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

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1 Title:

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

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Abstract

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

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

1. Introduction

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

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

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

2. Materials and methods

2.1 The SWETHRO network – measurements and chemical analyses

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

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

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

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

The water samples are analysed for pH, alkalinity and conductivity. The samples are then filtrated using a cellulose acetate filter (0.8 μ m). A small subsample is preserved with sulphuric acid (H₂SO₄) and analyzed for Kjeldahl-N and NH₄-N. Another subsample is preserved with nitric acid (HNO₃) for analysis of Fe and Al. The remaining sample volume is used for the remaining analyses. All samples are stored in a fridge before analysis.

SO₄-S, NO₃-N, Cl, Ca, Mg, Na, K, Mn are analysed by Ion Chromatography (IC) using Dionex chromatographs, the anions according to SS-EN ISO 10304-1 and the cations

according to SS-EN ISO 14911. $\text{NH}_4\text{-N}$ is analysed by Flow Injection Analysis (FIA) with spectrophotometric detection according to the modified SS-EN ISO 11732. During the FIA analysis the sample is mixed with sodium hydroxide. Ammonium is then transformed to ammonia, which is separated from the sample by passing it through a membrane. A color indicator takes up ammonia and the sample then passes through a spectrophotometer. The results are calculated from the absorbance at 590 nm. Kjeldahl-N is measured according to Foss-Tecators method AN 52212002-10-24. Fe and Al are measured with ICP-MS according to SS-EN ISO 17294-2:2005. Organic and inorganic Al is separated using ion exchange according to the “Driscoll method” (Driscoll, 1984). The analysis of DOC in soil water is done with NDIR. The DOC analysis leads to a small overestimation of the values since the filter size is 0.8 μm , whereas DOC is normally based on a filter size of 0.45 μm .

2.2 Study sites

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

FIG. 1

TABLE 1, 2

2.3 Data processing and time series analysis

The results from the soil water chemistry analysis were scrutinized, e.g. through the use of charge balance tests (de Vries et al., 2003), and obvious unrealistic data were removed.

At some sampling occasions no soil water samples could be obtained due to dry conditions. The time series contained between 51 and 68 data records per site. In all, 14 data records were not used due to small water amounts sampled (<50 ml). Information on water volume exists only from 1998 onwards, so possible earlier occasions with small water amounts could not be identified.

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

3. Results and discussions

3.1 Throughfall deposition

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

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

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

FIG. 2

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

FIG. 3

FIG. 4

3.2 Soil water chemistry

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

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

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

In order to separate short-term effects caused by sea salt episodes and storms from long-term trends caused by reduced acid deposition, the soil water trends for base cations, acidification indicators, N and DOC were interpreted in light of the soil water trends for $\text{SO}_4\text{-S}$ and Cl, along with information about storm events.

TABLE 3

3.2.1 $\text{SO}_4\text{-S}$ concentrations

The reduced $\text{SO}_4\text{-S}$ deposition is reflected in reduced $\text{SO}_4\text{-S}$ concentrations in eight of the nine sites (Fig. 5, Table 3). The most pronounced decrease occurred in ARK, where the concentration decreased from around 15 to 3 mg l^{-1} . This site also stands out through a large variation on short time-scales, seen in many of the parameters. A possible explanation could be large variations in the hydrological conditions on the site that is situated on a slope (Table 1). The decrease in $\text{SO}_4\text{-S}$ concentrations was also relatively large in RYS and ALA, from around 10 to 5 mg l^{-1} . On the other sites the concentration decreased from around 5 to 1-3 mg l^{-1} , with KNA as an exception, where the concentration was between 2 and 3 mg l^{-1} during most of the period. A comparison between the $\text{SO}_4\text{-S}$ deposition (Fig. 2) and S concentrations in soil solution (Fig. 5) shows that the decrease in $\text{SO}_4\text{-S}$ concentration in the soil solution was generally lower than the reduction in $\text{SO}_4\text{-S}$ deposition. The less pronounced effect in soil water can be explained

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

3.2.2 Cl and Na concentrations

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

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

3.2.3 Ca, Mg and K concentrations

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

The Mg concentration decreased significantly on seven of the sites (Fig. 9, Table 3). The large-scale decreasing trend can also be explained mainly by the decreased $\text{SO}_4\text{-S}$ deposition leading to reduced net charge. However, the trends are strengthened by the strong salt episodes in the beginning of the 1990s, due to increased deposition of Mg and increased release of Mg through ion exchange.

The K concentration showed a significantly decreasing trend on six of the sites (Fig. 10, Table 3). Just like for Ca and Mg, the reduced input of $\text{SO}_4\text{-S}$ and the sea salt episodes in the beginning of the 1990s can explain the major patterns. ALA had a decreasing trend before 2005, but after storm felling the concentrations increased substantially from below 0.5 mg l^{-1} to more than 4 mg l^{-1} due to disrupted uptake by the trees. In KNA, where the site was damaged in the storms 2005 and 2007, but not completely storm-felled, there was a smaller increase in K concentrations after the storm. The high concentrations in ARK in the beginning of the period coincide with high concentrations of $\text{NH}_4\text{-N}$ (Fig. 12). The reason for this is not known, but it is probably related to some kind of soil disturbance, possibly due to lysimeter installation.

3.2.4 Inorganic N concentrations

The concentrations of inorganic N below the root zone are generally low in undisturbed northern forest ecosystems, since they are generally nitrogen limited (Tamm, 1991). This was also the case in eight of the sites (Fig. 11-12). Only in ARK were highly elevated concentrations of both $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ regularly measured. The site was thinned in

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

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

3.2.5 pH, ANC and Ali

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

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

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

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

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

KNA and ALA were storm-damaged in 2005 and 2007, and the later measurements were strongly affected by the changed conditions. The increased input of organic material at a storm-felling, or at a normal clear-felling, may affect the pH positively (Nykqvist and Rosén, 1985; Piirainen et al., 2004). However, increased nitrification and NO₃-N leaching during the years after clear-cutting may temporarily counteract this (Akselsson et al., 2004). In ALA, ANC was negative during the whole period, -0.3 meq l⁻¹ at the lowest, pH was around 4.7 and the concentration of Ali 1-2 mg l⁻¹. There were no signs of recovery. On the contrary, there was a significant increase in Ali, which appeared before 2005 and thus cannot be explained by the storm felling. There was no clear effect of the storm-felling, except for a low pH, 4.1, in the last measurement in the period, which can be explained by nitrification and NO₃-N leaching following the clearcut (Fig. 11). In KNA, ANC was generally between 0 and -0.2 meq l⁻¹, pH between 4.5 and 4.7 and the concentration of Ali between 0.5 and 1.5 mg l⁻¹. There seemed to be a tendency towards somewhat increased ANC before 2005, but there was no significant trend for the whole period. There was no significant trend for Ali either. For pH there was a weak significant increase, but it was mainly due to a temporary increase in pH after the storm felling. The

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

3.2.6 DOC

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

FIG. 5-16

3.3 Acidification status and recovery

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

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

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

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

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

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

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

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

If the critical wind speeds from southern wind directions do increase in the future, it can increase the risk for storm-fellings. Changes to ground frost from warming and reduced snow cover can likewise increase the risk, as the “anchoring” of trees is affected. Storm-fellings can have about the same effect on $\text{NO}_3\text{-N}$ leaching and soil acidification as normal clear-fellings. A difference is, however, that storm-fellings can affect a large part of the landscape at the same time, which increases the risk of effects on surface waters. Increased nitrification during some years after clear-cutting leads to increased $\text{NO}_3\text{-N}$ leaching (Akselsson et al., 2004) and may lower pH temporarily. The effect on pH is counteracted by the increased input of organic material that stimulates decomposition and has a positive effect on pH (Nykqvist and Rosén, 1985; Piirainen et al., 2004). The net effect on pH depends on site-specific factors, for example the N status of the soil. For example, in KNA there was a pH increase after the storm-felling whereas ALA showed no clear effects except from the most recent pH measurement which showed a very low pH, probably due to nitrification and the subsequent $\text{NO}_3\text{-N}$ leaching. The clearcut effect on $\text{NO}_3\text{-N}$ leaching often last 5-6 years with a peak after a couple of years (Futter et al., 2010), thus effects can be expected over the next few years.

