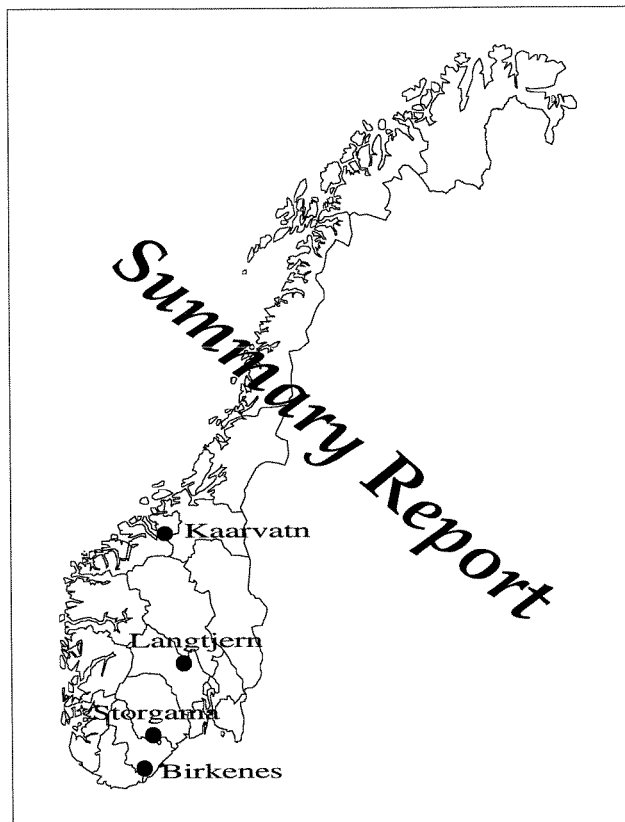


# Acid Rain Research


REPORT 34-B/1994

## Long-Term Monitored Catchments in Norway

- A Hydrologic and  
Chemical  
Evaluation -



# NIVA - REPORT

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**Abstract:**  
This report contains a thorough hydrologic and chemical evaluation of precipitation and runoff water, as well as relationships between precipitation chemistry and runoff chemistry from four long-term monitored catchments in Norway, i.e. Birkenes, Storgama, Langtjern and Kaarvatn. In addition time trends are evaluated in relation to the declining emissions of sulphur compounds in Europe since the late 70-thies. Because the major version was very voluminous, it was necessary to produce this summary report (B) with the same title and NIVA-number.

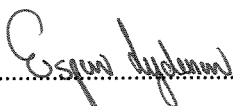
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2. Vannkjemi
3. Overvåking
4. Tidstrender

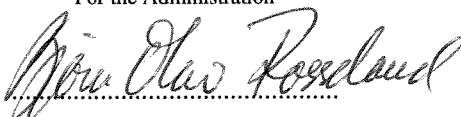
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For the Administration

  
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Bjørn Olav Rosseland

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# **SUMMARY REPORT**

**Q-475**

**LONG-TERM MONITORED CATCHMENTS IN NORWAY  
- A HYDROLOGIC AND CHEMICAL EVALUATION-**

*by*

*ESPEN LYDERSEN*

**NORWEGIAN INSTITUTE FOR WATER RESEARCH**

**Oslo 1994**

## PREFACE

About 20 years ago, long term monitoring of small Norwegian catchments were initiated, because of increasing concerns regarding acidification of surface water and damage to fish populations. Long range transported air pollutants were considered to be the major acidification factor, so both precipitation (wet- and dry- deposition) and runoff chemistry were included in the monitoring programme. The Royal Norwegian Council for Scientific and Industrial Research (NTNF), the Norwegian Agricultural Research Council (NLVF), and the Norwegian Ministry of Environment (MD) sponsored the programme until 1979, while the Norwegian State Pollution Control Authority (SFT) has been economical responsible since then. We hope the Norwegian monitoring programme on surface waters will continue within the economical frames of today, or even increase. All nations should always keep in mind that fresh water is the major article of food or nutrient for all life. Therefore it is a good and reasonable investment spending money on monitoring these important sources.

This report contains a thorough hydrologic and chemical evaluation of precipitation and runoff water separately as well as relationships between precipitation chemistry and runoff chemistry. In addition time trends are evaluated in relation to the declining emissions of sulphur compounds in Europe from the late 70-thies. Originally, this project was planned to last a few months, but because of the amounts of data that had to be put together into one data base, and because the author had too ambitious opinions of the final result, it took much more time. Accordingly, the major report ended up being relative voluminous, making it necessary to produce this summary report as a B version, but with the same title and NIVA-number as the major version. The statistical methods applied in this report are relatively simple, as was commented on by Dr. Nils Christophersen, University of Oslo, when he read the major version. We agree upon this criticism, but most of the relations presented and discussed are actual and real. The relationships could, however, have been more strongly confirmed by using other and more proper statistical methods. If other scientists want to use the data base for more enhanced statistical evaluation of various relationships, we will of course appreciate such initiatives. References and descriptions of analytical methods are omitted in the summary report, as well as more detailed hydrochemical relations and interpretations.

We will thank the Norwegian Institute for Air Research (NILU) which has been responsible for all precipitation data, and allowed the author to use their data without limitations, and of course my own institute, NIVA, and especially Dr. Arne Henriksen (NIVA) that have been very patient and understanding regarding the problems with finishing the report. He and Dr. Dick Wright (NIVA) have made many comments to this manuscript and related articles. Two articles, based on parts of the report, have already been accepted in international journals, and two more have been submitted. The man hours used for writing this report and related publications are all covered by NIVA. We also wish to acknowledge the important work carried out by our observers collecting water samples over many years during rain storms, intense cold and darkness at Birkenes (Håvard and Olaf Lien), Storgama (Per Øyvind Stokstad), Langtjern (Tone and Kolbjørn Sønsteby) and Kaarvatn (Erik Kårvatn).

Norwegian Institute for Water Research

Espen Lydersen (NIVA)

October 1994

# CONTENTS

<b>Introduction</b>	1
<b>Hydrology</b>	2
<b>Precipitation chemistry - wet deposition</b>	6
<b>Precipitation chemistry - dry deposition</b>	11
<b>Runoff chemistry</b>	15
The hydrologic effect on runoff chemistry	20
Sulphuric acid and other acidifying compounds	23
Seasalt episodes	27
Total organic carbon	29
Acid neutralising capacity (ANC)	33
Aluminium	36
<b>Time trends</b>	41
Dry deposition	41
Wet deposition	48
Runoff	55

## Introduction

\* This report is based on hydro-chemical data up to 1992, at four long-term monitored catchments in Norway, Birkenes, Storgama, Langtjern and Kaarvatn (Figure 1). At Birkenes and Langtjern, the precipitation and runoff has been monitored since 1974, at Storgama from 1975, and at Kaarvatn back to 1980.

\* All catchments are located in relatively acid-sensitive areas regarding geology; the soil covers are thin and the rocks or minerals present are slowly weatherable. At Birkenes and Storgama, granites are totally dominating, at Langtjern both granites and gneisses, while at Kaarvatn, gneisses and quartzites predominate.

\* The Kaarvatn catchment is located very close to the ocean in the county of Moere and Romsdal, and is the most precipitation rich and seasalt-influenced site. The Birkenes catchment is also located relatively close to the sea in the county of Aust-Agder, and is therefore also highly seasalt influenced. The Storgama catchment is located in a more typical inland region in the county of Telemark and thus less seasalt influenced. The Langtjern catchment is located far from the ocean in the county of Buskerud and is the most typical inland site. This catchment is also located in the rain shadow and only minor amounts of seasalts reach this catchment.

\* Annual mean temperatures ( $^{\circ}\text{C}$ ) during the monitoring periods at the weather-stations located nearby the four catchments are: Kaarvatn:  $7.0 \pm 0.8$ ; Birkenes:  $5.4 \pm 1.1$ ; Storgama:  $5.1 \pm 1.3$ ; and Langtjern:  $3.0 \pm 1.2$ .



Figure 1 The location of the four long-term monitored catchments.

## Hydrology

\* The weather-stations at Birkenes, Storgama and Langtjern, do relatively well reflect the real amounts of water precipitating into the catchments, while at Kaarvatn the weather-station underestimates the amount of water by about 35%. On the basis of annual input data from the beginning of the monitoring period up to 1990/91, the following regressions between measured ( $P_m$ ) and estimated ( $P_e$ ) inputs of water were found:

<b><u>Birkenes</u></b>	$P_e = 0.97P_m + 87$	$r^2 = 0.90$ (Calendar-year)
	$P_e = 1.13P_m - 155$	$r^2 = 0.96$ (Water-year)
<b><u>Storgama</u></b>	$P_e = 0.95P_m + 222$	$r^2 = 0.84$ (Calendar-year)
	$P_e = 1.06P_m + 103$	$r^2 = 0.95$ (Water-year)
<b><u>Langtjern</u></b>	$P_e = 1.09P_m + 56$	$r^2 = 0.47$ (Calendar-year)
	$P_e = 1.10P_m + 55$	$r^2 = 0.74$ (Water-year)
<b><u>Kaarvatn</u></b>	$P_e = 0.86P_m + 1004$	$r^2 = 0.65$ (Calendar-year)
	$P_e = 1.05P_m + 728$	$r^2 = 0.86$ (Water-year)

\* Calendar-year is very seldom the best hydrological year. At Birkenes and Langtjern, the best hydrological year begins June 1 and ends May 31, while at Storgama and Kaarvatn it begins September 1 and ends August 31. The largest difference between calendar-year and hydrological year is at Langtjern and Kaarvatn (Figure 2), but for annual mass-balance calculations, hydrological year should be used at all sites. Concerning annual concentration of chemical compounds, the differences between calendar-year and hydrological year are, however, small. The hydrology data and fluxes of chemical compounds are in this study based on water years.

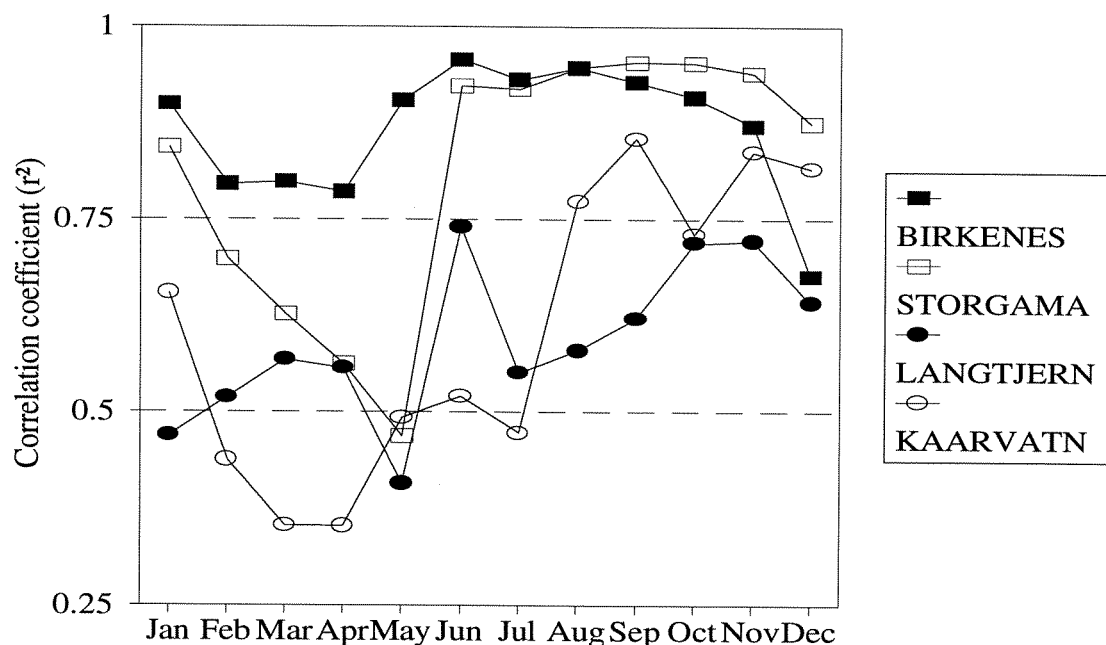


Figure 2 The correlation coefficients ( $r^2$ ) between precipitation and runoff at the four monitoring catchments, based on linear regressions for the different successive 12 month periods.

\* **Annual average precipitation** at the four catchments during the monitoring periods are: Kaarvatn:  $2175 \pm 275$  mm; Birkenes:  $1529 \pm 283$  mm; Storgama:  $1206 \pm 273$  mm; and Langtjern:  $864 \pm 159$  mm.

\* **Average intensity of rain** (mm/day of precipitation) during the monitoring periods are: Kaarvatn:  $10.3 \pm 0.9$ ; Birkenes:  $7.6 \pm 1.3$ ; Storgama:  $7.4 \pm 1.0$ ; and Langtjern:  $5.1 \pm 0.7$ .

\* **Average annual runoff** at the four catchments during the monitoring periods are: Kaarvatn:  $1856 \pm 306$  mm; Birkenes:  $1169 \pm 288$  mm; Storgama:  $947 \pm 287$  mm; and Langtjern:  $614 \pm 186$  mm

\* **Average annual evapotranspiration** at the four catchments during the monitoring period are estimated to be: Kaarvatn:  $319 \pm 125$  mm; Birkenes:  $360 \pm 70$  mm; Storgama:  $253 \pm 61$  mm; and Langtjern:  $250 \pm 94$  mm.

Table 1 Annual hydrological characteristics for the different catchments during the monitoring period.

	STATION			
	Birkenes	Storgama	Langtjern	Kaarvatn
Evapotransp.* mm	350	250	250	300
Evapotransp.** mm	$360 \pm 70$	$253 \pm 61$	$250 \pm 94$	$319 \pm 125$
<u>Calendar-year</u>				
No. of days $P_m > 0.1$ mm	$186 \pm 15$	$162 \pm 17$	$163 \pm 15$	$199 \pm 16$
Precipitation ( $P_m$ ) mm	$1480 \pm 216$	$1001 \pm 177$	$734 \pm 128$	$1369 \pm 262$
Intensity ( $P_m$ ) mm/day***	$7.4 \pm 0.9$	$5.7 \pm 0.7$	$4.4 \pm 0.6$	$6.6 \pm 0.9$
Precipitation ( $P_e$ ) mm	$1523 \pm 210$	$1173 \pm 168$	$856 \pm 140$	$2135 \pm 222$
Intensity ( $P_e$ ) mm/day***	$8.2 \pm 1.0$	$6.9 \pm 1.8$	$5.3 \pm 0.5$	$10.6 \pm 0.7$
Runoff ( $R_m$ ) mm	$1157 \pm 207$	$915 \pm 183$	$605 \pm 191$	$1826 \pm 278$
<u>Water-year</u>				
No. of days $P_m > 0.1$ mm	$188 \pm 15$	$163 \pm 19$	$164 \pm 12$	$200 \pm 20$
Precipitation ( $P_m$ ) mm	$1490 \pm 251$	$1040 \pm 258$	$735 \pm 145$	$1378 \pm 262$
Intensity ( $P_m$ ) mm/day***	$7.4 \pm 1.1$	$5.9 \pm 0.9$	$4.4 \pm 0.7$	$6.5 \pm 0.9$
Precipitation ( $P_e$ ) mm	$1529 \pm 283$	$1206 \pm 273$	$864 \pm 159$	$2175 \pm 275$
Intensity ( $P_e$ ) mm/day***	$7.6 \pm 1.3$	$7.4 \pm 1.0$	$5.1 \pm 0.7$	$10.3 \pm 0.9$
Runoff ( $R_m$ ) mm	$1169 \pm 288$	$947 \pm 288$	$614 \pm 187$	$1856 \pm 306$

\* Estimated evapotranspiration based on Soegnen, 1967; \*\* Estimated evapotranspiration during the monitoring period. i.e. Precipitation - Runoff; \*\*\* Precipitation/ No. of days with precipitation  $> 0.1$  mm;  $P_m$ : Precipitation measured;  $R_m$ : Runoff measured;  $P_e$ : Estimated precipitation based on the equations present in the text.

\* During cold winters at Birkenes, 60-80% of runoff during spring is melt-water from snow accumulated in the catchment, while during mild winters, minor amount of runoff during spring derives from snow. At the three other sites, normally 60-80% of the runoff during spring are melt-water, and whether it is a mild or cold winter is not very decisive, because the winter-temperatures at these sites are generally  $< 0^\circ\text{C}$ . Thus, precipitation during the winter, and the weather condition during spring are more important for the amount of melt-water at these sites (Figure 3).



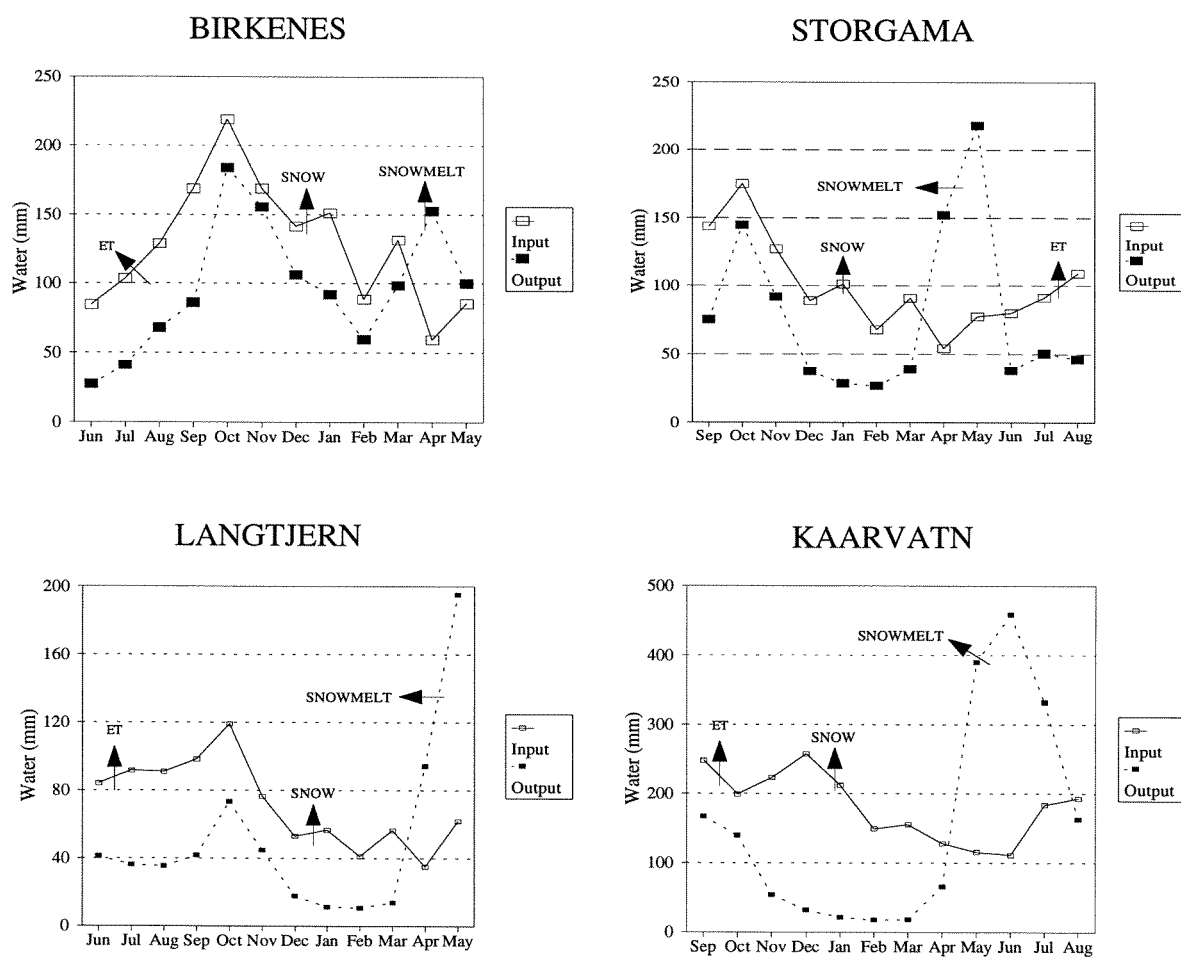


Figure 3 Average monthly precipitation and runoff at the four catchments during the monitoring periods.

\* In time, the precipitation events often occur simultaneously at Birkenes, Storgama and Langtjern, which means that when it rains at Birkenes, it usually rains at Storgama (but normally somewhat less), and very often at Langtjern too, but even less. This is primarily because most of the low pressures enter the southern Norway by western south-western winds, a typical pattern for the northern hemisphere. Kaarvatn undoubtedly belongs to another climatic region. Thus, precipitation events more seldom coincide with the other sites.

\* Typical for all four sites is high-flow periods during spring related to snow-melt, and during autumn related to very regular heavy rain periods (Figure 3). All catchments normally have a low-flow period during the winter, and at Birkenes, Storgama and Langtjern, low-flow-periods occur regularly also during summer and early autumn. Low-flow periods during summer and early autumn do normally not occur at Kaarvatn. This is primarily because of large altitude gradients within a relatively large catchment (25 km<sup>2</sup>), which means that snow-melt normally affects the hydrology during the whole summer (Figure 3).

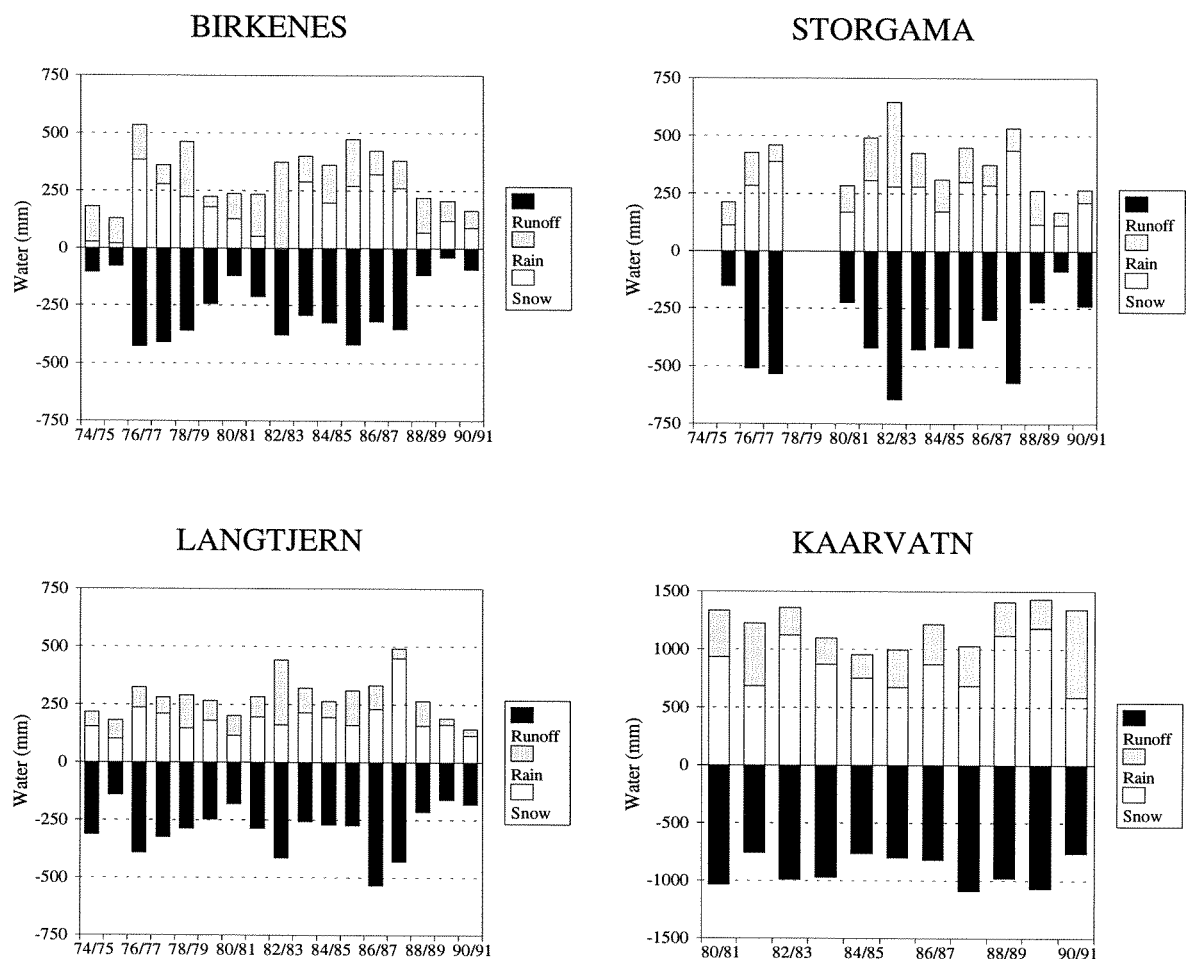


Figure 4 Annual accumulation of snow during winter (1 November-31 March), and precipitation and runoff the following spring (1 April-31 May) at the four catchments during the monitoring periods. Runoff is illustrated by negative values in the figure.

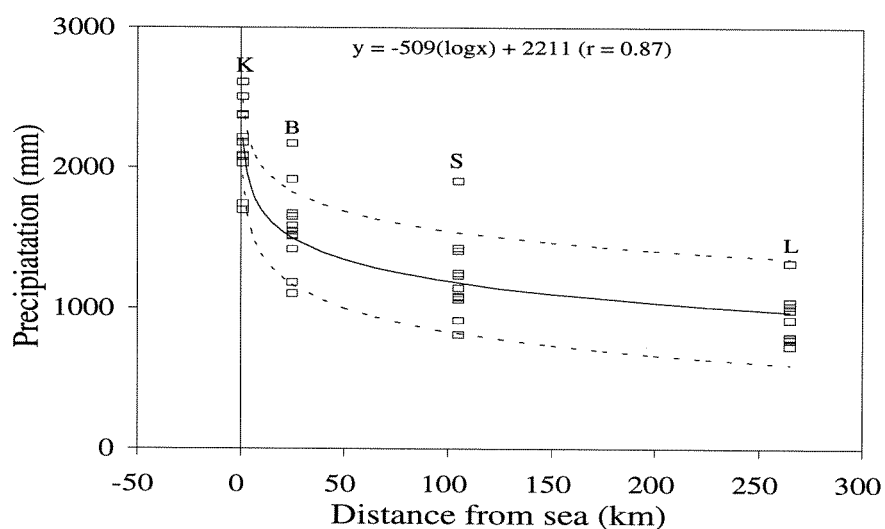


Figure 5 The annual amount of precipitation with distance from the sea, i.e. from Kaarvatn (K) to Langtjern (L).

## Precipitation chemistry - wet deposition

\* Wet-deposition is mainly a mixture of sodium-chloride, sulphuric acid and ammonium nitrate dissolved in water in varying concentrations and ratios (Figure 6).

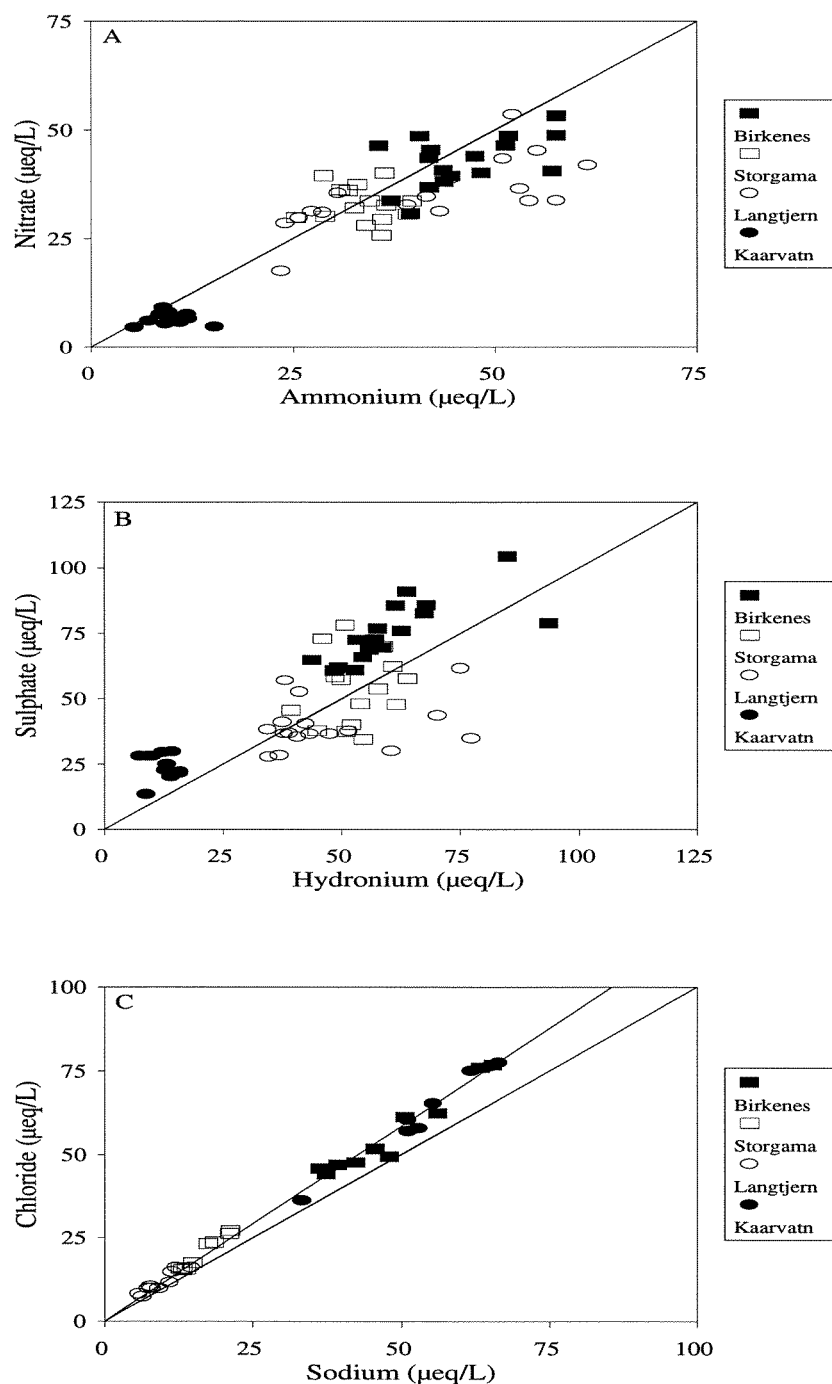


Figure 6 The ammonium/nitrate ratio (A), the hydronium/sulphate ratio (B), and the sodium/chloride ratio (C) in wet deposition from the different catchments, based on annual weighted averages during the respective monitoring periods. Continuous line represents the 1/1 line. The dotted line represents the Na/Cl ratio of sea water.

\* Birkenes normally receives the most ionic-rich precipitation, with an annual weighted average concentration of  $342 \pm 35 \mu\text{eq/L}$ . The corresponding averages at Storgama, Langtjern and Kaarvatn are  $219 \pm 19 \mu\text{eq/L}$ ,  $205 \pm 37 \mu\text{eq/L}$  and  $189 \pm 24 \mu\text{eq/L}$ , respectively.

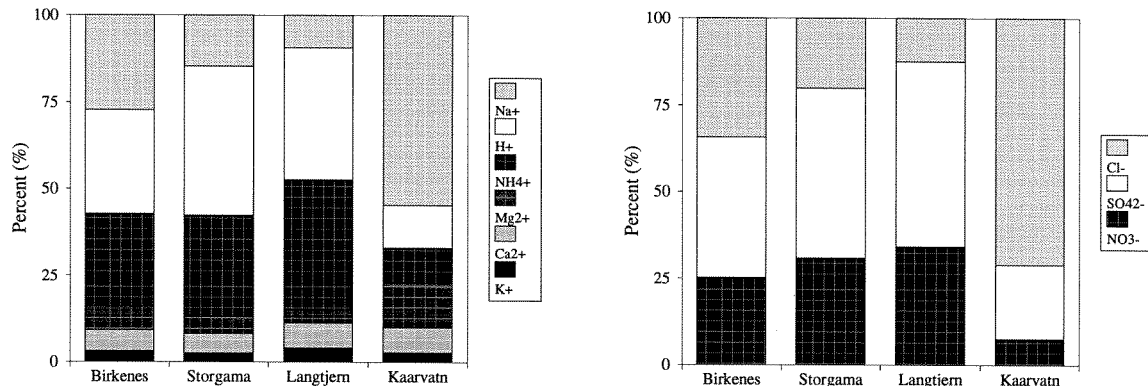


Figure 7 The percentage distribution of major cations and anions in wet deposition at the different catchments, based on annual weighted averages ( $\mu\text{eq/L}$ ) during the monitoring periods.

\* At Birkenes, an average of 30% of the cationic pool in wet-deposition is  $\text{H}^+$ -ions (Figure 7), while  $\text{NH}_4^+$  and  $\text{Na}^+$  both constitute by 27% each. The remaining 16% is  $\text{Ca}^{2+}$  (6%),  $\text{Mg}^{2+}$  (7%) and  $\text{K}^+$  (3%). The major anion is  $\text{SO}_4^{2-}$ , which on average constitutes 41% of the anionic pool, while  $\text{Cl}^-$  and  $\text{NO}_3^-$  contribute by 34% and 25%.

\* At Storgama, an average of 45% of the cationic pool in wet-deposition is  $\text{H}^+$ -ions (Figure 7), while  $\text{NH}_4^+$  and  $\text{Na}^+$  both constitute by 29% and 14%. The remaining 12% is  $\text{Ca}^{2+}$  (6%),  $\text{Mg}^{2+}$  (4%) and  $\text{K}^+$  (2%). The major anion is  $\text{SO}_4^{2-}$ , which on average constitutes 51% of the anionic pool, while  $\text{Cl}^-$  and  $\text{NO}_3^-$  contribute by 19% and 30%.

\* At Langtjern, an average of 40% of the cationic pool in wet-deposition is  $\text{H}^+$ -ions (Figure 7), while  $\text{NH}_4^+$  and  $\text{Na}^+$  both constitute by 35% and 8%. The remaining 17% is  $\text{Ca}^{2+}$  (9%),  $\text{Mg}^{2+}$  (4%) and  $\text{K}^+$  (4%). The major anion is  $\text{SO}_4^{2-}$ , which on average constitutes 57% of the anionic pool, while  $\text{Cl}^-$  and  $\text{NO}_3^-$  contribute by 11% and 32%.

\* At Kaarvatn,  $\text{Na}^+$  is the predominating cation, and on average constitutes 55% of the cationic pool in wet-deposition.  $\text{Mg}^{2+}$  and  $\text{H}^+$  both contribute by 12%, while  $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$  and  $\text{K}^+$  contribute by 10%, 9% and 3% (Figure 7). The major anion is  $\text{Cl}^-$ , which on average constitutes 69% of the anionic pool, while  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  contribute by 23% and 8%.

