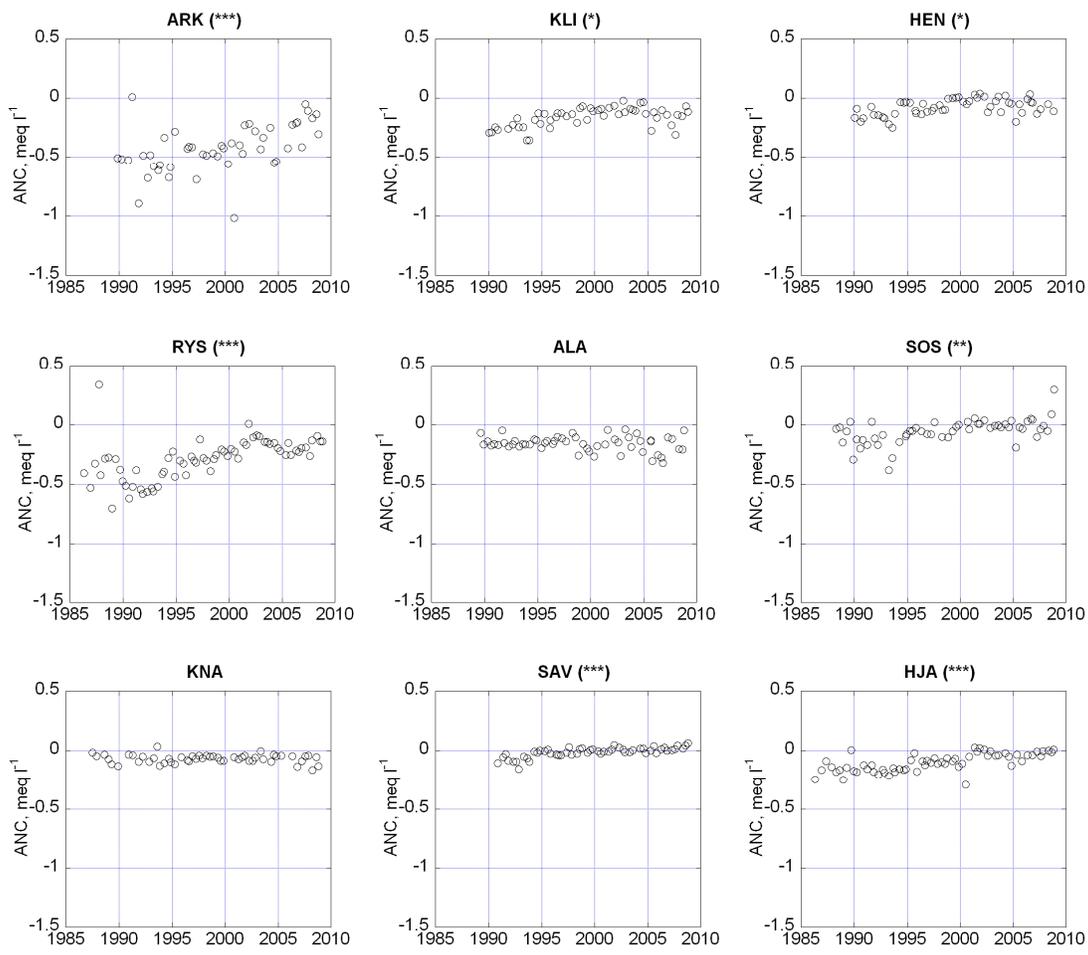
804
 805 Fig. 12. Ammonium nitrogen ($\text{NH}_4\text{-N}$) in soil water (mg l^{-1}). Significance level
 806 (Seasonal-Kendall) is given within brackets in the case of a significant trend, where one,
 807 two and three stars corresponds to $p < 0.05$, $p < 0.01$ and $p < 0.001$.