One of the sites, ARK, showed chronically elevated $\text{NO}_3\text{-N}$ concentrations in soil water, indicating N saturation. Since the nitrification process is acidifying if the $\text{NO}_3\text{-N}$ is leached, this also leads to acidification. There are several other sites with chronically

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

4. Conclusions

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

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

led to a marked acidification peak in the beginning of the period, it was difficult to evaluate the relative importance of reduced $\text{SO}_4\text{-S}$ deposition and “recovery” from sea salt episodes for the trends in pH, ANC and Ali in soil water. Sea salt episodes can be expected to continue to appear and will cause transient acidification episodes for soil water and surface water in southwestern Sweden as long as the soils are acidic.

- For most of the sites the $\text{SO}_4\text{-S}$ concentration in soil water did not decrease to the same extent as the $\text{SO}_4\text{-S}$ deposition, which highlights the importance of desorption of previously adsorbed SO_4^{2-} . The response differed widely between the sites, which could partly be explained by differences in DOC concentrations.
- One of the sites showed persistently elevated concentrations of $\text{NO}_3\text{-N}$, indicating that the N retention capacity is exceeded on the site. The high $\text{NO}_3\text{-N}$ concentrations coincided with very low pH. The results from the site highlight the importance of N retention in counteracting eutrophication and acidification.
- The two storm-felled sites showed substantially increased $\text{NO}_3\text{-N}$ concentrations, similar to the effects of clear-cutting. The initial effect on pH differed between the sites, but the time period was too short to allow general conclusions to be drawn. If a large part of a landscape is storm-felled in the regions where deposition of $\text{SO}_4\text{-S}$ and inorganic N has been high, there is a risk of episodes of N-leaching and surface water acidification.

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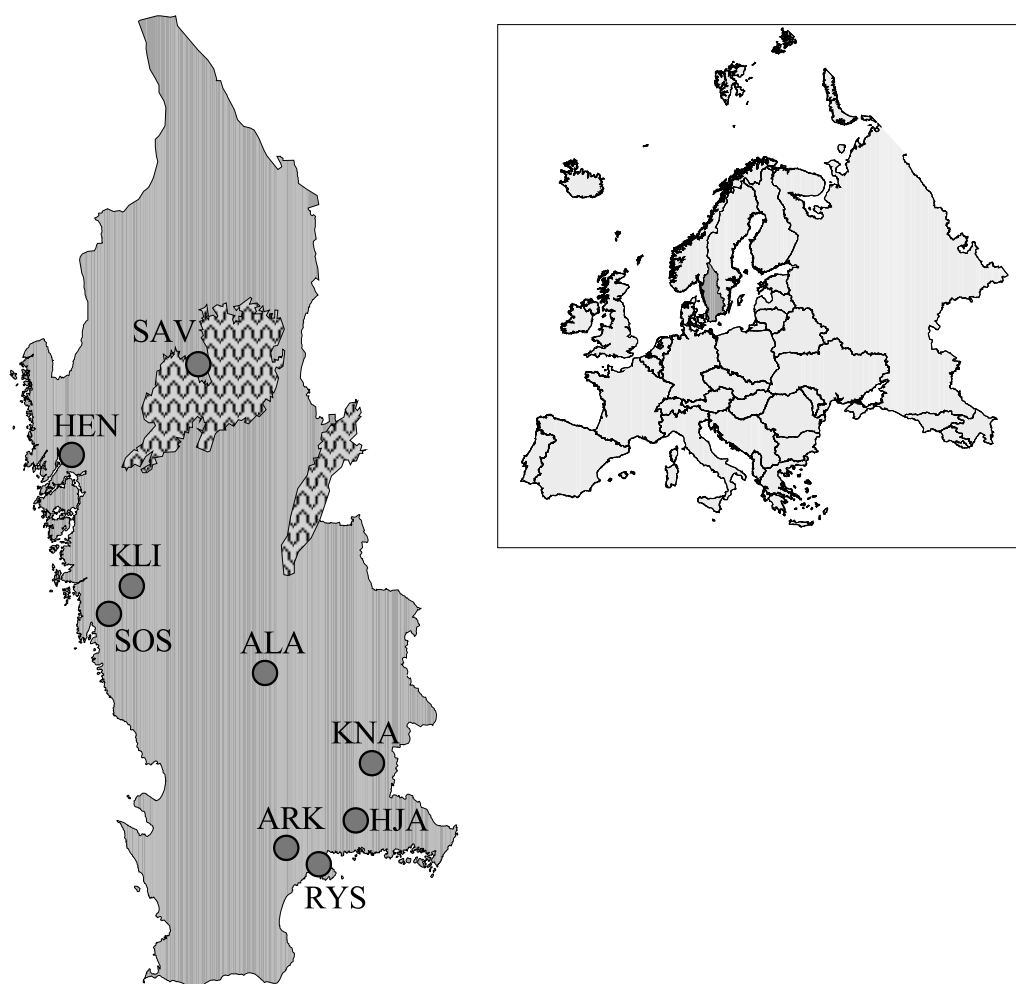
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750

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

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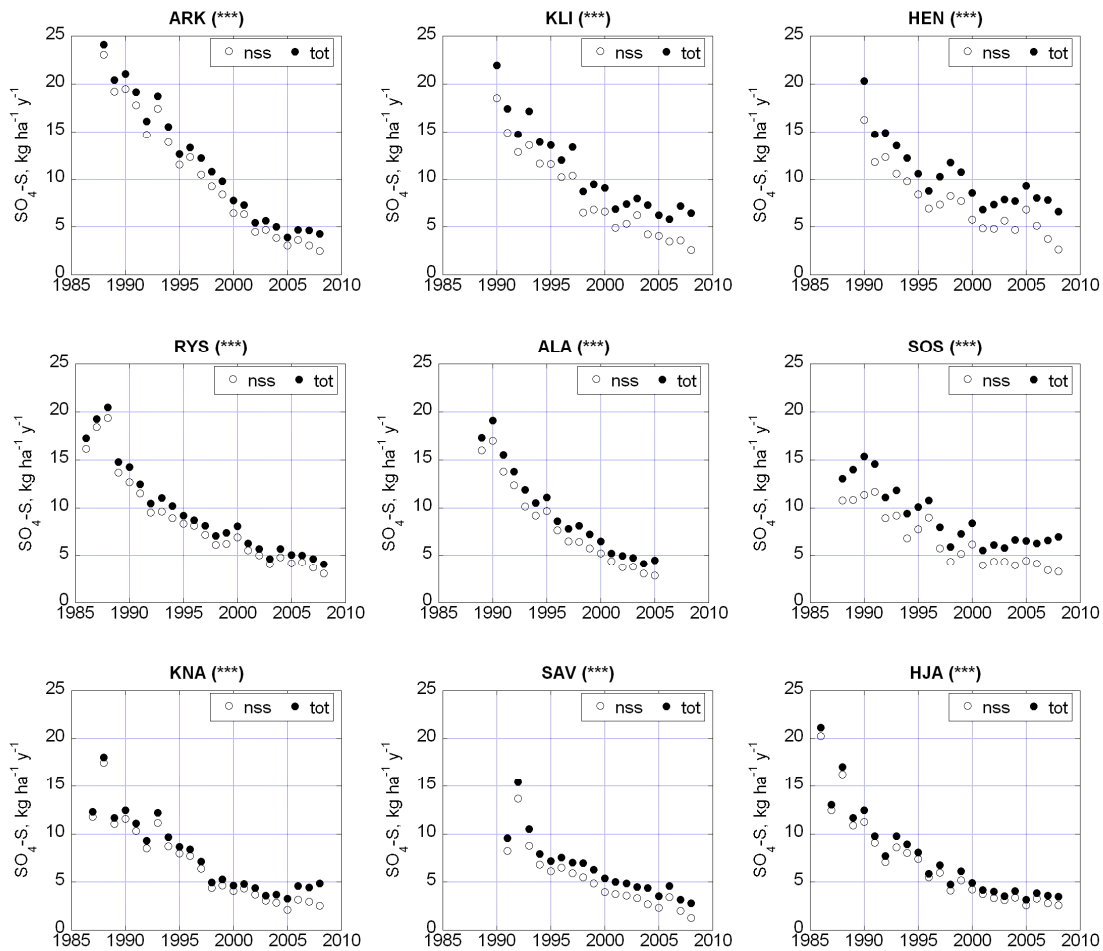


Fig. 2. Total (tot) and non sea salt (nss) throughfall deposition of $\text{SO}_4\text{-S}$. Significance level (Mann-Kendall) is given within brackets in the case of a significant trend, where one, two and three stars corresponds to $p < 0.05$, $p < 0.01$ and $p < 0.001$.