\* To estimate the origin of sulphate in wet-deposition, the concentration of marine sulphate is estimated as  $0.103[\text{Cl}^-]$ , which is the equivalent ratio present in sea water. By making a very simple assumption that all sulphate present in wet-deposition at Kaarvatn derives from natural source, on average 64% of sulphate in wet-deposition at Birkenes originates from anthropogenic sources, 27% from natural non-marine sources and the remaining 9% from marine sea-water. At Storgama, 49% of sulphate in wet-deposition originates from anthropogenic sources, 47% from natural non-marine sources and the remaining 4% from marine sea-water. Correspondingly at Langtjern, 41% of sulphate in wet-deposition originates from anthropogenic sources, 56% from natural non-marine sources and the remaining 2-3% from marine sea-water. Because anthropogenic sulphate to some extent also precipitates at Kaarvatn, the anthropogenic contribution is underestimated in these calculations.

\* Assuming all nitrate and ammonium present in wet-deposition at Kaarvatn representing the total natural source (background level) of nitrogen, 77% of nitrate and 70% of ammonium in wet-deposition at Birkenes originate from anthropogenic sources. Correspondingly at Storgama, 63% and 47% of nitrate and ammonium originate from anthropogenic sources, 53% and 56% at Langtjern. As for sulphate, a certain amount of anthropogenic derived nitrogen is also precipitating at Kaarvatn. Thus, the anthropogenic contributions are somewhat underestimated also in these calculations.

\* **The annual average weighted H<sup>+</sup>-concentrations in wet-deposition** for the monitoring periods are: Birkenes: 61 µeq/L (pH: 4.21); Storgama: 53 µeq/L (pH: 4.28); Langtjern: 48 µeq/L (pH: 4.32); Kaarvatn: 12 µeq/L (pH: 4.92).

\* **The highest monthly weighted H<sup>+</sup>-concentrations in wet-deposition** during the monitoring periods are: Birkenes: 168 µeq/L (pH: 3.77); Storgama: 158 µeq/L (pH: 3.8); Langtjern: 336 µeq/L (pH: 3.47); Kaarvatn: 45 µeq/L (pH: 4.35).

\* **The annual average weighted NH<sub>4</sub><sup>+</sup>-concentrations in wet-deposition** for the monitoring periods are: Birkenes: 46 µeq/L; Storgama: 34 µeq/L; Langtjern: 42 µeq/L; Kaarvatn: 10 µeq/L .

\* **The highest monthly weighted NH<sub>4</sub><sup>+</sup>-concentrations in wet-deposition** during the monitoring periods are: Birkenes: 152 µeq/L; Storgama: 161 µeq/L; Langtjern: 307 µeq/L; Kaarvatn: 127 µeq/L.

\* **The annual average weighted SO<sub>4</sub><sup>2-</sup>-concentrations in wet-deposition** for the monitoring periods are: Birkenes: 75 µeq/L; Storgama: 56 µeq/L; Langtjern: 62 µeq/L; Kaarvatn: 20 µeq/L.

\* **The highest monthly weighted SO<sub>4</sub><sup>2-</sup>-concentrations in wet-deposition** during the monitoring periods are: Birkenes: 210 µeq/L; Storgama: 231 µeq/L; Langtjern: 546 µeq/L; Kaarvatn: 76 µeq/L.

\* **The annual average weighted NO<sub>3</sub><sup>-</sup>-concentrations in wet-deposition** for the monitoring periods are: Birkenes: 43 µeq/L; Storgama: 33 µeq/L; Langtjern: 35 µeq/L; Kaarvatn: 6.5 µeq/L.

\* **The highest monthly weighted NO<sub>3</sub><sup>-</sup>-concentrations in wet-deposition** during the monitoring periods are: Birkenes: 121 µeq/L; Storgama: 99 µeq/L; Langtjern: 329 µeq/L; Kaarvatn: 29 µeq/L.

\* **The annual average weighted Cl<sup>-</sup>-concentrations in wet-deposition** for the monitoring periods are: Birkenes: 58 µeq/L; Storgama: 20 µeq/L; Langtjern: 12 µeq/L; Kaarvatn: 60 µeq/L.

\* **The highest monthly weighted Cl<sup>-</sup>-concentrations in wet-deposition** during the monitoring periods are: Birkenes: 191 µeq/L; Storgama: 123 µeq/L; Langtjern: 114 µeq/L; Kaarvatn: 264 µeq/L.

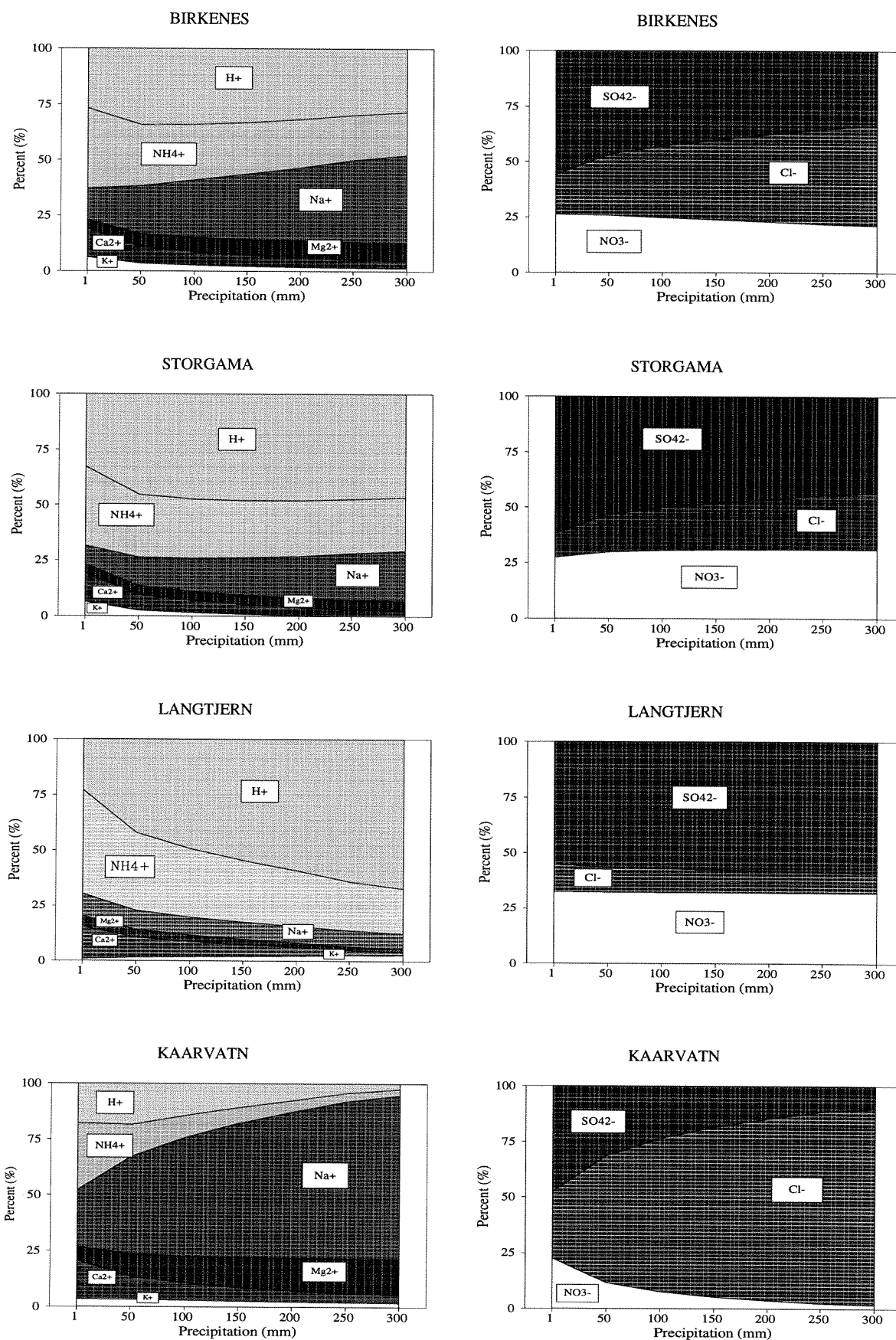


Figure 8 The percentage change in the distribution of cations and anions with respect to amount of precipitation based on monthly weighted averages.

\* Except for the typical seasalt ions (Na and Cl), the highest concentrations of ions in wet-deposition normally occur when the precipitation is low. This means that the amount of water plays an important role for the concentration of ions. This is best illustrated at Langtjern, the most precipitation poor sites, which normally exhibits the most extreme values. By large, the concentrations of non-marine ions decrease by increasing amounts of precipitation

\* At the most coast-near sites, Kaarvatn, Birkenes, the seasalt ions increase by increasing amounts of precipitation (Figure 8). This means that high amounts of precipitation normally mean strong low-pressures and strong winds, which increase the seasalt influence.

Table 2 Annual maximum, minimum and annual weighted averages of precipitation (mm) and concentrations of dissolved substances ( $\mu\text{eq/L}$ ) in bulk precipitation at the catchments during the monitoring periods.

Period		Birkenes 1974-1991	Storgama 1974-1991	Langtjern 1974-1991	Kaarvatn 1979-1991
H <sup>+</sup>	max	94	64	77	16
	mean	61 ± 12	53 ± 7	48 ± 14	12 ± 3
	min	44	39	34	7.4
NH <sub>4</sub> <sup>+</sup>	max	58	40	61	15
	mean	46 ± 7	34 ± 4	42 ± 13	10 ± 2
	min	36	25	24	5.5
Ca <sup>2+</sup>	max	19	11	22	12
	mean	12 ± 3	7.5 ± 1.6	11 ± 4.9	7.6 ± 2.7
	min	7.5	5.3	5.9	4.2
Mg <sup>2+</sup>	max	17	6.7	6.9	17
	mean	12 ± 2	4.8 ± 1.0	4.1 ± 1.3	12 ± 3
	min	8.8	3.6	2.3	7.7
Na <sup>+</sup>	max	66	21	15	66
	mean	49 ± 10	17 ± 3	9.3 ± 2.7	55 ± 10
	min	36	13	5.8	33
K <sup>+</sup>	max	6.6	4.5	6.6	3.2
	mean	5.4 ± 0.8	2.8 ± 1.0	4.4 ± 1.0	2.7 ± 0.4
	min	3.9	1.7	3.3	2.0
SO <sub>4</sub> <sup>2-</sup>	max	105	73	106	26
	mean	75 ± 12	56 ± 8	62 ± 18	20 ± 4
	min	61	43	37	11
Cl <sup>-</sup>	max	77	27	17	79
	mean	58 ± 12	20 ± 5	12 ± 3	60 ± 14
	min	44	13	7.2	36
NO <sub>3</sub> <sup>-</sup>	max	53	40	54	9.1
	mean	43 ± 6	33 ± 4	35 ± 8	6.5 ± 1.3
	min	31	26	18	4.5
Ionic strength ( $\mu\text{mol/L}$ )	max	240	164	170	136
	mean	215 ± 20	141 ± 13	138 ± 24	114 ± 14
	min	189	122	93	88
$\Sigma\text{Cations}$	mean	177 ± 17	114 ± 8	107 ± 17	99 ± 11
$\Sigma\text{Anions}$	mean	165 ± 18	105 ± 11	97 ± 20	89 ± 13

## Precipitation chemistry - dry-deposition

\* Long-term monitoring of dry-deposition compounds, primarily sulphur and nitrogen compounds, have been conducted at Birkenes and Kaarvatn only.

\* As for wet-deposition, Birkenes receives the highest amounts of sulphur and nitrogen compounds in dry-deposition.

\* Sulphur in dry-deposition is primarily present as SO<sub>2</sub>-gas and SO<sub>4</sub>-particles while the predominant nitrogen compounds are NO<sub>2</sub>-gas and NH<sub>4</sub>-particles. At Birkenes and Kaarvatn, these two nitrogen compounds constitute an average of 84% and 88% of total dry-deposited nitrogen.

\* **Annual average mean concentration of SO<sub>2</sub>-gas and SO<sub>4</sub>-particles** for the period 1979-1991 are: Birkenes: SO<sub>2</sub>-gas: 46 ± 15 neq/m<sup>3</sup>, SO<sub>4</sub>-particles: 61 ± 14 neq/m<sup>3</sup>; Kaarvatn: SO<sub>2</sub>-gas: 21 ± 8 neq/m<sup>3</sup>, SO<sub>4</sub>-particles: 26 ± 5 neq/m<sup>3</sup> (Figure 9). At both sites, 43% of sulphur in dry-deposition is SO<sub>2</sub>-gas, while the other 57% is SO<sub>4</sub>-particles.

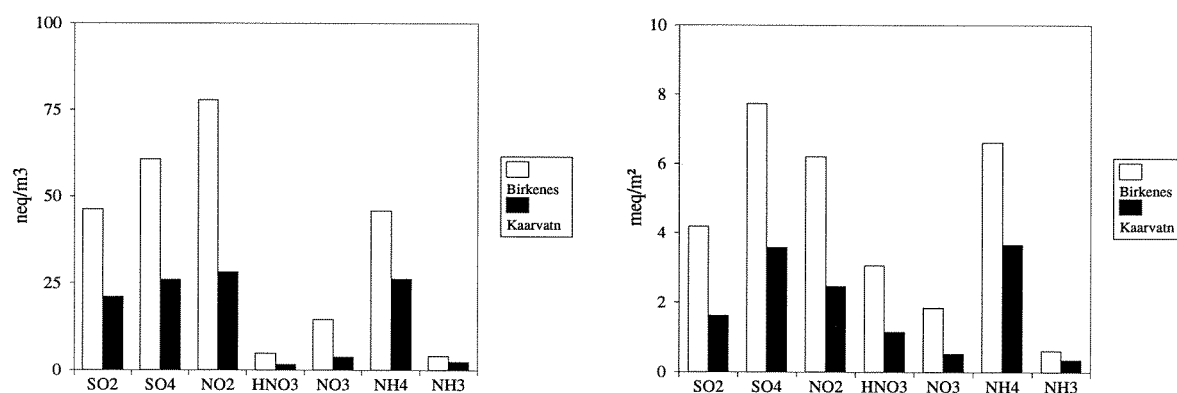


Figure 9 Annual average concentrations and fluxes of dry-deposition compounds of sulphur (from 1979-1991) and nitrogen (from 1988-1991) at Birkenes and Kaarvatn.

\* **Annual average concentration of nitrogen in dry-deposition at Birkenes** during 1988-1991 was 147 ± 7 neq/m<sup>3</sup> (Figure 9). During the same period, the annual average concentration of sulphur in dry-deposition was 82 ± 8 neq/m<sup>3</sup>.

\* **Annual average concentration of nitrogen in dry-deposition at Kaarvatn** during 1988-1991 was 62 ± 10 neq/m<sup>3</sup> (Figure 9). During the same period, the annual average concentration of sulphur in dry-deposition was 33 ± 9 neq/m<sup>3</sup>.

\* The annual average concentration of nitrogen in dry-deposition is 1.8 and 1.9 times higher than the corresponding dry-deposition concentration of sulphur at Birkenes and Kaarvatn.

\* In wet-deposition, the annual average concentration of nitrogen (ΣNH<sub>4</sub>,NO<sub>3</sub>) was 1.2 times higher than the concentration of sulphate at Birkenes, while at Kaarvatn the ΣNH<sub>4</sub>,NO<sub>3</sub> was 17% lower than the concentration of sulphate.



\* **Annual average dry-deposition influxes of sulphur** for the period 1979/80-1990/91 are: Birkenes:  $11.5 \pm 2.1$  meq/m<sup>2</sup>; Kaarvatn:  $5.0 \pm 1.0$  meq/m<sup>2</sup>. Thus, dry-deposition contributes by only 11% and 12% to the annual inputs of sulphate ( $\Sigma$ wet+dry) at Birkenes and Kaarvatn.

\* **Annual average dry-deposition influxes of nitrogen** for the period 1988/89-1990/91 are: Birkenes:  $18.3 \pm 0.9$  meq/m<sup>2</sup>; Kaarvatn:  $8.1 \pm 1.4$  meq/m<sup>2</sup>. Thus, dry-deposition contributes by 13% and 24% to the annual inputs of nitrogen ( $\Sigma$ wet+dry) at Birkenes and Kaarvatn.

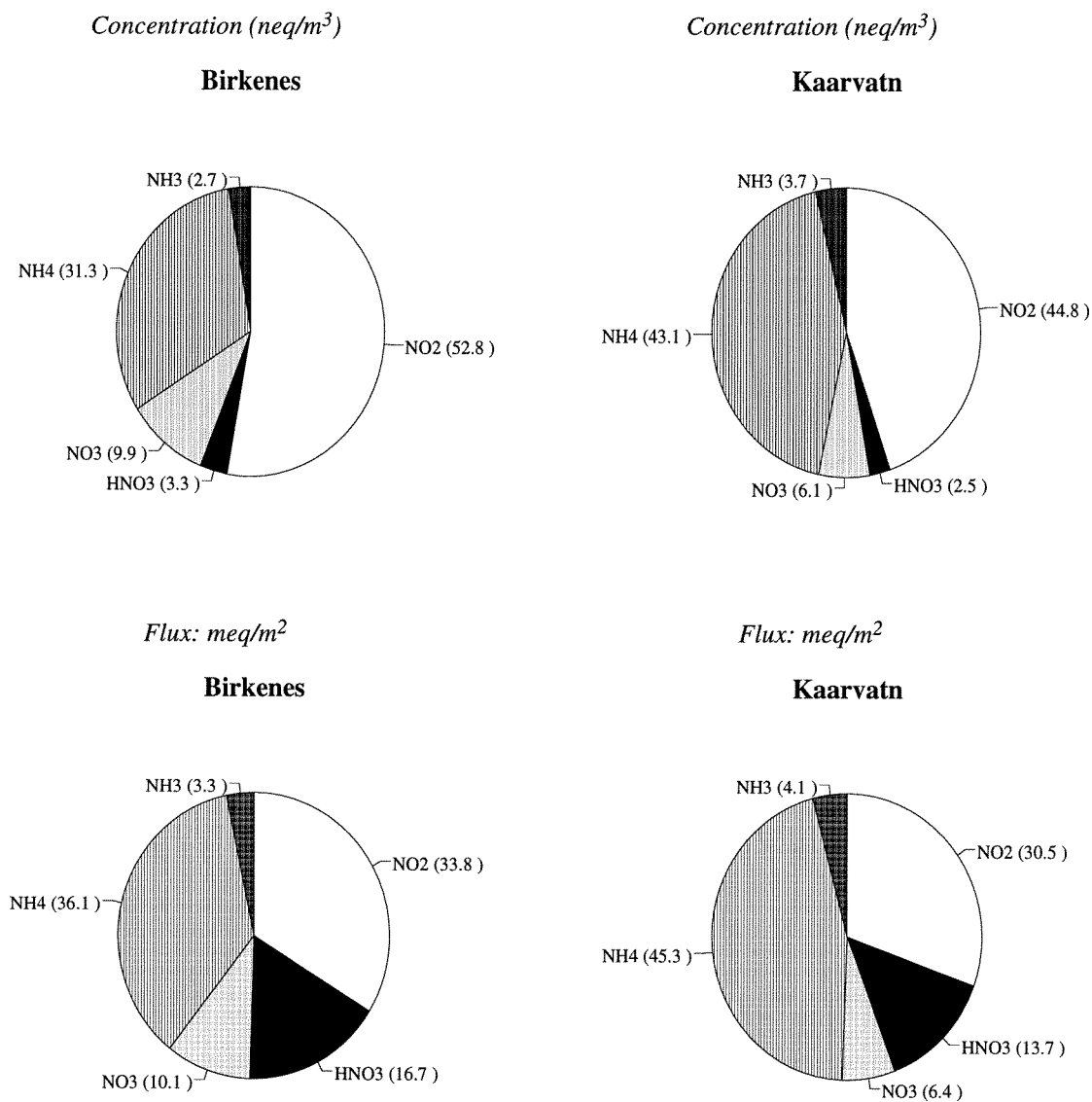


Figure 10 The percentage contributions of various dry-deposition compounds of nitrogen at Birkenes and Kaarvatn, based on average annual concentrations (neq/m<sup>3</sup>) and annual flux averages from 1988/89-1990/91.

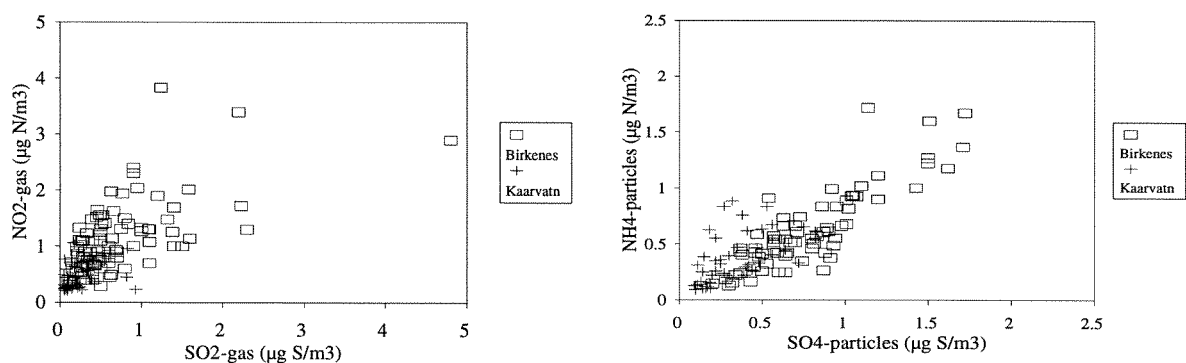


Figure 11 The relationship between monthly weighted concentration of  $SO_2$  and  $NO_2$ -gas and between  $SO_4^{2-}$ - and  $NH_4^+$ -particles ( $\mu g/m^3$ ) in dry-deposition at Birkenes and Kaarvatn.

\* Even though dry-deposition monitoring has been conducted for only a few years at Langtjern, this site seems to receive the relatively highest inputs of chemical compounds by dry-deposition. This should also be expected, because this site is the most precipitation poor site.

\* The dry-deposition velocities used for estimating fluxes cause significantly underestimates of dry-deposition fluxes at Birkenes. The most likely reasons for this are the high density of trees, and that the forest stand is old, i.e. large trees. By annual mass balance calculations, dry-deposition of sulphur and nitrogen constitute 30-40% of the total inputs of these elements at Birkenes. By using the deposition velocities estimated by the Norwegian institute for air research (NILU), dry-deposition of sulphur and nitrogen should only constitute about 10-15% of total inputs of these elements at Birkenes. No dry-deposition velocities are given for chloride. However, by mass balance calculation, annual dry-deposition of chloride, as for sulphur and nitrogen, seems to constitute 30-40% of total annual input at Birkenes.

\* At Kaarvatn, the weather-station is not representative for the chemical composition of dry- and wet-deposition for the whole catchment. Accordingly, no dry-deposition estimates are performed at this site.

\* The relative importance of seasalts, primarily from sodium and chloride, decreases by distance inland, from Kaarvatn to Langtjern (Figure 13). Concerning the more typical terrestrial derived compounds, Ca and K, it is the other way around.

\* The amount of chemical compounds that will dissolve or by other ways being washed out by precipitation depend on both quality and quantity of water (the chemical solvent) and the chemical compounds present in air.

\* Snow was found to remove sulphate from air about 40% less effective than rain. The precipitation was found to dissolve oxidised nitrogen compounds in dry-deposition ( $\Sigma NO_3$ ,  $HNO_3$ ) twice as effectively as reduced nitrogen ( $\Sigma NH_4$ ,  $NH_3$ ) and sulphate. This may indicate that the  $NH_4$  and  $SO_4$ -particles in air generally are less water-soluble compared with the oxidised nitrogen forms, or it indicates sampling and/or analytical problems due to oxidation of nitrogen by storage.

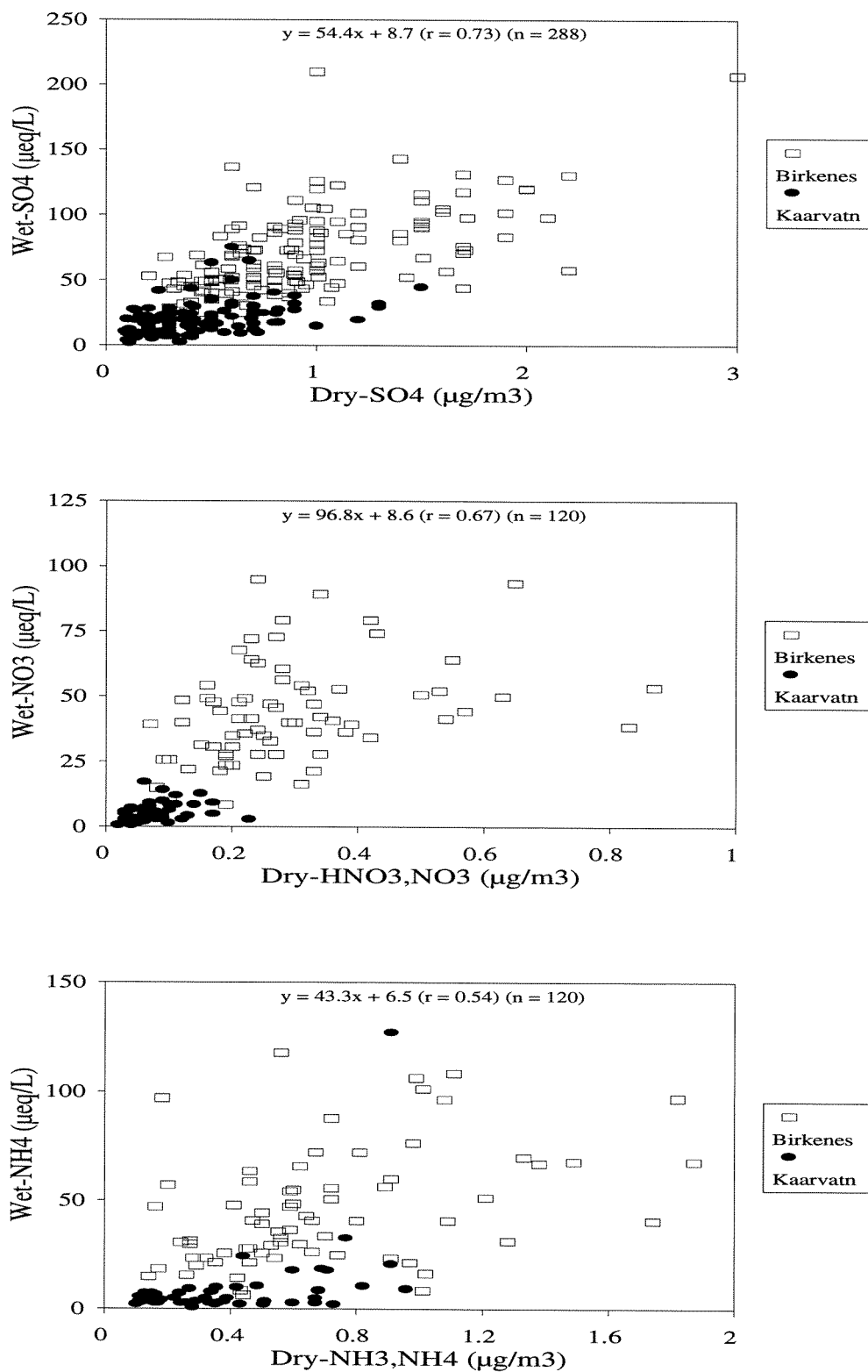


Figure 12 The concentration of sulphur and nitrogen compounds in air related to the concentrations in wet-deposition at Birkenes and Kaarvatn, based on monthly weighted averages. The sulphur data are from 1980-1991, while nitrogen data are from 1986-1991 (at Birkenes) or 1988-1991 (at Kaarvatn).

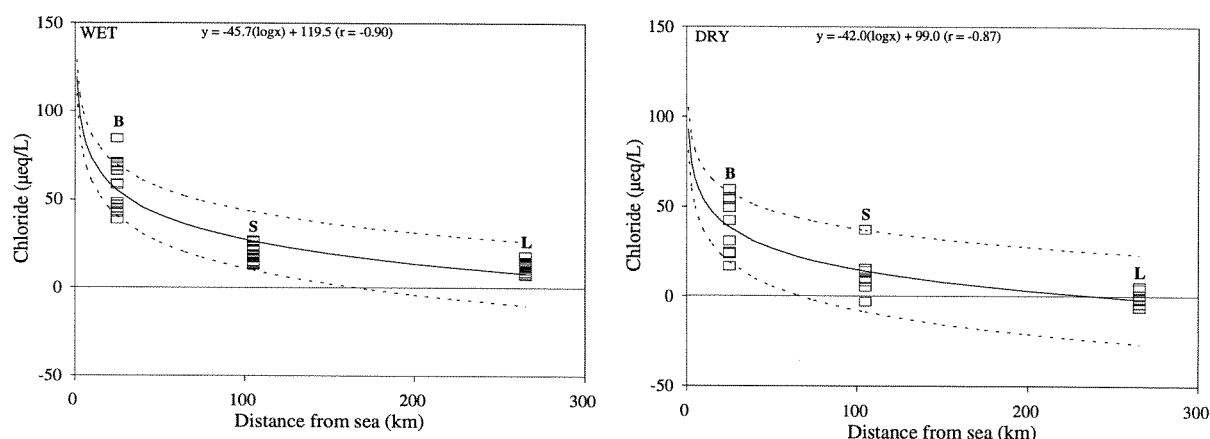


Figure 13 Decrease in concentration of chloride in wet- and dry- deposition with respect to distance from the coast, based on annual weighted averages. Dry-deposition of chloride is based on mass-balance calculations, i.e.  $Cl_{efflux} = Cl_{influx}$ . The dotted lines indicate  $\pm$  one std. deviation of mean.

## Runoff chemistry

\* **Annual average concentrations of ions ( $\Sigma$ Cations,Anions)** in runoff during the monitoring periods are: Birkenes:  $566 \pm 35$   $\mu\text{eq/L}$ ; Storgama:  $268 \pm 34$   $\mu\text{eq/L}$ ; Langtjern:  $242 \pm 33$   $\mu\text{eq/L}$ ; and Kaarvatn:  $214 \pm 22$   $\mu\text{eq/L}$ . On the basis of annual weighted flux averages, the total effluxes of ions ( $\Sigma$ Cations,Anions) are estimated to be 9%, 13%, and 13% less than the corresponding influxes ( $\Sigma$ wet-,dry-deposition) at Birkenes, Storgama and Langtjern. At Kaarvatn, a corresponding relation is not presented since the weather-station does not represent the weather-condition of the whole catchment.

\* **The annual average weighted  $H^+$ -concentrations in runoff** for the monitoring periods are: Birkenes: 24  $\mu\text{eq/L}$  (pH: 4.62); Storgama: 31  $\mu\text{eq/L}$  (pH: 4.51); Langtjern: 17  $\mu\text{eq/L}$  (pH: 4.77); Kaarvatn: 0.7  $\mu\text{eq/L}$  (pH: 6.15).

\* **The highest measured  $H^+$ -concentrations in runoff** during the monitoring periods are: Birkenes: 98  $\mu\text{eq/L}$  (pH: 4.01); Storgama: 100  $\mu\text{eq/L}$  (pH: 4.00); Langtjern: 41  $\mu\text{eq/L}$  (pH: 4.39); Kaarvatn: 3.4  $\mu\text{eq/L}$  (pH: 5.47).

\* **The annual average weighted concentrations of total Al (RAL, estimated as  $Al^{3+}$ ) in runoff** for the monitoring periods are: Birkenes: 49  $\mu\text{eq/L}$ ; Storgama: 18  $\mu\text{eq/L}$ ; Langtjern: 21  $\mu\text{eq/L}$ ; Kaarvatn: 2.1  $\mu\text{eq/L}$ .

\* **The highest measured concentrations of total aluminium (RAL) in runoff** during the monitoring periods are: Birkenes: 160  $\mu\text{eq/L}$  (1444  $\mu\text{g/L}$ ); Storgama: 56  $\mu\text{eq/L}$  (506  $\mu\text{g/L}$ ); Langtjern: 31  $\mu\text{eq/L}$  (276  $\mu\text{g/L}$ ); Kaarvatn: 5.6  $\mu\text{eq/L}$  (50  $\mu\text{g/L}$ ).

\* **The highest measured concentrations of inorganic monomeric Al (LAL) in runoff** during the monitoring periods (1985-1991) are: Birkenes: 785  $\mu\text{g/L}$ ; Storgama: 388  $\mu\text{g/L}$ ; Langtjern: 135  $\mu\text{g/L}$ ; Kaarvatn: 27  $\mu\text{g/L}$ .

- \* **The highest measured concentrations organic monomeric Al (ILAL) in runoff** during the monitoring periods (1985-1991) are: Birkenes: 1043 µg/L; Storgama: 131 µg/L; Langtjern: 172 µg/L; Kaarvatn: 41 µg/L.
- \* **The annual average weighted Ca-concentrations in runoff** for the monitoring periods are: Birkenes: 62 µeq/L; Storgama: 39 µeq/L; Langtjern: 61 µeq/L; Kaarvatn: 29 µeq/L.
- \* **The highest measured Ca-concentrations in runoff** during the monitoring periods are: Birkenes: 288 µeq/L; Storgama: 172 µeq/L; Langtjern: 104 µeq/L; Kaarvatn: 79 µeq/L.
- \* **The lowest measured Ca-concentrations in runoff** during the monitoring periods are: Birkenes: 17 µeq/L; Storgama: 9.0 µeq/L; Langtjern: 29 µeq/L; Kaarvatn: 9.0 µeq/L.
- \* **The annual average weighted SO<sub>4</sub>-concentrations in runoff** for the monitoring periods are: Birkenes: 131 µeq/L; Storgama: 78 µeq/L; Langtjern: 75 µeq/L; Kaarvatn: 20 µeq/L.
- \* **The highest measured SO<sub>4</sub>-concentrations in runoff** during the monitoring periods are: Birkenes: 271 µeq/L; Storgama: 196 µeq/L; Langtjern: 135 µeq/L; Kaarvatn: 60 µeq/L.
- \* **The annual average weighted NO<sub>3</sub>-concentrations in runoff** for the monitoring periods are: Birkenes: 9.0 µeq/L; Storgama: 10 µeq/L; Langtjern: 2.0 µeq/L; Kaarvatn: 1.4 µeq/L.
- \* **The highest measured NO<sub>3</sub>-concentrations in runoff** during the monitoring periods are: Birkenes: 107 µeq/L; Storgama: 74 µeq/L; Langtjern: 16 µeq/L; Kaarvatn: 12 µeq/L.
- \* **The annual average weighted Cl-concentrations in runoff** for the monitoring periods are: Birkenes: 127 µeq/L; Storgama: 35 µeq/L; Langtjern: 19 µeq/L; Kaarvatn: 62 µeq/L.
- \* **The highest measured Cl-concentrations in runoff** during the monitoring periods are: Birkenes: 330 µeq/L; Storgama: 166 µeq/L; Langtjern: 73 µeq/L; Kaarvatn: 339 µeq/L.
- \* **The annual average weighted TOC-concentrations in runoff** for the monitoring periods are: Birkenes: 4.9 mg C/L; Storgama: 4.1 mg C/L; Langtjern: 8.8 mg C/L; Kaarvatn: 1.0 mg C/L.
- \* **The highest measured TOC-concentrations in runoff** during the monitoring periods are: Birkenes: 20.3 mg C/L; Storgama: 7.3 mg C/L; Langtjern: 20 mg C/L; Kaarvatn: 3.2 mg C/L.
- \* **The lowest measured TOC-concentrations in runoff** during the monitoring periods are: Birkenes: 0.1 mg C/L; Storgama: 1.4 mg C/L; Langtjern: 4.8 mg C/L; Kaarvatn: 0.30 mg C/L.
- \* **The annual average weighted ANC-values in runoff** for the monitoring periods are: Birkenes: -50 µeq/L; Storgama: -33 µeq/L; Langtjern: 15 µeq/L; Kaarvatn: 22 µeq/L.
- \* **The highest measured ANC-values in runoff** during the monitoring periods are: Birkenes: 201 µeq/L; Storgama: 90 µeq/L; Langtjern: 75 µeq/L; Kaarvatn: 74 µeq/L.

