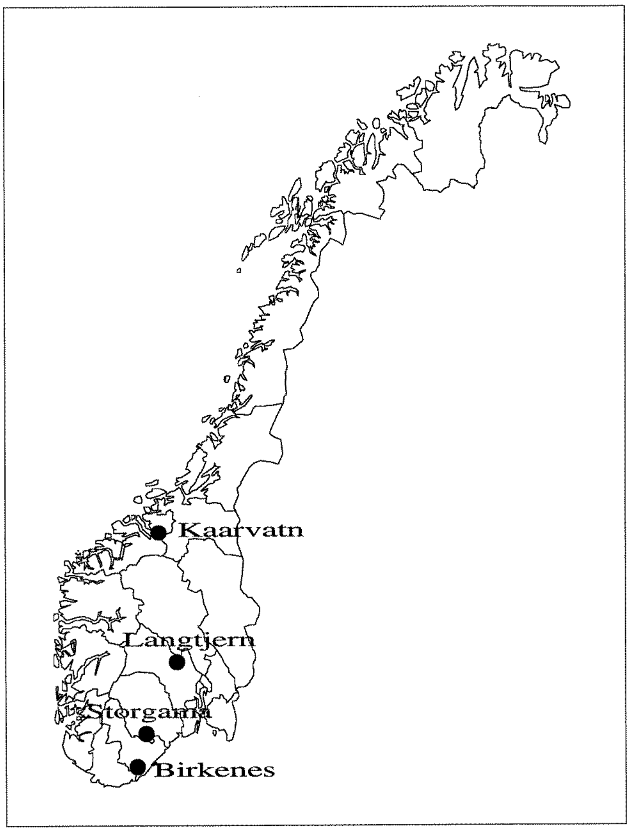
Acid Rain Research

REPORT 34-A/1994

Long-Term Monitored Catchments in Norway

- A Hydrologic and Chemical Evaluation -



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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 this main version (A) is very voluminous, it was necessary to produce a summary report (B) with the same title and NIVA-number.

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34-A/1994	Lydersen, E., 1994. Long term monitored catchments in Norway - a hydrologic and chemical evaluation -, 306 pp. + Appendix.
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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. More details concerning the programme are presented in the introduction chapter of this report, but we have to mention that 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 a summary report. The summary report is a B-version 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.

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 (Håvar 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

1. INTRODUCTION

This book is based on hydrochemical data of precipitation (wet and dry deposition) and runoff waters from 4 Norwegian catchments: Birkenes, Storgama, Langtjern and Kaarvatn, during the period 1974-1991 (Kaarvatn from 1978). The data were collected under the SNSF-project ("Acid precipitation - Effects on Forest and Fish") and the Norwegian Monitoring Programme for Long-Range Transported Air Pollutants. The SNSF-project was launched in 1972 in response to increasing concern about the loss of fish populations and the possible threat to forest productivity (Drabloes and Tollan, 1980). This research programme was jointly sponsored by the Royal Norwegian Council for Scientific and Industrial Research (NTNF), the Norwegian Agricultural Research Council (NLVF), and the Norwegian Ministry of Environment (MD). When this programme terminated in 1979, it was succeeded by the Norwegian Monitoring Programme for Long-Range Transported Air Pollutants, which started in 1980 and is still in progress. The aim of this programme is to describe the actual situation and trends in precipitation quality, in water and soil acidification, and in damage to fish and invertebrates. The Norwegian State Pollution Control Authority (SFT) is responsible for the co-ordination and implementation of the programme.

Long time-series of dry deposition of sulphur-compounds only exist in Birkenes and Kaarvatn. In Birkenes analyses of sulphate-particles are available continuously since 1974, and analyses of SO_2-gas exist continuously from 1978. At Kaarvatn both dry deposition compounds of sulphur are analysed continuously since 1980. At Langtjern corresponding datasets are available since 1988. Dry depositions of nitrogen compounds are available at Birkenes from 1986, at Kaarvatn from 1988, while some dry deposition data on nitrogen are available at Langtjern from 1990.

Chemical analyses of wet deposition are daily analysed (if precipitation), continuously during 1974 to 1991 at Birkenes, Storgama and Langtjern, except for one year (1979) at Storgama. At Kaarvatn similar continuous data series are available from 1980-1991.

Chemical analyses of runoff water are performed at least weekly at all sites. At Birkenes samples are continuously analysed from 1974-1978, from 1981-1983 and from 1985-1991. At Storgama weekly samples are analysed from 1975-1991, except for 1979. At Langtjern similar sample/analysis program exists back to 1974, except for the year 1984 and 1985. At Kaarvatn same kind of data set exists from 1980, except for 1985.

The scientific and technical work is carried out by research institutes under contract with SFT. At some of the station, the number of parameters analysed have increased as new aspects or problems arose. Today the monitoring programme includes the following parameters:

Dry deposition:
Gas: SO_2 and NO_2
Gas and particles: $\Sigma NH_4^+ + NH_3$ and $\Sigma NO_3^- + HNO_3$
Particles: SO_4^{2-}, Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-

Wet deposition:
Precipitation (mm),
Conductivity$^{20°C}$ (Conductivity $^{25°C}$/1.10 = Conductivity$^{20°C}$)
Major cations: H^+ (pH), Ca^{2+}, Mg^{2+}, Na^+, K^+, NH_4^+
Major anions: SO_4^{2-}, NO_3^-, Cl^-
Trace element: As, Pb, Cd, Cr, Co, Zn, Ni, Cu

Stream water:
Runoff (mm)
Conductivity$^{25°C}$
Major cations: H^+ (pH), Ca^{2+}, Mg^{2+}, Na^+, K^+, NH_4^+, acid-reactive Al (Al_r), labile Al (LAl), non-labile Al (ILAl)
Major anions: SO_4^{2-}, NO_3^-, Cl^-, HCO_3^-, total organic carbon (TOC).

SAMPLING AND ANALYSIS

2.1 Sampling

At Birkenes, Storgama and Langtjern, the weather stations are located some distance from the catchments, i.e. 1 km north-east of Birkenes; 8 km south-west of Storgama, and 5 km west of Langtjern. Thus, the amount of precipitation (mm) might differ from that really precipitates into these catchments. At Kaarvatn the weather-station is located at the outlet of the catchment. However, because of the large catchment area (25 km²) and the large latitude gradient within this catchment, the precipitation measured at the weather-station at the outlet might differ significantly from that really precipitating in this catchment. For all catchments, the amounts of precipitation are estimated, assuming the measured runoff data and the estimated evapotranspiration data to be the most accurate.

Wet deposition is collected in an open polyethylene bulk. The gages are positioned 2.0 m above the ground, and always located in open areas to avoid contamination, which might be a great problem if the collector is located in a forested area. No overhead obstruction is allowed above an angle of 45° from the opening of the collector. The collection area of the all gages is 314 cm². The design of the snow-sampler (winter-period) and the rain-sampler (summer-period) bulks differ to some extend (SFT-Report 26/81). The collectors are sampled daily, i.e. every morning at 8.00. Washing procedure is described in Norwegian Standard, N.S. 4864. The samples are stored at 4°C, and analysed at the Norwegian Institute for Air Research (NILU).

Atmospheric gases, aerosols and particles of different sulphur and nitrogen compounds are collected by pumping 17 m³ of air per day through the various types of filters. More details concerning the filters are present under description of the various analytical methods. The filters are collected weekly and analysed at NILU.

Runoff through a V-notch weir and water level recorder have been monitored continuously at all four locations. The stream water is collected using the "grab" spot method, using 500 mL high density polypropylene bottles. Samples are collected weekly. The samples are stored at 4°C, and analysed at NIVA. Stream water samples are collected weekly or more frequently during hydrologic episodes.

2.2 Analysis

Analysis of wet deposition.

pH (-log[H^+])
pH was measured potentiometrically using a pH-meter (type) and combined glass electrode.

Sulphate (SO_4^{2-})
Sulphate was measured by ion chromatography (IC), model Dionex 10.
Detection limit: 0.01 mg SO_4-S/L (0.63 µeq/L)

Nitrate(NO_3^-)
Nitrate was measured by IC, model Dionex 10.
Detection limit: 0.005 mg NO_3-N/L (0.36 µeq/L)

Ammonium (NH_4^+)
Ammonium was measured by the indophenolblue method, which is based on the reaction between ammonium, salicylic acid and sodiumhypochlorite using sodium- nitroprusside (sodium nitroferricyanide dihydrate) as catalyst in order to intensify the blue colour at room-temperature. The absorption measurement is carried out at 660 nm.
Detection limit: 0.04 mg NH_4-N/L (2.86 µeq/L)
Precision: 1-2%

Chloride (Cl^-)
Chloride was measured by IC, model Dionex 10.
Detection limit: 0.01 mg Cl/L (0.28 µeq/L)

Sodium (Na^+)
Sodium was measured by flame-emission spectroscopy at 589.6 nm.
Detection limit: 0.05 mg Na/L (2.17 µeq/L)

Calcium, magnesium, potassium (Ca^{2+},Mg^{2+},K^+)
Calcium, magnesium, potassium were measured by atomic absorption spectroscopy (air/acetylene flame) at 766.5, 422.7, 285.5 nm, respectively.
Detection limit calcium: 0.01 mg Ca/L (0.50 µeq/L)
Detection limit magnesium: 0.01 mg Mg/L (0.82 µeq/L)
Detection limit potassium: 0.01 mg K/L (0.26 µeq/L)

Analysis of dry deposition.

Sulphur-dioxide (SO_2)

Sulphur-dioxide was measured by adsorbing the gas onto a filter containing potassium-hydroxide (KOH). The filter was then extracted in water and then extracted in hydrogen-peroxide (H_2O_2). The SO_4-S that is formed is analysed by IC, model Dionex 10.
Detection limit: 0.1 µg SO_2-S m^{-3}
Estimated dry deposition velocity of SO_2:
Summer (1 April - 30 September): 0.7 cm s^{-1}
Winter (1 October - 31 March): 0.1 cm s^{-1}

Particulate sulphate (SO_4^{2-})

Particulate sulphate was measured by IC, model Dionex 10, from a water-extract of the particle filter Whatman 40.
Detection limit: 0.1 µg SO_4-S m^{-3}.
Estimated dry deposition velocity of SO_4-particles:
Summer (1 April - 30 September): 0.6 cm s^{-1}
Winter (1 October - 31 March): 0.2 cm s^{-1}

Nitrogen dioxide (NO_2)

Nitrogen dioxide was measured by the TGS-method (version of the Norwegian Standard 4855). NO_2 is absorbed in a solution containing tri-ethanol-amine, o- methoxy-phenol (guaiacol) and sodium-di-sulphite. The nitrite formed, reacts with sulphanilamide and N-(1-naphtyl)-ethylenediamine-dihydrochloride (NEDA), forming a coloured complex that is analysed spectrophotometrically at 550 nm.
Detection limit: 0.3-0.5 µg NO_2-N m^{-3}
Estimated dry deposition velocity of NO_2:
Summer (1 April - 30 September): 0.5 cm s^{-1}
Winter (1 October - 31 March): 0.1 cm s^{-1}

Ammonium + ammonia ($\Sigma NH_4^+, NH_3$)

Gas and particles of $\Sigma NH_4^+, NH_3$ retained on a filter containing oxalic-acid are extracted with water, and the extract is then analysed regarding ammonium by the indophenolblue method (see analysis of NH_4 above).
Detection limit: 0.05 µg NH_4-N m^{-3}
Estimated dry deposition velocity of NH_4 and NH_3 in air:
Summer (1 April - 30 September): 0.6 cm s^{-1} and 0.7 cm s^{-1}
Winter (1 October - 31 March): 0.2 cm s^{-1} and 0.1 cm s^{-1}
From this analysis, 8% is estimated to be NH_3 and 92% to be NH_4^+.

Nitrate + nitric acid ($\Sigma NO_3^-, HNO_3$)

Gas and particles of $\Sigma NO_3^-, HNO_3$ retained on a filter containing sodium-hydroxide are extracted with water, and the extract is then analysed with respect to nitrate by IC, model Dionex 10.
Detection limit: 0.01 µg NO_3-N m^{-3}
Estimated dry deposition velocity of NO_3 and HNO_3:

Summer (1 April - 30 September): 0.6 cm s^{-1} and 2.5 cm s^{-1}
Winter (1 October - 31 March): 0.2 cm s^{-1} and 1.5 cm s^{-1}
From this analysis, 25% is estimated to be HNO_3, 75% to be NO_3^-.

Calcium, magnesium, potassium (Ca^{2+},Mg^{2+},K^+)
Calcium, magnesium and potassium were measured from a water extract of a Whatman 40 sulphate filter by atomic absorption spectroscopy (air/acetylene flame) at 766.5, 422.7, and 285.5 nm, respectively. Dry deposition velocities for Ca, Mg, and K are not available, because the particle-size might differ significantly. Assuming chloride only originating from seasalts and also being a conservative ion, i.e. $Cl_{out} = Cl_{in}$, it is possible to estimate the marine dry-deposition parts of base cations by further assuming the equivalent ratios of chloride/base-cations still present as in sea-water.
Detection limit Ca: 0.02 μg m^{-3}
Detection limit Mg: 0.02 μg m^{-3}
Detection limit K: 0.02 μg m^{-3}

Chloride (Cl^-)
Chloride was measured by IC, model Dionex 10.
Detection limit: 0.01 mg Cl/L (0.28 μeq/ L)

Sodium (Na^+)
Sodium was measured by flame-emission spectroscopy at 589.6 nm.
Dry deposition velocity is not given, because the particle-size might differ significantly.
Detection limit: 0.05 mg Na/L (2.17 μeq/L)

After 1 March 1989, all air-compounds, except NO_2, are analysed from a filter-pack composed of a teflon particle filter (Zeflour 2 μm), an alkalic impregnated (by potassium-hydroxide and glycerol) Whatman 40 filter, and an acid impregnated (by oxalic acid) Whatman 40 filter. The particle filter is extracted with 10^{-4} M formic acid in an ultrasound bath. The potassium-hydroxide filter is extracted with water containing hydrogen-peroxide, and the oxalic-acid filter is extracted with 10^{-2} M nitric acid. The analyses are then performed as described earlier. The amount of $\Sigma NH_4^+,NH_3$ is calculated by adding the amount of NH_4 from the particle filter and the oxalic-acid filter. The amount of $\Sigma NO_3^-,HNO_3$ is calculated by adding up the amount of NO_3 from the particle filter and the potassium-hydroxide filter.

Analysis of stream water.

pH (-log[H^+])
The pH was measured potensiometrically using a pH-meter, Orion Research 901 Ion Analyser, with separate glass-electrode and reference-electrode. Reference: Norwegian Standard, NS 4720.
Results from internal calibration at NIVA:
pH: 5.51 ± 0.070 (n=15).

Calcium, Magnesium, Sodium, Potassium (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+})

These elements were analysed by Atomic Absorption flame Spectrophotmetry (AAS), Perkin Elmer 560, after acidifying the water samples by nitric acid (HNO_3) to $pH < 2.0$. References: Norwegian Standard, NS 4770, NS 4775 (Na, K), NS 4776 (Ca, Mg).

Detection limit Ca: 0.01 mg/L (0.5 μeq L^{-1})
Detection limit Mg: 0.001 mg/L (0.08 μeq L^{-1})
Detection limit Na: 0.002 mg/L (0.09 μeq L^{-1})
Detection limit K: 0.01 mg/L (0.26 μeq L^{-1})
Results from internal calibration at NIVA:
Ca: 1.00 ± 0.013 (n=34) (mg/L)
Mg: 1.00 ± 0.008 (n=20) (mg/L)
Na: 1.00 ± 0.013 (n=24) (mg/L)
K : 1.00 ± 0.009 (n=20) (mg/L)

Sulphate and chloride (SO_4^{2-}, Cl^-)

Sulphate and chloride were measured by ion chromatography (IC), model Waters ILC-1 Ion Chromatograph. Before October 1985, sulphate was analysed using the methyl thymol blue (MTB) method. It is well documented that the MTB method results in an overestimate of sulphate in dystrophic (coloured) natural waters (Cronan, 1979); Kerekes et al,. 1984). However, because total organic carbon (TOC) was not measured before 1985, and it is only the runoff-water from Langtjern that contains high concentrations of TOC, no corrections have been made. Even at Langtjern the influence from TOC on the MTB method is relatively small compared with the changes in sulphate during the monitoring period. For those who are interested in estimating the influence of TOC on the MTB method, the following equation should be used:

Sulphate^1 = Sulphate^2 - 0.046*TOC (mg C/L)
Sulphate^1 : IC-method; **Sulphate^2** : MTB method.

Detection limit sulphate (IC): 0.067 mg/L (4.17 μeq/L)
Detection limit chloride: 0.2 mg/L (5.64 μeq/L)

Results from internal calibration at NIVA (IC):
SO_4-S: 2.9 ± 0.07 (n=42) (mg/L)
Cl^- : 8.5 ± 0.19 (n=44) (mg/L)

Ammonium (NH_4^+)

Ammonium reacts with phenol and alkaline hypo-chlorite to give indophenol-blue. Sodium nitroprusside intensifies this blue colour at room temperature. The absorbance measurement is carried out at 630 nm. The analysis is conducted by autoanalysator, Technicon II Autoanalyser. Reference: Norwegian Standard, NS 4746.

Detection limit ammonium: 5 μg/L (0.4 μeq/L)
Precision: 1-2%
Results from internal calibration at NIVA:
NH_4-N : 205 ± 7.6 (n=35) (μg/L)

Nitrate and nitrite (NO_3^-, NO_2^-)

Nitrate is quantitatively reduced to nitrite by a cadmium-copper couple in alkaline NH_4-buffered solution (pH 8). In a strongly acid medium nitrite reacts with sulphanilamide to form diazonium compound, which react quantitatively with N-(1-naphtyl)ethylenediamine-dihydrochloride to form a strongly coloured azo compound. The absorbance measurement is carried out at 545 nm. The analysis is conducted by autoanalysator, Technicon II Autoanalyser. Reference: Norwegian Standard, NS 4745.
Detection limit ammonium: 1 µg/L (0.07 µeq/L)
Precision: 1,5%
Results from internal calibration at NIVA:
NO_3-N : 51 ± 1.7 (n=41) (µg/L)

Alkalinity (CO_3^{2-}, HCO_3^-, OH^-)

In most freshwaters, the alkalinity is basically the amount of CO_3^{2-}, HCO_3^- and OH^- present in solution. Alkalinity is measured by potentiometric titration with hydrochloric acid to pH 4.5 (total alkalinity). It should be noted that organic anions and some inorganic ions ($SiO(OH)_3^-$, $H_3BO_3^-$, NH_4^+, HS^-) will be included in the total alkalinity estimate, and so may colloidal and suspended $CaCO_3$. Reference: Norwegian Standard, NS 4754.

Aluminium

Aluminium reacts with pyrocatechol violet (PCV) at pH 5.9-6.4, forming a blue coloured complex. The absorbance measurement is carried out at 581 nm. The analysis is conducted by auto-analysator, Technicon II Autoanalyser.
Reference: Norwegian Standard, NS 4747.
Detection limit Al: 10 µg/L (1.1 µeq L^{-1})
Results from internal calibration at NIVA:
Al: 376 ± 5.3 (n=22) (µg L^{-1})

Total organic carbon (TOC)

The organic carbon is oxidised to CO_2 by peroxydisulphate and UV-radiation in strongly acidic environment. The CO_2 formed is then measured spectrometrically using an infra-red (IR) gas analysator with NDIR-detector, ASTRO 2001 TOC Analyser. Reference: Norwegian Standard, NS-ISO 8245.
Detection limit TOC: 0.1 mg C/L
Results from internal calibration at NIVA:
TOC: 4.99 ± 0.11 (n=30) (mg/L)

2.3 Definition of terms

All concentrations are primarily expressed in µeq/L. The following cations and anions are analysed in both wet deposition and runoff waters :

CATIONS: Ca^{2+}, Mg^{2+}, Na^+, K^+, H^+
ANIONS : SO_4^{2-}, HCO_3^-, NO_3^-, Cl^-

Ammonium (NH_4^+) is only measured in wet deposition, while two other parameters, aluminium and total organic carbon (TOC), are analysed in runoff water. The average charge of aluminium is estimated by the aluminium-speciation programme ALCHEMI-Version 4.0 (Schecher and Driscoll 1987,1988). The speciation programme is loaded with monthly weighted mean values of temperature, reactive Al, TOC and major cat- and anions. In the aluminium-speciation programme, the concentration of fluoride (F^-) and silicic acid (H_4SiO_4) are not measured, but estimated to be 100 µg F/L and 2 mg SiO_2/L at all field sites. All the applied equilibrium and complex-constants used are those originally present in the programme.

On the basis of the measured parameters the charge balance (CB) is calculated as:

$$CB = ([Ca^{2+}]+[Mg^{2+}]+[Na^+]+[K^+]+[NH_4^+]+[H^+]+[\Sigma Al^{n+}]) - ([SO_4^{2-}]+[Cl^-]+[NO_3^-]+[HCO_3^-]+[OH^-]+[A^-])$$

$[A^-]$ is an expression for the amount of organic anions. If the major ions incorporated in the charge balance equation are all measured, the amount of $[A^-]$ (µeq/L) can be estimated, so that charge balance is obtained. The concentration of ΣAl^{n+} is the sum of positively charged Al-ions, estimated by the Al-speciation programme, ALCHEMI-Version 4.0 (Schecher and Driscoll, 1987,1988).

In wet deposition, only minor amounts of aluminium (ΣAl^{n+}) are present, and because the pH of wet deposition usually is < 5, the amounts of bicarbonate (HCO_3^-) and hydroxide (OH^-) are minimal too. These parameters are therefore omitted in the charge balance of rain water.

In runoff water, only minor amounts of ammonium (NH_4^+) and hydroxide (OH^-) are present, and therefore omitted in the charge balance. If the runoff water pH < 5, the concentration of bicarbonate is also very low and omitted, but if pH > 5, bicarbonate is incorporated in the charge balance.

On the basis of the assumption above, one may calculate the acid neutralising capacity (ANC) of rain- and runoff water as:

ANC_{rain}:

$$([Ca^{2+}]+[Mg^{2+}]+[Na^+]+[K^+]+[NH_4^+]) - ([SO_4^{2-}]+[Cl^-]+[NO_3^-]) = [H^+]$$

ANC_{runoff}:

$$([Ca^{2+}]+[Mg^{2+}]+[Na^+]+[K^+]) - ([SO_4^{2-}]+[Cl^-]+[NO_3^-]) = ([A^-]+[HCO_3^-])-([H^+]+[\Sigma Al^{n+}])$$

Of the strong acid anions, Cl^- is the most mobile, usually following water through the ecosystem from precipitation to runoff, i.e. **$Cl_{in} = Cl_{out}$**. The major source of Cl^- is from pH-neutral seasalts, entering the terrestrial ecosystems both as wet- and dry-deposition. The equivalent relationship between Cl^- and other major ions of sea water is therefore used in order to estimate the contribution of non-marine ions in rain and surface water. This method seems very applicable when estimating the non-marine fraction of many major ions. The non-marine supply of ions (corrected for seasalt contribution) are always marked with asters, and the equivalent correction factors used are as follows:

$[Ca^{2+}]^* = [Ca^{2+}] - 0.037*[Cl^-]$
$[Mg^{2+}]^* = [Mg^{2+}] - 0.195*[Cl^-]$
$[K^+]^* = [K^+] - 0.018*[Cl^-]$
$[Na^+]^* = [Na^+] - 0.856*[Cl^-]$
$[SO_4^{2-}]^* = [SO_4^{2-}] - 0.103*[Cl^-]$

If the atmospheric input contains significant amounts of acid Cl^- ions, the concentration of Mg^{2+} can be used instead of Cl^-. Thus, the concentration of non-marine sulphate can be estimated as:

$$[SO_4^{2-}]^{**} = [SO_4^{2-}] - 0.520*[Mg^{2+}]$$

2.4 Statistics

Only simple linear regression is used for statistical evaluation of the long term trends, based on either monthly or annual weighted averages. Correlation coefficent at the 5% level is accepted as criterion for significance.

3. DESCRIPTION OF THE CATCHMENTS

Birkenes

The Birkenes catchment is situated in southernmost Norway, about 15 km north of Kristiansand in the county of Aust-Agder (Figure 3.1, 3.2). The catchment area is 0.41 km^2. Altitude in the catchment ranges from 200-300 m and the average catchment gradient is 1:6. The granite rock (biotite-granite) is overlain by a thin layer of soil (mean depth < 20 cm). Approximately 90 % of the soil is characterised as podzol and peaty podzol, low in pH and base-saturation. The forest is primarily Norwegian spruce and pine with some birch: The field vegetation does primarily consist of various heather-species (SFT Report 26/81).

Storgama

The Storgama catchment is situated 35 km north of the Birkenes catchment, approximately 50 km inland in the county of Telemark (Figure 3.1, 3.2). The catchment area is 0.6 km^2. Altitute in the catchment ranges from 580-690 m. About 22% of the catchment is exposed granitic bedrock, a further 49% has rankers and shallow podzols, while 19% of the area has a peat cover > 30 cm in depth (Christophersen et al., 1984). In the middle of the catchment is a small shallow lake. The vegetation of the peaty rankers consists of pine, birch and heather species (SFT Report 26/81).

Langtjern

The Langtjern catchment is situated about 100 km north-west of Oslo in the inland of the county of Buskerud (Figure 3.1, 3.2). The catchment area is 4.8 km². Altitude in the catchment ranges from 510-750 m. The geology is basically biotite-gneiss and granite from Precambrian. About 16% is exposed bedrock, 16% is peat, and 5% is open water (Wright and Henriksen, 1980). The soil cover is very thin with a low organic content. About 63% is open coniferous forest with some birch with heather-species predominate as field vegetation (SFT Report 26/81).

Kaarvatn

The Kaarvatn catchment is situated at the north-western part of southern Norway in the county of Moere and Romsdal (Figure 3.1, 3.2). The catchment area is 25 km². Altitude in the catchment range from 200-1375 m. The geology consists of heterogeneous and homogeneous gneisses and quartzites. The podzolic and peaty soil covers are thin. The vegetation is alpine, i.e. heather vegetation. Some birch is present, south in the catchment. The catchment is relatively unaffected by polluted rain, i.e. the chemical compounds of rain are mainly of marine origin (SFT Report 26/81).

Table 3.1 Some catchment-characteristics of the four monitored catchments.

	Birkenes	**Storgama**	**Langtjern**	**Kaarvatn**
Geographic description				
Latitude (N)	58°23'	59°01'	60°22'	62°47'
Longitude (E)	8°15'	8°32'	9°39'	8°53'
Catchment-area (km^2)	0.41	0.6	4.8	25
Altitude (m)	200-300	580-690	510-750	200-1375
Hydrology				
Mean annual precipitation(mm)	1490 ± 251	1040 ± 258	735 ± 145	1378 ± 262
Mean annual precipitation (mm)*	1529 ± 283	1206 ± 273	864 ± 159	2175 ± 275
Mean annual runoff	1169 ± 288	947 ± 287	614 ± 186	1856 ± 306
Area-distribution (%)				
Bare rock, and area with thin soil	3	59	74	76
Bog/Marsh	7	22	16	2
Forest with thicker soil profile	90	11	5	18
Water/lakes	-	8	5	4
Dominating bedrock	granite, biotite	granite	gneiss	gneiss, quartzite

*: Estimated precipitation, see Chapter 4 (Hydrology).

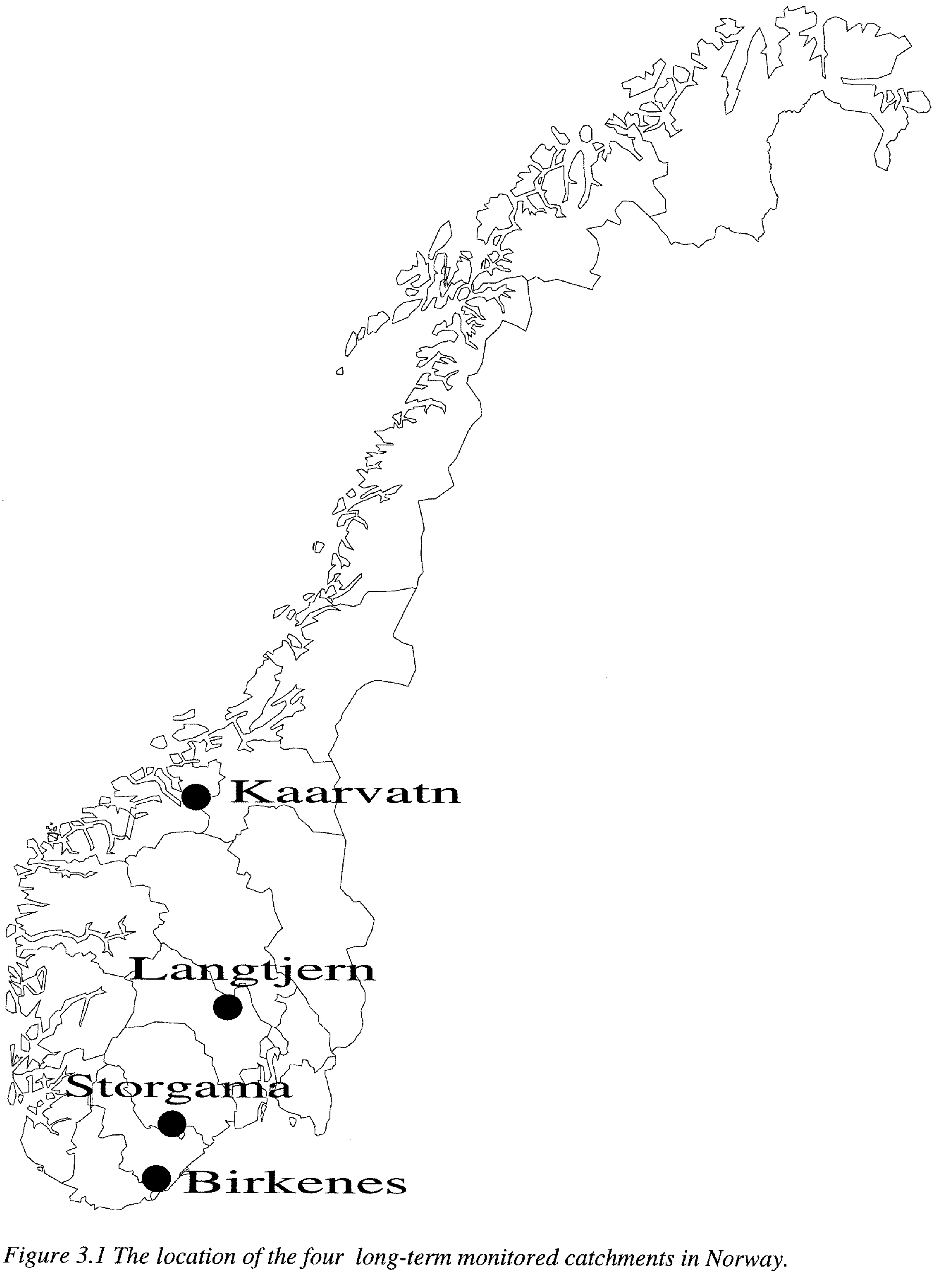


Figure 3.1 The location of the four long-term monitored catchments in Norway.

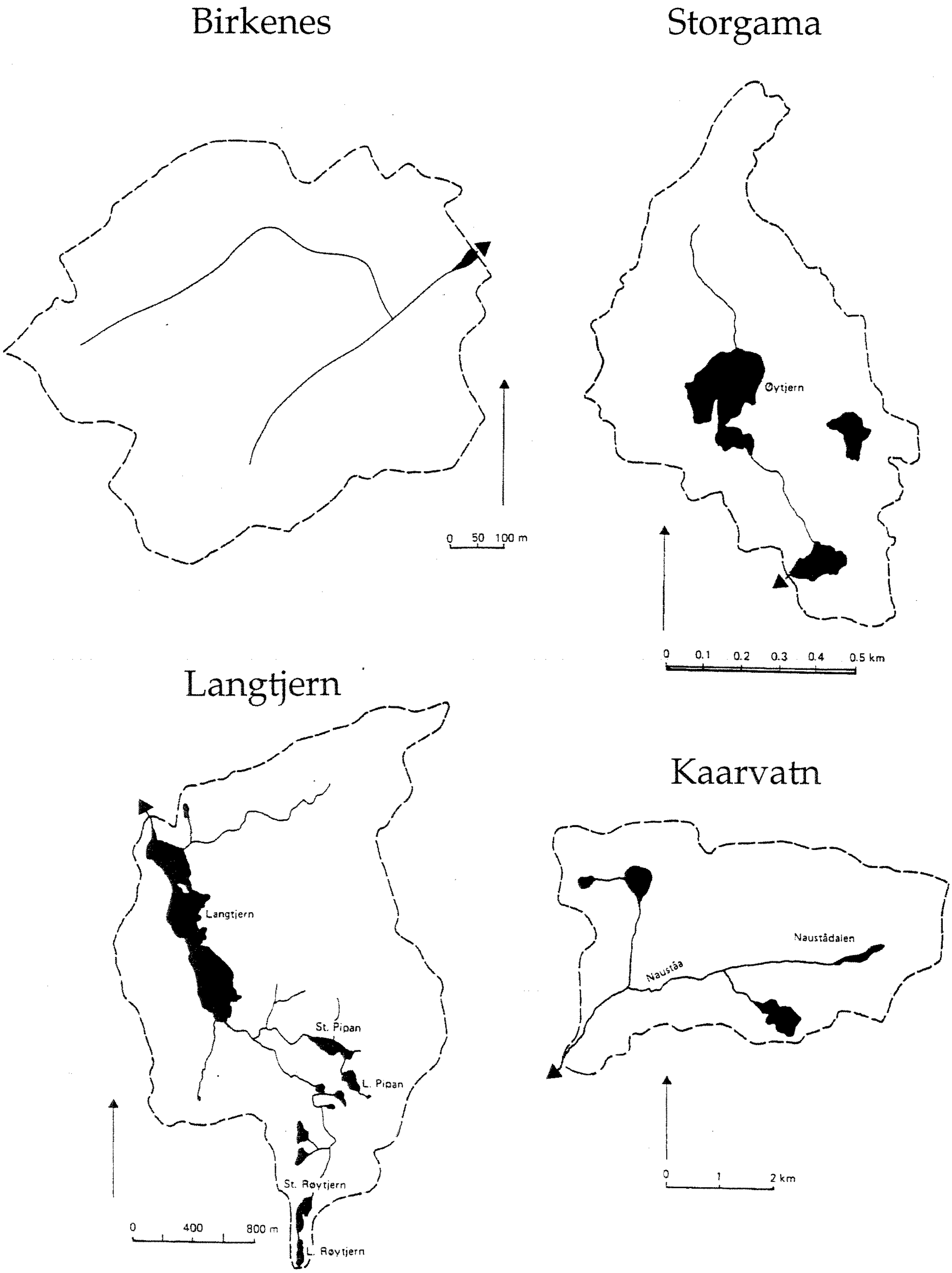


Figure 3.2 The four catchments, Birkenes, Storgama, Langtjern and Kaarvatn.

4. HYDROLOGY

4.1 Hydrologic year

The vital role of water as transporting agent, chemical solvent, and catalyst, means that the quality of hydrologic data are very important to understand and/or interpret the biogeochemical response of water entering a catchment.

In Norway, as in many corresponding climatic regions, the annual variations in air temperature have large impacts on the hydrology. The influence is most obvious at winter time when substantial amounts of precipitation are retained in the catchment as snow until spring melt. Other hydrological characteristics in most parts of Norway are dry periods during summer and early autumn, and significant precipitation periods during autumn and early winter. The calendar year (1 January to 31 December) is therefore very seldom the best water-year. Selection of a suitable water-year is a primary consideration for hydrological analyses and water-chemical interpretations. The ideal water-year is that successive 12-month period that most consistently, year after year, gives the highest correlation between precipitation and runoff. In such watersheds as presented in this investigation, runoff is largely dependant on: **(1)** Amount of precipitation; **(2)** Amount of water stored in the snow pack; **(3)** Amount of storage opportunity in the soil and thereby the amount of water stored in the soil at any time. **(4)** Evapotranspiration during summer.

After a large array of linear regressions for successive 12-months periods of precipitation and runoff had been examined, the water-year at Birkenes and Langtjern begins on June 1 and ends May 31, while at Storgama and Kaarvatn it starts on September 1 and ends August 31. The best water-years gave relatively high correlation between precipitation and runoff at all stations, i.e. the correlation coefficients (r^2) were 0.96, 0.95, 0.74, and, 0.86, at Birkenes, Storgama, Langtjern and Kaarvatn, respectively (Figure 4.1). The most important criteria for a good input/output correlation of water are: **(A)** Although the evapotranspiration during summer leaves the soils in variable states of water content, autumn rains completely replenish water depleted during the summer; **(B)** Water storage capacity in the catchment is relatively small; **(C)** The addition of water to the soil during melting of the snow pack is sufficient to fully recharge the soil.

Except at Birkenes, the correlation between precipitation and runoff are highly dependant on the water year chosen (Figure 4.1). This means that the runoff does continuously respond according to precipitation, without significant delay, during large parts of the year. The relatively high correlation at Birkenes also during winter indicates that the winter precipitation often falls as rain in this area, or if the precipitation comes as snow, it often melts relatively fast.

At the three other stations, far more of the winter precipitation is snow. Thus, the best correlation between annual inputs and outputs of water at these sites are far more dependant on the water-year chosen (Figure 4.1).

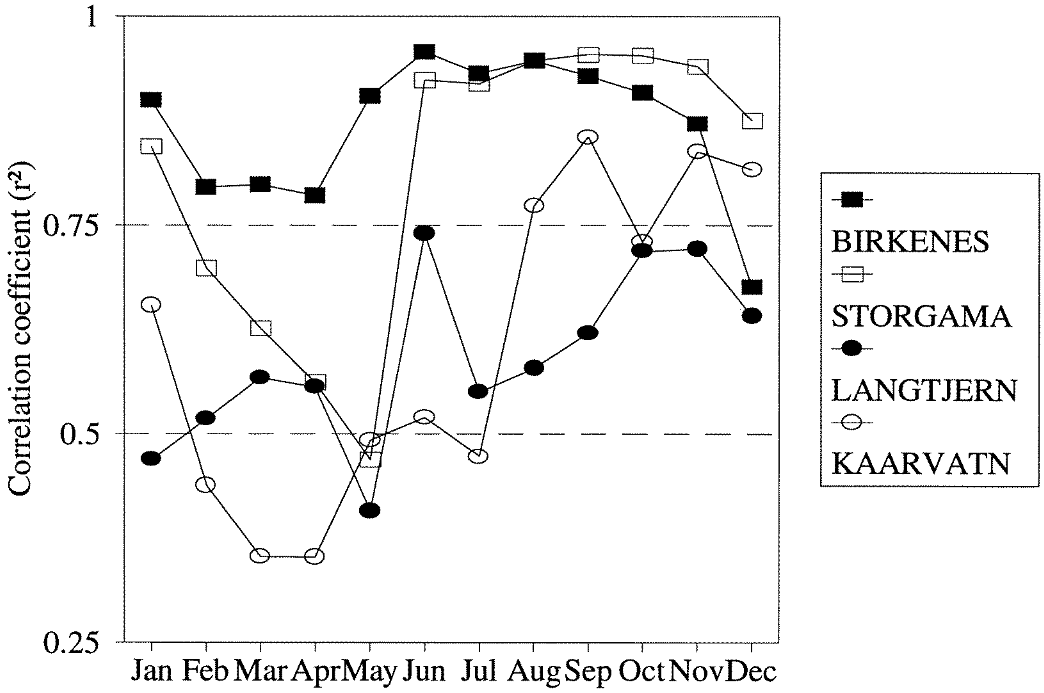


Figure 4.1 The correlation coefficients (r^2) between precipitation and runoff at the four catchments, based on linear regressions for the different successive 12 month periods.

Why lower correlations were found between annual inputs and outputs of water at Langtjern and Kaarvatn, compared with Birkenes and Storgama, may rely on different causes. At Langtjern, a lake, as well as boggy areas in the catchment act as important water sinks that buffer or moderate the hydrological extreme periods. Thus, the temporary storing capacity of water is higher in this catchment compared with at Birkenes and Storgama. At Kaarvatn, the weather-station is located at the outlet of the catchment. Because the catchment is very large, with large latitude variations and thus large orographic differences, the weather-station is not very representative for the whole catchment. In addition a large catchments per se often has more complex or inhomogenious hydrology compared with smaller catchments like Birkenes and Storgama.

4.2 Estimation of precipitation

Even though precipitation and runoff are monitored accurately, the 4 weather-stations do not necessarily represent the precipitation input to the catchments. At Kaarvatn, weather-station is located at the outlet of the catchment. However, measured runoff is much higher than measured precipitation. Because the catchment is very large (25 km²) and the altitude within the catchment range from 200-1375 m, the weather-station is not very representative for the weather-condition over the whole catchment. The weather-stations at the 3 other sites are located at some distance from the catchments, but the disagreements between measured precipitation and runoff are, however, much smaller. Linear regressions between annual precipitation and runoff during the monitoring period should reflect these relationships.