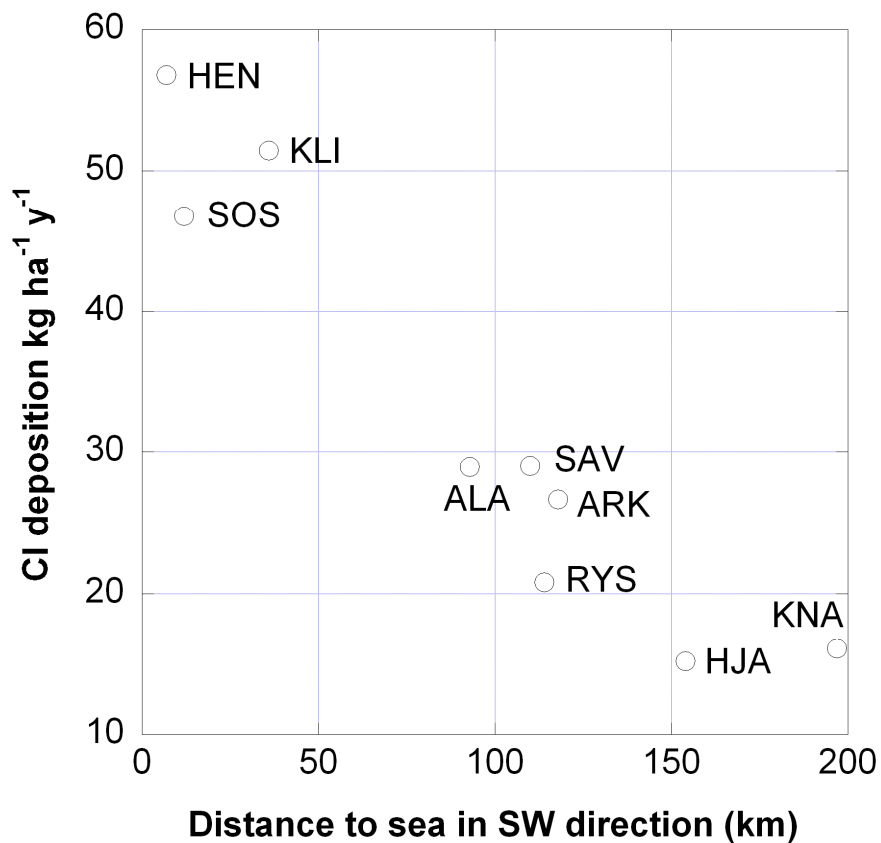


Fig. 3. Average chloride deposition (1991-2005) as a function of distance to sea in the southwest direction for the nine sites. For RYS, the winds from SW touches the coastline along the east coast, but the sea salt influence from there was assumed to be minor due to the short path over sea, and thus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

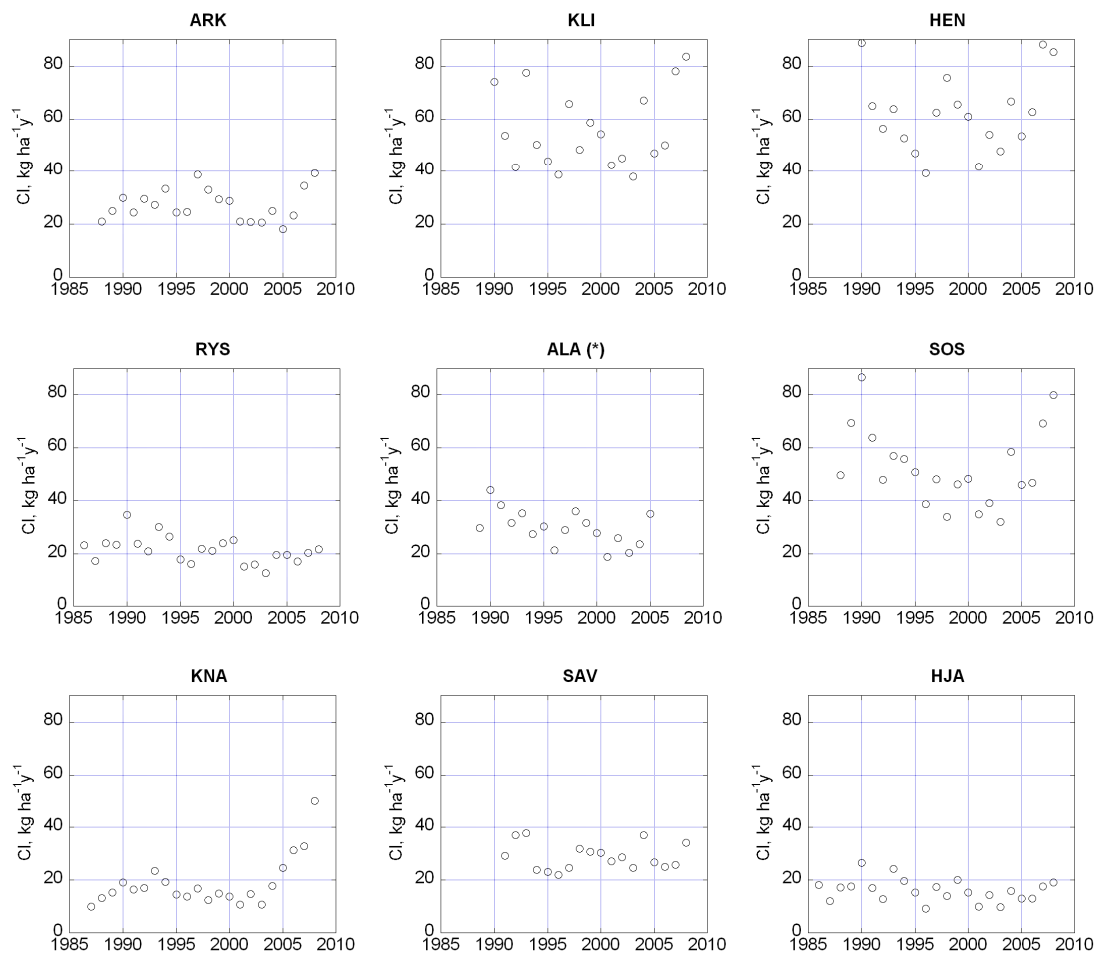


Fig. 4. Throughfall deposition of Cl. Significance level (Mann-Kendall) is given within brackets in the case of a significant trend, where one, two and three stars corresponds to $p < 0.05$, $p < 0.01$ and $p < 0.001$.

