

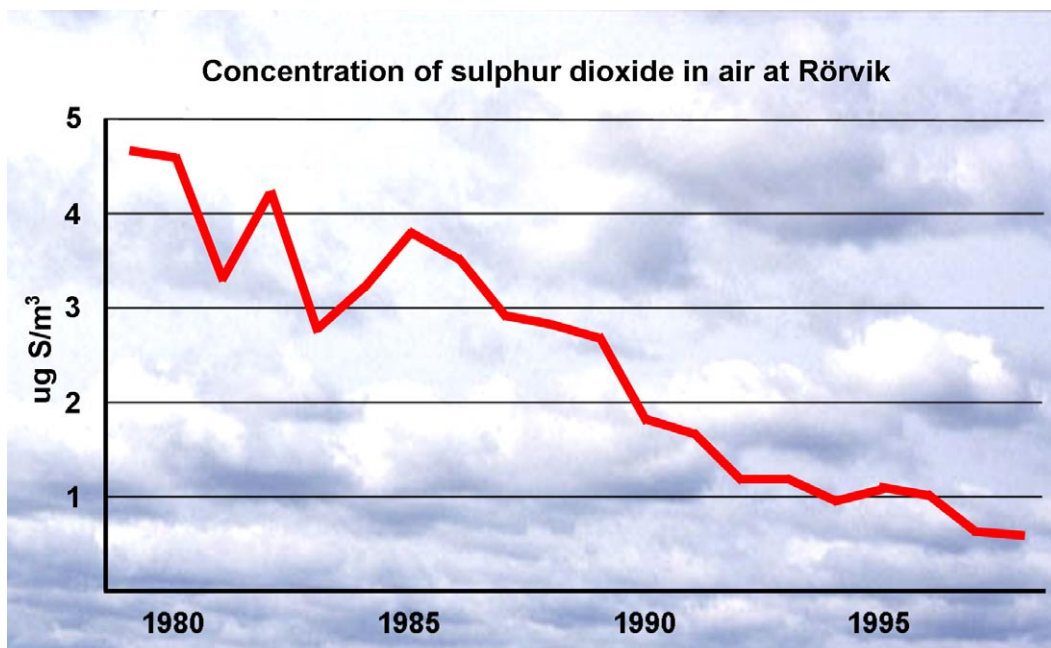


# report

IVL Swedish Environmental Research Institute

## Trends in air concentration and deposition at background monitoring sites in Sweden

- major inorganic compounds, heavy metals and ozone



Karin Kindbom, Annika Svensson, Karin Sjöberg, Gunilla Pihl Karlsson

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<b>Sammanfattning/Summary</b> <p>This report describes concentrations in air of sulphur compounds, soot, nitrogen compounds and ozone in Sweden between 1985-1998. Time trends of concentration in precipitation and deposition of sulphate, nitrate, ammonium, acidity, base cations and chloride in six different regions covering Sweden are evaluated during the period 1983-1998. Trends of heavy metals in precipitation have been analysed for the period 1983-1998 and the change in heavy metal concentration, 1975-1995, in mosses is described.</p> <p>Data used in the trend analyses originates from measurements performed at six Swedish EMEP stations and from approximately 25 stations within the national Precipitation Chemistry Network. Two different statistical methods, linear regression and the non-parametric Mann Kendall test, have been used to evaluate changes in annual mean values.</p>	
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## **SUMMARY**

This report describes concentrations in air of sulphur compounds, soot, nitrogen compounds and ozone in Sweden between 1985-1998. Time trends of concentration in precipitation and deposition of sulphate, nitrate, ammonium, acidity, base cations and chloride in six different regions covering Sweden are evaluated during the period 1983-1998. Trends of heavy metals in precipitation have been analysed for the period 1983-1998 and the change in heavy metal concentration, 1975-1995, in mosses is described.

Data used in the trend analyses originates from measurements performed at six Swedish EMEP stations and from approximately 25 stations within the national Precipitation Chemistry Network.

Two different statistical methods, linear regression and the non-parametric Mann Kendall test, have been used to evaluate changes in annual mean values.

Time trends of concentration of sulphur dioxide, particulate sulphate, soot, nitrogen dioxide, total nitrate and total ammonium in air show highly significant decreasing trends, except for soot at one station in northern Sweden. Concentrations of ozone have a strong seasonal variation with a peak occurring in spring every year. However, annual ozone concentrations show no obvious trends in spite of decreasing emissions of the precursors  $\text{NO}_x$  and VOC. A slight indication of a decreasing trend in the number of ozone episodes might be seen from 1990 to 1998.

Sulphate concentrations in precipitation and deposition show strongly significant decreasing trends in the whole country. Concentrations and deposition of nitrate and ammonium have been decreasing in all areas except for nitrate at stations in south-west and north-west Sweden and ammonium in south-west Sweden. Acidity has decreased in all areas since 1989, resulting in increasing pH values in Sweden.

The interannual variations of concentration and deposition of base cations and chloride are large and few general trends can be seen during 1983-1997.

Time trends of four heavy metals in precipitation have been evaluated for the period 1989-1998. The concentration of arsenic has decreased with statistical significance at all four stations in Sweden. Concentrations of cadmium, lead and nickel show decreasing trends at some of the stations. Time trends of mercury have not been statistically evaluated because the measurements cover a relatively short period of time.

The metal content of mosses represents a relative measure of the total (dry and wet) metal deposition. The concentrations of arsenic, cadmium, lead, nickel, mercury, chromium, iron, copper and zinc have been evaluated for the period 1970-1995. All metal concentrations show decreasing trends during the period.

# **Trends in air concentration and deposition at background monitoring sites in Sweden**

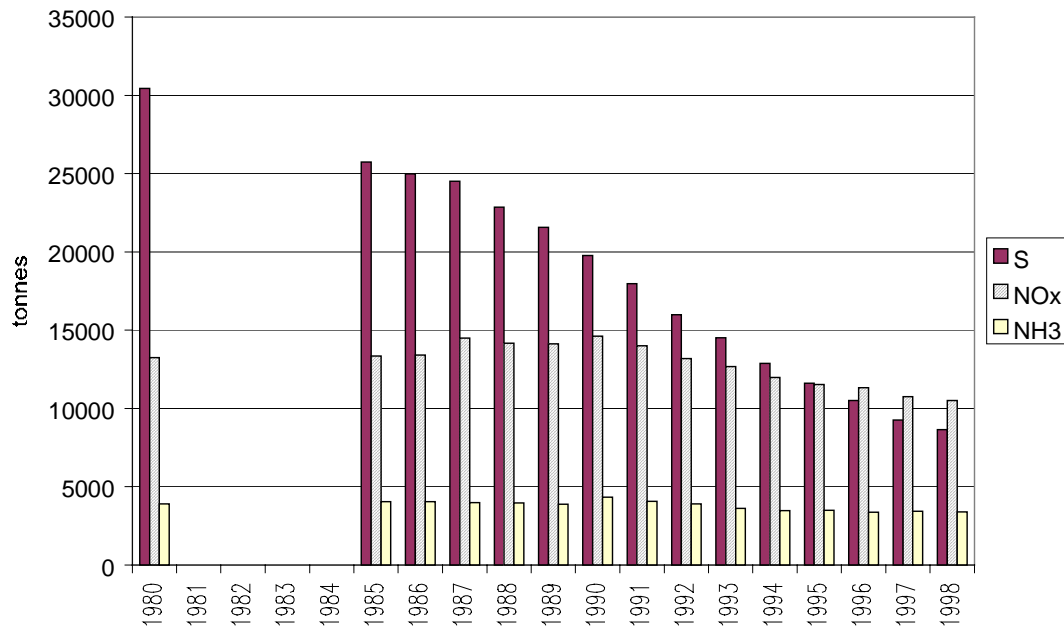
## **major inorganic compounds, heavy metals and ozone**

This study is based on results obtained within the national environmental monitoring programme in Sweden, financed by the Environmental Monitoring Department at the Swedish Environmental Protection Agency.

### **1. Introduction**

Sulphur and nitrogen compounds emitted to air can be transported over long distances and influence the environment not only in the region where they are emitted, but also in regions far from the source area. Historically, emissions of sulphur and nitrogen oxides steadily increased with the industrial expansion. The increase was especially rapid after the second world war. Since the beginning of the 1970's, international work has been directed towards understanding the dispersion and deposition processes of the pollutants emitted, and to achieve cooperation on abatement of the emissions in Europe. Under the Convention on Long Range Transboundary Air Pollution several protocols concerning emission reductions of a number of pollutants have been signed. In order to follow up the results of these protocols, The Cooperative Programme for Monitoring and Evaluation of the Long Range Transmission of Air Pollutants in Europe (EMEP) was initiated. Presently the EMEP monitoring network consists of approximately 100 monitoring stations across Europe. In addition to monitoring, the programme also includes emission inventories and model calculations for transport and deposition of pollutants emitted within Europe.

So far the most successful efforts to reduce emissions have been with sulphur. In the countries, which have the most significant influence on Swedish background air quality (including Sweden), the emissions of sulphur have decreased by approximately 70% from 1980 to 1998, about 20% for oxidized nitrogen and 13% for reduced nitrogen (Figure 1).



**Figure 1** Emissions of S, NO<sub>x</sub> and NH<sub>3</sub> in countries influencing air quality in Sweden 1980-1998 ([www.unece.org/env/lrtap/env\\_eb1.htm](http://www.unece.org/env/lrtap/env_eb1.htm))

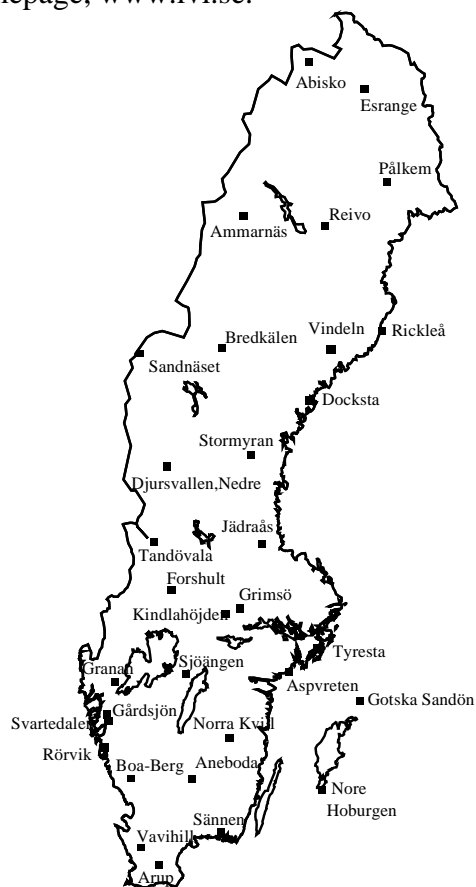
In view of the changes in European emissions over the last two decades it is of interest to study changes in air concentration and deposition measured at Swedish background monitoring stations during the same period of time. As mentioned earlier, the emissions of sulphur, oxidized nitrogen and reduced nitrogen in countries influencing Swedish air quality, have decreased since 1980 and a subsequent decrease in concentrations and depositions is expected.

## 2. Available data and statistical evaluation methods

### 2.1 Available monitoring data

The monitoring of air and precipitation concentrations of major inorganic compounds in background areas in Sweden started in the late 1970's. Heavy metals and ozone have been monitored since the mid 1980's. Measurement data are available from six Swedish EMEP stations and from the national Precipitation Chemistry Network, consisting of approximately 25 stations (Figure 2). Continuous monitoring has been performed at five EMEP stations and 21 Precipitation Chemistry Network stations during the period examined, 1985-1998. The EMEP station Erange started in 1990 and annual average values of concentrations in precipitation are presented in trend figures. The results from Erange are however not included in the trend analysis due to the short monitoring period. Vavihill and Breckälén are EMEP stations as well as Precipitation Chemistry Network stations. When these stations are displayed together in tables and figures, the EMEP stations are named VavihillE and BreckälénE. Different methods of sampling are used in the two networks. EMEP uses wet-only collectors for precipitation and impregnated filters for active air sampling. The Precipitation Chemistry Network uses bulk collectors for precipitation samplers and diffusive samplers for monitoring of air concentration.

More information about the monitoring networks, as well as monitoring results, are available at the IVL homepage, [www.ivl.se](http://www.ivl.se).



**Figure 2** Background monitoring stations in Sweden.

## 2.2 Statistical calculations

For the trend studies, changes in annual mean values have been evaluated using two different statistical methods, linear regression and the non-parametric Mann Kendall test (Gilbert, 1987).

**Linear regression** has been applied to study concentrations as a function of time for the different parameters and stations. In each case the slope of the line obtained, positive or negative, indicates whether there has been an increase or decrease in concentration with time. Furthermore, the slope also indicates the magnitude of the change. In addition, the assumption of a linear change with time can be verified or disproved.

The correlation coefficient,  $r$ , for the calculated regression line gives a measure of the degree of closeness of a possible linear relationship between the two variables, data and time. If the correlation coefficient is equal to +1 or -1 all the individual points are exactly on the line describing the relation. The possibility of a linear change with time is low if the correlation between the data sets and the regression line results in  $r < |0.6|$  (Nilsson, 1978).

The statistical significance is given by the  $p$ -value. A significance between two data sets with  $p < 0.05$  has been chosen to represent a statistically significant relationship. If  $p < 0.05$ , the probability is 95% or more that the line represents a real relation. Some of the data sets examined can be described by a linear relationship at least at the 95% significance level. For higher values of  $p$  ( $p > 0.05$ ) the relation has not been considered to be statistically significant.

The **Mann Kendall** is a non-parametric test for trend, using the relative magnitudes of the time-ordered data. Non-parametric methods generally have the advantage of being insensitive to outliers, missing values are allowed and data do not need to conform to any particular distribution. Anders Grimvall, University of Linköping, kindly provided the software used in the calculations.

The Mann Kendall test gives the trend direction and the significance of the detected upward or downward trend. A change with time that does not approximate to linearity might be detected using this non-parametric method.

The Sen's estimator of slope (Gilbert, 1987) can then be used to calculate the median of the annual change, as well as confidence intervals for the change. In the figures below, presenting these results, the 90% confidence interval around the median is shown.



### 3. Time trends of concentrations in air

#### 3.1 Sulphur compounds and soot

The results from the trend analysis of SO<sub>2</sub>, particulate SO<sub>4</sub>-S and soot in air are summarised in Table 1. Detailed discussions of the results are given in the paragraphs that follow. In Table 1 the calculated annual changes as well as the statistical significance levels of the changes are given for both statistical analysis methods. Highly significant decreasing trends were obtained in all cases, except for soot in Bredkålen in the northern part of Sweden. The trend analyses have been performed for the time period 1985-1998, even though older monitoring data exist for some compounds. All data available are however presented in the figures below.

**Table 1** Trend analysis results for sulphur dioxide, particulate sulphate and soot.

	Linear regression					Non parametric test	
	slope of the regression line (µg S/m <sup>3</sup> /year)	p	r	** change in concentration (%)	change in concentration (% / year)	median change (µg S/m <sup>3</sup> /year)	p
<b>SO<sub>2</sub>-S</b> <b>1985-1998</b>							
Bredkålen	-0.09	0.0000*	-0.89	-93	-7.1	-0.09	p<0.005
Aspvreten	-0.15	0.0000*	-0.92	-93	-7.2	-0.14	p<0.005
Hoburgen	-0.16	0.0000*	-0.90	-80	-6.1	-0.15	p<0.005
Rörvik	-0.25	0.0000*	-0.96	-93	-7.2	-0.24	p<0.005
Vavihill	-0.39	0.0000*	-0.69	-96	-7.4	-0.35	p<0.005
<b>SO<sub>4</sub>-S (part)</b> <b>1985-1998</b>							
Bredkålen	-0.034	0.0005	-0.80	-69	-5.3	-0.030	p<0.005
Aspvreten	-0.041	0.0004	-0.81	-47	-3.6	-0.041	p<0.005
Hoburgen	-0.052	0.0025	-0.74	-48	-3.7	-0.066	p<0.005
Rörvik	-0.084	0.0005	-0.80	-62	-4.8	-0.096	p<0.005
Vavihill	-0.069	0.0006	-0.80	-54	-4.1	-0.069	p<0.005
<b>Soot</b> <b>1985-1998</b>							
Bredkålen	-0.03	0.1458				-0.03	p<0.100
Hoburgen	-0.22	0.0012	-0.79	-58	-4.5	-0.28	p<0.005
Rörvik	-0.25	0.0000*	-0.93	-64	-4.9	-0.25	p<0.005
Vavihill	-0.32	0.0002	-0.85	-66	-5.1	-0.26	p<0.005

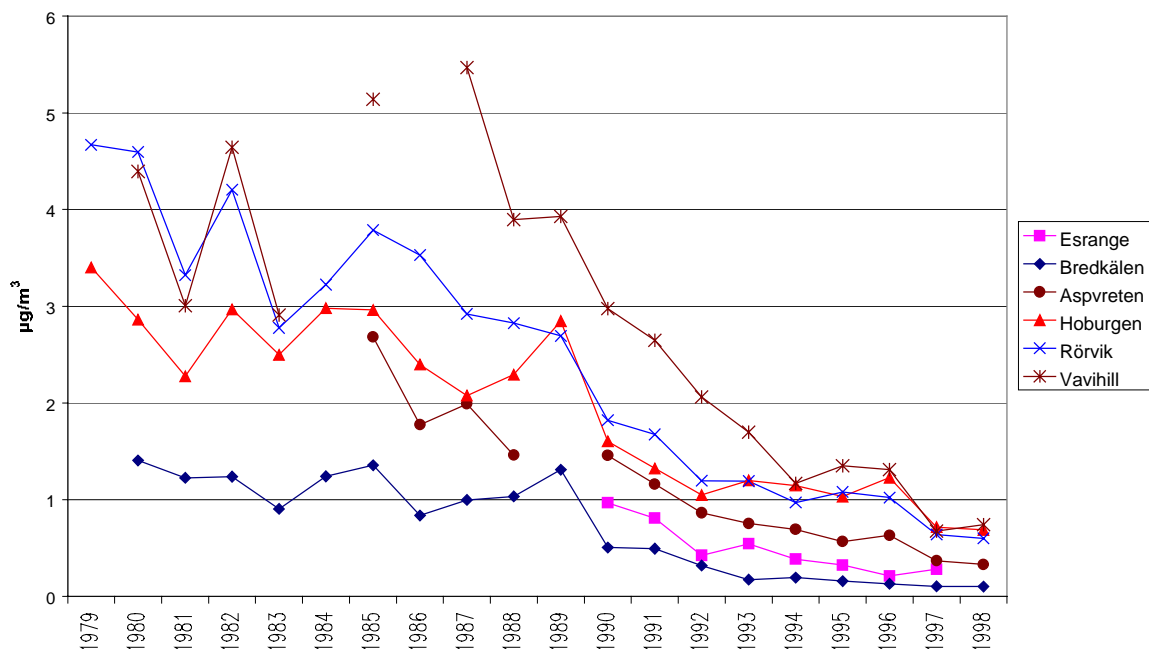
\*The p-value is less than 0.00001.

\*\* The change in concentration described by the regression line.

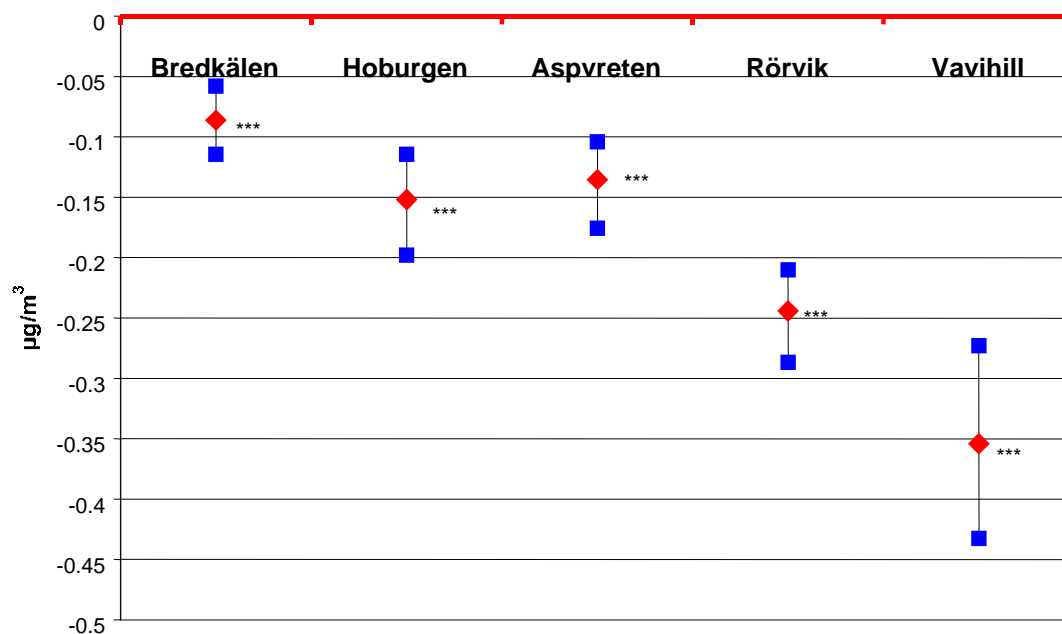
### 3.1.1 Sulphur dioxide in air

The annual average concentrations of sulphur dioxide in air have decreased at all sites during the measurement period, (Figure 3). The trend analyses show statistically significant decreases ( $p < 0.05$ ) at all stations for the period 1985-1998 irrespective of statistical method. The concentrations of  $\text{SO}_2$  in air have decreased by 80-95% during the 14 year period included in the study. In Figure 4 the results from the non-parametric trend test are presented, given as the calculated median change per year, with the 90% confidence interval indicated in the figure. The absolute decrease was largest in Vavihill in southern Sweden and smallest in Bredkålen in northern Sweden. This is probably a consequence of the originally lower background levels in the northern part of the country. The decrease is a result of measures taken to reduce emissions of sulphur dioxide in Sweden as well as in the rest of Europe (Figure 1).