It is possible to estimate the annual precipitation at each catchment. The relationship between annual measured runoff (**R_m**) and annual measured precipitation (**P_m**) is expressed by equation:

$$R_m = aP_m + b \qquad \text{(I)}$$

R_m : Measured runoff (mm)
P_m : Measured precipitation (mm)
a : P_m -coefficient
b : Constant ($R_m = b$ when $P_m=0$)

The evapotranspiration values are estimated (ET_e), based on an evapotranspiration map of southern Norway (Soegnen, 1967). Annual evapotranspirations are estimated to be 350, 250, 250, and 300 mm at Birkenes, Storgama, Langtjern and Kaarvatn, respectively (Table 4.1). Including evapotranspiration in the equation of hydrology, the annual amount of precipitation can be estimated (P_e) by the following equation:

$$P_e = R_m + ET_e \qquad \text{(II)}$$

By combining equation (I) and (II) it is possible to estimate the annual precipitation at each site as:

$$R_m = aP_m + b + ET_e \qquad \text{(III)}$$

On the basis of annual input data from the beginning of the monitoring period up to 1990/91, the following regressions between measured and estimated input of water exist:

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

Table 4.1 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 ± 70	253 ± 61	250 ± 94	319 ± 125
Calendar-year				
No. of days $P_m > 0.1$ mm	186 ± 15	162 ± 17	163 ± 15	199 ± 16
Precipitation(P_m) mm	1480 ± 216	1001 ± 177	734 ± 128	1369 ± 262
Intensity (P_m) mm/day***	7.4 ± 0.9	5.7 ± 0.7	4.4 ± 0.6	6.6 ± 0.9
Precipitation (P_e) mm	1523 ± 210	1173 ± 168	856 ± 140	2135 ± 222
Intensity (P_e) mm/day***	8.2 ± 1.0	6.9 ± 1.8	5.3 ± 0.5	10.6 ± 0.7
Runoff (R_m) mm	1157 ± 207	915 ± 183	605 ± 191	1826 ± 278
Water-year				
No. of days $P_m > 0.1$ mm	188 ± 15	163 ± 19	164 ± 12	200 ± 20
Precipitation (P_m) mm	1490 ± 251	1040 ± 258	735 ± 145	1378 ± 262
Intensity (P_m) mm/day***	7.4 ± 1.1	5.9 ± 0.9	4.4 ± 0.7	6.5 ± 0.9
Precipitation (P_e) mm	1529 ± 283	1206 ± 273	864 ± 159	2175 ± 275
Intensity (P_e) mm/day***	7.6 ± 1.3	7.4 ± 1.0	5.1 ± 0.7	10.3 ± 0.9
Runoff (R_m) mm	1169 ± 288	947 ± 288	614 ± 187	1856 ± 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.*

Accumulation of snow during the winter is estimated as $\text{Water}_{\textbf{input}}$ - $\text{Water}_{\textbf{output}}$, during 1 November to 31 March. Corresponding relation is used for runoff estimates during spring melt, at Birkenes, Storgama and Langtjern from 1 April to 31 May. At Kaarvatn, in addition the whole June is incorporated in the spring melt period due to the large catchment-area/latitude-gradient, which significantly elongates the melting period. It is not uncommon that the melting period at Kaarvatn may last until the end of July.

During autumn a runoff-percent for each month is estimated, which means the P_e/R_m-ratio (%). At late autumn the catchments are relatively water saturated. Thus, the precipitation during this period leaves the catchments relatively fast, i.e. runoff percent (P_e/R_m-ratio) is high.

4.3 Birkenes

At Birkenes, air-temperature is only recorded daily from 1980-1991. At the weather-station, Kjevik, located 25 km south of Birkenes, daily air-temperature data are available back to 1974. By linear regressions between monthly mean temperatures at the two sites during 1980-1991, the air temperature (°C) at Birkenes during the whole monitoring period (1974-1991) is calculated, quarterly and yearly (based on annual means) by the following regressions:

Yearly:	Birkenes: 1.02*Kjevik - 1.37	r=0.83	(n=11)
Jan-Mar:	Birkenes: 1.035*Kjevik - 1.43	r=0.97	(n=33)
Apr-Jun:	Birkenes: 1.063*Kjevik - 1.53	r=0.98	(n=33)
Jul-Sep:	Birkenes: 1.079*Kjevik - 2.32	r=0.90	(n=33)
Oct-Nov:	Birkenes: 0.921*Kjevik - 1.49	r=0.93	(n=33)

Air temperature at Birkenes during the monitoring period is present in Table 4.2. Annual mean air temperature at Birkenes during the period is 5.4 ± 1.1°C. During the monitoring period there is a tendency of elevated air temperatures for all time intervals present in Table 4.2, but the increases are not significant ($p < 0.05$). However, from 1985-1991 a significant increase in the annual mean temperature by 0.6°C per year ($r = 0.81$) is observed. This increase is a result of an increase for all quarters, but only the increases in the 1st quarter (Jan-Mar) and the 3rd quarter (Jul-Sep) are significant. In the 1st and 3rd quarter, the increase in air temperature is 1.4°C ($r = 0.76$) and 0.5°C ($r = 0.89$) per year. The increase in air temperature at Birkenes during the winter has large hydrological consequences, because the winter temperature the last years has been ≥ 0° C. Accordingly, large amounts of the winter-precipitation fall as rain, or if snow, it melts relatively fast. Thus, substantial amounts of the precipitation during winter are able to leave the catchment relatively fast, and no subsequent important spring melt occurs. Because, mild winters seem to occur no and then in this area (Table 4.2), more years of monitoring are needed to confirm the tendency of increasing winter-temperature being more than natural variations.

The annual precipitation mean at the weather-station at Birkenes during the monitoring period is 1490 ± 251 mm (water-year: Jun-May), distributed on 188 ± 15 precipitation days (input > 0.1 mm), with an average intensity of precipitation of 7.4 ± 1.1 mm. Estimated annual precipitation in the Birkenes catchment (P_e) during a water year is expressed by the following equation: $P_e = 1.13P_m - 155$ ($r = 0.98$). By this relationship, annual precipitation mean at Birkenes is 1529 ± 283 mm, with an average intensity of 7.6 ± 1.3 mm. On average, the weather-station at Birkenes underestimates the annual precipitation by 39 ± 33 mm (≈ 2%).

Lowest annual precipitation at Birkenes was recorded in 1975/76 with 1062 mm, the highest (2174 mm) in 1987/88 (Figure 4.2)

Highest monthly precipitation normally occurs in October (Figure 4.3) with a monthly average of 219 ± 122 mm. The precipitation in October is about 30% higher than the second most precipitation rich months, September and November. While on average 14.0 ± 6.3% of the annual precipitation enters the catchment in October, more than 35% of annual precipitation enters the catchment during the three wettest months, from 1 September to 30 November.

Table 4.2 Annual mean temperatures at Birkenes from 1974-1991, and mean temperatures during each successive three months period, during winter (1 Nov - 31 Mar) and spring (1 Apr. - 31 May).

Year	Annual Jan-Dec	1st quarter Jan-Mar	2nd quarter Apr-Jun	3rd quarter Jul-Sep	4th quarter Oct-Dec	Spring Apr-May	Winter Nov-Mar
1974	6.1	0.7	9.6	12.2	2.1	7.4	
1975	6.5	-0.0	8.2	14.3	3.3	6.0	0.5
1976	5.2	-2.4	9.3	13.2	0.5	6.7	-0.6
1977	4.7	-3.5	8.1	12.2	2.1	5.3	-2.8
1978	4.8	-2.8	8.5	11.9	1.5	6.0	-1.7
1979	3.6	-5.8	7.2	12.0	1.0	4.3	-3.9
1980	4.7	-5.2	9.4	13.4	1.3	7.1	-3.5
1981	4.6	-2.2	8.3	13.0	-0.6	6.8	-1.3
1982	5.6	-2.9	8.7	13.7	3.0	6.5	-3.0
1983	6.2	-0.1	8.3	13.9	2.9	6.1	0.5
1984	6.0	-2.4	9.3	13.1	4.1	6.9	-1.0
1985	3.8	-5.3	8.2	11.8	0.5	6.1	-2.2
1986	4.4	-5.0	8.1	11.5	3.1	5.1	-4.0
1987	4.1	-5.5	7.5	11.7	2.7	5.8	-2.7
1988	6.5	-0.1	10.0	13.5	2.5	6.7	0.2
1989	7.4	3.9	9.4	13.4	2.7	7.4	2.7
1990	7.4	3.6	10.1	13.2	2.4	8.5	2.5
1991	6.1	-0.7	7.9	14.3	3.1	6.7	-0.2
Mean	5.4 ± 1.1	-2.0 ± 2.9	8.7 ± 0.8	12.9 ± 0.9	2.1 ± 1.2	6.4 ± 0.9	-1.2 ± 2.0

The lowest amount of precipitation is normally recorded in April (60 ± 37 mm). On average this contributes by 3.8 ± 2.2% to the annual water input. Also May, June and February are precipitation poor months, i.e. normally < 100 mm.

The highest monthly precipitation was recorded in October 1976 with 575 mm, with an average intensity of 24 mm per day of precipitation. Monthly precipitation > 300 mm is only recorded 11 times during the monitoring period, and only four times with an intensity of rain > 15 mm per day of precipitation.

The lowest recorded monthly precipitation is 1 mm (August 1976). Monthly precipitation > 10 mm is only recorded 5 times during the monitoring period.

Annual runoff mean from the Birkenes-catchment during the monitoring period is 1169 ± 288 mm (water-year: Jun-May). As for the precipitation, lowest annual runoff was recorded in 1975/76 with 757 mm, and highest annual runoff was recorded in 1987/88 with 1865 mm (Figure 4.2)

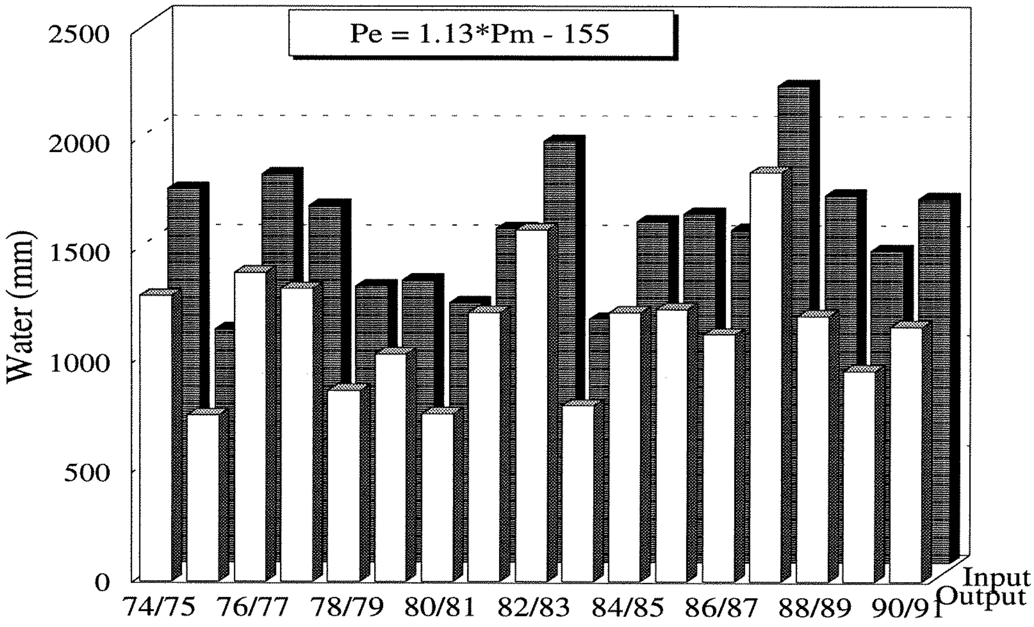


Figure 4.2 Annual precipitation and runoff at Birkenes during the monitoring period, 1974/75-1990/91. Pe = estimated precipitation; Pm = measured precipitation.

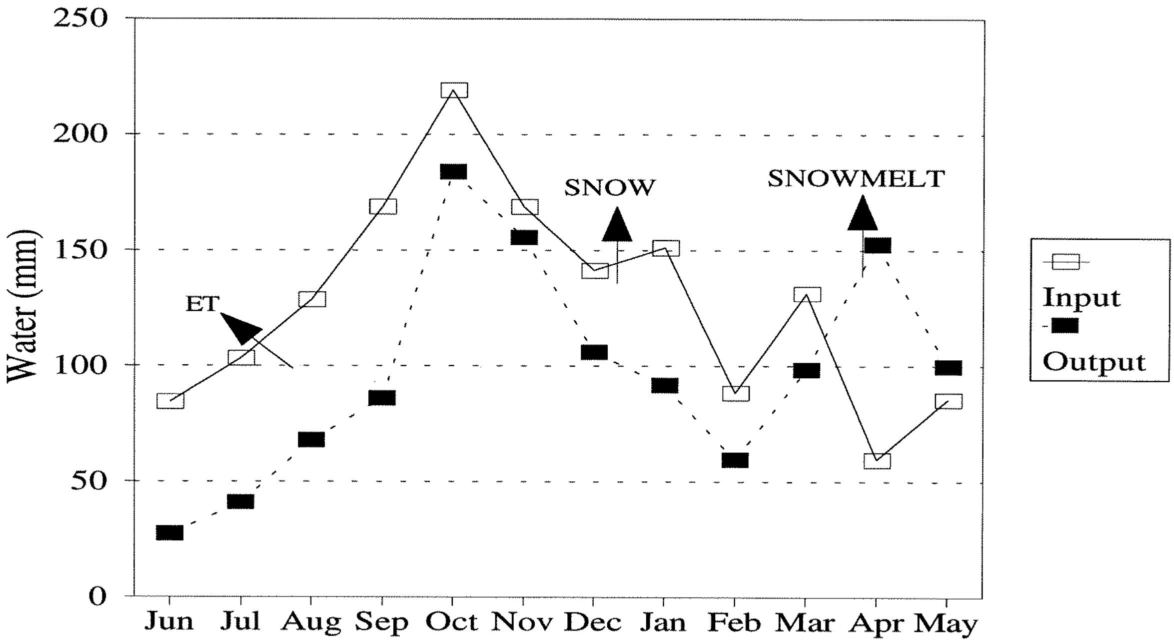


Figure 4.3 Average monthly precipitation and runoff at Birkenes during the monitoring period, 1974/75-1990/91.

Highest monthly runoff is normally recorded in October (Figure 4.3) with an average of 184 ± 119 mm. This is only slightly higher than the average output in November and in April during spring melt. Thus, both the highest inputs and outputs of water are normally recorded in October. On average 15.2 ± 7.8% of annual runoff leaf the catchment during October, while > 40% of annual runoff normally leaf the catchment during three runoff-rich autumn months.

Lowest monthly runoff (Figure 4.3) is normally recorded in June (27 ± 22 mm). On average the runoff this month contributes by only 2.6 ± 2.5% to total annual runoff. The runoff is normally very low also in July and August. High temperature, combined with minor precipitation during summer imply a large effect of evapotranspiration that subsequently leads to drought periods. No runoff during a month is, however, only recorded three times, in August (1976), in June and July (1989). Monthly runoff < 10 mm is recorded 30 times, and more than 80% of these recordings are from the summer months.

The highest monthly runoff was recorded in October 1976 with 511 mm, simultaneously with the highest recorded monthly precipitation. This month, 92% of the monthly input of water also left the catchment same month. The runoff in October 1976 is so far the only month with runoff > 400 mm. Monthly runoff values > 300 mm are only recorded three more times, in January 1975, in November 1983 and in October 1988.

Besides drought period during summer, two high flow periods normally occur yearly at Birkenes, i.e. during spring melt and autumn storms. The average runoff during spring melt at Birkenes (1 April-31 May) is 252 ± 130 mm. Melt water from snow accumulated during the winter (1 November-31 March), and the precipitation during spring (1 April - 31 May), on average contribute by about 50% each to the runoff during the two months of spring melt.

Low runoff values during spring melt (Runoff < 120 mm) are recorded the first two and the last three years of the monitoring period at Birkenes (Figure 4.4), lowest during spring 1990 (40 mm). Mild winters with mean air temperatures close to or ≥ 0°C are common for these years, and the contribution from precipitation to the runoff during April and May is high (Figure 4.5). During the winter 1982/83, almost no accumulation of snow occurred. The relatively high runoff the following spring was directly related to the large amount of precipitation during spring (356 mm). The precipitation this spring was approximately 19% of total annual precipitation this year.

On average 60-80% of runoff during spring melt originates from snow accumulated during cold winters (Figure 4.5). Consequently these winters normally cause the highest flow episodes the following spring. During the monitoring period, runoff during spring (1 April - 31 May) > 400 mm has only been recorded three times, in 1977, 1978 and 1986. Accumulated snow during the previous winters contributed by 72%, 77% and 57%, to the runoff during these springs.

High-flow periods also occur at late autumn in October and November. Then the catchment is often almost or totally water saturated. Thus, the precipitation is able to leave the catchment by runoff relatively fast. This is confirmed by the average runoff/precipitation- ratio(R/P-ratio) in October and November of 81 ± 19% and 87 ± 20%, respectively. Lowest R/P-ratios are normally recorded in July (26 ± 26%).

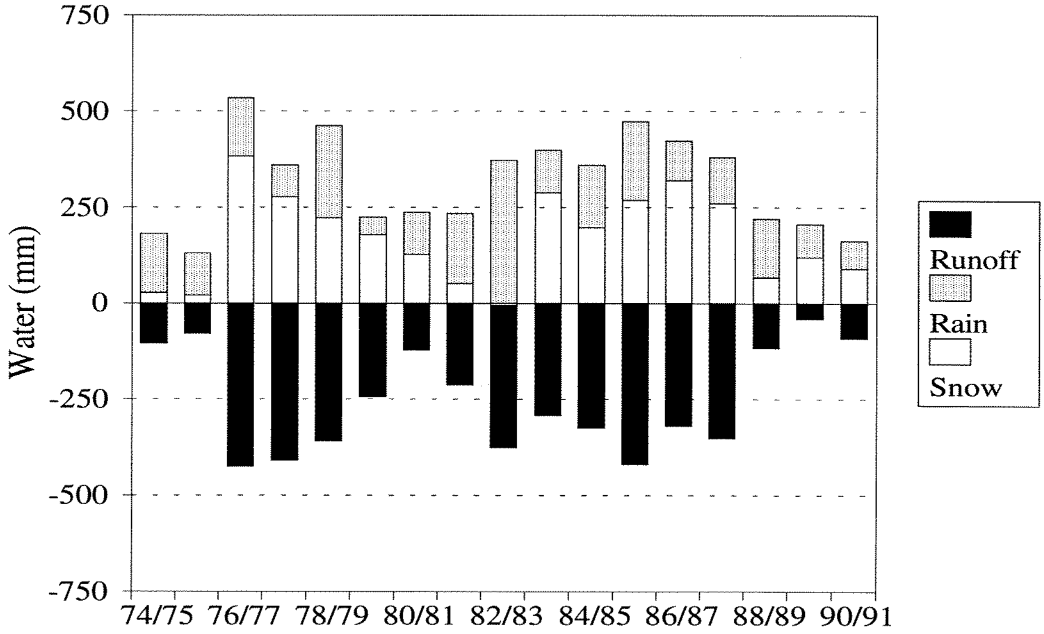


Figure 4.4 Annual accumulation of snow during winter (1 November-31 March), and precipitation and runoff the following spring (1 April-31 May) at the Birkenes catchment during the period 1974/75-1990/91. The runoff is illustrated by negative values in the figure.

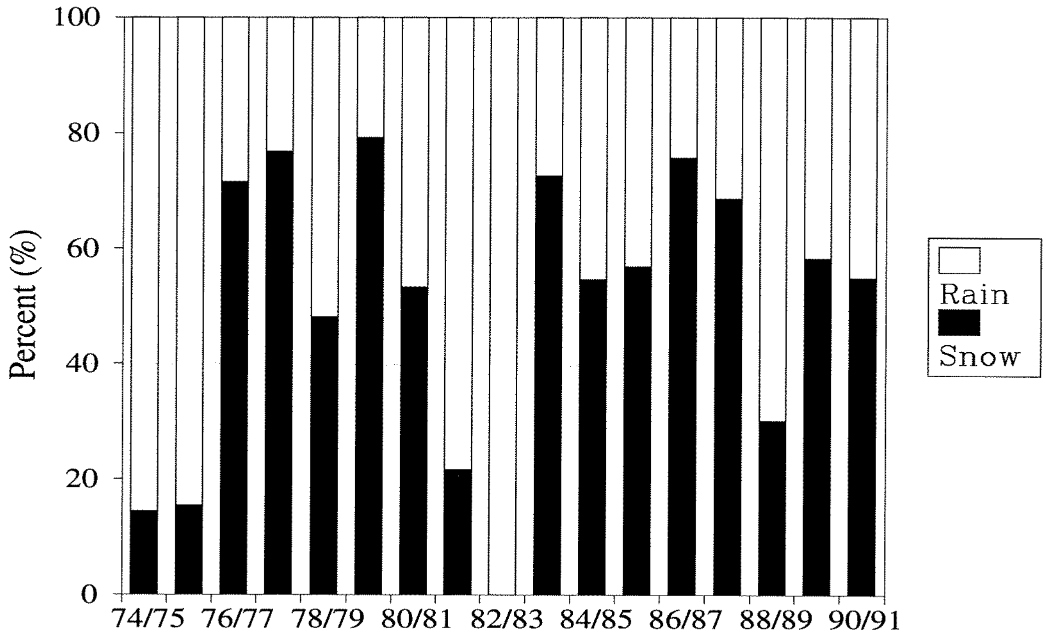


Figure 4.5 The percentage contribution of accumulated snow during winter (1 November- 31 March) and precipitation during spring (1 April-31 May) to the spring-runoff at the Birkenes catchment during 1974/75-1990/91.

Hydrologic characteristics at Birkenes are regularly drought periods during summer, high amounts of precipitation and runoff during autumn, and large variations in runoff at spring, mainly because of large variations in the quality (snow/rain) of precipitation during the winter, directly related to the winter temperature.

Estimated average annual evapotranspiration at Birkenes during the monitoring period is 360 ± 70 mm.

4.4 Storgama

Air-temperature at the weather-station Treungen, nearby Storgama, is daily recorded from 1974-1991 (Table 4.3). A weak tendency of elevated air temperatures during the monitoring period are also recorded at Storgama, but the increase is not significant ($p < 0.05$). However, a significant increase in the annual mean temperature by 0.6°C per year ($r = 0.83$) is recorded during the latest years, 1985-1991. The yearly increase is identical with the observations made at Birkenes for the same period. There are increases in air temperature for all quarters at Storgama, but only the increases for the 1st quarter (Jan-Mar) and the 3rd quarter (Jul-Sep) were significant, with an average increase in air temperature by 1.6°C ($r = 0.75$) and 0.4°C ($r = 0.88$) per year, respectively. At Storgama the average winter temperature is -3.1 ± 3.2°C compared with -2.0 ± 2.9°C at Birkenes. Similar to Birkenes, the tendency of elevated winter-temperatures has large hydrological consequences as the winter temperature has been ≥ 0° C. Thus. more of the winter precipitation falls as rain, or if it enters the catchment as snow or sleet, it often melts relatively fast so that the following spring will be significantly reduced. Since the winter temperature at Storgama normally is lower compared with at Birkenes, the effects of elevated winter temperatures on accumulation of snow and thereby runoff during spring, are so far smaller. As at Birkenes, because mild years (winters) occurs no and then at Storgama, more years of data are needed to confirm if the trend the last years is more than natural variations.

Annual precipitation mean during the monitoring period at Treungen is 1040 ± 258 mm (water-year: Sep-Aug), distributed on 163 ± 19 precipitation days (input > 0.1 mm), with an average intensity of precipitation of 5.9 ± 0.9 mm. Estimated annual precipitation (P_e) during a water year at Storgama is expressed by the following equation: $P_e = 1.06P_m + 103$ ($r=0.97$). By this relationship, the annual precipitation mean at Storgama is 1206 ± 273 mm, with an average intensity of 7.4 ± 1.0 mm. On the basis of the annual precipitation estimate, on average the weather-station underestimates the annual precipitation at Storgama by 166 ± 15 mm (≈ 16%).

As at Birkenes, the lowest recorded annual precipitation at Storgama was recorded in 1975/76 with 771 mm, while the highest was recorded in 1987/88 with 1906 mm (Figure 4.6). This coincidence with Birkenes is not surprising, because Storgama is located only 35 km north of Birkenes. The correlation between annual precipitation (mm) at Birkenes(x) and Storgama(y) is: $y = 0.68x + 148$ ($r = 0.70$, $n = 14$).

Highest monthly precipitation at Storgama does normally occur in October (Figure 4.7) with an average of 175 ± 76 mm, and is nearly 21% and 38% higher than the second most precipitation-rich months, September and November. On average 14.3 ± 4.0% of the annual precipitation enters the catchment in October, while more than 35% of annual precipitation normally enters the catchment during the three wettest months, i.e. from 1 September to 30 November. Lowest monthly precipitation, i.e. 54 ± 36 mm, is normally recorded in April. On average this contributes by 4.6 ± 3.5% to the annual precipitation February, May, June and December are slo precipitation poor months at Storgama, all with precipitation normally < 100 mm.

The highest recorded monthly precipitation at Storgama was recorded in October 1987 with 396 mm, with an average intensity of 18 mm per day of precipitation. Monthly precipitation > 300 mm was recorded in July 1988 (313 mm). Monthly precipitation > 200 mm has been recorded 14 times, and nearly 65% of these recordings were made during 1 August - 31 December. An average monthly intensity of rain > 12 mm per day of precipitation normally occurs once a year, primarily at autumn.

A month without any precipitation has so far only been recorded once, in May 1991. Only 1 mm/mth is recorded twice during the monitoring period, in May 1990 and July 1989, while monthly precipitation < 10 mm is recorded 8 times, 5 times during summer (June-August), twice in February and once in April.

Annual runoff mean at Storgama during the monitoring period is 947 ± 287 mm (water-year: Sep-Aug). As for input of water, lowest annual runoff was recorded in 1975/76 with 517 mm, the highest in 1987/88 with 1620 mm (Figure 4.6).

Highest monthly runoff is normally recorded in May (Figure 4.7), the main month of spring melt, with an average of 218 ± 170 mm. This is 43% higher than the second most runoff rich month, April, and more than 50% higher than the most runoff rich month during autumn, October. Nearly 40% of annual runoff at Storgama normally leaves the catctment during spring melt (1 April- 31 May).

Lowest monthly runoff (Figure 4.7) is normally recorded in January and February (29 ± 22 mm and 27 ± 44 mm), and runoff during these months only constitute 3.0 ± 2.4% and 3.0 ± 5.0% of annual average runoff. Low runoff values are regularly recorded also during summer (Jun-Aug), often with monthly runoff values < 5 mm. High summer temperature combined with minor precipitation leads to a large effect of evapotranspiration and subsequent drought periods. Since large areas of the catchment consist of bare rock so that the precipitation is able to leave the catchment relatively fast, the catchment is very drought sensitive. Accordingly, no runoff during a whole month is recorded 11 times, all during summer and early autumn (June to September). Low runoff values (< 10 mm) are normally recorded also during the winter.

Highest monthly runoff at Storgama was recorded in May 1977 with 461 mm. The main reason was the high amount of accumulated snow the previous winter combined with an unusual cold April. Together this lead to an intensive spring melt in May. About 44% of annual runoff this year left the catchment this single month. Highest recorded runoff during autumn was in October 1987 with 351 mm. The R/P-ration this month was 89%. Monthly runoff > 300 mm are recorded seven times, and by one exception, these observations were all made during spring melt.

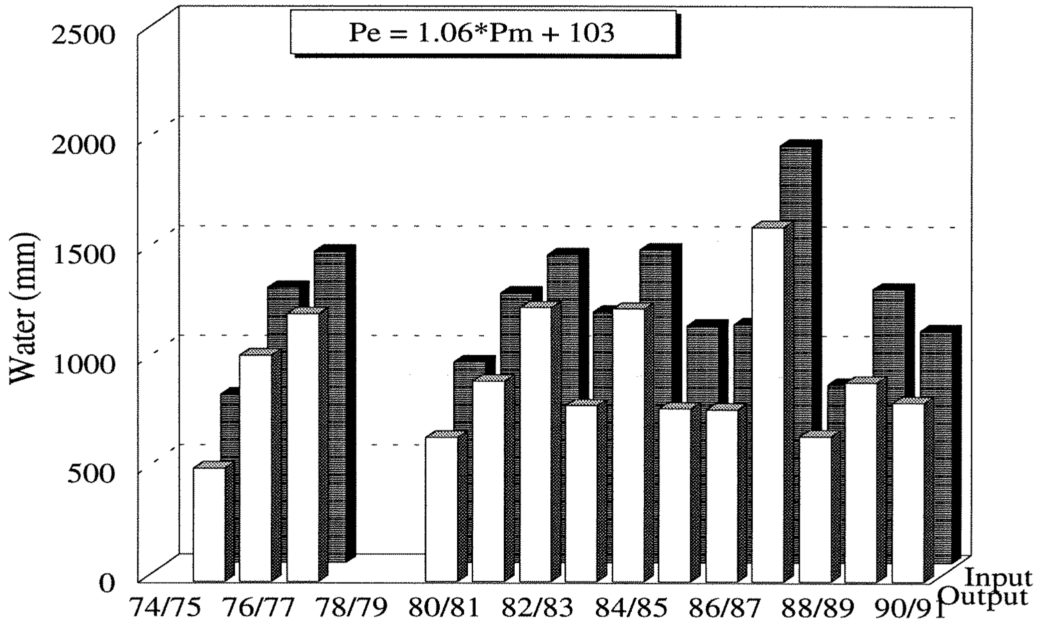


Figure 4.6 Annual precipitation and runoff at Storgama during the monitoring period, 1974/75-1990/91. Pe = estimated precipitation; Pm = measured precipitation.

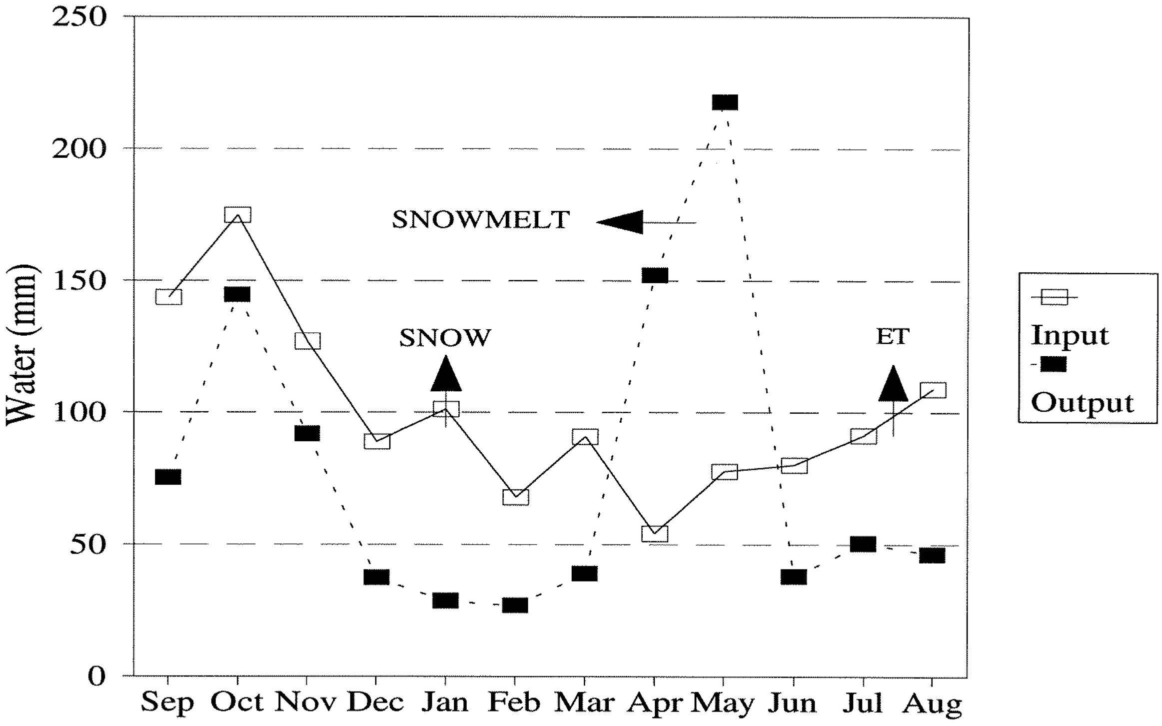


Figure 4.7 Average monthly precipitation and runoff at Storgama during the monitoring period, 1974/75-1990/91.

Table 4.3 Annual mean temperatures at Storgama from 1974-1991, and average temperatures during each successive three months period, during winter (1 Nov - 31 Mar) and spring (1 Apr. - 31 May).

Year	Annual Jan-Dec	1st quarter Jan-Mar	2nd quarter Apr-Jun	3rd quarter Jul-Sep	4th quarter Oct-Dec	Spring Apr-May	Winter Nov-Mar
1974	6.2	0.2	9.5	12.7	2.2	7.5	
1975	6.6	-0.9	8.5	15.0	3.8	6.1	-0.1
1976	5.2	-3.0	9.5	13.9	0.5	7.0	-0.9
1977	4.8	-3.9	8.1	12.7	2.1	5.3	-2.9
1978	4.7	-3.5	8.6	12.1	1.5	5.7	-2.1
1979	3.7	-6.2	7.8	12.4	0.7	4.8	-4.2
1980	4.3	-6.8	9.6	13.3	1.0	7.3	-4.6
1981	2.0	-6.9	8.4	12.6	-6.3	6.5	-4.3
1982	5.3	-4.2	8.8	14.1	2.5	6.6	-6.8
1983	6.2	-0.9	8.2	14.5	2.8	5.8	-0.2
1984	5.6	-4.1	9.4	13.4	3.8	7.1	-2.2
1985	3.5	-6.8	8.0	12.2	0.5	5.5	-3.3
1986	4.2	-6.3	8.0	11.9	3.1	4.6	-5.0
1987	3.8	-6.7	7.7	11.8	2.4	6.2	-3.4
1988	5.9	-1.1	9.6	13.2	1.7	6.1	-0.6
1989	7.1	3.3	9.1	13.5	2.6	6.8	2.0
1990	7.2	3.3	10.2	13.2	2.0	8.5	2.2
1991	5.9	-1.9	8.0	14.4	3.1	7.1	-1.2
Mean	5.1 ± 1.3	-3.1 ± 3.2	8.7 ± 0.7	13.2 ± 0.9	1.7 ± 2.2	6.3 ± 1.0	-2.2 ± 2.4

Besides drought period during summer and low flow during winter, high flow periods normally occur twice a year at Storgama, related to spring melt and autumn storms. The spring melt is quantitatively a far more important high flow period at Storgama than at Birkenes. At Storgama spring melt on average contributes with 39 ± 12% to the annual runoff, while at Birkenes it only contributes with 22 ± 11%. At Storgama, on average, 65% of the runoff during spring melt (April and May) normally originates from snow, while the remaining 35% originates from precipitation during the same period.

Extreme low runoff at Storgama during spring melt (Runoff < 120 mm) was recorded in 1976, 1989 and 1990 (Figure 4.8). Common to all these years are mild winters with mean air temp close to or ≥ 0°C, and the the low runoffs were a combination of a snow poor winter and a precipitation poor spring (Figure 4.8). The most extreme runoff during spring was recorded in 1983. The accumulation of snow during the winter (278 mm) was only slightly above normal (246 ± 98 mm), but the large amount of precipitation April and May (368 mm, which was nearly 2.6 times normal) was the main reason for the high runoff this spring. The precipitation during this spring constituted 26% of total annual input this year.

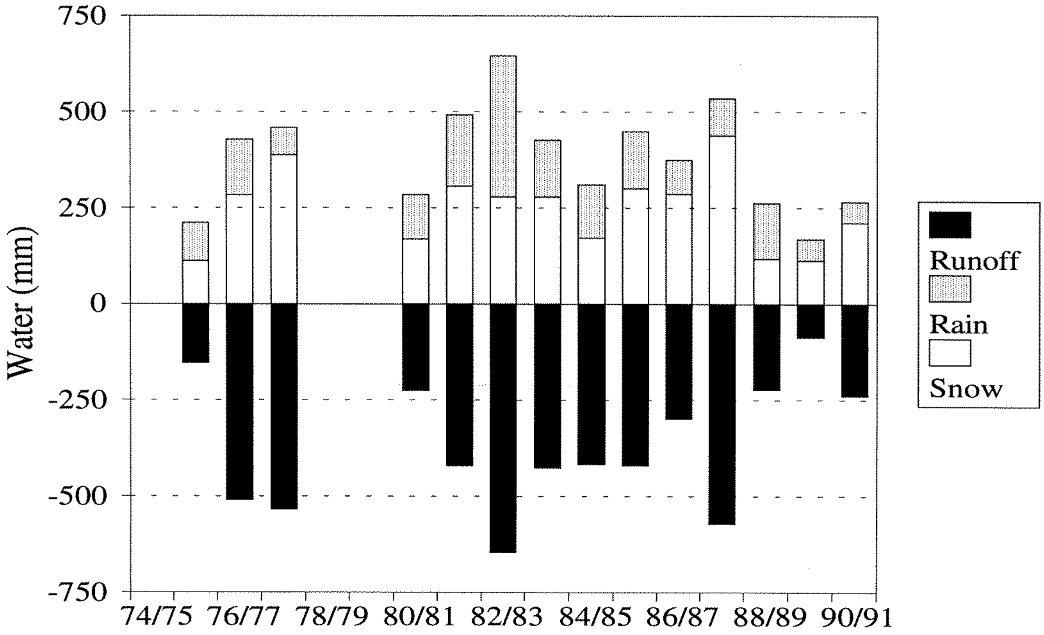


Figure 4.8 Annual accumulation of snow during winter (1 November-31 March), and precipitation and runoff the following spring (1 April-31 May) at the Storgama catchment during the period 1974/75-1990/91. The runoff is illustrated by negative values in the figure.

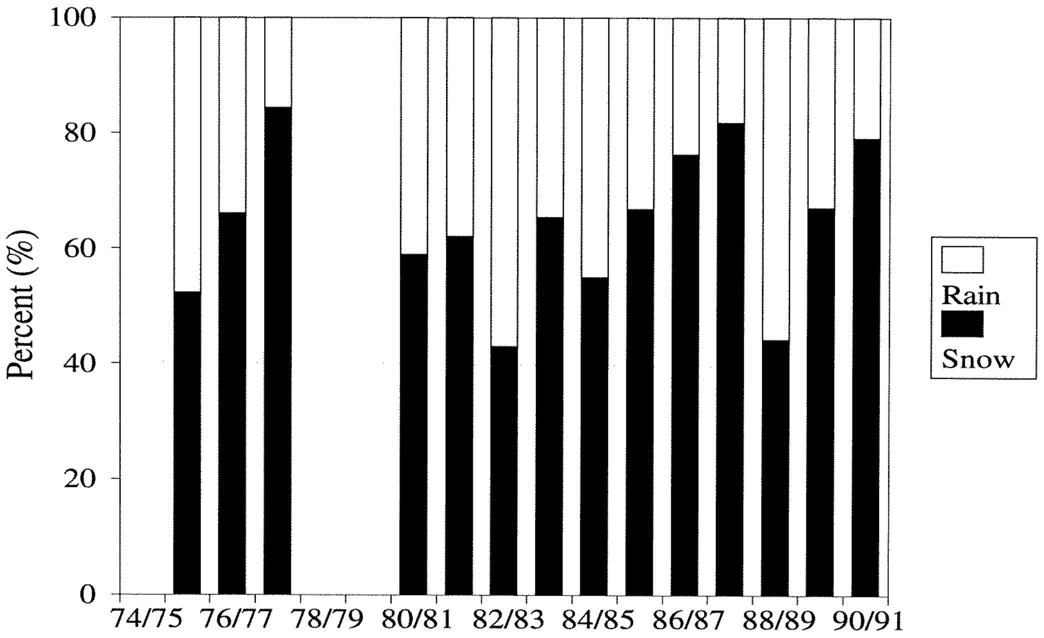


Figure 4.9 The percentage contribution of accumulated snow during winter (1 November- 31 March) and precipitation during spring (1 April-31 May) to the runoff during spring at Storgama during 1974/75-1990/91.

As during cold winters at Birkenes, on average 60-80% of the runoff during spring melt at Storgama originates from snow accumulated during the winter (Figure 4.9). Cold winters normally cause the most extreme high-flow episodes the following spring. While runoff during the spring melt period (1 April - 31 May) exceeded 400 mm at Birkenes only three times during the monitoring period (in 1977, 1978 and 1986), runoff-values > 400 mm have been recorded 8 times at Storgama. Average runoff during spring melt at Birkenes and Storgama are 252 ± 130 mm and 370 ± 162 mm, respectively.

As at Birkenes, high flow periods occur also at late autumn at Storgama, normally in October and/or November. Then the catchment is often almost water saturated, which means that the precipitation is able to leave the catchment relatively soon. The mean R/P-ratios for October and November at Storgama were estimated to be 81 ± 21% and 74 ± 20%, respectively. Lowest R/P-ratios generally occur in August (27 ± 27%).