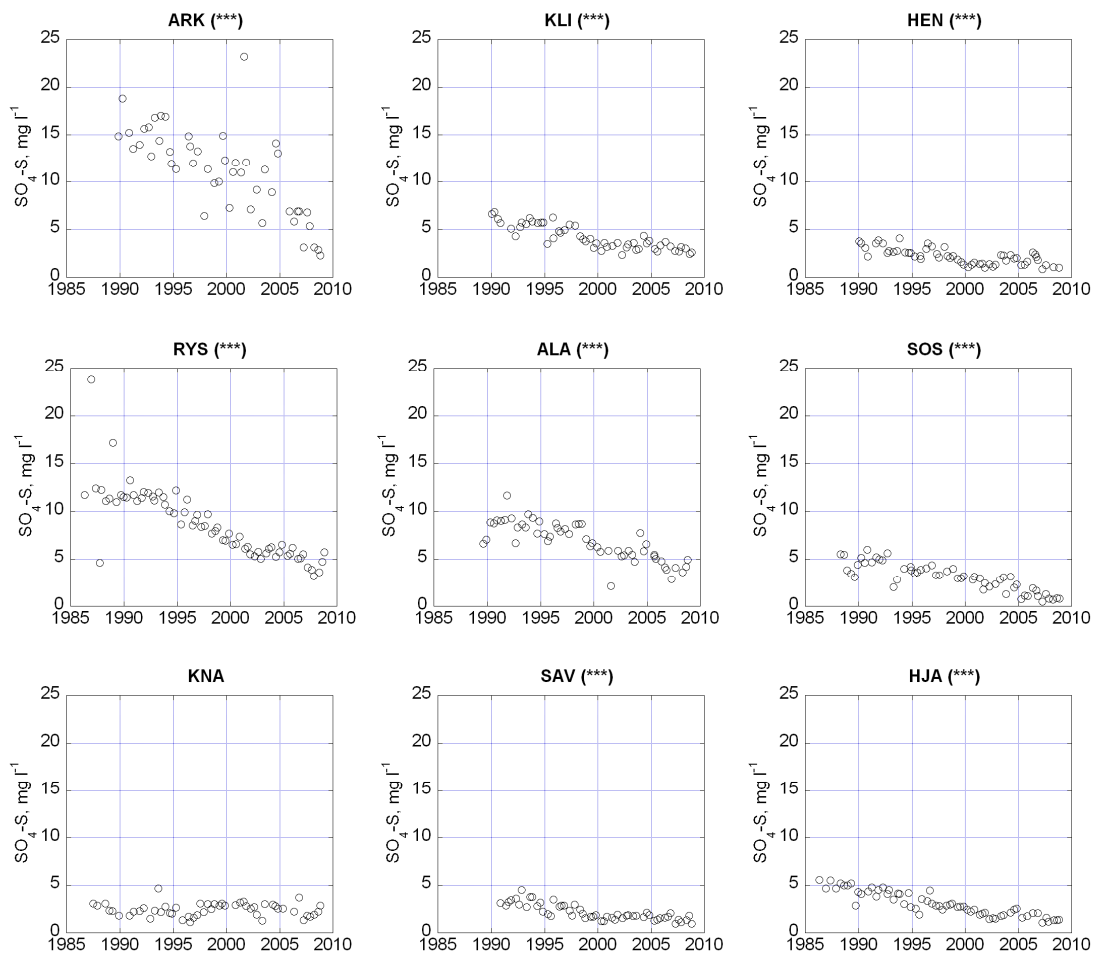


Fig. 5. Sulphur ($\text{SO}_4\text{-S}$) concentration (mg l^{-1}) in soil water. Significance level (Seasonal-Kendall) is given within brackets in the case of a significant trend, where one, two and three stars corresponds to $p < 0.05$, $p < 0.01$ and $p < 0.001$.

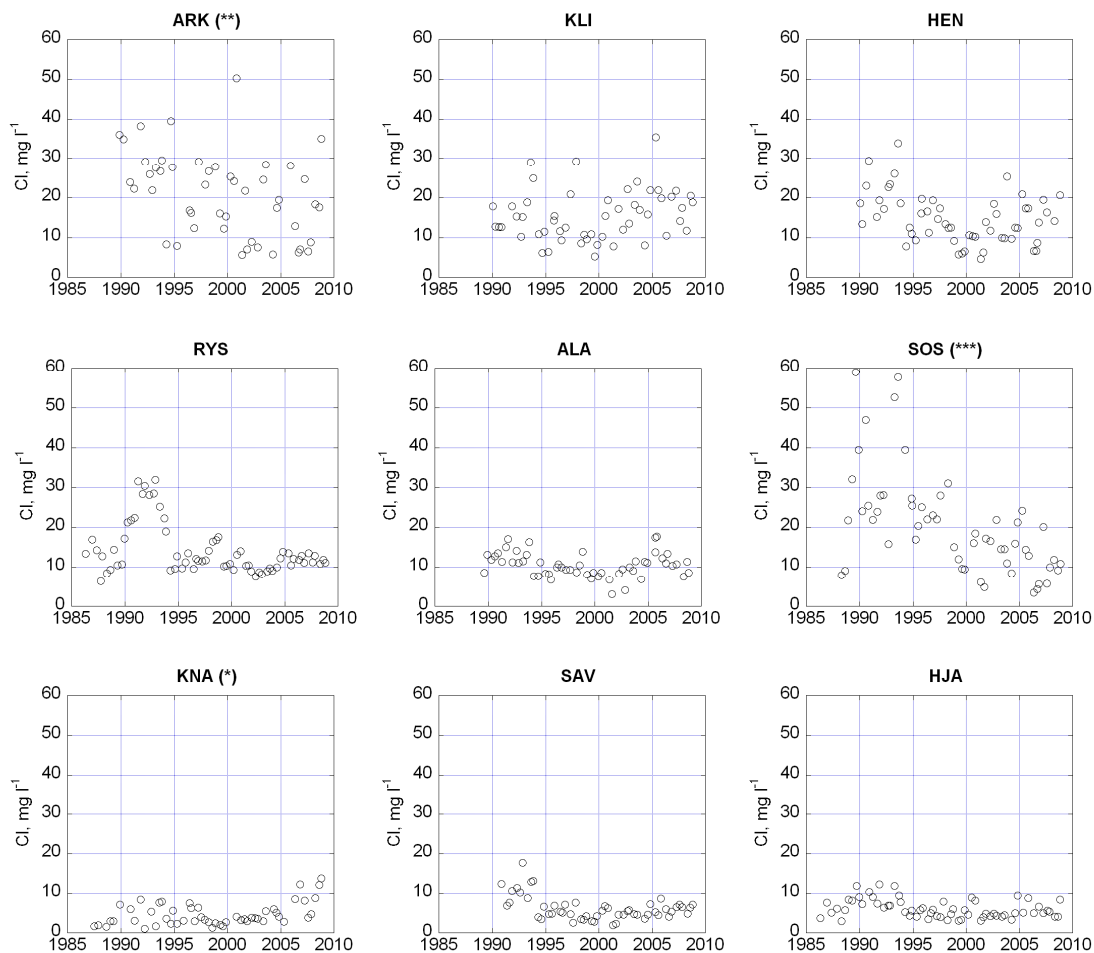


Fig. 6. Chloride (Cl) concentration (mg l^{-1}) in soil water. Significance level (Seasonal-Kendall) is given within brackets in the case of a significant trend, where one, two and three stars corresponds to $p < 0.05$, $p < 0.01$ and $p < 0.001$.

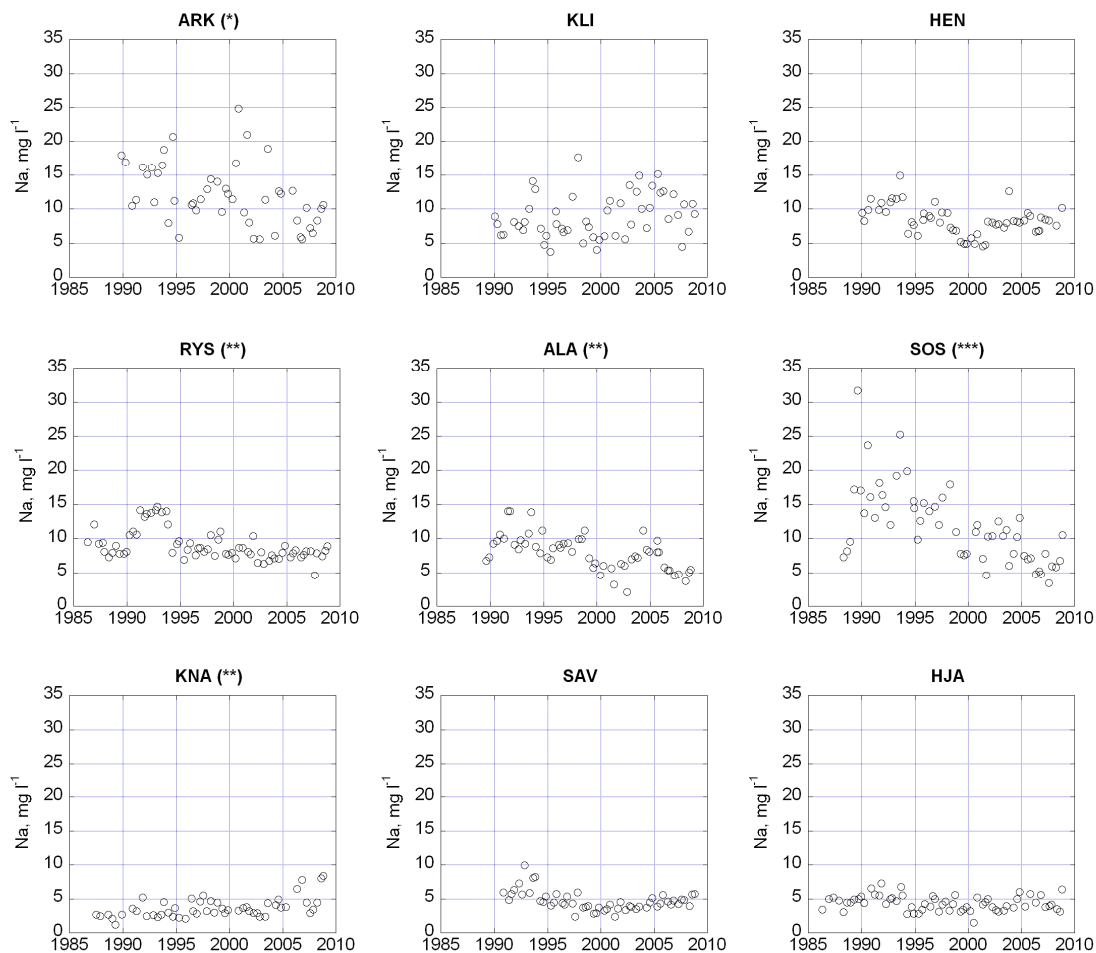


Fig. 7. Sodium (Na) concentration (mg l⁻¹) in soil water. Significance level (Seasonal-Kendall) is given within brackets in the case of a significant trend, where one, two and three stars corresponds to $p < 0.05$, $p < 0.01$ and $p < 0.001$.