\* **The lowest measured ANC-values in runoff** during the monitoring periods are: Birkenes: -333  $\mu\text{eq/L}$ ; Storgama: -130  $\mu\text{eq/L}$ ; Langtjern: -53  $\mu\text{eq/L}$ ; Kaarvatn: -8.3  $\mu\text{eq/L}$ .

Table 3 Annual weighted maximum, minimum and annual weighted mean values of runoff ( $\text{mm/m}^2$ ) and concentrations of dissolved substances ( $\mu\text{eq/L}$ ) in runoff from the catchments during the monitoring periods.

Period		Birkenes 1974-1991	Storgama 1974-1991	Langtjern 1974-1991	Kaarvatn 1980-1991
<b>H<sup>+</sup></b>	<i>max</i>	31	42	21	0.9
	<b>mean</b>	<b>24 ± 4</b>	<b>31 ± 5</b>	<b>17 ± 3</b>	<b>0.7 ± 0.1</b>
	<i>min</i>	18	13	1	0.6
<b>Al<sup>3+</sup></b>	<i>max</i>	56	22	28	2.5
	<b>mean</b>	<b>49 ± 3</b>	<b>18 ± 1</b>	<b>21 ± 3</b>	<b>2.1 ± 0.2</b>
	<i>min</i>	16	16	2	1.9
<b>Ca<sup>2+</sup></b>	<i>max</i>	77	60	81	31
	<b>mean</b>	<b>62 ± 8</b>	<b>39 ± 8</b>	<b>61 ± 9</b>	<b>29 ± 2</b>
	<i>min</i>	48	30	47	26
<b>Mg<sup>2+</sup></b>	<i>max</i>	41	19	25	20
	<b>mean</b>	<b>34 ± 4</b>	<b>13 ± 3</b>	<b>18 ± 3</b>	<b>17 ± 2</b>
	<i>min</i>	29	10	14	14
<b>Na<sup>+</sup></b>	<i>max</i>	136	51	35	71
	<b>mean</b>	<b>119 ± 10</b>	<b>35 ± 7</b>	<b>25 ± 4</b>	<b>58 ± 7</b>
	<i>min</i>	106	25	20	49
<b>K<sup>+</sup></b>	<i>max</i>	10	9	6	4
	<b>mean</b>	<b>6.1 ± 1.8</b>	<b>3.2 ± 1.9</b>	<b>3.4 ± 1.0</b>	<b>3.5 ± 0.2</b>
	<i>min</i>	3.6	1.5	2.4	3.2
<b>SO<sub>4</sub><sup>2-</sup></b>	<i>max</i>	155	103	99	22
	<b>mean</b>	<b>131 ± 15</b>	<b>78 ± 12</b>	<b>75 ± 12</b>	<b>20 ± 1</b>
	<i>min</i>	104	64	55	17
<b>Cl<sup>-</sup></b>	<i>max</i>	163	49	23	89
	<b>mean</b>	<b>127 ± 18</b>	<b>35 ± 6</b>	<b>19 ± 3</b>	<b>62 ± 13</b>
	<i>min</i>	100	22	13	46
<b>NO<sub>3</sub><sup>-</sup></b>	<i>max</i>	15	17	3	2
	<b>mean</b>	<b>9.0 ± 3.1</b>	<b>10 ± 3</b>	<b>2.0 ± 0.5</b>	<b>1.4 ± 0.2</b>
	<i>min</i>	4.5	5.8	1.5	1.1
<b>HCO<sub>3</sub><sup>-</sup></b>	<i>max</i>	0	0	0	29
	<b>mean</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>22 ± 4</b>
	<i>min</i>	0	0	0	15
<b>TOC</b> ( <i>mg C/L</i> )	<i>max</i>	5.5	5.1	9.1	1.1
	<b>mean</b>	<b>4.9 ± 0.4</b>	<b>4.1 ± 0.5</b>	<b>8.8 ± 0.4</b>	<b>1.0 ± 0.1</b>
	<i>min</i>	4.5	3.6	8.0	0.8
<b>Ionic strength</b> ( <i>μmol/L</i> )	<i>max</i>	456	283	274	165
	<b>mean</b>	<b>419 ± 29</b>	<b>211 ± 27</b>	<b>215 ± 28</b>	<b>142 ± 12</b>
	<i>min</i>	365	179	173	121
<b>ΣCations</b>	<b>mean</b>	<b>293 ± 20</b>	<b>139 ± 20</b>	<b>146 ± 16</b>	<b>109 ± 9</b>
<b>ΣAnions</b>	<b>mean</b>	<b>267 ± 20</b>	<b>123 ± 15</b>	<b>96 ± 14</b>	<b>105 ± 12</b>

\* At Birkenes, on the basis of annual weighted concentration means (Figure 14), Na<sup>+</sup> on average constitutes 40% of the cationic pool in runoff, while Ca<sup>2+</sup>, Al<sup>3+</sup>, Mg<sup>2+</sup> and H<sup>+</sup> on average contribute with 21%, 17%, 12% and 8%, respectively. Correspondingly, SO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup> both constitute 44% of the anionic pool, while NO<sub>3</sub><sup>-</sup> and negatively charged organic compounds (A<sup>-</sup>) constitute 3% and 9%.

\* At Storgama, on average Na<sup>+</sup> constitutes about 26% of the cationic pool in runoff, while Ca<sup>2+</sup>, Al<sup>3+</sup>, Mg<sup>2+</sup> and H<sup>+</sup> on average contribute with 27%, 13%, 10% and 22%, respectively. Correspondingly, SO<sub>4</sub><sup>2-</sup> constitutes 56% of the anionic pool, while Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and A<sup>-</sup> constitute 26%, 8% and 11%, respectively.

\* At Langtjern, Ca<sup>2+</sup> is the predominant cation and constitutes on average 41% of the cationic pool in runoff, while Na<sup>+</sup>, Al<sup>3+</sup>, Mg<sup>2+</sup> and H<sup>+</sup> contribute with 18%, 14%, 12% and 12%, respectively. Correspondingly, SO<sub>4</sub><sup>2-</sup> constitutes 50% of the anionic pool, while Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and A<sup>-</sup> constitute 13%, 1% and 35%, respectively.

\* At Kaarvatn, Na<sup>+</sup> is the predominant cation and constitutes on average 52% of the cationic pool in runoff, while Ca<sup>2+</sup>, Al<sup>3+</sup>, Mg<sup>2+</sup> and H<sup>+</sup> on average contribute with 27%, < 1%, 15% and 3%, respectively. Correspondingly, Cl<sup>-</sup> constitutes 56% of the anionic pool, while HCO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and A<sup>-</sup> constitute 21%, 18%, 1% and 3%, respectively.

\* HCO<sub>3</sub><sup>-</sup> is normally present only in the runoff water at Kaarvatn. Compared with the annual weighted average concentration of H<sup>+</sup> in wet-deposition, the H<sup>+</sup> concentrations are 55%, 38%, 57% and 94% lower in the runoff water at Birkenes, Storgama, Langtjern and Kaarvatn, respectively.

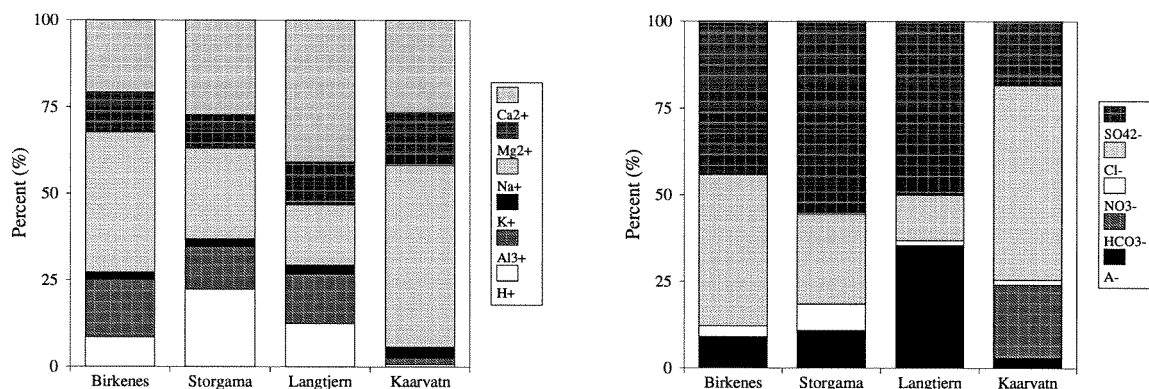


Figure 14 The percentage distribution of major cations and anions in runoff water from the four catchments based on annual weighted averages ( $\mu\text{eq/L}$ ) during the monitoring periods.

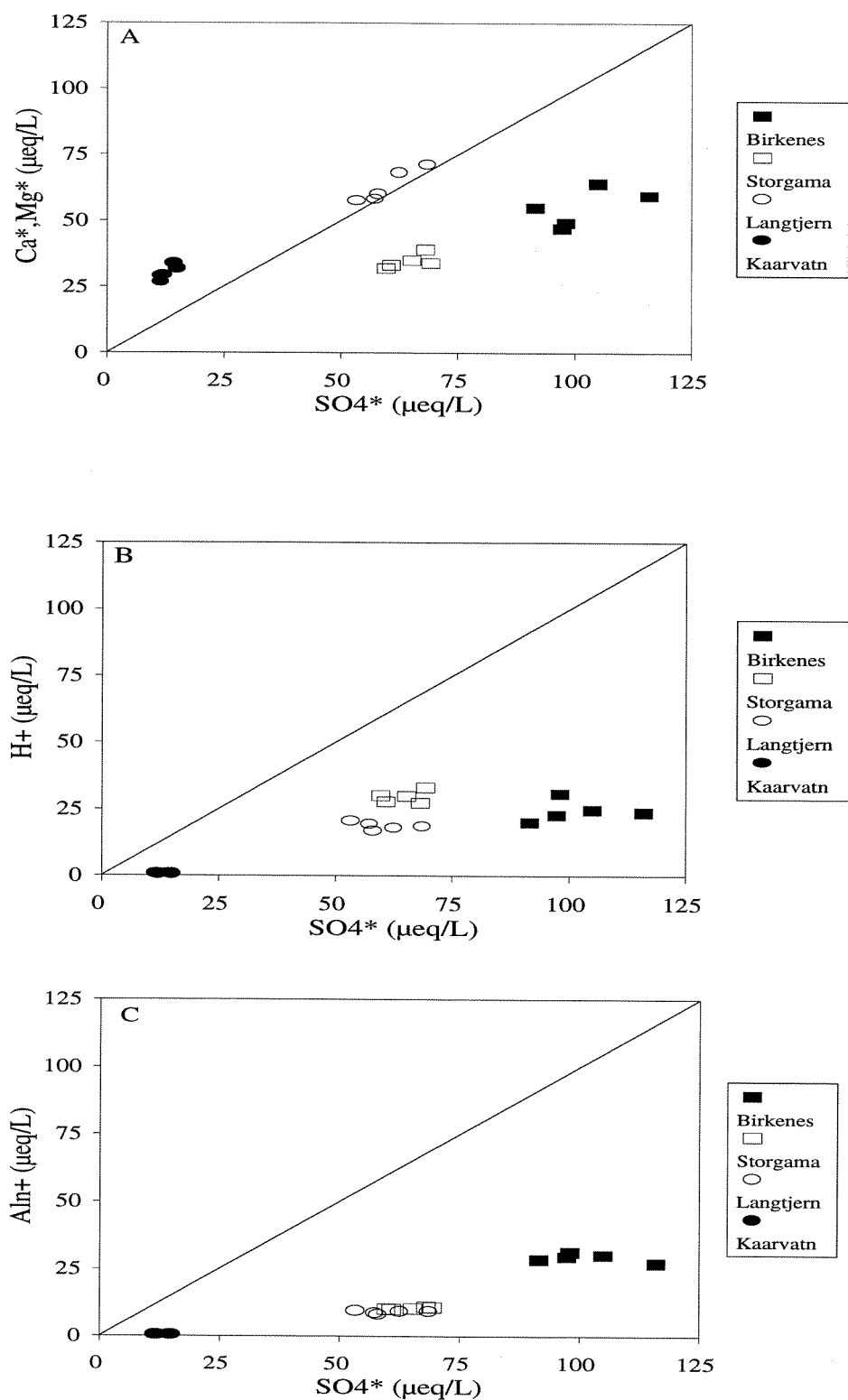


Figure 15 The  $[\text{SO}_4^*]/[\Sigma\text{Ca}^*, \text{Mg}^*]$  ratio (A),  $[\text{SO}_4^*]/[\text{H}^+]$  ratio (B), and the  $[\text{SO}_4^*]/[\text{Al}^{n+}]$  ratio (C) in runoff water from the different catchments, based on annual weighted averages during the period of monitoring when aluminium-speciation analyses have been performed at all sites, i.e. from 1986 to 1991. Continuous line represents the 1/1 line.



## The hydrologic effect on runoff chemistry

\* The concentrations of  $H^+$  in runoff are increasing by increasing runoff at all catchments (Figure 16), highest increase at Birkenes, followed by Storgama, Langtjern and Kaarvatn (Table 4). Increasing fluxes of  $H^+$  by increasing runoff are also found at all sites, highest at Birkenes, followed by Storgama, Langtjern and Kaarvatn.

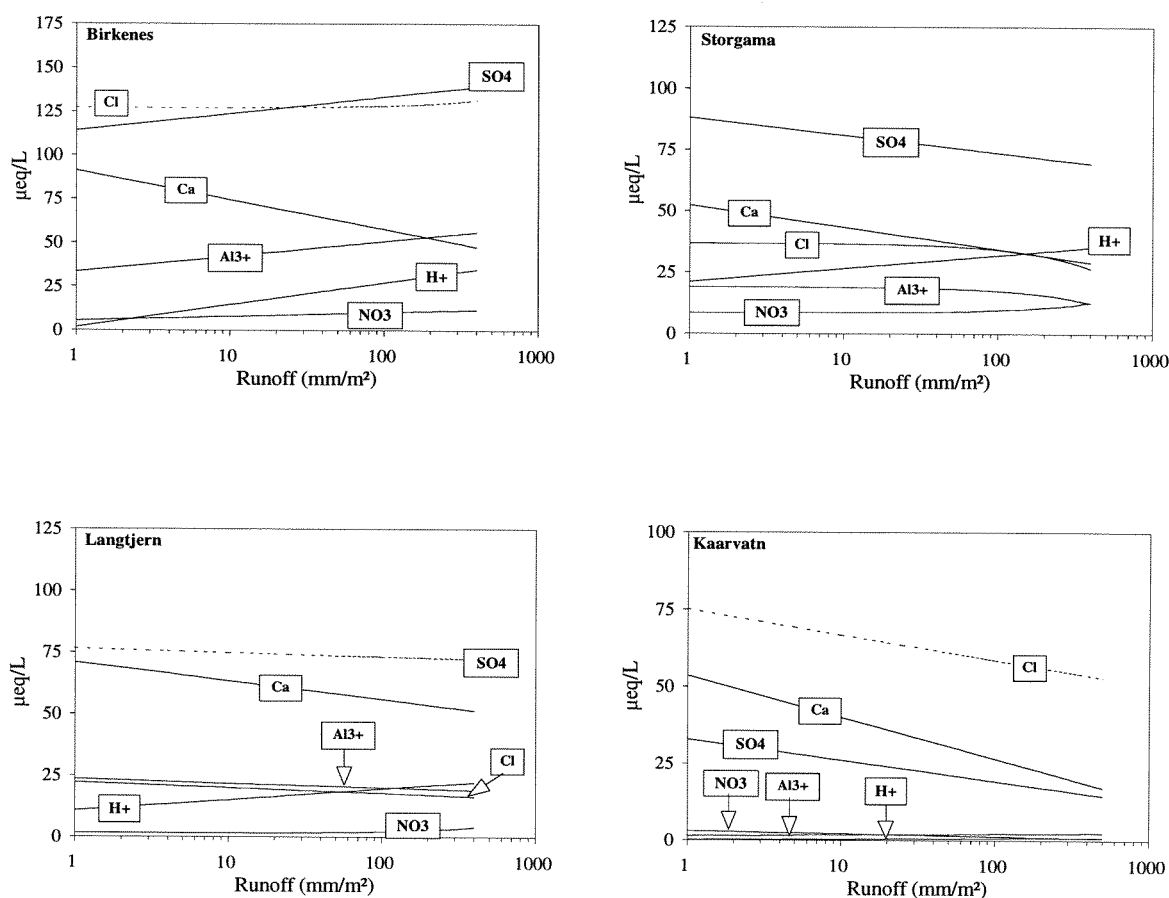


Figure 16 The relationships between monthly runoff ( $mm/m^2$ ) and monthly weighted concentrations of major dissolved ions in runoff ( $\mu eq/L$ ) at the four catchments during the monitoring period.

\* The concentrations of non-marine base cations ( $\Sigma Ca^*, Mg^*$ ) in runoff are decreasing by increasing runoff at all sites, highest decrease at Birkenes, followed by Kaarvatn, Storgama and Langtjern. However, increasing fluxes of  $\Sigma Ca^*, Mg^*$  by increasing runoff are found at all sites, highest at Langtjern, followed by Birkenes and Storgama  $\approx$  Kaarvatn.

\* At Birkenes and Kaarvatn, the concentrations of total aluminium in runoff (estimated as  $Al^{3+}$ ) are increasing by increasing runoff, highest increase at Birkenes of course. At Storgama and Langtjern, the concentrations of total aluminium are decreasing by increasing runoff, largest decrease at Langtjern. While the fluxes of total aluminium are increasing by increasing

runoff at Birkenes, Langtjern and Kaarvatn, highest at Birkenes, followed by Langtjern and Kaarvatn, the flux of aluminium is slightly decreasing by increasing runoff at Storgama.

\* The concentrations of non-marine sulphate ( $\text{SO}_4^*$ ) in runoff are decreasing by increasing runoff at Storgama, Kaarvatn and Langtjern, largest decrease at Storgama and Kaarvatn (about equal), followed by Langtjern. At Birkenes the concentration of  $\text{SO}_4^*$  in runoff increases by increasing runoff. At all sites, the fluxes  $\text{SO}_4^*$  are increasing by increasing runoff, highest at Birkenes, followed by Langtjern, Storgama and Kaarvatn

\* The concentrations of  $\text{NO}_3^-$  in runoff are increasing by increasing runoff at Birkenes, Storgama and Langtjern, highest increase at Birkenes, followed by Storgama and Langtjern, while for the least polluted catchment, Kaarvatn, the concentration of  $\text{NO}_3^-$  is decreasing by increasing runoff. At all sites, the fluxes of  $\text{NO}_3^-$  are increasing by increasing runoff, highest at Storgama, followed by Birkenes Langtjern and Kaarvatn. That the flux of  $\text{NO}_3^-$  is most runoff sensitive at Storgama is probably because both the concentration and flux of nitrate are generally very runoff dependent, and Storgama is probably the catchment with the shortest residence time of water.

\* The acid neutralizing capacity (ANC) is decreasing by increasing runoff at all sites, highest decrease at Birkenes, followed by Kaarvatn, Storgama and Langtjern.

\* Assuming the concentration of  $\text{H}^+$  and aluminium being the biological most harmful compounds in runoff, the most severe water quality changes by increasing runoff will occur at Birkenes, followed by Storgama, Langtjern, and Kaarvatn. At Kaarvatn, the water quality is still relatively good even at high flow periods, so that negative ANC-values seldom occur.

Table 4 The degree of concentration changes (positive/negative correlation) with respect to amount of runoff, based on monthly weighted averages.

Ion	Correlation	Degree of runoff sensitivity						
$\text{H}^+$	positive	Birkenes	>>	Storgama	>>	Langtjern	>>	Kaarvatn
$\text{Ca}^{2+}$	negative	Birkenes	>	Kaarvatn	>>	Storgama	>	Langtjern
$\text{Mg}^{2+}$	negative	Kaarvatn	>>	Langtjern	>	Birkenes*	>	Storgama
$\Sigma\text{Ca}^*,\text{Mg}^*$	negative	Birkenes	>	Kaarvatn	>>	Storgama	>	Langtjern
$\text{Na}^+$	negative	Kaarvatn	>>	Storgama	>>	Langtjern	>>	Birkenes*
$\text{K}^+$	positive	Langtjern	>	Storgama				
$\text{K}^+$	negative	Kaarvatn	>>	Birkenes*				
$\text{Al}^{3+}$	negative	Langtjern	>	Storgama				
$\text{Al}^{3+}$	positive	Birkenes	>>	Kaarvatn				
$\text{Cl}^-$	negative	Kaarvatn*	>>	Langtjern	>>	Storgama		
$\text{Cl}^-$	positive	Birkenes*						
$\text{NO}_3^-$	positive	Birkenes	>>	Storgama	>>	Langtjern		
$\text{NO}_3^-$	negative	Kaarvatn						
$\text{SO}_4^{2-}$	negative	Storgama	=	Kaarvatn	>>	Langtjern*		
$\text{SO}_4^{2-}$	positive	Birkenes						
$\text{SO}_4^*$	negative	Storgama	=	Kaarvatn	>>	Langtjern*		
$\text{SO}_4^*$	positive	Birkenes						
$\text{HCO}_3^-$	negative	Kaarvatn						
TOC	positive	Storgama*	>>	Kaarvatn*				
TOC	negative	Birkenes	>>	Langtjern*				
ANC	negative	Birkenes	>>	Kaarvatn	>>	Storgama	>	Langtjern

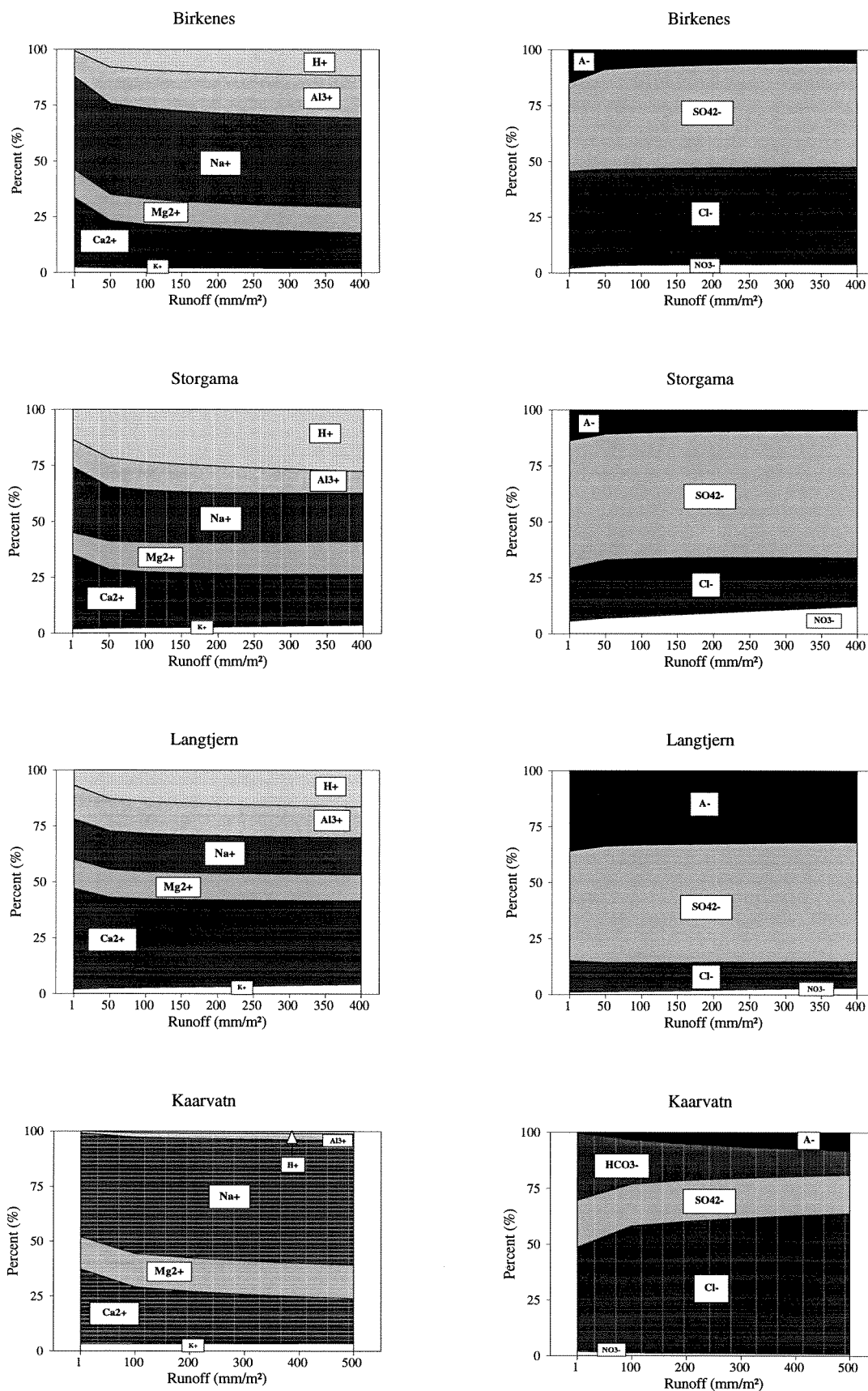


Figure 17 The percentage change in the distribution of inorganic cations and anions with respect to change in runoff, based on monthly weighted average values.

## Sulphuric acid and other acidifying compounds

\* Assuming the runoff concentration  $\text{SO}_4^*$  being the major factor for the runoff concentration levels of  $\text{Ca}^*$ ,  $\text{Mg}^*$ ,  $\text{Na}^*$ ,  $\Sigma\text{Al}^{n+}$ , and  $\text{H}^+$ , the concentration of  $\text{SO}_4^*$  in relation to  $\Sigma(\text{Ca}^*, \text{Mg}^*, \text{Na}^*, \Sigma\text{Al}^{n+}, \text{H}^+)$  expresses the amount of the acidification that is directly attributed to sulphuric acid. On the basis of monthly weighted averages from 1986-1991, on average 89% of the acidification at Birkenes is due to sulphuric acid, while 82%, 59% and 37% of the acidification at Storgama, Langtjern and Kaarvatn can be attributed to sulphuric acid. Most of the remaining 11% and 18% of the acidification at Birkenes and Storgama are primarily due to nitrate leakage, but also to some extent due to weak organic acids. The remaining 41% of the acidification at Langtjern that is not "sulphuric-acid-explainable" is primarily a consequence of the high amounts of weak organic acids. At Kaarvatn, 63% of the acidification is not directly related to sulphuric acid, but is most likely a consequence of carbonic acid. This is a weak inorganic acid that generally is present in relatively high amounts in the runoff water all catchments, but plays a minor role in catchments where strong acids totally predominate, as in Birkenes and Storgama.

\* Only at Birkenes, there has been a decrease in "sulphuric-acid-explanatory" acidification during the last years, i.e. from 1986-1992. At the other sites, the per cent of "sulphuric-acid-explanatory" acidification is about the same in 1986 as at the end of 1991, even though the concentration of sulphuric acid has decreased at all sites, both in precipitation and runoff.

\* At Birkenes, on average 79% of the input of free protons ( $\text{H}^+$ ) are consumed by various processes within the catchment. The corresponding consumption of  $\text{H}^+$ -ions at Storgama, Langtjern and Kaarvatn are 63%, 83% and 98%, respectively.

\* At Birkenes, on average 67% of the  $\text{H}^+$ -consumption can be attributed to base cation dissolution, while the remaining 33% is from dissolution of aluminium. At Storgama, 79% of the proton consumption can be attributed to base cation dissolution, while the remaining 21% is from dissolution of aluminium. At Langtjern, 89% of the proton consumption can be attributed to base cation dissolution, while the remaining 11% is from dissolution of aluminium, while at Kaarvatn, 98% of the proton consumption can be attributed to base cation dissolution, while only 2% is consumed by dissolution of aluminium. The importance of aluminium dissolution for pH-buffering of highly acidified catchments is well illustrated at Birkenes, where dissolution of aluminium on average neutralises > 30% of  $\text{H}^+$ -ions.

\* On the basis of monthly weighted averages from 1986-1991, the sulphuric acid explanatory acidification at Birkenes is at the lowest in August (78%), at the highest in November (96%). Correspondingly, the lowest influence from sulphuric acid at Storgama is normally in April (77%) while the highest influence normally occurs in May (98%). At Langtjern, the lowest influence from sulphuric acid normally occurs in April (54%), the highest in May (66%), while at Kaarvatn the lowest influence occurs in January (32%), the highest in April (57%).

\* At Birkenes the highest  $\text{H}^+$  concentration normally occurs in March and October, the same months when the concentration of  $\text{SO}_4^*$  is at the highest. The highest aluminium concentrations ( $\Sigma\text{Al}^{n+}$ ) normally occur in March and November.

Table 5 Mean concentrations of  $H^+$ ,  $\Sigma Al^{n+}$ ,  $\Sigma Ca^*$ ,  $Mg^*$ ,  $Na^*$  and  $SO_4^*$  in runoff from the four catchments, and the percentage amount of  $\Sigma(Ca^*, Mg^*, Na^*, \Sigma Al^{n+}, H^+)$  which can be directly attributed to sulphuric acid ( $SO_4^*$ ). The mean values are based on monthly weighted averages from 1986 to 1991.

	<b>A</b>	<b>B</b>	<b>C</b>	<b>D</b>	<b>E</b>	<b>F</b>
Site	$H^+$ $\mu eq/L$	$\Sigma Al^{n+}$ $\mu eq/L$	$\Sigma Ca^*, Mg^*, Na^*$ $\mu eq/L$	$A+B+C$ $\mu eq/L$	$SO_4^*$ $\mu eq/L$	$E/D$ %
Birkenes	24.2	29.2	60.0	113.4	101.4	89%
Storgama	29.0	10.4	39.4	78.8	64.4	82%
Langtjern	17.5	8.8	74.3	100.6	59.5	59%
Kaarvatn	0.70	0.61	34.3	35.6	13.2	37%

\* At Storgama the highest  $H^+$  concentration normally occurs in December, the same months when the concentrations of both  $SO_4^*$  and  $\Sigma Al^{n+}$  are at the highest. At Storgama, the highest concentrations of non-marine base cations also tend to occur in December.

\* At Langtjern, the highest  $H^+$  concentration normally occurs in December, the same months when the concentration of  $SO_4^*$  and  $\Sigma Al^{n+}$  are at the highest. At Langtjern, relatively high amounts of non-marine base cations normally occur in December.

\* At Kaarvatn, the highest concentration of  $SO_4^*$  normally occurs in December, while during the same months the concentration of  $\Sigma Al^{n+}$  and  $H^+$  only are at annual mean level. The highest concentrations of  $\Sigma Al^{n+}$  and  $H^+$  normally occur during spring melt, i.e. April 1 - June 30, but the concentrations are very low.

Table 6 Total concentration and the concentration and percentage distribution of various natural and anthropogenic sources of sulphate in wet-deposition, based on annual weighted concentration averages from 1980-1991. The wet-deposition at Kaarvatn is assumed to represent the background levels of non-marine  $SO_4^*$ . To account for concentration-variations due to various amounts of water entering the four sites, the concentration of sulphate at all weather-station is normalised to an annual input of water of 1000 mm/m<sup>2</sup>. Thus, normalised concentration is  $[SO_4 \text{ normalised}] = [SO_4 \text{ measured}] * [\text{Annual measured precipitation (mm)/1000 mm}]$ .