At Storgama the annual hydrology is characterised by regularly drought/low flow periods during summer and winter, large amounts of precipitation and high runoff during autumn, and large runoff variations during spring melt due to large variations in the quality of precipitation (snow/rain) at winter time. The average winter temperature at Storgama is somewhat lower than at Birkenes, which means that more precipitation during the winters at Storgama is normally stored as snow. Accordingly Storgama exhibits higher runoff during spring melt. The autumn precipitation at Storgama is quantitatively less important than at Birkenes. Large area of the Storgama catchment consists of bare rock, so the residence time of water is relatively short. Thus, the variations in runoff at Storgama are often more extreme compared with the more soil- and forest-rich Birkenes catchment.

Estimated annual average evapotranspiration during the monitoring period at Storgama is 253 ± 61 mm.

4.5 Langtjern

At the weather-station Gulsvik, nearby Langtjern, air-temperature is daily recorded from 1977-1991 (Table 4.4). Annual mean temperature during the monitoring period is 3.0 ± 1.2°C. A significant increase in the annual mean temperature by 0.2 °C per year (r = 0.58) has been observed during the period 1977-1991, mainly due to the significant increase by 0.4°C per year (r = 0.53 and r = 0.61, respectively) for 1st and 4th quarter. During the period 1985-1991, an even more significant increase in annual mean temperature by 0.6°C per year (r = 0.81) was found, and this annual increase was identical with that also observed at Birkenes and Storgama during the same period. The increase in annual air temperature at Langtjern from 1985 to 1991 is a result of increasing air temperatures for all quarters, but only significant for the 3rd quarter (0.4°C per year, r = 0.89), and almost significant for the 1st quarter (1.5°C per year, r = 0.70). Mean winter temperature at Langtjern during 1977-1991 is -6.8 ± 3.4°C. This is far colder than at Birkenes and Storgama. The tendency of increasing winter temperature has therefore has minimal hydrologic consequences at Langtjern so far, because the mean winter-temperature is still far below 0°C. However, by continuing winter temperature increases, the seasonal runoff pattern may change significantly in the years to come.

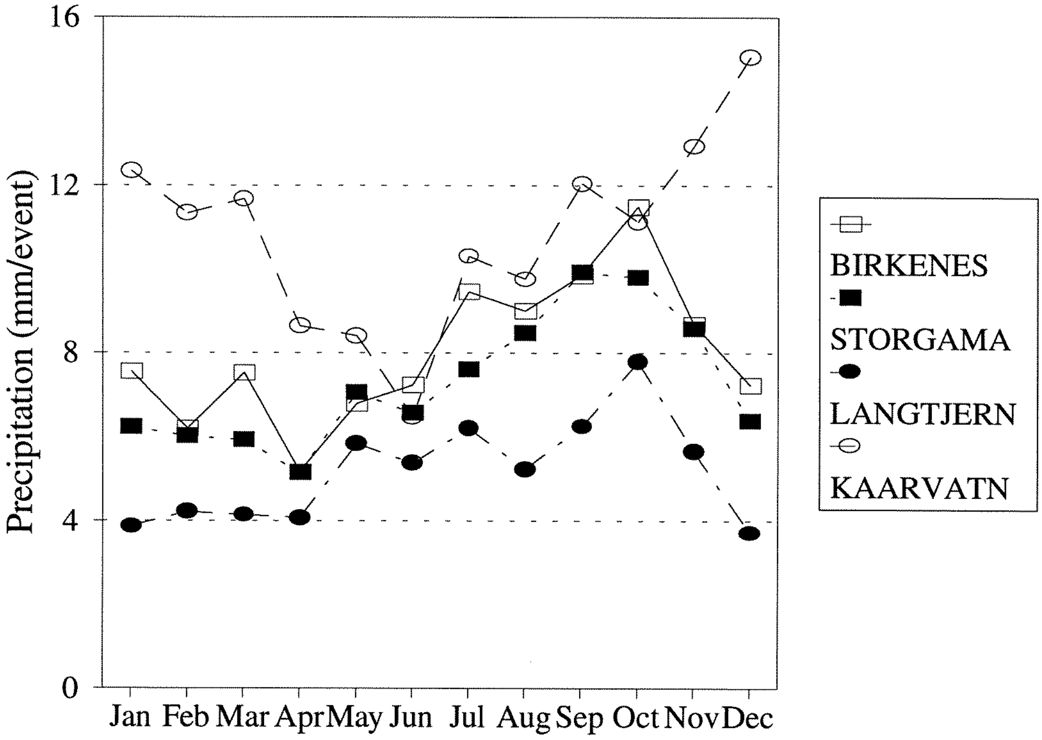


Figure 4.10 Average monthly intensity of precipitation at the four catchments during the monitoring period. Intensity: P_e/ no. of days with precipitation > 0.1 mm.

Annual average precipitation at the weather-station at Langtjern during the monitoring period is 735 ± 145 mm (water-year: Jun-May), distributed on 164 ± 12 precipitation days (input > 0.1 mm), with an average intensity of precipitation of 4.4 ± 0.6 mm. Estimated amount of precipitation (P_e) entering the Langtjern catchment during a water year is expressed by the following equation: $P_e = 1.10P_m + 55$ (r=0.86). By this relationship, the annual average precipitation at Langtjern is 864 ± 153 mm, with an average intensity of 5.1 ± 0.7 mm. On the basis of estimated annual precipitation, the weather-station underestimates the annual precipitation by 129 ± 14 mm (≈ 18%).

The low annual precipitation at Langtjern compared with the other sites, is mainly a consequence of geographical location. Langtjern is situated in the inland of eastern Norway, east of the north-south going mountain area of southern Norway. Because precipitation very often is associated with western and south-western winds, Langtjern often lies in the rain shadow.

Even though Langtjern is located far from Birkenes and Storgama, the lowest annual precipitation at Langtjern was also recorded in 1975/76 (577 mm). As at Birkenes and Storgama, the highest annual input was also recorded in 1987/88 with 1325 mm (Figure 4.11). The linear correlation between annual precipitation at Birkenes(x) and Langtjern(y) is: $y = 0.45x + 182$ ($r = 0.80$, $n = 17$). Thus, despite Langtjern is located far from Birkenes, the correlation between annual precipitation at the two sites is more relative significant.

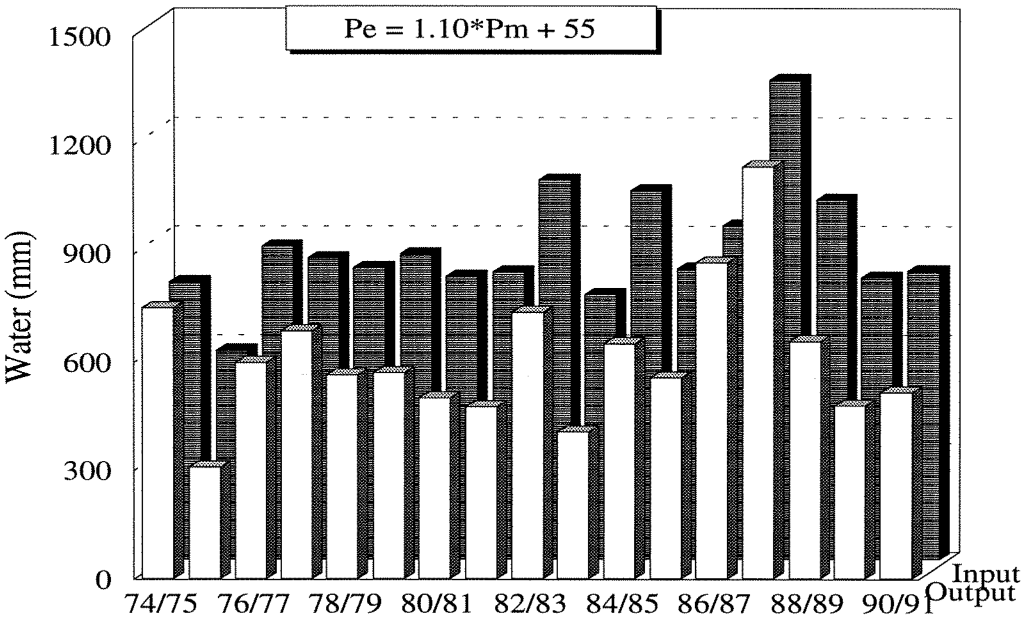


Figure 4.11 Annual precipitation and runoff at Langtjern during the monitoring period, 1974/75-1990/91. Pe = estimated precipitation; Pm = measured precipitation.

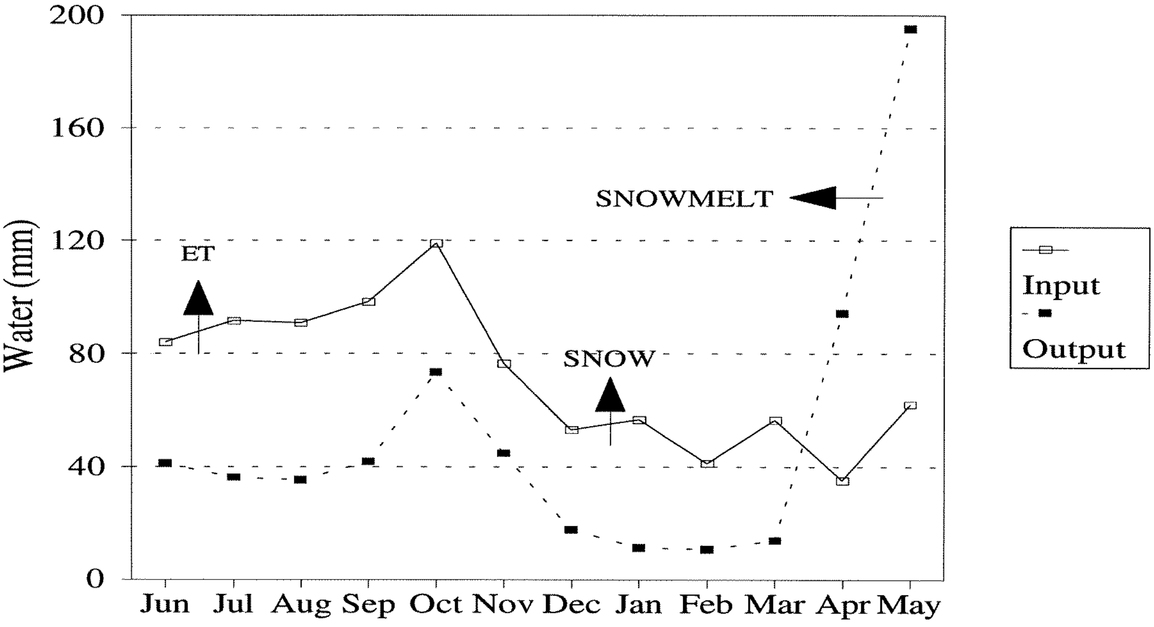


Figure 4.12 Average monthly precipitation and runoff at Langtjern during the monitoring period, 1974/75-1990/91.

As at Birkenes and Storgama, highest monthly precipitation at Langtjern is normally recorded in October (Figure 4.12) with an average of 119 ± 78 mm. October is the only month with precipitation normally > 100 mm. The average intensity of rain in October is 7.2 ± 3.0 mm per day of precipitation. The precipitation during October is on average 20% and 29% higher than the second most precipitation rich months, September and July. On average 13.4 ± 7.8% of annual precipitation enters the catchment in October, while more than 35% of total annual precipitation normally enters the catchment during the three wettest months.

Lowest monthly precipitation at Langtjern is normally recorded in April (33 ± 24 mm), a contribution to annual input by 3.8 ± 2.6%. From December to April, the monthly precipitation is normally < 60 mm.

The highest monthly precipitation at Langtjern was recorded in October 1987 with 276 mm, with an average intensity of 12 mm per day of precipitation. Monthly precipitation > 200 mm has been recorded six times, three times in October, once in July, August and May. Monthly intensity of rain > 12 mm per day of precipitation has been recorded three times, highest in July 1982 with as much as 24.4 mm per day of precipitation.

A whole month without precipitation is recorded three times at Langtjern, April 1981, February 1986, and May 1991. Monthly inputs < 10 mm has been recorded 13 times, always during the 5 first months of the year.

Annual average runoff at Langtjern during the monitoring period is 614 ± 186 mm (water-year: Jun-May). As for the precipitation, the lowest annual runoff (only 308 mm) was recorded in 1975/76, while the highest annual runoff was recorded in 1987/88 with 1138 mm (Figure 4.11).

Highest monthly runoff is normally recorded in May (Figure 4.12), the main month of spring melt. Average runoff in May is 195 ± 109 mm. This is 107% higher than the second most runoff rich month, April, and more than 167% higher than the most runoff rich month at autumn (October). On average, about 47% of annual runoff occurs during spring melt (1 April- 31 May).

Lowest monthly runoff (Figure 4.12) at Langtjern normally occurs from December to March, i.e. 18 ± 16 mm (Dec); 11 ± 7 mm (Jan), 11 ± 11 mm (Feb), and 14 ± 14 mm (Mar). The runoff these months on average contribute by 2.9 ± 2.6%, 1.8 ± 1.1%, 1.8 ± 2.2% and 2.5 ± 2.9%, respectively to total annual runoff. The runoff is normally very low also during summer (Jun-Aug), with monthly runoff often < 5 mm. High summer temperatures, combined with minor precipitation leads to high evapotranspiration, which causes regular drought periods during summer. Even though annual precipitation at Langtjern on average is 30% lower than the second most precipitation poor catchment (Storgama), the amount of precipitation during summer is nearly equal. Because of the bigger lake and more boggy areas within the Langtjern catchment, the runoff from this site less drought sensitive. While no monthly runoff has been recorded 6 times at Langtjern, a corresponding situation has been recorded 11 times at Storgama. All 6 recordings at Langtjern were made during summer and early autumn (June to September), and 5 of them in 1975 and 1976, typically after very snow poor winters (Figure 4.13) and precipitation poor summers. Low monthly runoff (< 10 mm) are normally recorded also during the winter.

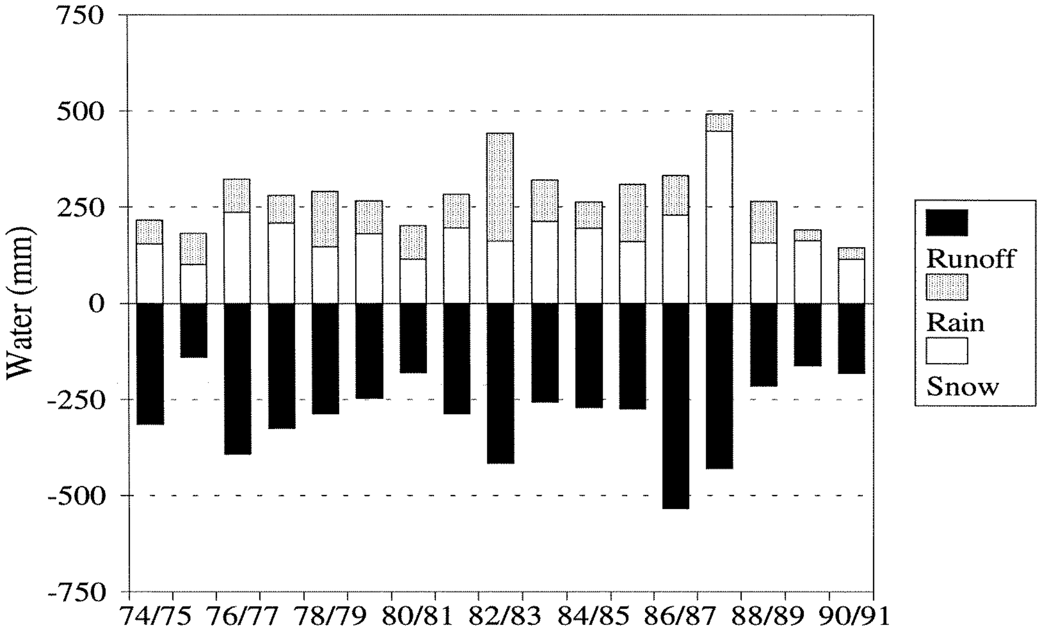


Figure 4.13 Annual accumulation of snow during winter (1 November-31 March), and precipitation and runoff the following spring (1 April-31 May) at the Langtjern catchment during the period 1974/75-1990/91. The runoff is illustrated by negative values in the figure.

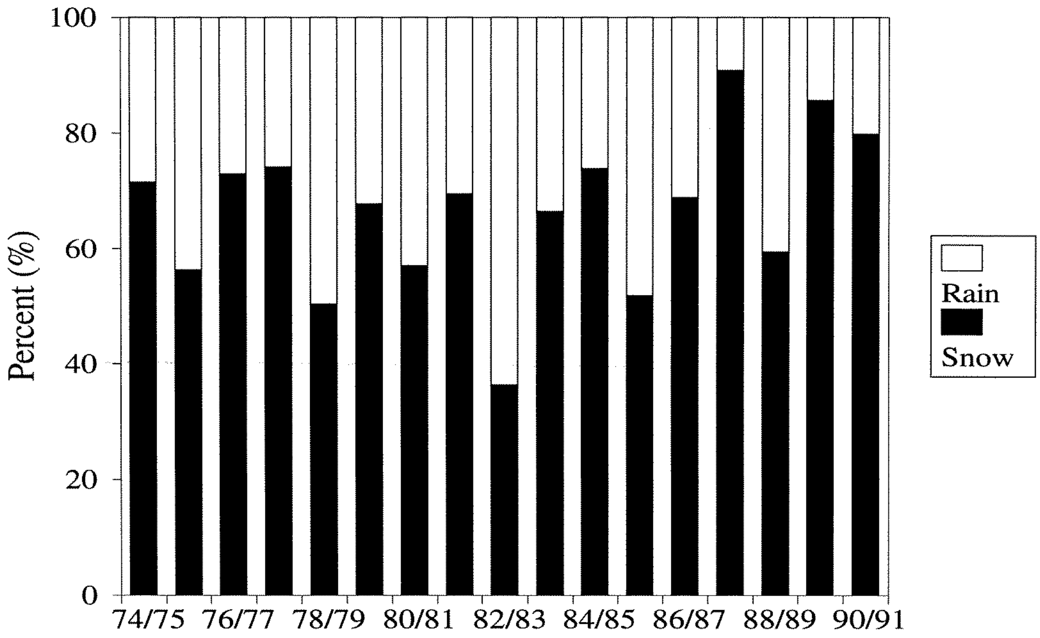


Figure 4.14 The percentage contribution of accumulated snow during winter (1 November- 31 March) and precipitation during spring (1 April-31 May) to the spring-runoff at the Langtjern catchment during 1974/75-1990/91.

Table 4.4 Annual mean temperatures at Langtjern from 1977-1991, and average temperatures during each successive three months period, during winter (1 Nov - 31 Mar) and spring (1 Apr. - 31 May).

		1st	**2nd**	**3rd**	**4th**		
	Annual	**quarter**	**quarter**	**quarter**	**quarter**	**Spring**	**Winter**
Year	**Jan-Dec**	**Jan-Mar**	**Apr-Jun**	**Jul-Sep**	**Oct-Dec**	**Apr-May**	**Nov-Mar**
1977	2.7	-8.1	7.9	12.5	-1.5	5.1	
1978	2.5	-7.9	8.9	11.8	-3.1	5.9	-6.6
1979	1.5	-9.7	8.7	11.8	-4.9	5.4	-8.6
1980	1.7	-10.5	9.9	12.9	-5.7	7.3	-9.6
1981	2.0	-6.9	8.4	12.6	-6.3	6.5	-7.8
1982	3.4	-6.6	8.9	13.8	-2.6	6.6	-8.2
1983	4.1	-4.5	8.6	13.9	-1.4	6.1	-5.1
1984	3.6	-8.3	9.7	12.8	0.3	7.6	-6.9
1985	1.3	-9.4	8.6	11.5	-5.4	6.2	-6.4
1986	2.6	-9.6	9.3	11.5	-0.8	5.7	-10.2
1987	1.7	-11.1	8.2	11.4	-1.6	6.4	-8.0
1988	3.9	-4.6	10.1	13.1	-3.0	6.3	-4.8
1989	5.1	0.7	9.0	12.7	-2.2	6.4	-1.7
1990	5.2	0.0	10.2	12.7	-2.1	8.2	-2.1
1991	3.9	-5.5	8.2	14.0	-1.2	6.9	-5.2
Mean	3.0 ± 1.2	-6.8 ± 3.4	9.0 ± 0.7	12.6 ± 0.8	-2.8 ± 1.9	6.4 ± 0.8	-6.5 ± 2.5

As at Storgama, the highest monthly runoff at Langtjern was recorded in May 1977 with 363 mm. The major cause was the relative large amount of accumulated snow during the winter (Figure 4.13), combined with the lowest mean April temperature ever recorded since 1977. Accordingly, an intensive spring melt occurred in May, and about 61% of annual runoff this year was recorded this single month. As at Storgama, the highest monthly runoff during autumn was recorded in October 1987 with 276 mm. This was a direct consequence of much rain not only in October, but also during the two previous months. The R/P-ratio this October was 75%. Monthly runoff values > 300 mm have only been recorded twice during the monitoring period, both in May 1977 and 1987.

Besides drought period during summer and low-flow during winter, two high flow periods occurs regularly at Langtjern, related to spring melt and autumn storms. High flow periods during autumn are, however, a far less important hydrologic event at Langtjern compared with the other sites. The spring melt at Langtjern is a more important hydrological event compared with at Storgama, and far more important compared with at Birkenes. Although more water normally leaves the Storgama catchment during spring melt (370 ± 162 mm) compared with at Langtjern (290 ± 103 mm), the percentage contribution of spring melt to the annual runoff is only 39 ± 12% at Storgama, while 47 ± 11% at Langtjern. While accumulated snow during the winter (1 November-31 March), and precipitation during spring (1 April-31 May), both on average contribute by 50% to total runoff during spring melt at Birkenes, 67 ± 13% of the runoff during spring at Langtjern can be directly attributed to snow melt, while the remaining 33 ± 13% is precipitation during April and May. This is very close to the situation also present at Storgama.

The lowest recorded runoff values during snow melt were recorded in 1976, 1981, 1990 and 1991 (Figure 4.13), lowest during spring melt in 1976 (141 mm). Common to all these years are snow poor winters followed by precipitation poor springs. The most extreme melting period was recorded in 1983. The accumulation of snow during the winter (161 mm) was only slightly lower than normal (187 ± 75 mm), so the high runoff this spring was primarily because of high amounts of precipitation in April and May (281 mm). This is about 3 times higher than normal. The precipitation these months contributed by 27% to total annual precipitation this year.

During cold winters at Langtjern, 70-90% of the runoff during spring melt may originate from accumulated snow (Figure 4.14), and the spring melts following cold winters normally cause the most extreme high-flow episodes at Langtjern. At Langtjern, runoff > 500 mm during spring (1 April to 31 May) has only been recorded once (1987). A corresponding high runoff value has never been recorded at Birkenes, but four times at Storgama. While average runoff during spring at Birkenes and Storgama is 252 ± 130 mm and 370 ± 162 mm, the average runoff at Langtjern is 290 ± 103 mm.

As at the other catchments, a high-flow period normally occurs at Langtjern during late autumn, primarily in October. Then, the catchment is often relatively water saturated, so that the precipitation is able to leave the catchment relatively fast. The mean R/P-ratio in October is 75 ± 37%, which is somewhat lower than at Birkenes and Storgama during the same month. The lowest R/P-ratio is normally present in August (29 ± 23%).

At Langtjern regular drought/low flow periods occur during summer, but especially during the winter, while high flow periods normally occur in October and during spring melt in April and May. Compared with Storgama, but particularly compared with Birkenes, the variations in runoff during spring melt are far less at Langtjern, mainly because of lower winter temperatures at Langtjern. Thus more of the winter precipitation usually accumulates as snow. The high flow periods during autumn are less hydrologic important at Langtjern compared with at Storgama, and far less important compared with Birkenes.

Average annual evapotranspiration at Langtjern during the monitoring period is estimated to be 250 ± 94 mm.

4.6 Kaarvatn

The weather-station at Kaarvatn is located at the outlet of the catchment. Air-temperature is daily recorded from 1984 (Table 4.5). Annual mean temperature during the monitoring period is 7.0 ± 0.8°C, and during the period an almost significant increase in annual mean temperature by 0.4 °C per year (r = 0.71) was observed. The increase in annual air temperature is a result of increasing temperatures for all quarters. Only the increase in temperature during 1st quarter by 1.0°C per year (r = 0.79) is significant. The average winter temperature at Kaarvatn is 1.8 ± 1.7°C, but an almost significant increase in the winter temperature by 0.6°C per year (r = 0.73) has been observed. Kaarvatn is the only weather-station of this investigation with mean winter temperatures normally < °C. However, the station does not represent the weather for the whole catchment. The large catchment area and the large altitude gradient cause large climatic variations that can not be reflected by one single weather-station. This is well illustrated by the winter temperatures. Despite winter temperatures > 0°C (which also has increased during the monitoring period), large amounts of the winter precipitation yearly accumulate as snow. However, if the winter temperature continues to increase, the seasonal hydrology flow pattern will change at Kaarvatn once in the future. However, only several years of monitoring will confirm if the tendency of increasing air temperature continues.

Annual average precipitation at the weather-station during the monitoring period (1980-1991) is 1378 ± 262 mm (water-year: Sep-Aug), distributed on 200 ± 20 precipitation days (input > 0.1 mm), with an average intensity of 6.5 ± 0.9 mm per day of precipitation. Estimated annual amount of precipitation (P_e) at Kaarvatn during a water-year is expressed by the following equation: $P_e = 1.05P_m + 728$ ($r = 0.93$). By this relationship, annual average precipitation at Kaarvatn is 2175 ± 275 mm, with an average intensity of 10.3 ± 0.9 mm per day of precipitation. On the basis of this estimate, the weather-station underestimates annual precipitation at Kaarvatn by 797 ± 13 mm (≈ 37%).

The substantial higher precipitation at Kaarvatn compared with the three other sites is primarily because of its location close to the sea, at the north-western corner of southern Norway. As for the other sites, the precipitation predominantly enters the catchment by western and/or south-western winds. Together with large altitude gradients within the catchment, the conditions are excellent for large precipitation amounts. While the three other catchment are approximately located in one meteorological region, Kaarvatn undoubtedly belongs to another meteorological region. This is further confirmed by a total different precipitation chemistry at Kaarvatn compared with the other sites (see later).

Lowest annual precipitation at Kaarvatn was recorded in 1981/82 with 1699 mm, highest annual precipitation was recorded in 1988/89 with 2612 mm (Figure 4.15).

Highest monthly precipitation is normally recorded in December (Figure 4.16) with an average of 259 ± 98 mm, but monthly precipitation amounts ≥ 200 mm are common from 1 September to 31 January, with an average intensitis between 9.7 ± 4.6 and 15.0 ± 4.5 mm per day of precipitation. Lowest amount of precipitation is normally recorded in June (111 ± 71 mm), which constitutes an average contribution to annual input of 5.1 ± 3.4%. Monthly precipitation at Kaarvatn is usually > 100 mm, so that precipitation is well distributed over the year.

The highest recorded monthly precipitation was in March 1990 with 500 mm, with an average intensity of 20 mm per day of precipitation. Monthly precipitation > 400 mm is recorded 6 times, 5 times during 1 September - 31 January. Monthly intensity of rain > 15 mm per day of precipitation occurs at least once a year, but so far never in June, July or in August.

A month without precipitation has never been recorded at Kaarvatn so far, but monthly precipitation < 20 mm is recorded 3 times, lowest in May 1983 (5 mm).

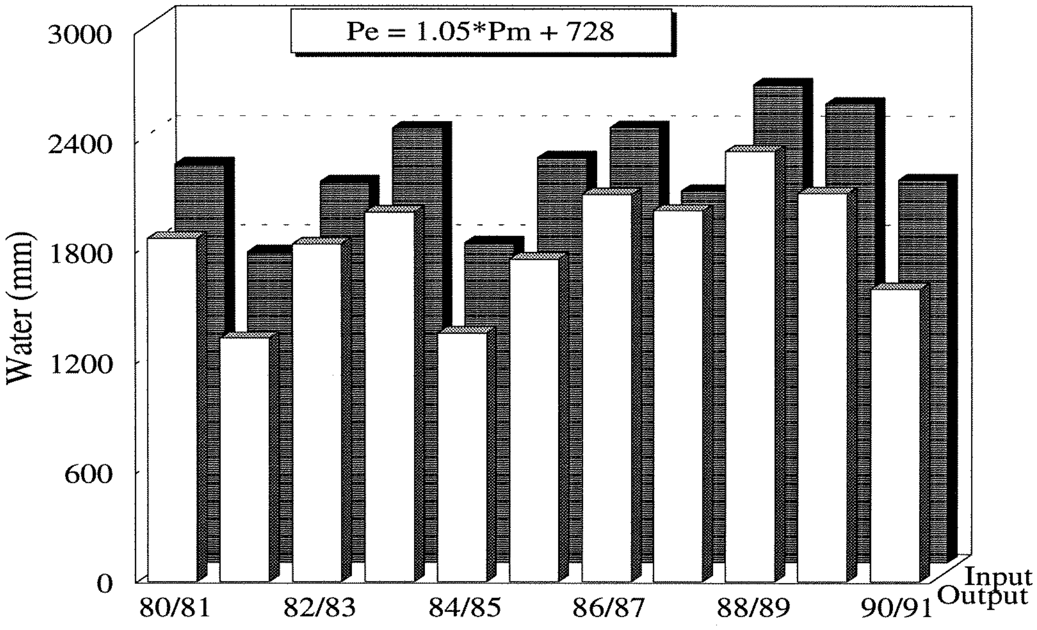


Figure 4.15 Annual precipitation and runoff at Kaarvatn during the monitoring period, 1980/81-1990/91. Pe = estimated precipitation; Pm = measured precipitation.

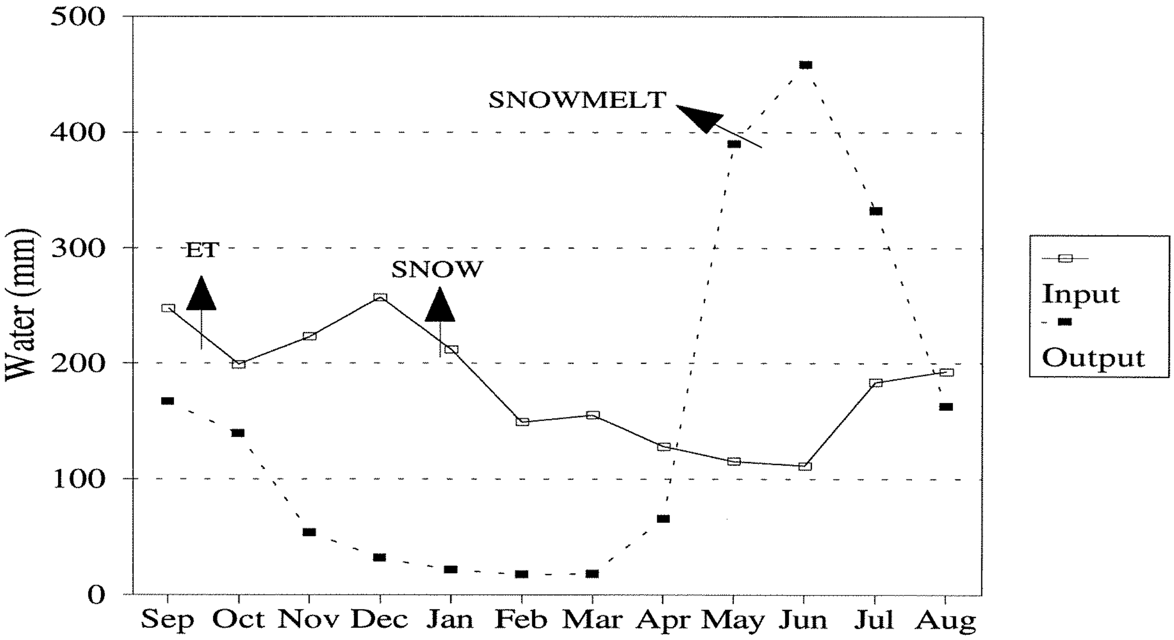


Figure 4.16 Average monthly precipitation and runoff at Kaarvatn during the monitoring period, 1980/81-1990/91.

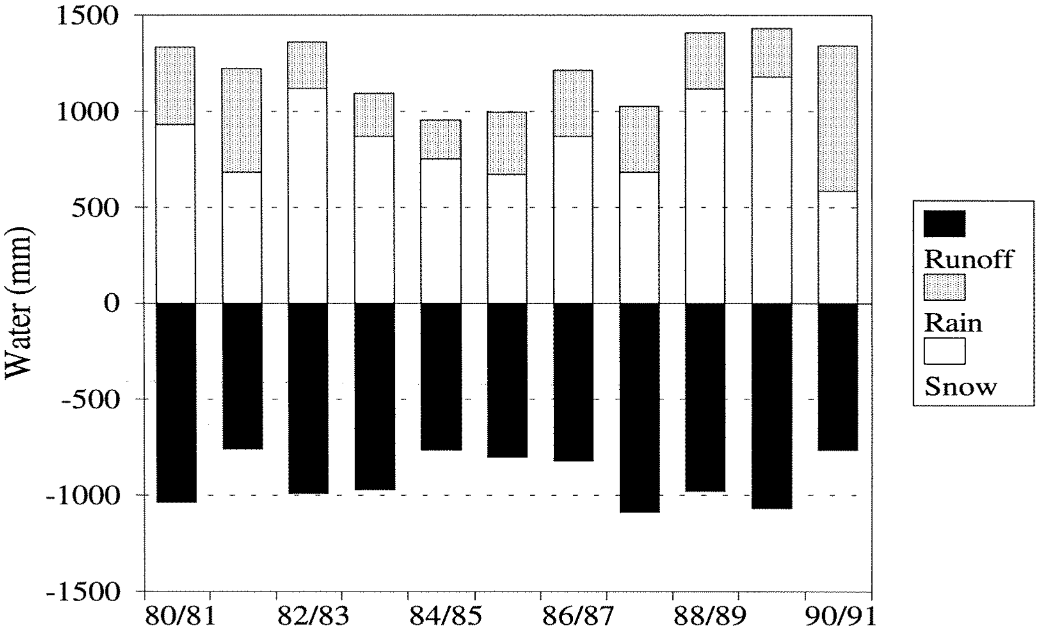


Figure 4.17 Annual accumulation of snow during winter (1 November-31 March), and precipitation and runoff the following spring (1 April-30 June) at the Kaarvatn catchment during the period 1980/81-1990/91. The runoff is illustrated by negative values in the figure.

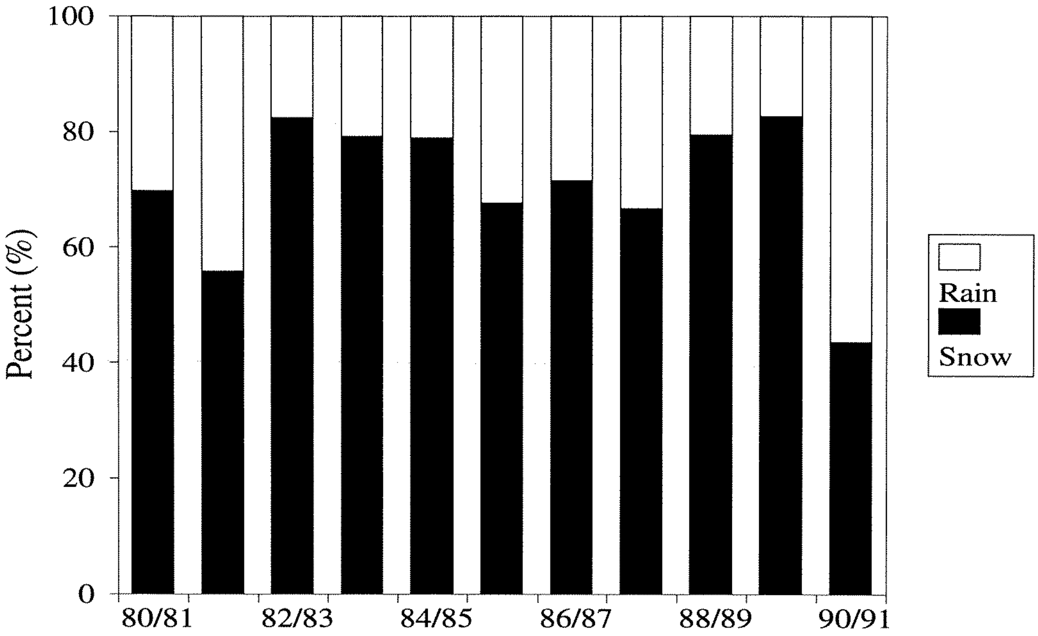


Figure 4.18 The percentage contribution of accumulated snow during winter (1 November- 31 March) and precipitation during spring (1 April-30 June) to the spring-runoff at the Kaarvatn catchment during 1980/81-1990/91.

Table 4.5 Annual mean temperatures at Kaarvatn from 1984-1991, and average temperatures during each successive three months period, during winter (1 Nov - 31 Mar) and spring (1 Apr. - 30 June).

Year	Annual Jan-Dec	1st quarter Jan-Mar	2nd quarter Apr-Jun	3rd quarter Jul-Sep	4th quarter Oct-Dec	Spring Apr-Jun	Winter Nov-Mar
1984	7.1	0.0	9.9	12.2	6.1	9.9	
1985	5.8	-1.0	9.2	12.9	2.1	9.2	1.4
1986	6.3	-1.1	9.9	11.7	4.9	9.9	-1.1
1987	6.2	-1.9	9.0	12.2	5.4	9.0	0.1
1988	7.2	1.4	9.2	14.5	3.8	9.2	1.9
1989	7.8	4.5	9.9	12.5	4.4	9.9	3.6
1990	8.3	4.6	10.4	13.0	5.1	10.3	4.0
1991	7.4	2.2	8.7	13.8	5.0	8.7	2.6
Mean	7.0 ± 0.8	1.1 ± 2.4	9.5 ± 0.5	12.8 ± 0.9	4.6 ± 1.1	9.5 ± 0.6	1.8 ± 1.7

Annual average runoff at Kaarvatn during the monitoring period is 1856 ± 306 mm (water-year: Sep-Aug). As for precipitation, the lowest annual runoff was recorded in 1981/82 (1331 mm), while the highest runoff was recorded in 1988/89 with 2352 mm (Figure 4.15).

Highest monthly runoff is normally recorded in June (Figure 4.16), the main month of spring melt, with 458 ± 65 mm. This is 17% higher than the second most runoff rich month, May, and about 3 times higher than the most runoff rich month during autumn, September. On average, 46% of annual runoff leaves the catctment during May and June.

Lowest monthly runoff (Figure 4.16) is normally recorded from December to March, i.e. 31 ± 20 mm (Dec), 21 ± 21 mm (Jan), 17 ± 11 mm (Feb), and 18 ± 12 mm (Mar). The runoff these months only constitute 1.7 ± 1.0%, 1.1 ± 0.8%, 0.9 ± 0.5% and 0.9 ± 0.6% of total annual runoff. November and April also exhibit low runoff values, i.e. 54 ± 28 mm and 66 ± 40 mm. Rest of the year, from May to October, the runoff is normally high. Because large amounts of snow accumulate in the catchment every winter besides a constant high precipitation, drought periods during the summer have never been recorded at Kaarvatn. Monthly runoff values < 100 mm are recorded 3 times from May to August, all in August, lowest in 1982 (51 mm).

The highest monthly runoff was recorded in May 1981 with 582 mm, mainly because of a precipitation rich April. No air temperature was recorded at that time (Table 4.5), but since the accumulation of snow during the winter was only somewhat higher than normal (Figure 4.17), and because 31% of annual runoff this year left the catchment during May, the air temperature in May 1981 was probably high. The highest runoff value at autumn was recorded in October 1983 with 335 mm, and was a direct consequence of high precipitation both in October and September. The R/P-ration in October (74%) was, however, lower than the average R/P-ratio for this month (83 ± 45%). Monthly runoff values > 500 mm are recorded 5 times and always in May or June.

Low runoff values during spring melt (1 April- 30 June) were recorded in 1982, 1985, 1991 (Figure 4.17), with 759 mm, 763 mm and 766 mm, respectively, while high runoff values were recorded in 1981, 1988 and 1990, with 1038 mm, 1090 mm and 1070 mm respectively. This demonstrates both the regularity and the quantitatively importance of snow melt at Kaarvatn. Average accumulation of snow during the winter is 860 mm ± 197, maximum accumulation during the winter 1989/90 (1182 mm) and minimum accumulation in 1990/91 (585 mm). During the snow richest winters, accumulated snow contributes by > 80% of the runoff during spring melt. Runoff values during spring melt > 1000 mm are recorded 3 times, and about 50% of total annual runoff these years were from spring melt.

During 1 August to 31 October the catchment is usually well water saturated. The mean R/P-ratios in August, September and October are estimated to be 83 ± 30%, 84 ± 46 and 83 ± 45% respectively. These ratios are very similar to that found at Birkenes and Storgama during the same period. It is not very informative to estimate the R/P-ratio during summer at Kaarvatn, since the whole summer is affected by melt water, which is "old" water accumulated as snow during the winter.

At Kaarvatn a significant high flow period always occurs during spring, i.e. from late April and until medio or ultimo July. Then the runoff continues to decrease almost until next spring melt, so that a low flow period may occur once during the winter. Highest precipitation normally occurs at autumn and early winter, while slightly lower amounts enter the catchment during the rest of the year, lowest in May and June. Among the four catchments, Kaarvatn exhibits the largest quantitative hydrologic variations, as well as the highest degree of seasonal regularity.