The decreasing sulphur dioxide trends in Sweden are consistent with decreasing concentrations of sulphur dioxide in air across Europe. EMEP Chemical Co-ordinating Centre has evaluated trends of atmospheric sulphur in Europe between 1978-1998 (Barett et al., 2000). Statistically significant trends were observed across the whole continent. Noticeable at many of the stations was a strong decline in the magnitude of episodes, which have had a decreasing influence on the monthly mean concentrations. Central Europe and Scandinavia have had the strongest decrease of sulphur dioxide in air during the period. Between 1980 and 1993 sulphur concentrations in air are estimated to have declined by between 40 and 80% depending on the station. Decreasing trends in Europe were uncertain only at the most remote stations on the north-west Atlantic coast.



**Figure 3** Annual averages of  $\text{SO}_2\text{-S}$  in air 1979-1998 ( $\mu\text{g S/m}^3$ ).



**Figure 4** Median annual change in  $SO_2$ -S concentration in air ( $\mu\text{g S}/\text{m}^3$ ) 1985-1998, calculated by Mann-Kendall and Sen's estimator of slope. The 90% confidence interval is indicated with filled squares in the figure. All decreases are significant at the 99.5% level, (\*\*\*)= $p < 0.005$ , (\*\*)= $p < 0.01$ , (\*)= $p < 0.05$ ).

### 3.1.2 Particulate sulphate in air

Measured concentrations of particulate sulphate in air have also been decreasing during the last two decades (Figure 5). The decrease 1985-1998 is statistically significant at all monitoring stations. During the time period studied the decrease has been in the order of 45-70% in Sweden, depending on the station. The decline of sulphate during the period has been smaller than the relative decrease in sulphur dioxide concentration. The calculated median change per year at each individual site using the Mann Kendall test is presented in Figure 6. The absolute decrease was largest in Rörvik on the Swedish west coast and smallest in Bredkålen in northern Sweden.

In correspondence with the Swedish results, the decreases in measured airborne particulate sulphate across Europe, have generally been slightly weaker than the decreases in sulphur dioxide (Barett et al., 2000). Between 1980 and 1993 the particulate sulphate concentrations in air were estimated to have declined by 30-70% depending on the station. Because decreases in sulphur dioxide concentration have been larger than the decreases of particulate sulphate, the ratio between the two compounds in air has been changing towards a larger relative fraction of sulphate than 20 years ago.

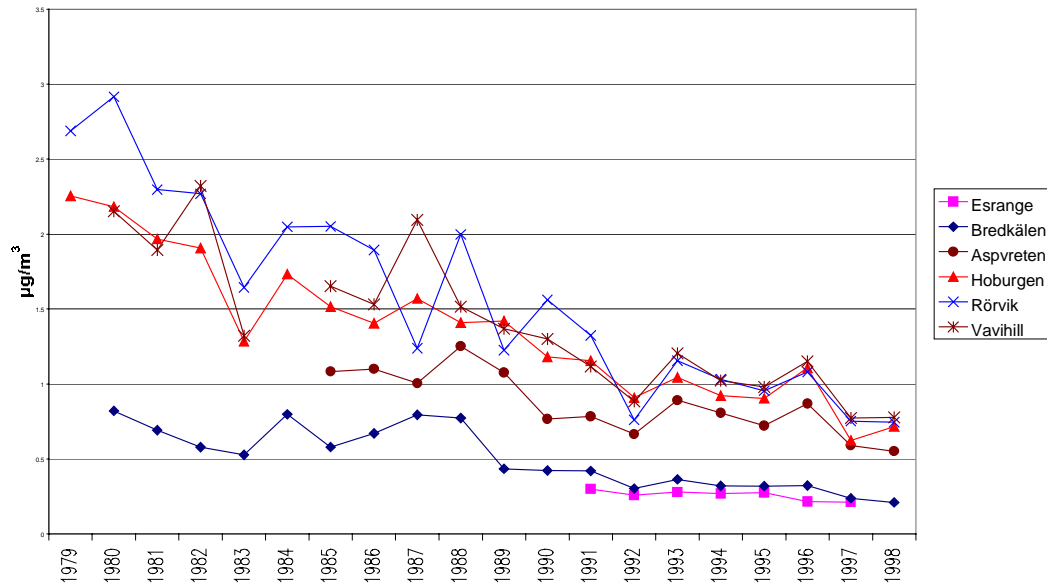


Figure 5 Annual averages of particulate SO<sub>4</sub>-S in air 1979-1998 (µg S/m<sup>3</sup>).

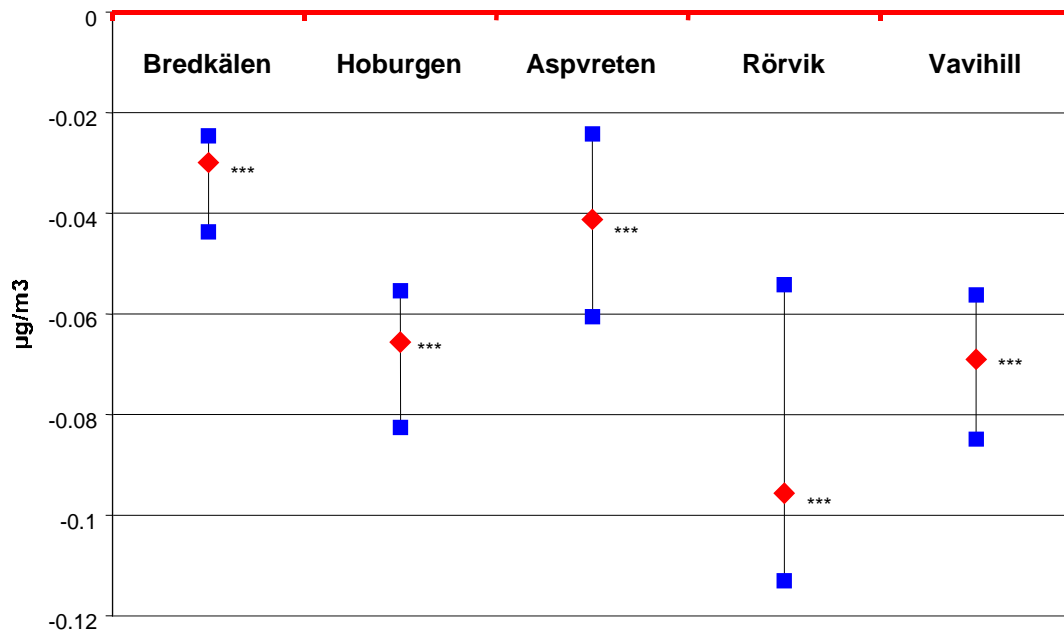
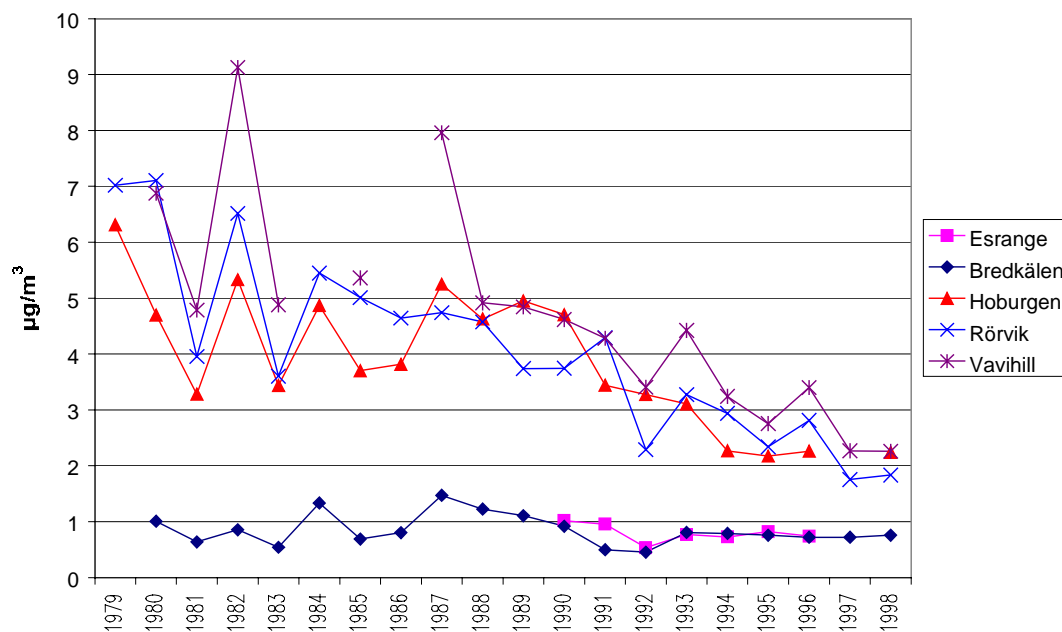


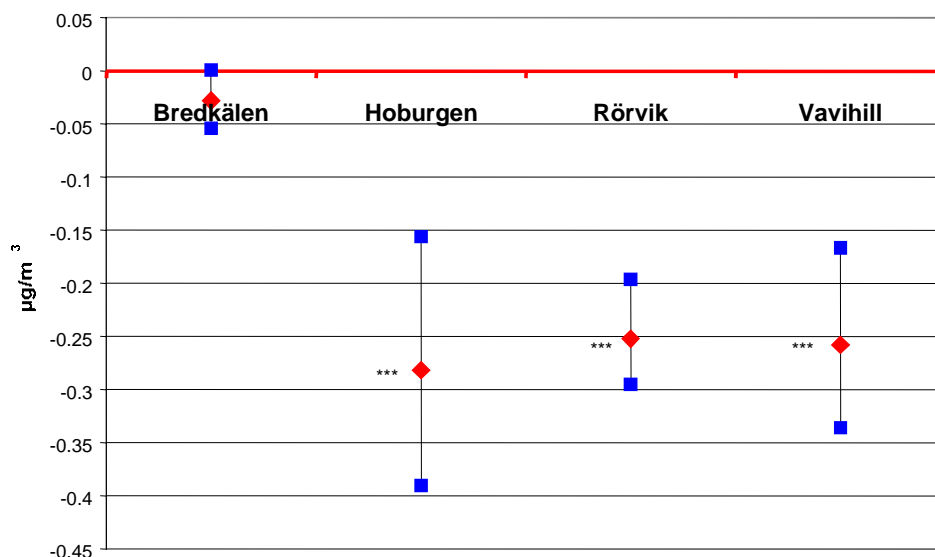
Figure 6 Median annual change in the concentration of particulate SO<sub>4</sub>-S 1985-1998 (µg S/m<sup>3</sup>). The 90% confidence interval is indicated in the figure. (\*\*\*=p<0.005, \*\*=p<0.01, \*=p<0.05)

### 3.1.3 Soot

There has also been a substantial decrease in concentrations of soot in air at many of the monitoring sites since 1979 (Figure 7). The decrease during the period 1985-1998 is significant at the three stations in the southern part of Sweden, while in Breckkälen in the north, there is no significant trend. In the last few years, measurements at this station have often been below detection limit of the analysis method and this is the most probable reason for the lack of a significant trend in the Breckkälen data. The decreases in the south have, however, been large, measured to be approximately 60% from 1985 to 1998. The calculated median change per year, as calculated by the non-parametric method, is presented in Figure 8. The absolute decreases were largest, and of approximately the same magnitude, at the three southern stations. The smallest absolute decrease was measured at Breckkälen in the north. Data measured at Hoburgen had the largest variation.



**Figure 7** Annual averages of soot, 1979-1998,  $\mu\text{g}/\text{m}^3$ .



**Figure 8** Median annual change of the concentration of soot in air 1985-1998,  $\mu\text{g}/\text{m}^3$ , calculated by the non-parametric method. The 90% confidence interval is indicated in the figure. (\*\*\*)= $p < 0.005$ , (\*\*)= $p < 0.01$ , (\*)= $p < 0.05$ )

## 3.2 Nitrogen compounds

### 3.2.1 Nitrogen dioxide in air

In an earlier study (Kindbom et al., 1994) time trends of measured concentrations of  $\text{NO}_2$  in air were studied for the period 1982-1992. At that time no significant trends in the annual averages of  $\text{NO}_2\text{-N}$  in air were detected. In this study, which analyses the time period 1985-1998, there are significant decreasing trends at least at the 95%-level at four out of five stations when applying linear regression. All five stations also show statistically significant decreasing trends if the non-parametric method is used (Table 2). The relative changes are, however, smaller than for  $\text{SO}_2$ , particulate  $\text{SO}_4$  and soot, and are in the order of 20-40% in Aspvreten, Rörvik and Vavihill from 1985-1998. In Bredkålen, where the concentration level has been considerably lower than at other sites since the monitoring began, the relative changes are larger, 84%. The absolute decreases are in the order of 0.02-0.05  $\mu\text{g N}/\text{m}^3/\text{year}$ , quite uniform for all stations (Table 2).

Plotted annual averages of  $\text{NO}_2\text{-N}$  in air 1982-1998 are presented in Figure 9. It is obvious from the figure that the concentration levels in the south-west, Vavihill and Rörvik, have been considerably higher than in the north, Bredkålen and Esrange, while at the stations in the south-east part of Sweden, Aspvreten and Hoburgen, the levels were intermediate.

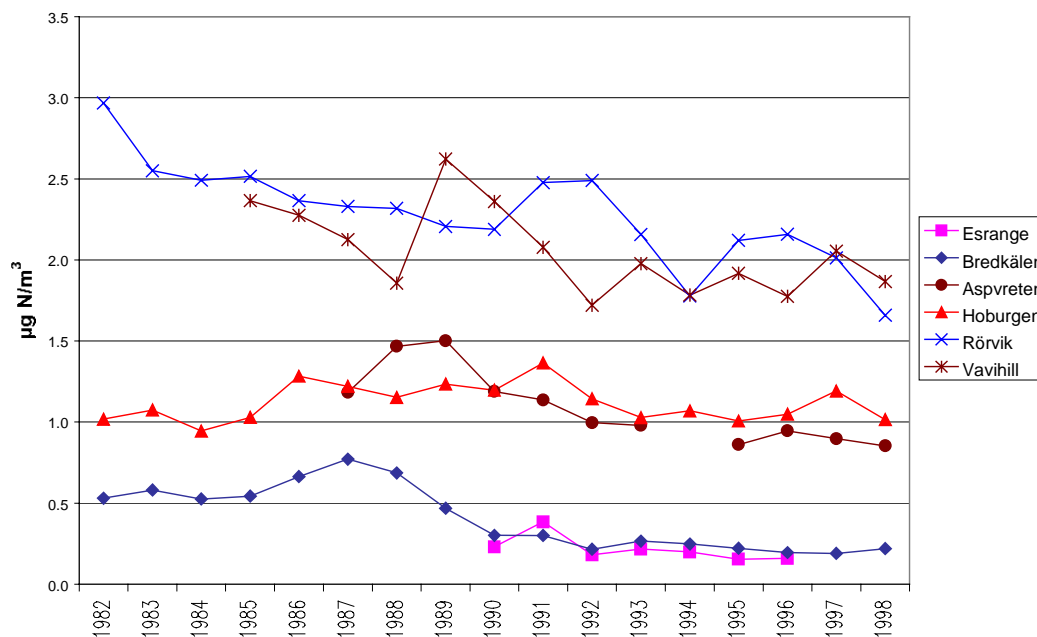
The median change per year, calculated with the Mann Kendall test, at each individual site is presented in Figure 10. In contrary to the results of the Mann Kendall test concerning sulphur compounds, where Bredkålen showed the smallest absolute decrease, the absolute decrease of nitrogen dioxide was smallest in Hoburgen.

Monitoring of nitrogen oxides in Europe has been more limited than the monitoring of SO<sub>2</sub> and particulate sulphur (Barett et al, 2000). Depending on area, trends have been increasing or decreasing, and some stations showed no trends at all during the last two decades.

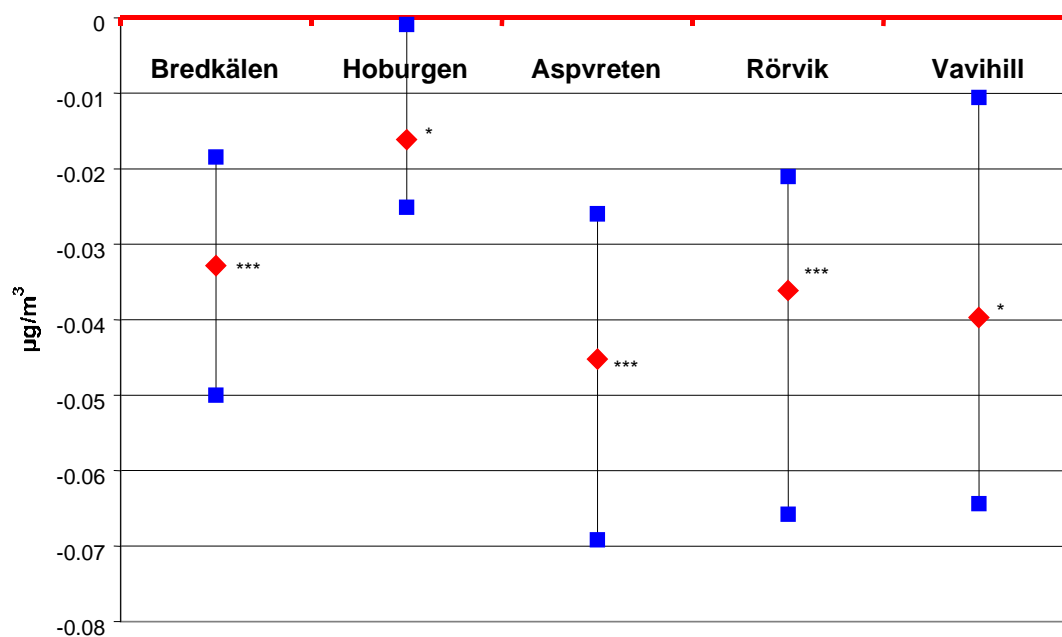
**Table 2** Trend analysis of annual averages of NO<sub>2</sub>-N in air, 1985-1998.

	Linear regression					Non parametric test	
	Slope of the regression line (µg N/m <sup>3</sup> /year)	p	r	change in concentration (%)	change in concentration (% / year)	median change (µg N/m <sup>3</sup> /year)	p
<b>NO<sub>2</sub>-N</b>							
<b>1985-1998</b>							
Bredkålen	-0.04	0.0001	-0.85	-84	-6.5	-0.03	p<0.005
Aspvreten*	-0.05	0.0011	-0.84	-38	-3.5	-0.05	p<0.005
Hoburgen	-0.01	0.120				-0.02	p<0.050
Rörvik	-0.04	0.003	-0.73	-23	-1.8	-0.04	p<0.005
Vavihill	-0.04	0.024	-0.60	-22	-1.7	-0.04	p<0.050

\*The data from Aspvreten covers the period 1987-1998.



**Figure 9** Annual averages of NO<sub>2</sub>-N in air 1982-1998 (µg N/m<sup>3</sup>).



**Figure 10** Median annual change of the concentration of  $\text{NO}_2\text{-N}$  in air 1985-1998,  $\mu\text{g N/m}^3$ . The 90% confidence interval is indicated in the figure. (\*\*= $p < 0.005$ , \*\*= $p < 0.01$ , \*= $p < 0.05$ )

### 3.2.2 Total nitrate and total ammonium in air

Total nitrate and total ammonium in air, the sum of gaseous and particulate matter (gaseous  $\text{HNO}_3$  + particulate  $\text{NO}_3^-$  and gaseous  $\text{NH}_3$  + particulate  $\text{NH}_4^+$ ) have been monitored since 1987 at most stations. The monitoring period is shorter than for the other compounds in air.

The results from the trend analysis (Table 3) show decreasing trends, statistically significant at least on the 95%-level, at all stations when applying linear regression, and at all stations except total  $\text{NO}_3\text{-N}$  in Rörvik using the non parametric test.

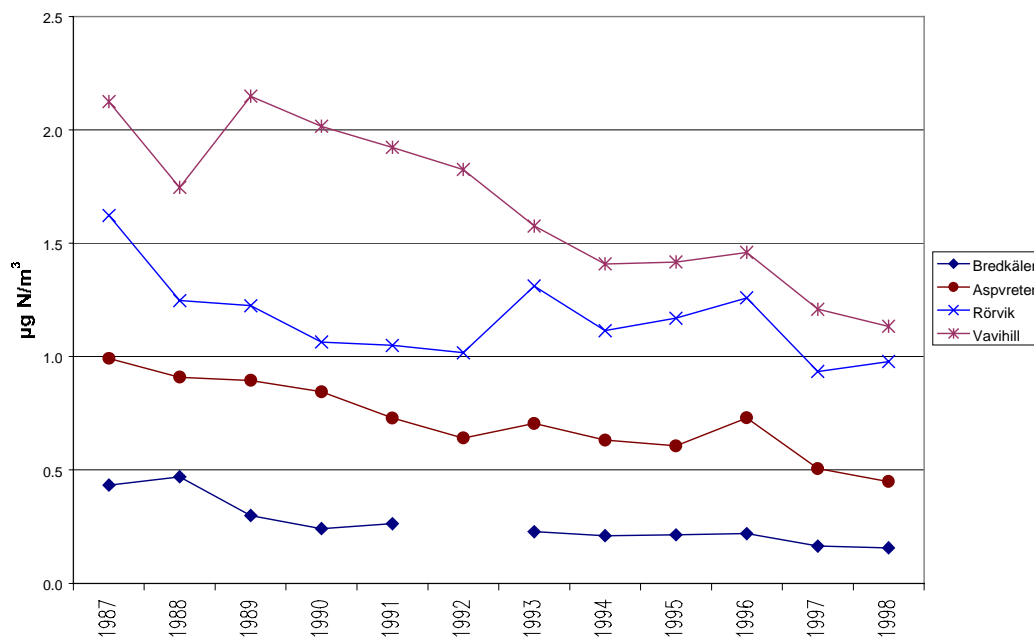
The largest absolute decrease for total  $\text{NH}_4\text{-N}$  has been measured at Vavihill in the very south of Sweden and for total  $\text{NO}_3\text{-N}$  in Aspvreten at the east coast (Figure 12 and Figure 14). In Bredkälén in the north the concentration levels were much lower than at the three southern stations during the whole period, especially pronounced for total  $\text{NO}_3\text{-N}$  (Figure 13).