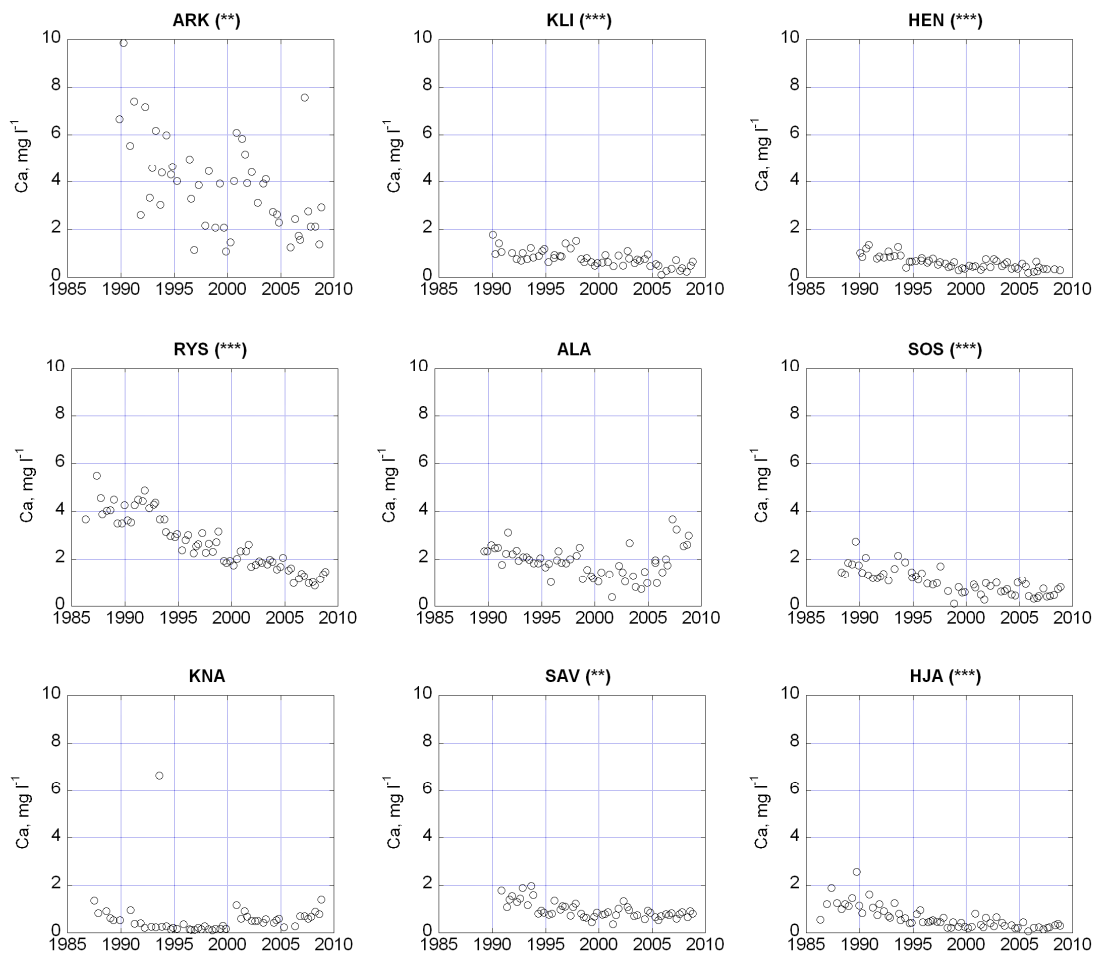


Fig. 8. Calcium (Ca) concentration (mg l⁻¹) in soil water. Significance level (Seasonal-Kendall) is given within brackets in the case of a significant trend, where one, two and three stars corresponds to $p < 0.05$, $p < 0.01$ and $p < 0.001$.

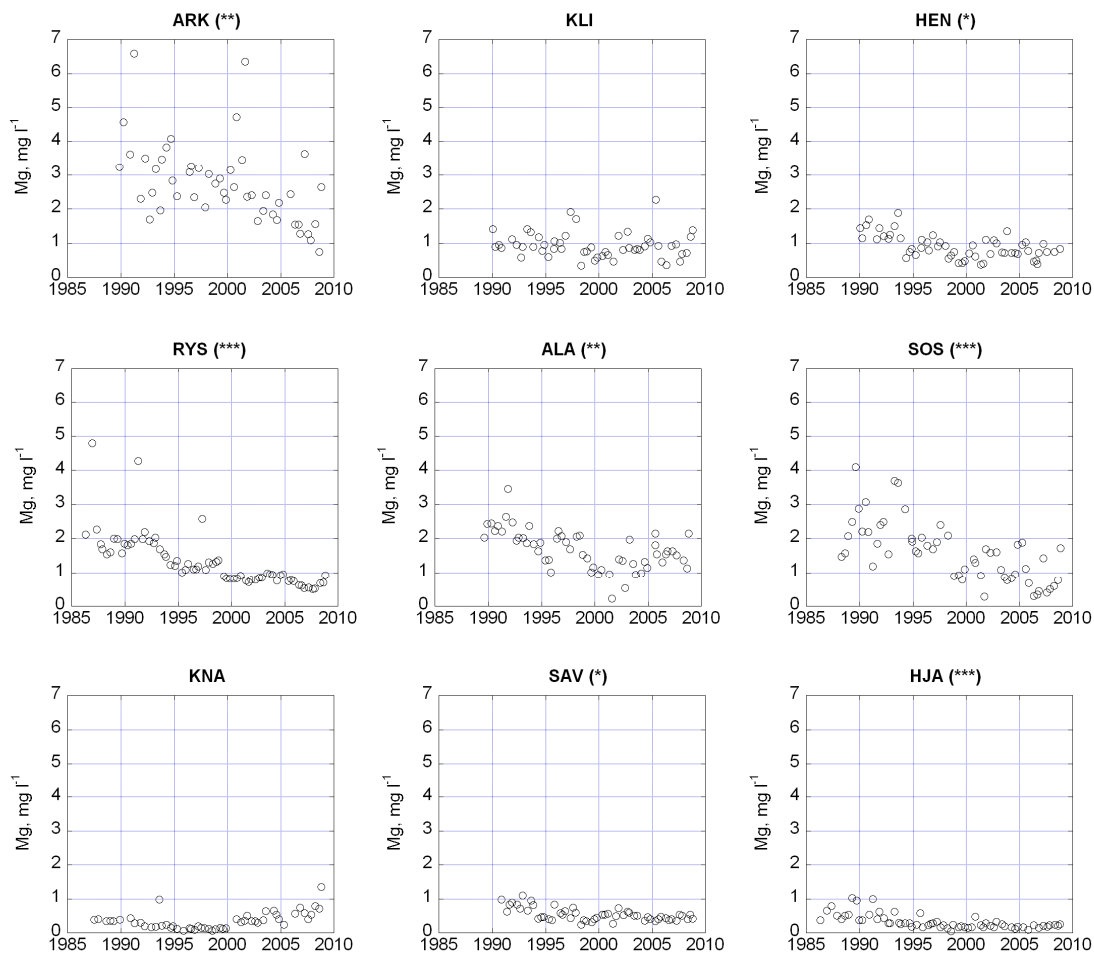


Fig. 9. Magnesium (Mg) concentration (mg l⁻¹) in soil water. Significance level (Seasonal-Kendall) is given within brackets in the case of a significant trend, where one, two and three stars corresponds to $p < 0.05$, $p < 0.01$ and $p < 0.001$.