Station	Unit	Total $SO_4$ A	Marine $SO_4$ -sources <sup>1</sup> B	Other natural $SO_4^*$ -sources <sup>2</sup> C	Anthropogenic $SO_4^*$ -sources D= A-B-C
Birkenes	$\mu eq/L$	110 ± 18	10 ± 3	29 ± 9	71 ± 17
	%	100	9 ± 2	27 ± 9	64 ± 8
Storgama	$\mu eq/L$	65 ± 17	3 ± 1	29 ± 9	33 ± 16
	%	100	4 ± 1	47 ± 16	49 ± 16
Langtjern	$\mu eq/L$	51 ± 8	1 ± 0.3	29 ± 9	21 ± 10
	%	100	2 ± 1	56 ± 18	41 ± 18
Kaarvatn	$\mu eq/L$	43 ± 8	14 ± 5	29 ± 9	0
	%	100	33 ± 14	67 ± 14	0

<sup>1</sup> Marine  $SO_4 = 0.103 * [Cl^-]$

<sup>2</sup> Natural  $SO_4^* = [SO_4^*]$  at Kaarvatn

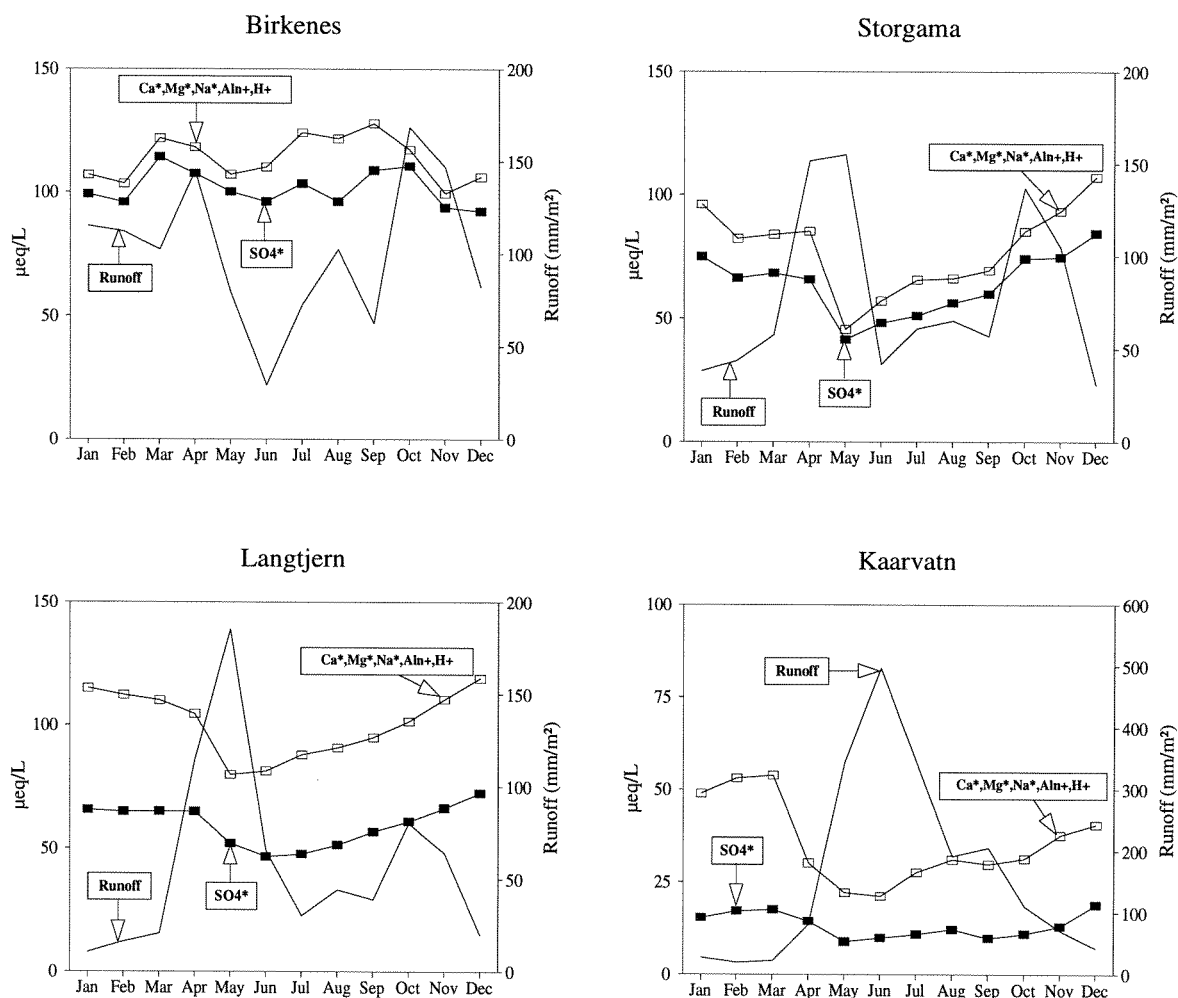


Figure 18 Seasonal variations in runoff and concentrations of non-marine sulphate ( $\text{SO}_4^*$ ) and  $\Sigma(\text{Ca}^*, \text{Mg}^*, \text{Na}^*, \Sigma\text{Aln}^+, \text{H}^+)$  at the four catchments, based on monthly weighted averages from 1986-1991.

Table 7 Total concentration and the concentration and percentage distribution of natural and anthropogenic sources of nitrate and ammonium in wet-deposition, based on annual weighted concentration averages from 1980 -1991. The wet-deposition at Kaarvatn is assumed to represent the background levels of nitrate and ammonium. To account for concentration-variations due to various amounts of water entering the four sites, the concentrations of nitrate and ammonium at all weather-station are normalised to an annual input of water of  $1000 \text{ mm/m}^2$ . Thus, normalised concentration is  $[\text{NO}_3 \text{ normalised}] = [\text{NO}_3 \text{ measured}] * [\text{Annual measured precipitation}(\text{mm})/1000 \text{ mm}]$ .

Station	Unit	Total	Nitrate		Total	Ammonium	
			Natural	Anthrop.		Natural	Anthrop.
Birkenes	$\mu\text{eq/L}$	$64 \pm 13$	$14 \pm 2$	$50 \pm 12$	$72 \pm 14$	$21 \pm 4$	$51 \pm 16$
	%	100	$23 \pm 6$	$77 \pm 6$	100	$30 \pm 11$	$70 \pm 11$
Storgama	$\mu\text{eq/L}$	$41 \pm 10$	$14 \pm 2$	$27 \pm 9$	$42 \pm 10$	$21 \pm 4$	$21 \pm 12$
	%	100	$37 \pm 9$	$63 \pm 9$	100	$53 \pm 17$	$47 \pm 17$
Langtjern	$\mu\text{eq/L}$	$33 \pm 5$	$14 \pm 2$	$19 \pm 4$	$45 \pm 7$	$21 \pm 4$	$24 \pm 10$
	%	100	$44 \pm 7$	$56 \pm 8$	100	$47 \pm 14$	$53 \pm 17$
Kaarvatn	$\mu\text{eq/L}$	$14 \pm 2$	$14 \pm 2$	0	$21 \pm 4$	$21 \pm 4$	0
	%	100	100	0	100	100	0

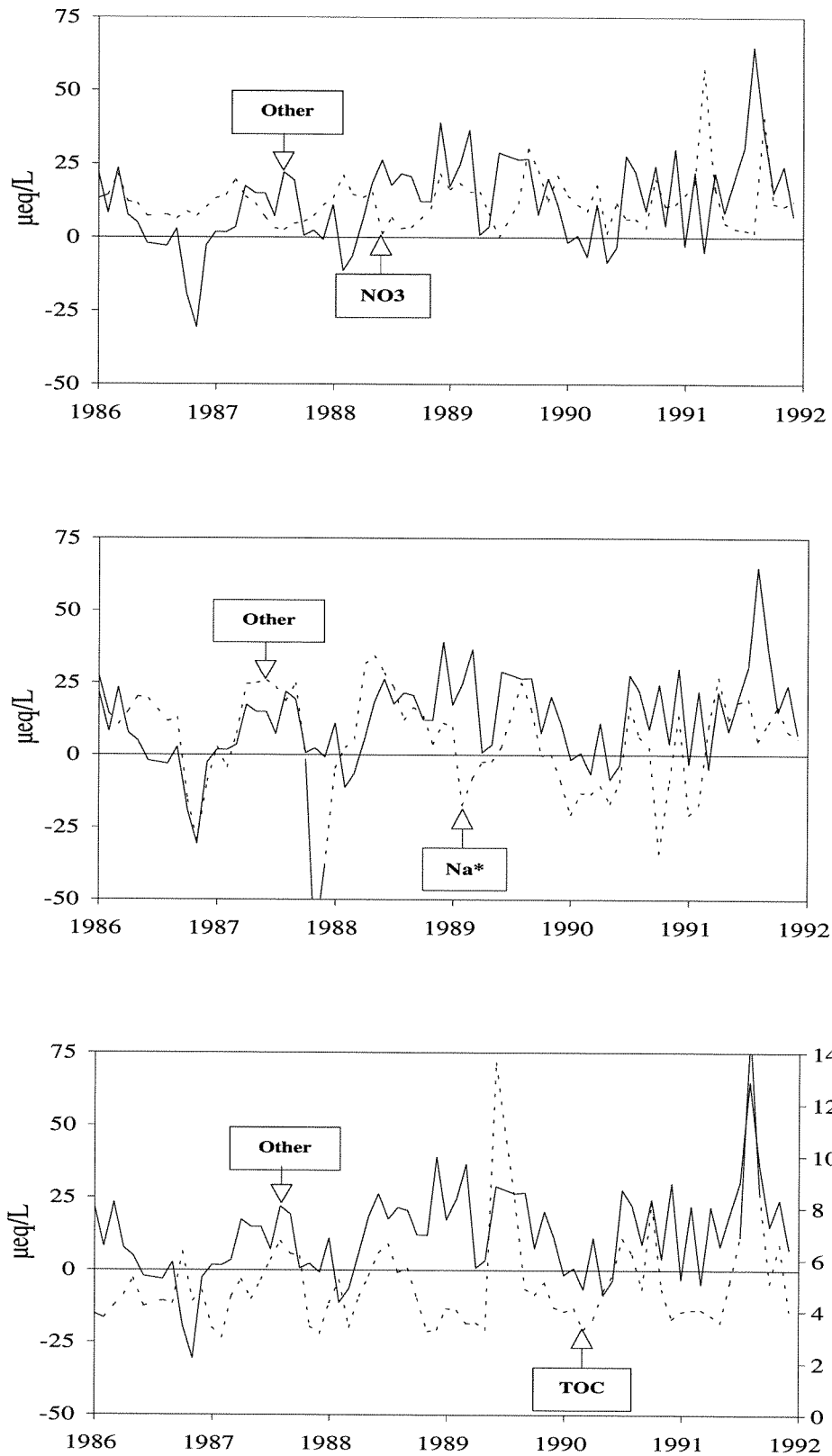


Figure 19 Monthly weighted concentrations of non-sulphuric-acid explanatory concentration of  $\Sigma\text{BC}^*, \text{Al}^{m+}, \text{H}^+$  (named Other), and the concentration of nitrate, non-marine sodium ( $\text{Na}^*$ ), and total organic carbon (TOC) at Birkenes from 1986 to 1991.

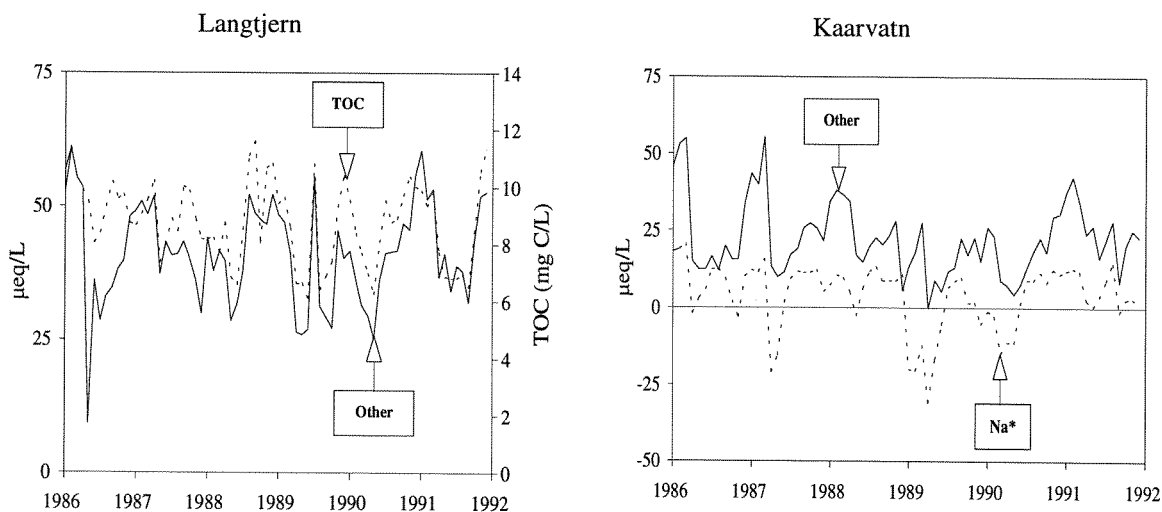


Figure 20 Monthly weighted concentrations of non-sulphuric-acid explanatory concentration of  $\Sigma BC^*$ ,  $Al^{n+}$ ,  $H^+$  (named Other), and the concentration of TOC (at Langtjern) and non-marine sodium,  $Na^*$  (at Kaarvatn) from 1986 to 1991.

\* The highest amounts of seasalts in runoff normally occur in October/November at Birkenes, November/December at Storgama, December-February at Langtjern, and in April at Kaarvatn.

\* On short-term basis, high seasalt inputs may cause significant cation exchange reactions, where marine sodium and magnesium are able to cation exchange with  $H^+$  and cationic Al ( $Al^{n+}$ ) in the soil. During these episodes, large amounts of  $H^+$  and cationic Al ( $Al^{n+}$ ) in runoff can be directly attributed to these processes, and the relative importance of sulphuric acid explainable acidification is therefore reduced.

## Seasalt episodes

\* Undoubtedly, sulphuric acid is the main cause of acidification and aluminium leakage, and therefore decisive for the aluminium concentration levels in runoff water. However, at least in acidified coast-near areas like at Birkenes, the seasalt variations are highly important for seasonal or short-term fluctuations in the aluminium concentration in runoff. Because aluminium most frequently is the major toxic compound in acidified surface waters, it is essential that the most significant difference between cold and warm years in coast-near areas of southern Norway, is the input of NaCl during the winter. Even though both Na and Cl are relative conservative ions, which means that input of these ions are about equal to their output during a certain time, i.e. within a year (Figure 21), the somewhat lower mobility of sodium due to its participation in cation exchange reactions in soil, cause temporarily acidification. Primarily at Birkenes receiving the highest inputs of strong acids, substantial amounts of negatively charged organic sites are protonated or contain cationic complexed aluminium. Thus, during seasalt episodes large amounts of sodium (and to a certain degree magnesium) will cation-exchange for  $H^+$  and cationic aluminium, which subsequent enter the surface waters.



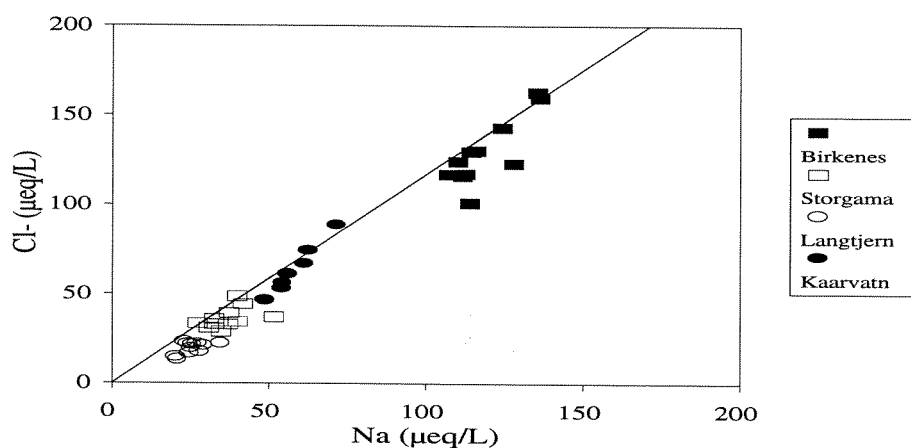


Figure 21 The sodium/chloride ratio in runoff at the different catchments, based on annual weighted averages during the respective monitoring periods. Continuous line represents the Na/Cl ratio of sea water.

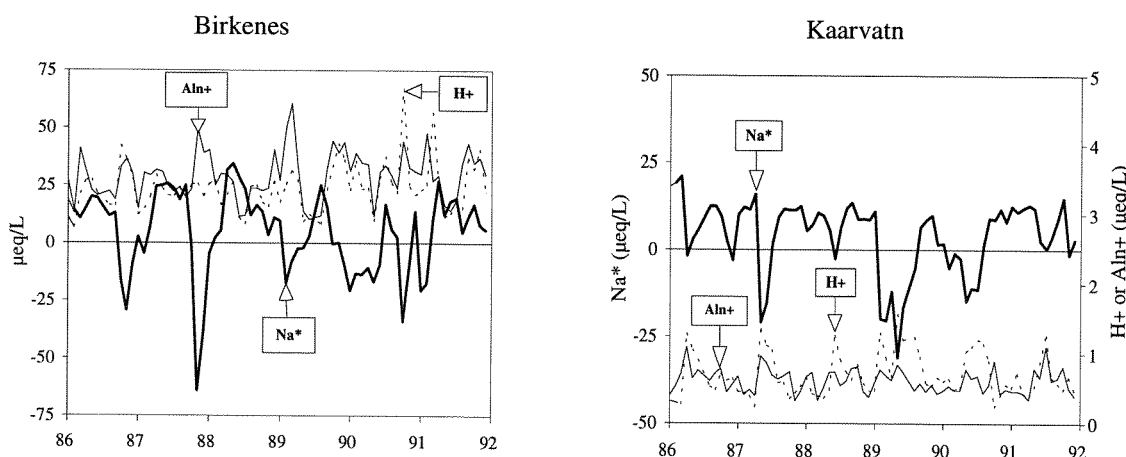


Figure 22 Monthly weighted average concentrations of non-marine sodium ( $\text{Na}^*$ ),  $\text{H}^+$  and  $\Sigma\text{Al}^{n+}$  in runoff water at Kaarvatn during 1986-1991.

\* The time of the year at which seasalt episodes occur is essential for the runoff chemistry at both Birkenes and Kaarvatn (Figure 22). Seasalt episodes during the winter do normally cause the most severe chemical conditions as far as  $\text{H}^+$  and aluminium are concerned. As described earlier, when low-pressures accompanied by strong winds and large amounts of precipitation enter the catchments as rain during the winter, the water is able to leave the catchments relatively fast as surface and subsurface discharge. This means that the water primarily flows through the uppermost soil layers, where sodium will cation exchange for aluminium and  $\text{H}^+$ . Of course this is also the case during seasalt episodes at autumn, but at that time of the year, often more water is able to penetrate deeper down into more inorganic soil layers. Much of the dissolved aluminium and  $\text{H}^+$ -ions from the cation-exchange reactions higher up in the soil, are therefore able to be retained in the catchment again by various neutralisation/ precipitation reactions.

\* If one of the main effects of global warming are warmer winters with stronger and more frequent seasalt episodes, it may have negative consequences for the surface water chemistry in acidified coast-near areas of southern Norway, primarily because of the elevated aluminium concentrations associated with such episodes.

## Total organic carbon in runoff

\* **The annual weighted concentration averages of total organic carbon (TOC) in runoff during the monitoring periods are:** Birkenes: 4.9 mg C/L; Storgama: 4.1 mg C/L; Langtjern: 8.8 mg C/L; and Kaarvatn: 1.0 mg C/L

\* On the basis of annual weighted concentration averages, organic ions ( $A^-$ ) constitute 35% of the anionic pool in runoff at the humic rich Langtjern site, while they constitute 10% or less at the other sites.

\* **The annual weighted averages of net charge [NC =  $(\Sigma\text{Cations} - \Sigma\text{Anions})/\text{TOC}$ ] of organic carbon ( $A^-$ ) are:** Birkenes: 5.5  $\mu\text{eq}/\text{mg C}$ ; Storgama: 3.7  $\mu\text{eq}/\text{mg C}$ ; Langtjern: 5.7  $\mu\text{eq}/\text{mg C}$ ; Kaarvatn: 4  $\mu\text{eq}/\text{mg C}$ .

\* No correlation was found between monthly average concentration of TOC and amount of runoff.

\* At Birkenes and Langtjern, the NC of organic compounds are decreasing significantly by increasing runoff pH. No corresponding significant trend was found at Storgama and Kaarvatn.

\* No correlation was found between NC of organic carbon and concentration of labile aluminium (LAL) or  $\Sigma\text{Al}^{n+}$  at any of the sites.

\* No correlation was found between NC of organic carbon and concentration of non-marine base cations  $\Sigma\text{Ca}^*, \text{Mg}^*$  at Birkenes, Storgama and Kaarvatn, while a positive correlation was found at Langtjern, the most precipitation-poor and TOC rich site.

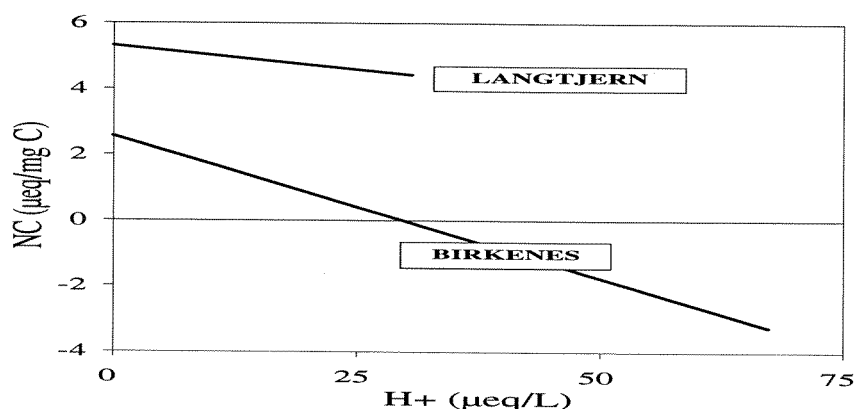


Figure 23 The relationships between concentration of  $H^+$  and NC ( $\mu\text{eq}$  of charges/ mg C) of organic compounds present in runoff water at Birkenes and Langtjern. The relationships rely on simple linear regression analyses by using monthly weighted means from 1986-1991. Birkenes:  $y = -0.086x + 2.56$  ( $r = -0.28$ ) ( $n = 70$ ); Langtjern:  $y = -0.029x + 5.31$  ( $r = -0.24$ ) ( $n = 72$ ). Positive NC-values mean net negative charges on organic carbon.

\* At all sites, a significant positive correlation was found between the concentration of non-marine sodium ( $\text{Na}^*$ ) and NC of organic carbon. This means that decreasing  $\text{Na}^*$  often indicates  $\text{Na}$  participating in cation-exchange reactions in the soil, so that the NC of organic carbon is getting less negative, or in extreme cases positive. Positive NC-values mean that the total charge on organic carbon is positive, i.e.  $\text{Al}^{3+} + [\text{R-COO}]^- = [\text{R-COOAl}]^{2+}$ . Positive NC-values are most frequently found at Birkenes and Kaarvatn, most often during the winter and spring-melt period, while positive NC-values are only observed no end then at Storgama. Positive NC-values are so far never recorded at Langtjern. Thus, positive NC-values primarily occur in coast-near, seasalt influenced areas, because of cation-exchange processes with sodium in the key role.

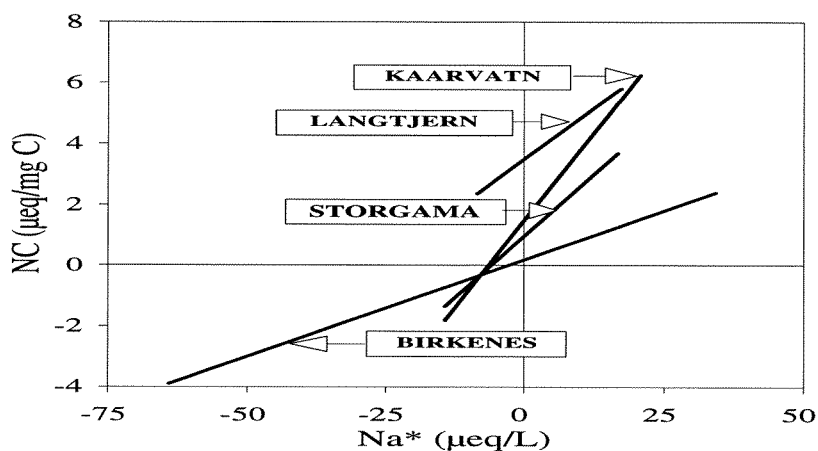


Figure 24 The relationship between concentration of non-marine sodium ( $\text{Na}^*$ ) and NC ( $\mu\text{eq}$  of charges/ mg C) of organic compounds present in runoff water at the four catchments. The relationships rely on simple linear regression analyses by using monthly weighted means from 1986-1991. Birkenes:  $y = 0.063x + 0.19$  ( $r = 0.35$ ) ( $n = 70$ ); Storgama:  $y = 0.161x + 0.96$  ( $r = 0.46$ ) ( $n = 68$ ); Langtjern:  $y = 0.133x + 3.48$  ( $r = 0.63$ ) ( $n = 72$ ) and Kaarvatn:  $y = -0.229x + 1.47$  ( $r = 0.30$ ) ( $n = 72$ ). Positive NC-value means net negative charges on organic carbon.

\* Changes in NC of organic carbon in runoff water are best related to the concentration of non-marine sodium ( $\text{Na}^*$ ) and  $\text{H}^+$  in runoff (Figure 25 and 26). There are several explanations to this:

1) Except for  $\text{NH}_4^+$ -ions, which are taken up by the vegetation relatively fast, the predominant cations in precipitation at all sites are  $\text{H}^+$ -ions and/or  $\text{Na}^+$ -ions. Because most of the organic compounds are present in the uppermost soil-horizons, the majority of rainwater has to pass these layers on its way to rivers and lakes. The  $\text{H}^+$ - and  $\text{Na}^+$ -ions may therefore very well be the most important cations for the quality of organic compounds. When water penetrates further down into more inorganic soil layers, or when water from these deeper layers is pressed up into the uppermost organic soil horizon, divalent base cations and aluminium may substitute for  $\text{H}^+$  and  $\text{Na}^+$ , but due to the lack of correlation between base-cation or aluminium and NC of organic carbon, these cation substitutions seem to play a minor role for the NC of organic substances.

2) Organic complexes with cationic aluminium and divalent base cations form stronger or more stable complexes compared with the corresponding complexes with  $\text{Na}^+$  and  $\text{H}^+$ . They will therefore be more or less unaffected by normal variation in the concentration of  $\text{H}^+$  and  $\text{Na}^+$ .

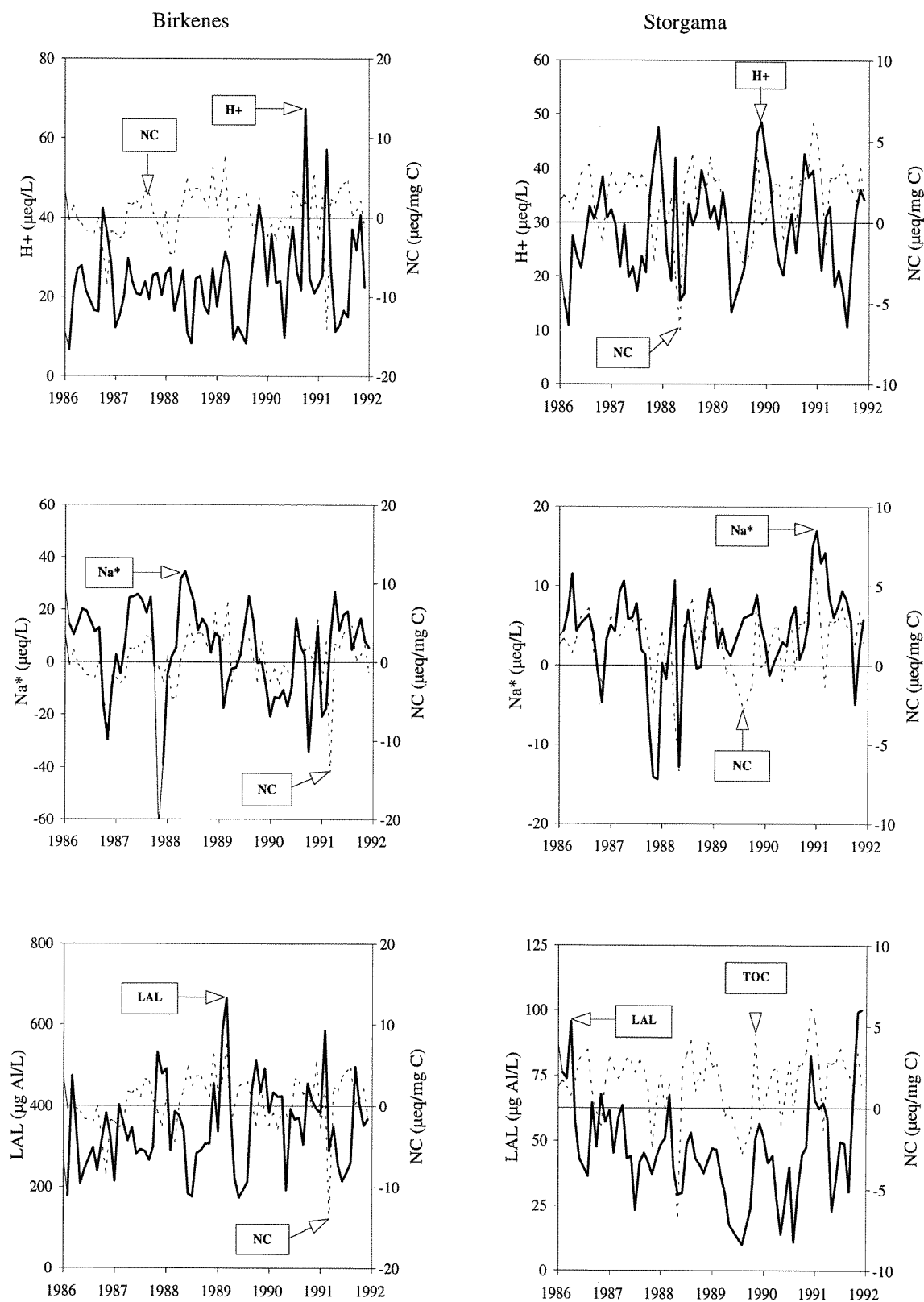


Figure 25 Monthly variations in the NC ( $\mu\text{eq}$  of charges/ $\text{mg C}$ ) of organic compounds and the concentration of  $\text{H}^+$ , non-marine sodium ( $\text{Na}^*$ ), and labile aluminium (LAL) at Birkenes and Storgama during 1986-1991. Positive NC-value means that the organic carbon are negatively charged and vice versa.

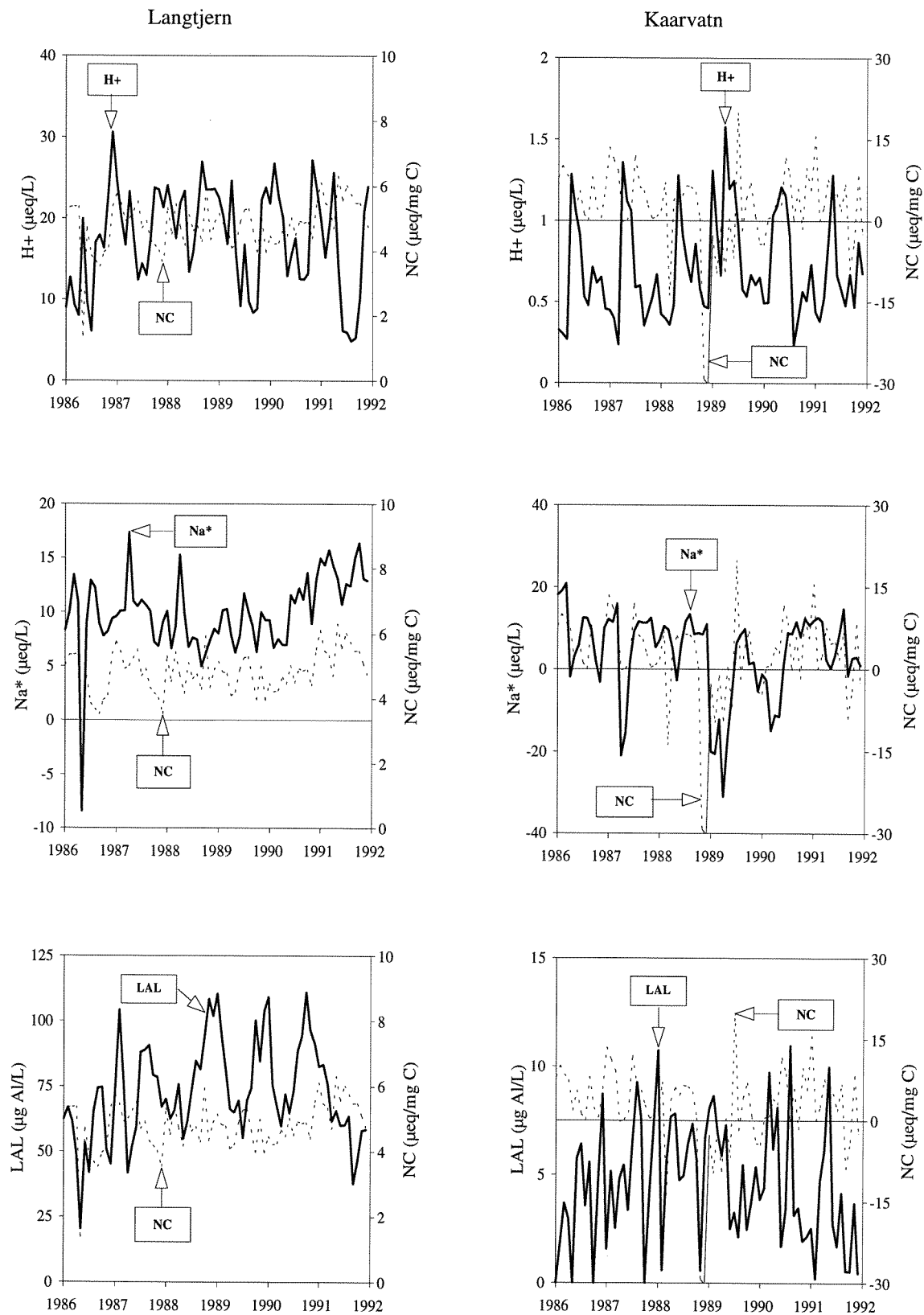


Figure 26 Monthly variations in the NC ( $\mu\text{eq}$  of charges/mg C) of organic compounds and the concentration of  $\text{H}^+$ , non-marine sodium ( $\text{Na}^*$ ), and labile aluminium (LAL) at Birkenes and Storgama during 1986-1991. Positive NC-value means that the organic carbon are negatively charged and vice versa.

3) Similar to the organic acids, aluminium itself acts as a pH-buffer, where H<sup>+</sup>-ions are taken up during dissolution or released during precipitation of Al. Thus, a pH change will affect both the average charge of organic acids and aluminium.

4) The negative correlation between NC of organic carbon and H<sup>+</sup> concentration at the two most TOC-rich sites, Langtjern and Birkenes, may indicate that humic acids to a certain degree are able to affect the runoff-water pH, when the concentration of TOC is relatively high.

## ANC in runoff

\* The acid neutralising capacity (ANC) can be defined as the ability of a solution or a catchment to neutralise inputs of strong acids. ANC can be estimated as the difference between base cations and strong acid anions in runoff water, i.e.:

$$\text{ANC} = [\text{Ca}^{2+}] + [\text{Mg}^{2+}] + [\text{Na}^{+}] + [\text{K}^{+}] - [\text{SO}_4^{2-}] + [\text{Cl}^{-}] + [\text{NO}_3^{-}]$$

Basically, ANC is a collective term for the concentration of organic anions (A<sup>-</sup>), alkalinity (as HCO<sub>3</sub><sup>-</sup>) in relation to the concentration of H<sup>+</sup>, and aluminium (ΣAl<sup>n+</sup>), i.e. ANC = ([A<sup>-</sup>] + [HCO<sub>3</sub><sup>-</sup>]) - ([H<sup>+</sup>] + [ΣAl<sup>n+</sup>]). In low organic carbon water, positive ANC-values normally means a bicarbonate-buffered system, like at Kaarvatn. Positive ANC-values are often present in high organic carbon waters too, despite the water-pH is < 5.0. This is primarily due to pH-buffering from weak organic acids, which means that the concentration of organic anions (A<sup>-</sup>) is high, like at Langtjern. When negative ANC-values occur, aluminium is able to enter into solution in relatively high inorganic concentrations, and pH is normally < 5.0, like at Birkenes and Storgama. High concentrations of aluminium may also be present in organic rich water (with positive ANC-values), but in these waters, aluminium is primarily present as aluminium-organic complexes. These Al-forms have no acute toxic effect on biota. In water with negative ANC-values, acute toxic inorganic Al-species predominate. The average charge of aluminium is estimated from the ALCHEMI-speciation programme, and Al-fractionation analyses have only been conducted since 1985/86.