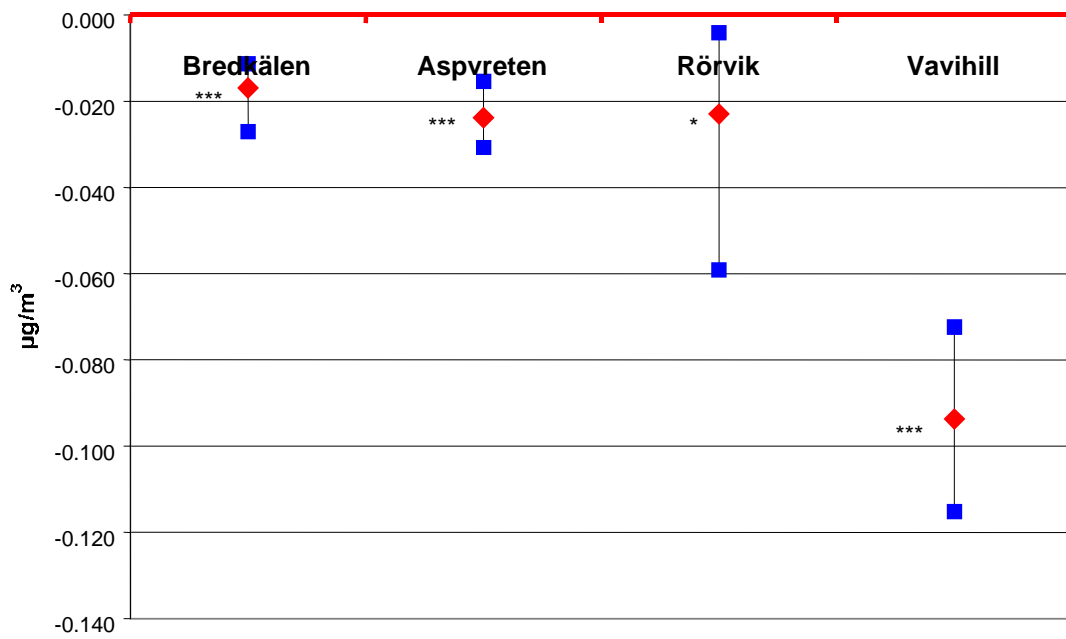
Monitoring of total nitrate across Europe did not begin until the late 1980's. The trends have been weak over large areas of continental Europe and in some cases the seasonal changes may have had larger influence than changes between the years. Monitoring of reduced nitrogen concentrations is less comprehensive than for oxidised nitrogen and no trend studies have been documented (Barett et al, 2000).



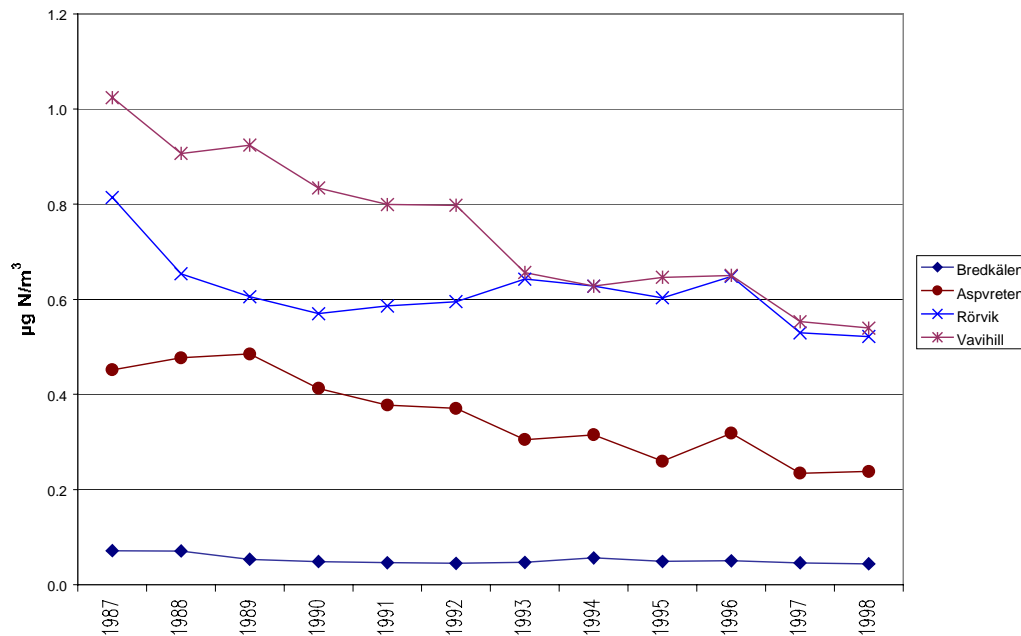
**Table 3** Trend analysis of annual averages of total-NH<sub>4</sub>-N and total-NO<sub>3</sub>-N 1987-1998.

	Linear regression					Non parametric test	
	slope of the regression line (µg N/m <sup>3</sup> /year)	p	r	change in concentration (%)	change in concentration (% / year)	median change (µg N/m <sup>3</sup> /year)	p
<b>Total-NH<sub>4</sub>-N 1987-1998</b>							
Bredkålen	-0.02	0.0005	-0.87	-65	-5.9	-0.02	p<0.005
Aspvreten	-0.04	0.0000	-0.93	-45	-4.1	-0.02	p<0.005
Rörvik	-0.03	0.0470	-0.58	-25	-2.3	-0.02	p<0.050
Vavihill	-0.09	0.0000	-0.92	-45	-4.1	-0.09	p<0.005
<b>Total-NO<sub>3</sub>-N 1987-1998</b>							
Bredkålen	-0.002	0.0150	-0.68	-32	-2.9	-0.002	p<0.050
Aspvreten	-0.02	0.0000	-0.95	-49	-4.4	-0.05	p<0.005
Rörvik	-0.01	0.0330	-0.61	-21	-1.9	-0.01	p<0.100
Vavihill	-0.04	0.0000	-0.97	-47	-4.3	-0.04	p<0.005

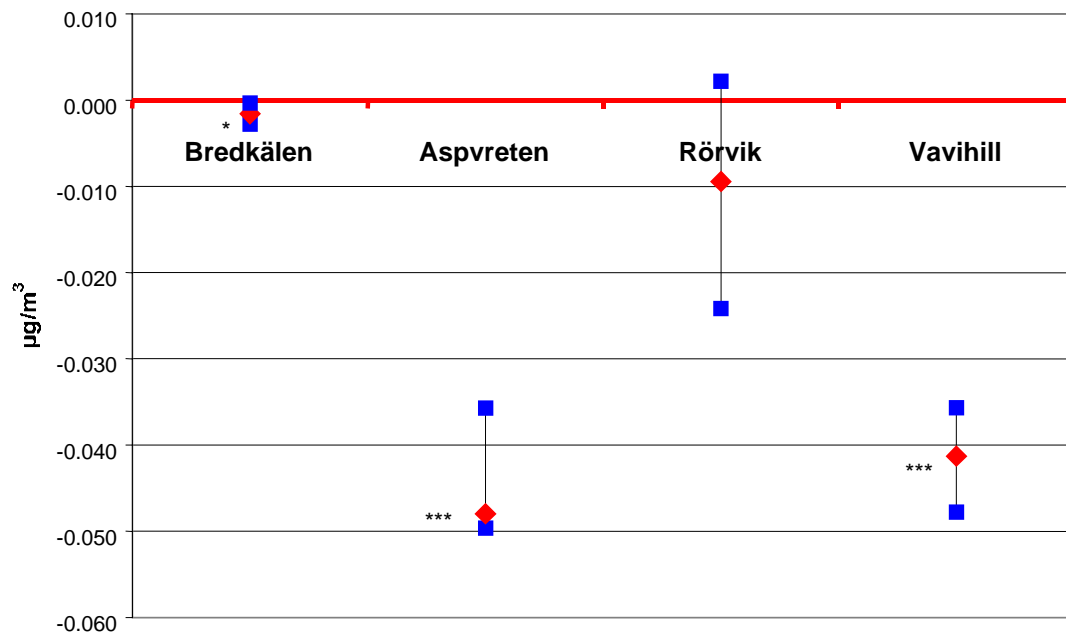
**Figure 11** Annual average concentrations of total-NH<sub>4</sub>-N in air 1987-1998 (µg N/m<sup>3</sup>).



**Figure 12** Median annual change of the concentration of total-NH<sub>4</sub>-N in air 1987-1998, µg N/m<sup>3</sup>. The 90% confidence interval is indicated in the figure. (\*\*\*=p<0.005, \*\*=p<0.01, \*=p<0.05)



**Figure 13** Annual average concentrations of total NO<sub>3</sub>-N in air 1987-1998 (µg N/m<sup>3</sup>).



**Figure 14** Median annual change of the concentration of total  $\text{NO}_3\text{-N}$  in air 1987-1998,  $\mu\text{g N/m}^3$ . The 90% confidence interval is indicated in the figure. (\*\*= $p < 0.01$ , \*= $p < 0.05$ )

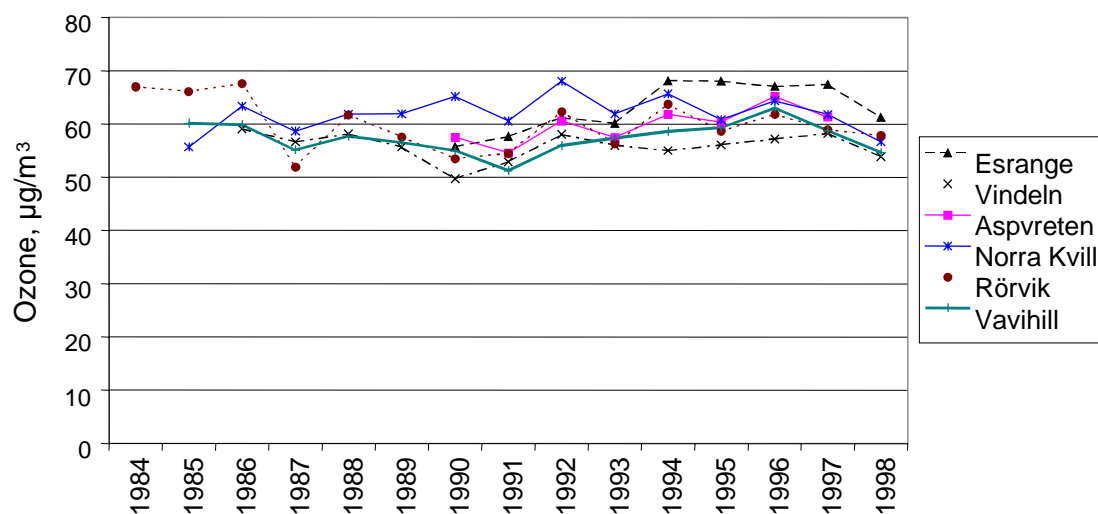
### 3.3 Ozone

Ozone, O<sub>3</sub>, is formed by photochemical oxidation processes in warm and sunny weather with low wind speeds. Ozone is continuously formed and decomposed to obtain a state of equilibrium. The presence of precursors is necessary for a net production of ozone to occur. Such precursors are nitrogen oxides, NO<sub>x</sub>, and volatile hydrocarbons, VOC. The main sources of NO<sub>x</sub> and VOC are anthropogenic emissions, such as combustion and traffic. Ozone is a large scale pollutant and ozone formed in airmasses over the European continent contributes to the ozone concentrations in Sweden.

Monitoring of ground-level ozone concentrations in Swedish background areas has been performed since 1984 in Rörvik (Figure 2). The monitoring network was enlarged to four stations in 1985 when measurements started in Vindeln, Vavihill and Norra Kvill. Monitoring started in Esrange and Aspvreten 1990 and hourly values have been registered at six stations during a period from 1990 to 1998.

#### 3.3.1 Annual variations

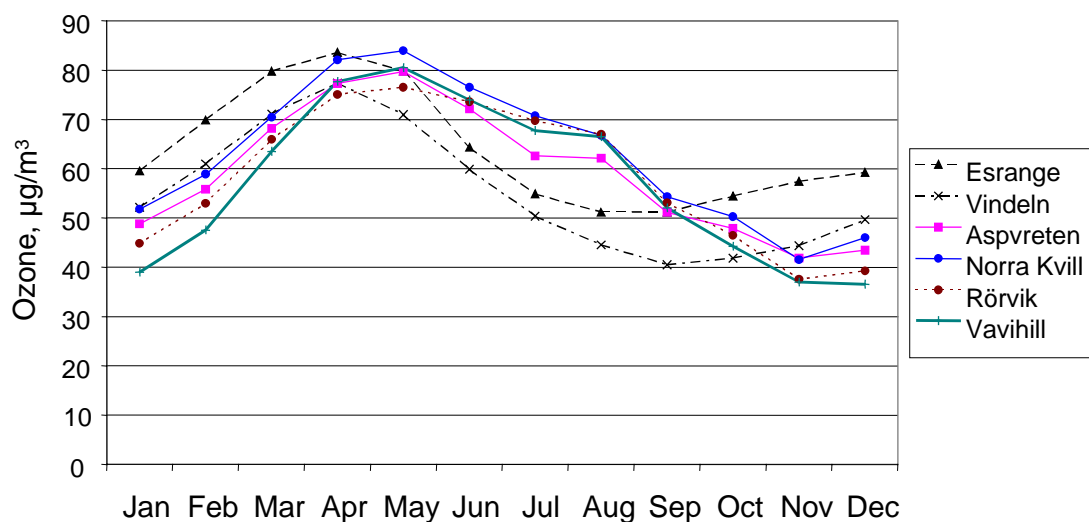
The annual average concentrations of ozone (Figure 15) show no apparent time trend. Since the levels of ozone measured in Sweden are influenced by long-range transport, one might expect differences depending on how far north the station is situated in relation to the main source areas of the precursors NO<sub>x</sub> and VOC in continental Europe. The average percentage emission reduction for the whole EMEP area in Europe in NO<sub>x</sub> between 1990 and 1998 was 21% and the reduction in NMVOC emissions was 26% (Vestreng & Støren, 2000). Because the emissions of the precursor have decreased in areas influencing the conditions in Sweden a decreasing trend in ozone concentrations would have been expected. The annual averages did, however, not show any consistent or large differences, neither depending on geographical location of the station nor on time.



**Figure 15** Annual average concentrations of ozone ( $\mu\text{g}/\text{m}^3$ ).

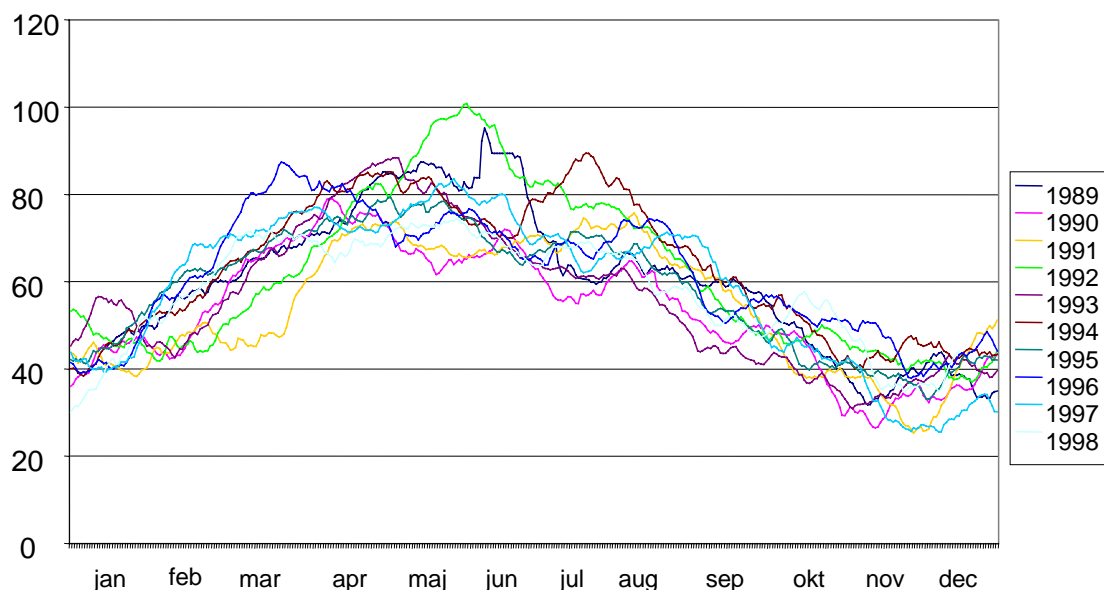
### 3.3.2 Seasonal variations

Unlike many other air pollutants, which usually have higher concentrations in wintertime, the seasonal variations of ozone show a spring peak (Figure 16). In southern Sweden (Vavihill, Rörvik, Norra Kvill and Aspvreten) the spring peak usually occurs in April or May while in the north (Vindeln and Esrange) the peak occurs somewhat earlier.



**Figure 16** Seasonal variation (1990-1998) in ozone concentration (monthly averages) at the Swedish monitoring sites ( $\mu\text{g}/\text{m}^3$ ). Stations in the legend are given from north to south.

Since the formation of ozone is highly dependent on the meteorological situation, there are large interannual variations, both regarding peak values measured during episodes and the time of occurrence of the spring peak. In Figure 17 the 30-days moving average of ozone concentrations at Rörvik on the west coast, for each year 1989-1998, is presented. It is clear that although the general pattern is of a spring peak in April-May, episodes of high concentrations may occur both earlier and later during the year and the magnitudes within a given season differ considerably in different years.

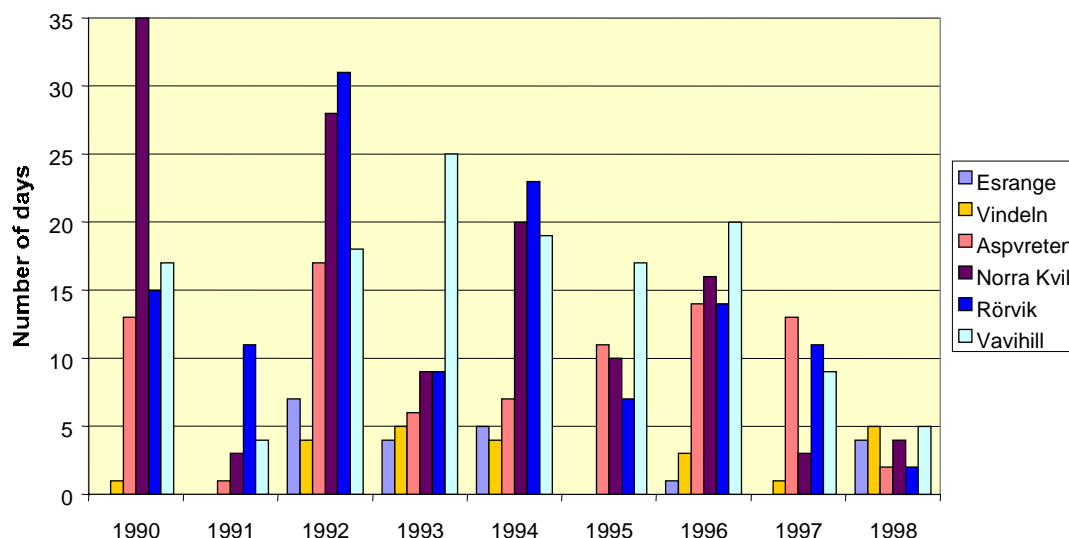


**Figure 17** 30-days moving average ozone concentrations at Rörvik, 1989-1998 ( $\mu\text{g}/\text{m}^3$ ).

### 3.3.3 Episodes

Episodes with high concentrations of ozone, represented by the number of days with 8-hour average ozone concentrations above  $120 \mu\text{g}/\text{m}^3$  each year, are presented in Figure 18. The number of episodes has possibly been decreasing from 1990 to 1998, but the tendency is not clear, as the interannual variations are large. For example in 1991, there was “bad summer weather” with few high-pressure situations with warm and sunny weather, which resulted in low ozone concentrations.

Episodes with high concentrations of ozone are generally less common at the two northerly stations, Vindeln and Esrange, than in the southern part of the country.