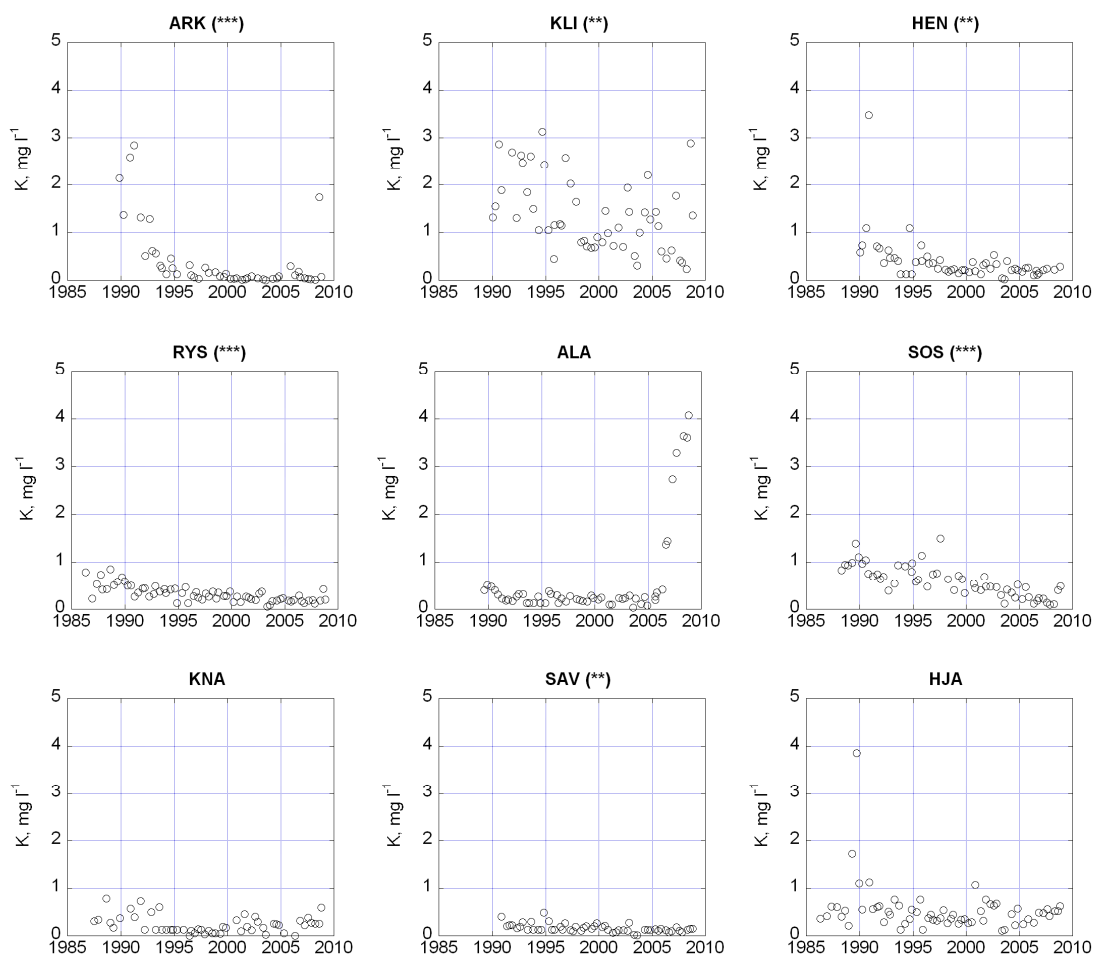


Fig. 10. Potassium (K) concentration (mg l⁻¹) in soil water. Significance level (Seasonal-Kendall) is given within brackets in the case of a significant trend, where one, two and three stars corresponds to $p < 0.05$, $p < 0.01$ and $p < 0.001$.

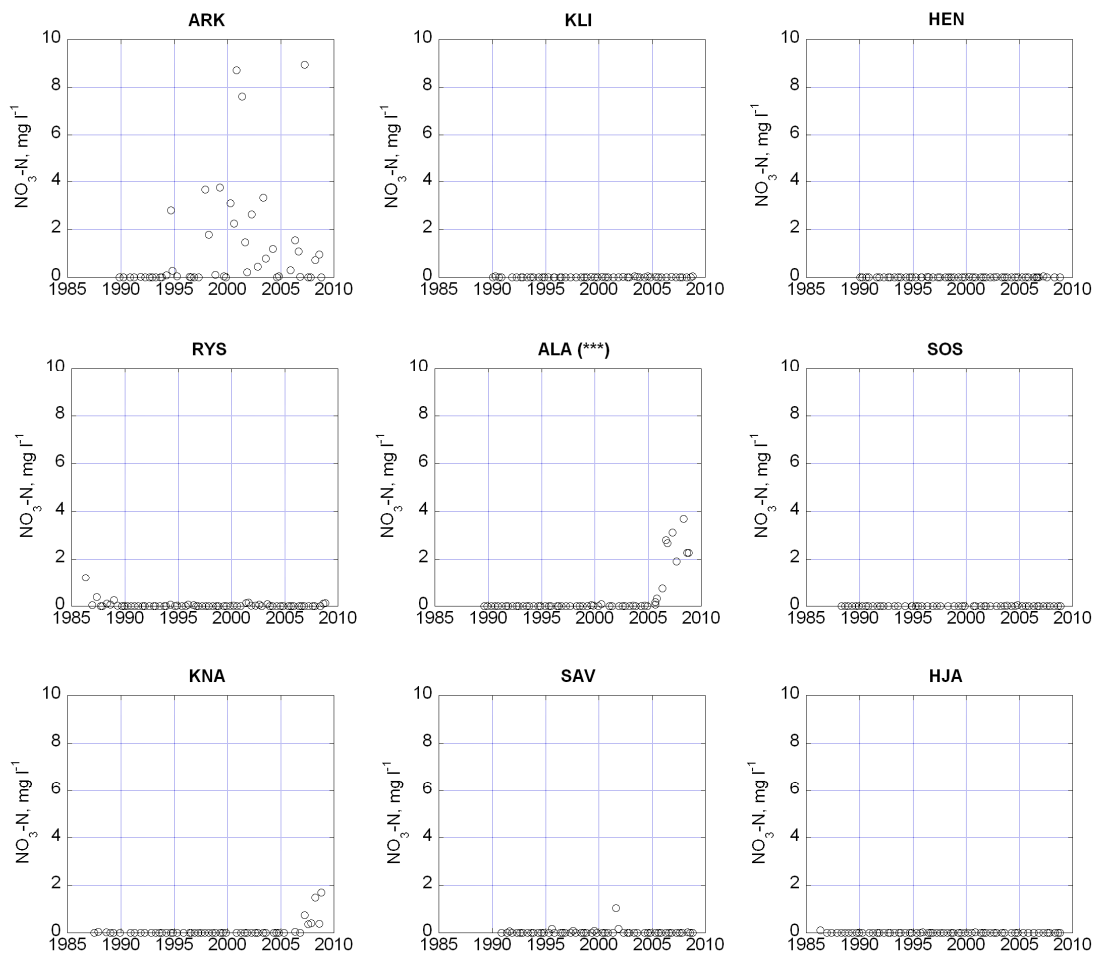


Fig. 11. Nitrate nitrogen ($\text{NO}_3\text{-N}$) in soil water (mg l^{-1}). Significance level (Seasonal-Kendall) is given within brackets in the case of a significant trend, where one, two and three stars corresponds to $p < 0.05$, $p < 0.01$ and $p < 0.001$.