\* **The monthly weighted ANC-averages** during 1986-1991 are: Birkenes: -49 ± 28 µeq/L; Storgama: -33 ± 14 µeq/L; Langtjern: 16 ± 10 µeq/L; and Kaarvatn: 22 ± 12 µeq/L.

\* All sites exhibit a significant positive correlation between the concentration of organic anions (A<sup>-</sup>) and ANC (Figure 27). This means that when the ANC is low, the concentration of negative charges is low. This should be expected, because most of the organic anions are weak acid anions, which act as a pH-buffers. During episodes with low ANC, pH and aluminium normally increases, which mean that more organic anions will complex with H<sup>+</sup> and cationic aluminium so that the concentration of A<sup>-</sup> will decrease.

\* All sites exhibit negative correlations between ANC and the concentration of aluminium (ΣAl<sup>n+</sup>) in runoff water, but at Langtjern the correlation is not significant (Figure 28). Due to high concentration of TOC in runoff water at Langtjern, ANC-variations tend to have minor influence on the aluminium chemistry. The most significant negative correlations between ANC and ΣAl<sup>n+</sup> were present at Storgama (r = -0.70) and Birkenes (r = -0.65)

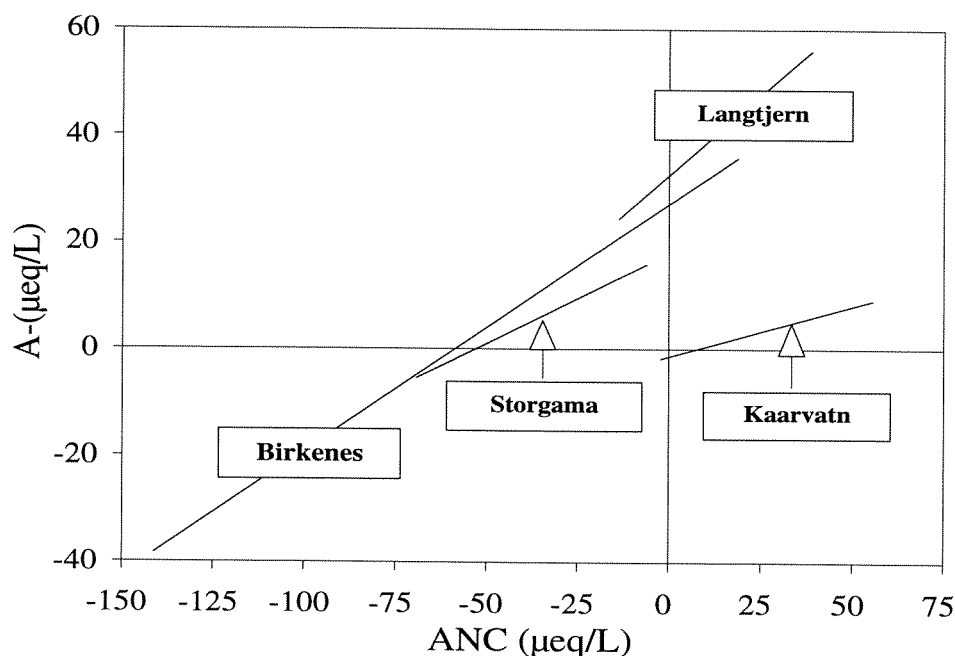


Figure 27 The relationships between acid neutralising capacity (ANC) and concentration of organic anions ( $A^-$ ), based on monthly weighted averages from 1986-1991. The correlations are based on linear regression analyses, and the correlations are assumed to be significant when  $p < 0.05$ . Continuous line means  $p < 0.05$ , dotted line means  $p > 0.05$ . The regression lines are: Birkenes:  $y = 0.46x + 27.1$  ( $r = 0.76$ ) ( $p < 0.01$ ); Storgama:  $y = 0.34x + 17.9$  ( $r = 0.56$ ) ( $p < 0.01$ ); Langtjern:  $y = 0.60x + 32.6$  ( $r = 0.69$ ) ( $p < 0.01$ ); Kaarvatn:  $y = 0.19x - 1.44$  ( $r = 0.33$ ) ( $p < 0.01$ ).

\* All catchments exhibit significant negative correlations between the concentration of chloride and ANC in runoff (Figure 28). Correspondingly there are significant positive correlations between ANC and the concentration of non-marine sodium ( $Na^*$ ) in runoff water at all sites (Figure 28). This means that when the  $Na^*$ -value is decreasing, more sodium is temporarily retained in the catchment due to cation-exchange, and more  $H^+$  and/or  $\Sigma Al^{n+}$  will be present in runoff water.

\* All catchments exhibit significant negative correlations between ANC and the concentration of  $H^+$  in runoff water (Figure 28).

\* Significant negative correlations were found between the monthly weighted concentration of non-marine sulphate ( $SO_4^*$ ) and ANC in runoff at Birkenes, Storgama and Langtjern, while a significant positive correlation was found at Kaarvatn. At Kaarvatn this is basically because of the significant negative correlation that exists between monthly runoff and monthly weighted concentrations of  $SO_4^*$ , which means that the highest concentration of  $SO_4^*$  normally is present at low runoff. Because  $SO_4^*$  primarily expresses the concentration of sulphuric acid, a long residence time of water within the catchment often leads to an increase in the acid neutralising capacity (ANC) of the catchment. This may also indicate that the sulphuric acid to some extent may act as a catalyst in weathering/dissolution reactions, particularly in the weakly acidified Kaarvatn catchment.

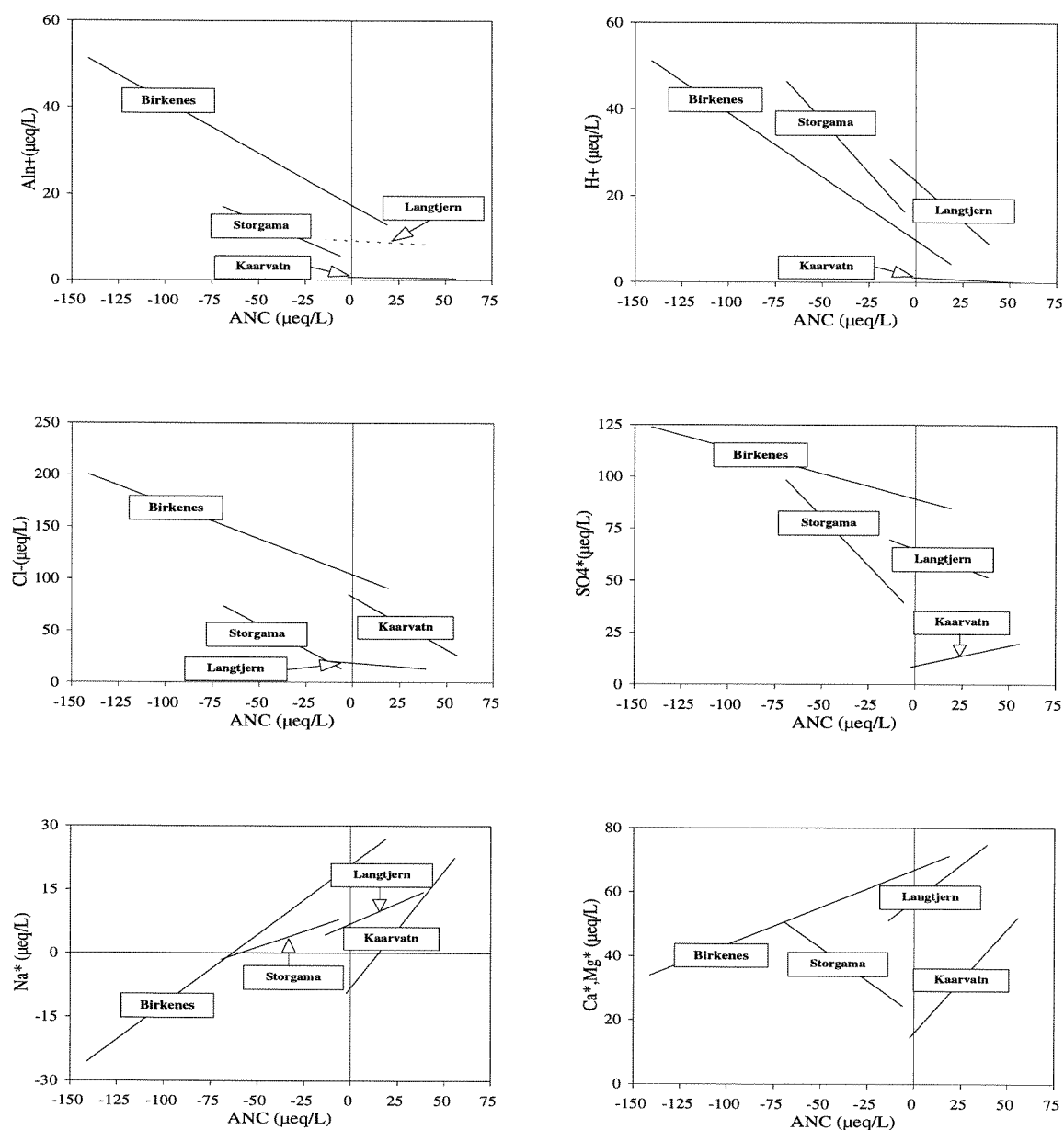


Figure 28 The relationships between acid neutralising capacity (ANC) and the concentration of aluminium ( $\Sigma Al^{n+}$ ), chloride ( $Cl^-$ ), non-marine sodium ( $Na^*$ ),  $H^+$ , non-marine sulphate ( $SO_4^*$ ) and non-marine base cations ( $\Sigma Ca^*, Mg^*$ ) in runoff water, based on monthly weighted averages from 1986-1991. The correlations are based on linear regression analyses, and the correlations are assumed to be significant when  $p < 0.05$ . Continuous line means  $p < 0.05$ , dotted line means  $p > 0.05$ . The regression lines are:  $\Sigma Al^{n+}$ : Birkenes:  $y = -0.24x + 17.4$  ( $r = -0.65$ ) ( $p < 0.01$ ); Storgama:  $y = -0.18x + 4.50$  ( $r = -0.70$ ) ( $p < 0.01$ ); Langtjern:  $y = -0.02x + 9.12$  ( $r = -0.13$ ) ( $p > 0.05$ ); Kaarvatn:  $y = -0.005x + 0.71$  ( $r = -0.32$ ) ( $p < 0.01$ ).  $Cl^-$ : Birkenes:  $y = -0.68x + 104.0$  ( $r = -0.48$ ) ( $p < 0.01$ ); Storgama:  $y = -0.96x + 7.71$  ( $r = -0.74$ ) ( $p < 0.01$ ); Langtjern:  $y = -0.14x + 18.9$  ( $r = -0.32$ ) ( $p < 0.01$ ); Kaarvatn:  $y = -1.01x + 82.5$  ( $r = -0.31$ ) ( $p < 0.01$ ).  $Na^*$ : Birkenes:  $y = 0.33x + 20.7$  ( $r = 0.52$ ) ( $p < 0.01$ ); Storgama:  $y = 0.15x + 8.89$  ( $r = 0.37$ ) ( $p < 0.01$ ); Langtjern:  $y = 0.19x + 6.89$  ( $r = 0.57$ ) ( $p < 0.01$ ); Kaarvatn:  $y = 0.55x - 8.31$  ( $r = 0.65$ ) ( $p < 0.01$ ).  $H^+$ : Birkenes:  $y = -0.29x + 9.73$  ( $r = -0.78$ ) ( $p < 0.01$ ); Storgama:  $y = -0.48x + 13.4$  ( $r = -0.78$ ) ( $p < 0.01$ ); Langtjern:  $y = -0.37x + 23.5$  ( $r = -0.62$ ) ( $p < 0.01$ ); Kaarvatn:  $y = -0.02x + 1.11$  ( $r = -0.71$ ) ( $p < 0.01$ ).  $SO_4^*$ : Birkenes:  $y = -0.25x + 89.3$  ( $r = -0.35$ ) ( $p < 0.01$ ); Storgama:  $y = -0.94x + 33.9$  ( $r = -0.75$ ) ( $p < 0.01$ ); Langtjern:  $y = -0.35x + 56.0$  ( $r = -0.31$ ) ( $p < 0.01$ ); Kaarvatn:  $y = 0.20x + 8.84$  ( $r = 0.43$ ) ( $p < 0.01$ ).  $\Sigma Ca^*, Mg^*$ : Birkenes:  $y = 0.23x + 66.8$  ( $r = 0.38$ ) ( $p < 0.01$ ); Storgama:  $y = -0.41x + 21.9$  ( $r = -0.51$ ) ( $p < 0.01$ ); Langtjern:  $y = 0.45x + 57.2$  ( $r = 0.41$ ) ( $p < 0.01$ ); Kaarvatn:  $y = 0.65x + 16.0$  ( $r = 0.66$ ) ( $p < 0.01$ ).



\* At Birkenes, Langtjern and Kaarvatn, significant positive correlations were found between monthly weighted ANC-values and monthly weighted concentrations of non-marine base cations, i.e.  $\Sigma\text{Ca}^*,\text{Mg}^*$  (Figure 28). This means that the ANC is high, as expected, the concentration of base cations is high. At Storgama, however, a corresponding significant negative correlation was found. As for the other sites, a very significant positive correlation was found between the concentration of non-marine sulphate ( $\text{SO}_4^*$ ) and  $\Sigma\text{Ca}^*,\text{Mg}^*$  in runoff water at Storgama, but opposite to the other sites, a significant positive correlation was found between the concentrations of  $\Sigma\text{Ca}^*,\text{Mg}^*$  and  $\text{H}^+$ . This means that when the concentration of acid neutralising compounds as  $\text{Ca}^*$  and  $\text{Mg}^*$  are increasing in runoff water at Storgama, a simultaneous and paradoxical increase of  $\text{H}^+$  occurs. The most likely reason for the positive correlation between the concentration of  $\text{H}^+$  and  $\Sigma\text{Ca}^*,\text{Mg}^*$  is that sulphide-oxidation takes place within the catchment during drought-periods. Since the ANC of the catchment is low, both  $\text{H}^+$  and  $\Sigma\text{Ca}^*,\text{Mg}^*$  are thus able to increase simultaneously. The source of the sulphide being oxidised, is most likely sulphate from the atmosphere which previously has been reduced to sulphides.

\* Variations in the concentration of  $\text{H}^+$  and organic anions ( $\text{A}^-$ ) cause the most statistical significant changes in ANC of runoff at Birkenes and Langtjern. At Storgama the variations in the concentration of  $\text{H}^+$  and  $\text{SO}_4^*$  are the most significant causes for ANC variations, while at Kaarvatn it is the variations in the concentrations of  $\text{H}^+$  and alkalinity ( $\text{HCO}_3^-$ ) which exhibit the strongest correlations with ANC.

\* All sites exhibit a decrease in ANC by increasing runoff, largest decrease at Birkenes, followed by Kaarvatn, Storgama and Langtjern. By assuming the concentration of  $\text{H}^+$  and aluminium being the most biological harmful compounds in runoff-water at the for sites, the most severe consequences of increasing runoff will occur at Birkenes, followed by Storgama, Langtjern, and Kaarvatn. At Kaarvatn, the water quality is still relatively good even at high flow, which means that negative ANC-values seldom occur at Kaarvatn.

## Aluminium

\* Three aluminium-fractions have been measured back to 1985/86, i.e. total reactive Al (RAL), labile Al (LAL) and non-labile Al (ILAL), while RAL has been monitored from the very beginning of the monitoring. RAL is the sum of LAL and ILAL, and the acute toxic Al-species are primarily present in the LAL-fraction.

\* To obtain high concentration of aluminium in runoff water, the acid neutralising capacity (ANC) has to be negative (as in Birkenes and Storgama), otherwise, high amounts of dissolved organic carbon must be present, as in the Langtjern catchment.

\* At Birkenes, the monthly weighted mean concentration of total reactive aluminium (RAL) is  $454 \pm 34 \mu\text{g Al/L}$ , and on average 78% of RAL is present as LAL. Monthly weighted average charge of aluminium ( $\Sigma\text{Al}^{n+}$ ) at Birkenes is  $29.6 \pm 1.4 \mu\text{eq/L}$ . The average charge of each Al-ion is calculated to be +1.80.

\* At Storgama, the monthly weighted mean concentration of RAL is  $164 \pm 8 \mu\text{g Al/L}$ , and on average 70% of RAL is present as LAL. The total average charge of aluminium ( $\Sigma\text{Al}^{n+}$ ) at

Storgama is  $10.6 \pm 0.4 \mu\text{eq/L}$ . The average charge of each Al-ion is calculated to be +1.76.

\* At Langtjern, the monthly weighted mean concentration of RAL at Langtjern is  $175 \pm 9 \mu\text{g Al/L}$ , and on average 42% of RAL is present as LAL. The total average charge of aluminium ( $\Sigma\text{Al}^{n+}$ ) at Langtjern is  $8.9 \pm 0.5 \mu\text{eq/L}$ . The average charge of each Al-ion is calculated to be +1.39.

\* At Kaarvatn, the high ANC in runoff means that only minor amounts of aluminium are able to leak out into the surface water. Thus, the monthly weighted mean concentration of RAL is low ( $18.2 \pm 0.7 \mu\text{g Al/L}$ ) and on average only 25% of RAL is present as LAL. The total average charge of aluminium ( $\Sigma\text{Al}^{n+}$ ) at Kaarvatn is  $0.62 \pm 0.03 \mu\text{eq/L}$ , which gives an calculated average charge of each Al-ion of +0.90.

\* Based on the ALCHEMI-speciation programme (Table 7), the predominant inorganic dissolved aluminium-species at Birkenes are:  $\text{Al}^{3+} > \text{AlF}^{2+} > \text{AlH}_3\text{SiO}_4^{2+}$ , while the corresponding order of predominance at Storgama and Langtjern is:  $\text{AlF}^{2+} > \text{Al}^{3+} > \text{AlF}_2^+$ . At Kaarvatn the concentrations of dissolved inorganic Al-species in general are very low

\* At Birkenes, the highest concentration of LAL normally occurs during autumn and early spring, while the highest concentration of ILAL, i.e. predominantly the organic Al-forms, occurs during August (Figure 29). At Storgama, the concentration of LAL is more or less continuously increasing from May to December. At December the maximum values normally occur, but LAL remains high until next spring melt. The concentration of ILAL does not exhibit large seasonal fluctuation, but the highest concentration normally occurs during autumn and winter. At Langtjern, the concentrations of both LAL and ILAL are more or less continuously increasing from May until maximum occur once during the winter and remain relatively high until spring melt. During spring melt the concentrations both LAL and ILAL are at the lowest. At Kaarvatn, the concentrations of both LAL and ILAL are normally at the highest during April and August, but the total concentration of aluminium during these months is only somewhat higher than  $20 \mu\text{g Al/L}$

\* At all sites, there are several significant chemical relations with the concentration of aluminium, i.e. ILAL, LAL and RAL ( $\text{RAL} = \text{ILAL} + \text{LAL}$ ). On the basis of monthly weighted averages, the three most significant factors for the concentration of LAL at the coast-near Birkenes catchment are the concentration of  $\text{Cl}^- > \text{Na}^* > \text{H}^+$ , positive correlation concerning  $\text{Cl}^-$  and  $\text{H}^+$  and negative for  $\text{Na}^*$ . Correspondingly at Kaarvatn, the other coast-near catchment, the concentrations of  $\text{Cl}^-$  and  $\text{Na}^*$  are the most important factors for the concentration of labile aluminium. At both Birkenes and Kaarvatn, no significant correlations were found between monthly weighted concentration of  $\text{SO}_4^*$  and LAL, which indicates that short-term changes in the concentration of sulphate have minor influence on the short-term or periodical changes in concentration of LAL. However, as mentioned earlier, the concentration of  $\text{SO}_4^*$  is undoubtedly decisive for the level of aluminium present in runoff water, but in coast-near areas, seasalt-episodes seem to be most important for the fluctuation of LAL.

\* At Storgama the most significant correlations were found between the monthly weighted concentration of LAL and the concentrations of  $\text{SO}_4^*$  and  $\Sigma\text{Ca}^*, \text{Mg}^*$ , with chloride as the third most significant. That positive correlations were found between LAL and both  $\text{SO}_4^*$  and  $\Sigma\text{Ca}^*, \text{Mg}^*$ , must be due to sulphide oxidation in the catchment. Also in the runoff water at Storgama, a high positive correlation was found between the concentration of  $\text{Cl}^-$  and LAL,

which indicates that seasalt episodes may play an important role even for the aluminium chemistry at Storgama. The negative correlation between  $\text{Na}^*$  and LAL at both Birkenes and Kaarvatn, is however, not present at Storgama. This may rely on the highly significant and positive base cation ( $\Sigma\text{Ca}^*, \text{Mg}^*$ )/aluminium correlation present at Storgama, which probably means that the concentration  $\text{Na}^*$  also increases during sulphide oxidation. Thus, in the soil-poor, draught sensitive Storgama catchment, sulphide oxidation processes within the catchment often seem to overshadow the seasalt-effect. As described earlier, the major seasalt effect is that sodium from precipitation is retained in the catchment due to cation-exchange, so that the calculated concentration of  $\text{Na}^*$  is decreasing or often reaches negative values.

\* At Langtjern, variations in runoff and changes in the concentration of organic carbon are the most significant factors for the concentrations of LAL. This means that at Langtjern, the organic chemistry is decisive for the aluminium chemistry. The negative correlation between monthly runoff and monthly weighted concentration of LAL at Langtjern, means that the concentration of LAL is decreasing by increasing runoff. There is no significant correlation between the monthly weighted concentration of TOC and runoff, but on the other hand, it is a weak but significant negative correlation between runoff and charge density of organic carbon. Since the amounts of negative charges on organic complexes are decreasing by increasing runoff, it means that qualitatively changes in TOC occur, despite no significant change in the concentration of TOC.

*Table 8 Monthly mean concentrations of measured Al-species (RAL, ILAL, and LAL) and estimated concentrations of inorganic and organic Al-species and fractions in runoff water from the four catchments, based on the ALCHEMI-speciation programme. Silicon and fluoride are not measured, but estimated to be 2 mg  $\text{SiO}_2/\text{L}$  and 100  $\mu\text{g F}/\text{L}$ . The mean values are based on monthly weighted averages from 1986-1991. The organic Al-fractions are based on a triprotic acid with the dissociation constants:  $pK_1 = 6.86$ ;  $pK_2 = 12.8$ ;  $pK_3 = 14.9$ , and complex-constants:  $\text{Al}^{3+} + \text{A}^{3-} = \text{Al}(\text{A})$  ( $pK = 8.38$ ) and  $\text{Al}^{3+} + \text{HA}^{2-} = \text{Al}(\text{HA})^+$  ( $pK = 13.1$ ). The constants are identical with those present in the ALCHEMI-version 4.0.*

<i>Al-species</i>	<i>unit</i>	<b>Birkenes</b>	<b>Storgama</b>	<b>Langtjern</b>	<b>Kaarvatn</b>
RAL	$\mu\text{g Al}/\text{L}$	$454 \pm 34$	$164 \pm 8$	$175 \pm 9$	$18.2 \pm 0.7$
ILAL	"	$100 \pm 34$	$48 \pm 11$	$103 \pm 15$	$13.6 \pm 1.4$
LAL	"	$354 \pm 22$	$116 \pm 7$	$73 \pm 11$	$4.6 \pm 1.1$
$\Sigma\text{Al}^{n+}$ (tot.)	$\mu\text{eq}/\text{L}$	$29.6 \pm 1.4$	$10.6 \pm 0.4$	$8.9 \pm 0.5$	$0.62 \pm 0.03$
$\text{Al}^{3+}$	$\mu\text{eq}/\text{L}$	$13.6 \pm 1.1$	$2.5 \pm 0.2$	$1.25 \pm 0.2$	
$\text{Al}(\text{OH})^{2+}$	"	$0.9 \pm 0.1$	$0.11 \pm 0.01$	$0.11 \pm 0.01$	$0.01 \pm 0.001$
$\text{Al}(\text{OH})_2^+$	"				$0.03 \pm 0.01$
$\text{AlF}^{2+}$	"	$7.9 \pm 0.3$	$5.7 \pm 0.1$	$4.7 \pm 0.4$	$0.11 \pm 0.01$
$\text{AlF}_2^+$	"		$0.7 \pm 0.01$	$0.8 \pm 0.02$	$0.12 \pm 0.01$
$\text{AlOHF}^+$	"	$0.7 \pm 0.1$	$0.4 \pm 0.03$	$0.6 \pm 0.05$	$0.29 \pm 0.02$
$\text{AlSO}_4^+$	"	$0.2 \pm 0.02$			
$\text{AlH}_3\text{SiO}_4^{2+}$	"	$3.6 \pm 0.2$	$0.6 \pm 0.06$	$0.5 \pm 0.03$	$0.04 \pm 0.002$
$\Sigma\text{Al}^{n+}$ (inorg.)	"	$27.0 \pm 1.2$	$10.0 \pm 0.3$	$7.9 \pm 0.5$	$0.6 \pm 0.02$
$\text{Al}(\text{organic})^0$	$\mu\text{mol}/\text{L}$	$2.2 \pm 0.5$	$0.35 \pm 0.10$	$1.1 \pm 0.22$	$0.09 \pm 0.02$
$\text{Al}(\text{H-organic})^+$	"	$2.7 \pm 0.6$	$0.55 \pm 0.13$	$1.0 \pm 0.11$	$0.004 \pm 0.001$
$\Sigma\text{Al}^{n+}$ (org.)	$\mu\text{eq}/\text{L}$	$2.7 \pm 0.6$	$0.55 \pm 0.13$	$1.0 \pm 0.11$	$0.004 \pm 0.001$

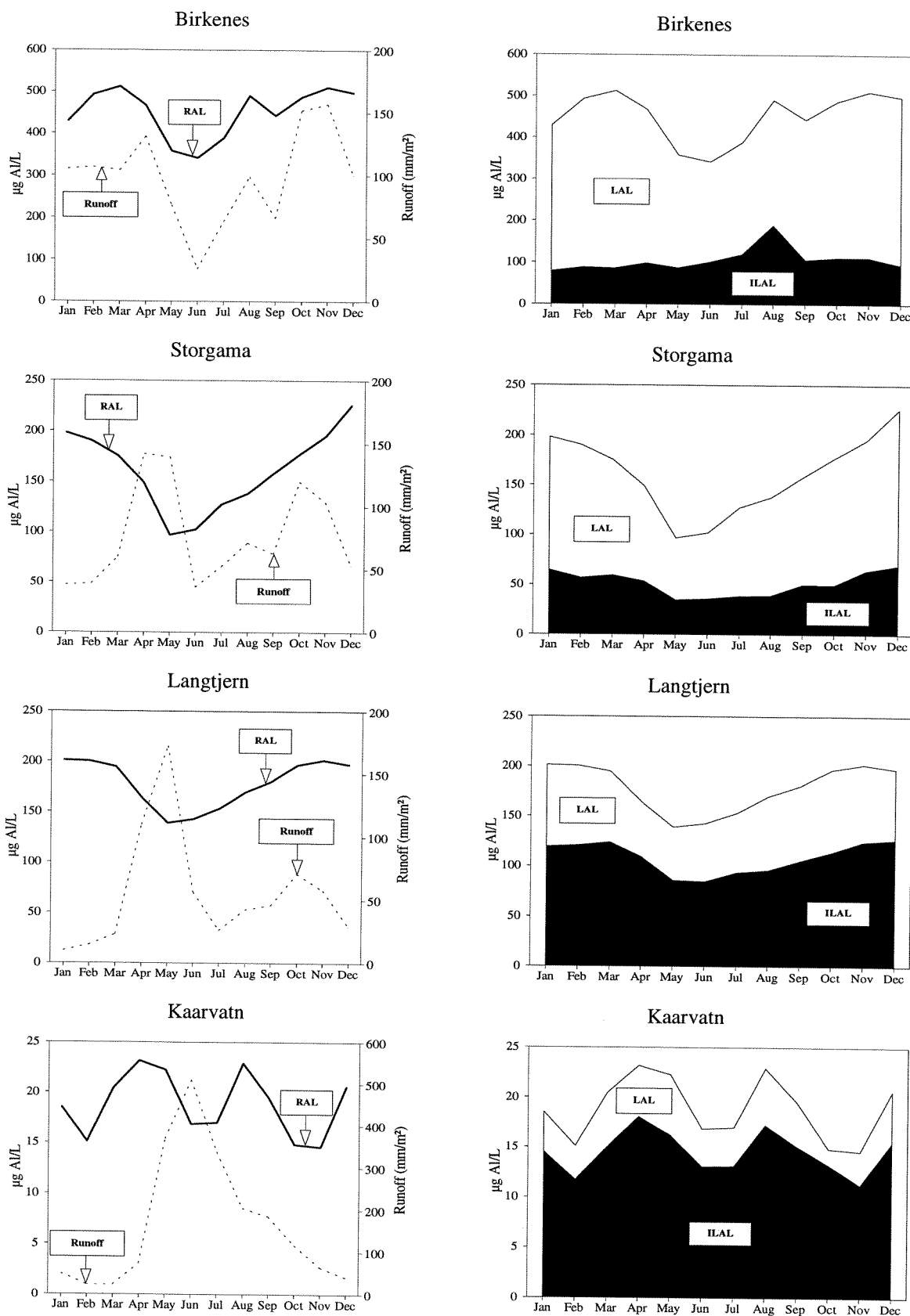


Figure 29 Monthly runoff-means and monthly mean concentrations of reactive aluminium (RAL), non-labile (ILAL) and labile (LAL) aluminium at the four catchments, based on monthly weighted averages from 1986-1991. RAL = LAL + ILAL

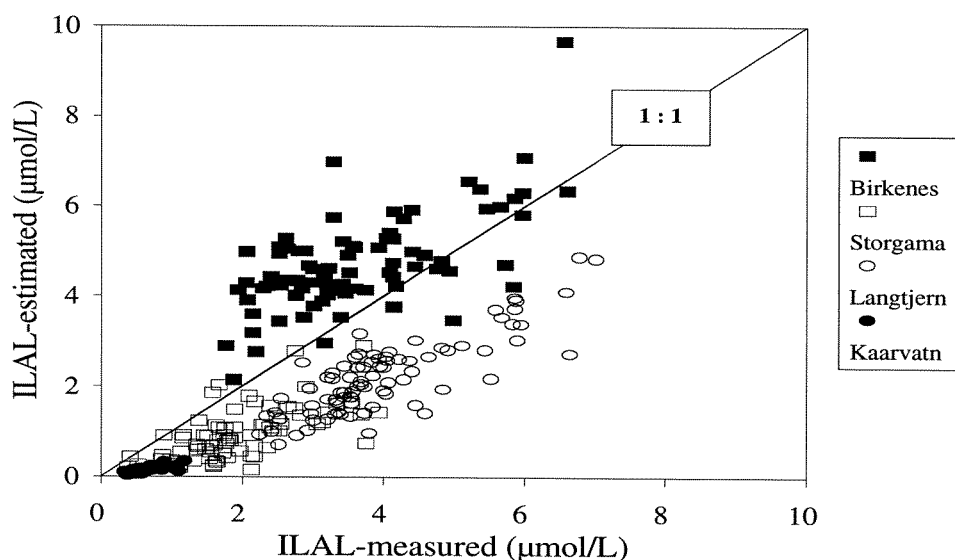


Figure 30 The relationship between measured and calculated (by the ALCHEMI-speciation programme) concentration of non-labile aluminium (LAL) at the four catchments, based on monthly weighted averages during 1986-1991. Birkenes:  $y = (1.11 \pm 0.03)x$  ( $r = 0.79$ ); Storgama:  $y = (0.48 \pm 0.02)x$  ( $r = 0.64$ ); Langtjern:  $y = (0.56 \pm 0.01)x$  ( $r = 0.82$ ); Kaarvatn:  $y = (0.20 \pm 0.007)x$  ( $r = 0.80$ ).

\* The lower organic complexing-constants for aluminium that seems to be present at Birkenes compared with the other sites (see Figure 30) is an important observation, because qualitative changes in the functional-groups of organic substances seem to occur during acidification, i.e. a decrease in the carboxylic-acidity and an increase in phenolic acidity by acidification. Thus, the lowest organic Al-complexing-constants should be expected at Birkenes, because the complexing strength of phenolic-groups normally are weaker compared with carboxylic-groups. In addition, it has been shown that the molecular weight of dissolved organic carbon seems to increase by declining pH. This may also lead to a reduction in the complexing capacity, because the concentration of negative sites/mg C most likely will decrease when the organic complexes are increasing in size.

## Time trends

\* The time trends are based on simple linear regression analysis by use of monthly (concentrations) or annual (fluxes) weighted average data from the beginning of the monitoring and up to January 1993.

## Dry deposition

Time trends of dry-deposition are estimated at Birkenes and Kaarvatn, because dry-deposition measurements are only conducted at these sites.

### *Sulphur*

\* On the basis of the regression line (Figure 31), the monthly weighted concentrations of SO<sub>2</sub>-gas and SO<sub>4</sub>-particles in air at Birkenes have decreased by 81% and 53% during the period 1978-1992. The concentration of ΣSO<sub>2</sub>,SO<sub>4</sub> has decreased by 67% from a monthly weighted concentration average of 2.63 µg S/m<sup>3</sup> at the beginning of 1978 to 0.86 µg S/m<sup>3</sup> at the end of 1992.

\* On the basis of the regression line (Figure 32), the monthly weighted fluxes of SO<sub>2</sub>-gas and SO<sub>4</sub>-particles in air at Birkenes have decreased by 60% and 48% during the period 1978-1992. The flux of ΣSO<sub>2</sub>,SO<sub>4</sub> has decreased by 57% from a monthly weighted flux average of 22.8 mg S/m<sup>2</sup> at the beginning of 1978 to 9.76 mg S/m<sup>2</sup> at the end of 1992.

\* On the basis of the regression line (Figure 31), the monthly weighted concentrations of SO<sub>2</sub>-gas and SO<sub>4</sub>-particles in air at Kaarvatn have decreased by 81% and 49% during the period 1980-1992. The concentration of ΣSO<sub>2</sub>,SO<sub>4</sub> has decreased by 64% from a monthly weighted concentration average of 1.05 µg S/m<sup>3</sup> at the beginning of 1980 to 0.38 µg S/m<sup>3</sup> at the end of 1992.