**Figure 18** Number of days/year with 8-hour moving average ozone concentration above  $120 \mu\text{g}/\text{m}^3$ .

### 3.3.4 Statistical calculations of ozone data

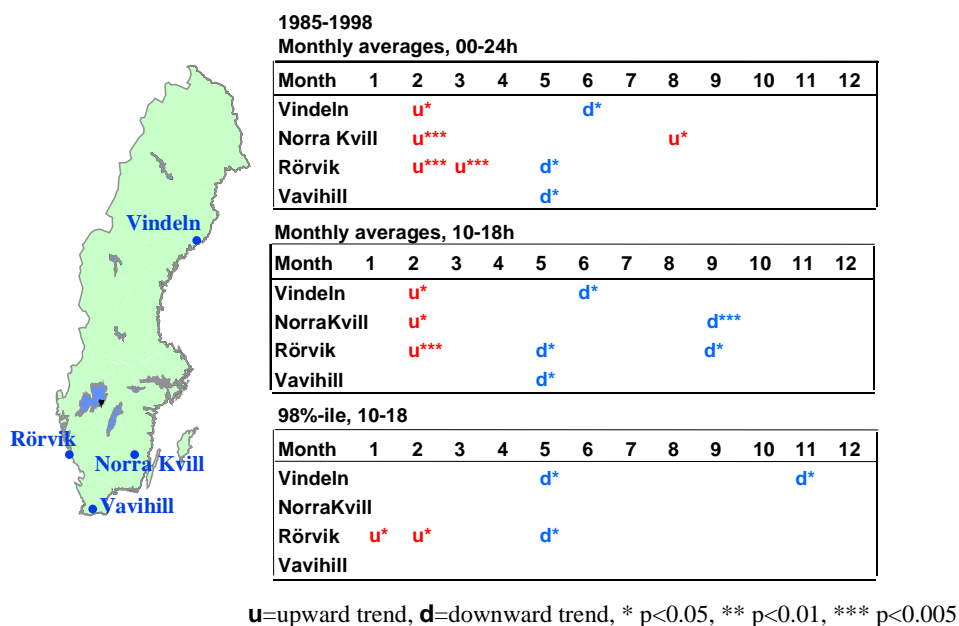
Decreasing ozone concentrations have been expected during the last decade since the emissions of precursors have reduced. Decreasing trends in ozone concentrations are however not easily detectable. Ozone data show no visible trends in annual average concentrations (Figure 15). The number of episodes with elevated ozone concentrations (Figure 18) may have decreased during the period, but the interannual variation makes trend evaluation difficult.

The non-parametric Mann Kendall test has been performed using ground-level ozone concentrations from four Swedish as shown on the map in Figure 19. The time trend analyses were made for separate months, in order to try to detect if there has been seasonal differences in ozone concentration trends. The analyses were based on monthly averages of all data, monthly averages of daytime data (10-18 local time) and on the 98%-ile of monthly daytime data (10-18 local time). The results are summarised in Figure 19. The Mann Kendall analysis showed increasing concentrations of ozone in late winter-early spring and decreasing trends in late spring-early summer. The increasing trends during winter are statistically more significant than the spring decreases. Furthermore, the increasing winter trends were stronger when both daytime and nighttime data were used.

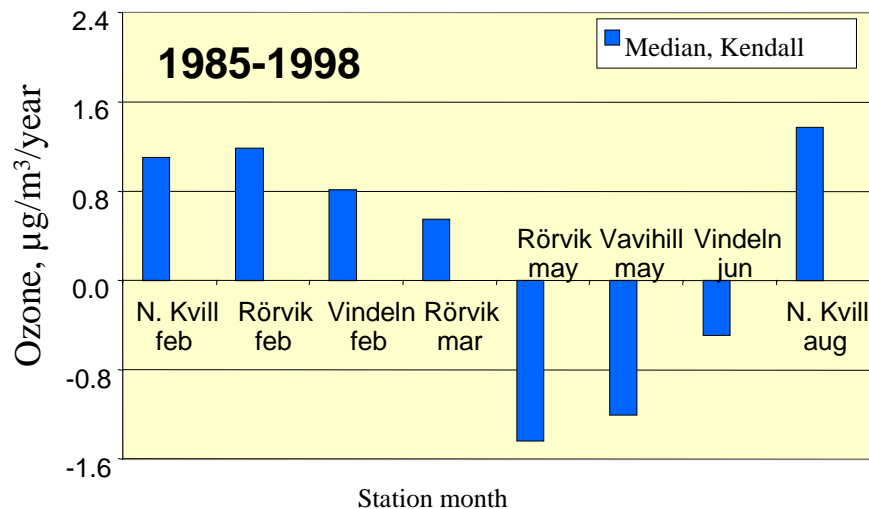
The 98%-ile did not show as many statistically significant increasing trends. This might strengthen the assumption from section 3.3.3 of possibly fewer occasions of episodes.

The magnitudes of the changes of the monthly averages (from Figure 19) were calculated for data sets found to be statistically significant, at least on the 95 % level. The results are presented in Figure 20. The increases in February and March and the

decreases in May, June and August were calculated to be in the order of 0.5-1.5  $\mu\text{g}/\text{m}^3$  per year (Sen's estimator of slope).



**Figure 19** Statistically significant time trends of monthly averages of ozone concentrations in air from 1985-1998 calculated by the non parametric Mann Kendall test for trend.



**Figure 20** Median annual change in monthly averages of ozone at stations and months where a trend has been at least 95% significant according to the Mann Kendall test.

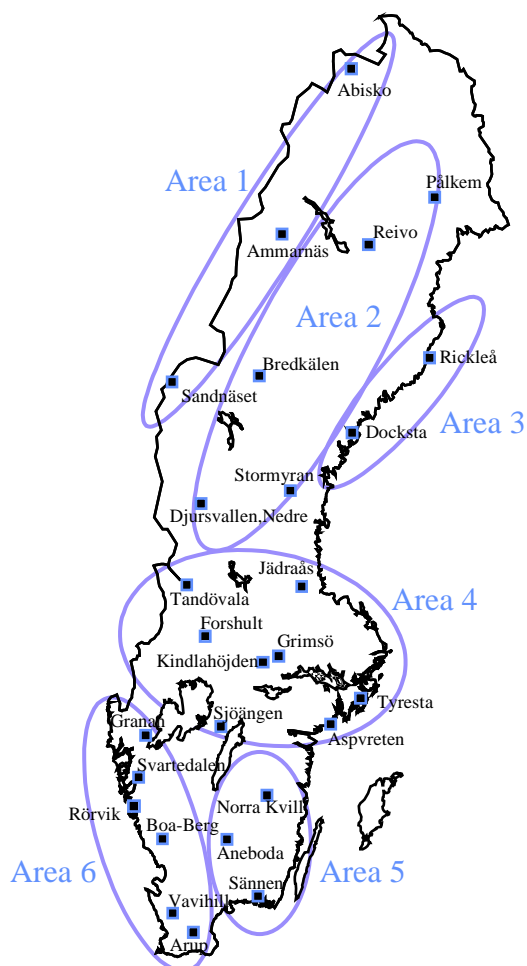


## 4. Time trends of concentrations in precipitation and deposition

### 4.1 Regions of different exposure

The changes in precipitation and deposition over time of major inorganic compounds have been studied in six different regions in Sweden. The geographical regions were chosen on the basis of known differences in exposure, with the criteria of having at least two measurement sites within each region (Figure 21 and Table 4).

The measurement network has changed somewhat over the years, many sites have been in use since 1983 but some were added in 1988. Only stations with measurements since 1983 have been included in the analysis.



**Figure 21** The six regions with monitoring stations indicated.

**Table 4** The six regions, with stations and measurement period, included in the trend analysis.

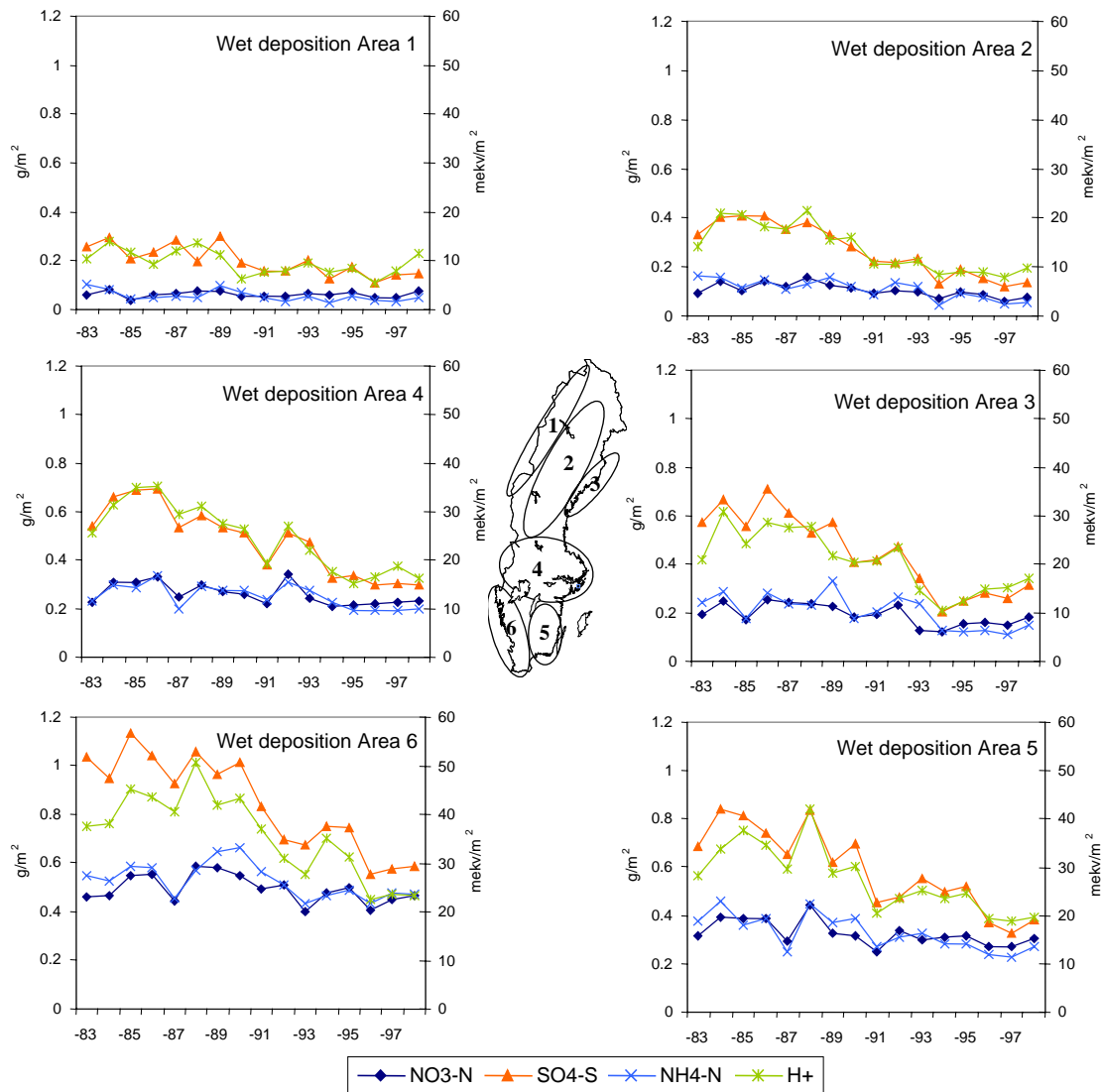
Period	Area	Number of sites	Name of station
1983-98	1	3	Abisko, Ammarnäs, Sandnäset
1983-98	2	4	Bredkålen (2), Pålkem, Reivo
1983-98	3	2	Docksta, Rickleå
1983-98	4	4	Aspvreten, Forshult, Grimsö/Kindlahöjden, Sjöängen
1983-98	5	3	Aneboda, Norra Kvill, Sännen
1983-98	6	7	Arup (2), Boa-Berg, Granan, Rörvik, Svartedalen, Vavihill

## 4.2 Sulphate, nitrate, ammonium and acidity

The calculated annual averages of wet deposition of sulphur, nitrate, ammonium and acidity in six different areas in Sweden, 1983-1998, are presented in Figure 22. The pollution load has been lower in the northern inland areas, area 1 and 2, than in the rest of the country. Area 6 in the south-west, has had the highest deposition levels of sulphur, nitrogen and acidity.

Sulphur and acidity show substantial decreases in deposition, while the deposition of nitrate and ammonium has changed to a lesser extent from 1983-1998. Annual median changes in wet deposition have been examined with the Mann Kendall test and the results are presented in Figures 25, 27, 28 and 30.

Concentrations of sulphate, nitrate, ammonium and acidity in precipitation are summarised in the three following sections. Trend analyses of the concentrations in precipitation in the six regions have been performed with linear regression, which displays decreasing trends all over the country (Tables 5, 6 and 7). The changes at individual stations are presented in Figures 24, 26 and 29.

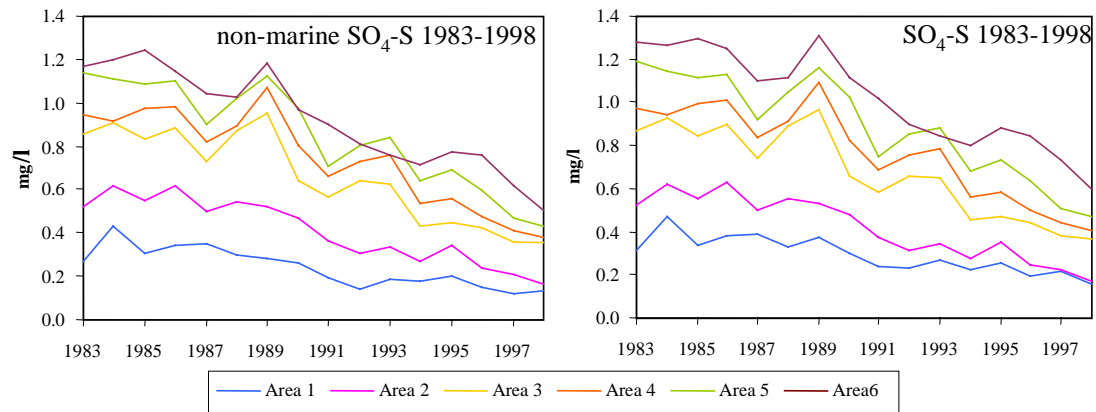


**Figure 22** Annual average wet deposition of  $\text{NO}_3\text{-N}$ ,  $\text{SO}_4\text{-S}$ ,  $\text{NH}_4\text{-N}$  ( $\text{g}/\text{m}^2$ ) and  $\text{H}^+$  ( $\text{meqv}/\text{m}^2$ ) 1983-1998

#### 4.2.1 Sulphate

In precipitation the concentrations of sulphate, as well as the concentrations of sulphate corrected for influences from sea-salt, have decreased at all stations in Sweden (Figure 23). The decrease has been in the order of 50-70% from 1983-1998 (Table 5), similar in magnitude to the relative decrease of emissions in Europe (Figure 1). Consequently, the wet deposition of non-marine sulphur (Figure 24) shows distinct decreasing trends over the whole country. The absolute change is larger at the southern stations, where the load has been greater since the beginning of the period.

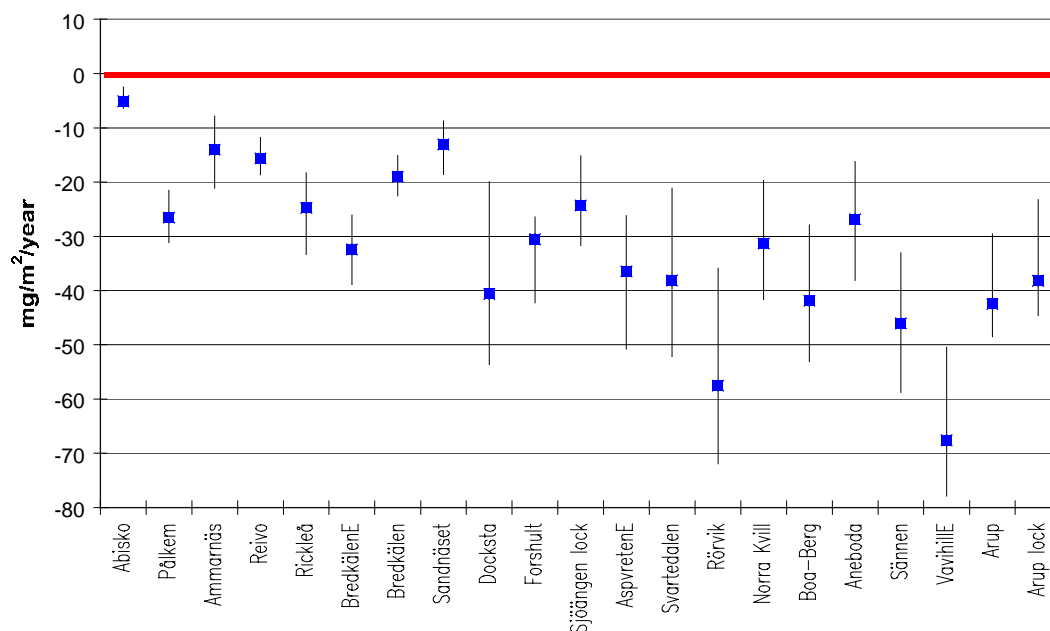
Sulphate concentrations in precipitation and deposition of sulphate also show decreasing trends across Europe (Barett et al., 2000).



**Figure 23** Weighted average SO<sub>4</sub>-S and non-marine SO<sub>4</sub>-S concentrations in precipitation, 1983-1998 in six different regions in Sweden (mg S/l).

**Table 5** Trend analysis of annual average concentrations of SO<sub>4</sub>-S and non-marine SO<sub>4</sub>-S 1983-1998 (mg S/l). Linear regression.

	Area	Slope of the regression line (mg/l/year)	p	r	change in concentration (%)	change in concentration (% / year)
<b>non-marine SO<sub>4</sub>-S 1983-1998</b>	1	-0.017	0.0000	-0.87	-69	-4.6
	2	-0.029	0.0000	-0.94	-70	-4.7
	3	-0.040	0.0000	-0.91	-63	-4.2
	4	-0.041	0.0000	-0.90	-59	-3.9
	5	-0.047	0.0000	-0.93	-59	-3.9
	6	-0.046	0.0000	-0.95	-54	-3.6
<b>SO<sub>4</sub>-S 1983-1998</b>	1	-0.015	0.0000	-0.86	-56	-3.7
	2	-0.029	0.0000	-0.93	-68	-4.5
	3	-0.040	0.0000	-0.91	-61	-4.1
	4	-0.041	0.0000	-0.90	-57	-3.8
	5	-0.047	0.0000	-0.93	-56	-3.8
	6	-0.045	0.0000	-0.93	-49	-3.3



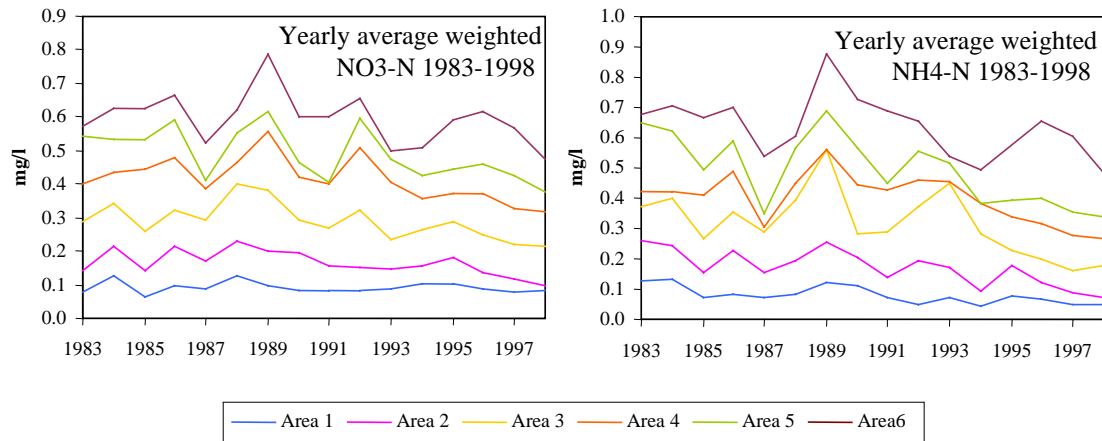
**Figure 24** Annual median change in wet deposition of non marine sulphur at individual stations, 1985-1998 (mg/m<sup>2</sup>/year). Stations from left to right are arranged from north to south. The 90% confidence interval is indicated in the figure.

#### 4.2.2 Nitrate and ammonium

Concentration of nitrate and ammonium in precipitation show decreasing gradients from the southern to the northern part of Sweden (Figure 25). In an earlier trend study (Kindbom et al., 1994), examining the period 1980-1992, time trends of nitrate and ammonium showed slightly increasing trends. In contrast to the earlier study, decreasing concentrations were found to be statistically significant in several of the areas during the period 1983-1998. Area 2, 3, 4 and 5 show significantly decreasing trends of nitrate at least at the 95% level (Table 6). Significantly decreasing trends in the concentration of ammonium were detected in all areas, except area 6.

Annual median changes in wet deposition of NO<sub>3</sub>-N at individual stations are presented in Figure 26. Overall the absolute annual median decrease in deposition seem to have been somewhat larger at the stations in the southern part of the country than in the north. The variations, and thus the uncertainty, in the calculated annual median change have, however, also been larger as represented by the wider 90% confidence intervals indicated in Figure 26.