The annual average evapotranspiration at Kaarvatn during the monitoring period is estimated to be 319 ± 125 mm.

4.7 Summary

The catchments exhibit large hydrologic variations both regarding quantity of water and the seasonal flow patterns. It is, however, a significant relationship (Figure 4.19) between annual precipitation and distance from the coast (km):

$$\text{Precipitation (mm)} = y = -509*\log(\text{km}) + 2211 \ (r = 0.87). \qquad \text{(I)}$$

A corresponding relation is well documented in the literature, and should therefore be expected. Nevertheless, Kaarvatn undoubtedly belongs to another climatic region compared with the other sites, This is confirmed by the precipitation chemistry at Kaarvatn compared with the other sites (See Chapter 5).

Both yearly (Figure 4.20) and monthly variations in precipitation coincide very well at Birkenes, Storgama and Langtjern. This means that when it rains at Birkenes, it usually rains at Storgama and very often at Langtjern, but at Storgama less than at Birkenes and at Langtjern less than at Storgama. This is because most depressions enter southern Norway by western and south-western

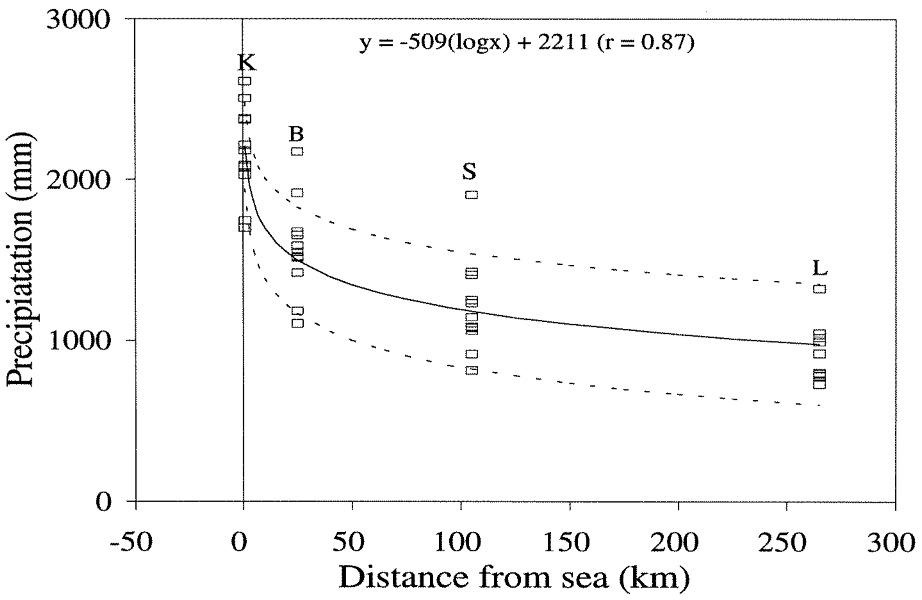


Figure 4.19 The annual amount of precipitation with distance from the sea.

winds, a typical pattern for the northern hemisphere. Birkenes, Storgama and Langtjern are located approximately on a south-southern line (Figure 4.21), with a relatively nice gradient regarding distance from the sea. The relationship between annual input of water with distance from the sea (km), along this line, from Birkenes to Langtjern, is:

Precipitation (mm) = $y = -643 * \log(km) + 2436$ ($r = 0.84$) (II)

The lower significance in equation II compared with equation I where Kaarvatn is incorporated, only illustrates that the relationship between amount of precipitation with distance from the sea may vary a lot from one precipitation event to another both regarding quantitative (amount of water) and qualitative differences (velocity of depression).

Even though the three southernmost sites exhibit relatively similar precipitation patterns, the runoff patterns do vary a lot, primarily because of different winter temperatures, warmest at Birkenes, coldest at Langtjern. While minor or sometimes no snow is accumulated during a winter at Birkenes, a similar situation is very uncommon or rarely at Storgama and Langtjern.

Kaarvatn and Langtjern are the catchments which year by year exhibit the most regular seasonal hydrological patterns, while Birkenes exhibits the highest irregularity, mainly because the winter temperature is often close to 0°C. Small changes in winter temperature at Birkenes may therefore be decisive to which extent the precipitation accumulates as snow or not.

Table 4.6 Hydrology relationships between the four catchments based on annual averages during the monitoring period. = : The difference is > 2.5%; > : The difference is < 25%; >> : The difference is > 25%; >>> : The difference is > 50%.

Annual precipitation	Kaarvatn	>>	Birkenes	>	Storgama	>>	Langtjern
Precipitation days	Kaarvatn	>	Birkenes	>	Langtjern	=	Storgama
Intensity of rain	Kaarvatn	>>	Birkenes	=	Storgama	>>	Langtjern
Evapotranspiration	Birkenes	>	Kaarvatn	>	Storgama	=	Langtjern
Accumulation of snow	Kaarvatn	>>>	Storgama	>>	Langtjern	>	Birkenes
Snow/annual precip. (%)	Kaarvatn	>>	Langtjern	>	Storgama	>>	Birkenes
Autumn rain*	Kaarvatn	>	Birkenes	>	Storgama	>>	Langtjern
Pe/Rm *	Kaarvatn	=	Birkenes	=	Storgama	>	Langtjern
Annual runoff	Kaarvatn	>>	Birkenes	>	Storgama	>>	Langtjern
Runoff 1st quarter	Birkenes	>>>	Storgama	>>	Kaarvatn	>	Langtjern
Runoff 2nd quarter	Kaarvatn	>>>	Storgama	>	Langtjern	>	Birkenes
Runoff 3rd quarter	Kaarvatn	>>>	Birkenes	>	Storgama	>>	Langtjern
Runoff 4th quarter	Kaarvatn	>>	Birkenes	>>	Storgama	>>	Langtjern
Spring melt	Kaarvatn	>>>	Storgama	>	Langtjern	>	Birkenes
Spring melt/annual runoff (%)	Kaarvatn	>	Langtjern	>	Storgama	>>	Birkenes

***:** The highest monthly input of water during autumn. The P_e/R_m ratio is also based on this month.

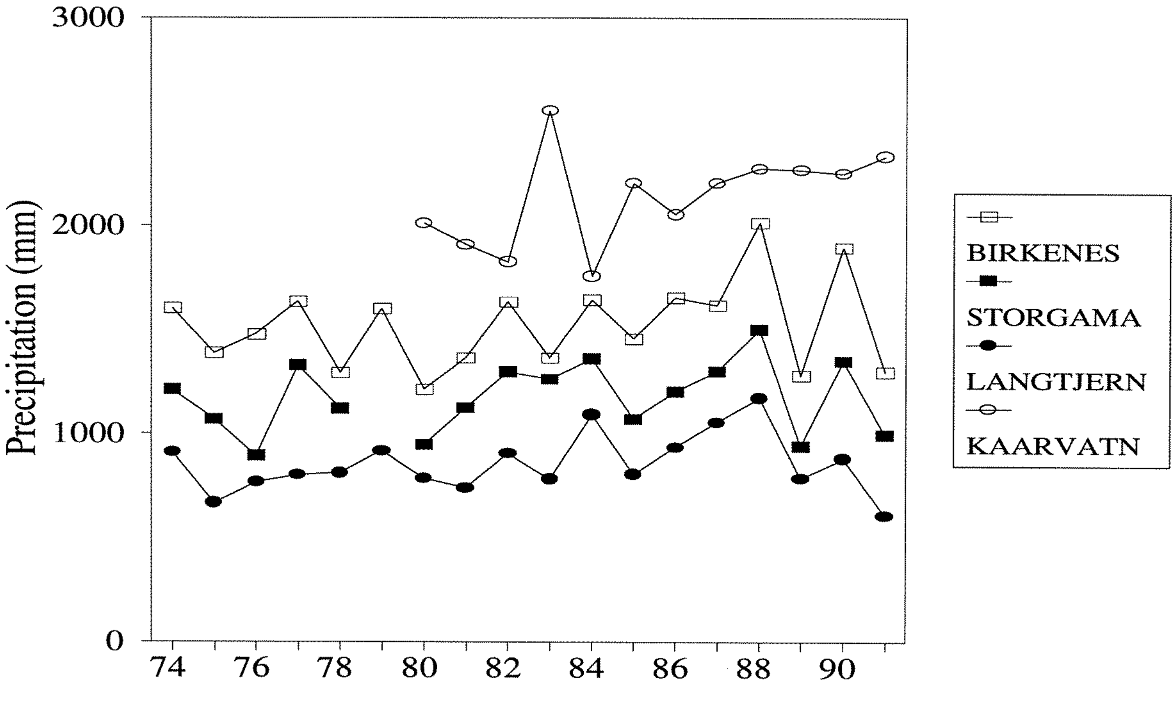


Figure 4.20 Annual precipitation at the four sites during the monitoring period.

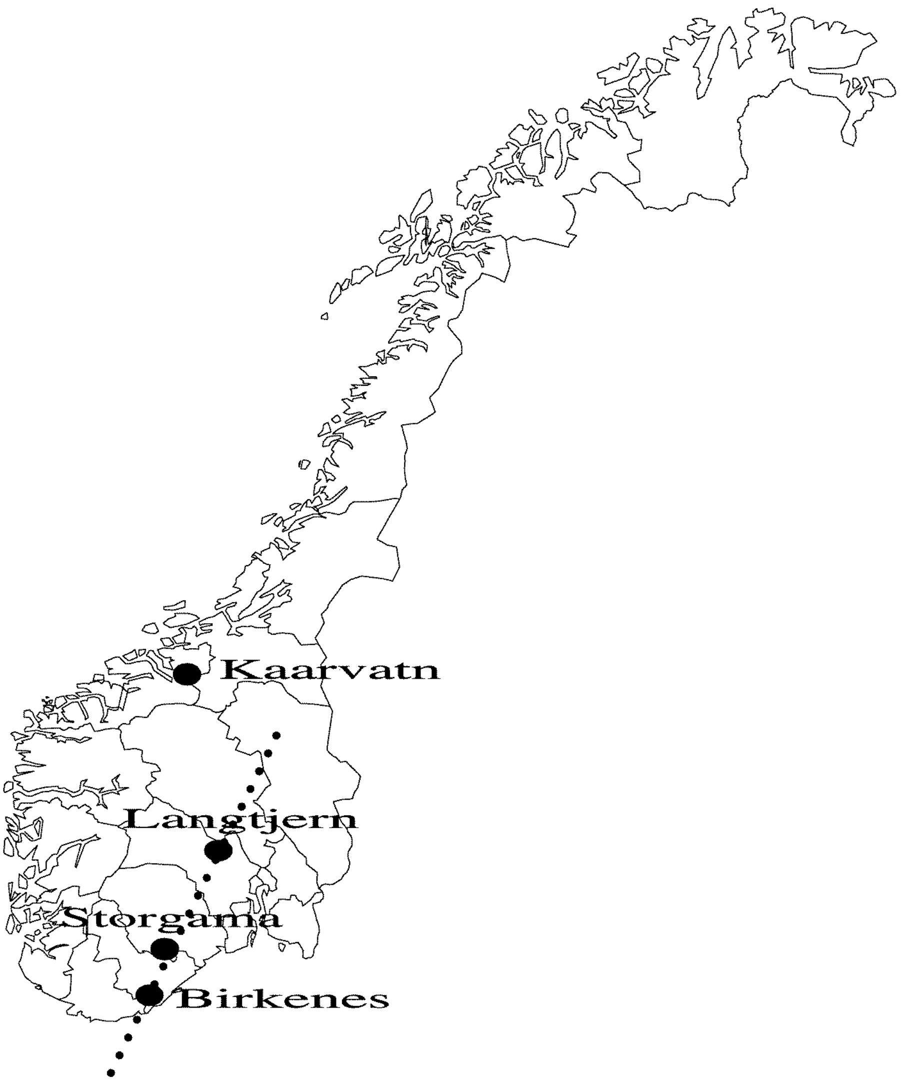


Figure 4.21 The location of Birkenes, Storgama and Langtjern along a stipulated south-western line.

5. CHEMISTRY

Weekly samples of dry deposition and runoff water, and daily samples of precipitation (wet deposition) are obtained from the watersheds for chemical analysis. Dry deposition is sampled on different filters, while rain and snow are sampled with continuously open plastic collectors. Samples of runoff water are collected well upstream from each wire in clean polyethylene bottles. This is necessary because water collected from the ponding basin close to the wire would be contaminated by calcium and bicarbonate from the cement in the weir itself. More details concerning sampling and analysis are present in Chapter 2.

The concentrations of dissolved chemicals characterizing a period of time are reported as weighted averages. These averages are computed by summing the amount of chemical from individual samples of precipitation or runoff water during the period and then dividing this value by the total amount of water during the period. Chemical fluxes across ecosystems boundaries is determined (1) by multiplying the measured concentration of dissolved chemicals in the accumulated composite sample precipitation by the amounts of precipitation during the interval (day) and (2) by multiplying the average of measured concentrations of dissolved chemicals from runoff water samples taken at the beginning and at the end of the interval (week) by the amount of runoff during the period.

The concentration of dry deposition compounds characterizing a period of time are also reported as weighted averages. These averages are computed by dividing the amount of dry deposition retained on the filter during the collection period (week) with the volume of air that has passed through during the correspondent period. The fluxes of dry deposition is further calculated on the basis of the deposition velocities presented in Chapter 2.

It has been shown that sampling according to a standard time series may seriously underestimate or overestimate a highly variable parameter (e.g. Claridge, 1970). However, even though the concentrations of chemicals fluctuate a lot, the fluctuations are not that extreme. Thus, serious errors are not produced by daily sampling of rainwater or by continuously sampling of dry-deposition. For streamwater where only spot samples are collected once a week, larger errors may arise when weekly weighted means are estimated on the basis of one sample.

Preciptation chemistry has been monitored at Birkenes, Storgama, and Langtjern more or less continuously from 1974, while the monitoring programme at Kaatvatn was initiated in 1979, and more or less continuously monitored since then (see Chapter 1).

Dry deposition of both SO_2-gas and SO_4-particles have been continuously monitored at Birkenes from 1978, at Kaarvatn from 1979, and at Langtjern from 1988, while at Storgama these compounds were only measured in 1978. Dry deposition of nitrogen compounds (NO_2-gas and gas and particles of $\Sigma NO_3,HNO_3$ and $\Sigma NH_4,NH_3$) have been continuously monitored at Birkenes from 1986 and at Kaarvatn since 1988. Dry deposition of base cations and chloride has only been monitored at Birkenes, base cations continuously since 1986, chloride since 1988, except 1989.

5.1 Wet-deposition.

Annual weighted concentrations

The precipitation at Birkenes, undoubtedly, contains the highest concentration of chemical compounds, i.e. ΣCations+Anions = 342 ± 35 μeq/L (Table 5.2). This is 1.6 times higher than at Storgama, and 1.7 and 2.2 times higher compared with the precipitation at Langtjern and at Kaarvatn.

The major cations in precipitation (μeq/L) at Birkens is dominated by H^+-, NH_4^+- and Na^+-ions, which averagely constitute 30 ± 4%, 27 ± 3% and 27 ± 5% of the total cationic pool, respectively (Figure 5.1). The remaining 16% is distributed on Ca^{2+} (6 ± 1%), Mg^{2+} (7 ± 1%) and K^+ (3 ± 1%). The anions in precipitation are dominated by SO_4^{2-}, which constitutes 41 ± 4%, while Cl^- and NO_3^- constitute 34 ± 5% and 25 ± 3% of the total anionic pool.

At Storgama, H^+ is the predominant cation, and constitutes by 45 ± 3% of the total cationic pool, while NH_4^+ and Na^+ constitute 29 ± 3% and 14 ± 2%, respectively (Figure 5.1). The remaining 12% is Ca^{2+} (6 ± 1%), Mg^{2+} (4 ± 1%) and K^+ (2 ± 1%). The anionic pool is dominated by SO_4^{2-}, which constitutes 51 ± 5%, while Cl^- and NO_3^- constitute 19 ± 4% and 30 ± 3%.

At Langtjern, H^+ and NH_4^+ are the predominant cations, and contribute by 40 ± 6% and 35 ± 7% of the total cationic pool, while Na^+ only constitutes 8 ± 3% of the cation pool (Figure 5.1). The remaining 17% is Ca^{2+} (9 ± 1%), Mg^{2+} (4 ± 1%) and K^+ (4 ± 1%). The anionic pool is dominated by SO_4^{2-}, which constitutes 57 ± 3%, while Cl^- and NO_3^- constitute 11 ± 3% and 32 ± 3%.

At Kaarvatn, Na^+ is the predominant cation, and contributes by 55 ± 6% to the total cationic pool. Mg^{2+} and H^+ both contribute by 12 ± 3%, while NH_4^+ constitute 10 ± 2 (Figure 5.1). The remaining 11% is Ca^{2+} (8 ± 4%) and K^+ (3 ± 0.4%). The anionic pool is dominated by Cl^- which constitutes 69 ± 8%, while SO_4^{2-} and NO_3^- constitute 23 ± 6% and 8 ± 3%.

Table 5.1 Annual weighted concentration ratios (μeq/L) of basecation/chloride in relation to the correspondant ratios of seawater, and annual weighted concentration ratios of ***A****: $[H^+]/[SO_4^*]$;* ***B****: $[NH_4]/[NO_3^-]$; and* ***C****: $\Sigma[Ca^{2+}]_{marine} + ([NH_4^+]-[NO_3^-])/[SO_4]_{marine}$ in precipitation at the four catchments.*

Locality	Distance from sea (km)	Ca/Cl	Mg/Cl	Na/Cl	K/Cl	A	B	C
Seawater		0.037	0.195	0.856	0.018			
Kaarvatn	0	0.14	0.20	0.87	0.04	0.98	1.60	0.91
Birkenes	25	0.20	0.21	0.86	0.10	0.88	1.09	1.15
Storgama	105	0.39	0.24	0.80	0.14	0.99	1.03	0.92
Langtjern	265	0.88	0.33	0.81	0.39	0.80	1.19	7.04

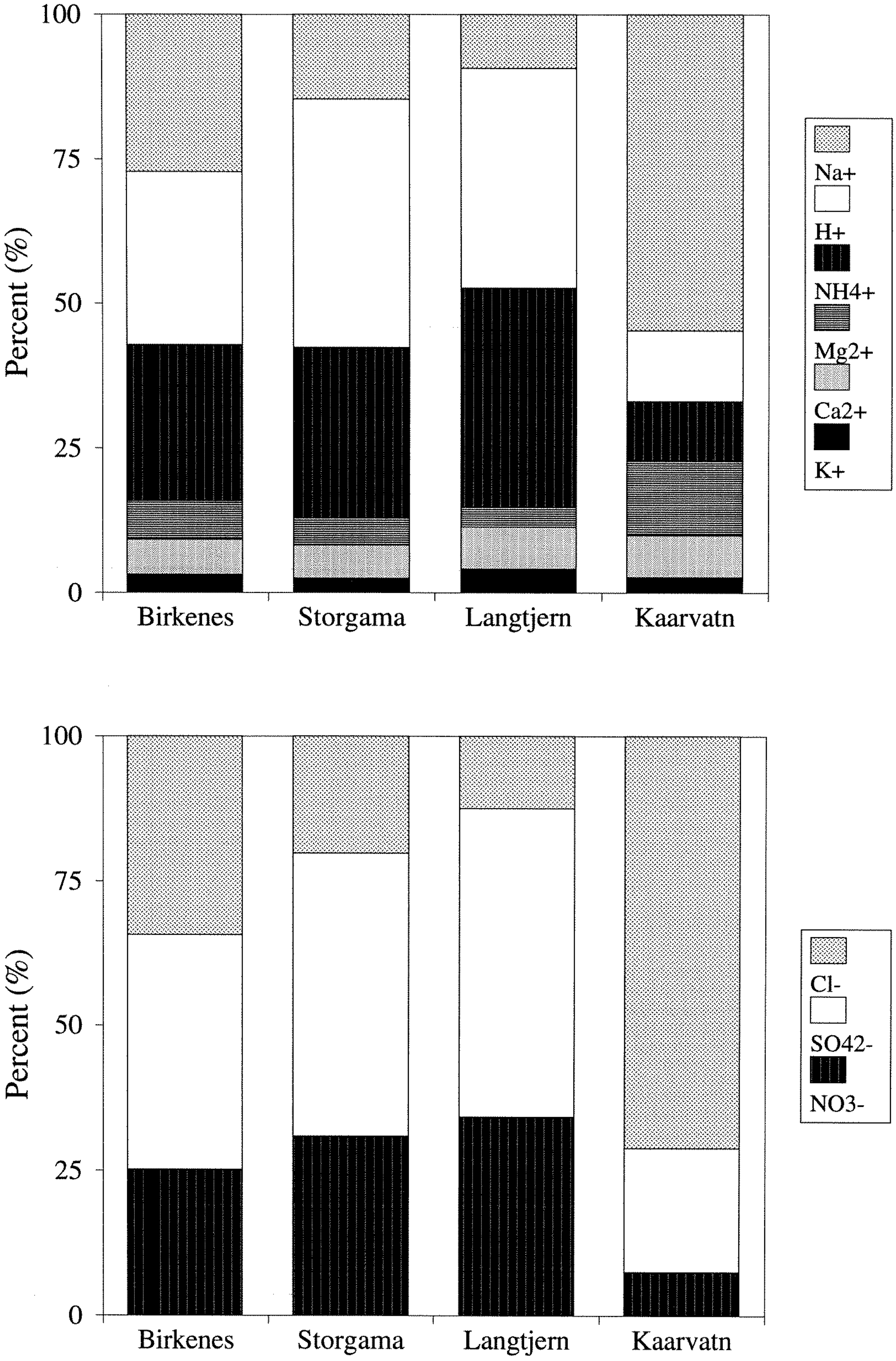


Figure 5.1 The percent distribution of major cations and anions in wet deposition at the different catchments, based on annual weighted means (µeq/L) during the monitoring period.

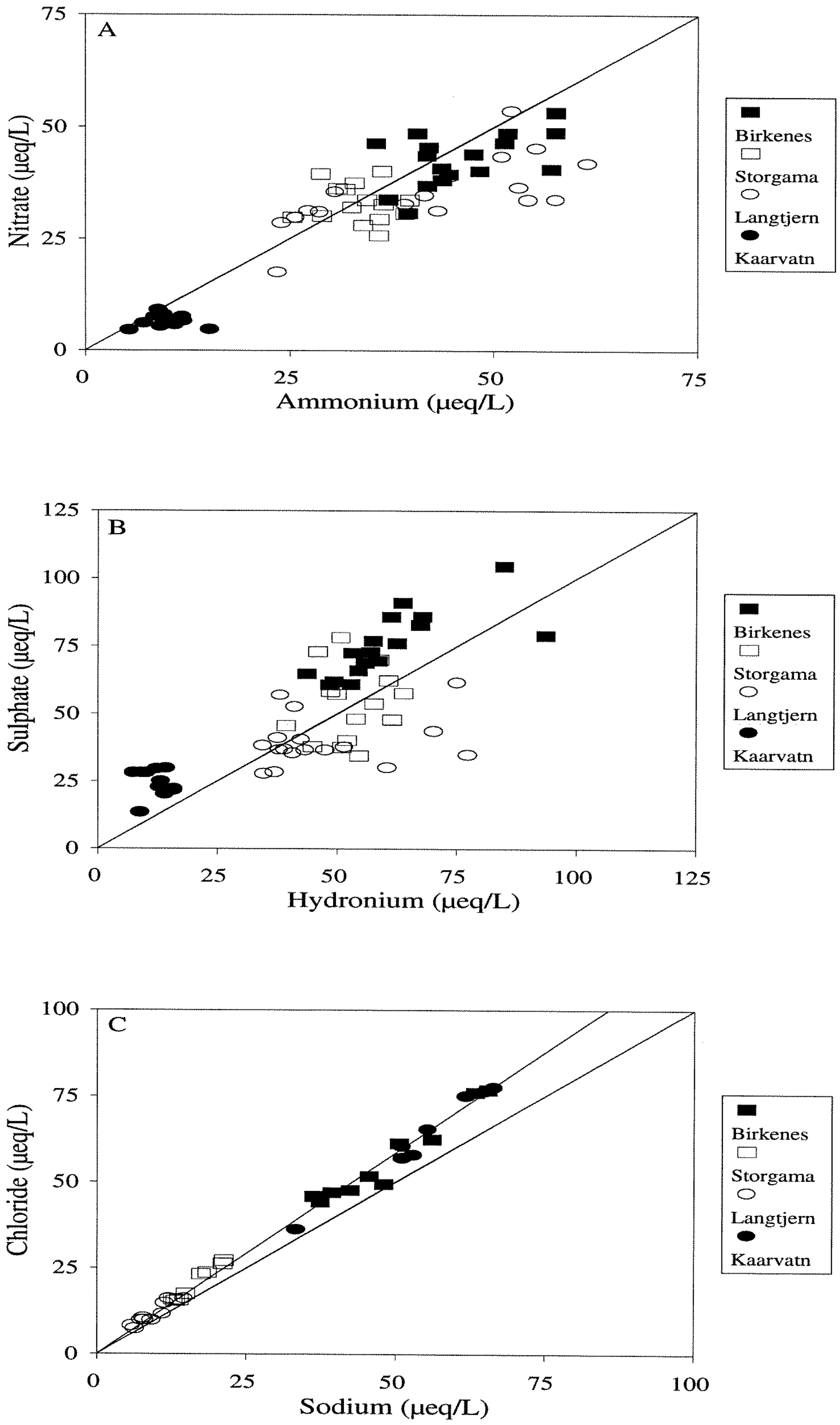


Figure 5.2 The ammonium/nitrate ratio (A), the hydronium/sulphate ratio (B), and the sodium/chloride ratio (C) in wet deposition from the different catchments, based on annual weighted averages during the respective monitoring periods. Continuous line represents the 1/1 line. The dotted line represents the Na/Cl ratio of seawater.

As relatively well documented, the chemisty of wet deposition at the four sites can be characterized as a solution of sulphuric-acid, ammonium-nitrate and sodium-chloride, but with large differences in the concentration and the relative distribution of these chemical compounds between the different sites (Figure 5.2). High input of ammonium-nitrate and sulphuric-acid indicates high influence from manmade activitites (combustion of coal and gasoline, and fertilization of agricultural areas) from both long-range and more local sources. In addition, all catchments are more or less influenced by seasalts, depending on the location of the catchment with respect to distance from the sea. Typically, the most coastnear catchments, Kaarvatn and Birkenes, receive the highest amounts of sodiumchloride, magnesiumchloride and sulphate-salts, the last probably with divalent basecations (as calcium and magnesium) and/or with ammonium as the predominant counter-ion (Table 5.1). Both the Na/Cl and Mg/Cl ratios in the precipitation at Birkenes and Kaarvatn are approximately equal to that present in seawater (Table 5.1). Langtjern, the most typical inland catchment, is on the other hand, far more influenced by terrestrial sources than by marine. The basecations/chloride ratios of precipitation do therefore differ a lot from that present in seawater.

On a long term basis, ΣCation, is not significantly different from ΣAnion (Table 5.2). However, it is a general tendency of higher ΣCation compared with ΣAnion. This fact might probably be explained by the analysis programme, where ions like HCO_3^-, PO_4^{3-}, Br^-, F^-, I^- and organic anions (A^-) are omitted. Despite this fact, these anions may only constitute a minor part of the anionic pool. These ions may originate from both sea and seaspray as well as from earth dust, and are expected to vary due to climatic/seasonal variation. Another explaination for the excess of cations in precipitation, is that soil particles and aerosols in the atmosphere may be chemically altered to produce cations. The ubiquitous hydrogen ions in precipitation may react with the entrained soil particles and release cations into solution. Therefore, some of the cations may have been derived from an "artificial weathering" reaction within the continuously open bulk collector. Such reactions would not change the total amount of cations input to the ecosystem, but might alter their chemical forms and underestimate the input of hydrogen ion in precipitation.

Surprising concentrations of dissolved organic carbon were found in both snow and rain at the Hubbard Brook, a monitored forested ecosystem in New Hampshire, U.S.A. Average carbon concentrations falling on the Hubbard Brook watershed were 2.4 mg C/L (Jordan and Likens, 1975), but only a small fraction was present as dissociated organic acids (Likens et al. 1976; Galloway et al., 1976). On the basis of a few storm analyses, volatile caboxylic acids, carbohydrates, and tannin-lignin contributed $\leq 30\%$ of the organic matter in precipitation at Hubbard Brook. The actual composition of the dissolved organic carbon in precipitation is probably a mixture of many organic species, all of which are present in trace amounts. The high amounts of organic compounds found in the precipitation at Hubbard Brook is very interesting, especially as this pool may represent an important additional energy source for ecosystems. However, since it is most likely that the organic pool of wet- and dry-deposition basically originates from local sources, transport of organic compounds from the catchment should also have been measured, but that is very difficult. Thus, the net effect of atmospheric organic input to the catchment compared with organic output from the catchment is impossible to evaluate.

Table 5.2 Annual maximum, minimum and annual weighted averages of precipitation (mm) and concentrations of dissolved substances (µeq/L) in bulk precipitation at the catchments during the monitoring periods.

Period		**Birkenes 1974-1991**	**Storgama 1974-1991**	**Langtjern 1974-1991**	**Kaarvatn 1979-1991**
	max	*2174*	*1906*	*1325*	*2612*
Precipitation	**mean**	**1529 ± 283**	**1206 ± 273**	**864 ± 159**	**2175 ± 275**
	min	*1062*	*771*	*577*	*1699*
	max	*94*	*64*	*77*	*16*
H^+	**mean**	**61 ± 12**	**53 ± 7**	**48 ± 14**	**12 ± 3**
	min	*44*	*39*	*34*	*7.4*
	max	*58*	*40*	*61*	*15*
NH_4^+	**mean**	**46 ± 7**	**34 ± 4**	**42 ± 13**	**10 ± 2**
	min	*36*	*25*	*24*	*5.5*
	max	*19*	*11*	*22*	*12*
Ca^{2+}	**mean**	**12 ± 3**	**7.5 ± 1.6**	**11 ± 4.9**	**7.6 ± 2.7**
	min	*7.5*	*5.3*	*5.9*	*4.2*
	max	*17*	*6.7*	*6.9*	*17*
Mg^{2+}	**mean**	**12 ± 2**	**4.8 ± 1.0**	**4.1 ± 1.3**	**12 ± 3**
	min	*8.8*	*3.6*	*2.3*	*7.7*
	max	*66*	*21*	*15*	*66*
Na^+	**mean**	**49 ± 10**	**17 ± 3**	**9.3 ± 2.7**	**55 ± 10**
	min	*36*	*13*	*5.8*	*33*
	max	*6.6*	*4.5*	*6.6*	*3.2*
K^+	**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*
	max	*105*	*73*	*106*	*26*
SO_4^{2-}	**mean**	**75 ± 12**	**56 ± 8**	**62 ± 18**	**20 ± 4**
	min	*61*	*43*	*37*	*11*
	max	*77*	*27*	*17*	*79*
Cl^-	**mean**	**58 ± 12**	**20 ± 5**	**12 ± 3**	**60 ± 14**
	min	*44*	*13*	*7.2*	*36*
	max	*53*	*40*	*54*	*9.1*
NO_3^-	**mean**	**43 ± 6**	**33 ± 4**	**35 ± 8**	**6.5 ± 1.3**
	min	*31*	*26*	*18*	*4.5*
	max	*240*	*164*	*170*	*136*
Ionic strength	**mean**	**215 ± 20**	**141 ± 13**	**138 ± 24**	**114 ± 14**
(µmol/L)	*min*	*189*	*122*	*93*	*88*
ΣCations	**mean**	**177 ± 17**	**114 ± 8**	**107 ± 17**	**99 ± 11**
ΣAnions	**mean**	**165 ± 18**	**105 ± 11**	**97 ± 20**	**89 ± 13**
ΣCat + ΣAn	**mean**	**342 ± 35**	**219 ± 19**	**205 ± 37**	**189 ± 24**
ΣCat - ΣAn	**mean**	**12 ± 6**	**9 ± 5**	**10 ± 4**	**10 ± 5**

Annual weighted influxes

The influxes of chemical compounds from precipitation (wet-deposition) do not only depend on the concentrations, but are, of cause, highly dependent on the amount of precipitation. Since Birkenes is the second most precipitation-rich catchment and undoubtedly receives the highest concentrations of dissolved chemical compounds, this catchment also receives the highest inputs of chemical compounds (Table 5.3), i.e. 536 ± 98 meq/m^{2}yr. While the annual weighted concentration average of ions in wet-deposition at Birkenes is 2.2 times higher than at Kaarvatn, the correspondant total influx of ions at Birkenes is only 1.2 times higher. This clearly demonstrates the importance of water input for the influx of chemical componds. Annual precipitation at Kaarvatn is averagely 2175 ± 275 mm, which is a factor 1.4 higher compared with that normally precipitating at Birkenes. Total annual influx of ions by wet-deposition at Birkenes is 2.1 higher compared with at Storgama and 3.4 higher than at Langtjern, the most precipitation-poor catchment.

The major cations in wet-deposition (meq/m^2 yr) at Birkens are H^+-, NH_4^+-and Na^+-ions, which constitute 30 ± 5%, 24 ± 3% and 31 ± 5% of the total wet-deposition influx of cations, respectively. The remaining 15% is distributed on Ca^{2+} (5.3 ± 1.1%), Mg^{2+} (7.4 ± 1.2%) and K^+ (2.5 ± 0.3%). The wet-deposition input of anions are dominated by SO_4^{2-} and Cl^- which constitute 38 ± 6% and 38 ± 7% of the input of anions, while the remaining 24 ± 2% originates from wet-deposition of NO_3^-.

At Storgama, H^+ is the predominant cation, and constitutes 44 ± 3% of the total annual wet-deposition influx of cations, while NH_4^+ and Na^+ constitute 28 ± 2% and 16 ± 3%, respectively. The remaining 12% is Ca^{2+} (4.9 ± 0.9%), Mg^{2+} (4.6 ± 0.9%) and K^+ (1.8 ± 0.9%). The anion influx is dominated by SO_4^{2-}, which constitutes 48 ± 5%, while Cl^- and NO_3^- constitute 21 ± 3% and 31 ± 3%, respectively.

At Langtjern, H^+ and NH_4^+ are the predominant cations, and contributes by 45 ± 8% and 33 ± 7% to the total annual wet-deposition influx of cations, while Na^+ only constitutes 8.8 ± 1.4% of the cationic pool. The remaining 13% is Ca^{2+} (6.4 ± 0.7%), Mg^{2+} (3.1 ± 0.6%) and K^+ (3.9 ± 0.5%). The anion input is dominated by SO_4^{2-}, which constitutes 55 ± 5%, while Cl^- and NO_3^- constitute 12 ± 2% and 33 ± 4%, respectively.

At Kaarvatn, Na^+ is the dominating cation, and contributes by 60 ± 5% of the total annual wet-deposition influx of cations, while the second most typical marine cation, magnesium, contribute by 14 ± 1%. The remaining cations, H^+, NH_4^+, Ca^{2+}, and K^+ contribute by 10 ± 3%, 7.4 ± 2.1%, 5.9 ± 1.5% and 2.6 ± 0.4, respectively. Chloride contributes by 76 ± 5% of the annual wet-deposition influx of anions, while SO_4^{2-} and NO_3^- constitute 18 ± 4% and 5.4 ± 2%, respectively.

Table 5.3 Annual maximum, minimum, and annual weighted averages of precipitation (mm/m^2 yr) and wet-deposition influxes of major dissolved substances ($meq/\ m^2$ yr) at the four catchments during the monitoring periods.

Period		**Birkenes 1974-1991**	**Storgama 1974-1991**	**Langtjern 1974-1991**	**Kaarvatn 1979-1991**
Precipitation	*max*	*2174*	*1906*	*1325*	*2612*
	mean	**1529 ± 283**	**1206 ± 273**	**864 ± 159**	**2175 ± 275**
	min	*1062*	*771*	*577*	*1699*
H^+	*max*	*113*	*90*	*63*	*29*
	mean	**87 ± 18**	**61 ± 13**	**39 ± 11**	**22 ± 4**
	min	*57*	*41*	*24*	*17*
NH_4^+	*max*	*84*	*54*	*43*	*22*
	mean	**63 ± 14**	**36 ± 9**	**29 ± 10**	**17 ± 4**
	min	*38*	*21*	*13*	*9.9*
Ca^{2+}	*max*	*21*	*13*	*14*	*26*
	mean	**14 ± 2**	**7.5 ± 2.5**	**7.0 ± 2.7**	**15 ± 5**
	min	*11*	*4.1*	*4.2*	*9.5*
Mg^{2+}	*max*	*30*	*9.8*	*4.4*	*51*
	mean	**20 ± 5**	**5.7 ± 1.6**	**2.7 ± 0.7**	**31 ± 10**
	min	*11*	*3.7*	*1.7*	*18*
Na^+	*max*	*115*	*34*	*9.2*	*222*
	mean	**84 ± 25**	**21 ± 6**	**7.1 ± 1.5**	**142 ± 46**
	min	*41*	*12*	*4.1*	*88*
K^+	*max*	*9.5*	*3.4*	*4.7*	*7.9*
	mean	**6.8 ± 1.5**	**2.3 ± 0.8**	**3.1 ± 0.8**	**6.0 ± 1.2**
	min	*4.4*	*1.1*	*1.7*	*4.6*
SO_4^{2-}	*max*	*140*	*88*	*72*	*47*
	mean	**104 ± 20**	**62 ± 14**	**47 ± 10**	**39 ± 7**
	min	*74*	*42*	*33*	*22*
Cl^-	*max*	*157*	*41*	*12*	*260*
	mean	**99 ± 29**	**25 ± 8**	**8.7 ± 2.0**	**153 ± 54**
	min	*49*	*15*	*5.5*	*84*
NO_3^-	*max*	*84*	*59*	*39*	*13*
	mean	**61 ± 13**	**37 ± 9**	**25 ± 6**	**11 ± 1**
	min	*35*	*20*	*13*	*8.8*
ΣCations	**mean**	**275 ± 51**	**130 ± 33**	**88 ± 18**	**235 ± 57**
ΣAnions	**mean**	**264 ± 49**	**127 ± 27**	**81 ± 17**	**203 ± 57**
ΣCat + ΣAn	**mean**	**536 ± 97**	**251 ± 64**	**168 ± 34**	**451 ± 115**

The effect of precipitation on the ionic concentrations and fluxes

The percentage contributions of major ions in wet-deposition differ to some extend depending on whether it is concentrations (µeq/L) or fluxes (meq/ m^2yr) which are to be evaluated. This means that the amount of precipitation affects the concentrations of each ion in a varying degree. Based on simple linear regression analyses, a half-logaritmic relationships seems to be most adequate in most cases to express changes in the concentration of chemical dissolved compounds with respect to changes in the amount of precipitation. The exceptions are the concentrations of Na^+,Cl^- and H^+, where a linear relationships seems somewhat more cosistent. This is the case for all three compounds at the three most coastnear sites, Kaarvatn, Birkenes and Storgama, while a significant half-logaritmic relationship is more consistent concerning the concentration of Na^+ and Cl^- at Langtjern. Monthly weighted relationships, of cause, illustrate the water-dependent concentration changes far better than a correspondant regression made up by annual weighted averages. Concerning fluxes of dissolved chemical compounds, a linear-linear relationship describe the water-dependance best, and annual relationships are almost as good as the correspondant regressions made up by monthly averages. The water dependant changes in concentrations and fluxes based on both monthly and annual weigthed averages, are present in Appendix A and B.

As earlier described, the most coastnear sites, Birkenes and Kaarvatn, are highly influenced by seasalts, primarily sodium- and magnesium-chloride. At these sites, there are positive correlations between amount of precipitation and concentration of these compounds ($p < 0.05$), and the concentrations of Na^+, Mg^{2+} and Cl^- exhibit a linear increase by increasing input of water (Figure 5.3 and 5.6). Most extreme is the Kaarvatn catchment, where the monthly concentrations of Na^+, Mg^{2+} and Cl^- increase by averagely 24, 5, and 26 µeq/L per 100 mm of precipitation, which is more than two times higher than at Birkenes. At Storgama, a correspondent significant relationship does not exist, (Figure 5.4), while at Langtjern the concentrations of the typical seasalt-ions exhibit a logaritmic decrease by increasing amounts of precipitation. At Langtjern, the concentrations of Na^+, Mg^{2+} and Cl^- decrease by averagely 13, 8 and 18 µeq/L during an increase in precipitation from 10 mm to 100 mm (Figure 5.5). A positive correlation between seasalts and amount of precipitation should be expected at the most coastnear sites, because high amounts of precipitation is normally associated with strong winds, which significantly increases the influence of seaspray to coastnear sites. Even though seaspray primarely is aerosols of seawater, also seasalt particles will readily dissolve in rainwater due to the very high solubility of sodium- and magnesium-chlorides.