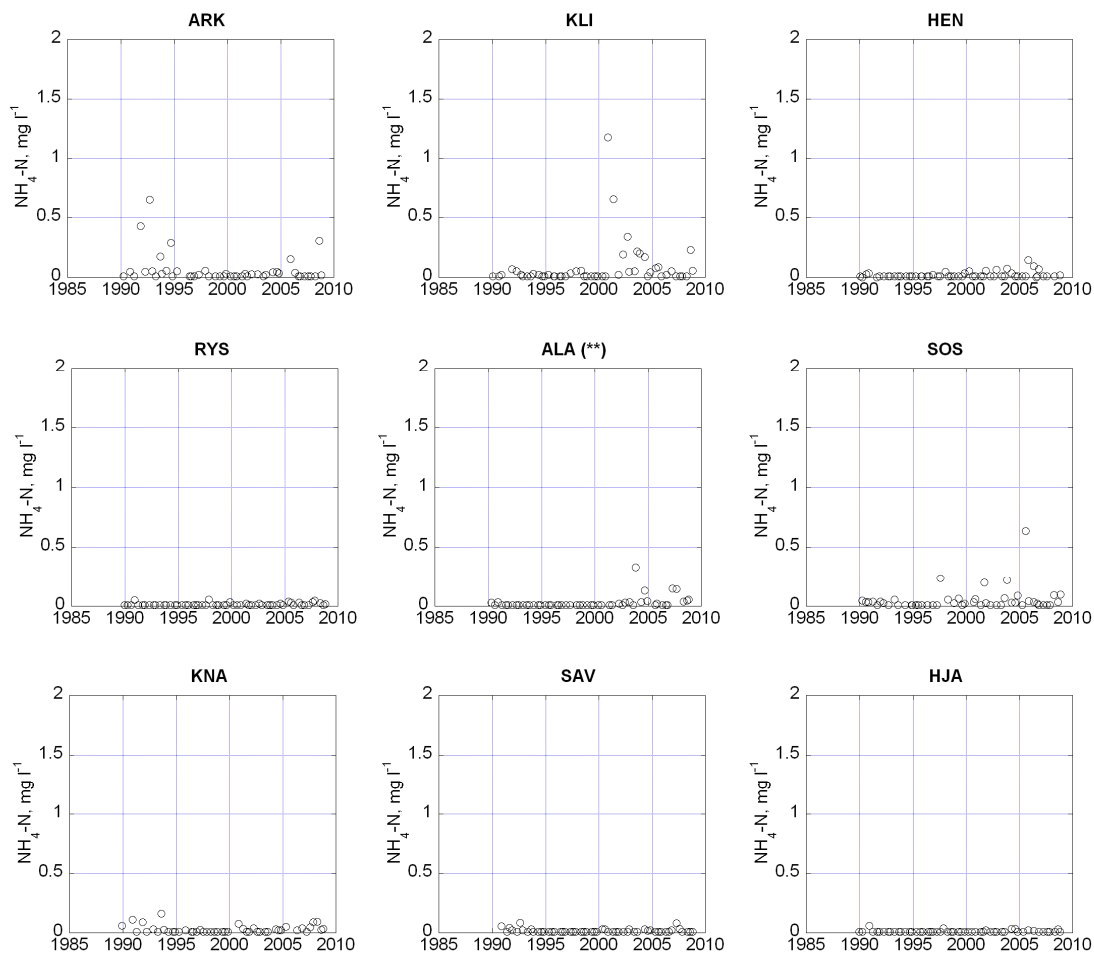


Fig. 12. Ammonium nitrogen (NH₄-N) in soil water (mg l⁻¹). Significance level (Seasonal-Kendall) is given within brackets in the case of a significant trend, where one, two and three stars corresponds to p<0.05, p<0.01 and p<0.001.

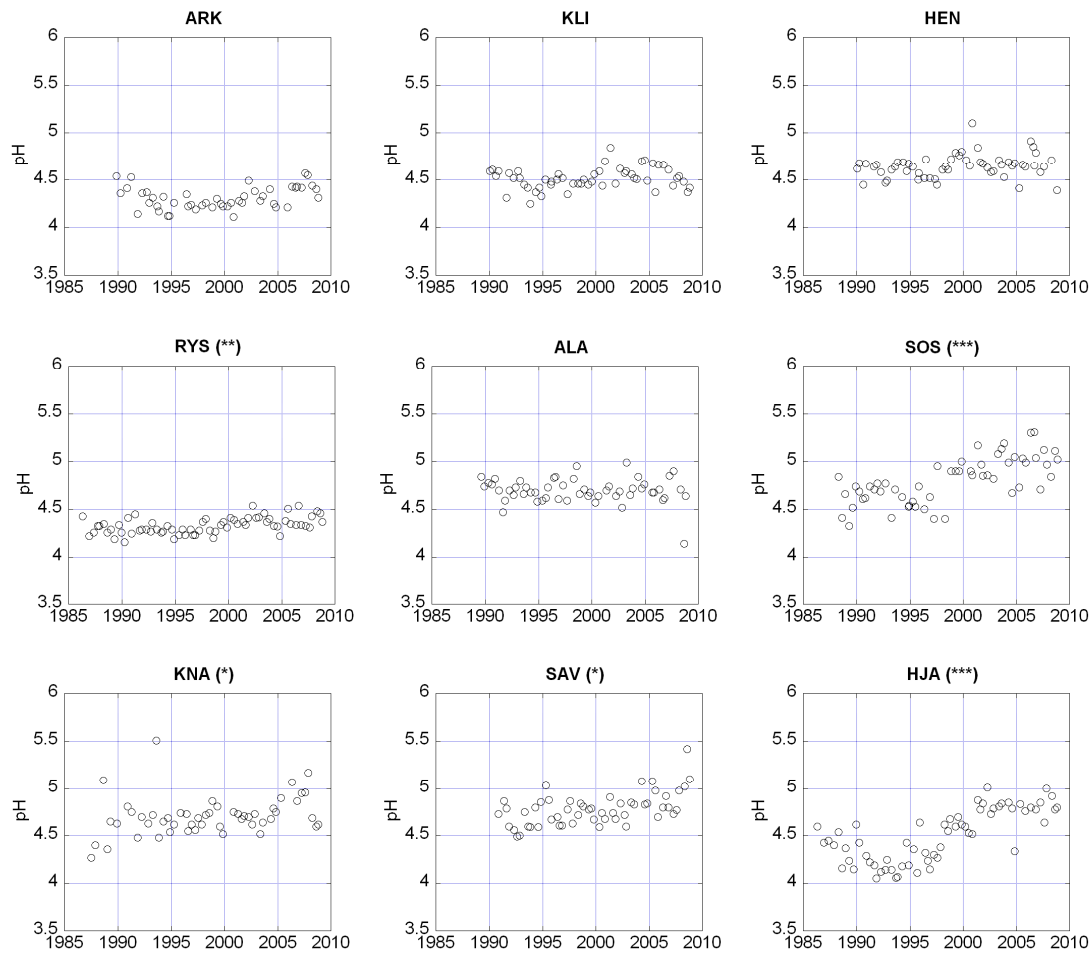


Fig. 13. pH in soil water. Significance level (Seasonal-Kendall) is given within brackets in the case of a significant trend, where one, two and three stars corresponds to $p < 0.05$, $p < 0.01$ and $p < 0.001$.

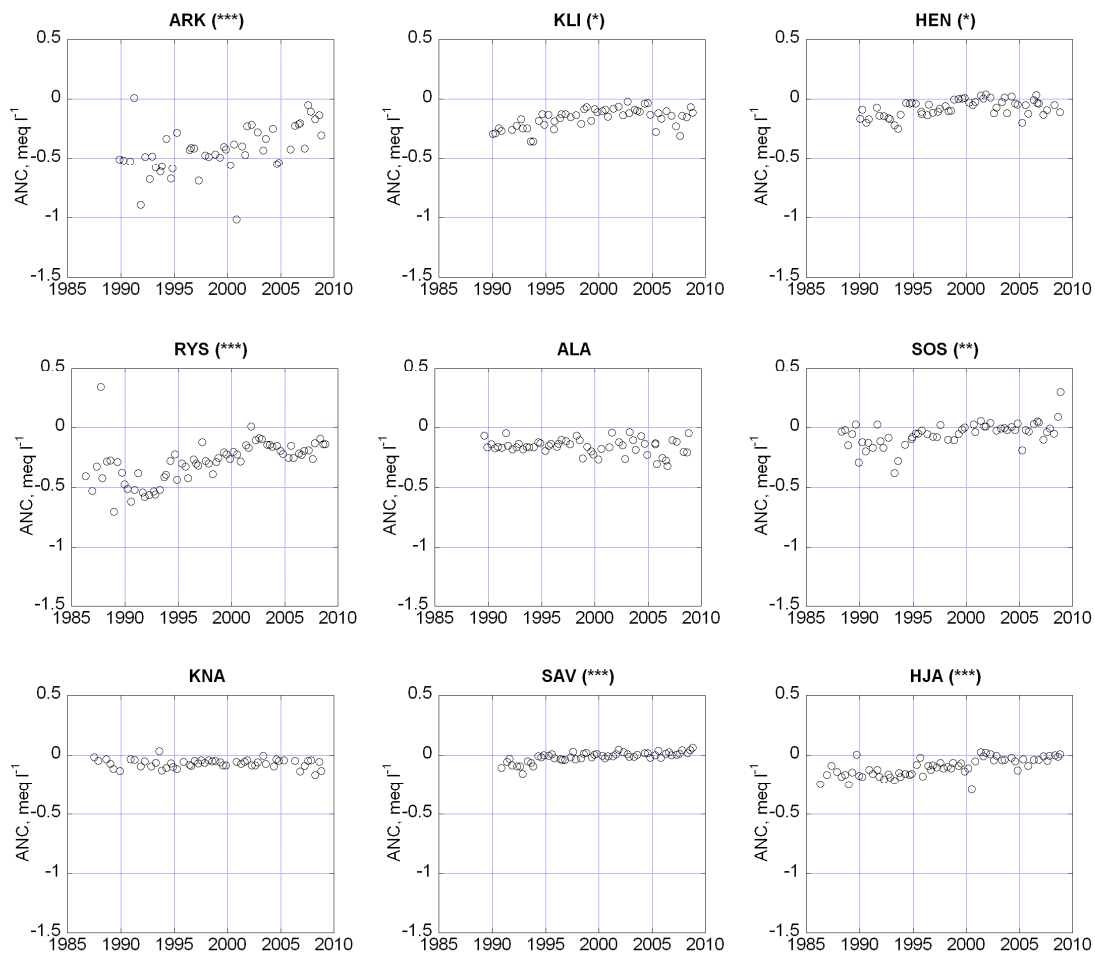


Fig. 14. ANC in soil water (meq l⁻¹). Significance level (Seasonal-Kendall) is given within brackets in the case of a significant trend, where one, two and three stars corresponds to $p < 0.05$, $p < 0.01$ and $p < 0.001$.