\* On the basis of the regression line (Figure 32), the monthly weighted fluxes of SO<sub>2</sub>-gas and SO<sub>4</sub>-particles in air at Kaarvatn have decreased by 69% and 46% during the period 1980-1992. The flux of ΣSO<sub>2</sub>,SO<sub>4</sub> has decreased by 54% from a monthly weighted concentration average of 9.22 mg S/m<sup>2</sup> at the beginning of 1980 to 4.24 mg S/m<sup>2</sup> at the end of 1992.

\* The percentage declines of sulphur in dry-deposition are very similar at the two sites. Thus, even at Kaarvatn which is considered to be almost protected against anthropogenic sulphur deposition, a significant respond was found, well related to the decline in sulphur emission in Europe from the end of the 70-thies.

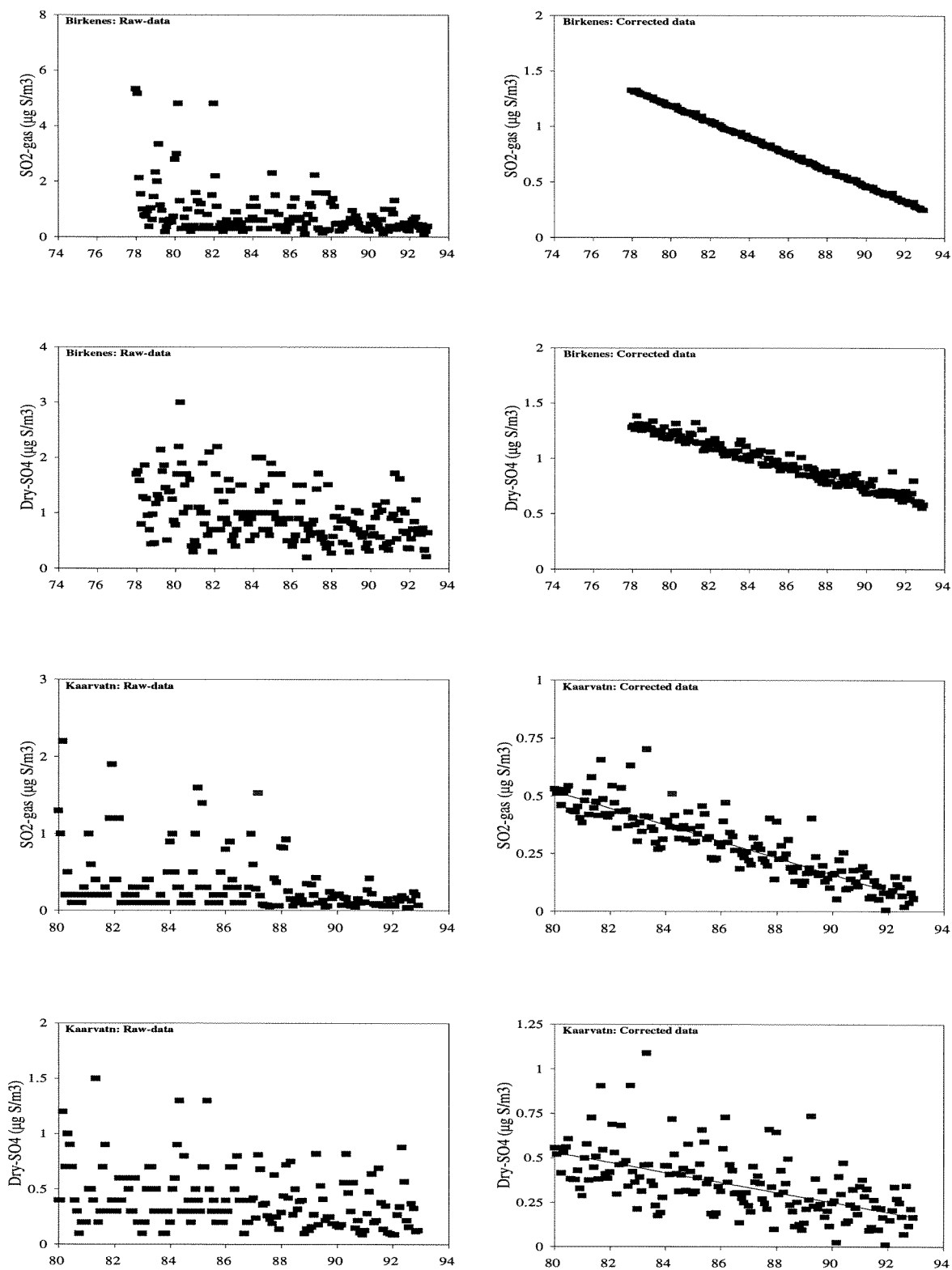


Figure 31 The monthly weighted concentration of SO<sub>2</sub>-gas and SO<sub>4</sub>-particles in air (µg S/m<sup>3</sup>) at Birkenes (1978-1992) and Kaarvatn (1980-1992), present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualises the influence of water on the concentration of each chemical compound, i.e. large scattering means high water dependence and vice versa. Continuous line means that the linear regression is significant, i.e.  $p < 0.05$ , while a dotted line means no significance,  $p > 0.05$ .

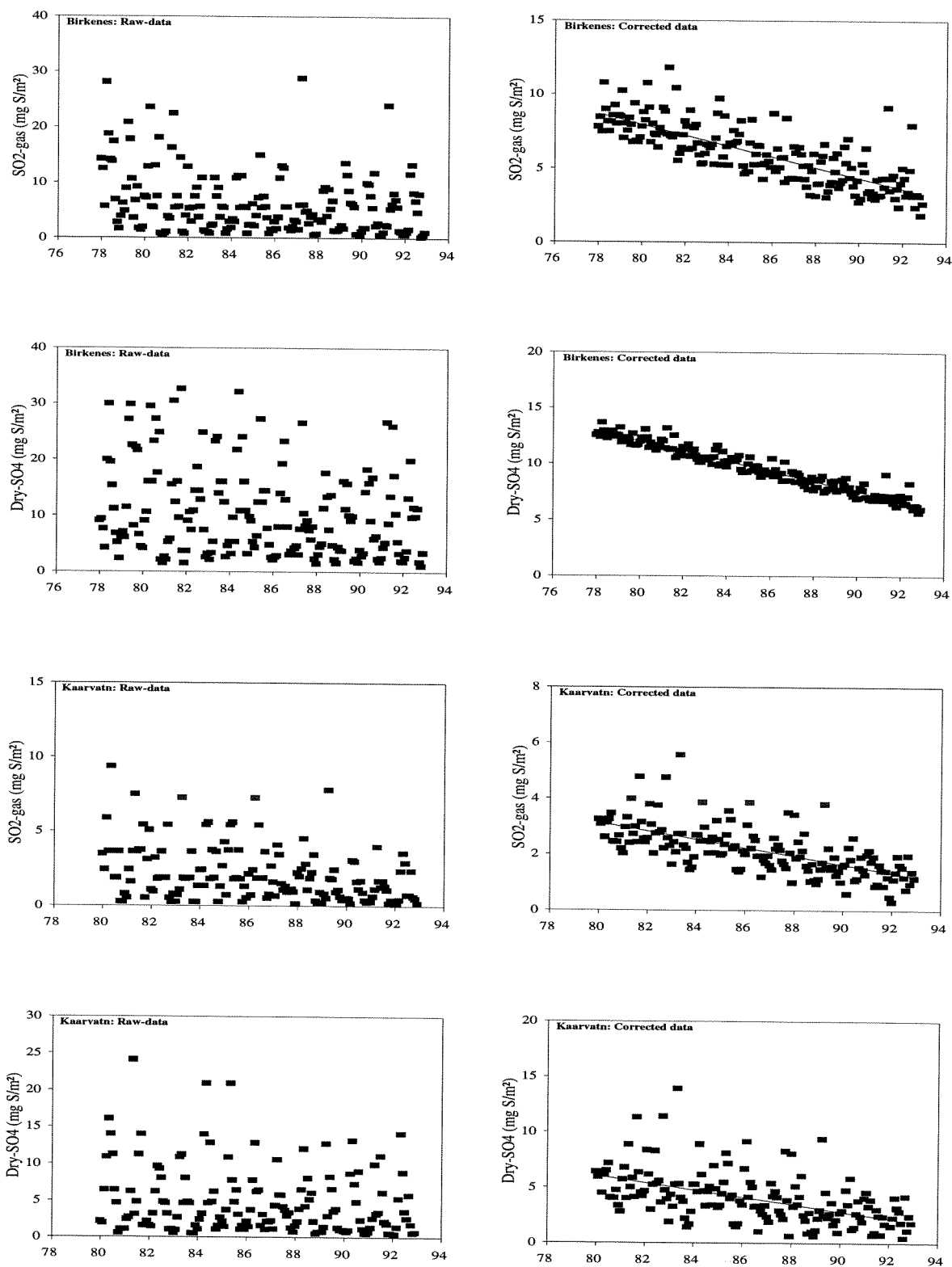


Figure 32 The monthly weighted influxes of  $\text{SO}_2$ -gas and  $\text{SO}_4$ -particles in air ( $\text{mg S/m}^2$ ) at Birkenes (1978-1992) and Kaarvatn (1980-1992), present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualises the influence of water on the concentration of each chemical compound, i.e. large scattering means high water dependence and vice versa. Continuous line means that the linear regression is significant, i.e.  $p < 0.05$ , while a dotted line means no significance,  $p > 0.05$ .



## *Nitrogen*

\* The major compounds of nitrogen in dry-deposition are NO<sub>2</sub>-gas and NH<sub>4</sub>-particles. At Birkenes dry-deposition of nitrogen has been monitored since 1986, while at Kaarvatn back to 1988.

\* On the basis of the regression line (Figure 33), the monthly weighted concentrations of NO<sub>2</sub>-gas and NH<sub>4</sub>-particles in air at Birkenes have decreased by 40% and 6% during the period 1986-1992. The decrease in NH<sub>4</sub> is, however, far from significant. The concentration of total nitrogen in dry-deposition ( $\Sigma$ NO<sub>2</sub>,HNO<sub>3</sub>,NO<sub>3</sub>,NH<sub>3</sub>,NH<sub>4</sub>) has decreased by 30% from a monthly weighted concentration average of 2.32 µg N/m<sup>3</sup> at the beginning of 1986 to 1.63 µg N/m<sup>3</sup> at the end of 1992.

\* On the basis of the regression line, (Figure 34), there are no significant declines in the fluxes of any nitrogen compounds at Birkenes, but tendencies of decreasing NO<sub>2</sub>-gas flux and increasing flux of NH<sub>4</sub>-particles are present.

\* On the basis of the regression line (Figure 33), the monthly weighted concentrations of NO<sub>2</sub>-gas and NH<sub>4</sub>-particle in air at Kaarvatn have decreased by 75% and 18% during the period 1988-1992. As at Birkenes, the decrease in NH<sub>4</sub> is far from significant. The concentration of total nitrogen in dry-deposition ( $\Sigma$ NO<sub>2</sub>,HNO<sub>3</sub>,NO<sub>3</sub>,NH<sub>3</sub>,NH<sub>4</sub>) has decreased by 49% from a monthly weighted concentration average of 1.08 µg N/m<sup>3</sup> at the beginning of 1988 to 0.55 µg N/m<sup>3</sup> at the end of 1992.

\* On the basis of the regression line (Figure 34), it has been a significant decline in the influx of NO<sub>2</sub>-gas at Kaarvatn by 74%, from a monthly average of 4.34 ± 2.54 mg N/m<sup>2</sup> at the beginning of 1988 to 1.12 ± 1.15 mg N/m<sup>2</sup> at the end of 1992. A very weak (not significant) decline in the influx of NH<sub>4</sub>-particles is also found during the same period.

\* While a significant decline was found in the concentration of NO<sub>2</sub>-gas at both Birkenes and Kaarvatn, most significant at Kaarvatn, the concentrations of NH<sub>4</sub>-particles have been approximately constant during the same periods, i.e. from 1986 at Birkenes and from 1988 at Kaarvatn. Concerning the fluxes of N in dry-deposition, it is only the decrease in influx of NO<sub>2</sub> at Kaarvatn that has been significant during the period 1988-1992.

\* At the end of 1992, the concentrations and fluxes of nitrogen in dry-deposition are generally higher than the corresponding concentration of sulphur at both Birkenes and Kaarvatn.

\* The monthly weighted concentrations of SO<sub>2</sub>-gas and SO<sub>4</sub>-particles in air are relatively unaffected by variation in precipitation at Birkenes. At Kaarvatn, however, the concentration of SO<sub>4</sub>-particles in air is highly influence by the amount of precipitation. This confirms that the input of SO<sub>4</sub>-particles at Kaarvatn to large extent derives from sea spray and not from anthropogenic sources. The negative correlation between monthly weighted concentration of SO<sub>4</sub>-particles in air and monthly amount of precipitation, means that the highest concentration of SO<sub>4</sub>-particles occurs during precipitation poor-periods. During such periods, the SO<sub>4</sub>-particles being transported up in the air by sea-waves and winds are less able to be removed from the air by precipitation as wet-deposition.

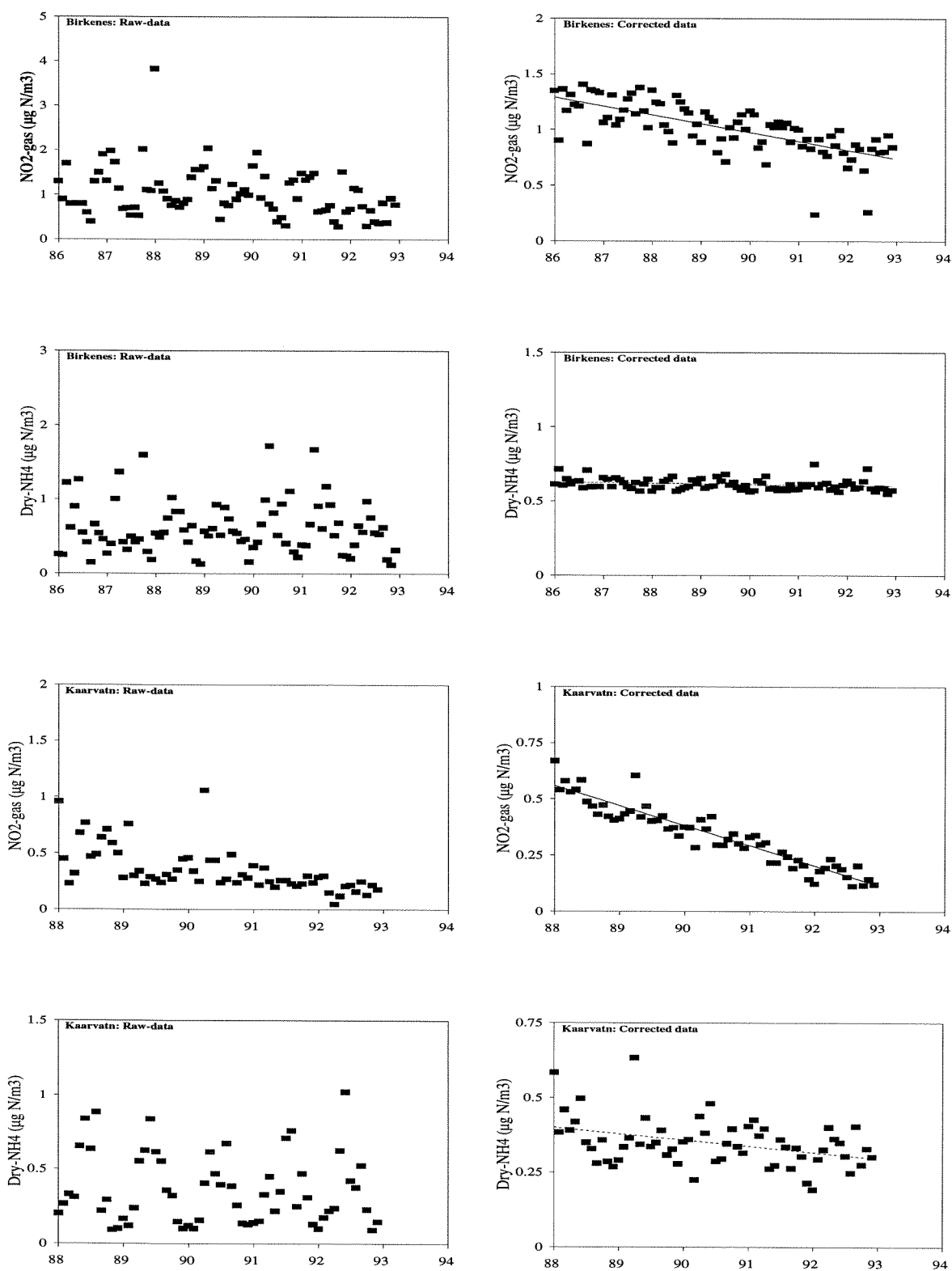


Figure 33 The monthly weighted concentration of NO<sub>2</sub>-gas and NH<sub>4</sub>-particles in air (µg S/m<sup>3</sup>) at Birkenes (1986-1992) and Kaarvatn (1988-1992), present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualises the influence of water on the concentration of each chemical compound, i.e. large scattering means high water dependence and vice versa. Continuous line means that the linear regression is significant, i.e.  $p < 0.05$ , while a dotted line means no significance,  $p > 0.05$ .

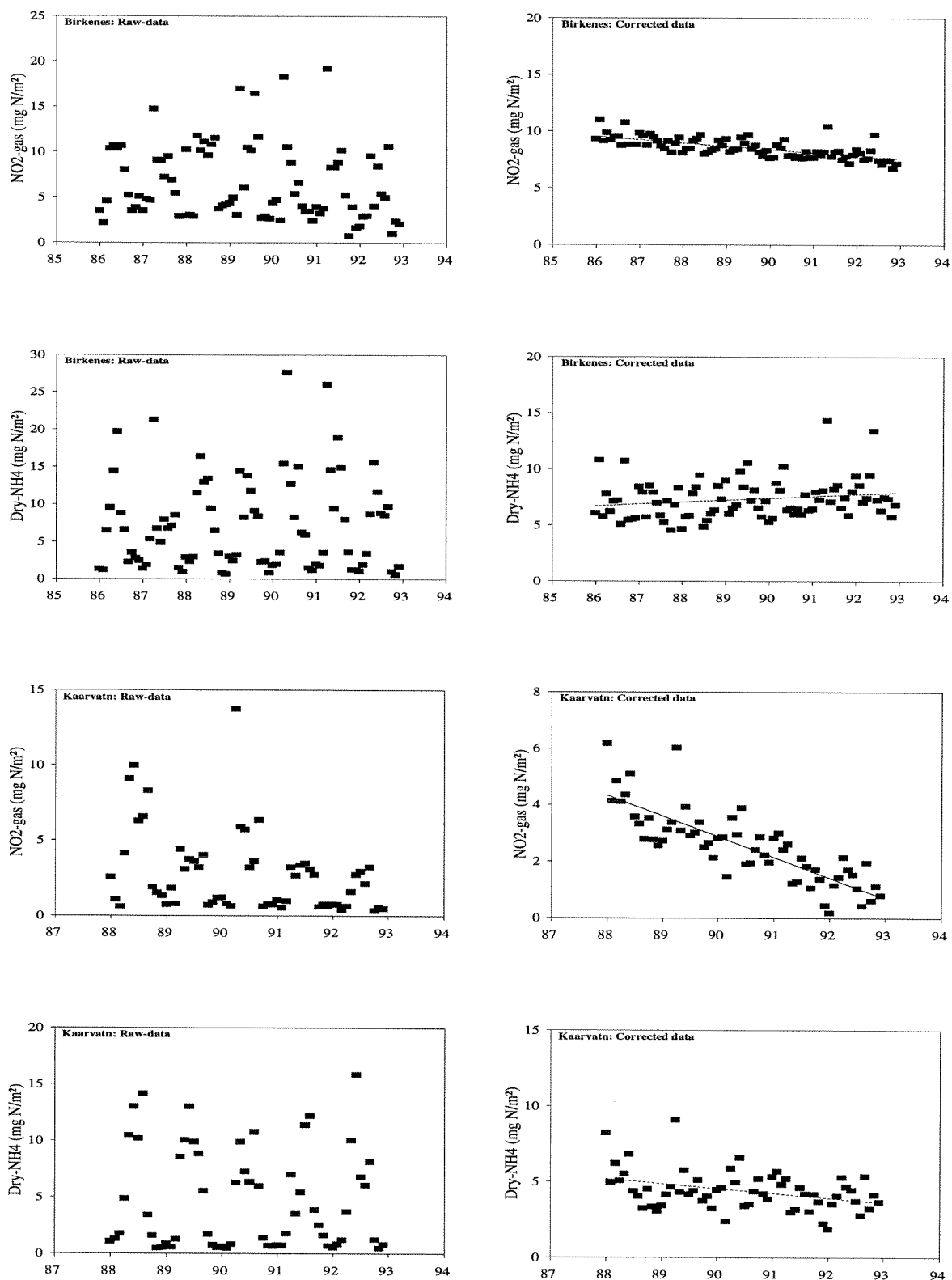


Figure 34 The monthly weighted influxes of NO<sub>2</sub>-gas and NH<sub>4</sub>-particles in air (mg N/m<sup>2</sup>) at Birkenes (1986-1992) and Kaarvatn (1988-1992), present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualises the influence of water on the concentration of each chemical compound, i.e. large scattering means high water dependence and vice versa. Continuous line means that the linear regression is significant, i.e.  $p < 0.05$ , while a dotted line means no significance,  $p > 0.05$ .

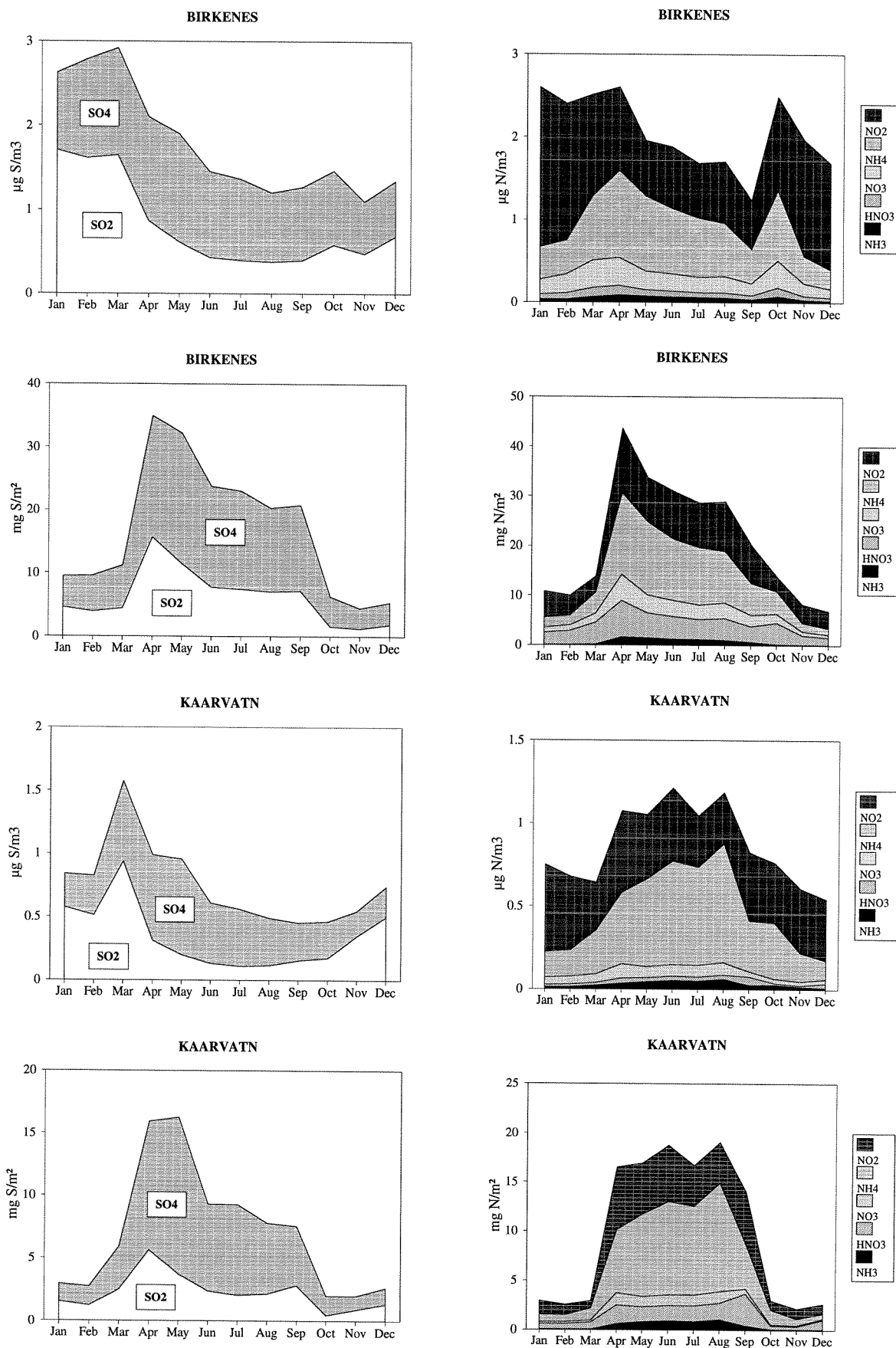


Figure 35 The monthly weighted concentration averages ( $\text{mg}/\text{m}^3$ ) and input averages ( $\text{mg}/\text{m}^2$ ) of  $\text{SO}_2$ -gas,  $\text{NO}_2$ -gas,  $\text{SO}_4$ -particles, and  $\text{NH}_4$ -particles in dry-deposition at Birkenes and Kaarvatn.

## Wet deposition

\* The only significant trends in the monthly concentration of dissolved chemical compounds in wet-deposition at all sites are the decrease in sulphate and  $H^+$ , which means that the concentration of sulphuric acid in precipitation has decreased at all sites during the monitoring periods.

\* On the basis of the regression line (Figure 36), the monthly average concentration of sulphate at Birkenes at the beginning of 1974 was  $86.1 \pm 33.9 \mu\text{eq/L}$ . At the end of 1992, the monthly concentration has decreased by 27%, down to an average of  $62.7 \pm 7.80 \mu\text{eq/L}$ . The monthly average concentration of  $SO_4^*$  at the beginning of 1977 (not Cl measurements before 1977) was  $83.0 \pm 33.8 \mu\text{eq/L}$ . At the end of 1992, the monthly average concentration of  $SO_4^*$  has by 36% down to  $52.8 \pm 8.48 \mu\text{eq/L}$ .

\* On the basis of the regression line (Figure 36), the average monthly concentration of sulphate at Storgama at the beginning of 1974 was  $68.2 \pm 32.3 \mu\text{eq/L}$ . At the end of 1992, the concentration has decreased by 34% down to  $44.8 \pm 7.60 \mu\text{eq/L}$ . The monthly average concentration of  $SO_4^*$  at the beginning of 1977 was  $62.5 \pm 30.5 \mu\text{eq/L}$ . At the end of 1992, the monthly average concentration of  $SO_4^*$  has decreased by 31% down to  $43.1 \pm 8.00 \mu\text{eq/L}$ .

\* On the basis of the regression line (Figure 36), the average monthly concentration of sulphate at Langtjern at the beginning of 1974 was  $77.0 \pm 51.7 \mu\text{eq/L}$ . At the end of 1992, the monthly average concentration has decreased by 47% down to  $40.7 \pm 12.0 \mu\text{eq/L}$ . At the beginning of 1975 the monthly concentration of  $SO_4^*$  was  $78.8 \pm 51.8 \mu\text{eq/L}$ . At the end of 1992, the monthly average concentration of  $SO_4^*$  has decreased by 53% down to  $36.9 \pm 12.2 \mu\text{eq/L}$ .

\* On the basis of the regression line (Figure 36), the monthly average concentration of sulphate at Kaarvatn at the beginning of 1980 was  $25.6 \pm 10.6 \mu\text{eq/L}$ . At the end of 1992, the concentration has decreased by 44% down to a monthly average of  $14.4 \pm 2.99 \mu\text{eq/L}$ . The monthly average concentration of  $SO_4^*$  at the beginning of 1980 was  $19.8 \pm 10.8 \mu\text{eq/L}$ . At the end of 1992, the monthly average concentration of  $SO_4^*$  has decreased by 62% down to  $7.6 \pm 2.99 \mu\text{eq/L}$ .

\* On the basis of the regression line (Figure 37), the average monthly concentration of  $H^+$  in wet-deposition at Birkenes at the beginning of 1974 was  $71.2 \pm 24.2 \mu\text{eq/L}$  (pH = 4.15). At the end of 1992, the concentration has decreased by 33%, down to a monthly average of  $47.6 \pm 5.70 \mu\text{eq/L}$  (pH = 4.32) at the end of 1992.

\* On the basis of the regression line (Figure 37), the average monthly concentration of  $H^+$  in wet-deposition at Storgama at the beginning of 1974 was  $60.7 \pm 22.7 \mu\text{eq/L}$  (pH = 4.22). At the end of 1992, the concentration has decreased by 26%, down to a monthly average of  $44.8 \pm 5.32 \mu\text{eq/L}$  (pH = 4.32) at the end of 1992.

\* On the basis of the regression line (Figure 37), the average monthly concentration of  $H^+$  in wet-deposition at Langtjern at the beginning of 1974 was  $64.8 \pm 34.3 \mu\text{eq/L}$  (pH = 4.19). At the end of 1992, the concentration has decreased by 58%, down to a monthly average of  $27.4 \pm 7.98 \mu\text{eq/L}$  (pH = 4.56) at the end of 1992.

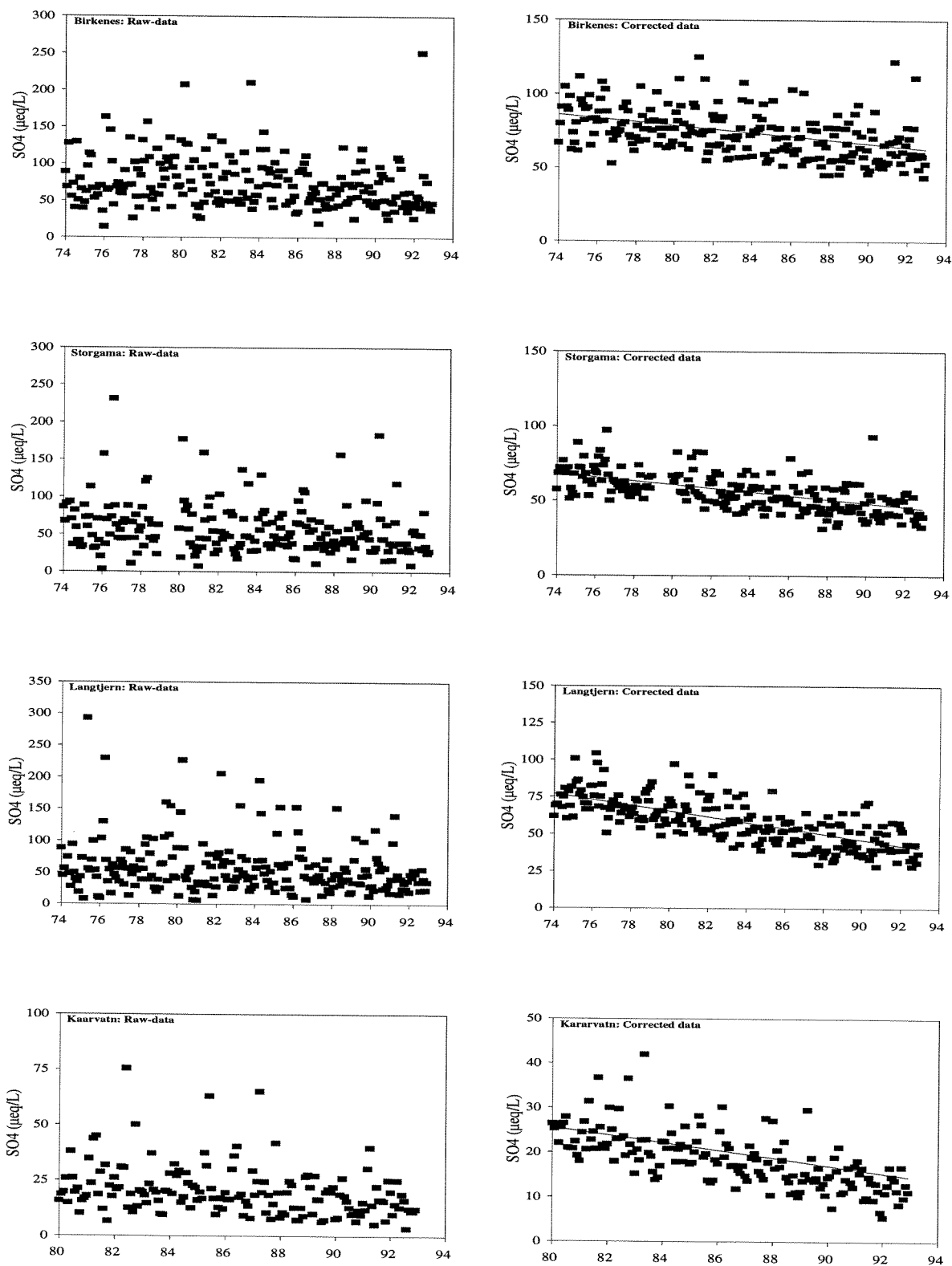


Figure 36 The monthly weighted concentration ( $\mu\text{eq/L}$ ) of  $\text{SO}_4^{2-}$  in wet-deposition at the four catchments, present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualises the influence of water on the concentration/flux of each chemical compound, i.e. large scattering means high water dependence and vice versa. Continuous line means that the linear regression is significant, i.e.  $p < 0.05$ , while a dotted line means no significance,  $p > 0.05$ .