For the remaining dissolved chemical compounds analysed, there are a generally an significant logaritmic decrease in the concentrations by increasing amount of precipitation, except for H^+ at Langtjern and K^+ at Kaarvatn, where no significant relationships with the amount of precipitation were found (Figure 5.3-5.6). The degree of concentration changes due to variation in precipitation are schematically presented in Table 5.4. The lack of correlation between K^+-concentration and amount of precipitation at Kaarvatn, should rely on the high seawater influence at this site. The major sources of potassium is primarily of terrestric origins, geological (natural) and/or manmade (agricultural). Thus, a negative correlation with increasing precipitation should normally be expected. However, at Kaarvatn where the concentration of potassium is low, the potassium contribution from seawater to the concentration of this element in precipitation is highly important. This may explain why potassium normally increases by increasing inputs of water at this site. Based on the regression line for potassium (see Figure 5.6) at Kaarvatn, only 18% of potassium in precipitation normally originates from seawater by a monthly precipitation of 5 mm, while about 80% of potassium originates from seawater by a monthly precipitation of 500 mm.

The fact that there is no significant negative correlation between the H^+-concentration and the amount of precipitation at Langtjern, while correspondent significant relationships exist at the other three sites, does probably rely on several factors. The weather station at Langtjern is located in an agricultural area. In addition, Langtjern receives the lowest amount of precipitation, which means that the wet-deposition/dry-deposition ratio is low. These factors cause increased sampling problems and accompanying analytical difficulties. As commented on earlier, in areas receiving high proportion of dry-deposition compounds, the ability of hydrogen ions in precipitation to react with the entrained soil particles in the bulk collector will increase, and more cations will enter into solution. This can, to a certain extent, be illustrated by the increase in H^+/SO_4^* ratio at Langtjern by increasing amount of precipitation (Figure 5.12). Low wet-deposition inputs at Langtjern often occurs in April and May (see Figure 4.22). During these months, both forest floor and agricultural areas are very sensitive for wind-erosion, because "new" vegation is not yet established. In addition, agricultural activities such as ploughing, fertilizing and liming occur at large scale at that time. Thus, the contribution from dry-deposition is probably at the highest, and may explain why the lowest H^+/SO_4^* ratios most often occur at the same time. Simultaneously, high ammonium and calcium concentration are also registrated, which further confirm this assumtion (Figure 5.13). Similar tendencies during spring are also observed at the other three sites, but less extreme, which probably rely on higher wet-deposition/dry-deposition ratios at these sites.

An increase in the total concentration of ions in precipitation (ΣCations+Anions) by increasing amount of precipitation is the net result at both Birkenes and Kaarvatn, but only Kaarvatn exhibits a significant and logaritmic increase (Figure 5.11). At Langtjern and Storgama, the total concentration of ions (ΣCations+Anions) exhibit a significant logaritmic decrease by increasing amounts of precipitation (Figure 5.11). Concerning charge balance, cation excesses normally exist in wet-deposition at all sites, but the excess seems to decrease by increasing amount of precipitation at all sites, but only significant at Birkenes and Langtjern. This, confirm the theory presented above, about wet-deposition/dry-deposition ratios, but it may also rely on the fact that anions like organic anions, bicarbonate and phosphate are not being analysed.

Because most ions in precipiatation exhibit a statistical significant concentration changes with respect to amount precipitation, ions with a positive correlation, obviously exhibit correspondent positive correlations as far as fluxes are concerned. Several of the negatively correlated ions (decreasing concentration with increasing inputs of water) may not necessarely exhibit a correspondant positive correlation between ionic fluxes and precipitation. A linear regression between fluxes of ions and amount of precipitation are made up on the basis of monthly weighted averages. However, at all stations, a positive significant correlation ($p < 0.05$) was found between monthly ionic influxes (meq/m^2mth) and monthly inputs of water (mm/m^2mth) for all ions. The only exception was the ammonium flux at Kaarvatn, but also this relationship was close to significant, i.e. $p \approx 0.05$. (see Appendix B).

The most marine influenced sites which normally exhibit a significant increase in concentration of marine compounds in precipitation by increasing amount of precipitation, do also receive the highest inputs of water. Accordingly, these sites exhibit the strongest correlation between influxes of marine derived ions and input of water (Table 5.5, Figure

5.14). Most extreme is the Kaarvatn catchment which increase the monthly influxes of sodium, magnesium and chloride by averagely 10.2, 2.1 and 10.8 meq/m² per 100 mm of precipitation, a gradient which is approximately 30% higher compared with at Birkenes (Figure 5.14). Even for the more typical inland catchments, Storgama and Langtjern, a positive and significant correlation exists between influxes of marine compounds and inputs of water, but the gradients are 76.0% and 93.5% lower compared with at Kaarvatn (Figure 5.14). For the more terrestrial derived compounds, e.g. calcium and potassium, it is the other way around, which means that the most terrestrial influenced sites (Langtjern and Storgama) exhibit the highest positive correlation between influxes of terrestrial derived ions and inputs of water, despite these sites do not necessarely receive the highest concentrations of these ions (Table 5.2).

The Birkenes catchment which receives the highest concentration of "pollution compounds", also exhibits the highest increase in the influxes of these compounds by increasing inputs of water. Averagely, the monthly influxes of SO_4^{2-} and NO_3^- increase by 6.0 and 3.4 meq/m² per 100 ml of precipitation at Birkenes (Figure 5.14). At Storgama the correspondent increase is 4.7 (SO_4^{2-}) and 2.7 (NO_3^-) meq/m² per 100 ml of water, while at Langtjern the average increase is 4.9 (SO_4^{2-}) and 2.4 (NO_3^-) meq/m² per 100 ml of water. For the relatively unpolluted Kaarvatn catchment, the correspondent increases were far less, 1.2 (SO_4^{2-}) and 0.2 (NO_3^-) meq/m² per 100 ml of precipitation (Figure 5.14).

The concentration and influx of chemical compounds, e.g., H^+, NH_4^+,SO_4^{2-}, NO_3^- as well as the change in this parameters with respect to amount of precipitation, do to a certain extent, reveal the degree of atmospheric pollution at the different sites. This will be more firmly described later in this chapter (See Chapter 5.5, Acid precipitation).

Table 5.4 The degree of concentration changes (positive/negative correlation) with respect to the amount of precipitation, based on monthly weighted averages. The table is based on the linear regressions presented in Appendix A.

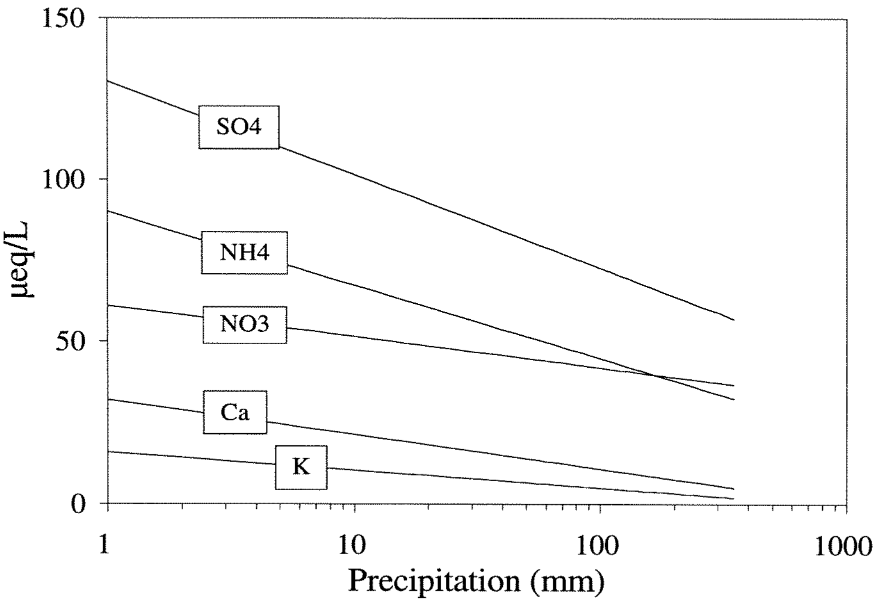
Ion	**Correlation**	**Degree of water dependence**						
H^+	negative	Birkenes	>	Storgama	=	Kaarvatn	>>	Langtjern*
NH_4^+	negative	Langtjern	>>	Birkenes	>>	Storgama	>>	Kaarvatn
Ca^{2+}	negative	Langtjern	>	Birkenes	>>	Storgama	>>	Kaarvatn
Mg^{2+}	negative	Langtjern	>>	Storgama				
Mg^{2+}	positive	Kaarvatn	>>	Birkenes				
Na^+	negative	Langtjern						
Na^+	positive	Kaarvatn	>>	Birkenes	>>	Storgama*		
K^+	negative	Birkenes	>	Storgama	>>	Kaarvatn	>>	Langtjern
Cl^-	negative	Langtjern						
Cl^-	positive	Kaarvatn	>>	Birkenes	>>	Storgama*		
NO_3^-	negative	Langtjern	>>	Birkenes	>	Kaarvatn	>	Storgama
SO_4^{2-}	negative	Langtjern	>	Birkenes	>	Storgama	>>	Kaarvatn

= : Difference < 5% compared with the foregoing site.
\> : Difference > 5% compared with the foregoing site.
\>> : Difference > 25% compared with the foregoing site.
* : not statistical significant, i.e. $p > 0.05$.

Table 5.5 The degree of changes in ionic fluxes (positive/negative correlation) with respect to the amount of precipitation, based on monthly weighted averages. The table is based on the linear regressions presented in Appendix B.

Annual precipitation		Kaarvatn	>>	Birkenes	>	Storgama	>>	Langtjern
Ion	**Correlation**	**Degree of water dependence**						
H^+	positive	Birkenes	=	Storgama	=	Langtjern	>>	Kaarvatn
NH_4^+	positive	Birkenes	>	Langtjern	>>	Storgama	>>	Kaarvatn*
Ca^{2+}	positive	Birkenes	>	Kaarvatn	>	Storgama	>	Langtjern
Mg^{2+}	positive	Kaarvatn	>>	Birkenes	>>	Storgama	>>	Langtjern
Na^+	positive	Kaarvatn	>>	Birkenes	>>	Storgama	>>	Langtjern
K^+	positive	Birkenes	>	Kaarvatn	>	Langtjern	>>	Storgama
Cl^-	positive	Kaarvatn	>>	Birkenes	>>	Storgama	>>	Langtjern
NO_3^-	positive	Birkenes	>	Storgama	>	Langtjern	>>	Kaarvatn
SO_4^{2-}	positive	Birkenes	>	Langtjern	>	Storgama	>>	Kaarvatn

= : Difference < 5% compared with the foregoing site.
> : Difference > 5% compared with the foregoing site.
>> : Difference > 25% compared with the foregoing site.
* : not statistical significant, i.e. $p > 0.05$.



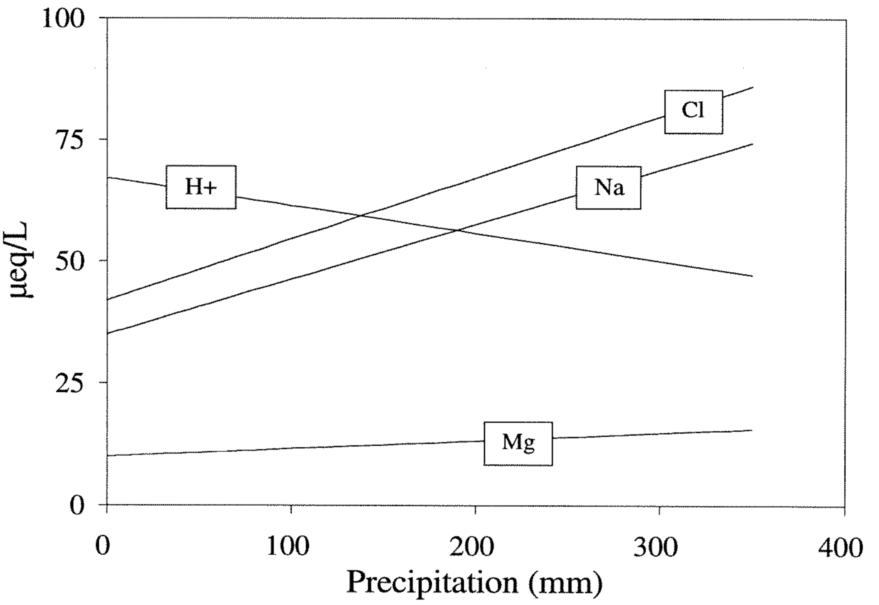
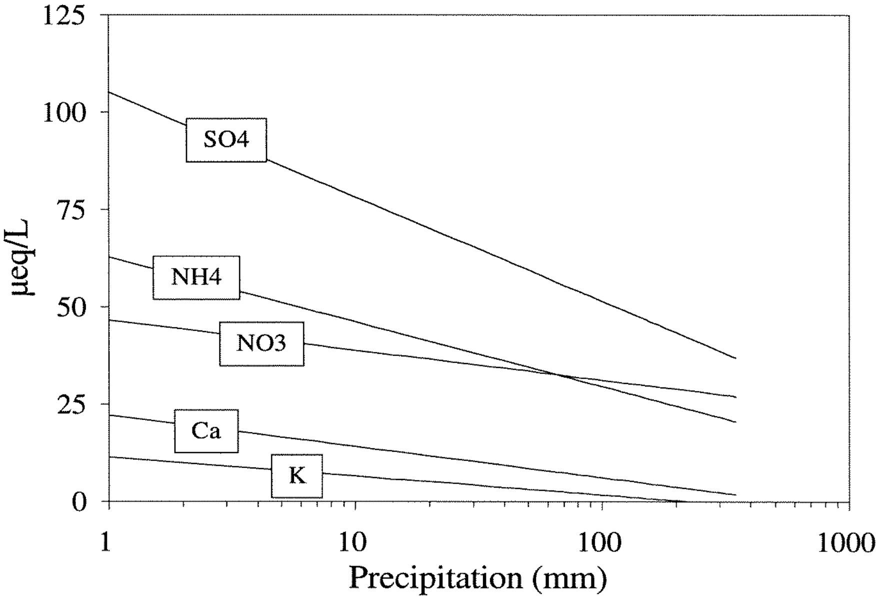


Figure 5.3 The relationships between monthly inputs of water (mm) and monthly weighted concentrations of major chemical dissolved species in precipitation (µeq/L) at Birkenes during the monitoring period. The relationships rely on linear regression analyses. The regression lines are: $[H^+]$: $y = -0.06x + 67.2$; $[NH_4^+]$: $y = -22.6(\log x) + 90.1$; $[Ca^{2+}]$: $y = -10.7(\log x) + 32.2$; $[Mg^{2+}]$: $y = 0.02x + 10.0$; $[Na^+]$: $y = 0.11x + 35.0$; $[K^+]$: $y = -5.5(\log x) + 15.9$; $[Cl^-]$: $y = 0.13x + 41.9$; $[NO_3^-]$: $y = -9.6(\log x) + 61.2$; $[SO_4^{2-}]$: $y = -28.9(\log x) + 131$. Continuous line indicates a significant relationship ($p < 0.05$), while a dotted line indicates no significance, i.e. $p > 0.05$. More details from the regression analyses are present in Appendix A.



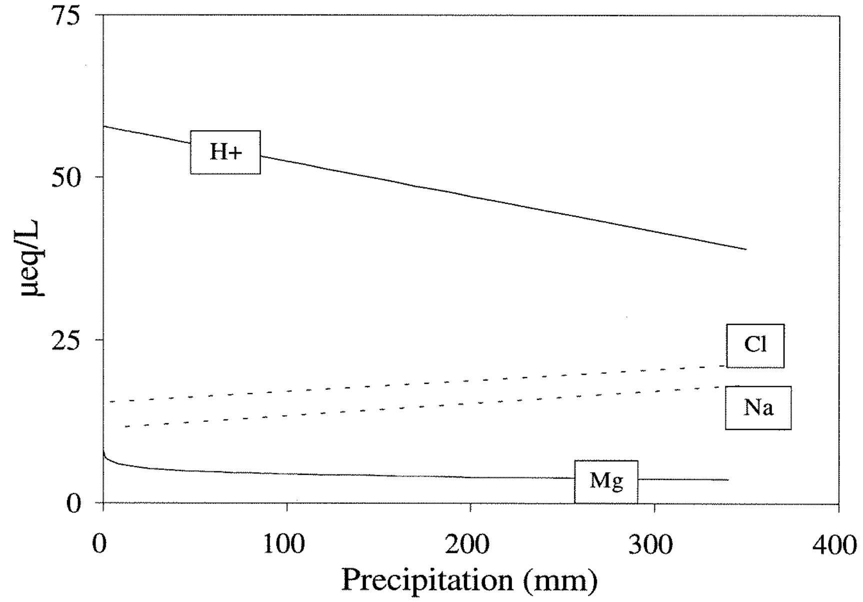
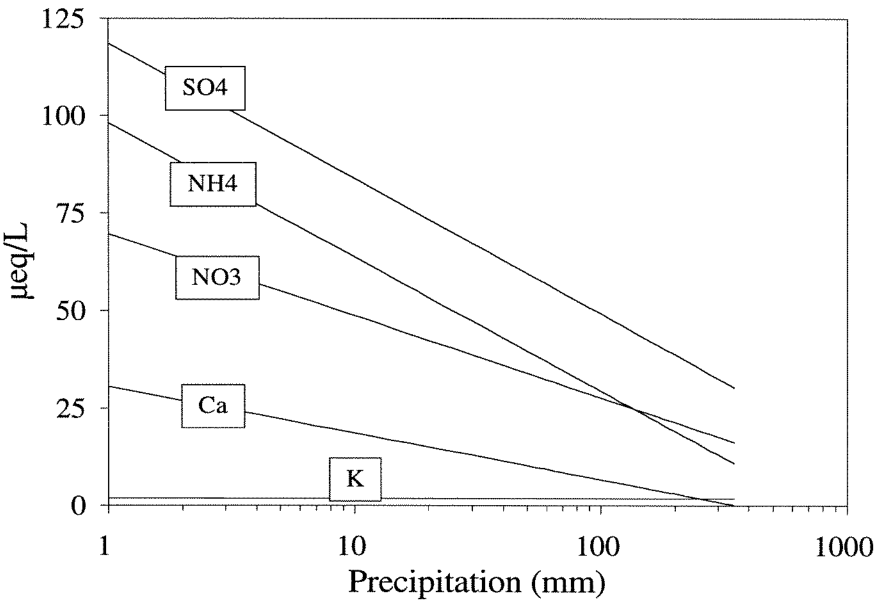


Figure 5.4 The relationships between monthly inputs of water (mm) and monthly weighted concentrations of major chemical dissolved species in precipitation (µeq/L) at Storgama during the monitoring period. The relationships rely on linear regression analyses. The regression lines are: $[H^+]$*:* $y = -0.05x + 57.8$*;* $[NH_4^+]$*:* $y = -16.6(\log x) + 62.8$*;* $[Ca^{2+}]$*:* $y = -8.0(\log x) + 22.1$*;* $[Mg^{2+}]$*:* $y = -1.5(\log x) + 7.4$*;* $[Na^+]$*:* $y = 0.02x + 14.7$*;* $[K^+]$*:* $y = -4.8(\log x) + 11.3$*;* $[Cl^-]$*:* $y = 0.02x + 18.3$*;* $[NO_3^-]$*:* $y = -7.7(\log x) + 46.6$*;* $[SO_4^{2-}]$*:* $y = -26.8(\log x) + 105$*. Continuous line indicates a significant relationship (*$p < 0.05$*), while a dotted line indicates no significance, i.e.* $p > 0.05$*. More details from the regression analyses are present in Appendix A.*



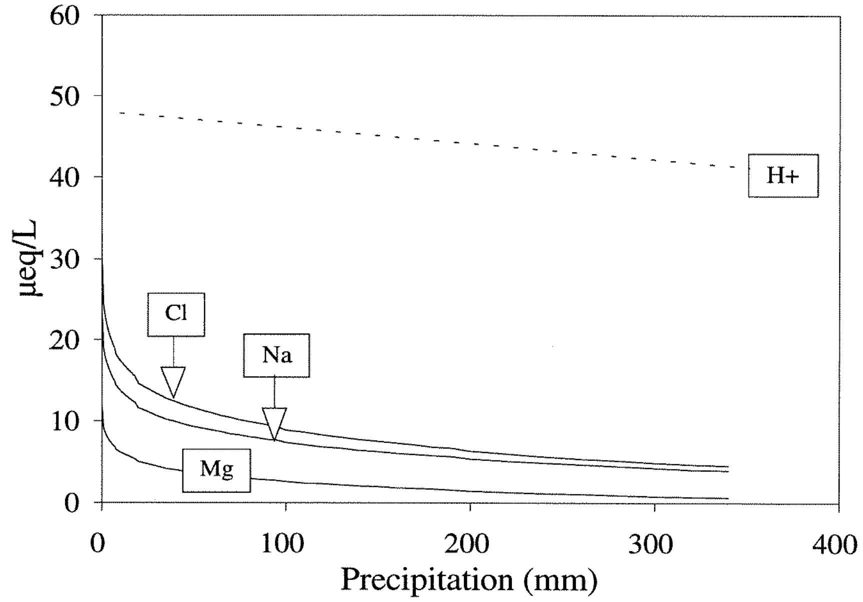
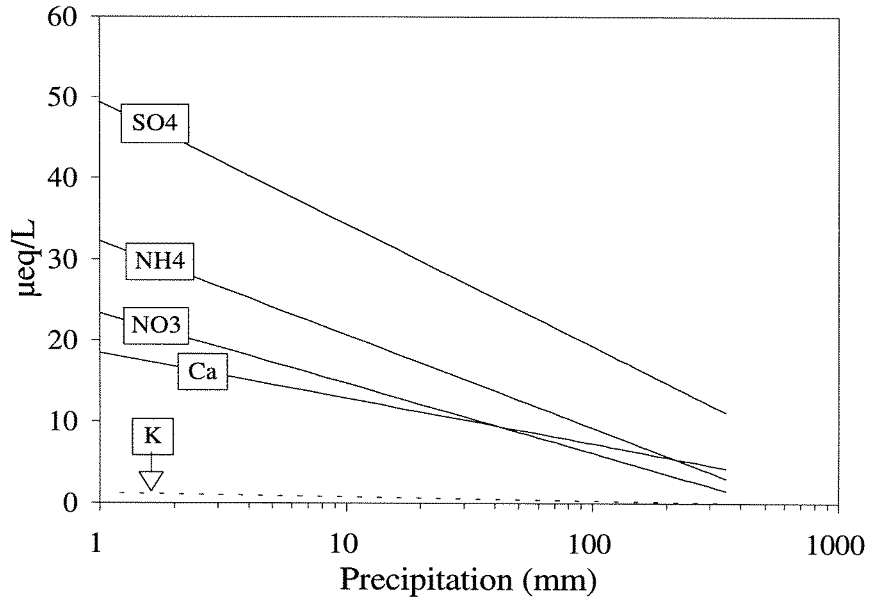


Figure 5.5 The relationships between monthly inputs of water (mm) and monthly weighted concentrations of major chemical dissolved species in precipitation (µeq/L) at Langtjern during the monitoring period. The relationships rely on linear regression analyses. The regression lines are: $[H^+]$: $y = -0.02x + 48.2$; $[NH_4^+]$: $y = -34.3(\log x) + 98.1$; $[Ca^{2+}]$: $y = -12.0(\log x) + 30.6$; $[Mg^{2+}]$: $y = -3.8(\log x) + 10.4$ $[Na^+]$: $y = -6.7(\log x) + 21.0$; $[K^+]$: $y = -0.04(\log x) + 1.82$; $[Cl^-]$: $y = -8.8(\log x) + 27.0$; $[NO_3^-]$: $y = -21.0(\log x) + 69.7$; $[SO_4^{2-}]$: $y = -34.7(\log x) + 119$. Continuous line indicates a significant relationship ($p < 0.05$), while a dotted line indicates no significance, i.e. $p > 0.05$. More details from the regression analyses are present in Appendix A.



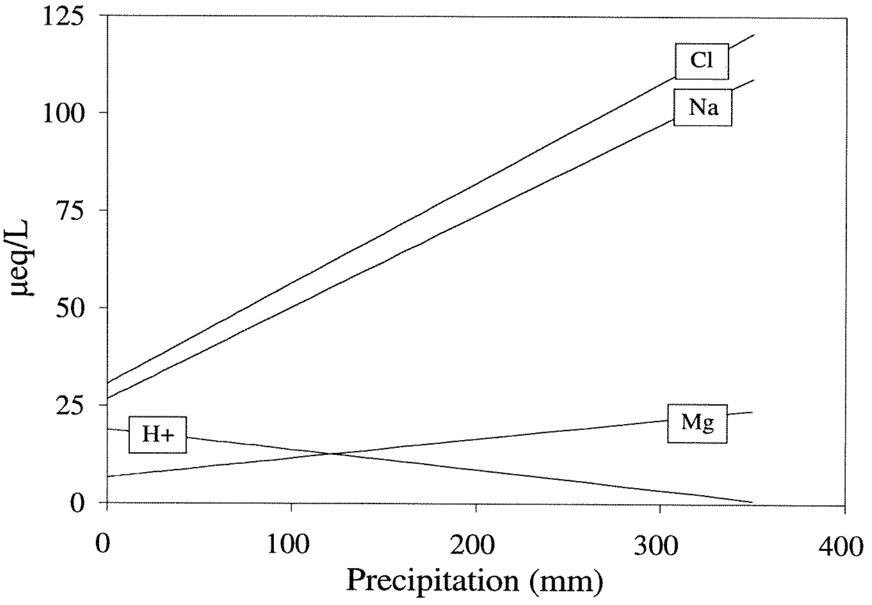


Figure 5.6 The relationships between monthly inputs of water (mm) and monthly weighted concentrations of major chemical dissolved species in precipitation (µeq/L) at Kaarvatn during the monitoring period. The relationships rely on linear regression analyses. The regression lines are: $[H^+]$: $y = -0.05x + 18.9$; $[NH_4^+]$: $y = -11.5(\log x) + 32.2$; $[Ca^{2+}]$: $y = -5.6(\log x) + 18.5$; $[Mg^{2+}]$: $y = 0.05x + 6.6$; $[Na^+]$: $y = 0.24x + 26.6$; $[K^+]$: $y = -0.40(\log x) + 3.5$; $[Cl^-]$: $y = 0.26x + 30.6$; $[NO_3^-]$: $y = -8.6(\log x) + 23.4$; $[SO_4^{2-}]$: $y = -15.0(\log x) + 49.4$. *Continuous line indicates a significant relationship (*$p < 0.05$*), while a dotted line indicates no significance, i.e.* $p > 0.05$. *More details from the regression analyses are present in Appendix A.*

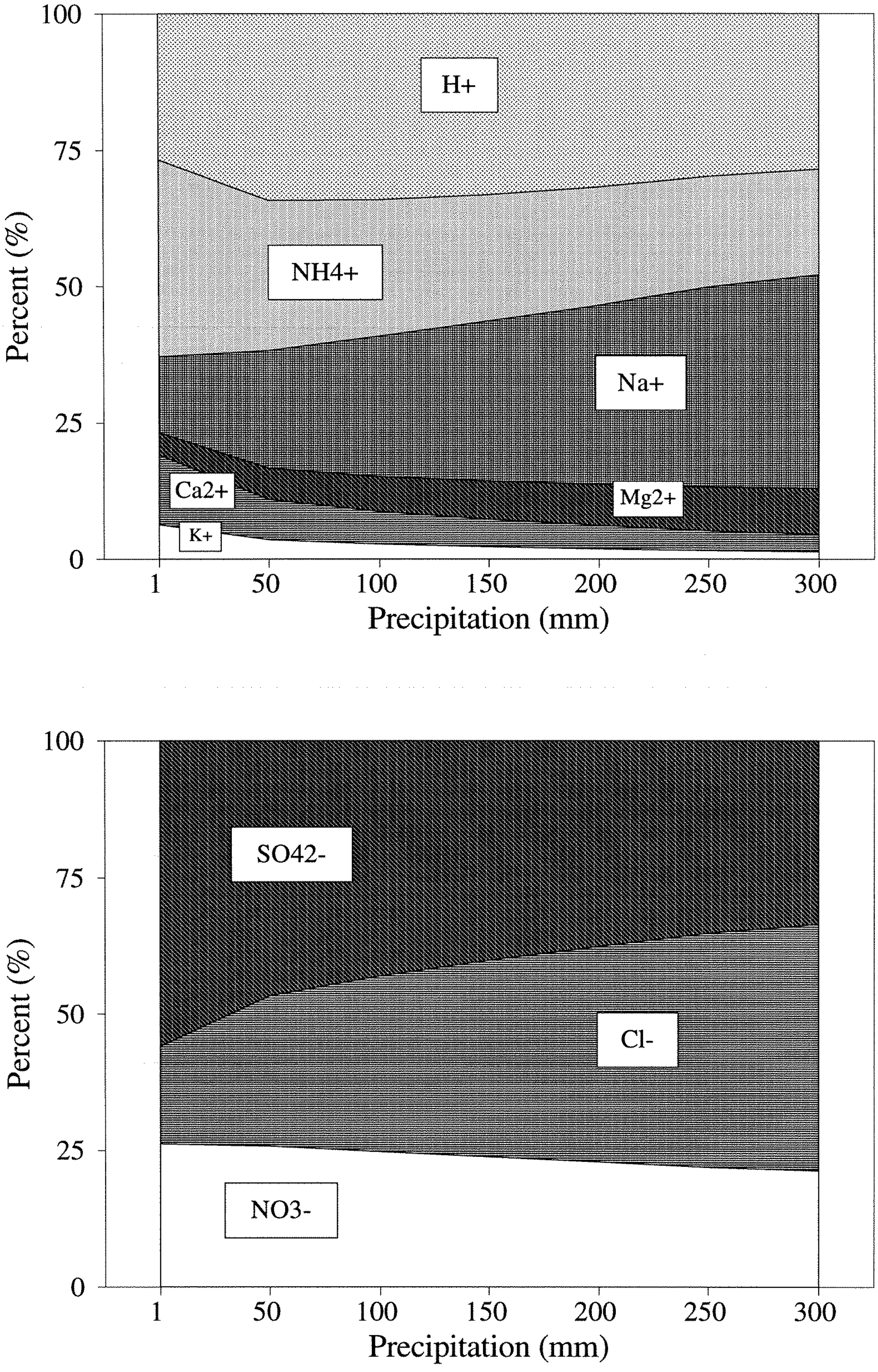
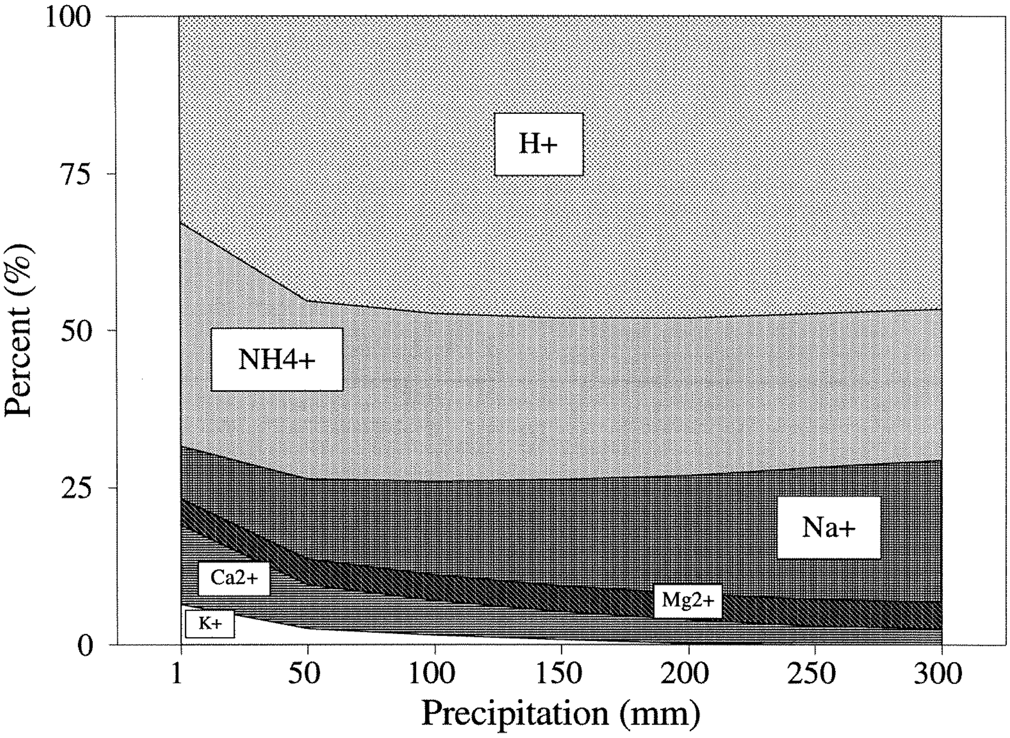


Figure 5.7 The percentage change in the distribution of cations and anions with respect to amount of precipitation at Birkenes, based on monthly weighted averages. The figure relies on the regression lines presented in Appendix A.



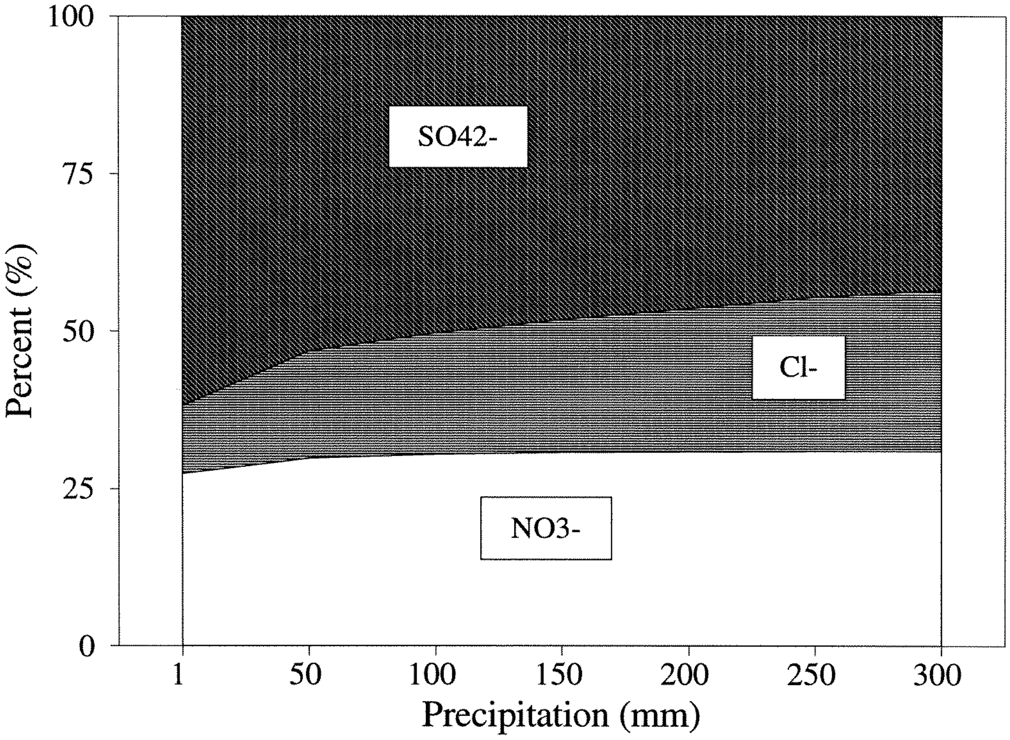


Figure 5.8 The percentage change in the distribution of cations and anions with respect to amount of precipitation at Storgama, based on monthly weighted averages. The figure relies on the regression lines presented in Appendix A.

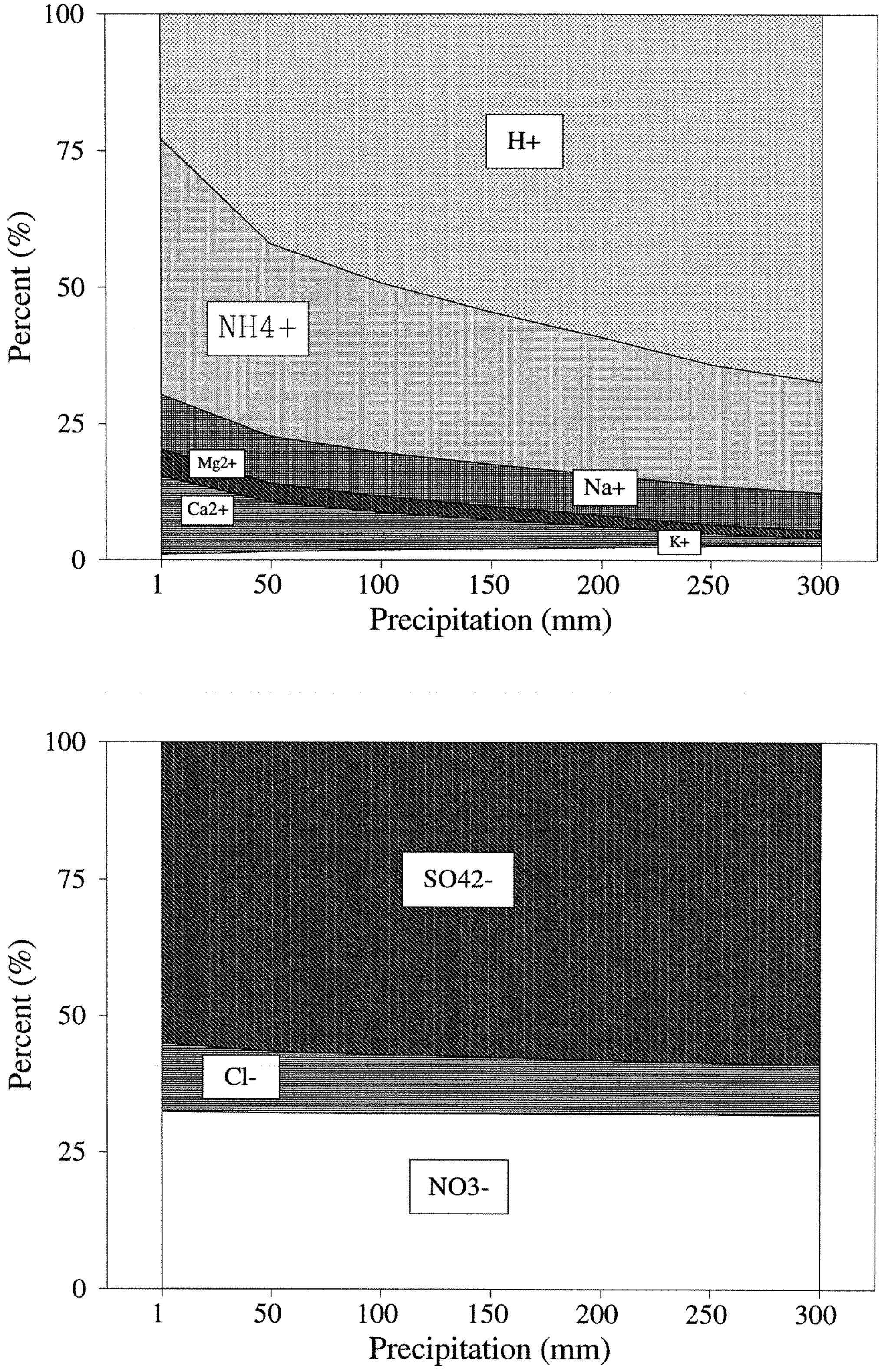


Figure 5.9 The percentage change in the distribution of cations and anions with respect to amount of precipitation at Langtjern, based on monthly weighted averages. The figure relies on the regression lines presented in Appendix A.