808



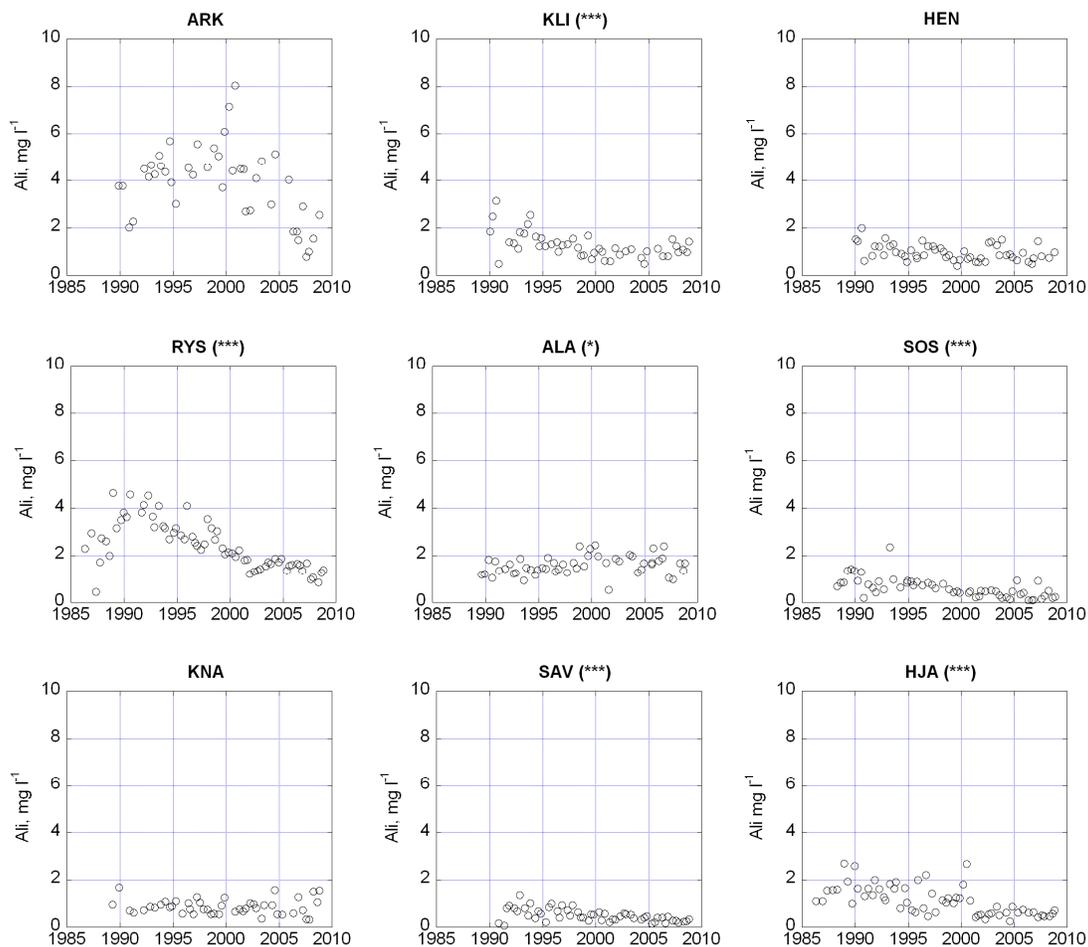
809
 810 Fig. 13. pH in soil water. Significance level (Seasonal-Kendall) is given within brackets
 811 in the case of a significant trend, where one, two and three stars corresponds to $p < 0.05$,
 812 $p < 0.01$ and $p < 0.001$.