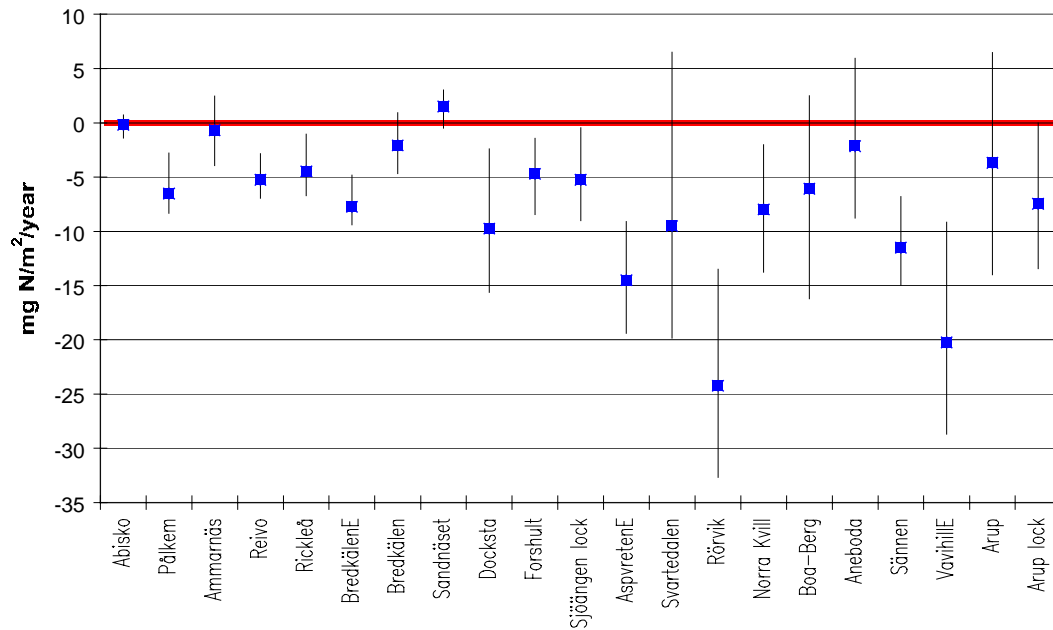
Annual median changes in wet deposition of NH<sub>4</sub>-N for each station are presented in Figure 27. The calculated absolute changes were largest at some stations in the southern part of the country.



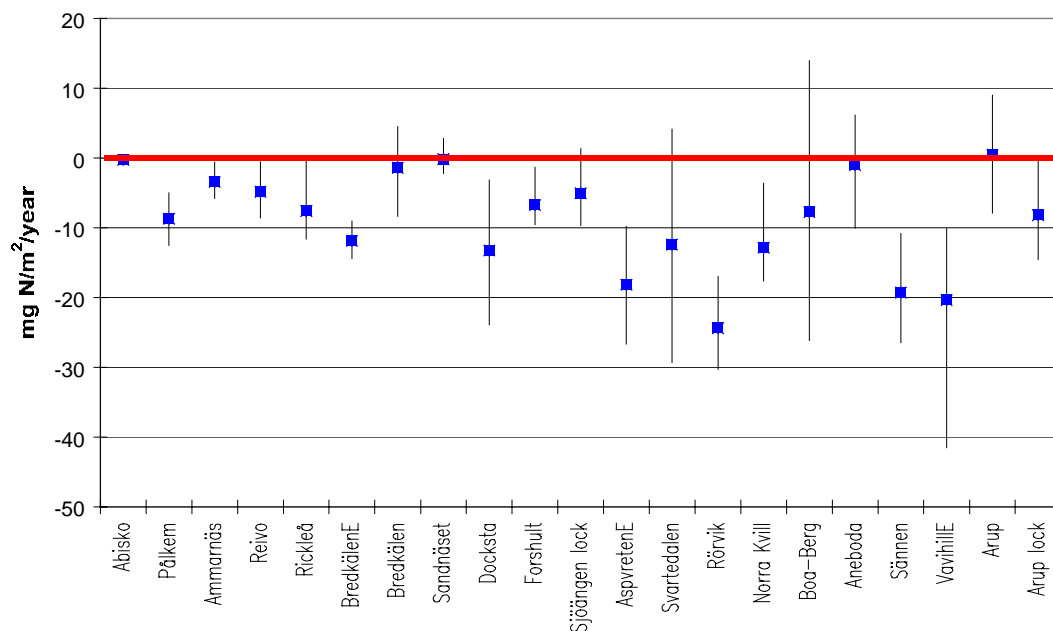
**Figure 25** Weighted average  $\text{NO}_3\text{-N}$  and  $\text{NH}_4\text{-N}$  concentrations in precipitation, 1983-1998 in six different regions in Sweden (mg N/l).

**Table 6** Trend analysis of annual average concentrations of  $\text{NO}_3\text{-N}$  and  $\text{NH}_4\text{-N}$  1983-1998 (mg N/l). Linear regression.

	Area	Slope of the regression line (mg/l/year)	p	r	change in concentration (%)	change in concentration (%/year)
<b><math>\text{NO}_3\text{-N}</math> 1983-1998</b>	1	-0.001	0.5132	-0.18		
	2	-0.004	0.0222	-0.57	-33	-2.2
	3	-0.006	0.0202	-0.57	-28	-1.9
	4	-0.008	0.0256	-0.56	-24	-1.6
	5	-0.009	0.0164	-0.59	-25	-1.7
	6	-0.006	0.1527	-0.37		
<b><math>\text{NH}_4\text{-N}</math> 1983-1998</b>	1	-0.004	0.0031	-0.69	-55	-3.7
	2	-0.009	0.0006	-0.76	-58	-3.9
	3	-0.012	0.0297	-0.54	-44	-3.0
	4	-0.009	0.0281	-0.55	-30	-2.0
	5	-0.017	0.0028	-0.69	-41	-2.7
	6	-0.010	0.0645	-0.47		



**Figure 26** Annual median change in wet deposition of  $\text{NO}_3\text{-N}$  at individual stations, 1985-1998 ( $\text{mg}/\text{m}^2/\text{year}$ ). Stations from left to right are arranged from north to south. The 90% confidence interval is indicated in the figure.



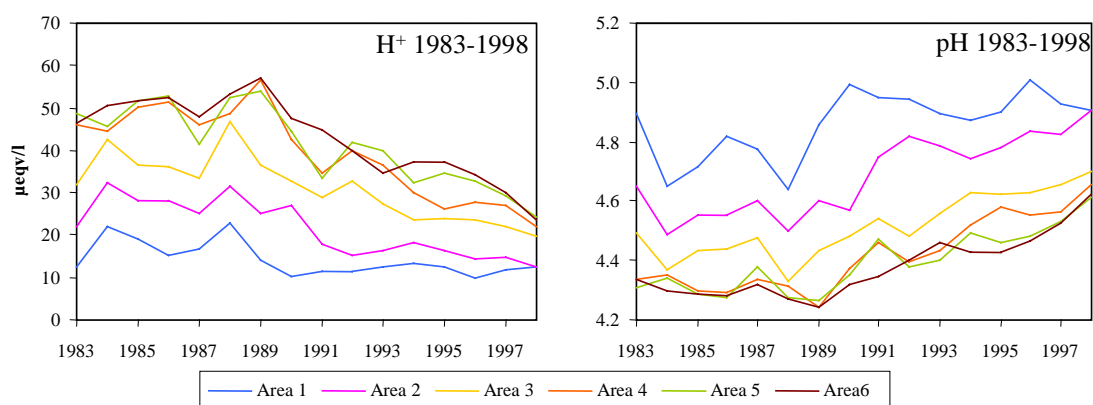
**Figure 27** Annual median change in wet deposition of  $\text{NH}_4\text{-N}$  at individual stations, 1985-1998 ( $\text{mg}/\text{m}^2/\text{year}$ ). Stations from left to right are arranged from north to south. The 90% confidence interval is indicated in the figure.

### 4.2.3 pH in precipitation and deposition of $H^+$

The atmospheric deposition of acidic substances, such as sulphur and nitrogen compounds emitted from combustion processes, have caused acidification of soil and water. Low pH values and a large content of  $H^+$  ions in precipitation are indicators of “acid rain”. The emissions of sulphur have declined since 1980 (Figure 1), which has resulted in a decrease of sulphur compounds in air and precipitation (Figures 3, 5, 23 and 24). A smaller reduction of nitrogen ( $NO_x$  and  $NH_3$ ) emissions has been accomplished during the 1990’s (Figure 1). No signs of decreasing nitrogen trends could be seen in an earlier report on sulphur and nitrogen compounds in Sweden 1980-1992 (Kindbom et. al, 1994), but results from 1983-1998 show a tendency of decreasing nitrogen compounds in air and precipitation at several stations in Sweden (Chapters 3.2 and 4.2.2).

Weighted average annual  $H^+$  concentrations and pH in precipitation 1983-1998 are summarised in Figure 28. The concentrations of hydrogen ions show a decreasing gradient from southern to northern Sweden, and consequently pH values are higher in the north than in the south.  $H^+$  has decreased and pH has increased in all areas since 1989. The linear regression of annual concentration of  $H^+$  in precipitation shows a strong decrease in all areas ( $p < 0.05$ ), as can be seen in Table 7. The concentration of  $H^+$  has decreased by approximately 50 % in all areas between 1983 and 1998.

The deposition of hydrogen ions has decreased at all stations except in the very north of Sweden (Figure 29).  $H^+$  in Area 1, where Abisko and Ammarnäs are situated, has had the lowest concentration of  $H^+$  in precipitation of all areas at least since 1983. The decreasing sulphur emissions of acidifying substances might not have had such a strong impact on the relatively low  $H^+$  load in northern Sweden as on the originally higher load in southern Sweden.

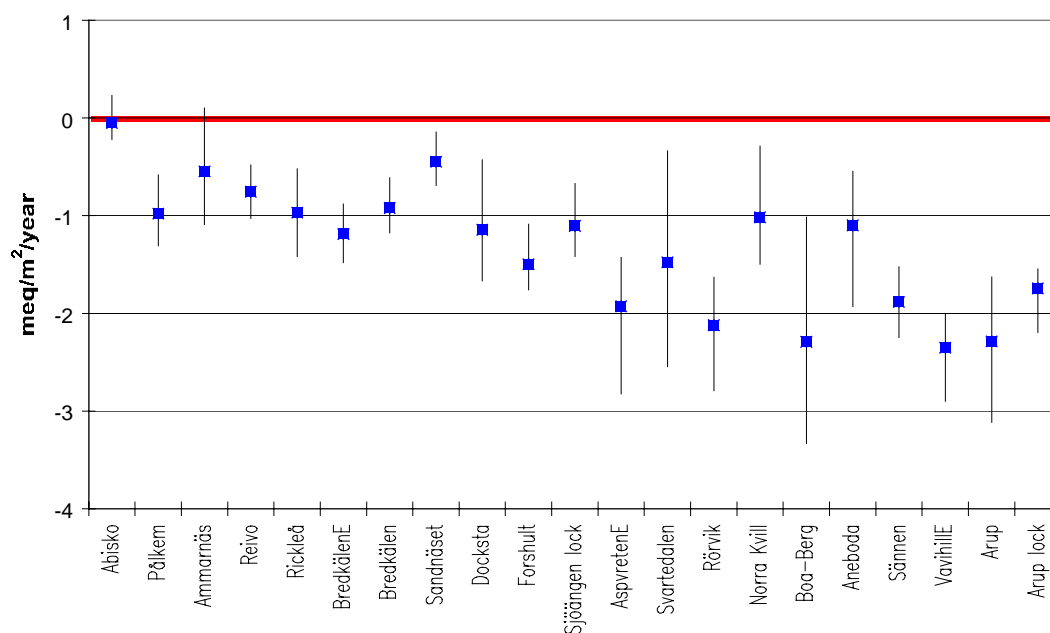


**Figure 28** Weighted average  $H^+$  concentrations ( $\mu eqv/l$ ) and pH in precipitation, 1983-1998 in six different regions in Sweden.



**Table 7** Trend analysis of annual average concentrations of  $H^+$  1983-1998 ( $\mu\text{eqv } H^+/l$ ). Linear regression.

	area	slope of the regression line ( $\mu\text{ekv}/l/\text{year}$ )	p	r	Change in concentration (%)	Change in concentration (%/year)
<b><math>H^+</math></b>						
<b>1983-1998</b>						
	1	-0.505	0.0132	-0.60	-42	-2.8
	2	-1.161	0.0000	-0.84	-58	-3.8
	3	-1.299	0.0001	-0.81	-48	-3.2
	4	-1.892	0.0000	-0.86	-53	-3.5
	5	-1.661	0.0000	-0.85	-46	-3.1
	6	-1.707	0.0000	-0.85	-46	-3.1

**Figure 29** Annual median change in wet deposition of  $H^+$  at individual stations, 1985-1998 ( $\text{meq}/\text{m}^2/\text{year}$ ). Stations from left to right are arranged from north to south. The 90% confidence interval is indicated in the figure.

### 4.3 Base cations and chloride

Base cations are important nutrients for forest trees and plant life. In the acidification process of soils, base cations are leached from the soil and replaced by hydrogen and aluminium ions. Base cation leakage can, on a long time scale, result in nutrient shortage and impaired forest growth. Sources of base cation supply to soils are soil erosion, sea salt, agricultural activity and deposition from industrial processes and combustion emissions.

Linear regression has been applied to study the base cation concentration in precipitation as a function of time. A minority of the linear regressions show a statistical significance higher than the 95 % level. The figures show that the interannual variations are large and no general trends can be found. The concentration, especially of potassium, may be highly influenced by contamination of biological material or throughfall. The sites are however visited for inspection regularly, when the specific requirements for an open field location are controlled. A possible contamination from throughfall in the samples is therefore generally not considered to be a major problem. Another aspect is the subjective judgement when evaluating data, for accepting or rejecting measurement results, which may have changed somewhat during the period.

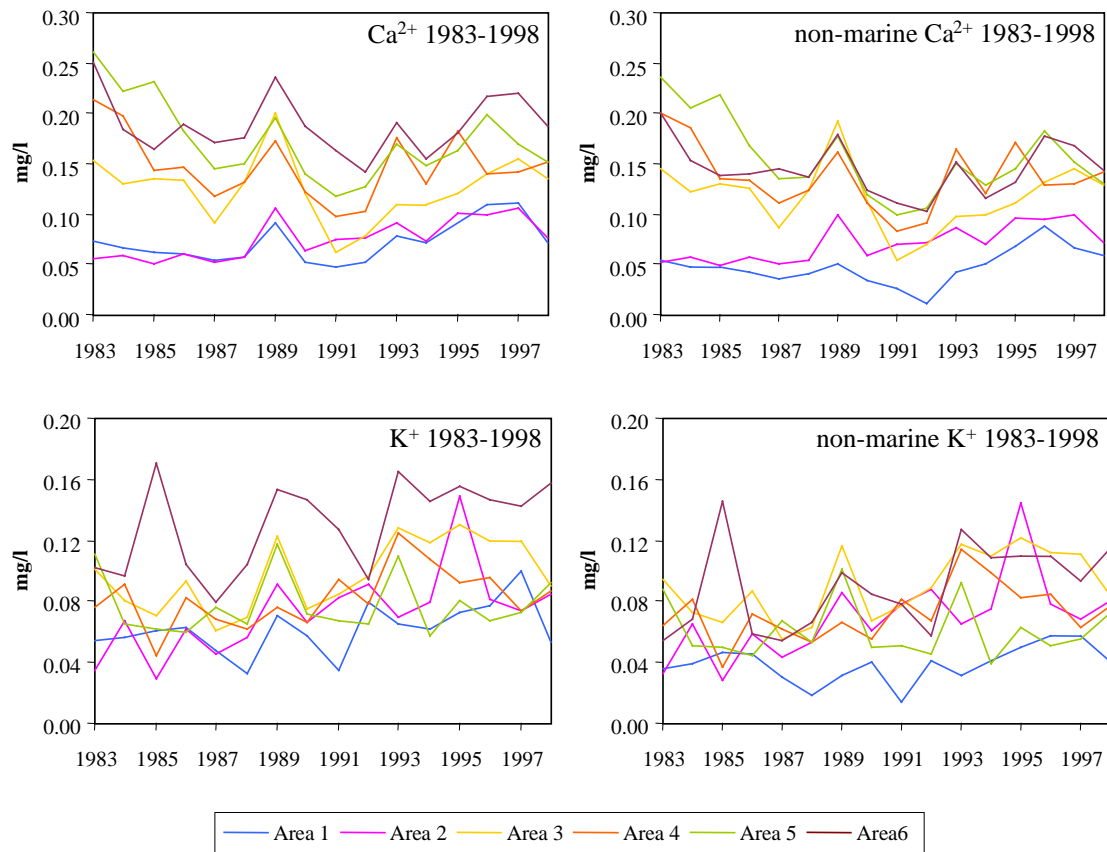
The linear regression tests with results above the 95 % level are summarised in Tables 8-11. Results with lower statistical significance have been left out.

#### 4.3.1 Calcium (Ca) and potassium (K)

The variations in the concentrations of calcium and potassium in precipitation between different years and stations are large (Figure 30). The concentrations of calcium and potassium however show decreasing gradients from south to north. The largest marine influence can be observed in Areas 1, 5 and 6.

The concentration of **calcium** in precipitation between 1983-1998 appears to have increased in the northern areas of Sweden and decreased in Area 5 (Table 8). No trends can be detected in the remaining areas. Sandnäset and Ammarnäs in Area 1 are highly influenced by the sea. This might explain why the total amount of calcium in Area 1 has increased, while non-marine calcium in the same area show random variations. The concentration of calcium in especially Sandnäset might attain high levels when strong winds from the west are predominant.

The concentration of **potassium** in precipitation appears to have increased in several areas (Table 9) although the predominant picture is of random and large inter-annual variations. As in the discussion above, concerning marine influence, the sea influences the stations in area 6.



**Figure 30** Weighted average of  $\text{Ca}^{2+}$ , non-marine  $\text{Ca}^{2+}$ ,  $\text{K}^{+}$  and non-marine  $\text{K}^{+}$  concentrations in precipitation, 1983-1998 in six different regions in Sweden (mg/l).

The annual median changes in wet deposition of non-marine calcium and non-marine potassium at individual stations are presented in Figure 31 and Figure 32 respectively. The statistical significance levels are above 95 % in Sandnäset and Bredkålen concerning an increase of both compounds. Furthermore, calcium at VavihillE shows a statistically significant decrease and potassium at Arup, Rickleå and Reivo show statistically significant increases. The concentrations at the remaining stations have been fluctuating during the period.

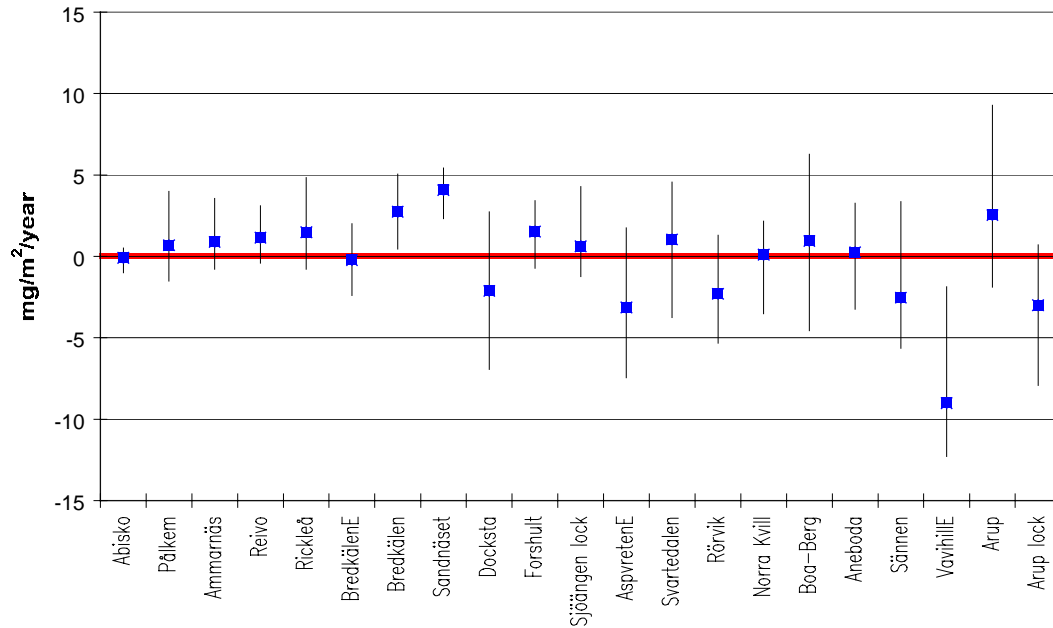
No general trend can be found for calcium and potassium throughout the country.