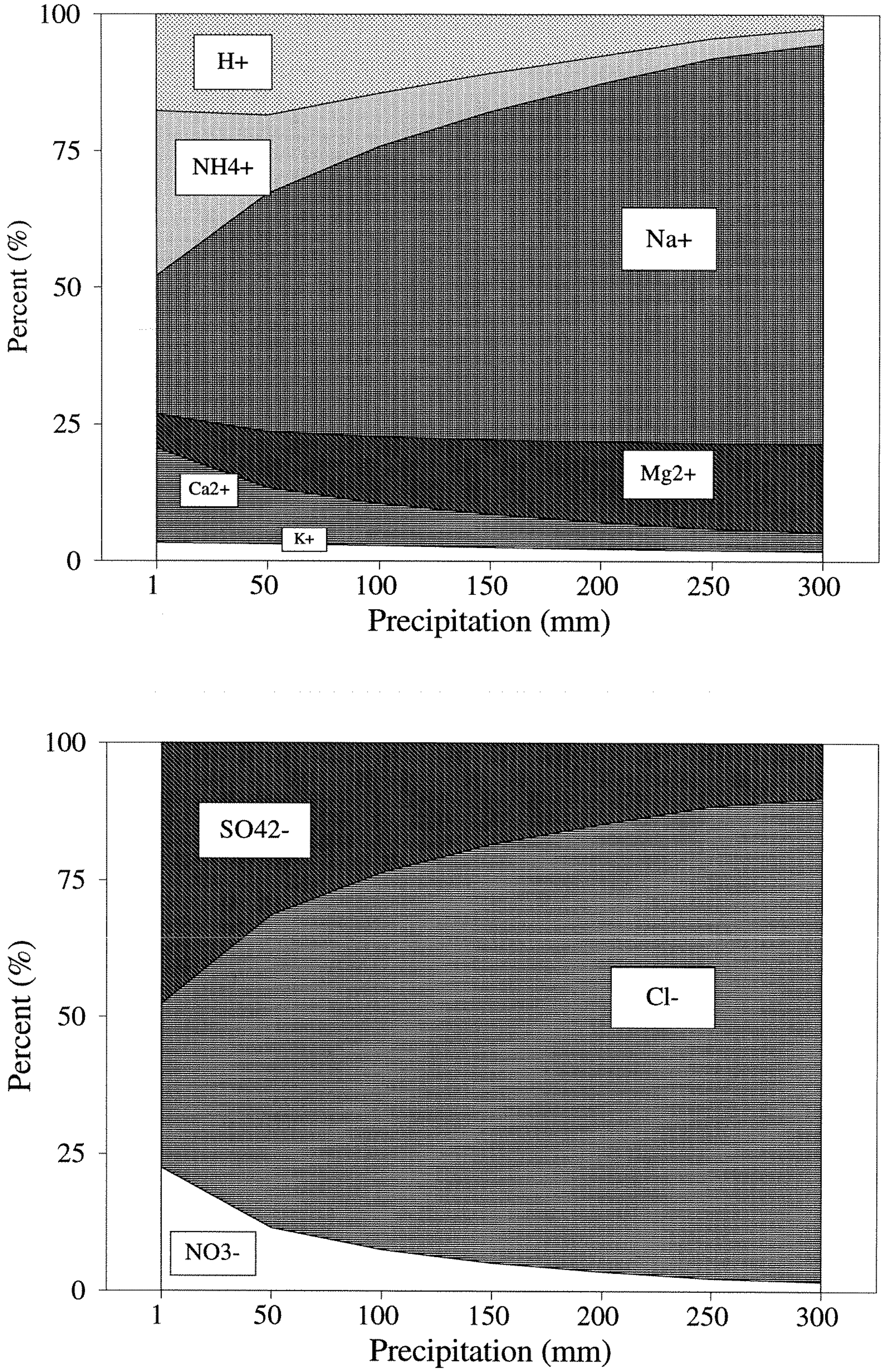
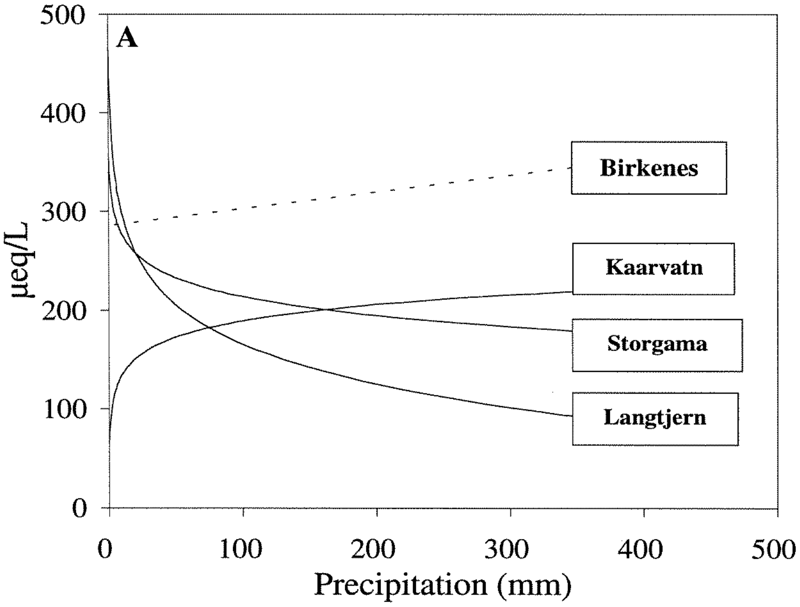


Figure 5.10 The percentage change in the distribution of cations and anions with respect to amount of precipitation at Kaarvatn, based on monthly weighted averages. The figure relies on the regression lines presented in Appendix A.



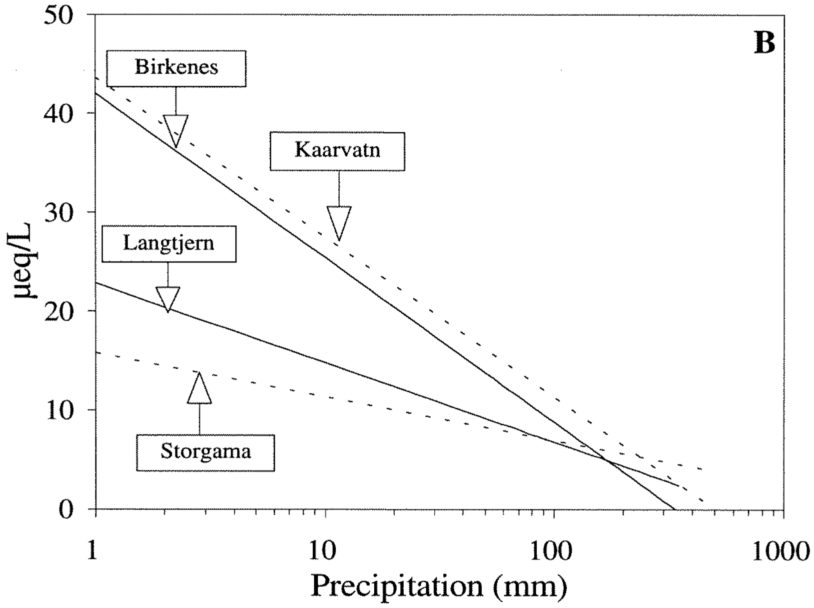
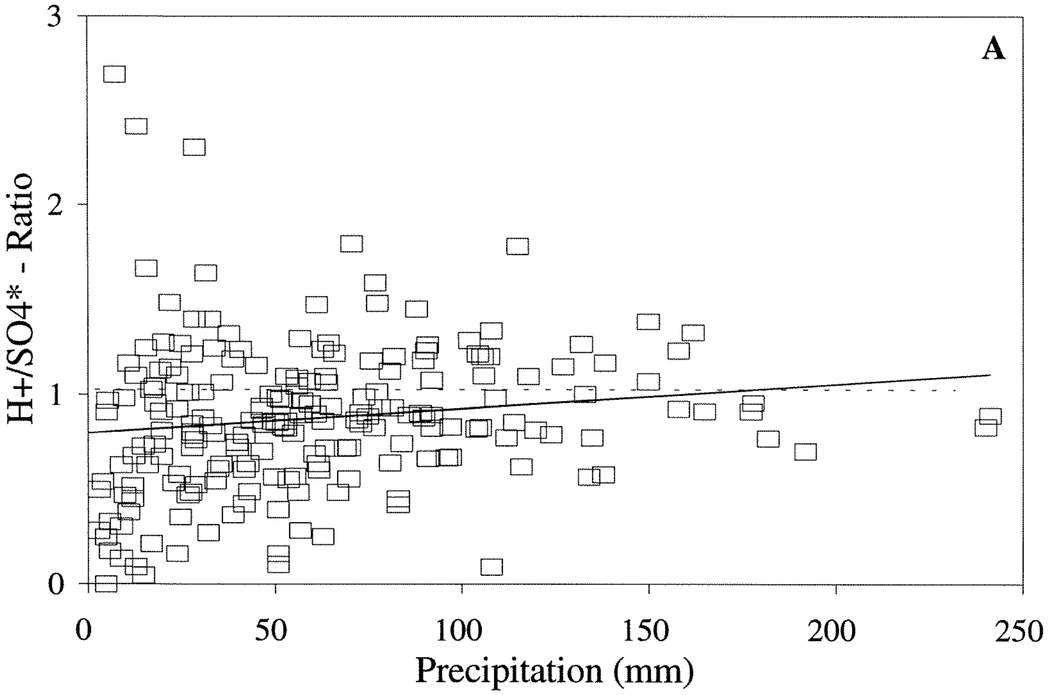


*Figure 5.11 The relationships between monthly inputs of water (mm) and monthly weighted ΣCations+Anions (**A**) and charge balance ΣCations-Anions (**B**) at the four catchment during the monitoring period, based on simple regression analyses. The regression lines are as follows: Figure **A**: Birkenes (y = 0.18x + 283, r = 0.13, n = 108); Storgama (y = -63.8(log x) + 342, r = -0.25, n=106); Langtjern (y = -134.6(log x) + 435, r = -0.39, n = 105); Kaarvatn (y = 55.5(log x) + 78.1, r = 0.23, n = 108). Figure **B**: Birkenes (y = -16.6(log x) + 42.0, r = -0.36, n = 108); Storgama (y = -4.41(log x) + 16.4, r = -0.12, n=106); Langtjern (y = -8.00(log x) + 22.8, r = -0.28, n = 105); Kaarvatn (y = -16.3(log x) + 43.4, r = -0.28, n = 108). Continuous line means that the regression is statistical significant, i.e. p < 0.05, while a dottet line means not significant, i.e. p > 0.05.*



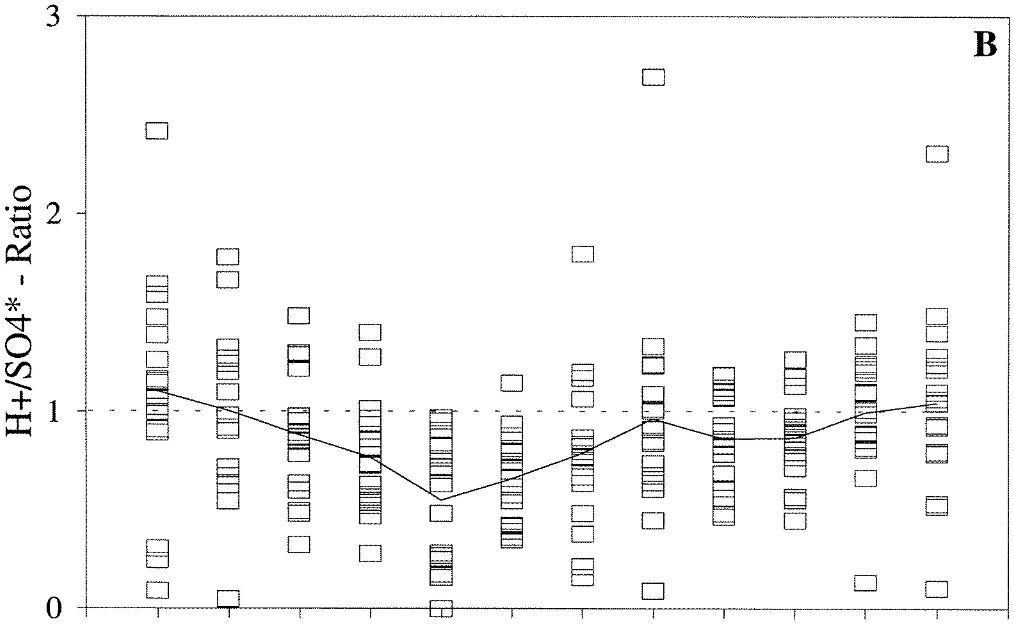
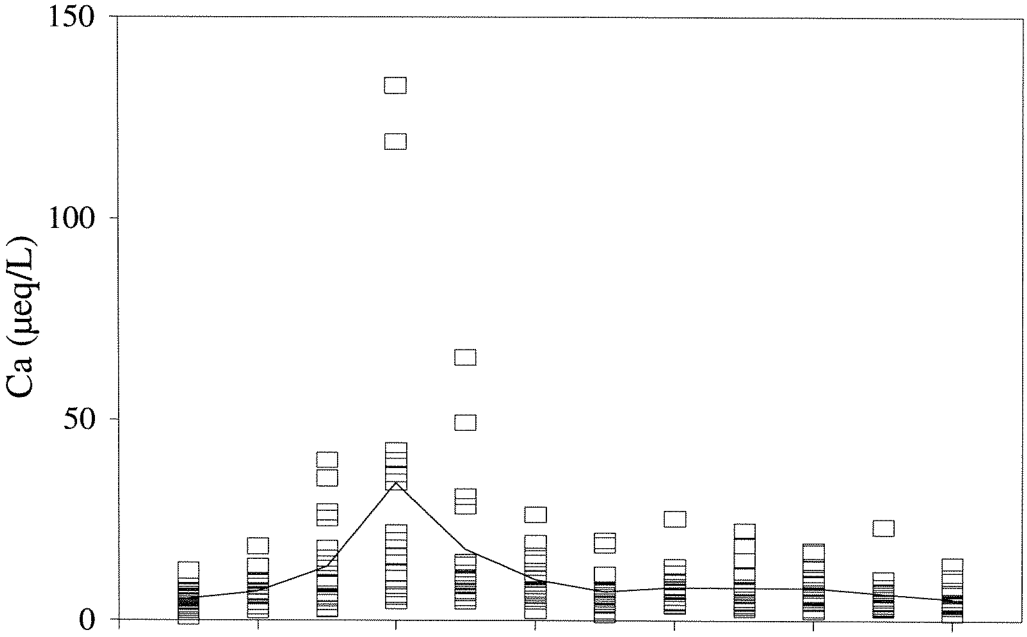


Figure 5.12 The equivalent H^+/SO_4 (non-marine sulphate) ratio in precipitation with respect to (A): The amount of precipitation; and (B) seasonal changes, based on monthly weighted averages (Jan - Dec) at Langtjern during the monitoring period. The dotted line indicates the 1 : 1 line. The regression line is : $y = 0.0013x + 0.80$ ($r = 0.15$) ($n = 201$).*



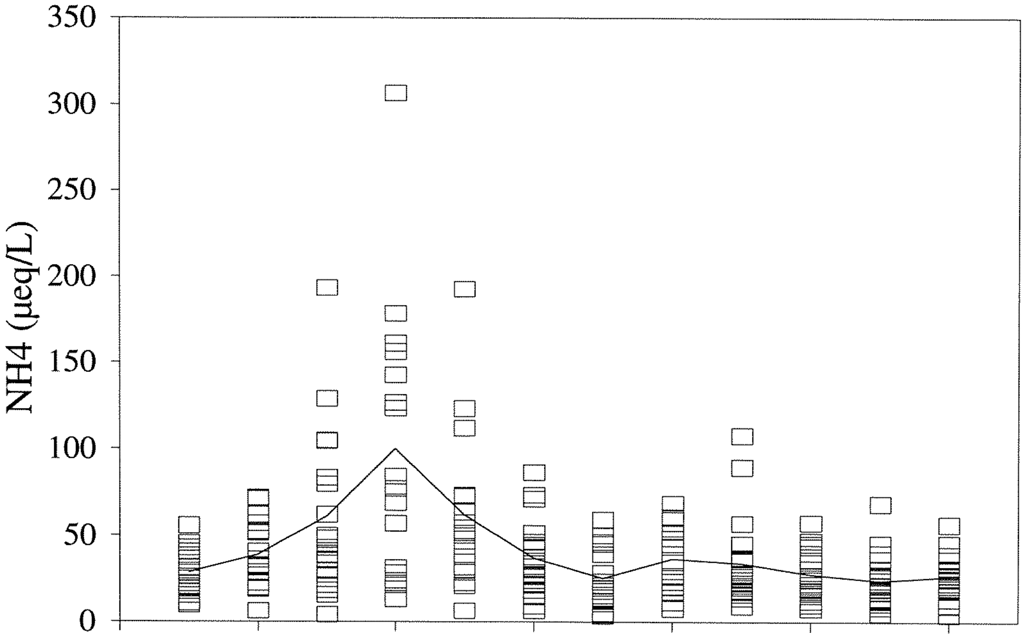


Figure 5.13 Variation in monthly weighted averages of Ca^{2+} *and* NH_4^+ *at Langtjern during the monitoring period. The continuous lines indicates the monthly mean values.*

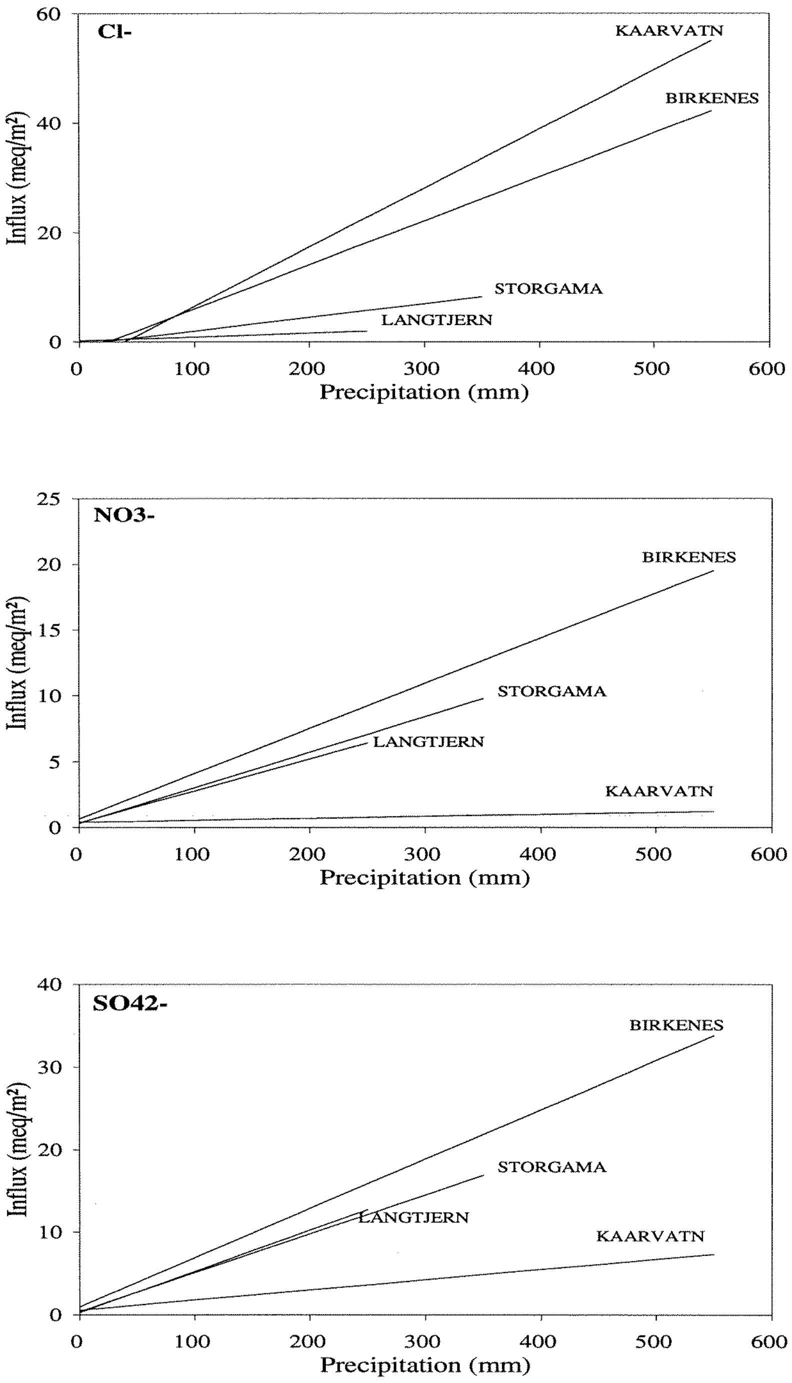


Figure 5.14 The relationship between monthly influxes of strong acid anions and monthly influxes of water at the four catchments, based on simple linear regression analyses. The predominant counterions are $Na^+(Cl^-)$, $NH_4^+(NO_3^-)$, and $H^+(SO_4^{2-})$. The regression lines are: ***Chloride****: Birkenes: $y = 0.08x - 2.0$; Storgama: $y = 0.03x - 0.5$; Langtjern: $y = 0.01x + 0.2$; Kaarvatn: $y = 0.11x - 4.3$.* ***Nitrate****: Birkenes: $y = 0.03x + 0.7$; Storgama: : $y = 0.03x - 0.3$; Langtjern: $y = 0.02x + 0.4$; Kaarvatn: $y = 0.002x + 0.4$.* ***Sulphate****: Birkenes: $y = 0.06x + 1.0$; Storgama: $y = 0.05x + 0.4$; Langtjern: $y = 0.05x + 0.3$; Kaarvatn: $y = 0.01x + 0.6$. Continuous line indicates a significant relationship ($p < 0.05$), while a dotted line indicates no significance, i.e. $p > 0.05$. More details from the regression analyses are presented in Appendix B.*

5.2 Dry-deposition.

Annual weighted concentrations

It is only dry-position of major inorganic sulphur compounds, i.e. SO_2-gas and SO_4-particles, which have been monitored from the very beginning of the progamme (1974), and only at Birkenes. However, due to some difficulties by measuring SO_2-gas during the first years, only sulphur-data back to 1978 will be used, but from that on, both sulphur compounds have been continuously measured at Birkenes. At Storgama, dry-deposition data of sulphur only exists for one year, 1978, while at Langtjern and Kaarvatn continuously data exist back to 1988 and 1979, respectively. Dry-deposition of nitrogen compounds (NO_2-gas, ΣHNO_3-gas,NO_3-particles, ΣNH_3-gas,NH_4-particles) have been monitored at Birkenes and Kaarvatn only, at Birkenes from 1986 and at Kaarvatn back to 1988. At Birkenes, NO_2-gas has been measured back to 1982, except 1983. At Storgama, dry-deposition of nitrogen compounds have never been measured, while at Langtjern only $\Sigma HNO_3,NO_3$ has been measured from 1990 and on. Dry deposition measurements of major base cations, Ca, Mg, Na and K and Cl are only conducted at Birkenes, Ca, Mg and K continuously back to 1986, while Na and Cl have been continuously monitored back to 1988, except for Cl in 1989.

A short presentation of the dry-deposition programme is also given in the indroduction of this chapter, while more details, concerning frequency of sampling and applied analytical methods ect. are presented in Chapter 2.

Table 5.6 Weighted annual maximum, minimum and annual mean concentrations of major dry-deposition compounds of sulphur and nitrogen ($\mu g/m^3$) at the catchments during the monitoring periods. Based on Ferm (1988), HNO_3 and NO_3^- contribute with 25% and 75% of the $\Sigma HNO_3,NO_3$, while NH_3 and NH_4 contributes by 8% and 92% to the $\Sigma NH_3,NH_4$.

Parameter			**Birkenes**	**Storgama**	**Langtjern**	**Kaarvatn**
	Period		1978-1991	1977-1978	1988-1991	1979-1990
		max	*1.76*	*0.95*	*0.53*	*0.55*
SO_2-gas		**mean**	**0.81 ± 0.35**	**0.95**	**0.32 ± 0.13**	**0.34 ± 0.14**
		min	*0.48*	*0.95*	*0.22*	*0.12*
		max	*1.41*	*0.90*	*0.66*	*0.54*
SO_4-particles		**mean**	**1.01 ± 0.21**	**0.81 ± 0.09**	**0.54 ± 0.07**	**0.42 ± 0.08**
		min	*0.67*	*0.72*	*0.48*	*0.30*
	Period		1982-1991		1990-1991	1988-1991
		max	*1.30*			*0.57*
NO_2-gas		**mean**	**1.08 ± 0.13**			**0.39 ± 0.11**
		min	*0.83*			*0.26*
		max	*0.36*		*0.21*	*0.09*
ΣHNO_3, NO_3		**mean**	**0.29 ± 0.03**		**0.21 ± 0.01**	**0.07 ± 0.01**
		min	*0.26*		*0.20*	*0.06*
		max	*0.77*			*0.44*
$\Sigma NH_3,NH_4$		**mean**	**0.68 ± 0.06**			**0.40 ± 0.03**
		min	*0.63*			*0.35*

As for wet-deposition of sulphur (sulphate), Birkenes normally receives the highest dry-deposition concentrations of this element (Table 5.6), but because dry-deposition recordings have been conducted during different time period at the weather stations, the annual means present in Table 5.6 are not directly comparable, especially because there also has been a significant decrease in the concentration of sulphur compounds during the monitoring period (See Chapter 6). Highest sulphur values are normally recorded during the first years of monitoring, while the lowest values are recorded the last years. As a consequence, only dry-deposition data from Birkenes (the most polluted site) and Kaarvatn (the least polluted site) for sulphur- (1979-1991) and nitrogen-compounds (1988-1991) will be focused on, because they are the only sites which have been continuously monitored during these periods. The data used for comparing the sites are transformed into equivalents, which means that the dry-deposition compounds of sulphur are assumed to be divalent, while for the nitrogen compounds, all are assumed to be or transformed to monovalent compounds.

Annual average mean concentrations of SO_2-gas and SO_4-particles at Birkenes during 1979-1991 were 46 ± 15 neq/m^3 and 61 ± 14 neq/m^3, respectively (Figure 5.15), while the correspondent concentrations at Kaarvatn were 21 ± 8 neq/m^3 and 26 ± 5 neq/m^3 (Figure 5.15), This means that the annual mean concentration of sulphur in dry-deposition at Kaarvatn is less than half (44%) the concentration at Birkenes. The percentage distribution between SO_2-gas and SO_4-particles is almost equal at the two sites, 43% (SO_2-gas) and 57% (SO_4-particles).

Annual average mean concentration of nitrogen compounds in dry-deposition at Birkenes during 1988-1991 was 147 ± 7 neq/m^3, while the annual average concentration of sulphur during the same period was 82 ± 8 neq/m^3. During the same time period, the annual average concentrations of nitrogen and sulphur compounds at Kaarvatn were 62 ± 10 neq/m^3 and 33 ± 9 neq/m^3, respectively. As for sulphur, the annual average concentration of nitrogen at Kaarvatn is less than half (42%) the concentration at Birkenes. The annual mean concentration of dry-deposited nitrogen compounds during 1988-1991 were 1.8 and 1.9 times higher than the correspondent dry-deposition concentrations of sulphur at Birkenes and Kaarvatn, respectively.

At both sites (Birkenes and Kaarvatn), NO_2-gas and NH_4-particles are the predominant dry-deposition compounds of nitrogen. At Birkenes, NO_2-gas and NH_4-particles contributed by 53% and 31% to the total annual mean concentration of nitrogen in dry-deposition, while the correspondant contributiuon at Kaarvatn was 45% (NO_2-gas) and 43% (Figure 5.16). The relatively lower contribution of NO_2-gas and the relatively higher contribution of NH_4-particles at Kaarvatn compared with at Birkenes, indicates a relatively higher agricultural and lower industrial influence at Kaarvatn compared with at Birkenes. This conclusion can be drawn since NH_4-particles predominantly originate from agricultural activities (fertilization and animal husbandry), while NO_2-gas predominantly derives combustion of oil and gasoline. However, the annual mean concentrations of both NO_2-gas and NH_4-particles are 2.8 and and 1.7 times higher at Birkenes, which means that the dry-deposition concentrations of nitrogen at Birkenes, as for sulphur, is much higher at this site compared with at Kaarvatn.

Dry-deposition compounds, other than nitrogen and sulphur compounds, have only been measured at Birkenes, where base cations and chloride have been more or less continuously monitored since 1986 (Table 5.7). As for wet-deposition at Birkenes, sodium is also the predominant base cation in dry-deposition. Based on annual average concentrations (neq/m^3),

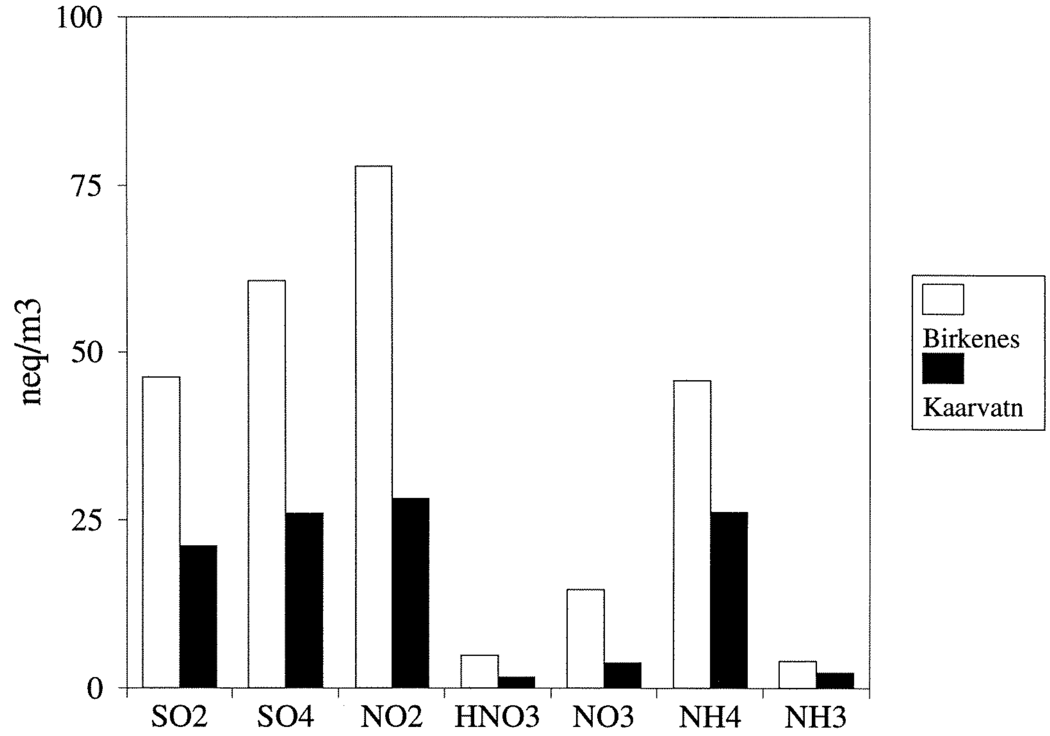


Figure 5.15 Annual average concentrations of dry-deposition compounds of sulphur (from 1979-1991) and nitrogen (from 1988-1991) at Birkenes and Kaarvatn.

sodium constitutes 27 ± 2% of the cationic pool of dry-deposition, while calcium, magnesium, and potassium contribute by 4.8 ± 1.8%, 5.8 ± 0.4% and 2.9 ± 0.5%, respectively, The remaining 59 ± 2% is ammonium, which means that the percentage contribution of ammonium in dry-deposition at Birkenes is more than twice that present in wet-deposition. The percentage contribution of sodium in dry-deposition is about equal its contribution in wet-deposition at Birkenes. The percentage contribution from chloride to the total anionic pool of dry-deposition is 14 ± 3%. This is less than half the contribution compared with that present in wet-deposition. The percentage contributions of calcium, magnesium and potassium in dry-deposition are only somewhat lower than the correspondent contribution of these ions in wet-deposition.

Charge balance of dry-deposition is estimated as $\Sigma NH_4^+, Ca^{2+}, Mg^{2+}, Na^+, K^+ - \Sigma NO_3^-, Cl^-, SO_4^{2-}$. The remaining dry-deposition compounds measured are gases, and thus omitted from the charge balance calculations. Based on annual average concentrations, charge balance of dry deposition at Birkenes is 4.3 ± 7.1 neq/m^3, which means an excess of cations.

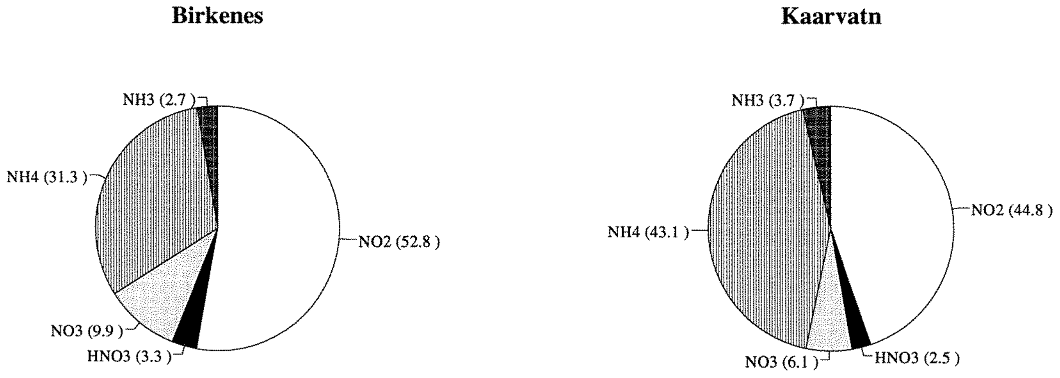


Figure 5.16 The percentage contributions from the various dry-deposition compounds to the total dry-deposition concentration of nitrogen at Birkenes and Kaarvatn, based on average annual concentrations averages (neq/m³) from 1988 to 1991.

Table 5.7 Annual average concentrations (µg/m³) of calcium, magnesium, sodium, potassium and chloride in dry-deposition at Birkenes.

Period: **Element:**	**1986-1991** **Ca**	**1986-1991** **Mg**	**1988-1991** **Na**	**1986-1991** **K**	**1988-1991** **Cl**
max	*0.10*	*0.07*	*0.61*	*0.11*	*0.44*
mean	**0.07 ± 0.02**	**0.05 ± 0.01**	**0.50 ± 0.07**	**0.08 ± 0.02**	**0.37 ± 0.09**
min	*0.06*	*0.04*	*0.43*	*0.05*	*0.25*

By comparing the various base-cation/chloride ratios in dry-deposition with the correspondent ratios present in wet-deposition and in seawater (Table 5.8), the highest ratios is present in dry-deposition. This means that chloride is less predominant as counter-ions for base-cations in dry-deposition compared with wet-deposition. This makes sence, because basecation-chlorides are very soluble and should therefore be expected to be present in higher amounts in the wet-deposition fraction as dissolved ions, while basecation-particles with other anions like HCO_3^-, CO_3^{2-}, PO_4^{3-} and SO_4^{2-} are less soluble and therefore more likely present in higher amounts in the dry-deposition fraction. The NH_4^+/SO_4^{2-} and the $\Sigma NH_4^+,Ca^{2+}/SO_4^{2-}$ ratio (Table 5.8) in dry-deposition, indicates that sulphate are predominantly accompanied by ammonium as cation (counter-ion), but also, to some extend, accompanied by divalent base-cations as calcium and magnesium. However, even though, the ammonium/sulphate ratio is approximately 1:1, the two ions do not primarely originate from the same sources. While ammonium primarily originates from agricultural activities, sulphate primarely originates from combustion of fossil organic materials (coal, oil, ect.), and to some extend from natural sources due to oxidation of organic and inorganic sulphides.

The dry-deposition analyses of nitrogen and sulphut clearly demonstrate that NO_2 and SO_2 are the predominant gases, while NH_4^+ and SO_4^{2-} are the predominant ions in the particles (Figure

5.17 og 5.18). Base cations are only present in particles, and most likely associated with chloride and sulphate as counteranions. The concentration of basecation in air is probably highly dependent on the location of the weather station with respect to distance from sea or distance from agricultural areas.

*Table 5.8 Annual average concentration ratios (neq/m^3) of base-cation/chloride in wet- and dry-deposition in relation to the correspondent ratios of seawater, and annual average concentration ratios of **A**: $[NH4^+]/[SO_4^{2-}]$; **B**: $\Sigma[NH4^+],[Ca^{2+}]/[SO_4^{2-}]$ in dry-deposition at Birkenes.*

	Ca/Cl	**Mg/Cl**	**Na/Cl**	**K/Cl**	**A**	**B**
Seawater	0.037	0.195	0.856	0.018		
Wet-deposition	0.14	0.20	0.87	0.04		
Dry deposition	0.41	0.46	2.14	0.22	0.95	1.02

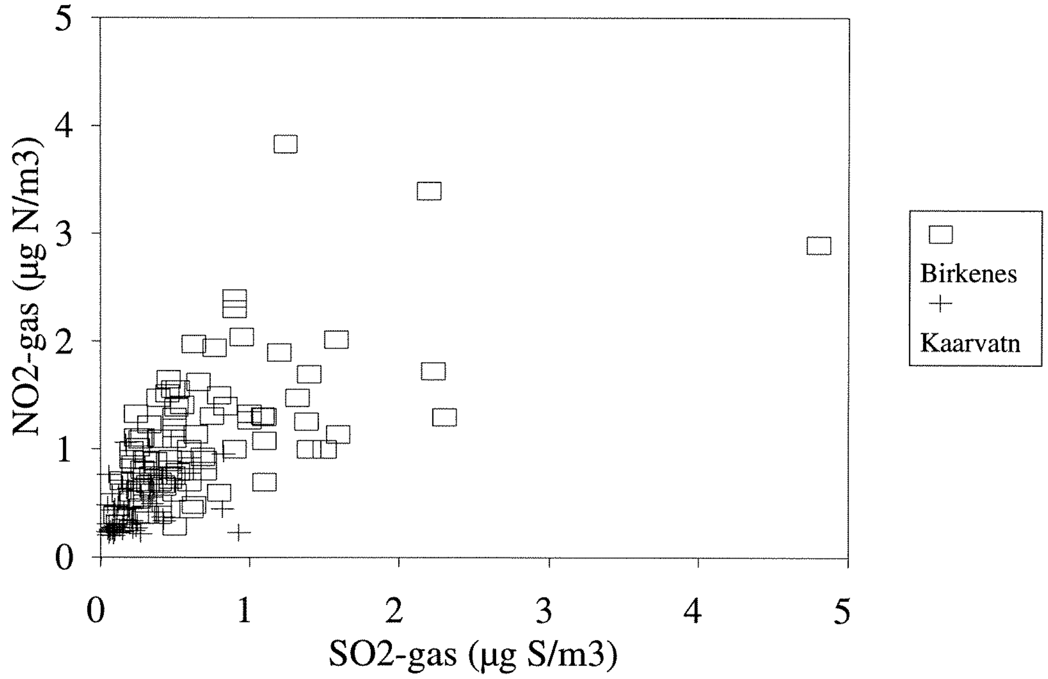


Figure 5.17 The relationship between monthly weighted concentration of SO_2 and NO_2 gas (µg/m^3) in dry-deposition at Birkenes and Kaarvatn. The relationships rely on linear regression analyses. The regression lines are: Birkenes: $y = 0.6x + 0.7$ ($r = 0.61$) ($n = 108$); Kaarvatn: $y = 0.2x + 0.4$ ($r = 0.24$) ($n = 48$). Continuous line indicates a significant relationship ($p < 0.05$), while a dotted line indicates no significance, i.e. $p > 0.05$.

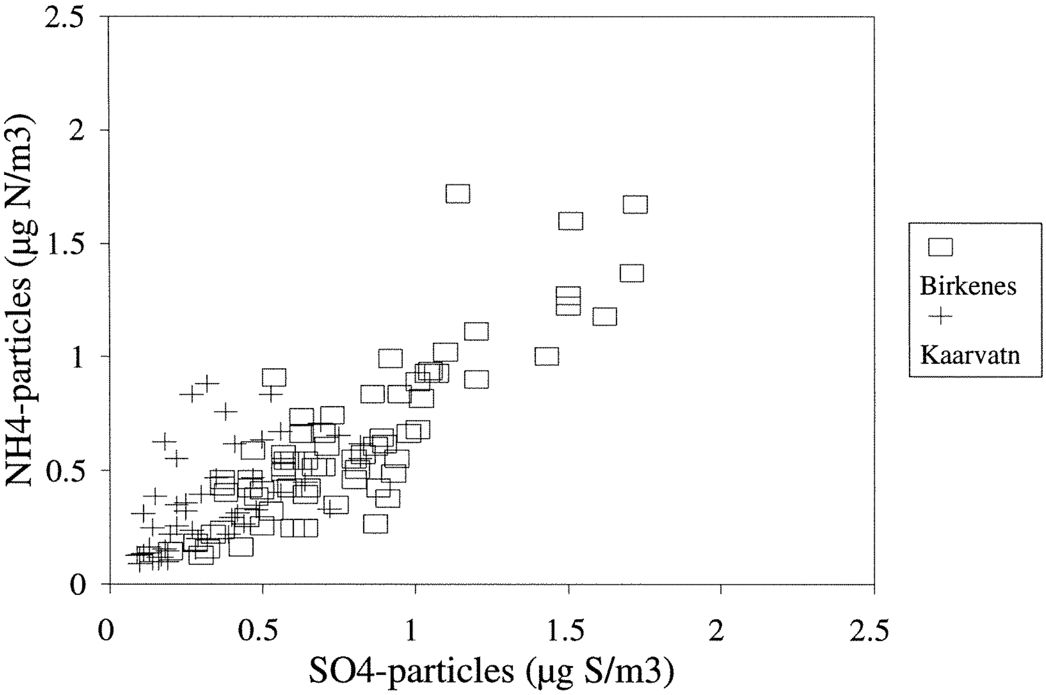


Figure 5.18 The relationship between monthly weighted concentration of SO_4^{2-}-and NH_4^+-particles (µg/m³) in dry-deposition at Birkenes and Kaarvatn. The relationships rely on linear regression analyses. The regression lines are: Birkenes: $y = 0.9x - 0.05$ ($r = 0.86$) ($n = 72$); Kaarvatn: $y = 0.7x + 0.15$ ($r = 0.59$) ($n = 48$). Continuous line indicates a significant relationship ($p< 0.05$), while a dotted line indicates no significance, i.e. $p > 0.05$.