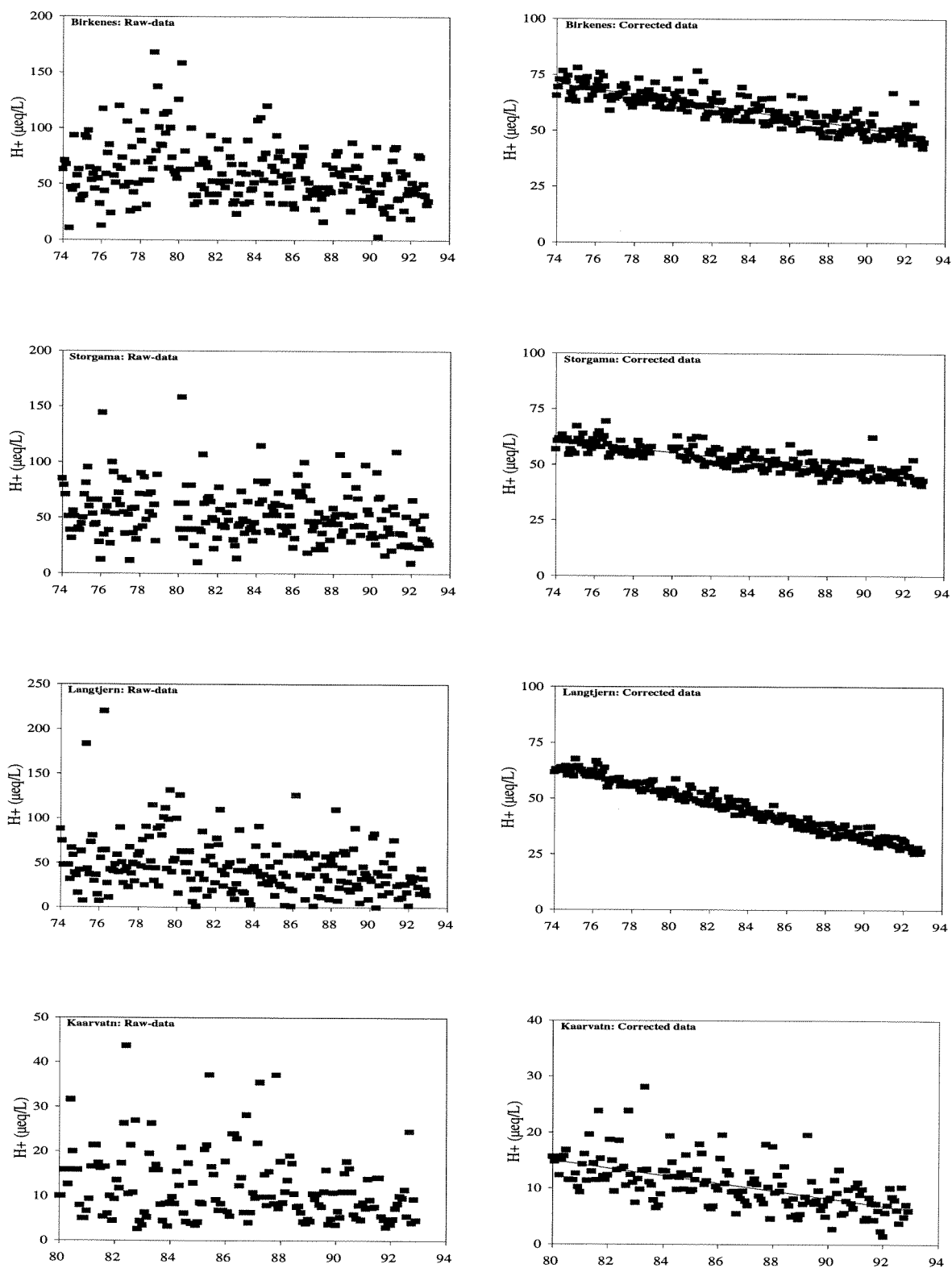


Figure 37 The monthly weighted concentration ( $\mu\text{eq/L}$ ) of  $H^+$  in wet-deposition at the four catchments, present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualises the influence of water on the concentration/flux of each chemical compound, i.e. large scattering means high water dependence and vice versa. Continuous line means that the linear regression is significant, i.e.  $p < 0.05$ , while a dotted line means no significance,  $p > 0.05$ .

\* On the basis of the regression line (Figure 37), the average monthly concentration of  $H^+$  in wet-deposition at Kaarvatn at the beginning of 1980 was  $15.0 \pm 7.34 \mu\text{eq/L}$  ( $\text{pH} = 4.82$ ). At the end of 1992, the concentration has decreased by 43% down to a monthly average of  $8.51 \pm 2.08 \mu\text{eq/L}$  ( $\text{pH} = 5.07$ ) at the end of 1992.

\* On the basis of the regression lines, weak but significant tendencies of decreasing concentrations of Ca were found at all sites, except at Birkenes.

\* On the basis of the regression lines, the only significant trends in the annual fluxes of major dissolved ions in wet-deposition are the reductions in non-marine sulphate ( $\text{SO}_4^*$ ) at Birkenes, Storgama and Kaarvatn (Figure 40). At Birkenes and Storgama the flux of  $\text{SO}_4^*$  has decreased by 36% and 37% from 1977 to 1992, while a 34% decrease was found at Kaarvatn from 1980-1992. The decrease in  $\text{SO}_4^*$  at Langtjern from 1975-1992 by 20% was not significant. This may rely on the relative high increase in annual amount of precipitation during the period, because increasing amounts of precipitation means increasing influx of sulphate. All catchments exhibit decreasing fluxes of  $H^+$  in wet-deposition during the period of monitoring (Figure 41), i.e. Birkenes (24%), Storgama (19%), Langtjern (27%) and Kaarvatn (13%). These trends are, however, not significant.

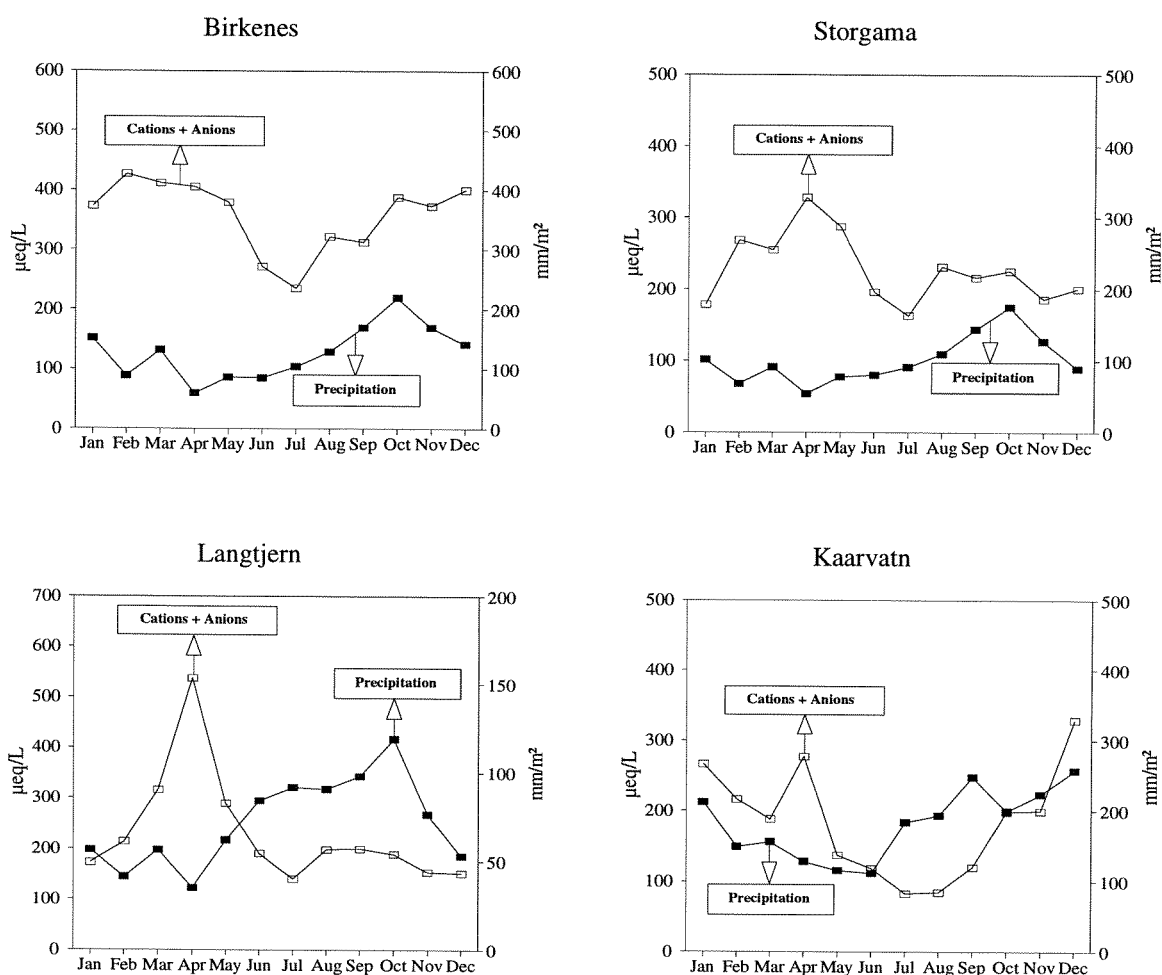


Figure 38 Seasonal changes in ionic concentration and precipitation amounts at the four catchments, based on monthly weighted averages during the monitoring periods.



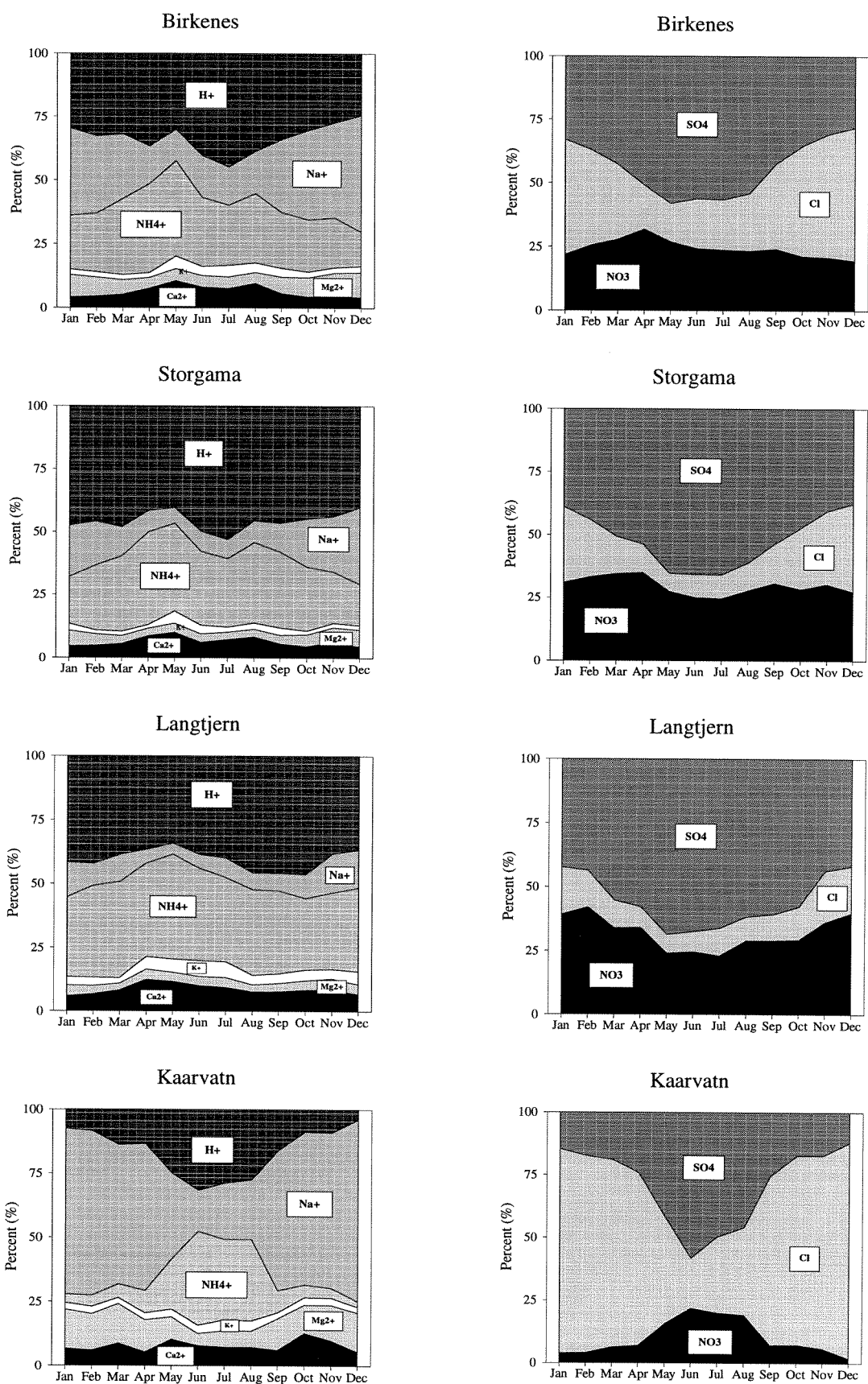


Figure 39 Seasonal changes in the percentage distribution of cations and anions in precipitation at the four catchments, based on monthly weighted averages during the monitoring periods.

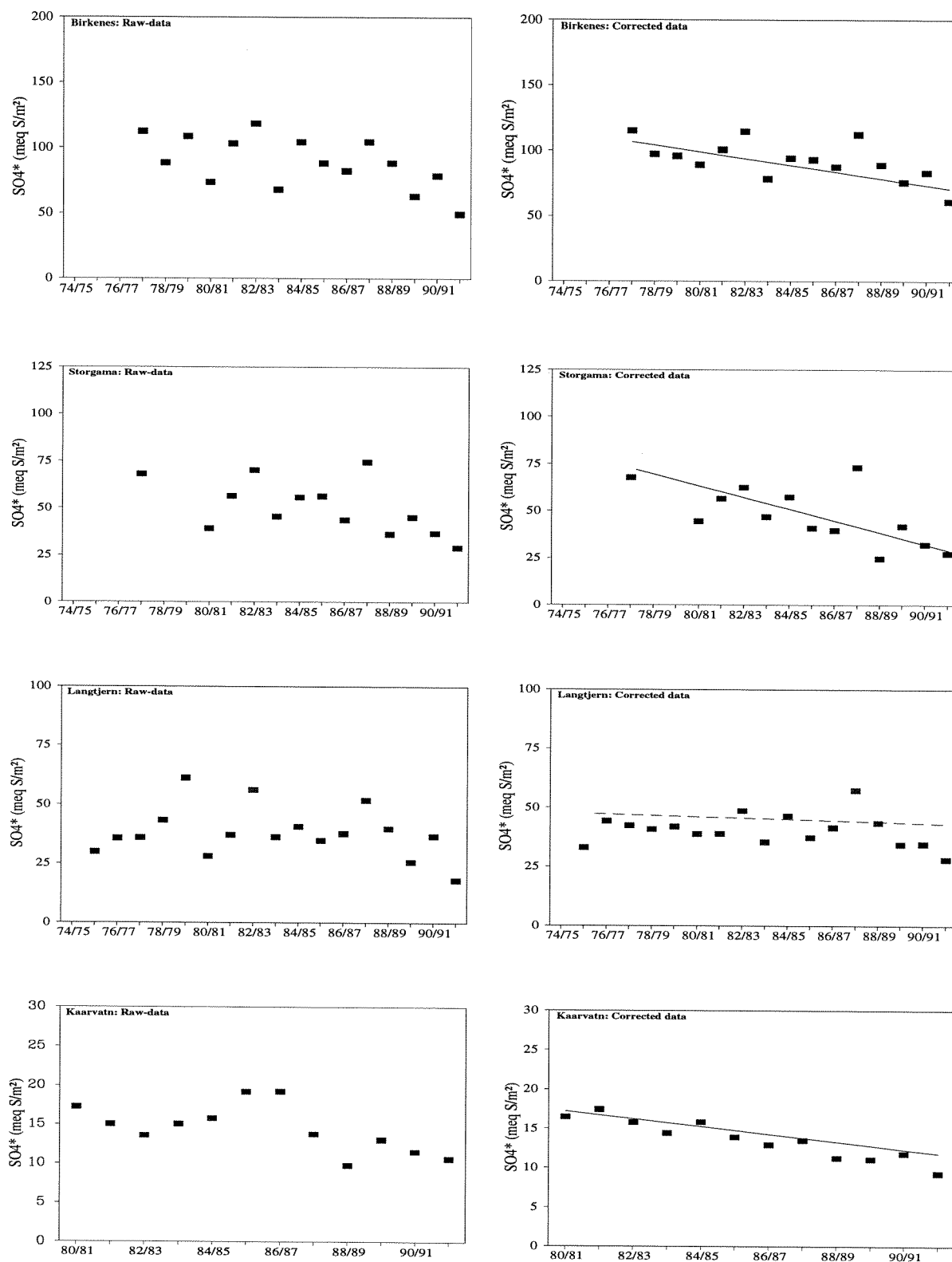


Figure 40 Annual weighted fluxes (meq/m<sup>2</sup>) of non-marine sulphate ( $SO_4^*$ ) in wet-deposition at the four catchments, present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualises the influence of water on the concentration/flux of each chemical compound, i.e. large scattering means high water dependence and vice versa. Continuous line means that the linear regression is significant, i.e.  $p < 0.05$ , while a dotted line means no significance,  $p > 0.05$ .

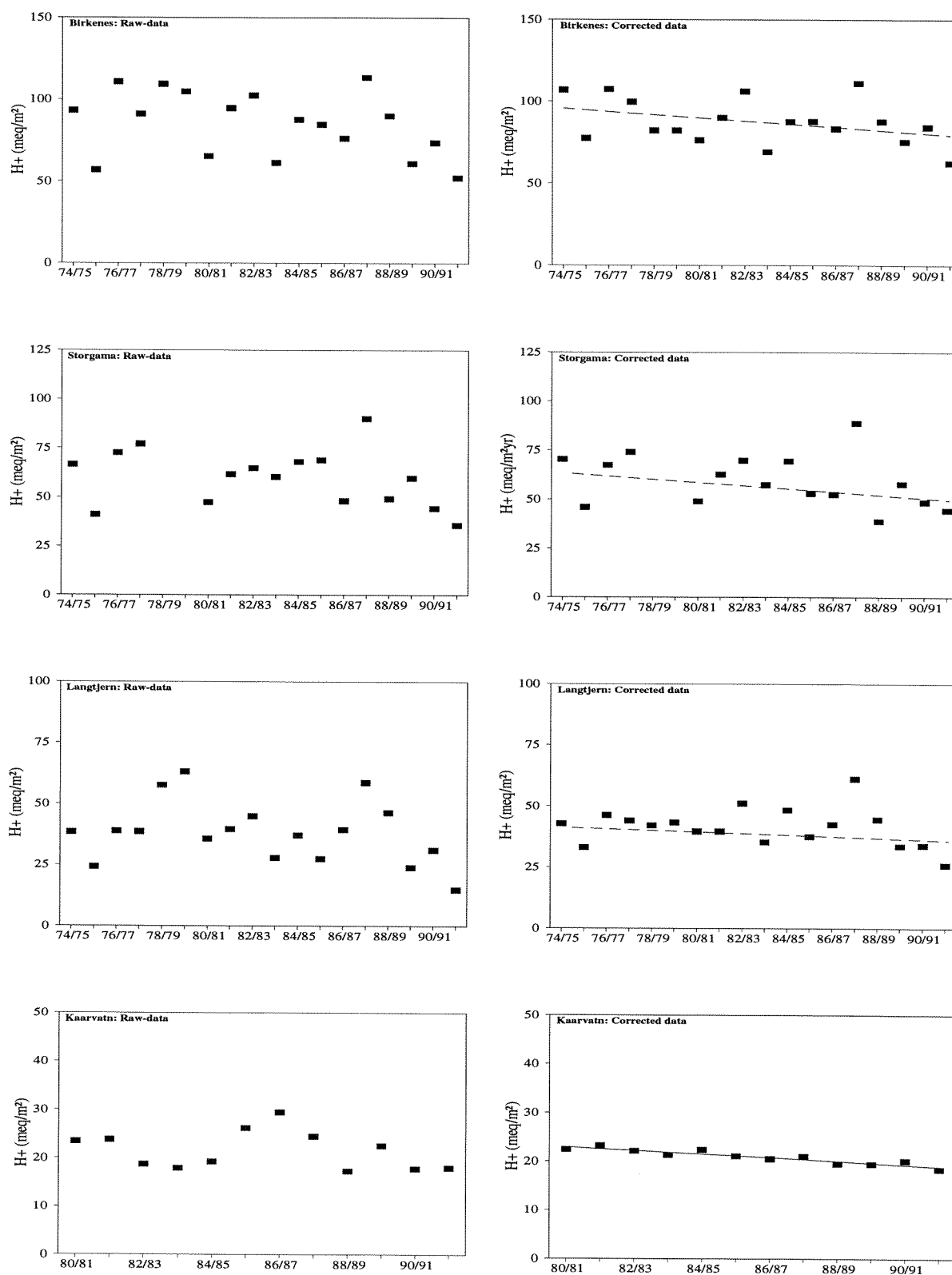


Figure 41 Annual weighted fluxes (meq/m<sup>2</sup>) of  $H^+$  in wet-deposition at the four catchments, present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualises the influence of water on the concentration/flux of each chemical compound, i.e. large scattering means high water dependence and vice versa. Continuous line means that the linear regression is significant, i.e.  $p < 0.05$ , while a dotted line means no significance,  $p > 0.05$ .

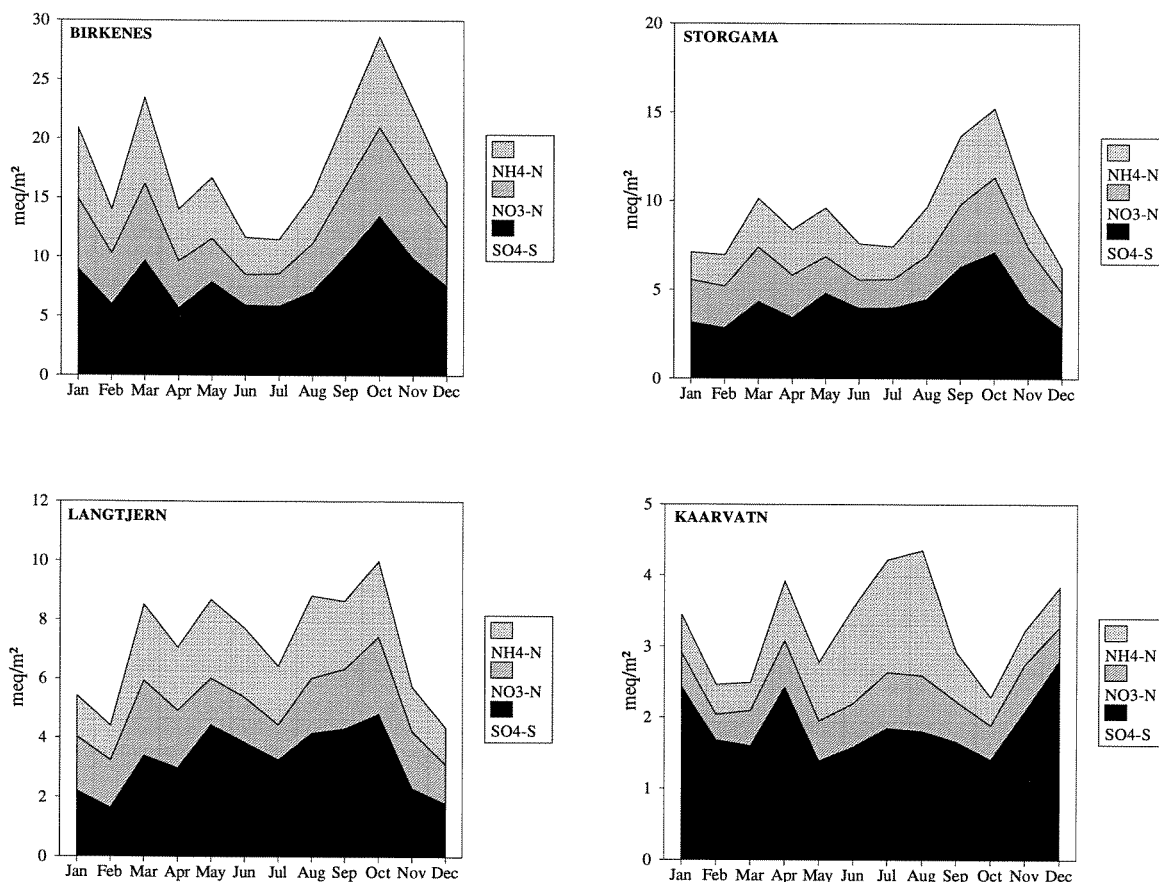


Figure 42 Seasonal influxes of  $SO_4^{2-}$ ,  $NO_3^-$  and  $NH_4^+$  by wet-deposition at the four catchments, based on monthly weighted averages during the monitoring periods.

## Runoff

\* On the basis of the regression line (Figure 43), the average monthly concentration of  $SO_4^*$  in runoff water at Birkenes was  $139 \pm 19.4 \mu\text{eq/L}$  at the beginning of 1974, and  $SO_4^*$  constituted 92% of total dissolved inorganic sulphur in runoff. At the end of 1992, the monthly concentration of  $SO_4^*$  has decreased by 31% (Table 8), down to a monthly weighted average of  $96 \pm 4.8 \mu\text{eq/L}$ , and  $SO_4^*$  constituted 87% of total dissolved inorganic sulphur.

\* On the basis of the regression line (Figure 43), the average monthly concentration of  $SO_4^*$  in runoff water at Storgama was  $87 \pm 19.4 \mu\text{eq/L}$  at the beginning of 1974, and  $SO_4^*$  constituted 97% of total dissolved inorganic sulphur in runoff. At the end of 1992, the monthly concentration of  $SO_4^*$  has decreased by 32% (Table 8), down to a monthly weighted average of  $59 \pm 5.3 \mu\text{eq/L}$ , and  $SO_4^*$  constituted 93% of total dissolved inorganic sulphur.

\* On the basis of the regression line (Figure 44), the average monthly concentration of  $SO_4^*$  in runoff water at Langtjern was  $87 \pm 14.2 \mu\text{eq/L}$  at the beginning of 1974, and  $SO_4^*$  constituted 98% of total dissolved inorganic sulphur in runoff. At the end of 1992, the monthly concentration of  $SO_4^*$  has decreased by 35% (Table 8), down to a monthly weighted average of  $56 \pm 3.4 \mu\text{eq/L}$ , and  $SO_4^*$  constituted 97% of total dissolved inorganic sulphur.

\* On the basis of the regression line (Figure 44), the average monthly concentration of  $\text{SO}_4^*$  in runoff water at Kaarvatn was  $16 \pm 4.9 \mu\text{eq/L}$  at the beginning of 1980, and  $\text{SO}_4^*$  constituted 74% of total dissolved inorganic sulphur in runoff. At the end of 1992, the average concentration of  $\text{SO}_4^*$  has decreased by 34% (Table 8), down to a monthly weighted average of  $11 \pm 1.4 \mu\text{eq/L}$ , and  $\text{SO}_4^*$  constituted 61% of total dissolved inorganic sulphur.

\* On the basis of the regression line (Figure 43), the average monthly concentration of  $\Sigma\text{Ca}^*,\text{Mg}^*$  in runoff water at Birkenes was  $86 \pm 17.4 \mu\text{eq/L}$  at the beginning of 1974, while at the end of 1992 the average concentration was  $48 \pm 4.2 \mu\text{eq/L}$ . This is a 44% decrease from 1974-1992 (Table 8).

\* On the basis of the regression line (Figure 43), the average monthly concentration of  $\Sigma\text{Ca}^*,\text{Mg}^*$  in runoff water at Storgama was  $59 \pm 13.9 \mu\text{eq/L}$  at the beginning of 1974, while at the end of 1992 the average concentration was  $34 \pm 3.8 \mu\text{eq/L}$ . This is a 42% decrease from 1974-1992 (Table 8).

\* On the basis of the regression line (Figure 44), the average monthly concentration of  $\Sigma\text{Ca}^*,\text{Mg}^*$  in runoff water at Langtjern was  $89 \pm 14.2 \mu\text{eq/L}$  at the beginning of 1974, while at the end of 1992 the average concentration was  $63 \pm 3.2 \mu\text{eq/L}$ . This is a 28% decrease from 1974-1992 (Table 8).

\* On the basis of the regression line (Figure 44), the average monthly concentration of  $\Sigma\text{Ca}^*,\text{Mg}^*$  in runoff water at Kaarvatn was  $39 \pm 13.9 \mu\text{eq/L}$  at the beginning of 1980, while at the end of 1992 the average concentration was  $34 \pm 3.9 \mu\text{eq/L}$ . This is a 13% decrease from 1980-1992 (Table 8).

\* The decrease in the concentration of  $\text{SO}_4^*$  is almost equal to the decrease in the concentrations of base cations,  $\Sigma\text{Ca}^*,\text{Mg}^*$ . Thus, the pH of runoff have not changed significantly during the periods of monitoring.

\* Site specific trends in runoff are: The increase in nitrate at Birkenes; The decrease in K and nitrate at Storgama; The tendency of increasing seasalt influence at the most coast-near sites, Birkenes, Storgama and Kaarvatn.

Table 8 Percentage change in the monthly weighted concentration of various S-compounds,  $\text{H}^+$ , and  $\Sigma\text{Ca}^*,\text{Mg}^*$  at the four sites during the monitoring periods, i.e. from the middle of the 70thies at Birkenes, Storgama and Langtjern (from 1980 at Kaarvatn) and up to 1992. Negative values mean a decreasing trend. Significant trends ( $p < 0.05$ ) are marked with asterisks.

Compound		Percentage (%) change			
		Birkenes	Storgama	Langtjern	Kaarvatn
Dry-dep.	$\text{SO}_2$ -gas	-81%*			-81%*
	$\text{SO}_4$ -part.	-53%*			-49%*
	Total-S	-67%*			-64%*
Wet-dep.	$\text{SO}_4^*$	-36%*	-31%*	-53%*	-62%*
	$\text{H}^+$	-33%*	-26%*	-58%*	-43%*
Runoff	$\text{SO}_4^*$	-31%*	-32%*	-35%*	-34%*
	$\text{H}^+$	13%	-10%	6%	16%
	$\Sigma\text{Ca}^*,\text{Mg}^*$	-44%*	-42%*	-28%*	-13%

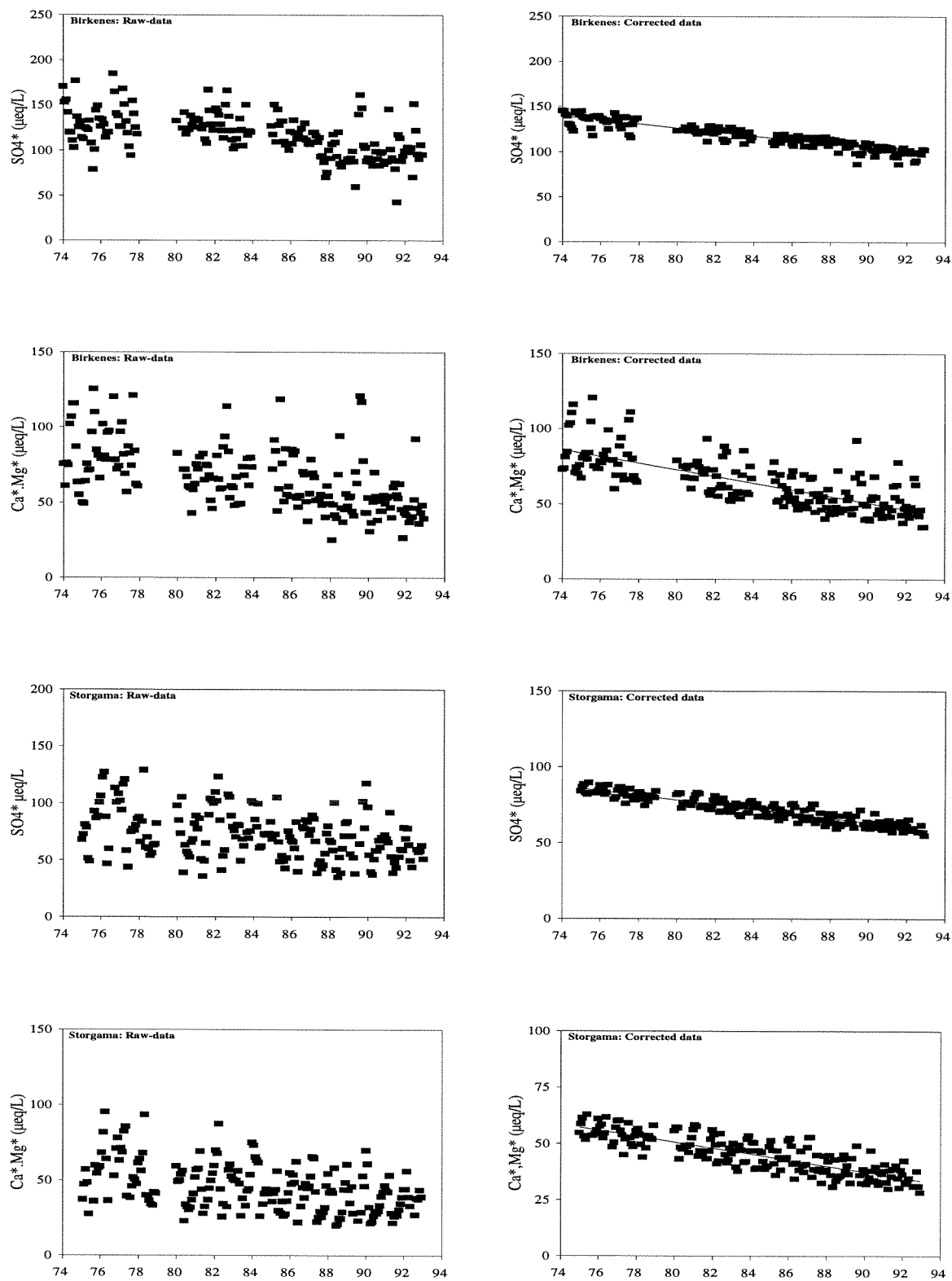


Figure 43 The monthly weighted concentration of  $SO_4^*$  and  $\Sigma Ca^*, Mg^*$  in runoff ( $\mu eq/L$ ) at Birkenes and Storgama from 1974-1992, present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualises the influence of water on the concentration/flux of each chemical compound, i.e. large scattering means high water dependence and vice versa. Continuous line means that the linear regression is significant, i.e.  $p < 0.05$ , while a dotted line means no significance,  $p > 0.05$ .