**Table 8** *Trend analysis of annual average concentrations of calcium 1983-1998 (mg Ca/l). Linear regression.*

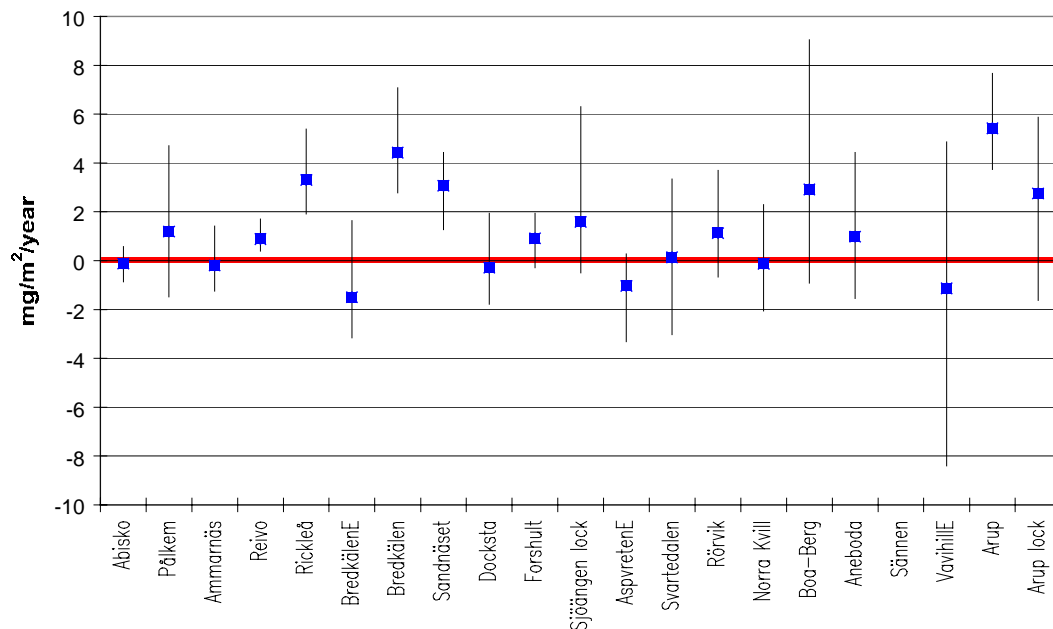
	area	slope of the regression line (mg/l/year)	p	r	change in concentration (%)	change in concentration (%/year)
<b>1983-1998</b>						
<b>Ca<sup>2+</sup></b>	1	0.002	0.0374	0.52	59	3.9
	2	0.003	0.0011	0.74	88	5.9
	5	-0.004	0.0374	-0.52	-32	-2.1
<b>non-marine Ca<sup>2+</sup></b>	2	0.003	0.0012	0.73	87	5.8
	5	-0.005	0.0266	-0.55	-36	-2.4

**Table 9** *Trend analysis of annual average concentrations of potassium 1983-1998 (mg K/l). Linear regression.*

	area	slope of the regression line (mg/l/year)	p	r	change in concentration (%)	change in concentration (%/year)
<b>1983-1998</b>						
<b>K<sup>+</sup></b>	2	0.004	0.0078	0.64	123	8.2
	3	0.003	0.0241	0.56	53	3.5
	6	0.003	0.0359	0.53	45	3.0
<b>non-marine K<sup>+</sup></b>	2	0.004	0.0097	0.62	124	8.2
	3	0.003	0.0286	0.55	53	3.6



**Figure 31** Annual median change in wet deposition of non-marine  $\text{Ca}^{2+}$  at individual stations, 1985-1998 ( $\text{mg}/\text{m}^2/\text{year}$ ). Stations from left to right are arranged from north to south. The 90% confidence interval is indicated in the figure.



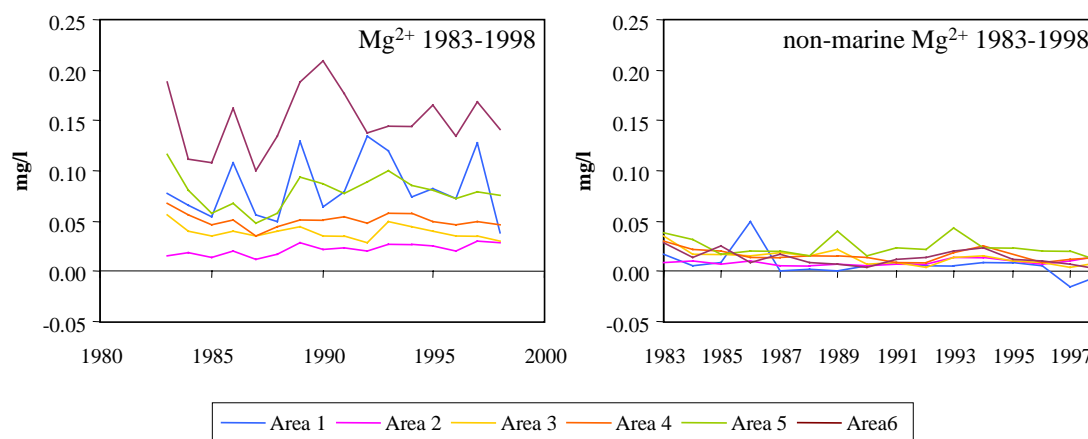
**Figure 32** Annual median change in wet deposition of non-marine  $\text{K}^+$  at individual stations, 1985-1998 ( $\text{mg}/\text{m}^2/\text{year}$ ). Stations from left to right are arranged from north to south. The 90% confidence interval is indicated in the figure. The results from Sännen have been excluded because of contamination.

### 4.3.2 Magnesium (Mg)

The sea is a great contributor to the total amount of magnesium in precipitation (Figure 33), especially in areas 1, 5 and 6. The fluctuations between the years are large in these areas, probably because of the concentration's dependence of wind speed and direction in relation to the sea. Area 2 has had the lowest concentration of total magnesium.

Linear regression analysis was undertaken of the concentrations in precipitation of magnesium and non-marine magnesium in the six areas. Two, out of twelve, linear regression analyses resulted in regression lines with statistical significances above the 95 % level (Table 10).

The calculations of the marine influence are based on the assumption that all sodium in the precipitation sample originates from sea salt. Contributions from other sources might, however, influence the sodium concentration in precipitation. Due to the relatively low levels of magnesium, the calculation of non-marine magnesium at rare occasions results in negative values. For that reason the annual median change in wet deposition of magnesium has been left out.



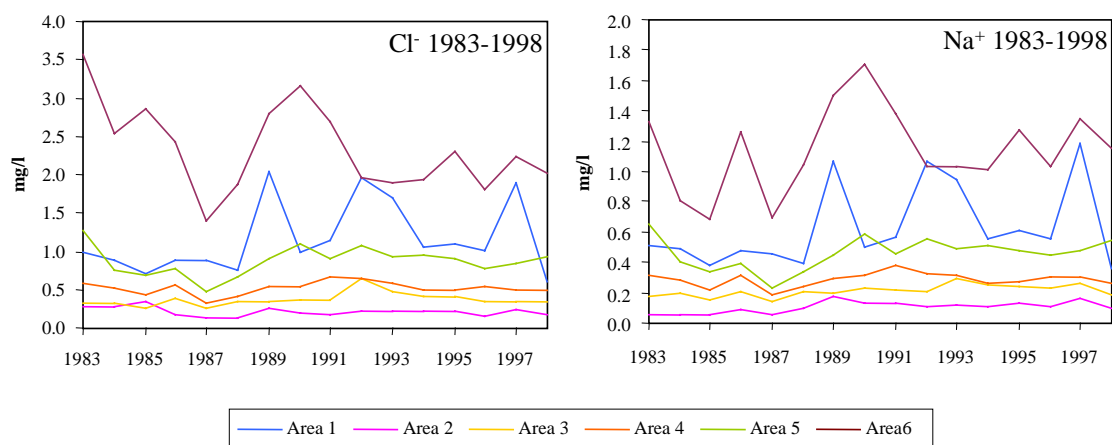
**Figure 33** Weighted average  $Mg^{2+}$  and non-marine  $Mg^{2+}$  concentration in precipitation, 1983-1998 in six different regions in Sweden (mg/l).

**Table 10** Trend analysis of annual average concentrations of magnesium 1983-1998 (mg Mg/l). Linear regression.

	area	slope of the regression line (mg/l/year)	p	r	change in concentration (%)	change in concentration (%/year)
<b>1983-1998</b>						
<b><math>Mg^{2+}</math></b>	2	0.001	0.0007	0.76	86	5.7
<b>non-marine <math>Mg^{2+}</math></b>	3	-0.001	0.0016	-0.72	-78	-5.2

### 4.3.3 Sodium (Na) and chloride (Cl)

The concentrations of sodium and chloride in precipitation depend to the greatest extent on marine contribution. Area 1 and 6 have had the highest sodium and chloride content in precipitation, while area 2 has had the lowest (Figure 34). This is in correspondence with the results for magnesium. The variations amongst the years have been large in areas 1 and 6. In areas 2, 3 and 4 the interannual variations have been smaller.



**Figure 34** Weighted average  $\text{Cl}^-$  and  $\text{Na}^+$  concentrations in precipitation, 1983-1998 in six different regions in Sweden (mg/l).

Areas 2 and 3 show a statistically significant increase of **sodium** concentration in precipitation during the period (Table 11). The analyses of **chloride** did not exhibit any statistically significant results.

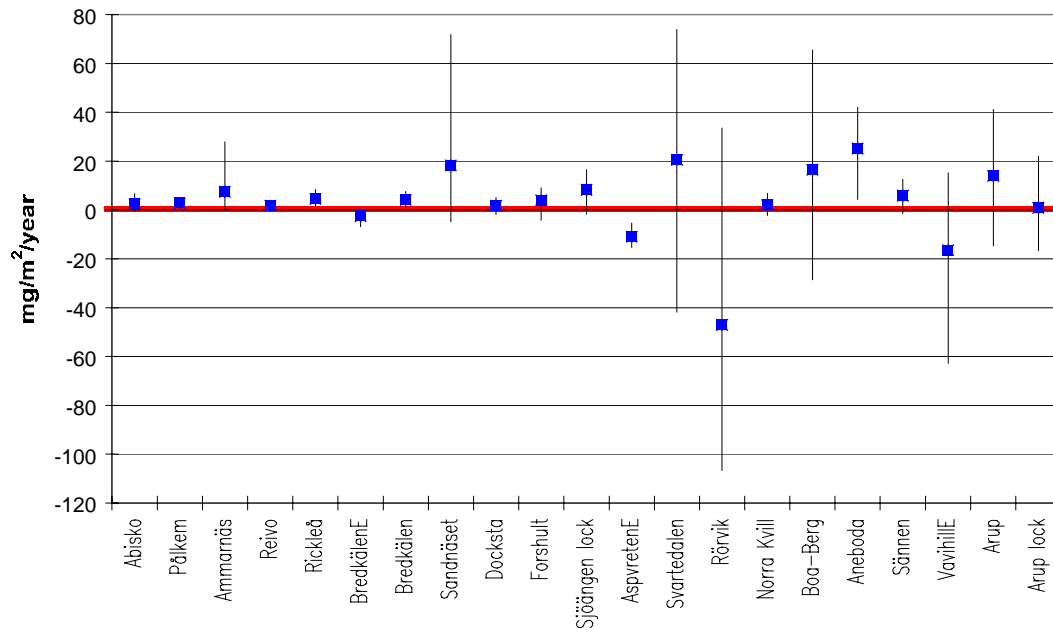
**Table 11** Trend analysis of annual average concentrations of sodium 1983-1998 (mg Na/l). Linear regression.

	area	slope of the regression line (mg/l/year)	p	r	change in concentration (%)	change in concentration (%/year)
<b>1983-1998</b>						
<b>Na<sup>+</sup></b>	2	0.005	0.0064	0.65	113	7.5
	3	0.005	0.0156	0.59	44	2.9

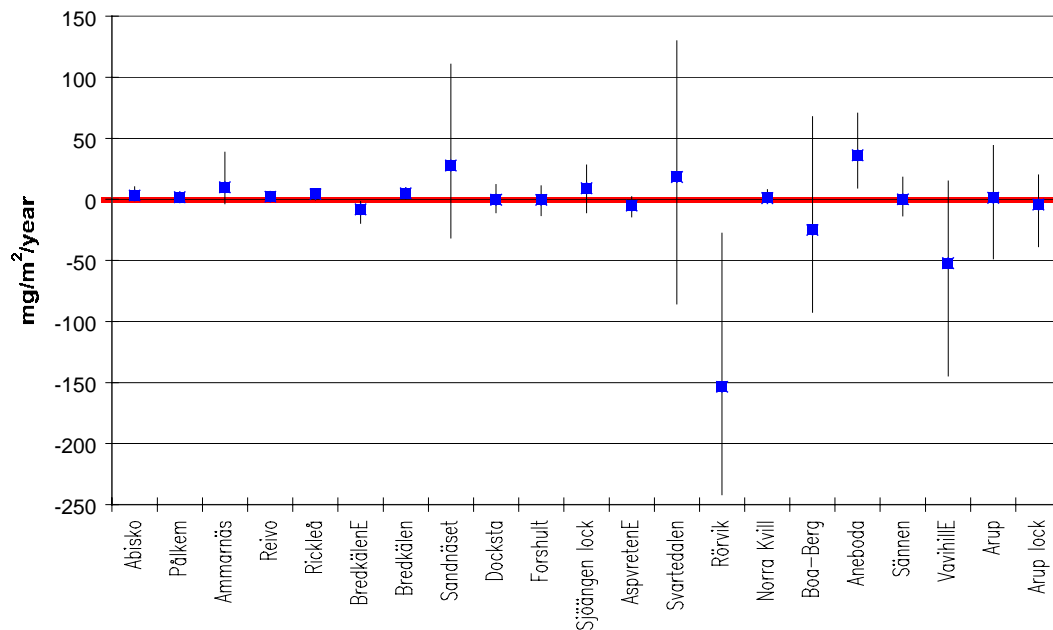
The deposition of sodium and chloride at the individual stations during the period (Figures 35 and 36) show the greatest variation in pollution load at the stations along the coast (Arup, Vavihill, Boa-berg, Rörvik and Svartedalen) and at Sandnåset in area 1. The variations in deposition were, as expected, larger at the stations under marine influence, than at stations situated in interior parts of the country.

Because of the dominating marine influence it is difficult to discern any trends in the concentrations of magnesium, sodium and chloride. The variations in the marine contribution have probably been much larger than variations from other sources. The trend analyses of annual average concentrations have only given statistically

significant results in area 2 and 3 concerning an increase of magnesium and sodium. These areas are the ones with the smallest marine influence.



**Figure 35** Annual median change in wet deposition of Na<sup>+</sup> at individual stations, 1985-1998 (mg/m<sup>2</sup>/year). Stations from left to right are arranged from north to south. The 90% confidence interval is indicated in the figure.



**Figure 36** Annual median change in wet deposition of Cl<sup>-</sup> at individual stations, 1985-1998 (mg/m<sup>2</sup>/year). Stations from left to right are arranged from north to south. The 90% confidence interval is indicated in the figure.

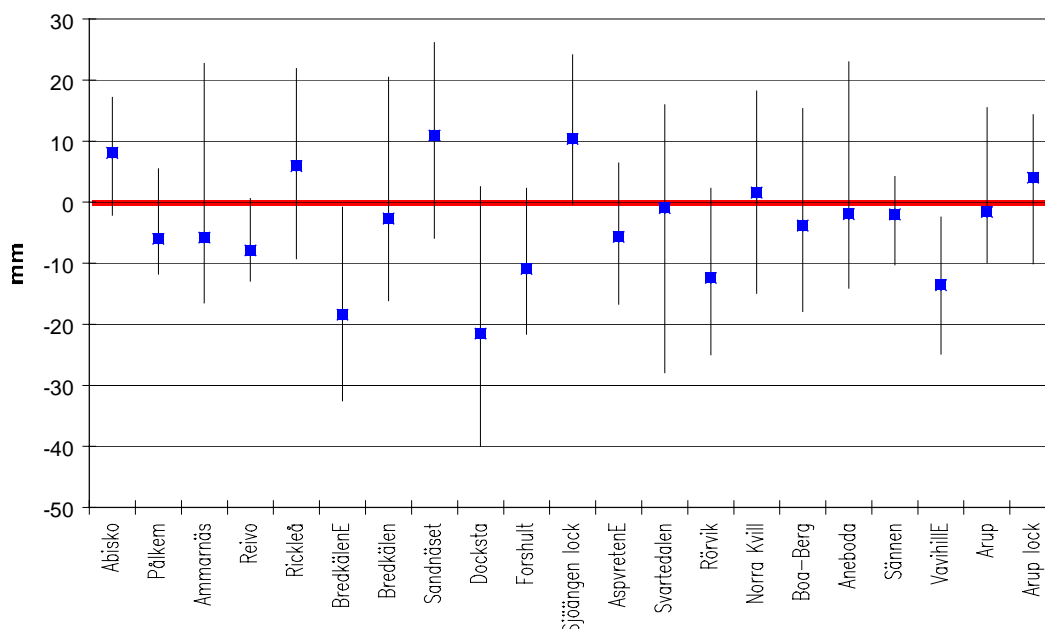


## 4.4 Precipitation amount

To evaluate trends of deposition it is essential to analyse possible trends in annual precipitation data. The amount of the deposition of different compounds is highly dependent on the precipitation amount. Likewise, the concentration in precipitation might also depend on the amount of precipitation. Heavy rain or snowfalls have the ability to dilute the concentration of its contents, while smaller amounts often contain higher concentrations. The variability of concentration in precipitation due to precipitation amount is probably more of a seasonal phenomenon, while the precipitation amount has great influence on the annual values of wet deposition.

Statistically significant trends of decreasing precipitation amount could be seen in BredkälenE, Docksta and Vavihill. The Mann Kendall tests of wet deposition of non-marine sulphur, nitrate, ammonium and H<sup>+</sup> showed that these three stations had statistically significant decreasing trends concerning all the compounds during the period. It should be noticed that all stations showed decreasing trends of sulphur, all stations except Abisko showed decreasing trends of H<sup>+</sup> and that decreasing trends were discovered at more than half of the stations concerning the nitrate and ammonium.

The strongest tendencies of an increasing trend of precipitation amount were discovered in Abisko and Sjöängen lock, But the statistical significances were below the 95 % level, chosen to represent statistical significance in this study. Abisko is the only station without a statistically significant decrease of H<sup>+</sup> deposition and one of the stations showing no trends in the analysis of deposition of nitrate and ammonium. Abisko is, however, situated in the very north, with a low annual precipitation amount and low load of pollutants.



**Figure 37** Annual median change in precipitation amount at individual stations, 1985-1998 (mm/year). Stations from left to right are arranged from north to south. The 90% confidence interval is indicated in the figure.

## 5. Time trends of heavy metals

### 5.1 Heavy metals in precipitation

Heavy metals in precipitation have been sampled and analyzed at four sites, Arup, Svartedalen, Aspvreten and Breckålen, in Sweden since 1986. Average concentration in precipitation, median annual change in concentration and the results from the statistical calculations concerning arsenic, cadmium, lead, nickel and mercury are summarised in Figures 38-45. Arsenic, cadmium and nickel are in the focus of the interest within EU, while cadmium, lead and mercury are priority metals within the EMEP cooperation.

Emissions of heavy metals to air are associated with high temperature processes like coal combustion, waste incineration and metal industries. **Arsenic** (As) is emitted to the atmosphere mainly from coal combustion. Examples of local sources are mining industries, glass industries and the use of arsenic in pesticides and wood preservatives (Rühling, 1996). The main sources of **cadmium** (Cd) is the use of phosphate fertilizers, in which cadmium is a constituent, and combustion of fossil fuels and waste incineration. The greater part of the emissions of **lead** (Pb) has its origin in combustion of leaded fuel. The use of leaded petrol has decreased in western Europe but is still used in eastern Europe. **Nickel** (Ni) is mainly spread to the environment by oil and coal combustion.

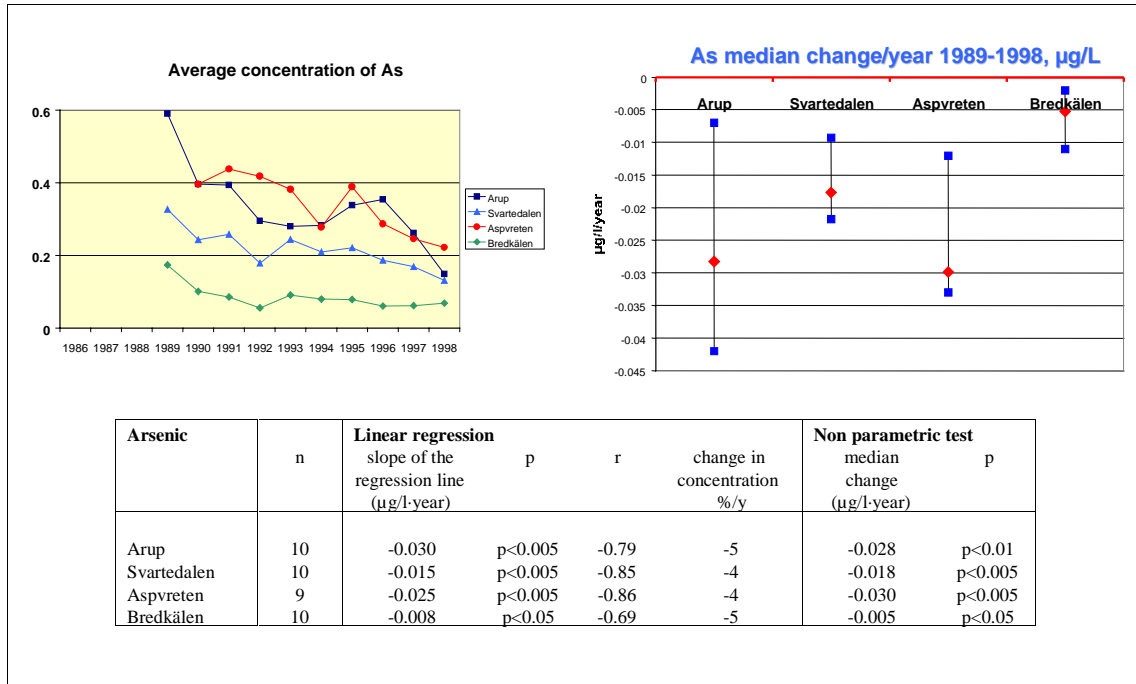
The Swedish emissions of heavy metals have decreased to a small fraction of the rather large emissions during the 1970's ([www.environ.se](http://www.environ.se)). The long-range transport from Europe is, at the present time, responsible for the major part of the heavy metal deposition in Sweden, especially cadmium, lead and zinc.