Annual weighted fluxes

When calculating dry-deposition fluxes, the deposition velocities have to be known. The applied deposition velocity data are presented in Table 5.9. These are empirical values, made up by the Norwegian Institute for Air Research (NILU), based on a standardized area, containing a defined open and forested area. In addition, a several other factors are also accounted for, like seasonal vegetation changes, temperature ect. Studies at Gårdsjöen, Sweden, indicate that dry-deposition of sulphur was directly related to the amount of forest cover and age of stand (Hultberg and Greenfelt, 1986), and in Norway, a decrease in the sulphur flux from the catchment was observed after clearfelling of a 80-year-old Norway spruce stand (Wright, 1991). Clearfelling also apparantly reduced the inputs of seasalt aerosols, i.e. fluxes of Na, Mg and Cl in runoff declined during the first two years following treatment (Hultberg, 1987). It is also well known that the deposition rates of gases and particles are dependant on the wind-speed, and for gases like SO_2, NO_2, HNO_3 and NH_3, the deposition also depends on the photosynthetic activity of vegatation, and the fact that deposition onto wet surfaces are far higher than onto dry surfaces. It is further well known that an air-layer often is established close to the surface/ground, especially during the winter. This layer may prevent/reduce the amount of chemical compounds in air from precipitate onto the ground. Therefore, the deposition velocity of gases and particles are very uncertain values, and may vary a lot both in time and space. However, the deposition velocity applied may fit relatively well for some catchment, while being unsiutable for other sites. Concerning the base cations and chloride, deposition velocities are impssible to estimate, primarily because basecation particles are varying a lot in particle size.

Based on the deposition velocities given, annual average dry-deposition influx of sulphur at Birkenes from 1979/80/-1990/91 was 11.5 ± 2.1 meq/m², while the correspondant average annual influx at Kaarvatn during the same period was 5.0 ± 1.0 meq/m². These annual influxes averagely constitutes 11 ± 3% and 12 ± 2% of the total input of sulphur (ΣWet+Dry) at Birkenes and Kaarvatn, respectively. The annual average dry-deposition influx of nitrogen at Birkenes from 1988/89 to 1990/91 was 18.3 ± 0.9 meq/m², while the correspondent average annual influx at Kaarvatn during the same period was 8.1 ± 1.4 meq/m². These annual influxes constitutes 13 ± 2% and 24 ± 7% of the total input of nitrogen (ΣWet+Dry) at Birkenes and Kaarvatn, respectively. This indicates that dry-deposition of nitrogen is a more important nitrogen source at Kaarvatn compared with at Birkenes. Annual dry-deposition influxes of sulphur and nitrogen are present i Table 5.11.

The dry-deposition velocities is not only dependent on whether it is a gas or particle or which types. It is also important whether it is summer or winter. Thus, the percentage distribution of various dry-deposition compounds will differ a lot dependent on whether it is concentrations (μeq/m³) or influx (meq/m²yr) that are to be evaluated. While the percentage concentration distribution of SO_2-gas and SO_4-particles at Birkenes is 43 ± 4% and 57 ± 4%, the correspondant flux-distribution is 35 ± 4% (SO_2-gas) and 65 ± 4% (SO_4-particles). At Kaarvatn, the percentage concentration distribution of SO_2-gas and SO_4-particles is 43 ± 7% and 57 ± 7%, while the correspondant flux-distribution is 31 ± 4% and 69 ± 4%. Most extreme is the difference beween concentration and influx of HNO_3-gas. While HNO_3-gas only constitutes 3.3 ± 0.1% and 2.5 ± 0.5% of the total nitrogen concentration in dry-deposition at Birkenes and Kaarvatn, respectively, it accordingly contributes by 17 ± 1% and 14 ± 5% to the total dry-deposition influx (See Figure 5.16 and 5.20). The main explanation for this is the high deposition velocity of this gas, i.e. 1.5 cm/sec during the winter (October-March) and 2.5 cm/sec during the summer (April-September). This is much higher than the correspondant deposition velocity of NO_2-gas which is 0.1 cm/sec during the winter and 0.5 cm/sec during the summer (Table 5.9).

Concerning influxes of the predominant dry-deposition compounds (SO_2-gas, NO_2-gas, SO_4-particles and NH_4-particles), the montly influxes of the two gases or the two particle compunds are quantitatively very similar (Figure 5.21 and 5.22), especially at Birkenes, but also at Kaarvatn. Despite the significant reduction in the influxes of both sulphur compounds

Table 5.9 The applied dry-deposition velocities (cm/sec) of nitrogen and sulhpur compounds during summer (April-September) and winter (October-March).

	SO_2	SO_4^{2-}	NO_2	NO_3^-	HNO_3	NH_3	NH_4
Summer	0.7	0.6	0.5	0.6	2.5	0.7	0.6
Winter	0.1	0.2	0.1	0.2	1.5	0.1	0.2

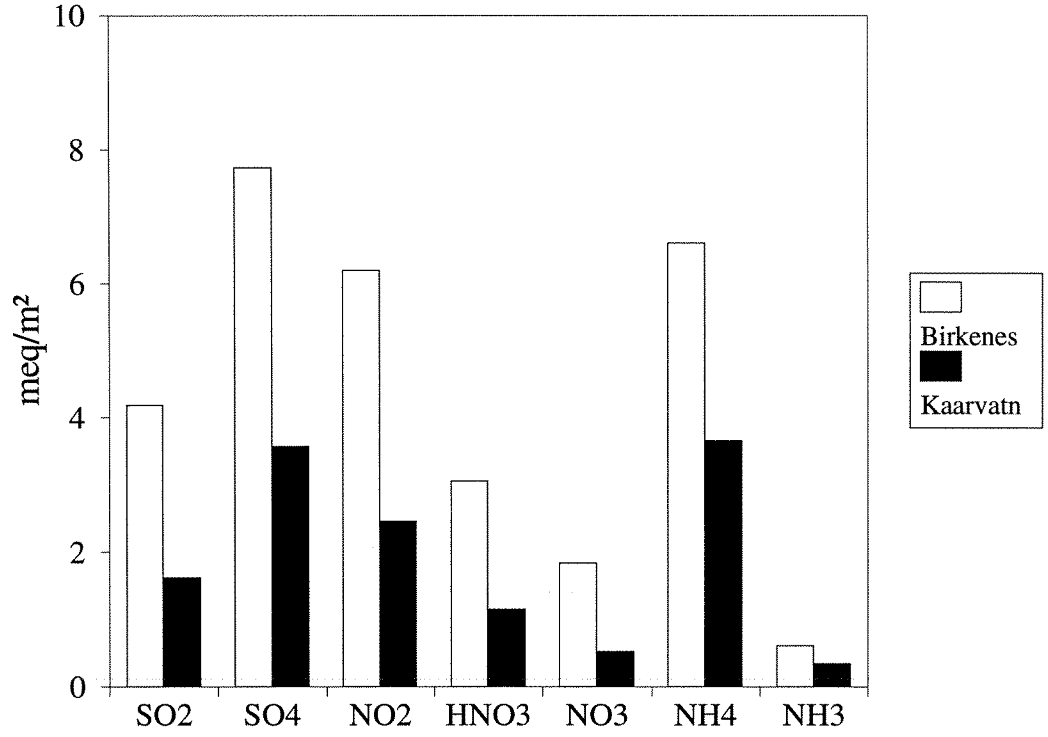


Figure 5.19 Annual average dry-deposition influxes (meq/m^2) of sulphur (from 1979/80-1990/91) and nitrogen (from 1988/89-1990/91) compounds at Birkenes and Kaarvatn.

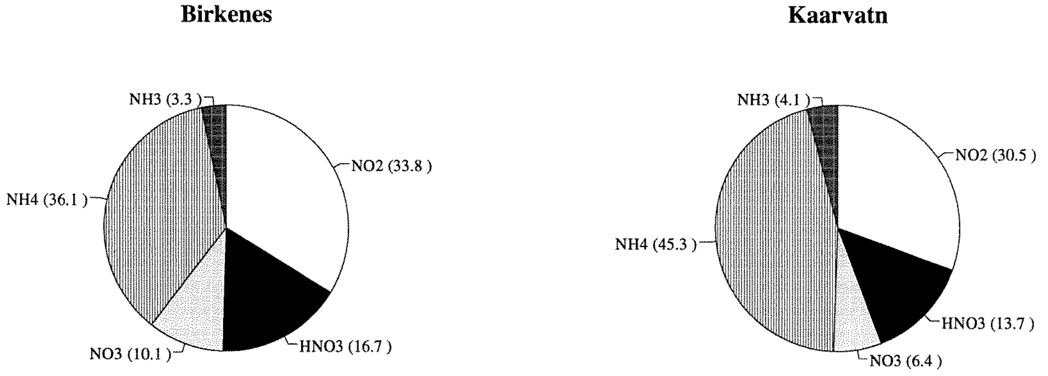


Figure 5.20 The percentage contribution of the various dry-deposition compounds of nitrogen in relation to the annual average influx of nitrogen (meq/m^2) at Birkenes and Kaarvatn from 1988/89-1990/91.

during the monitoring period at both catchment (Birkenes: 1978-1991; Kaarvatn: 1979-1991), it has been minor changes in the ratio between the two gases or the two particle compounds in air. Birkenes exhibits the most significant relationship between SO_2-gas and NO_2-gas and between SO_4-particles and NH_4-particles (Figure 5.21 and 5.22). At Kaarvatn, the weakest relationship (but significant) was found between SO_2-gas and NO_2-gas. This rely on the fact that there has been a significant ($p < 0.05$) decrease in monthly dry-deposition of SO_2 by averagely 0.023 meq/m^2 and an almost significant decrease in dry-deposition of NO_2 by averagely 0.045 meq/m^2 during the period 1988-1991, i.e. the period where all nitrogen and sulphur compounds have been monitored.. Thus, there has been a relative change in the influx of the two gases during the period, which of cause will weaken the relationship. At both sites, the SO_4/NH_4 relationship in particles is far the most significant. This is natural, because, these two ions are chemically directly assosiated in the particles, even though they primarily originates from different sources (described earlier in this chapter), The two gases (SO_2 and NO_2), on the other hand, are present more or less undependant of each other, even though they both predominately arise from industrial/urban sources.

Table 5.10 Weighted annual maximum, minimum and annual mean fluxes of major dry-deposition compounds of sulphur and nitrogen (meq/m^2 yr) at the catchments during the monitoring periods.The deposition rates are given in Chapter 2.2.2.

			Birkenes	**Storgama**	**Langtjern**	**Kaarvatn**
Parameter	*Period*		78/78-90/91	77/78	88/89-90/91	79/80-90/91
		max	*7.5*		*2.3*	*2.4*
SO_2-gas		**mean**	**4.4 ± 1.2**		**1.9 ± 0.3**	**1.6 ± 0.5**
		min	*3.1*		*1.7*	*0.87*
		max	*10.7*	*7.3*	*4.9*	*4.8*
SO_4-particles		**mean**	**8.0 ± 1.6**	**7.3**	**4.6 ± 0.3**	**3.6 ± 0.7**
		min	*5.3*	*7.3*	*4.3*	*2.7*
	Period		82/83-90/91		90/91	88/89-90/91
		max	*7.0*			*3.0*
NO_2-gas		**mean**	**6.0 ± 0.6**			**2.5 ± 0.4**
		min	*5.1*			*1.9*
		max	*3.7*		*2.8*	*1.9*
HNO_3-gas		**mean**	**3.2 ± 0.3**		**2.8**	**1.2 ± 0.6**
		min	*3.0*		*2.8*	*0.8*
		max	*2.2*		*1.7*	*0.7*
NO_3-particles		**mean**	**1.9 ± 0.2**		**1.7**	**0.5 ± 0.1**
		min	*1.8*		*1.7*	*0.4*
		max	*0.7*			*0.4*
NH_3-gas		**mean**	**0.6 ± 0.1**			**0.3 ± 0.1**
		min	*0.5*			*0.3*
		max	*7.1*			*4.2*
NH_4-particles		**mean**	**6.2 ± 0.7**			**3.7 ± 0.5**
		min	*5.3*			*3.1*

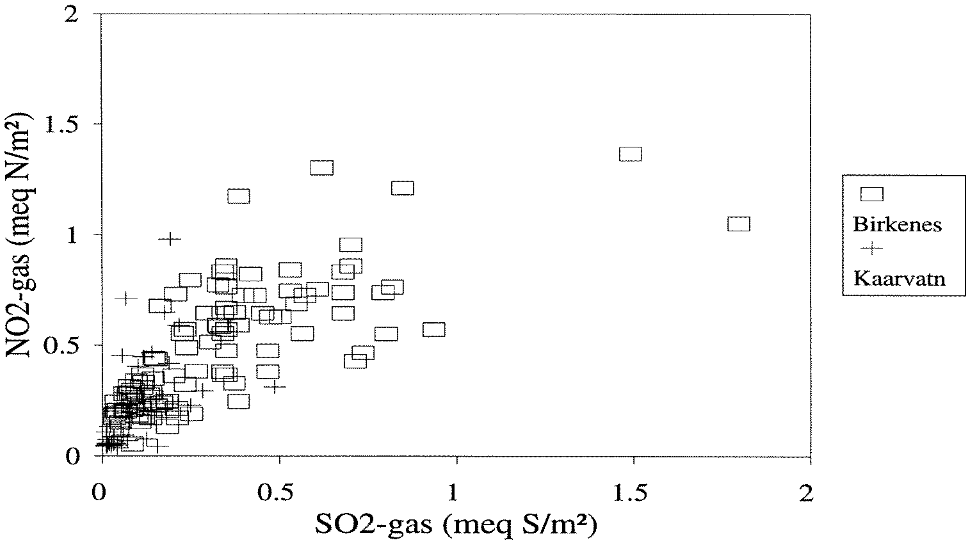


Figure 5.21 The relationship between monthly weighted dry-deposition influxes of SO_2 *and* NO_2 *gas (meq/m²) at Birkenes (1982-1991) and Kaarvatn (1988-1991). The relationships rely on liniar regression analyses. The regression lines are: Birkenes: y = 0.7x + 0.25 (r = 0.74) (n = 108); Kaarvatn: y = 1.1x + 0.12 (r = 0.49) (n = 48). Continuous line indicates a significant relationship (p< 0.05), while a dotted line indicates no significance, i.e. p > 0.05.*

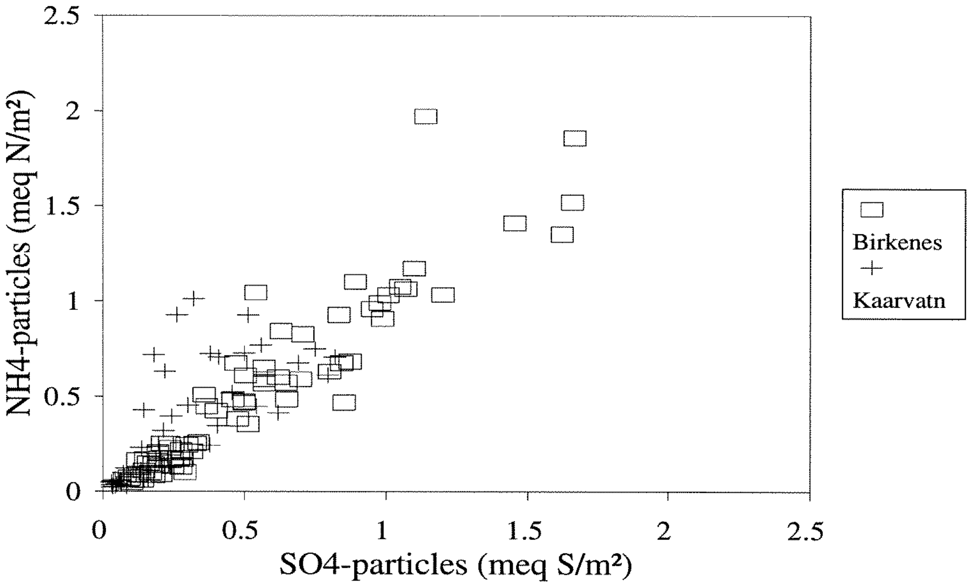


Figure 5.22 The relationship between monthly weighted dry-deposition influxes of SO_4^{2-}*-and* NH_4^+*-particles (meq/m²) at Birkenes (1986-1991) and Kaarvatn (1988-1991). The relationships rely on linear regression analyses. The regression lines are: Birkenes: y = 1.0x - 0.03 (r = 0.94) (n = 72); Kaarvatn: y = 1.0x + 0.07 (r = 0.76) (n = 48). Continuous line indicates a significant relationship (p< 0.05), while a dotted line indicates no significance, i.e. p > 0.05.*

Table 5.11 Annual dry-deposition influxes of sulphur and nitrogen compounds (meq/m²) and the percentage dry-deposition contribution of sulphur and nitrogen in relation to total input (Σwet, dry).

	Sulphur-compounds				**Nitrogen-compounds**						
	SO_2	SO_4	ΣDry	%*	NO_2	NO_3	HNO_3	NH_4	NH_3	ΣDry	%*
Birkenes											
1974/75	a	6.6	a	a	a	a	a	a	a	a	a
1975/76	a	9.9	a	a	a	a	a	a	a	a	a
1976/77	a	9.0	a	a	a	a	a	a	a	a	a
1977/78	a	8.3	a	a	a	a	a	a	a	a	a
1978/79	7.5	9.3	16.7	15.0	a	a	a	a	a	a	a
1979/80	5.8	10.7	16.4	12.2	a	a	a	a	a	a	a
1980/81	5.8	9.9	15.8	16.7	a	a	a	a	a	a	a
1981/82	4.6	8.3	12.8	10.1	a	a	a	a	a	a	a
1982/83	3.5	8.9	12.4	8.2	a	a	a	a	a	a	a
1983/84	3.7	9.0	12.7	14.1	a	a	a	a	a	a	a
1984/85	4.2	8.7	13.0	10.0	6.1	a	a	a	a	a	a
1985/86	3.6	6.6	10.2	9.4	5.1	a	a	a	a	a	a
1986/87	4.8	6.9	11.8	11.3	6.0	2.2	3.7	5.9	0.5	18.3	12.9
1987/88	3.1	5.3	8.3	6.4	5.9	1.8	3.1	5.3	0.5	16.5	9.3
1988/89	3.5	6.1	9.8	8.8	6.5	1.9	3.1	5.6	0.5	17.6	10.4
1989/90	3.3	5.9	9.2	10.6	7.0	1.8	3.0	7.1	0.7	19.6	14.7
1990/91	4.1	6.6	10.7	10.4	5.2	1.8	3.1	7.1	0.7	17.8	12.6
Storgama											
1977/78	a	7.3	a	a	a	a	a	a	a	a	a
Langtjern											
1988/89	2.3	4.9	7.2	13.3	a	a	a	a	a	a	a
1989/90	1.7	4.7	6.4	16.3	a	a	a	a	a	a	a
1990/91	1.7	4.3	6.0	12.5	a	1.7	2.8	a	a	a	a
Kaarvatn											
1980/81	2.0	3.9	5.9	11.3	a	a	a	a	a	a	a
1981/82	1.9	4.0	5.9	12.5	a	a	a	a	a	a	a
1982/83	1.5	3.4	4.8	11.6	a	a	a	a	a	a	a
1983/84	1.9	4.5	6.3	12.9	a	a	a	a	a	a	a
1984/85	2.2	4.4	6.5	15.0	a	a	a	a	a	a	a
1985/86	1.7	3.1	4.8	10.8	a	a	a	a	a	a	a
1986/87	1.4	2.9	4.3	8.7	a	a	a	a	a	a	a
1987/88	1.4	3.2	4.6	12.3	a	a	a	a	a	a	a
1988/89	1.3	2.9	4.2	9.4	2.5	0.7	1.9	4.2	0.4	9.7	24.6
1989/90	0.9	3.3	4.2	9.1	3.0	0.5	0.8	3.7	0.4	8.3	30.7
1990/91	0.9	2.7	3.6	14.1	1.9	0.4	0.8	3.1	0.3	6.4	17.4

***:** Dry-deposition as percent of total atmospheric input (Σwet,dry).

a: Data are lacking for some months or for a whole year.

Estimated catchment specific dry-deposition velocities.

The dry-deposition velocities used (Table 5.9), may often cause wrong dry-deposition influxes, and very the fluxes will be underestimated. The degree of underestimation is highly catchment specific, but also within a catchment, the dry-deposition velocity may deviate a lot both in time and space, due to factors like continuous vegetation growth which alter the forest cover and age of stand and climatic changes (e.g. temperature, wind-speed and wind-direction). For the relatively forested Birkenes catchment, more relevant dry-deposition velocities or fluxes can be estimated for chlorine and sulphate by assuming both element being concervative. In this context, it means that annual effluxes (runoff) is equal to the annual influxes (Σwet,dry) of these elements. At Birkenes, this is a reasonable assumption, because the influxes of both elements are relatively high, so no biogeochemical processes do affect the annual average mass-balance calculations significantly. Thus, dry-deposition influxes of chlorine and sulphate can be calculated as the difference between annual average efflux and wet-deposition influx of chloride and sulphate (Table 5.13). By transforming these fluxes into concentrations (μeq/L), the annual average concentration of dry-deposition compounds of sulphur and chloride can be estimated by multiplying the annual weighted average concentrationws of these elements in runoff-water by the annual hydrological runoff/precipitation-ratio, because this factor directly express the evapotranspiration factor. The concentration difference between the adjusted evapotranspiration value of runoff and the measured concentration in wet-deposition, then directly expresses the annual average concentration in dry-deposition.

Because of the very mild years at Birkenes in 1988/89 and 1990/91, with no significant accumulation of water during the winter (snow or frozen ground), it is also possible to calculate dry-deposition velocities for half-year periods (Winter: October-March; Summer: April-September) for both chlorine and sulphur at this site, by assuming both ions to be conservative also within this 6 month periods. It should be underlined that these half-year estimates only rely on two years of data.

Because the concentration of sulphate in runoff-water from the Birkenes catchment is relatively high compared to the chemistry of wet-deposition, it is also necessary to assess if important sulphate-producing sources are present within the catchment. During 1989/90, water from to very nearby lakes was sampled and analysed every forthnight with respect to major chemical dissolved compounds. If important sulphur-producing sources are present in the Birkenes catchment and/or within the catchment of the two lakes, the SO_4^{2-}/Cl^--ratio of runoff-water from Birkenes should deviate from that present in the two lakes or in the rain-water. Even though the chemical quality and quantity of wet-deposition (precipitation) might show large local variations, we assume the weather-station at Birkenes also being representative for the wet-deposition chemistry at the two very nearby lakes. Despite this assumption, the runoff-chemistry from the Birkenes catchment and the chemisty of the two lakes differred a lot. However, the Na/Cl-ratio and the SO_4/Cl-ratio are approximately identical at all three sites (Table 5.12). This means that no significant sulphate producing sources are present in the Birkenes catchment. The variation in concentrations between the sites are primarily a result of different hydrology and dry-deposition influxes. Two important reasons for the lower concentrations of sodium, sulphate and chloride in the lakes are: **1)** Extensive clearfelling during the last years in these catchments, and **2)** The lake areas constitute relatively large parts of the catchments, while no lake is present in the well forested

Birkenes catchment. Thus, far higher influxes of dry-deposition compounds should be expected in the Birkenes catchment compared with the two other sites.

Table 5.12 Annual weighted concentration of major chemical compounds (µeq/L) in precipitation and runoff water at Birkenes and correspondant lake-water chemistry from two lakes located very nearby the Birkenes catchment during 1989/90.

Site	**Water**	**H^+**	**Ca^{2+}**	**Na^+**	**SO_4^{2-}**	**Cl^-**	**Na/Cl**	**SO4/CL**
Birkenes	Precipitation	44	11	66	65	77	0.86	0.84
Birkenes	Runoff	25	66	136	122	163	0.83	0.75
Repstadvatn	Lake-water	18	47	106	98	134	0.79	0.73
Barkevatn	Lake-water	20	48	111	102	137	0.81	0.74

Because it is possible to claim that sulphur-producing processes within the Birkenes catchment have minor influence on the annual mass-balance budget, mass-balance calculations are used for estimating catchment-specific dry-deposition velocities for chloride and sulphate. During the period when all sulphur-compounds have been monitored at Birkenes (1980/81 to 1990/91, except 1983/84 and 1984/85), the annual dry-deposition velocity of sulphur was estimated to be 1.8 ± 0.8 cm/sec. This is 2.6 times higher than the highest dry-deposition velocity used, i.e. 0.7 cm/sec, estimated for SO_2 during summer (Table 5.9). Thus, the dry-depositon flux of sulphur averagely constitute about 30% (33 ± 7%) of total annual influx of sulphur at Birkenes. Using the dry-deposition velocities given in Table 5.9, dry-deposition should only constitute 10% (10 ± 3%) of total annual sulphur input. As earlier mentioned, it is also possible to estimate dry-deposition velocities for half-year intervals based on the very mild years at Birkenes (1988/89 and 1990/91) assuming sulphur also being concervative within a 6 month period. During these two years, the average dry-deposition velocity of sulphur during summer was estimated to be 0.4 ± 0.05 cm/sec, while the correspondent deposition velocity during winter was 2.2 ± 0.5 cm/sec. The annual average deposition velocity for the two years was 1.3 ± 0.3 cm/sec. Doing the same calculation for dry-deposition of chloride during the two mild years, the average dry-deposition velocity of this element was estimated to be 17 ± 3 cm/sec during summer and 11 ± 0.5 cm/sec during winter, while the annual average dry-deposition velocity was estimated to be 13 ± 0.4 cm/sec. The far higher deposition rate for chloride compared with sulphate does probably rely on the fact that chloride primarily derives from local marine sources. Because the Birkenes is sited relatively close to the sea, large amounts of seasalt aerosols/particles are able to be transported into the catchment. It is therefore likely that the molecular-weight of these compounds is far higher than the molecular-weight of the more long-ranged transported sulphur compounds. Consequently, the dry-deposition velocity of chloride at Birkenes has to be higher than the correspondent dry-deposition velocity of sulphur. Because the seasalt aerosols may vary significantly with respect to molecular-weight, not only from site to site, but during a year at one site, estimates on dry-deposition velocity of chloride is not present in the literature. The estimated dry-deposition rates of chloride at Birkenes are therefore only valid for this site and only for the two years incorporated.

It is impossible to do the same kind of dry-deposition velocity estimates for nitrogen compounds, because the atmospheric input of nitrogen is almost totally retained in the catchment, primarely by biological uptake and by numerous chemical/biochemical redoks-reactions. However, as the predominant dry-deposition compounds of nitrogen are NO_2-gas and NH_4-particles, it is reasonable to assume that the real dry-deposition of nitrogen is close to that estimated for sulphur, since NO_2/SO_2-ratio and the NH_4/SO_4-ratio is ≈ 1:1 (See Figure 5.21 and 5.22). This means that the dry-deposition of nitrogen also contributes by about 30% to the total annual influx of nitrogen at Birkenes.

At the three other sites, it is impossible, for several reasons, to estimate site-specific dry-deposition velocities. At Storgama it is primarely due to a total lack of dry-deposition data (Table 5.11). However, only small parts of the Storgama catchment is covered by forest, and approximately 60% of the catchment is bare rock. Thus, it is should be acceptable to use mass-balance calculations for sulphur and chloride (Table 5.13) to estimate the dry-deposition influxes of these elements at this site. By doing so, dry-deposition influxes of sulphur and chloride averagely constitute 10% and 19% of the total annual influxes of these elements at Storgama.

Table 5.13 Annual average effluxes (runoff=R), influxes (wet-deposition=W) and the difference between mean annual average effluxes and influxes (D=R-W) of sulphate and chloride (meq/m² yr) during the period of monitoring.

		Sulphate			**Chloride**	
Site	**R**	**W**	**D**	**R**	**W**	**D**
Birkenes	163 ± 43	104 ± 20	59 ± 25	163 ± 49	105 ± 31	58 ± 27
Storgama	69 ± 21	62 ± 14	7 ± 11	32 ± 12	25 ± 8	6 ± 6
Langtjern	46 ± 13	47 ± 11	- 2 ± 12	11 ± 2	9 ± 2	2 ± 2
Kaarvatn	31 ± 6	39 ± 7	- 8 ± 5	107 ± 31	168 ± 49	- 61 ± 23

At Langtjern, dry-deposition data on sulphur does only exists for the last three years, but as shown in Table 5.13, it seems to be a retention of sulphur within the catchment, which exlude mass-balance calculation as a suitable method for estimating dry-deposition fluxes of sulphur. Because a lake also is present in the catchment, as well as it contains relatively large areas of bogs, substantial amounts of sulphate might very well be "tied up" in the catchment by sulphate-reducing processes forming immobile sulphide-compounds. Bogs are effective zinks for sulphur, which means that sulphide-compounds accumulate, and are able to be present on immobile forms for hundreds of years. The mass-balance calculation of chloride indicates an annual average dry-deposition of this element of about 7% of total annual influx at Langtjern (Table 5.13)

At Kaarvatn, it is also impossible to use mass-balance calculations to estimate dry-deposition fluxes, primarely because the weather-station is very unrepresentative for the precipitation-chemistry for the whole catchment, especially with respect to seasalts (Table 5.13). Because, the weather-station is located at the outlet of the catchment, very close to the sea, the chloride is overestimated by a factor 1.6.

The use of mass-balance calculations to estimate dry-deposition velocities is somewhat speculative. This is clearly demonstrated for sulphur, because for this element, it implies the highest "dry-deposition velocities" during the winter period, the period which physically and biologically should give the lowest deposition rates. The most important reason for this, is the far higher combustion of fossil fuels during winter, which causes higher concentration of SO_2-gas and SO_4-particles, compared with at summer. Thus, the calculated or "fitted" dry-deposition velocities are only catchment-specific deposition-rates which only express reasonable dry-deposition estimates for each single catchment.

5.3 Concentration of marine compounds with distance from the sea

In unpolluted areas, the sea is the major source of atmospheric supply of sodium and chloride, but also of magnesium and sulphate. Sea spray carries large amount of sea water into the atmosphere which, on evaporation, forms salt particles and aerosols that are capable of acting as nuclei for cloud and raindrop condensation. Atmospheric salinity can be carried for great distances inland over continents, although a majority of it is precipitated with rainfall in the coastal regions, and decreases with distance inland.

Because the Kaarvatn catchment undoubtedly belongs to another climatic region compared with the other sites, this catchment is omitted when the seasalt-concentration in precipitation with respect to distance from sea is evaluated. The calculation of distance from sea is based on the stipulated northeastern line drawn in Figure 4.21 Because this part of Norway belongs to the uppermost part of the northern westwind-belt, defined as the area between 35th and 65th parallel, it means that western winds dominate. Thus, the drawn line presented in Figure 4.23 is found to be reasonable for estimating the seasalt gradient from Birkenes to Langtjern.

Based on annual weighted concentration in both wet- and dry-deposition (estimated by mass-balance calculations), a very significant half-logarithmic relationship was found between concentration of chloride and distance from sea (log km). The the regression equation (Figure 5.23) shows that the concentration of chloride in wet-deposition is reduced by 50% and 90%, 20 km and 226 km distance inland, along the stipulated northeastern line. Correspondingly, the concentration of chloride in dry-deposition is reduced by 50% and 90%, 15 km and 132 km distance inland (Figure 5.24). Directly related to the three catchments, this means that less than 50% of the chloride concentration present in wet-deposition at sea, is present in the precipitation at Birkenes, located 25 km from the sea, while about 20% and less than 10% are left in the wet-deposition at Storgama and Langtjern, respectively. By the equation present in Figure 5.24, dry-deposition of chloride will normally not reach the Langtjern catchment, which is located 265 km inland with respect to the stipulated northeastern line. By this equation, no dry-deposition of chlorid should normally be expected in areas located more than 228 km distance inland.

A correspondent seasalt investigation was conducted in the Sogn og Fjordane county, Norway (Ryghaug and Bølviken, 1987), based on stream water samples. This investigation showed a 50% and 90% reduction in concentration of chloride within a distance of 12 km and 100 km from the coast. This is a stronger decrease by distance from the coast compared with the gradient present along the northeastern line from Birkenes to Langtjern. However, the deviation can easily be explained by topographic differences. Sogn og Fjordanen is located in the western part of Norway, characterized by high mountains at the coast, which implies very steep altitude-gradients, compared with the gradient from Birkenes to Langtjern. This fact, obviously implies large orographic differences between the areas compared, and is therefore the most likely explanation for the different seasalt gradients in precipitation with respect to distance from the coast.

Table 5.14 The percentage reduction of chloride concentration in wet-deposition and dry-deposition with respect to distance from sea, based on the regressions present in Figure 5.23 and 5.24.

Site	**At coast**	**Birkenes**	**Storgama**	**Langtjern**
Distance from sea (km)	0	25	105	265
Wet-Cl	100%	47%	23%	7%
Dry-Cl	100%	41%	14%	0%

Continental rain generally contains more sulphate, calcium, magnesium and potassium in relation to chloride compared with more coastnear areas. At least for sulphate, this may not necessarily be so, because the concentration of this ion is highly dependent on the influence from antropogenic sources. However, since the concentration differences of sulphur in precipitation between the three southernmost catchments are relatively small (Table 5.2), an increase in the SO_4/Cl ratio with respect to distance inland should be expected. This is also clearly demonstrated in Figure 5.25, where the annual average SO_4/Cl ratio of wet-deposition increased from 1.2 at Birkenes to 3.4 and 4.9 at Storgama and Langtjern, respectively. Concerning the relationships beween base-cations, e.g. Ca, Mg and K, and Cl, a corresponding, but smaller, increase was found with respect to distance inland. At Birkenes, the annual average ratios of Ca/Cl, Mg/Cl and K/Cl were 0.15, 0.20 and 0.06 (Figure 5.25). The corresponding ratios at Storgama were 0.56 (Ca/Cl), 0.27 (Mg/Cl), and 0.23 (K/Cl), while at Langtjern 0.83 (Ca/Cl), 0.31 (Mg/Cl) and 0.34 (K/Cl). There was no significant change in the annual average Na/Cl ratio with distance from sea, which means that the chloride deposition is about equal to the deposition of sodium. While the expected Na/Cl ratio of seawater is 0.86, the annual average ratio at Birkenes, Storgama and Langtjern was 0.86 ± 0.05, 0.80 ± 0.04 and 0.81 ± 0.03.

In accordance with the chloride ratios presented above, it has to be a statistical significant increase in the ratio between the total concentration of sulphate and base cations (Ca, Mg and K) and theire marine contributions, because the marine fractions are estimated on the basis of theire equivalente ratios with respect to chlorid in seawater. The marine fraction is estimated using the equations given in Chapter 2.3. Based on the regression line present in Figure 5.26, the annual average $SO_4/SO_{4marine}$ ratio at Birkenes is 11 and increase to 33 and 48 at Storgama and Langtjern. The ratios of Ca/Ca_{marine}, Mg/Mg_{marine} and K/K_{marine} at Birkenes are 4, 1 and 3 while the corresponding ratios at Storgama are 15 (Ca/Ca_{marine}), 1 (Mg/Mg_{marine}) and 13 (K/K_{marine}) and 22 (Ca/Ca_{marine}), 2 (Mg/Mg_{marine}) and 19 (K/K_{marine}) at Langtjern. These results clearly demonstrates the increasing importance of terrestrial sources in atmospheric deposition by distance inland. In other words, this means that the percentage contribution of more typical terrestrial derivated ions in precipitation, like calcium and potassium, increases by increasing distance from sea.

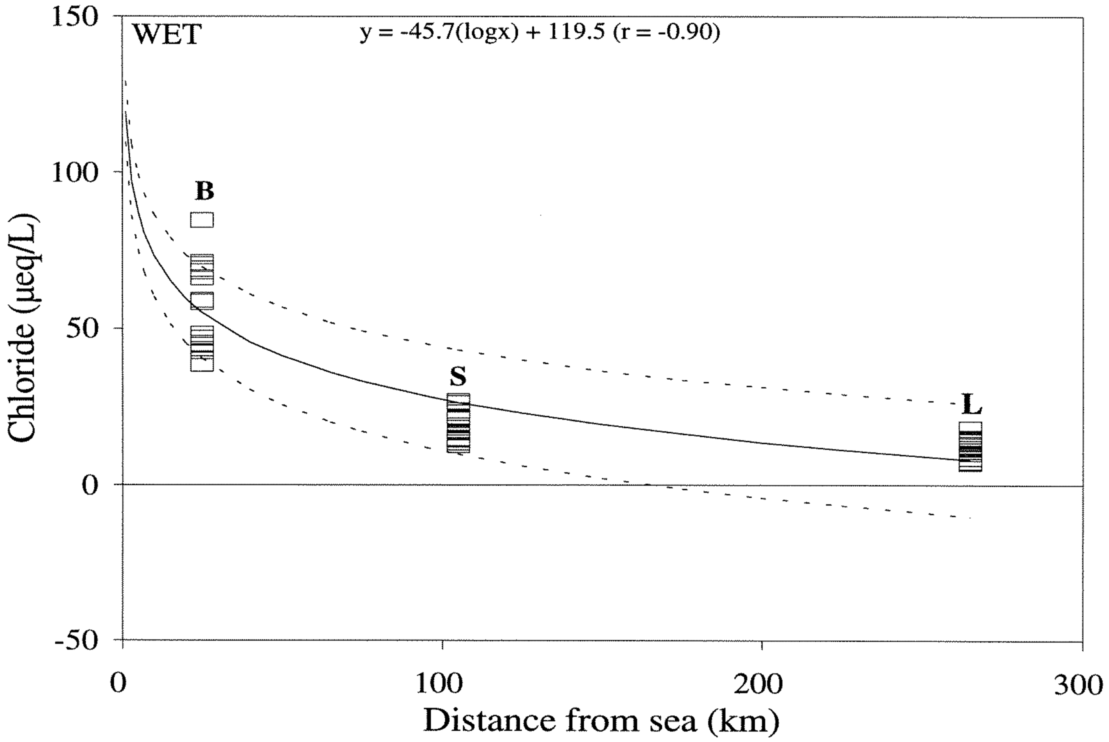


Figure 5.23 Decrease in concentration of chloride in wet-deposition with respect to distance from the coast, based on annual weighted averages. The dotted lines indicate ± one std. deviation of mean.