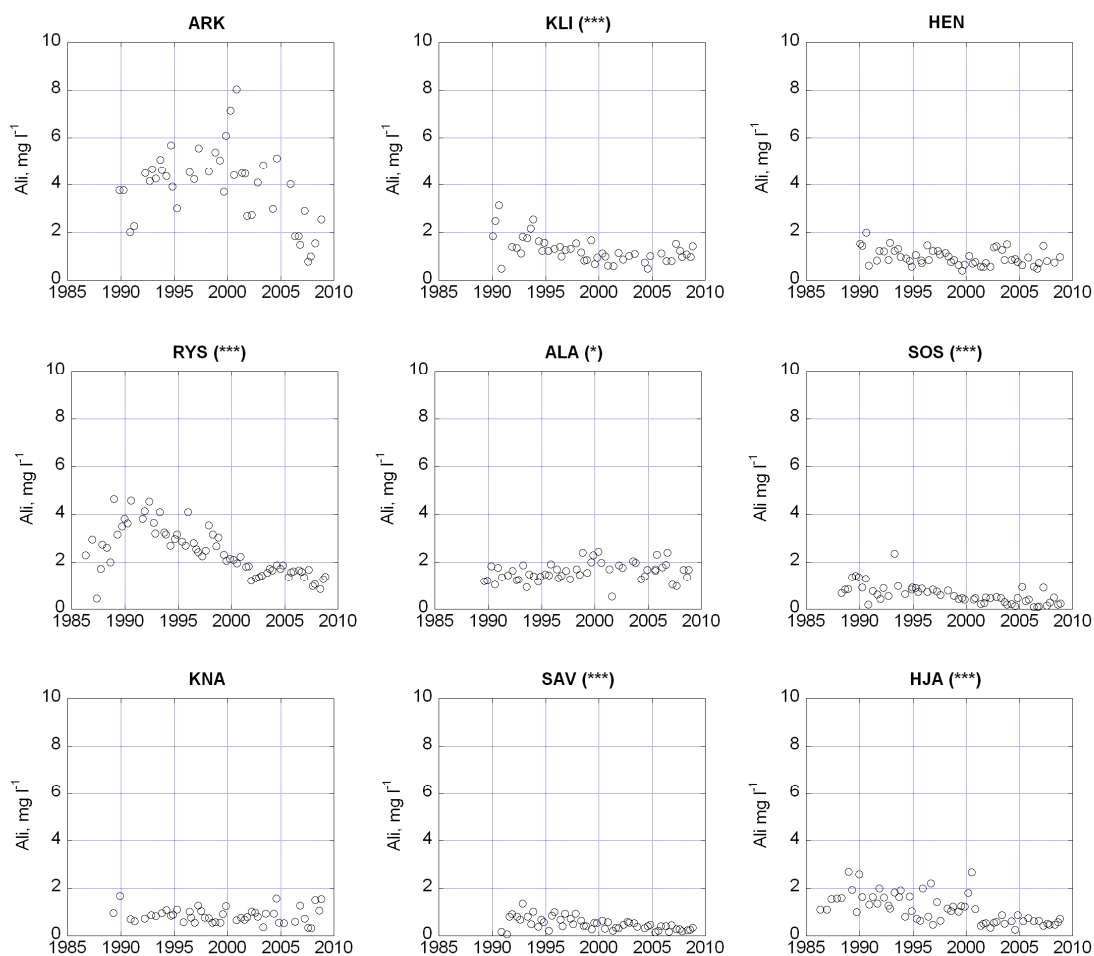


Fig. 15. Inorganic aluminium, Ali, in soil water (mg l^{-1}). Significance level (Seasonal-Kendall) is given within brackets in the case of a significant trend, where one, two and three stars corresponds to $p < 0.05$, $p < 0.01$ and $p < 0.001$.

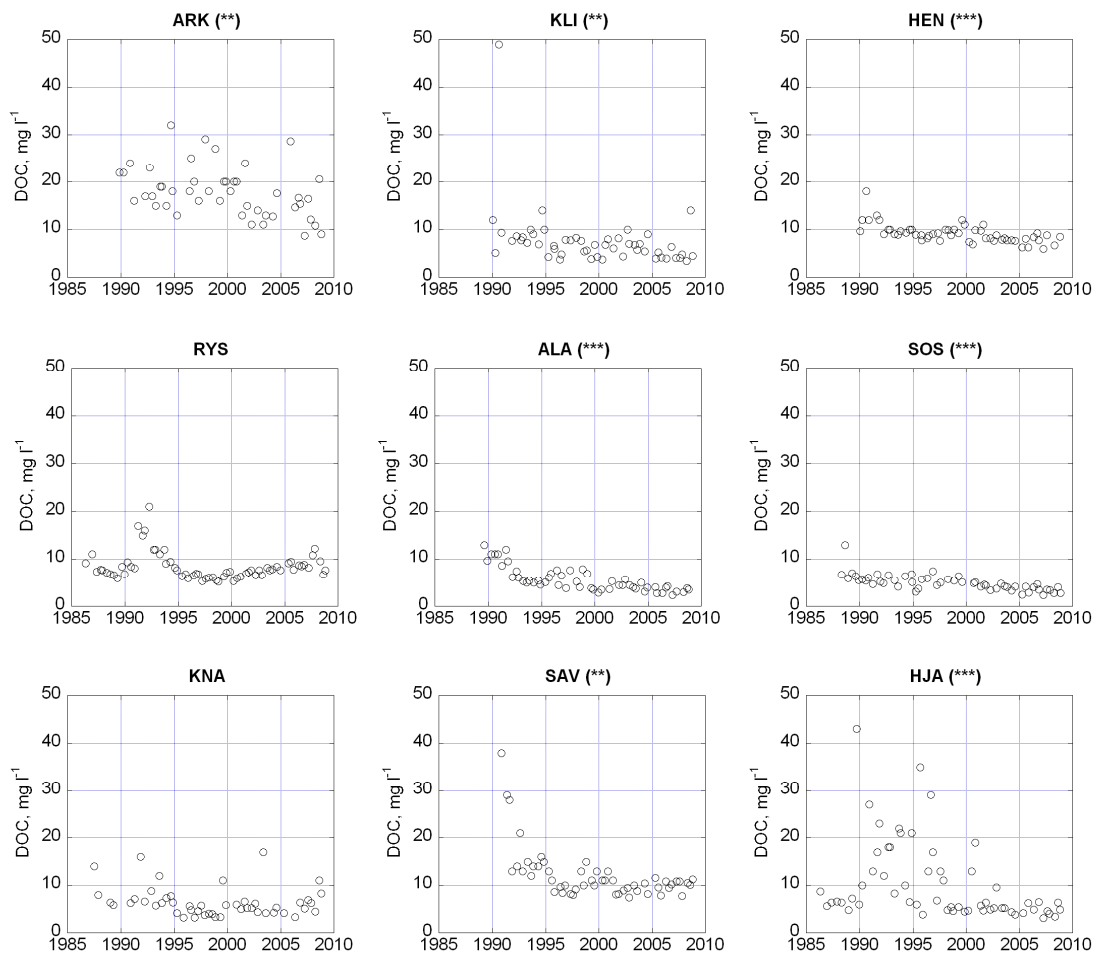


Fig. 16. DOC in soil water (mg l^{-1}). Significance level (Seasonal-Kendall) is given within brackets in the case of a significant trend, where one, two and three stars corresponds to $p < 0.05$, $p < 0.01$ and $p < 0.001$. Note that the filter size used was $0.8 \mu\text{m}$ in contrast to the standard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

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).

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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} .

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