#### 5.1.1 Arsenic, cadmium, lead and nickel

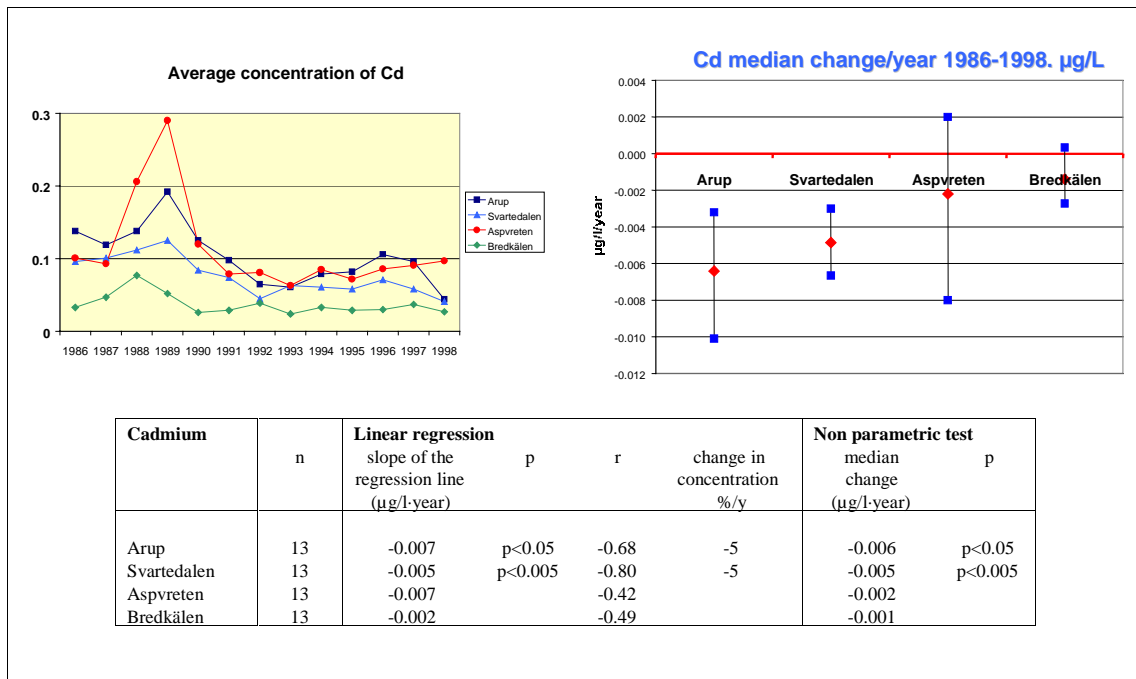
The annual average concentrations of arsenic, cadmium, lead and nickel, as well as the results of the trend analyses are presented in figures 38-41.

The concentration of **arsenic** has decreased at all four stations between 1989 and 1998. The largest absolute decrease in concentration can be seen in Arup in southern Sweden and the smallest in Breckålen in northern Sweden. **Cadmium** has decreased in Arup and Svartedalen with at least a significance of 95 %. The trends at the remaining two stations are more vague. The linear regression and the non parametric test both resulted in statistically significant decreasing trends of **lead** in Svartedalen and Breckålen. The concentration of **nickel** in precipitation has decreased at Arup, Svartedalen and Breckålen.

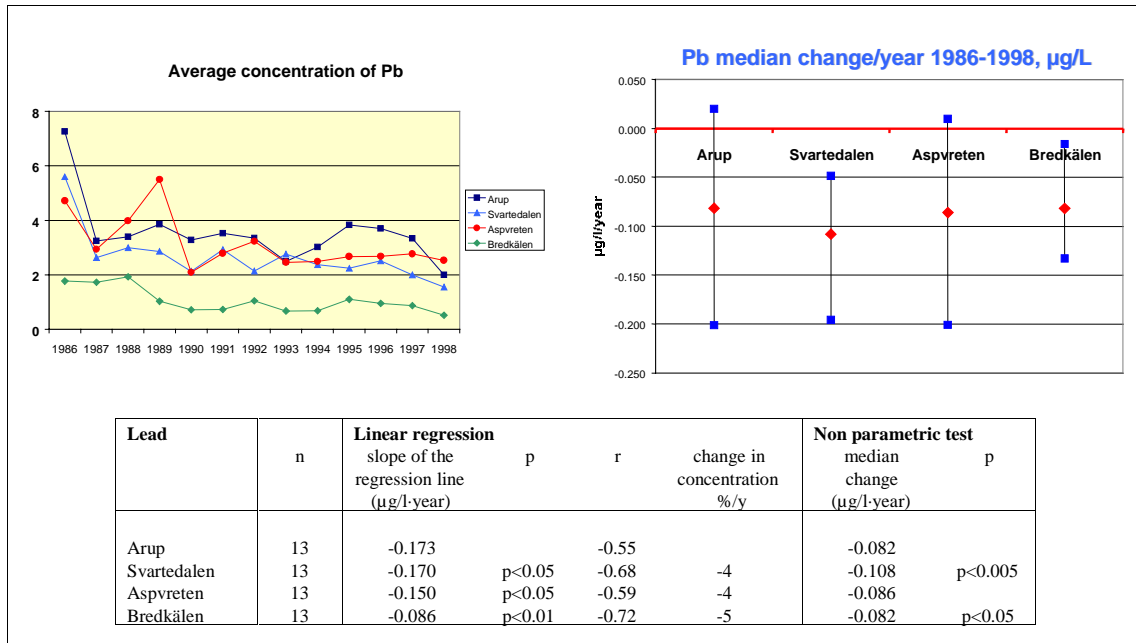
All heavy metals show statistically significant decreasing trends of concentration in precipitation in Svartedalen at the Swedish west coast.



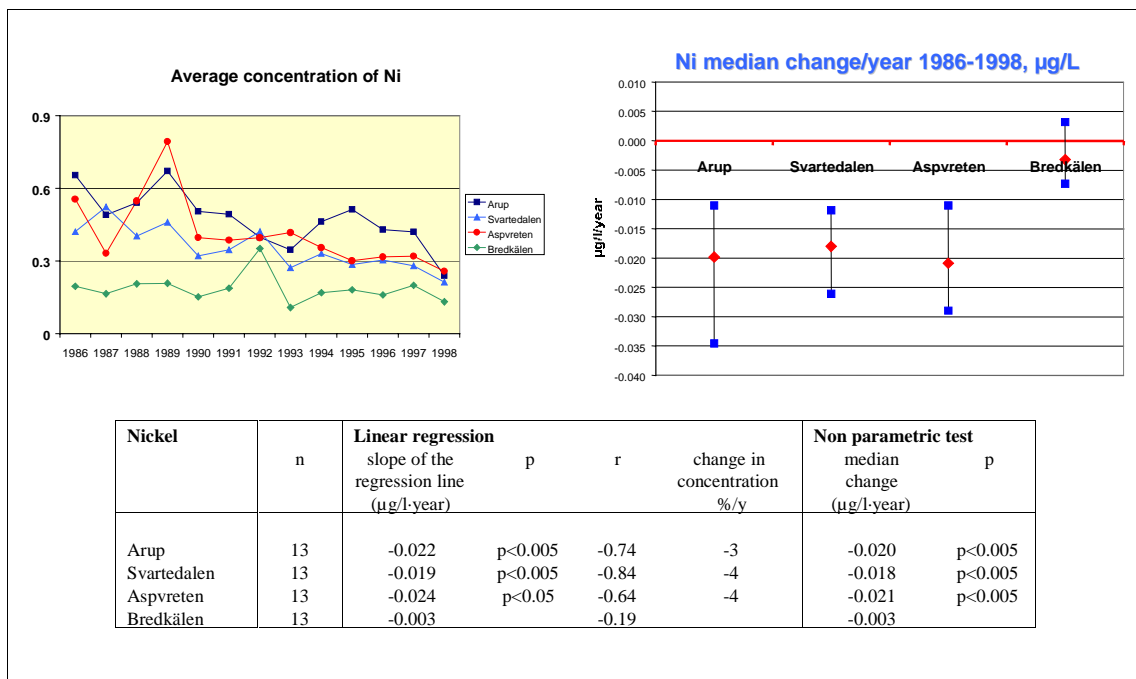
**Figure 38** Annual average concentration of (µg/l), annual median change in concentration and trend analysis of arsenic 1989-1998 (Aspvreten 1990-1998).



**Figure 39** Annual average concentration (µg/l), annual median change in concentration and trend analysis of cadmium 1986-1998.

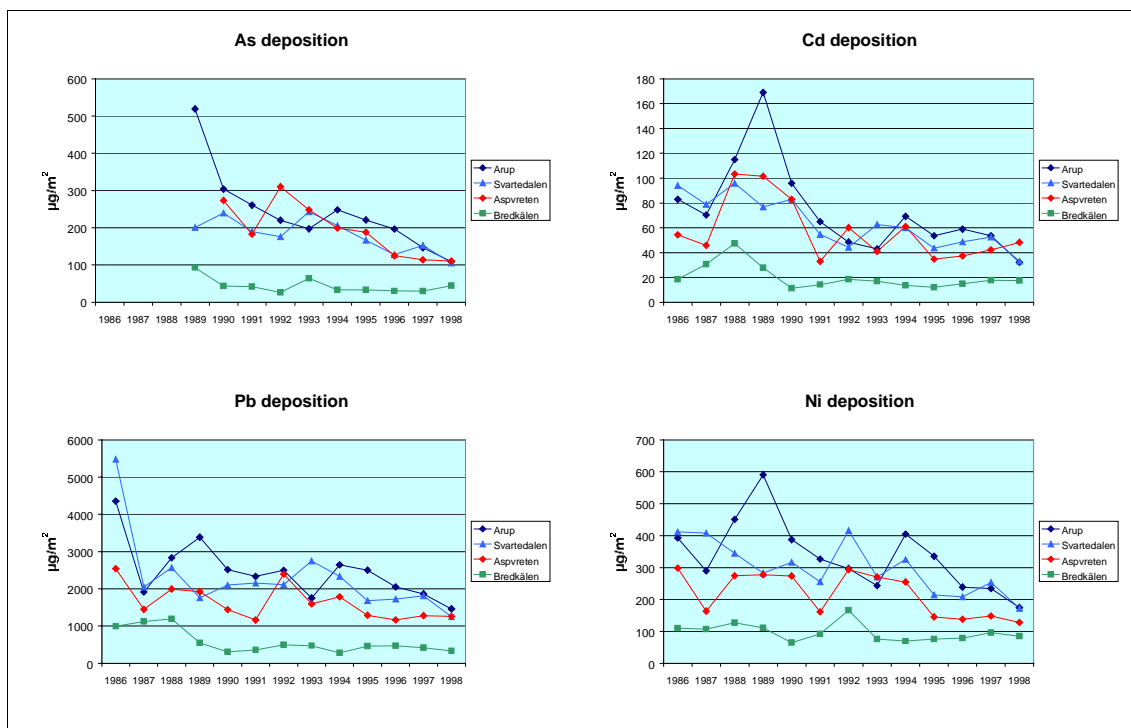


**Figure 40** Annual average concentration (µg/l), annual median change in concentration and trend analysis of lead 1986-1998.



**Figure 41** Annual average concentration (µg/l), annual median change in concentration and trend analysis of nickel 1986-1998.

The annual wet deposition of arsenic, cadmium, lead and nickel are presented in Figure 42. The deposition load has been lowest at Breckkälen in the north of Sweden during the whole period. Although the variations from year to year have been large, the figures indicate generally decreasing trends in the deposition of all the heavy metals during the period.

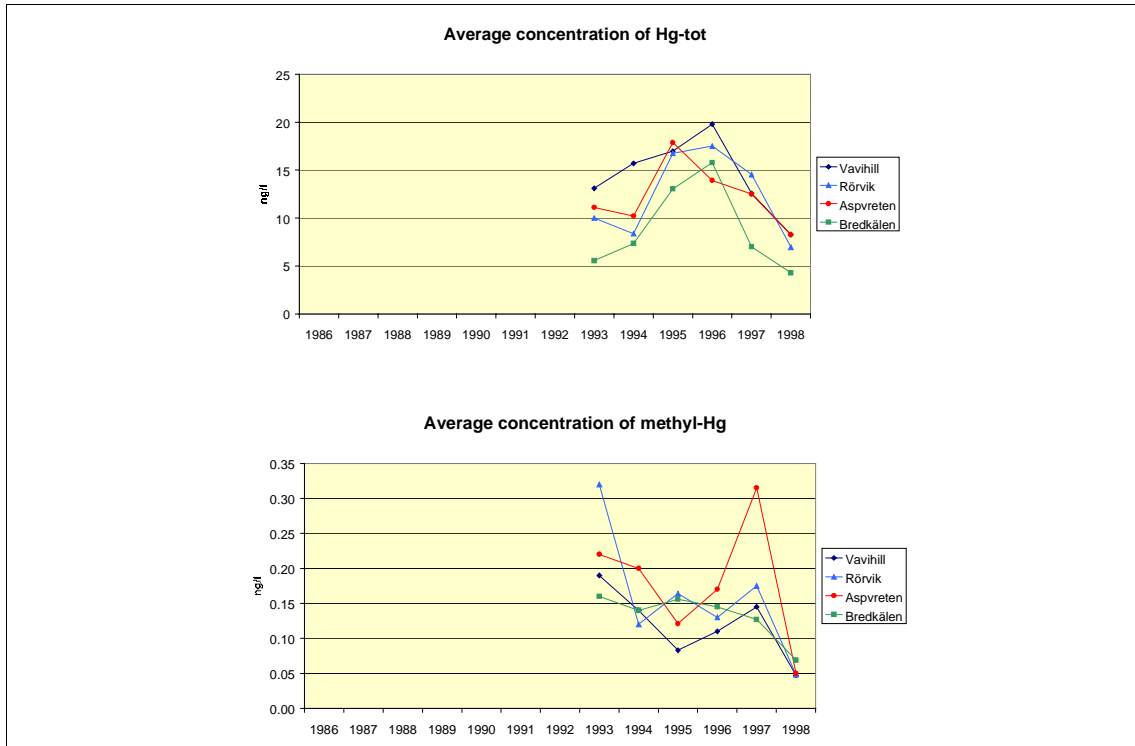


**Figure 42** Annual wet deposition of arsenic, cadmium, lead and nickel ( $\mu\text{g}/\text{m}^2$ ).

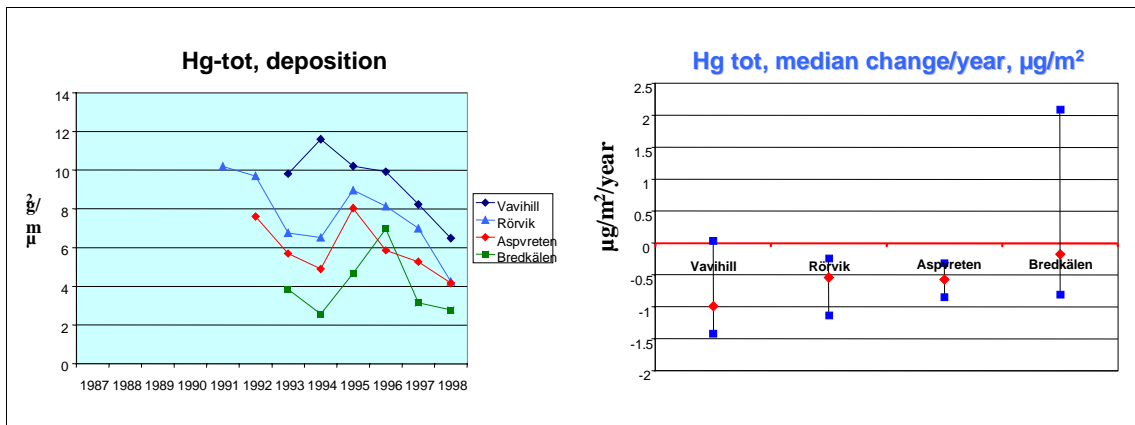
### 5.1.2 Total-mercury and methyl-mercury

Mercury is emitted to the atmosphere from coal and waste combustion and through chlorine-alkali industrial processes. Another source is the former use of amalgam for dental purposes (Rühling, 1996). The aim of the Swedish Environmental Protection Agency is to gradually shelve or restrict the use of mercury to eliminate the supply to the environment in the long run ([www.environ.se](http://www.environ.se)). Mercury is easily spread over large areas because its chemical and physical properties make it possible for mercury compound to remain in air and water during long periods of time (Swedish Environmental Protection Agency, 1997). Mercury exists in many different species and the most toxic compound is methyl-mercury. Methyl-mercury accumulates in the biological food chain and predators at the top of the chain have the highest exposure.

Concentration of total-mercury and methyl-mercury in precipitation has been measured as monthly values at four stations since 1993. Annual average concentration values of total-mercury and methyl-mercury in precipitation are presented in Figure 43. The highest concentrations of total-mercury were registered in Aspvreten 1995 and at the remaining three stations one year later, 1996. Time trends have not been statistically evaluated since the measurements cover a relatively short period of time.



**Figure 43** Annual averages of total-mercury and methyl-mercury in precipitation. (ng/l) 1993-1999.



**Figure 44** Annual average deposition and annual calculated median change in deposition of total-mercury ( $\mu\text{g}/\text{m}^2/\text{year}$ ).

## 5.2 Heavy metals in mosses

The relative change in deposition of heavy metals from the atmosphere has been investigated by analysis of the metal content in mosses in Sweden since 1970. The method is based on the ability of mosses to almost exclusively extract metals from air and precipitation and not from the surface they grow on (Rühling, 1998). The metal content of mosses will therefore reflect the atmospheric deposition.

Mosses are excellent bio indicators of metal deposition because:

- They extract the main part of their nutrients from precipitation or from deposited airborne particles.
- They have a high capacity to absorb most heavy metals.
- They have a strongly reduced cuticle, which makes it easy for metals to bind to the cell walls.
- The cells of mosses are effectively exposed to the surrounding air, as the leaves only consist of one cell layer.

The Swedish environmental monitoring of heavy metals in moss species have been conducted with a regular interval of five years. The number of analysed samples has expanded from 120 in 1970 to 1172 in 1995. The two moss species used are *Hylocomium splendens* and *Pleurozium schreberi*. In 1970 mostly *Hylocomium splendens* was collected and analysed but today *Pleurozium schreberi* is the dominant test specie.

### 5.2.1 Heavy metal content in mosses and atmospheric heavy metal deposition

The changes in median concentrations of the different heavy metals in mosses in Sweden, 1970-1995, are presented in Figure 45. All heavy metals show decreasing trends during the period. The concentration of lead shows the strongest decline, with a decrease of the median value of almost 90% since 1970. For **chromium** and **iron** the decreases have been in the order of 80-85%, while the content of **cadmium** and **nickel** have decreased by 70-75%. The concentration of **mercury** has decreased with ~60% during the period. **Copper** and **zinc** have decreased with ~50% since 1970. The analysis of **arsenic** started in 1975 and since then a 25-35% decrease in median concentrations has been observed.

The changes in deposition of heavy metals with time in different geographical areas in Sweden is presented in Figure 46, represented by the median metal concentration in mosses from 1970 to 1995. The presentation is divided into four areas from southern to northern Sweden, Götaland, Svealand, Lower Norrland and Upper Norrland.

The load of heavy metals has been higher in the southern part of the country, Götaland and Svealand, compared to the northern part, lower and upper Norrland (Figure 46). All metals show decreasing trends from 1970 to 1995. The metal concentrations in Götaland and Svealand have decreased to a larger extent than the concentrations in Norrland. As a result, the strong southerly-northerly gradient over the country has been declining since 1970.