813



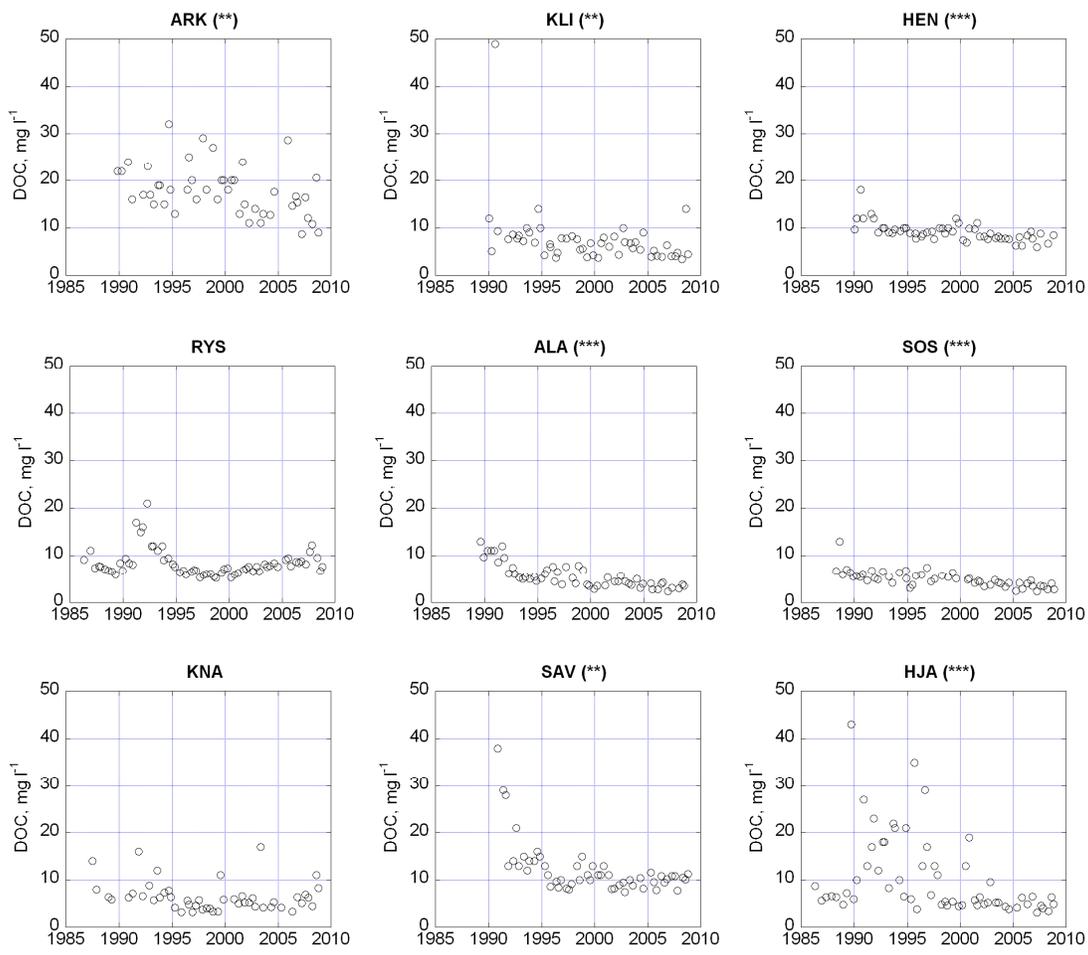
814
 815 Fig. 14. ANC in soil water (meq l^{-1}). Significance level (Seasonal-Kendall) is given
 816 within brackets in the case of a significant trend, where one, two and three stars
 817 corresponds to $p < 0.05$, $p < 0.01$ and $p < 0.001$.

818



819
 820 Fig. 15. Inorganic aluminium, Ali, in soil water (mg l^{-1}). Significance level (Seasonal-
 821 Kendall) is given within brackets in the case of a significant trend, where one, two and
 822 three stars corresponds to $p < 0.05$, $p < 0.01$ and $p < 0.001$.

823



824
 825 Fig. 16. DOC in soil water (mg l^{-1}). Significance level (Seasonal-Kendall) is given within
 826 brackets in the case of a significant trend, where one, two and three stars corresponds to
 827 $p < 0.05$, $p < 0.01$ and $p < 0.001$. Note that the filter size used was $0.8 \mu\text{m}$ in contrast to the
 828 standard size $0.45 \mu\text{m}$, which leads to a small overestimation of DOC concentration.
 829

830 **Tables**

831 Table 1. Basic information for the nine sites.

Site	Original name ^a	Lat	Long	Altitude (m)	Distance to sea (km) ^b	Data period	Number of lysimeters	Special features
ARK	Arkelstorp	56.18	14.25	105	21 (SE)	1989-2008	3	S slope. High content of stones, boulders. Thinned in July 1995.
KLI	Klippan	57.69	12.48	120	34 (W)	1990-2008	3	Top of ridge. Nature reserve. Bark beetle attack reported 2008 ^d .
HEN	Hensbacka	58.44	11.74	120	2 (W)	1990-2008	3	Lower part of slight N slope.
RYS	Ryssberget	56.08	14.60	125	3 (S)	1986-2008	6	Top of hill. Lysimeters in depression near deposition samplers.
ALA	Alandsryd	57.20	13.98	220	91 (SW)	1989-2008 ^c	3	SW slope. Slightly hilly area. Completely storm felled 2005.
SOS	Söstared	57.52	12.25	100	12 (SW)	1988-2008	5	Established after fire 1923.
KNA	Knapanäs	56.68	15.15	160	58 (S)	1987-2008	5	Flat area. Severely damaged in the storms 2005 and 2007 ^c .
SAV	S. Averstad	59.01	13.12	65	115 (W)	1990-2008	5	Flat area. NW of a big lake, highly exposed to SW winds.
HJA	Hjärtsjömåla	56.34	14.98	100	18 (S)	1986-2008	5	Slightly hilly area. High stone content.

832 ^a The sites are ordered based on average S deposition 1991-2005, from highest to lowest.833 ^bThe closest distance to sea is given. The direction is given in brackets.834 ^c1989-2005 for deposition.835 ^dAll spruces on the site have been attacked.836 ^cThree of the lysimetres were damaged and replaced by new ones after the storm 2005.