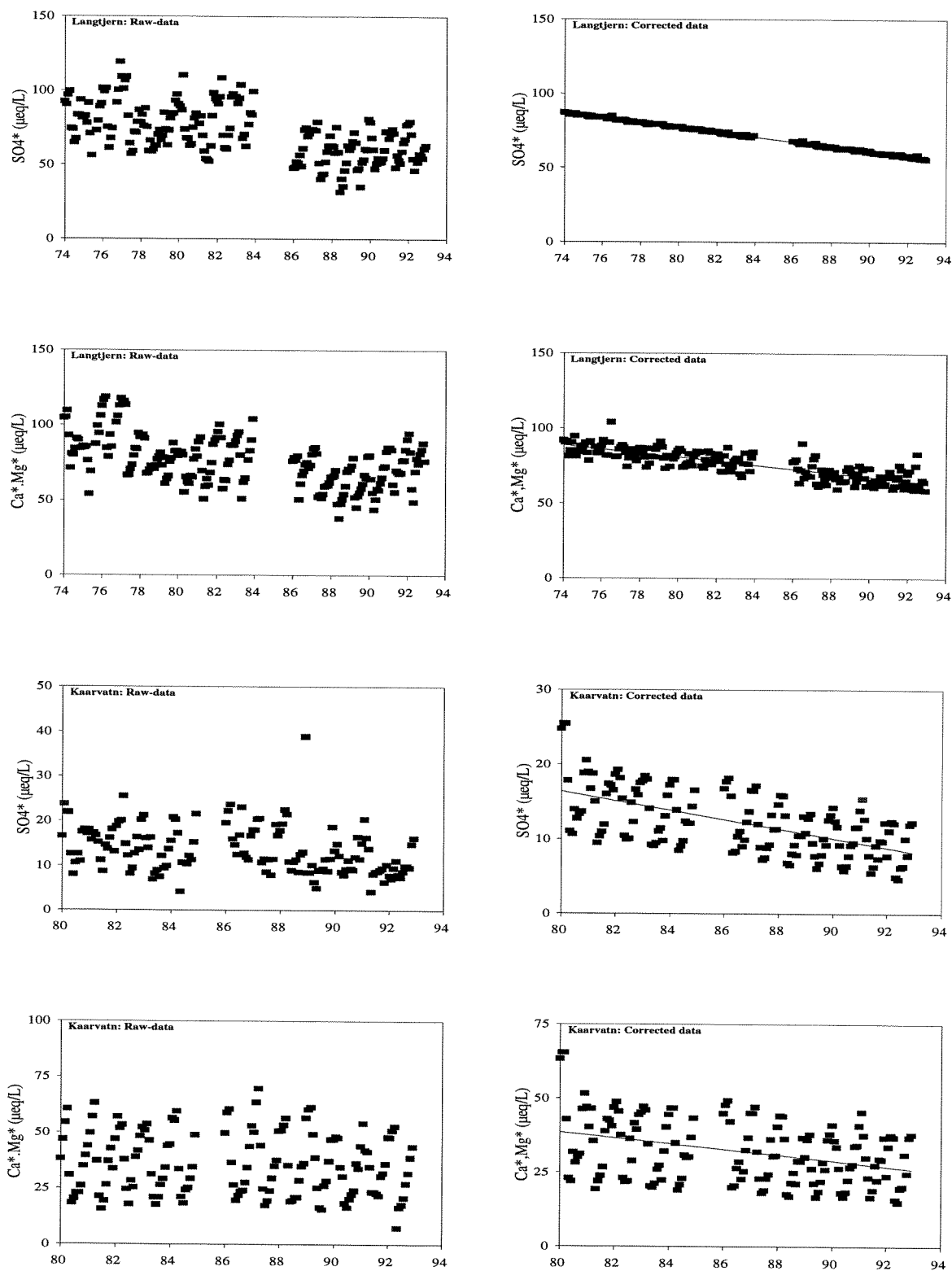


Figure 44 The monthly weighted concentration of  $\text{SO}_4^*$  and  $\Sigma\text{Ca}^*,\text{Mg}^*$  in runoff ( $\mu\text{eq/L}$ ) at Langtjern (1974-1992) and Kaarvatn (1980-1992), present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualises the influence of water on the concentration/flux of each chemical compound, i.e. large scattering means high water dependence and vice versa. Continuous line means that the linear regression is significant, i.e.  $p < 0.05$ , while a dotted line means no significance,  $p > 0.05$ .

Table 9 Percentage change in the annual fluxes of various S-compounds, H<sup>+</sup>, and  $\Sigma$  Ca\*,Mg\* at the four sites during the monitoring periods, i.e. from the middle of the 70thies at Birkenes, Storgama and Langtjern (from 1980 at Kaarvatn) and up to 1992. Negative values mean a decreasing trend. Significant trends ( $p < 0.05$ ) are marked with asterisks.

Compound		Percentage (%) change			
		Birkenes	Storgama	Langtjern	Kaarvatn
Dry-dep.	SO <sub>2</sub> -gas	-60%*			-69%*
	SO <sub>4</sub> -part.	-48%*			-46%*
	Total-S	-57%*			-54%*
Wet-dep.	SO <sub>4</sub> *	-36%*	-37%*	-20%	-34%*
	H <sup>+</sup>	-24%	-19%	-27%	-13%
Runoff	SO <sub>4</sub> *	-37%	-33%	-28%	-4%
	H <sup>+</sup>	-14%	-11%	6%	14%
	$\Sigma$ Ca*,Mg*	-44%*	-48%*	-20%	4%

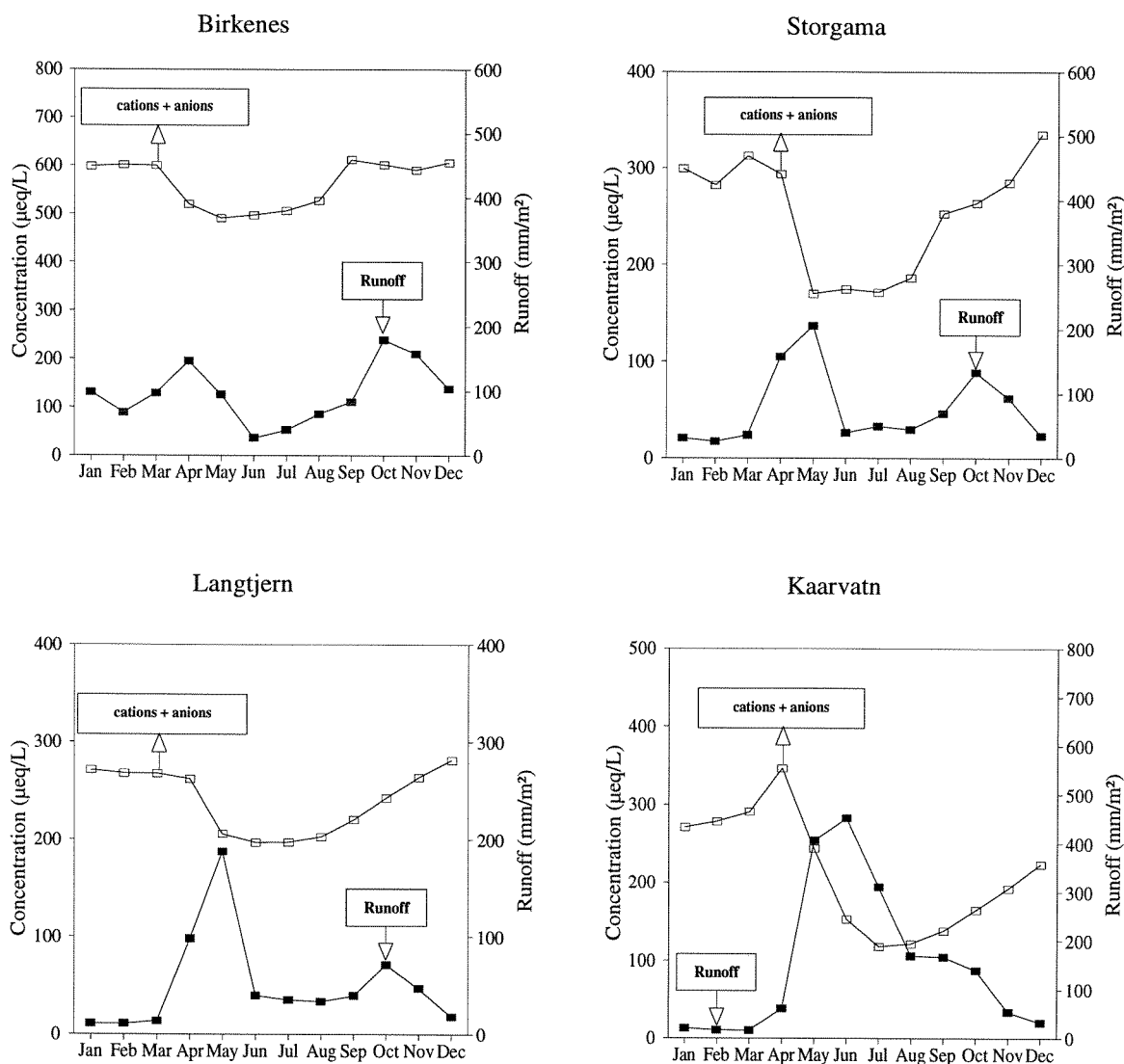


Figure 45 Seasonal changes in the ionic concentration and runoff during a year at the four catchments, based on monthly weighted averages during the monitoring periods.



\* At all sites, the concentrations of sulphate in wet-deposition were relatively sensitive to variations in amount of precipitation. The corresponding water-dependences were much less in runoff-water, but it varies a lot from catchment to catchment. The concentration of  $\text{SO}_4$  or  $\text{SO}_4^*$  in runoff-water at Kaarvatn was most runoff-sensitive, followed by Birkenes and Storgama, while at Langtjern the concentration of  $\text{SO}_4/\text{SO}_4^*$  in runoff water was almost insensitive to variations in runoff (Figure 44). This may rely on at least two important factors. The Langtjern catchment contains large boggy areas, and the sampling site is at the outlet of a relatively big lake. The residence time of water is therefore most likely higher at this site compared with the other, so that the ability of the catchment to moderate hydrologic and chemical extremes are far the best at Langtjern.

\* At all sites, the concentrations of  $\Sigma\text{Ca}^*,\text{Mg}^*$  are much more dependent on variation in hydrology compared with the concentration of  $\text{SO}_4$  and  $\text{SO}_4^*$  (Figure 43 and 44). This should also be expected, as long as non-marine base cations primarily derive from physico-chemical soil-water processes, while sulphate enters the catchments primarily as atmospheric dry- and wet-deposition compounds, and acts as a relative conservative ion. The concentration of non-marine base cations ( $\Sigma\text{Ca}^*,\text{Mg}^*$ ) are decreasing by increasing runoff at all sites, most significantly at Birkenes and Kaarvatn.

\* The most significant time trends in output/effluxes of chemical compounds at the three most acidified catchments, were the decrease in  $\Sigma\text{Ca}^*,\text{Mg}^*$  and  $\text{SO}_4^*$  (Table 9). These time trends are, however, not very significant (Figure 47 and 48). At Kaarvatn, the relatively large increase in annual input/output of water during the monitoring period, has almost "compensated" for the decrease in the concentration of  $\Sigma\text{Ca}^*,\text{Mg}^*$  and  $\text{SO}_4^*$ , so that these fluxes exhibit no significant time-trends. The most significant changes in output of other chemical compounds by time were the increase in output of nitrate at Birkenes, and the decrease in potassium at Storgama from 1974/75 to 1991/92.

\* During the period 1974-1992, on average  $\text{ANC}'$  ( $\Sigma\text{Ca},\text{Mg},\text{K} - \Sigma\text{SO}_4,\text{NO}_3$ ) explained  $65 \pm 5\%$  of the monthly variations in ANC in runoff water at Birkenes (Figure 50), while the remaining  $35 \pm 5\%$  was explained by the difference between sodium and chloride (Na-Cl), i.e. the seasalt effect. During the last years, 1985-1992,  $\text{ANC}'$  explained  $59 \pm 8\%$  of the monthly variations in ANC, while the remaining  $41 \pm 8\%$  was explained by Na-Cl.

\* During the period 1975-1992, on average  $\text{ANC}'$  explained  $81 \pm 3\%$  of the monthly variations in ANC at Storgama, while the remaining  $19 \pm 3\%$  was explained by Na-Cl. During the period 1985-1992,  $\text{ANC}'$  explained  $74 \pm 5\%$  of the monthly variations in ANC, while the remaining  $26 \pm 5\%$  was explained by Na-Cl.

\* During the period 1974-1992, on average  $\text{ANC}'$  explained  $79 \pm 2\%$  of the monthly variations in ANC at Langtjern, while Na-Cl explained the remaining  $21 \pm 2\%$ . During the last years, 1985-1992,  $\text{ANC}'$  explained  $81 \pm 3\%$  of the monthly variations in ANC, while Na-Cl explained the remaining  $19 \pm 3\%$ .

\* During the period 1980-1992, on average  $\text{ANC}'$  explained  $32 \pm 9\%$  of the monthly variations in ANC, while Na-Cl explained the remaining  $68 \pm 9\%$ . During the period 1985-1992,  $\text{ANC}'$  explained  $27 \pm 11\%$  of the monthly variations in ANC, while the remaining  $71 \pm 11\%$  was explained by Na-Cl.

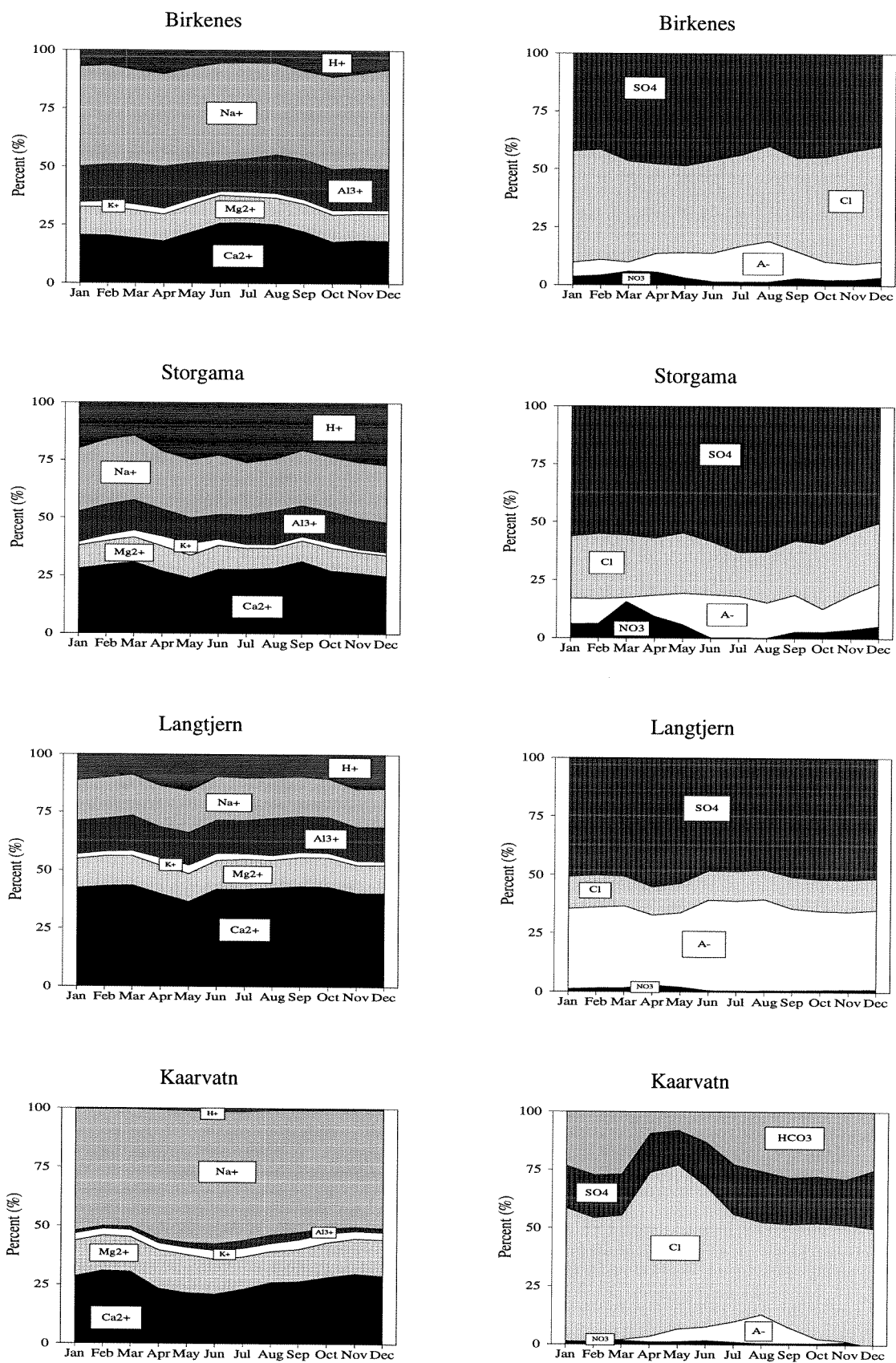


Figure 46 Seasonal changes in the percentage distribution of cations and anions in runoff at the four catchments during the monitoring periods.

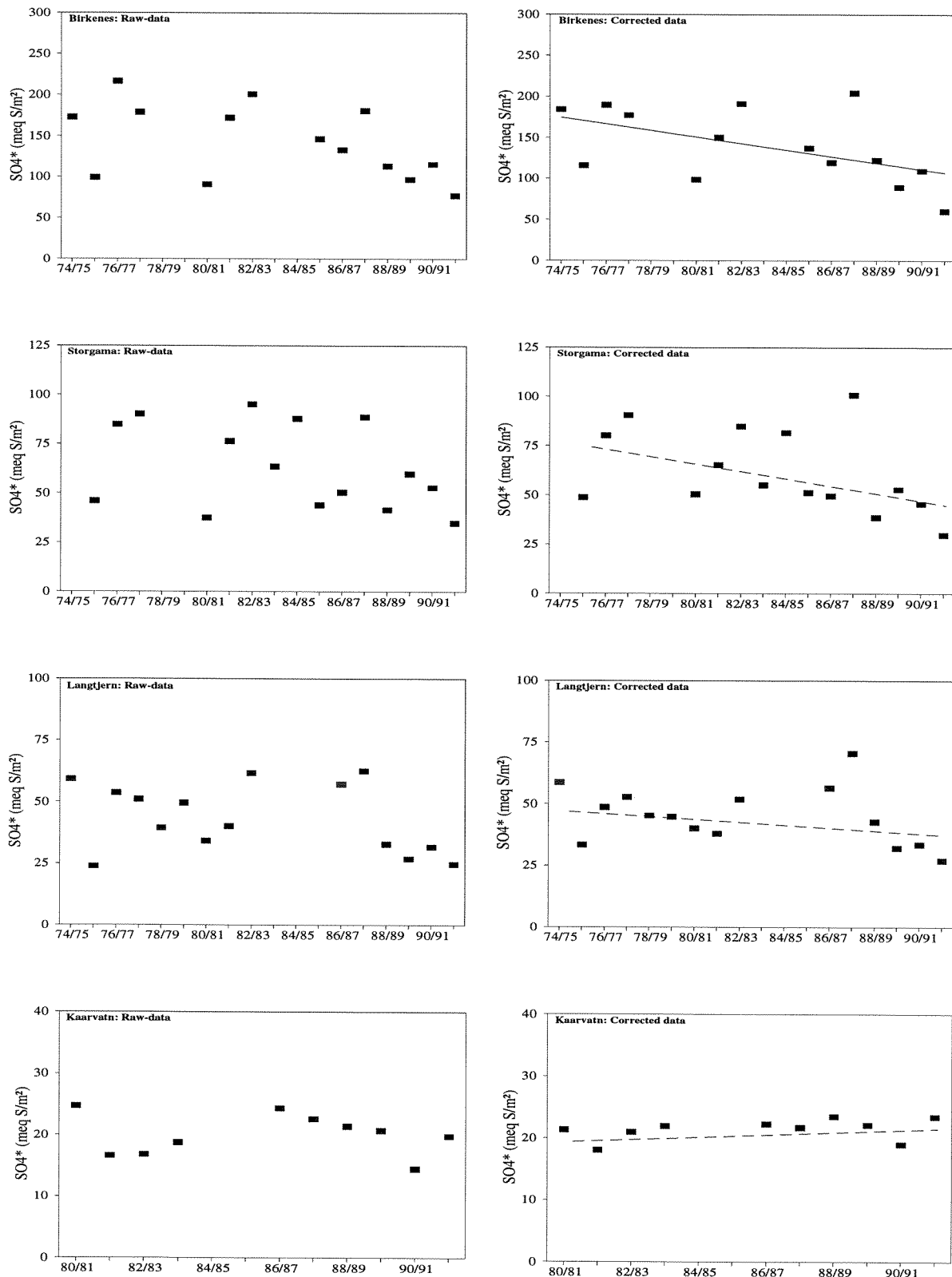


Figure 47 Annual weighted fluxes (meq  $S/m^2$ ) of non-marine sulphate ( $SO_4^*$ ) in runoff at the four catchments, present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualises the influence of water on the concentration/flux of each chemical compound, i.e. large scattering means high water dependence and vice versa. Continuous line means that the linear regression is significant, i.e.  $p < 0.05$ , while a dotted line means no significance,  $p > 0.05$ .

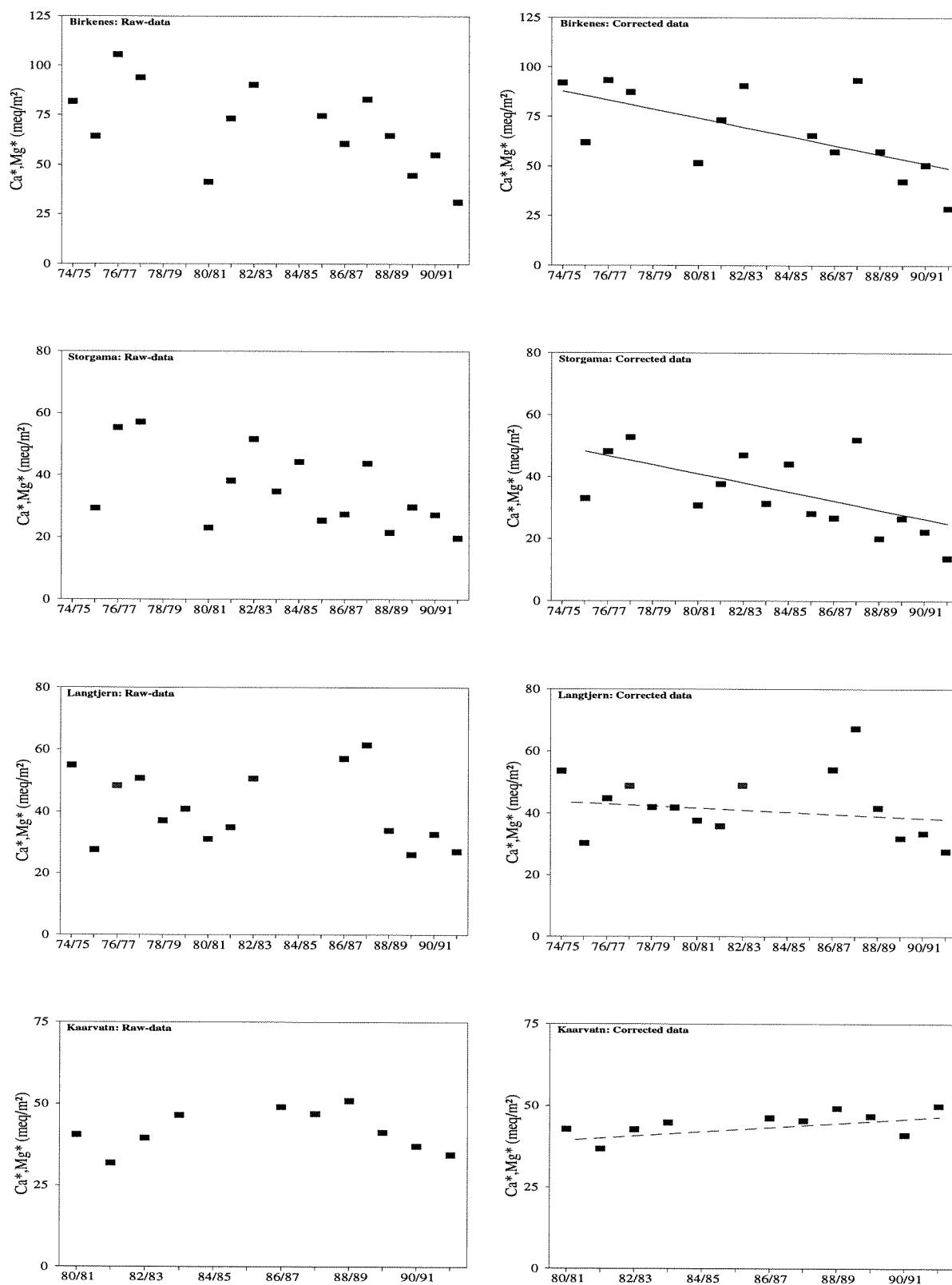


Figure 48 Annual weighted fluxes (meq/m<sup>2</sup>) of non-marine base-cations ( $\Sigma\text{Ca}^*,\text{Mg}^*$ ) in runoff at the four catchments, present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualises the influence of water on the concentration/flux of each chemical compound, i.e. large scattering means high water dependence and vice versa. Continuous line means that the linear regression is significant, i.e.  $p < 0.05$ , while a dotted line means no significance,  $p > 0.05$ .

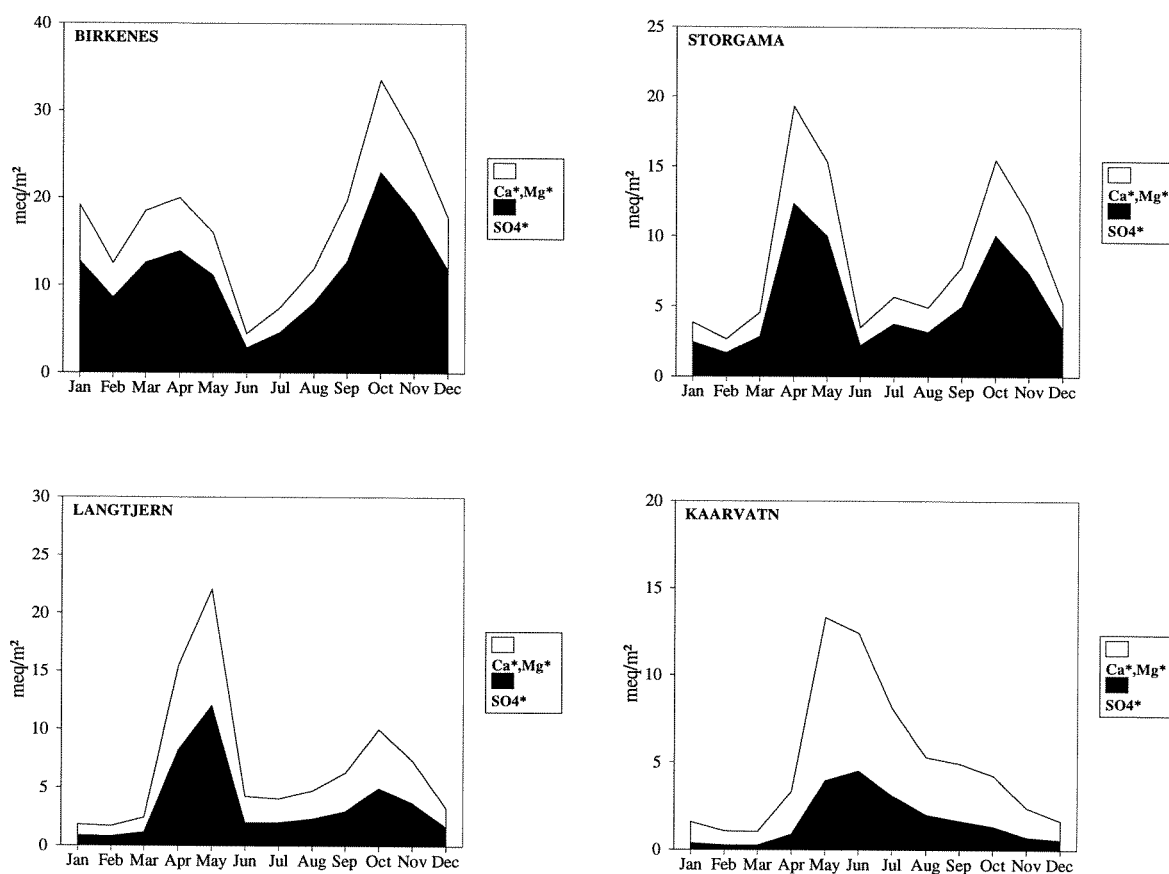


Figure 49 Seasonal output ( $\text{meq/m}^2\text{mth}$ ) of  $\text{SO}_4^*$  and  $\Sigma\text{Ca}^*,\text{Mg}^*$  in runoff at the four catchments during the monitoring periods.

\* At Birkenes, the monthly weighted runoff concentration of  $\text{SO}_4^*$  has decreased by  $43 \mu\text{g/L}$  during the period 1974-1992, while the corresponding decrease in  $\Sigma\text{Ca}^*,\text{Mg}^*$  was  $38 \mu\text{g/L}$ . At Storgama, the monthly weighted concentration of  $\text{SO}_4^*$  on average has decreased by  $28 \mu\text{g/L}$  during the period 1974-1992, while the corresponding decrease in  $\Sigma\text{Ca}^*,\text{Mg}^*$  was  $25 \mu\text{g/L}$ . At Langtjern, the monthly weighted concentration of  $\text{SO}_4^*$  on average has decreased by  $31 \mu\text{g/L}$  during the period 1974-1992, while the corresponding decrease in  $\Sigma\text{Ca}^*,\text{Mg}^*$  was  $26 \mu\text{g/L}$ . At Kaarvatn, the monthly weighted concentration of  $\text{SO}_4^*$  on average has decreased by  $5.6 \mu\text{g/L}$  during the period 1980-1992, while the corresponding decrease in  $\Sigma\text{Ca}^*,\text{Mg}^*$  was  $5.1 \mu\text{g/L}$ . Because the decrease in concentration of  $\text{SO}_4^*$  during the monitoring periods is slightly higher than the decrease in  $\Sigma\text{Ca}^*,\text{Mg}^*$  at all sites, an increase in ANC should be expected. A weak tendency of an increase in ANC is also observed at all sites during the last years i.e. from 1985-1992, but the decreases in Na-Cl at Birkenes and Kaarvatn are almost overshadowing this improvement at these sites. A decrease in Na-Cl in runoff water, means that the base saturation of the soil is temporarily improved, because sodium is retained in the catchment. That the base cations tend to decline with a slower rate than sulphate, means that the base cations are "strengthening" their position versus sulphate. If the concentration of nitrate in runoff water does not increase in the years to come, all together, this may indicate an improvement, not only for the runoff-water, but also for the base-cation status in soil in the long run. Thus, the very weak improvement in base cation status versus strong acid anions ( $\text{SO}_4$  and  $\text{NO}_3$ ) during the last years, may therefore be a signal of a slowly improving surface-water chemistry in southern Norway.

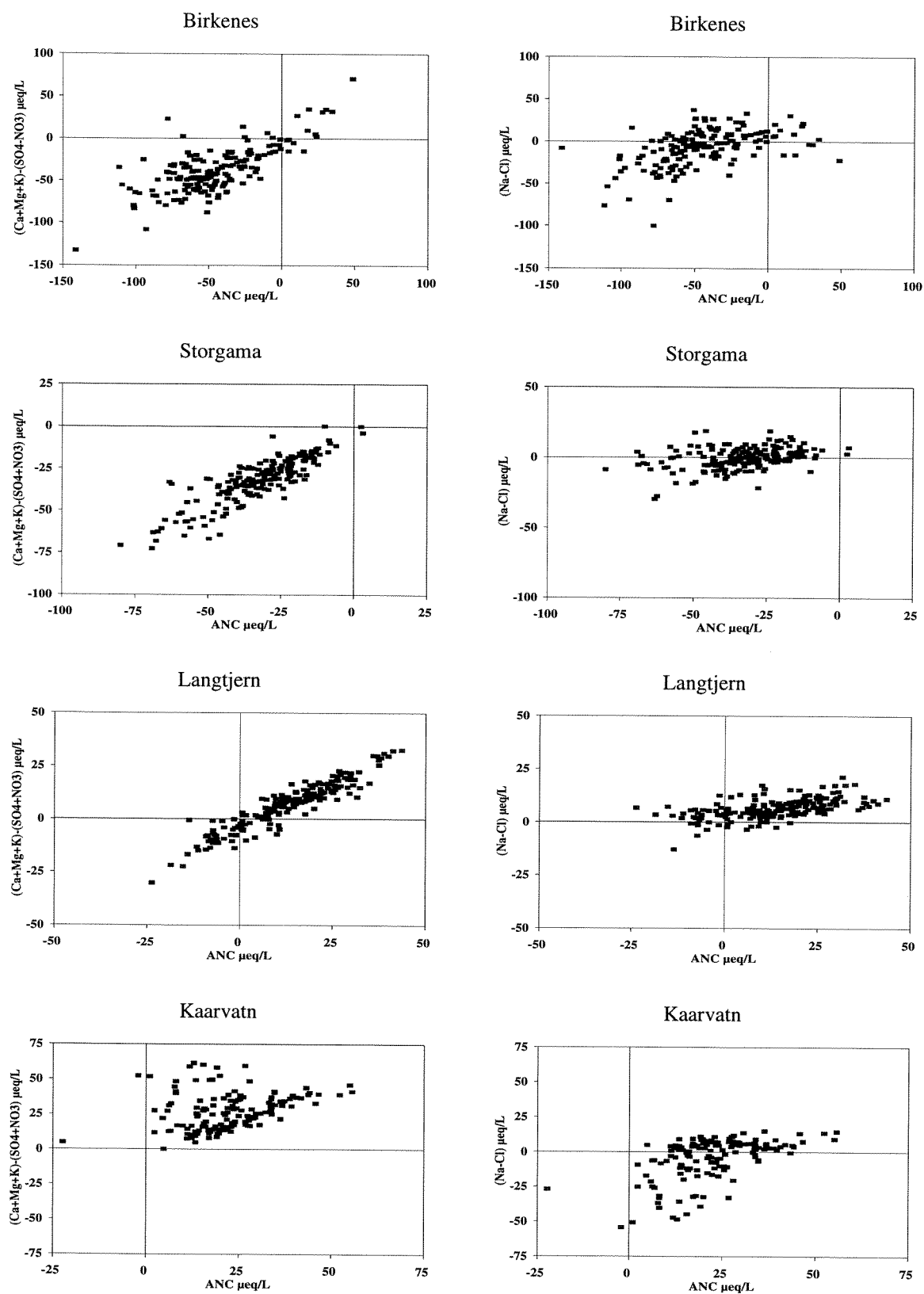


Figure 50 The relationships between ANC and  $ANC'$  ( $\Sigma Ca, Mg, K - \Sigma SO_4, NO_3$ ) and ANC and  $Na-Cl$  in runoff-water at the four catchments, based on monthly weighted averages during the monitoring periods. The regression lines are: **Birkenes**:  $y = 0.65ANC' - 8.56$  ( $r = 0.73$ );  $y = 0.35(Na-Cl) + 8.56$  ( $r = 0.50$ ) ( $n = 180$ ); **Storgama**:  $y = 0.81ANC' - 5.76$  ( $r = 0.86$ );  $y = 0.19(Na-Cl) + 5.76$  ( $r = 0.37$ ) ( $n = 192$ ); **Langtjern**:  $y = 0.79ANC' - 3.57$  ( $r = 0.94$ );  $y = 0.21(Na-Cl) + 3.57$  ( $r = 0.59$ ) ( $n = 198$ ); **Kaarvatn**:  $y = 0.32ANC' + 19.9$  ( $r = 0.28$ );  $y = 0.68(Na-Cl) - 19.9$  ( $r = 0.54$ ) ( $n = 144$ ).



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