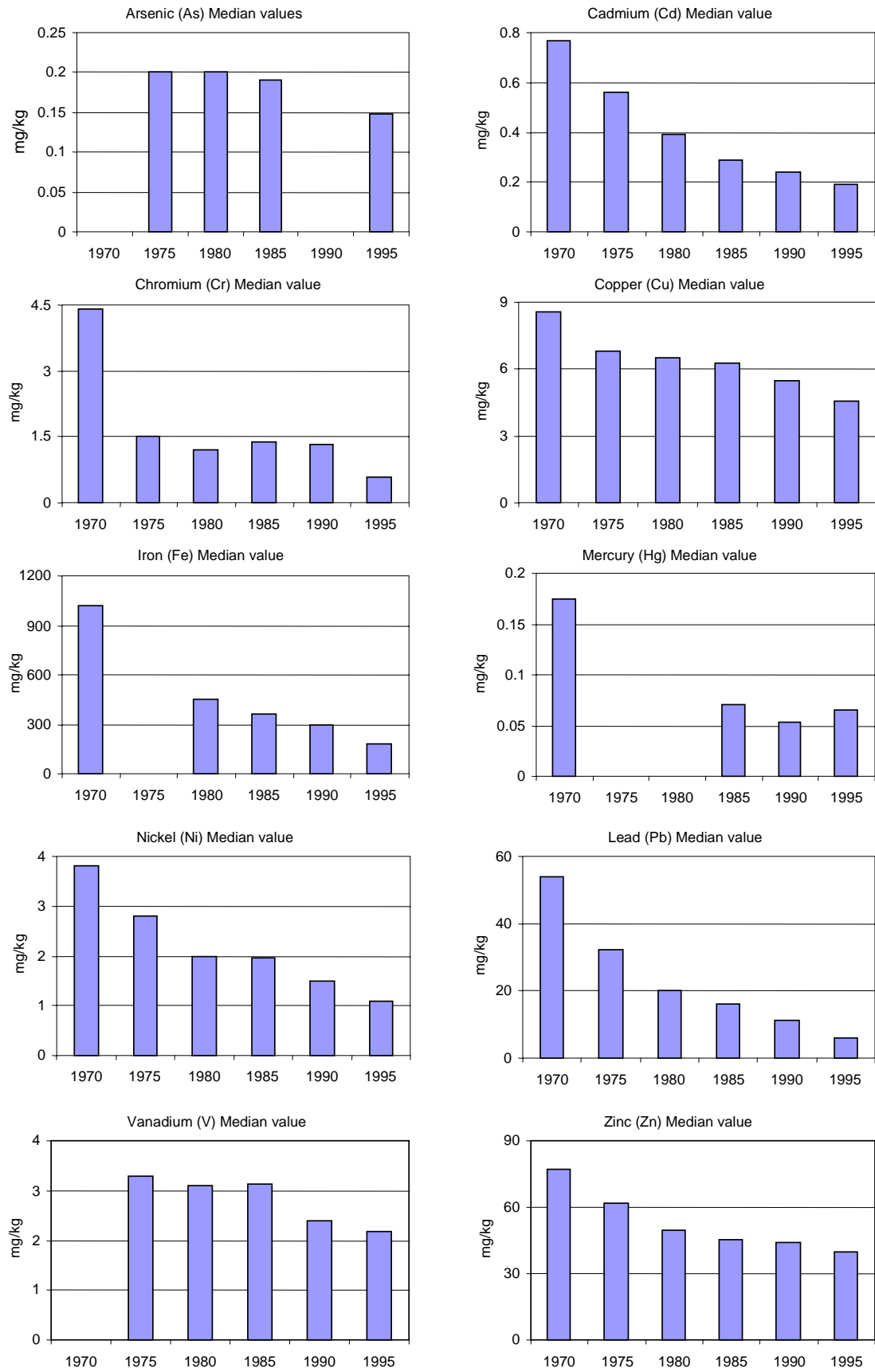
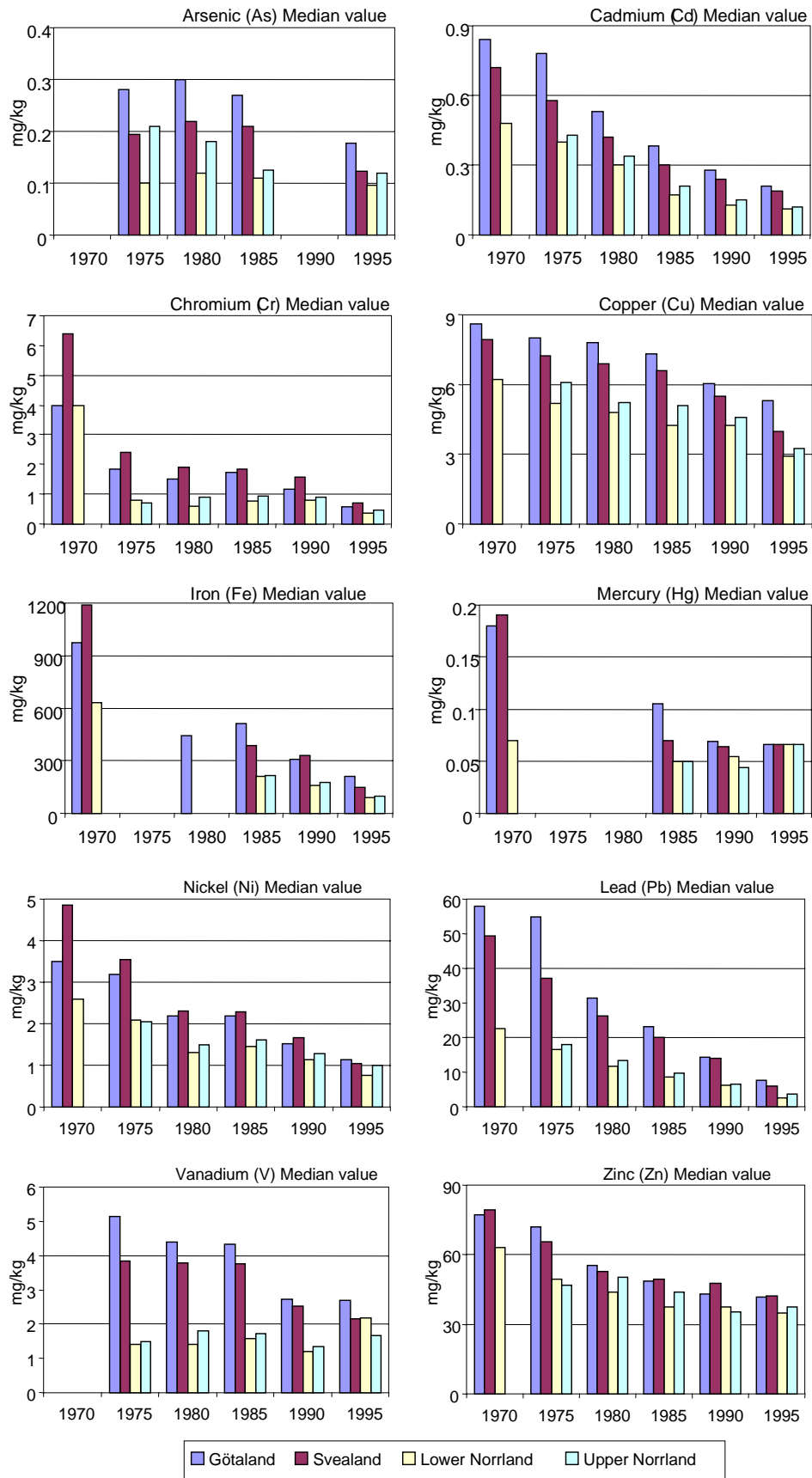


Figure 45 Median metal content in mosses in Sweden 1970-1995 (mg/kg).





**Figure 46** Median metal concentration in mosses in different regions in Sweden 1970-1995 (mg/kg).

### 5.2.2 Geographical mapping of heavy metal deposition

Since the moss surveys include a large number of samples, well representing different geographical areas, it is possible to interpolate the results, giving gradient maps of the metal deposition over Sweden. Gradient maps for arsenic, cadmium, mercury, nickel and lead for every fifth year since 1975 are presented in Figure 47.

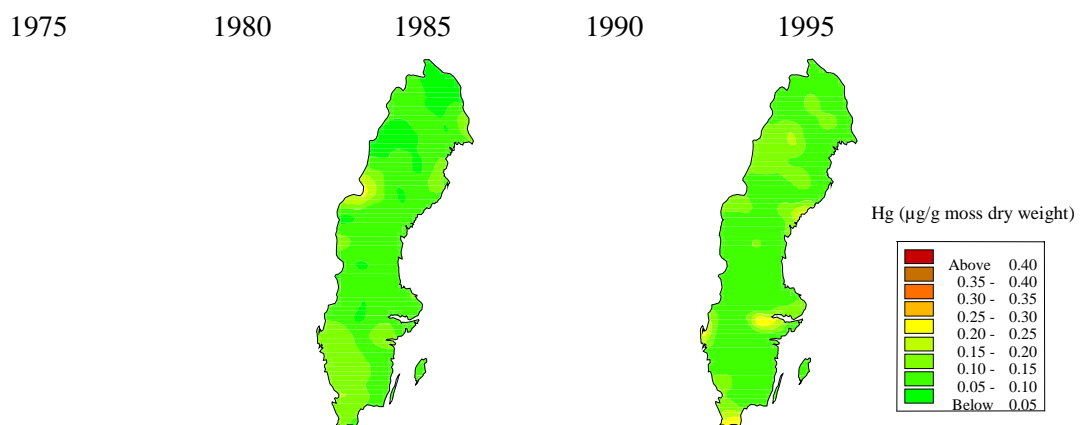
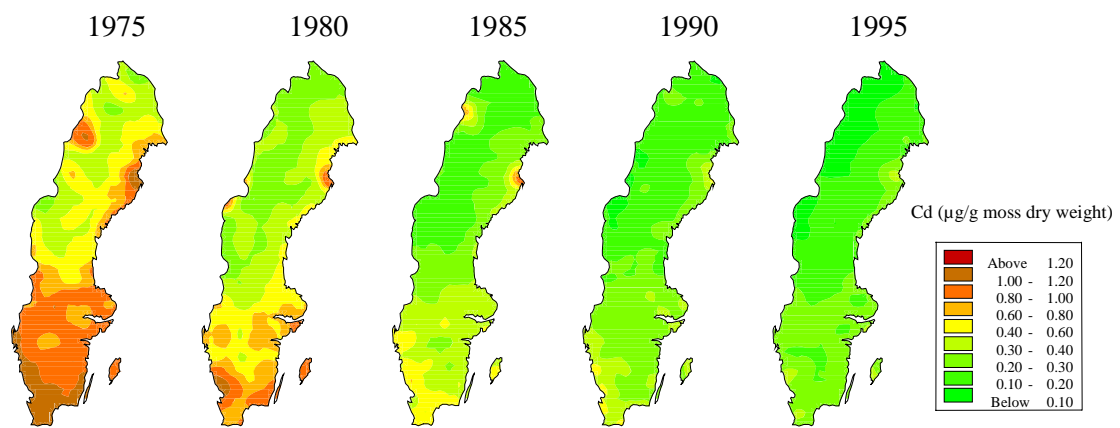
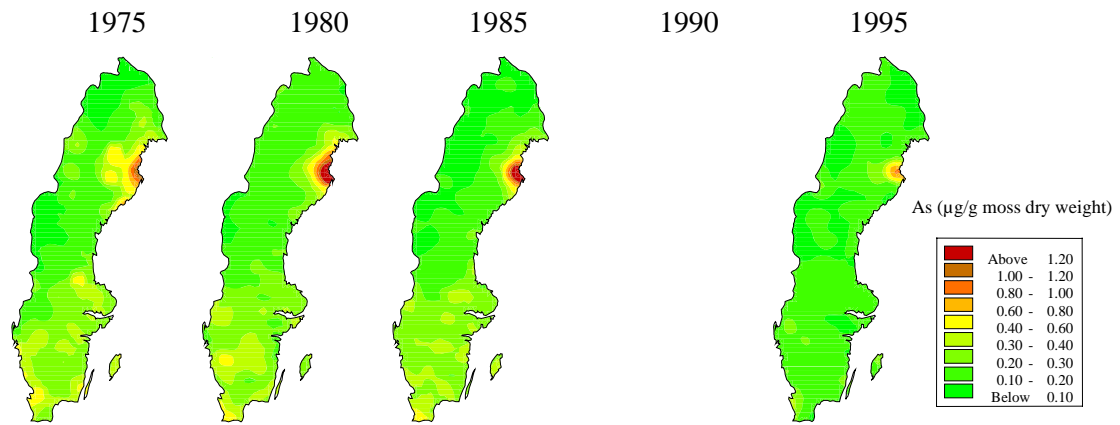
The metal concentrations in mosses represent a relative measurement of the total deposition. Comparison with deposition data shows that the moss technique can describe time trends of heavy metal deposition satisfactorily. Calibration of the concentration is necessary to get a measure of the actual deposition. A simple method described in Rühling 1985 assumes the metal concentration in mosses multiplied by 0.15 gives the actual deposition. Another method, which can be more precise, consists of calibration of the concentrations in the moss versus deposition measurements. Berg and Steinnes (1998) have performed the most extensive study.

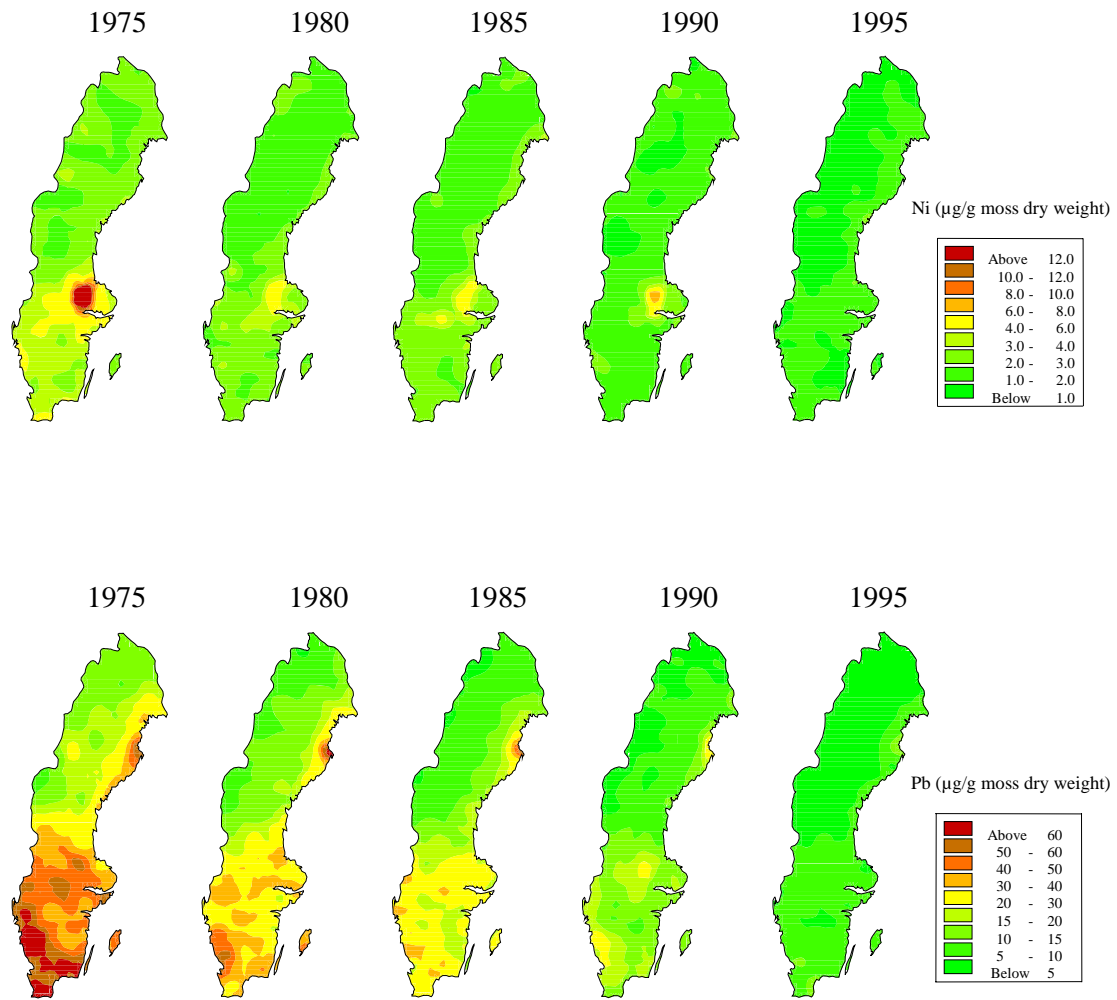
The early maps of **arsenic** and **nickel** show considerable influence from local point sources while the magnitude of the deposition of **cadmium** and **lead** are highly dependent of the contribution from long-range transport of metals from the European continent (Rühling et al. 1996). This is evident because of the generally higher load in the southern part of the country. But local point sources are of importance as well, which is obvious in Figure 47. **Mercury** is dispersed more evenly across the country.

A distinct local source is the smelter at Rönnskär in the north-east of Sweden. It can be seen on the maps of arsenic, cadmium and lead. Another local source is the emissions of nickel from steel industries west of Lake Mälaren. The deposition from these two sources has decreased between 1975-1995. The emissions of arsenic and cadmium from the smelter at Rönnskär were still detectable in 1995, but the large deposition of nickel around Lake Mälaren in 1975 was not noticeable in 1995.

The long-range transport of cadmium and lead has decreased considerably since 1975 and the deposition shows strongly decreasing trends all over the country. Another explanation to the decreasing cadmium deposition in southern Sweden might be a change in the use of fertilisers. Cadmium is a constituent in phosphate fertilisers used in agricultural areas.

Gradient maps for mercury are available for 1985 and 1995. Background values appear to have remained on comparable levels during the period.





**Figure 47** Geographical mapping of the heavy metal deposition of arsenic, cadmium, mercury, nickel and lead in Sweden by moss analysis.

## 6. Discussion

The concentrations of **sulphur dioxide and particulate sulphate** in air showed statistically significant decreasing trends already in the earlier Swedish trend report (Kindbom et al., 1994) covering the years 1980-1992. The decreasing trends are confirmed in this trend study, with statistically significant decreases of the two compounds at all stations 1985-1998. These results were expected because the emissions of sulphur have continued to decrease during the 1990's in countries influencing Swedish air quality (Figure 1).

The concentration in precipitation and deposition of sulphate has decreased in all six areas across Sweden. The decreasing trend of sulphate in precipitation was less marked in the earlier trend report, and these last results strengthen the perception of decreasing concentrations in precipitation as well as in air.

The concentrations of total nitrate and total ammonium in air showed decreasing trends in the earlier study from 1980-1992. Other **nitrogen compounds** in air did not show any statistically significant trends. The present trend analysis of nitrogen dioxide (1985-1998), nitrate and ammonium (1987-1998) in air resulted in statistically significant decreasing trends at all stations except NO<sub>2</sub>-N at Hoburgen (linear regression) and NO<sub>3</sub>-N in Rörvik (Mann Kendall). The emissions of NO<sub>x</sub> in countries influencing Swedish conditions started to decrease from the beginning of the 1990's (Figure 1), which is later than the starting-point of the decrease in sulphur emissions.

Nitrogen concentrations in precipitation showed increasing tendencies between 1980-1992, but the trend, 1983-1998, appears to have turned towards decreasing concentration in most areas in Sweden. The trend analysis of wet deposition of nitrate and ammonium resulted in a more vague picture than the concentrations in precipitation, although a decrease could be seen at many of the stations.

As a consequence of the decrease in deposition, of especially sulphur, the deposition of **acidity** has decreased between 1983-1998. This has resulted in increasing pH values in all areas in Sweden.

It was likely to expect the concentration of **ozone** in air to be decreasing as the emissions of the precursors, NO<sub>x</sub> and VOC, have decreased. However, air concentrations of ozone only show a recurrent seasonal variation, without any distinct annual trends.

If any trend was expected concerning the **base cations** it would have been of the decreasing kind, since the emissions from combustion processes have decreased during the period. A minority of the trend analyses resulted in statistically significant trends, which were either decreasing or increasing. The concentrations of base cations in precipitation in Sweden are relatively low and the interannual variations in concentration and deposition are large, which might obstruct the chances of finding a possible trend.

The concentrations in precipitation of the **heavy metals** arsenic, cadmium, lead and nickel have decreased between 1989-1998. The decreases of arsenic and nickel are

probably a cause of the decrease of emissions from combustion processes. Lead is decreasing because of the diminishing use of leaded fuel.

The content of arsenic, cadmium, chromium, copper, iron, mercury, nickel, lead, vanadium and zinc in mosses all show decreasing tendencies during 1970-1995. Lead shows the strongest decline with a decrease of almost 90% since 1970. Geographical mapping shows that both background concentrations and emission from large point sources of heavy metals in Sweden have been decreasing during the period.

## 7. References

- Barett K., Schaug, J., Bartonova A., Semb A., Hjellbrekke A., Hanssen J. E. (2000). Europe's changing air environment. Two decades of observed trends in acidifying atmospheric sulphur and nitrogen in Europe; 1978-1998. EMEP/CCC-Report 7/2000.
- Berg, T. & Steinnes, E. (1998). Use of mosses (*Hylocomium splendens* and *Pleurozium schreberi*) as bio monitors of heavy metal deposition: from relative to absolute deposition values. *Environmental Pollution* 98: 61–71.
- Gilbert, R.O. (1987). *Statistical Methods for Environmental Pollution Monitoring*. Van Nostrand Reinhold, New York.
- Kindbom K., Lövblad G., Sjöberg K. (1994). Sulphur and Nitrogen Compounds in Air and Precipitation in Sweden 1980-1992. IVL-report B 1144.
- Munthe, J., Kindbom K., Pleijel K., Parkman H., Wennberg L., Dock L., Svensson M., Norman F. (1997). Kviksilver i miljön-förekomst och effekter. Swedish Environmental Protection Agency. Report 4767.
- Nilsson, L. Y. (1978). *Praktisk statistik. Del 1-begrepp och metoder*.
- Rühling, Å. (1984) Atmospheric Heavy Metal Deposition in Europe-estimation based on moss analysis. *Nord* 1994:9.
- Rühling, Å. et al. (1996). Atmospheric Heavy Metal Deposition in Northern Europe 1995. *Nord* 1996:37.
- Rühling, Å. (1998). Unpublished material from Åke Rühling.
- Vestreng V., Støren E. (2000). Analysis of UNECE/EMEP emission data. MSC-W Status Report 2000. EMEP/MSC-W Note 1/00. Norwegian Meteorological Institute. Research note no 37.



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IVL Svenska Miljöinstitutet AB

P.O.Box 210 60, SE-100 31 Stockholm  
Hälsingegatan 43, Stockholm  
Tel: +46 8 598 563 00  
Fax: +46 8 598 563 90

IVL Swedish Environmental Research Institute Ltd

P.O.Box 470 86, SE-402 58 Göteborg  
Dagjämningsgatan 1, Göteborg  
Tel: +46 31 725 62 00  
Fax: +46 31 725 62 90

Aneboda, SE-360 30 Lammhult  
Aneboda, Lammhult  
Tel: +46 472 26 77 80  
Fax: +46 472 26 77 90

[www.ivl.se](http://www.ivl.se)