837 Table 2. Forest and soil properties, climate and N deposition for the nine sites.

Site	Tree species	Tree age years	SI ^c	Soil type	Temp ^f °C	Prec ^f mm	N dep ^g kg ha ⁻¹ y ⁻¹
ARK	Norway spruce	53 ^c	32	Transition	7.6	731	10.2
KLI	Norway spruce ^a	117 ^c	22	Transition	6.9	1055	9.2
HEN	Norway spruce	89 ^c	26	Podzol	6.7	1070	9.2
RYS	Beech	132 ^c	30	Cambisol	7.7	663	10.3
ALA	Norway spruce	80 ^d	30	Transition	6.2	899	9.3
SOS	Scots pine ^b	85 ^c	24	Podzol	7.6	1128	10.6
KNA	Norway spruce	51 ^d	32	Podzol	6.9	721	9.8
SAV	Norway spruce	77 ^c	30	Podzol	6.7	743	9.3
HJA	Scots pine	73 ^c	23	Podzol	7.2	771	10.2

838 ^aNorway spruce is the dominating species but the stand also comprises pines.

839 ^bAn old pine forest with a dense stand of young spruces underneath (7-8 meters high).

840 ^cStand age in 2008.

841 ^dStand age in 2005, when the site was storm damaged.

842 ^eSite index, i.e. height in metres at the age of 100 years, based on assessment at site establishment.

843 ^fYearly mean (1981-2010) from SMHI (<http://luftweb.smhi.se/>).

844 ^gModelled yearly mean (2007-2009) of inorganic N deposition to forest, from the MATCH model (Langner
845 et al., 1996).

846

847

848 Table 3. Median values in soil water and significant ($p < 0.05$) increases (\uparrow) and decreases
 849 (\downarrow) for the time series. Medians are given in mg l^{-1} , except for ANC which is given in
 850 meq l^{-1} .

Site	SO ₄ -S	Cl	Na	Ca	Mg	K	NO ₃ -N ¹	NH ₄ -N ²	pH	ANC	Ali	DOC
ARK	11.9 \downarrow	22.0 \downarrow	11.4 \downarrow	3.9 \downarrow	2.5 \downarrow	0.1 \downarrow	0.08	<0.03	4.3	-0.43 \uparrow	4.2	17.3 \downarrow
KLI	3.8 \downarrow	15.2	8.1	0.8 \downarrow	0.9	1.2 \downarrow	<0.01	<0.03	4.5	-0.14 \uparrow	1.2 \downarrow	6.8 \downarrow
HEN	2.2 \downarrow	13.8	8.2	0.6 \downarrow	0.8 \downarrow	0.3 \downarrow	<0.01	<0.03	4.6	-0.06 \uparrow	0.9	8.9 \downarrow
RYS	8.4 \downarrow	12.0	8.2 \downarrow	2.6 \downarrow	1.1 \downarrow	0.3 \downarrow	<0.01	<0.03	4.3 \uparrow	-0.27 \uparrow	2.3 \downarrow	7.7
ALA	6.9 \downarrow	10.5	8.0 \downarrow	1.8	1.6 \downarrow	0.2	<0.01 \uparrow	<0.03 \uparrow	4.7	-0.16	1.6 \uparrow	5.0 \downarrow
SOS	3.1 \downarrow	17.9 \downarrow	11.0 \downarrow	1.0 \downarrow	1.6 \downarrow	0.5 \downarrow	<0.01	<0.03	4.8 \uparrow	-0.04 \uparrow	0.5 \downarrow	4.9 \downarrow
KNA	2.5	3.7 \uparrow	3.2 \uparrow	0.4	0.3	0.2	<0.01	<0.03	4.7 \uparrow	-0.06	0.8	5.9
SAV	1.9 \downarrow	5.5	4.4	0.9 \downarrow	0.5 \downarrow	0.1 \downarrow	<0.01	<0.03	4.8 \uparrow	-0.01 \uparrow	0.5 \downarrow	10.8 \downarrow
HJA	2.8 \downarrow	5.6	4.3	0.5 \downarrow	0.3 \downarrow	0.5	<0.01	<0.03	4.5 \uparrow	-0.10 \uparrow	1.1 \downarrow	6.4 \downarrow

851 ¹ Quantification limit for NO₃-N is 0.01 mg l^{-1} .

852 ² Quantification limit for NH₄-N is 0.03 mg l^{-1} .
 853