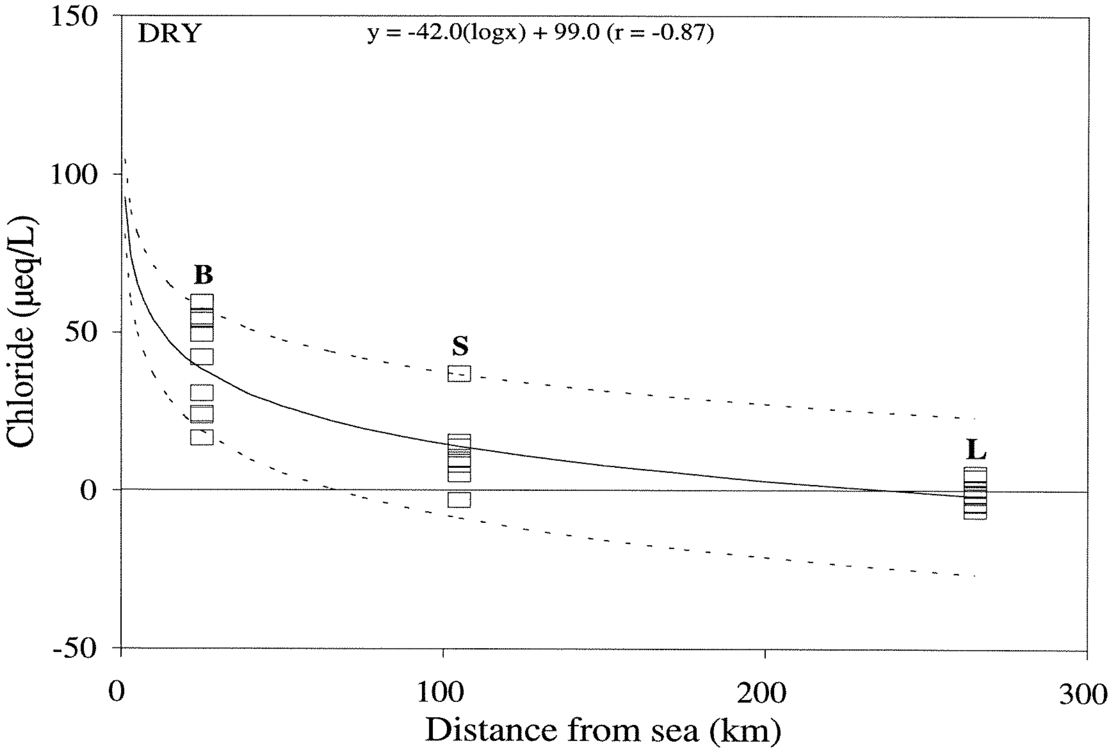


Figure 5.24 Decrease in concentration of chloride in dry-deposition with respect to distance from the coast, based on annual weighted averages. Dry-depositon of chloride is based on mass-balance calculations, i.e. $Cl_{efflux} = Cl_{influx}$. *The dotted lines indicate ± one std. deviation of mean.*

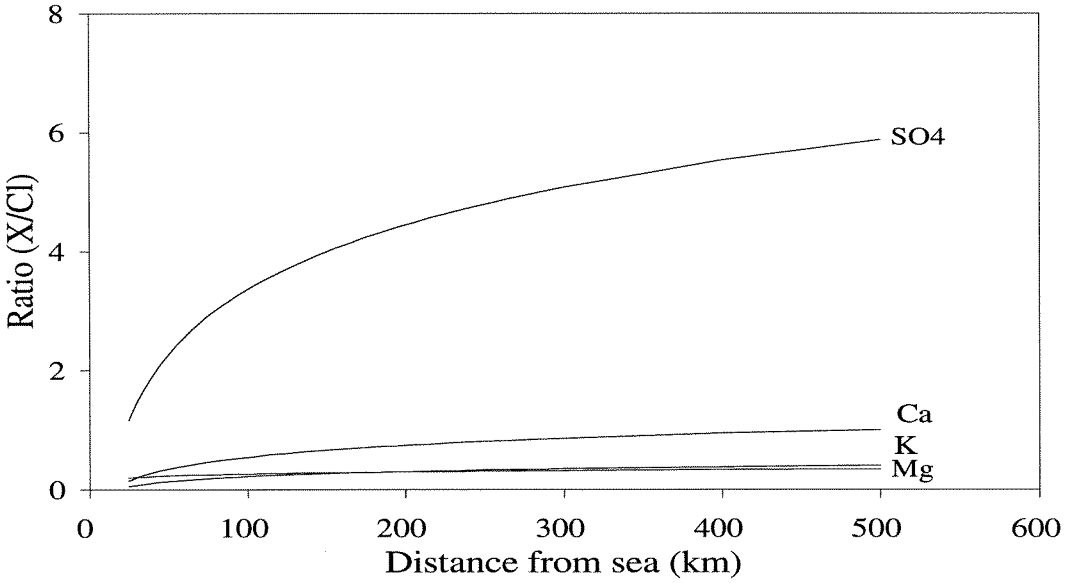


Figure 5.25 Changes in the sulphate, calcium, magnesium and potassium ratios with respect to chloride in relation to distance from sea, based on monthly weighted wet-deposition averages. The regression lines are: SO_4/Cl*: y = 3.6 logx -3.9 (r=0.80) (n=44); Ca/Cl: y = 0.7 logx - 0.8 (r=0.69) (n=44); Mg/Cl: y = 0.1logx + 0.04 (r=0.71) (n= 44); K/Cl: y = 0.3 logx - 0.3 (r=0.76) (n=27).*

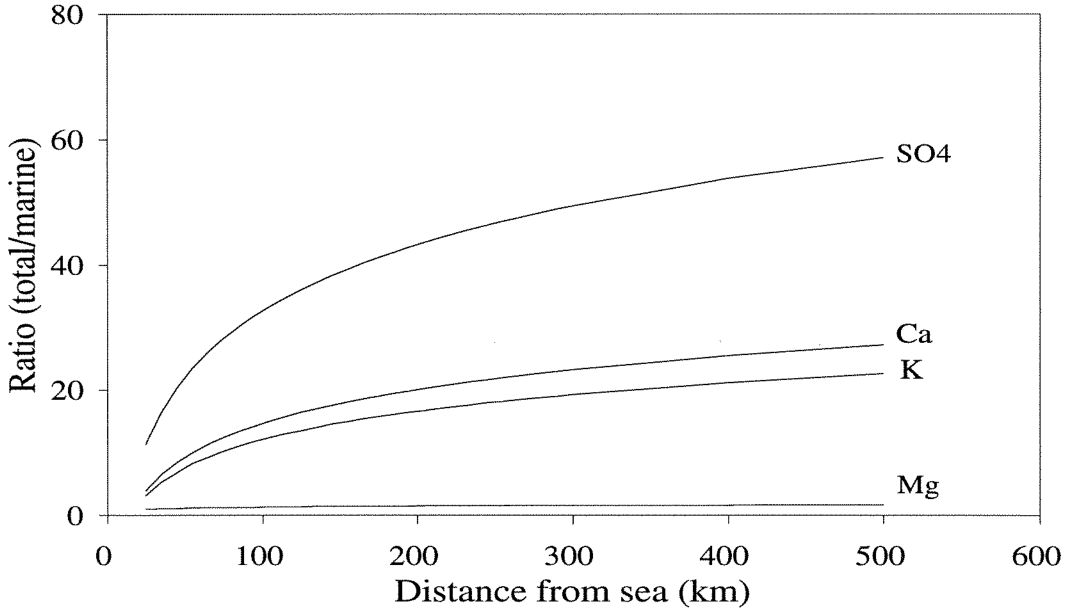


Figure 5.26 The relationships between total concentration of sulphate, calcium, magnesium and potassium in wet-deposition and their marine contributions with respect to distance from the coast, based on monthly weighted averages. The regression lines are: $SO_4/SO_{4marine}$*: y = 35logx -38 (r=0.80) (n=44);* Ca/Ca_{marine}*: y = 18logx - 22 (r=0.69) (n=44);* Mg/Mg_{marine}*: y = 0.6logx + 0.2 (r=0.71) (n= 44);* K/K_{marine}*: y = 15logx - 18 (r=0.76) (n=27).*

5.4 Acid precipitation

An overview

Urban acid deposition was probably first reported by Smith (1852, 1872). His work was, however, "forgotten" until a century later when the spread of acid deposition, largely sulphuric acid, became apparent far from urban sources (Barrett and Brodin, 1955; Houghton, 1955; Gorham, 1955). This means that the more local acid deposition problems described by Smith got a large regional problems within a 100 year period. The effects of acid deposition upon lake pH were probably first described by Mackereth (1957) and Gorham (1957, 1958a) in England. Although Huitfeld-Kaas (1922), Dahl (1926), and Sunde (1926) claimed that acid freshwater caused mortality of salmon and trout, Dannevig (1959) was the first who correlated fish death in Norway with acidification of surface waters by acid deposition. The broad ecological consequences of long-range transport of acidifying air pollutants were first recognized by Odèn (1968). From that time, acidification of surface waters has been reported as a major problem in large areas of the northern temperate regions:

In the United States: Likens et al., 1972; Likens and Bormann, 1974; Schofield, 1976; Davies et al.,1978; Driscoll et al. 1984; NAPAP, 1990.

In Canada: Gorham and Gordon, 1960; Beamish and Harvey, 1972; Conroy et al., 1974; Scheider et al., 1975; Dillon et al., 1978; LaZerte, B.D., 1984; RMCC, 1990.

In Scandinavia: Odèn, 1968; Wicklander, 1973; Almer et al.,1974; Leivestad et al., 1976; Gjessing et al., 1976; Wright et al., 1977; Dickson, W. 1978; Henriksen and Seip, 1980; Overrein et al., 1980; Rebsdorf, 1980.

In Scotland: Wright et al., 1980; Skiba et al., 1989.

In Germany: Ulrich et al., 1980; Schoen et al., 1984; Steinberg et al., 1984.

In Belgium: Vangenechten and Vanderborght, 1980; Vangenechten et al., 1981.

In the Netherlands: van Dam et al., 1980; Van Breemen et al., 1982; Mulder et al., 1987.

In Switzerland: Schnoor et al., 1983; Fuhrer, 1986.

In eastern European countries : Zytkowicz, 1982; Babiakovà and Bodis, 1987.

Common to all these areas are low pH buffering capacity in the catchment, combined with large depositions of directly acidifying (e.g. strong acids) and/or indirectly acidifying (e.g. NH_4^+) compounds.

The magnitude of the consequences of air pollution on the chemistry of surface waters during the last decades has reach such major proportions that global action is required to curtails it effects. Although much of the atmospheric pollution returns to the ground in the areas immediately adjacent to the industrial concentrations, large amounts enter the atmosphere to influence the precipitation and surface waters of entire countries or portion of continents. Acid atmospheric deposition enters the ecosystems in a variety of forms and via a number of pathways. The most common strong acids in precipitaion are sulphuric (H_2SO_4) and nitric (HNO_3) acid. Occasionally other mineral acids [e.g. hydrochloric (HCl) or phosphoric acid (H_3PO_4)], organic acids [e.g. formic acid (HCOOH) or acetic acid (CH_3COOH) may be present, but normally in unsignificant quantities, at least as their contribution to the acidity of precipitation are concerned. Although a substantial amount of the strong acid anion, Cl^- , may be present in precipitation, it generally derives from neutral salts, usually of marine origin, rather than from HCl (Henriksen, 1979, 1980). This is undoubtedly the case as far as the Norwegian monitored catchments are concerned. Other acids are also present as carbonic acid (H_2CO_3), formed by the reaction between atmospheric CO_2 and water, but the carbonic acid is a relatively weak acid. Thus, the contribution of this acid to the acidity of water decreases as the contribution from strong acids increases. However, the carbonic acid may be an important acid in natural, low acidified systems, because the amount of present in soil solutions is generally much higher than in the atmosphere. This implies that the amount of CO_2 which actually enters via precipitation is of minor importance.

Except the very coastnear seasalt-influenced areas (high in NaCl), the H^+ ion is the dominant cation in acid deposition, but other cations may accompany the acid anions. Among those commonly encountered are Ca^{2+}, Mg^{2+}, K^+ and NH_4^+. Thus, acid precipitation is usually a complex mixture of acids and salts. The degree to which the strong acid anions (SO_4^{2-}, NO_3^- and Cl^-) exceed the base cations, on chemical equivalent basis, determine the qualitative capacity of precipitation to acidify the system. In addition the NH_4^+ can enhance the capacity of precipitation to acidify the system.

Atmospheric deposition includes not only wet-deposition but also deposition of gases and particles, often termed dry-deposition. The most important gases are SO_x, primarily SO_2, NO_x, primarily NO_2. These compounds may be adsorbed on soil and plant surfaces or absorbed within the plants through the stomata and eventually converted into H_2SO_4 and HNO_3. Ammonia gas may also be deposited and converted to NH_4^+. Dry deposited particles may contain salts of any of the acid anions or base cations. The total acidifying capacity of dry-deposition sources may exceed that of the direct acidity of precipitation (wet-deposition), particulary in areas far from the coast, characterized with an arid climate. At more precipitation rich sites (humid climate), wet-deposition is the dominating atmospheric source of acidification. The latter is the situation within most parts of Norway and Scandinavia.

The effects of acid atmospheric compounds on the acidification of surface waters is very complexed, because numerous acid-neutralizing and acid-producing processes take place within the catchment when precipitation impinges the vegetation (e.g. interaction with the canopy) and percolate the soil system. This means that the surface waters may necessarely not be less acidic than the precipitation, even though this is the most common result. Undependent on acid rain, acidification of surface waters may also arise due to special conditions in the catchment, as aeration (oxidation) of different sulphide compounds (Alasaarela, 1982; Erviö and Palko, 1984; Björkqvist and Weppling, 1987). In addition, natural sources to soil and freshwater acidification exist (Ulrich, 1980), mainly due to:

1) Nutrient uptake by plants.
2) Production of CO_2 by plant roots and micro-organisms.
3) Oxidation of N- and S-compounds.
4) Humification of organic substances.

Knowledge about the acidification phenomenon has increased tremendously since Odèn (1968) suggested that the increasing acidity of precipitation was resposible for the decline in fish populations in many areas. In the first years of the acid precipitation science, it was generally accepted that the deposition of acidic substances from the atmosphere into soil and aquatic systems was the dominant cause of surface water acidification (Wright and Gjessing, 1976; Seip and Tollan, 1978; Likens et al., 1979). Based on this assumption, Henriksen (1980) claimed that the acidification process could be described as a large scale titration, where the effect of acid precipitation on a catchment could be compared with an acid titration of a hydrogen carbonate solution. Other scientists, especially Rosenqvist (1977, 1978, 1981, 1990), claimed that the main reason for the acidification of surface waters is the change in the biogeochemical buffering level of the catchment, and in addition to the chemistry of precipitation, the chemistry of runoff water may also be dependant on both the amount and intensity of precipitation, parameters which influence the residence time and flow-pattern of water through the catchments.

Reeve and Fergus (1982) showed that podzol soils can naturally create highly acidic clearwaters containing high amounts of inorganic dissolved aluminium. These observations were made in coastal Australia areas that do not receive acidic H_2SO_4 in precipitation, but receive high amounts of neutral chloride salts from sea spray. The proposed mechanism is that sea salt cations (Na^+, Ca^{2+}, Mg^{2+}) are taken up by soils or vegetation and replaced by H^+-ions, resulting in acidic waters. The effect of neutral salt on soil and surface water acidification is earlier reported by several scientists (Wicklander, 1975; Rosenqvist, 1977; Skartveit, 1980; Sullivan et al., 1988; Seip et al., 1989).

One of the most significant consequences of soil acidification is the mobilization of aluminium from edaphic to aquatic environments is (Magistad, 1925; Scheider et al., 1975; Wicklander, L., 1975; Wright et al., 1977; Dickson, 1978; Cronan and Schofield, 1979; Cronan, 1980; Dickson, 1980; Driscoll, 1980; Driscoll et al., 1980; Vangenechten and Vanderborght, 1980; Wright et al., 1980; Krug and Isaacson, 1984; Mulder et al., 1989). In addition to Rosenqvist (1977,1978,1981,1990), many scientists have stressed the importance of the biogeochemistry of the catchment for the surface water chemistry (Brosset, 1979; Glover and Webb, 1979; Overrein et al., 1980; Seip et al., 1980, 1989; Stuanes, 1980; Ulrich, 1980; Groeterud, 1981; Johnson et al., 1981; Christophersen, 1983; Reuss and Johnson, 1985; Van Breemen and Mulder, 1987; Mulder et al., 1990; Sullivan et al., 1990, Krug, 1989, 1991), and Sullivan et al. [1990] claimed that the role of catchment for neutralization of acidic input is more important than generally assumed so far. Similar conclusions were also made by Krug (1989) based on an extensive review of literature conserning theories of the acidification of freshwaters. Model-based estimates of future chemical changes and biological responses should therefore be re-evaluated in the light of these results (Sullivan et al., 1990). Similar conclusion was also drawn in the final report from the Surface Water Acidification Programme (SWAP, 1990).

The interactions of acid rain and acid soils have generally been concerned with major inorganic constituents of precipitation, soil, and leachate. The leaching of basic cations from extremely acid soil materials is therefore often observed to be small relative to the H^+ additions of acid rain. (Wicklander, 1973; Abrahamsen, 1980; Bache, 1980; Smith, 1981). Consequently, the release of Al by dissolution or exchange are considered to be the major acid neutralization processes (Ulrich et al., 1979; Mulder and Van Breemen, 1987; Mulder et al., 1987), because the dissolution of solid Al is a proton consuming process. That means that a dissolved Al- specie, like Al^{3+}, acts as a mobile temporary proton sink enabling acidity to be transported by this ion in large quantities in the draining water. The fate of these ions is determined by secondary reactions, like adsorption, complexation and precipitation processes during which protons are released again. These observations have led to the hypothesis that such soil materials are poorly buffered against H^+ addition (Overrein et al., 1980; Seip, 1980).

The buffering capacity against H^+ in a cathment is also shown to be highly dependant on the mobility of the accompanying anions, mainly the strong acid anions Cl^-, SO_4^{2-} and NO_3^- (Seip, 1980; Reuss and Johnson, 1985). In acid soils, the introduction of mobile anions, whether as salts or acids, can cause sufficient increase in soil solution ionic strenght to reduce the alkalinity of the soil solutions significantly. Within certain critical ranges this will lead to a switch from positive to negative alkalinity in the solution (Reuss and Johnson, 1985). If Cl^-, which is the most mobile anion, predominates, a relatively fast acidification response will occur. The SO_4^{2-} ion is less mobile and the acidification effect by this ion is highly dependent on the sulphate retention in the catchment. This was already pointed out by Gorham (1958b). The effects of the NO_3^--ion on the acidification is difficult to evaluate. This ion is often totally resorbed by the vegetation, and effects of plant growth on soil acidification is difficult to quantify, but as for NH_4^+, a more firmly discussion dealing with this ion wil be presented later in this chapter.

Most areas considered highly sensitive to acidification by acid rain, often have high proportions of extremely acid, organic-rich lithic soils and peats (Braekke, 1976; Krug and Frink, 1983]. Even though Hedin et al. [1990] claimed that organic, acid-base systems have a very limited capacity to buffer inputs of strong mineral acids, several experiments in acid, organic-rich soils show that they are not poorly buffered. Treatments (additions of strong acid) more acidic than pH 4 are required to significantly reduce pH and significantly increase the quantity of cation leaching from these soils (Overrein, 1972; Seip et al., 1979, 1980; Abrahamsen, 1980; Abrahamsen and Stuanes, 1980; Cronan, 1980; Overrein et al., 1980; Smith, 1981). Since cation exchange reactions predominate in the organic soil horizions, cation exchange reactions are important in regulating the solution chemistry. However, it is unreasonable to assume that cation exchange is the only mechanism by which soil organic matter influences solution chemistry. Very little is known about how the solubility and mobility of organic matter and its complexes are influenced by acid input, and how such interactions influence cation flux and leachate acidity (Krug and Frink, 1983). The results obtained by Krug and Isaacson (1984) indicate that soil organic matter buffers against strong acid additions by a number of other mechanisms than exchange of base-cations and aluminium for H^+. Complex changes in both the organic and inorganic composition of leachate is suggested (Ritchie and Posner, 1982). The organic acid buffering mechanism may be an alternative explanation to the observation that humic-coloured lakes in Scandinavia are becoming clearer. This effect is previously attributed to precipitation of humic acid by iron and aluminium dissolved by acid rain (Almer et al., 1974; Dickson, 1978).

Acid precipitation at the monitoring sites.

At all four sites, precipitation chemistry has been daily measured i the period 1980-1991. During this compareable period, annual average weighted concentration of strong acid anions (SAA: $\Sigma SO_4^{2-}, NO_3^-, Cl^-$) at Birkenes was 173 ± 20 µeq/L, while the correspondent concentrations at Storgama, Langtjern and Kaarvatn were 106 ± 12 µeq/L, 100 ± 15µeq/L, and 87 ± 16 µeq/L. During this period, averagely 39 ± 6% of SAA was present as non-marine sulphate (SO_4*) at Birkenes, while the percent contributions from NO_3^- and Cl^- were 25 ± 3% and 33 ± 6%. The remaining 3-4% was marine sulphate. At Storgama, 48 ± 5% of SAA was present as SO_4*, while NO_3^- and Cl^- contributed by 31 ± 3% and 20 ± 4%, respectively. The remaining 1-2% was marine sulphate. At Langtjern, SO_4* averagely constituted 52 ± 4% of the concentration of SAA, while NO_3^- and Cl^- contributed by 33 ± 3% and 13 ± 3%. The remaining 1-2% was marine sulphate. At Kaarvatn, which receives far the most unpolluted rainwater, chloride constituted 60 ± 6% of SAA, while SO_4* and NO_3^- constituted 23 ± 7% and 11 ± 2%. The remaining 6% was marine sulphate.

Typically for the three most air-polluted sites, is the decrease in concentration of SAA by distance from sea, from Birkenes towards Langtjern, primarily due to the substantial decrease in chloride concentration by distance inland, from an annual average Cl^--concentration of 58 ± 14 µeq/L at Birkenes to 20 ± 5 µeq/L at Storgama and 12 ± 3 µeq/L at Langtjern, based on the period 1980-1991. The differences in the concentrations of SO_4* and NO_3^- between the sites are, however, small. At Birkenes, the annual average concentration of SO_4* and NO_3^- were 65 ± 12 µeq/L and 43 ± 6 µeq/L, at Storgama 52 ± 8 µeq/L (SO_4*) and 33 ± 5 µeq/L (NO_3^-), while at Langtjern the average annual concentrations of SO_4* and NO_3^- were 55 ± 11 µeq/L and 34 ± 5 µeq/L, respectively. This means that the concentrations of SO_4* and NO_3^- at the three sites are within one standard deviation of mean. Thus, if using the concentration of SO_4* and NO_3^- as criterion for air-pollution/acid-precipitation, there are only small differences in the atmospheric pollution between the three sites. However, the annual atmospheric loading of sulphur and nitrogen is highest at Birkenes, because this site receives the highest annual amount of precipitation. The annual average inputs of SO_4* and NO_3^- through wet-deposition at Birkenes during 1980-1991 were 86 ± 17 meq/m² and 59 ± 11 meq/m². The correspondant wet-deposition influxes at Storgama were 49 ± 12 meq/m² (SO_4*) and 32 ± 8 meq/m² (NO_3^-), while at Langtjern, the influxes of SO_4* and NO_3^- were 37 ± 8 meq/m² and 22 ± 6 meq/m², respectively. Even though Langtjern receives the lowest inputs of water and thus the lowest wet-deposition influxes of sulphate and nitrate, the highest monthly weighted concentration (µeq/L) of these or other chemical compounds is often recorded here. Despite that fact, the highest monthly influxes (meq/m²) of the same chemical constituents are never recorded here. Thus, when comparing the degree of pollution from airborned acidifying compounds at different sites, the ranking might deviate significantly depending on if concentrations or fluxes are used. This may further be illustrated by comparing the annual weighted concentration at 35 monitored long-term monitored weather-stations in Norway during 1991. Some areas sited at the very north of Norway, have very high concentrations of SO_4* in wet-deposition (Figure 5.27), like the weather-station at Karpdalen with an annual average concentration of SO_4* in 1991 of 57 µeq/L. It was only the weather station at Soegne (Søgne), situated at the very south of Norway, which had a higher annual average concentration of SO_4* this year (59 µeq/L). The annual average concentration of SO_4* in wet-deposition at Birkernes, Storgama and Langtjern in 1991 was 47 µeq/L, 37 µeq/l and 38 µeq/L. Annual mean concentration of SO_4* for the 35 stations during 1991 was 29 µeq/L. On the other hand, when comparing the annual weighted fluxes in 1991 (Figure 5.28), the stations sited nearby the city of Bergen, at the western coast of Norway, received the highest annual inputs of SO_4* in 1991. Highest annual influx of SO_4* in wet-deposition in 1991 was recorded at Vikedal by 81 meq/m², while the mean influx of SO_4* for the 35 stations in 1991 was 29 meq/m². The annual influxes of SO_4* at Birkenes, Storgama and Kaarvatn in 1991 were 58 meq/m², 30 meq/m² and 19 meq/m², respectively.

Because a separate evaluating of either concentrations (C) or fluxes (F) tends to give an incomplete ranking of the effect one pollutant like sulphuric acid may have on the runoff-water chemistry, we have tried to combine the two, by simply multiplying them (C*F), making a concentration-flux product (CF), i.e. $CF = [C]^2 * [Waterflux]$. This is of cause a simple assumption. However, by doing so, the southern parts of Southern-Norway will be placed at the top of the list with respect to influence from acid rain (Figure 5.29). With respect to water chemistry and fish status, a such approximation seems resonable, because it is these areas which exhibit the most severe surface water acidification, a fact which can not be explained by different geology only.

By comparing the CF-products at the 35 weather-stations in 1991 (Figure 5.29), it is clear that the southern parts of Southern-Norway receive the highest "loadings" (CF-products) of SO_4*, followed by the weather-station at the western coast of Southern-Norway, south of Bergen. The highest CF-product in 1991 was recorded at Soegne (3.9), while the CF-product at Birkenes; Storgama and Langtjern were 2.7, 1.1, and 0.7. The annual mean CF-product of the 35 station in 1991 was 1.0. All weather-stations located in at Norther- Norway had CF-products of SO_4* < 1.0 in 1991. The weather-stations sited south of Bergen with CF-products of SO_4* < 1.0 are all located quite a long distance inland from the coast. The same pattern is present for other non-marine chemical compounds in wet-deposition like H^+, NO_3^-, NH_4^+ (Table 5.15).

Table 5.15 Annual mean CF-products of SO_4, H^+, NO_3^-, NH_4^+ and Cl^- for the 35 weather-station in 1991, and the correspondent annual CF-products at Birkenes, Storgama, Langtjern, and Kaarvatn during the same year. The CF-product is defined as:[Annual concentration, $\mu eq/L]^2$*[Annual precipitation]*10^{-6}.*

	SO_4*	H^+	NO_3^-	NH_4^+	Cl^-
Mean of 35 stations	1.0	0.9	0.7	0.5	9.7
Birkenes	2.7	2.7	2.1	1.6	7.7
Storgama	1.1	1.2	0.9	0.5	0.5
Langtjern	0.7	0.4	0.5	0.6	0.1
Kaarvatn	0.1	0.1	0.03	0.1	13.5

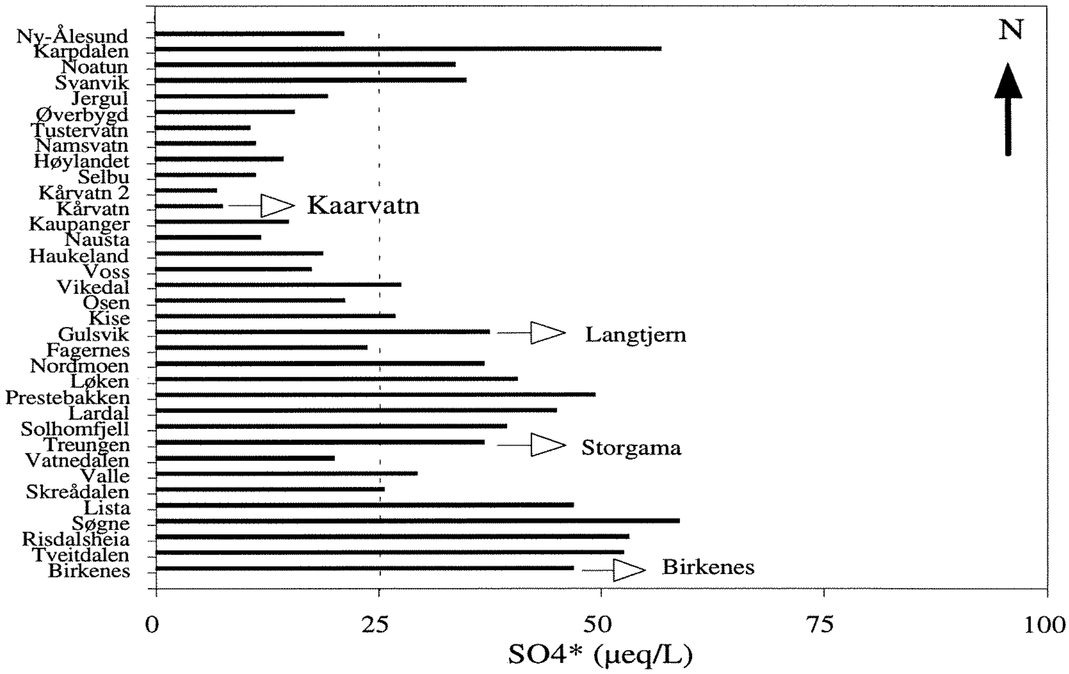


Figure 5.27 Annual weighted concentrations of non-marine sulphate (SO_4) in wet-deposition at 35 Norwegian weather-stations in 1991. The dotted line is the mean value of the 35 stations. The weather-stations are placed in the figure approximately in a south-north gradient, with the southernmost stations at the bottom, the northernmost at the top.*

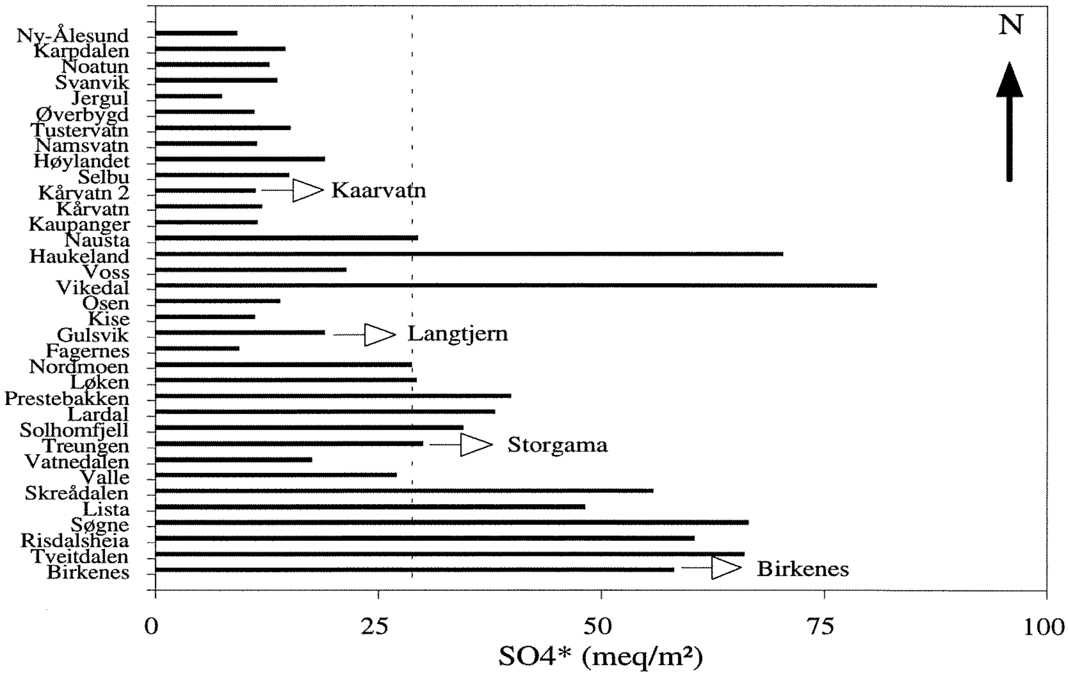


Figure 5.28 Annual weighted wet-deposition fluxes of non-marine sulphate (SO_4) at 35 Norwegian weather-stations in 1991. The dotted line is the mean value of the 35 stations. The weather-stations are placed in the figure approximately in a south-north gradient, with the southernmost stations at the bottom, the northernmost at the top.*

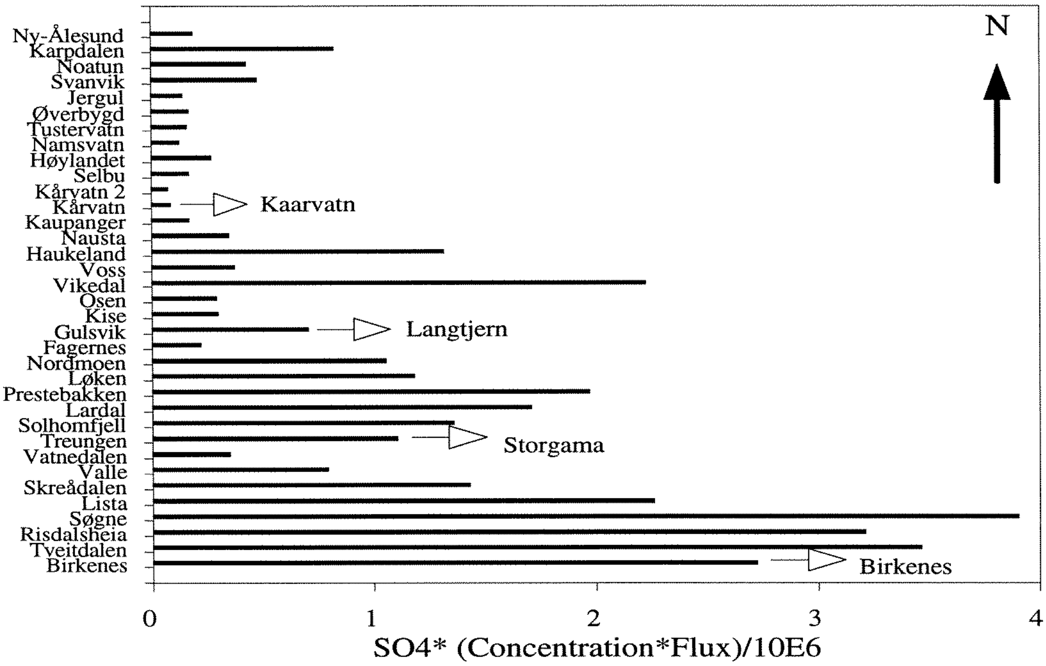
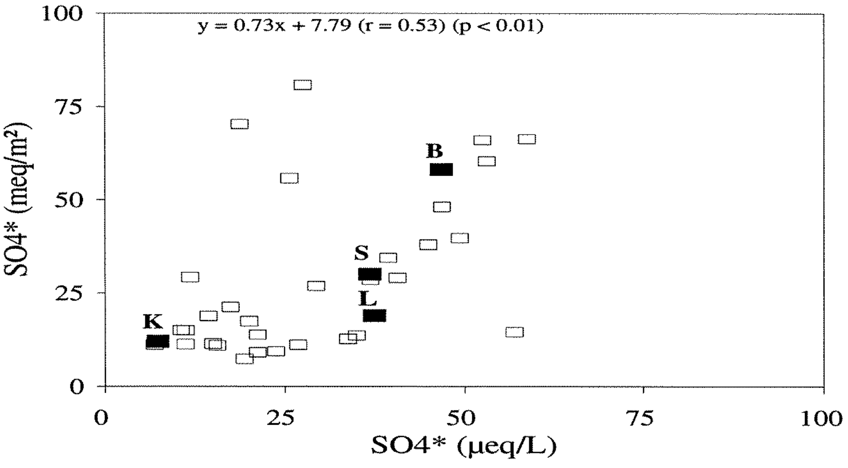
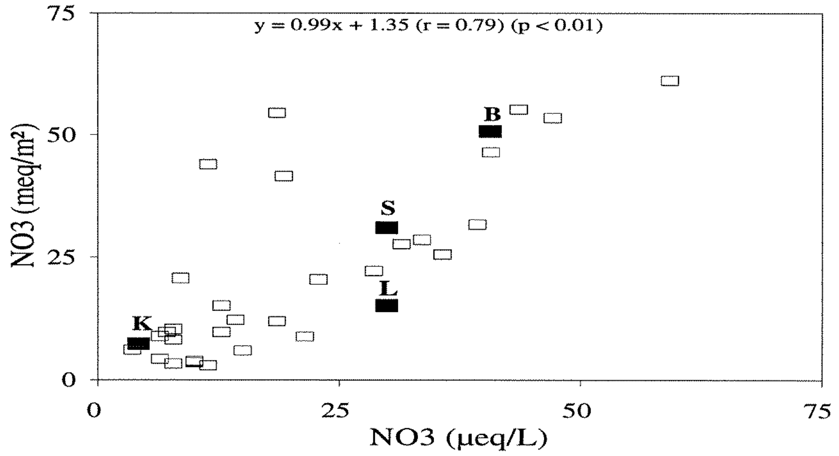


Figure 5.29 Annual weighted concentration-flux product (CF-product) of non-marine sulphate (SO_4) in wet-deposition at 35 Norwegian weather-stations in 1991. The dotted line is the mean value of the 35 stations. The weather-stations is placed in the figure approximately in a south-north gradient, with the southernmost stations at the bottom, the northernmost at the top. The CF-product is defined as: [Annual concentration, $\mu eq/L]^2$*[Annual precipitation]*10^{-6}.*

Concentration-flux relationships.

Based on annual weighted data from the 35 weather-station in Norway in 1991, there are relatively significant relationships between concentrations and fluxes of the major non-marine chemical ions of wet-deposition, NH_4^+, SO_4^{2-*} and NO_3^-(Figure 5.30), even though the concentrations as well as annual water input vary a lot, i.e. from 256 mm to 3744 mm. It is far from obvious that such linear relationships should exist, even though the majority of stations (60%) is located south of Bergen, which is the region of Norway which receives the highest loadings of atmospheric pollutants. Thus, this relationships indicates that areas receiving high inputs of water, most effectively remove chemical components from the atmosphere. It might be several reasons for this. First of all, most of NH_4^+, SO_4^{2-*} and NO_3^- which precipitates over Southern-Norway is carried over long distance from England and the sentral European continent. Thus, the highest influxes of pollutants consequently occur in the coast-near areas of Southern-Norway, which is the area of Norway which first will be exposed to the initial and therefore the most polluted atmospheric fallouts. In addition it rains more, and normally also more frequently at coast-near areas compared with more inland sites. This means that the atmosphere over coast-near areas of southern Norway is better "cleaned" from atmospheric pollutants every rain events due to a higher intensity of rain, and is "cleaned" more frequently because the annual number of precipitation days is higher. Consequently when the rain or low-pressures are going further inland , both the concentration of chemical compounds in the





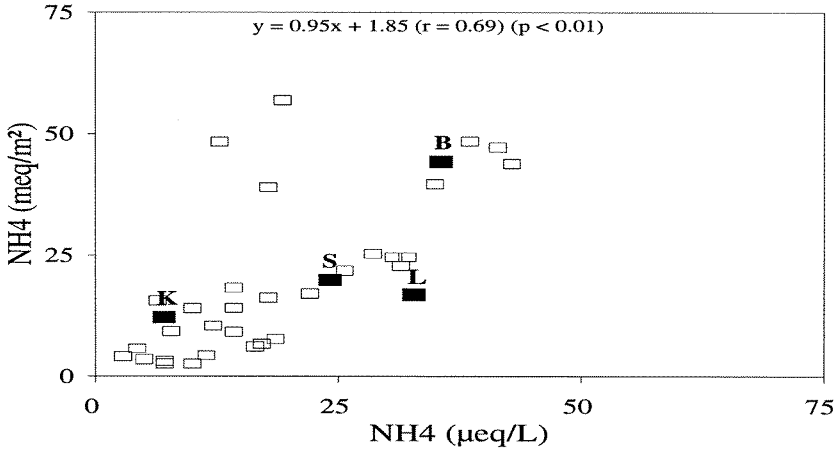


Figure 5.30 The relationships between annual weighted concentrations and fluxes of SO_4, NO_3^-, and NH_4^+ at 35 Norwegian weather-stations in 1991, based on a liniar regression analyses. The weather-stations sited at the four monitoring catchments is illustrated by filled squares and by their first letter, i.e. B = Birkenes.*

Table 5.16 The relationships between monthly inputs of water (x in mm) and the concentrations (y in µeq/L) of NH_4^+, SO_4^{2-} and NO_3^- in wet-deposition at Birkenes, Storgama and Langtjern during the monitoring period 1974-1991. The relationships are assumed to be significant when $p < 0.05$. n.s. = not significant.*

		$y = ax + b$	r	p	n
SO_4^{2-}					
	Birkenes	$y = -28.9(\log x) + 86.5$	-0.34	< 0.01	214
	Storgama	$y = -26.8(\log x) + 67.5$	-0.32	< 0.01	202
	Langtjern	$y = -34.7(\log x) + 73.2$	-0.24	< 0.05	212
NO_3^-					
	Birkenes	$y = -9.6(\log x) + 61.2$	-0.18	< 0.01	214
	Storgama	$y = -7.7(\log x) + 46.6$	-0.16	< 0.05	202
	Langtjern	$y = -21.0(\log x) + 69.7$	-0.22	< 0.01	212
NH_4^+					
	Birkenes	$y = -22.6(\log x) + 90.1$	-0.31	< 0.01	214
	Storgama	$y = -16.6(\log x) + 62.8$	-0.25	< 0.01	202
	Langtjern	$y = -34.3(\log x) + 98.1$	-0.34	< 0.01	212
Cl^-					
	Birkenes	$y = 0.13x + 41.9$	0.25	< 0.01	180
	Storgama	$y = 0.02x + 18.3$	0.05	n.s.	166
	Langtjern	$y = -8.8(\log x) + 27.0$	-0.31	< 0.01	201

atmosphere and the amount of precipitating water are decreasing. Thus, Storgama should receive lower influxes of atmospheric pollutants than Birkenes, and Langtjern even lower. However, because the concentrations of chemical compounds in the atmosphere and the amount of water both are decreasing by distance inland, the concentration of chemical compounds in wet-deposition (µeq/L) may not necessarily decrease, because the decrease in concentration may be compensated by the decrease in water input. Therefore the high concentration of pollutants recorded in wet-deposition at Langtjern, is highly related to the low inputs of water.

It is also well known that the initial phase of precipitation contains the highest concentations of ions, and the concentrations decrease as the precipitation period proceeds, until approximately distilled water is precipitating at the very end of heavy precipitation periods, especially in typically inland areas, like at Langtjern. In coast-near areas like Birkenes, heavy rains means heavy seasalt influence, which means that all ions other than those originating from seawater, decrease to approximately cero at the very end of heavy rain events. This is well illustrated in Table 5.16. As also well documented in this table, is that the smallest decreases in the concentration of SO_4^{2-}*, NO_3^- and NH_4^+ by increasing inputs of water are generally recorded at Birkenes, while the far highest decrease in concentrations by increasing inputs of water is recorded at Langtjern. This means that less water is needed to "clean" the atmosphere from chemical compounds at Langtjern compared with at Birkenes, which confirms the atmospheric pollutant gradient from Birkenes towards Langtjern.

As long as there are chemical compounds left in the wet-deposition, the influx of ions will of cause increase by increasing inputs of water. By deviding monthly inputs of water by the numbers of days with precipitation during the same months, an average intensity estimate during each precipitation day is obtained. At Birkenes, Storgama and Langtjern, the relationships between average intensity of rain (mm/m²day of precipitation) and the correspondant average influxes of SO_4* (meq/m²day of precipitation) are approximately identical at all three sites, i.e. the influx of SO_4* increase by approximately 0.5 meq/m² per 10 mm of precipitation.

Due to a certain pollution gradient from Birkenes towards Langtjern, it means that if 10 mm of rain is falling in the catchments during a day, averagely 0.61 meq/m² of SO_4* is entering the Birkenes catchment by wet-deposition, while 0.51 meq/m² and 0.49 meq/m² is entering the catchment of Storgama and Langtjern. But it is also well known that rain better than snow, removes chemical compounds from air, i.e. rain is a better "cleaning" agent than snow. By comparing the intensity of precipitation by removal of SO_4* during three typical winter months (December, January and February) when the precipitation predominantly falls as snow with three autumn months (August, September and October) when predominantly rain is falling, it is clearly demonstrated that rain better or more effectively removes chemical compounds from air (Table 5.17). The concentration of sulphur compounds in air during the winter and autumn period is about identical at each site. At Birkenes, this means that if 10 mm of precipitation is falling during the winter about 12% less SO_4* is entering the catchment compared if the same amount of water is falling during autumn. At Storgama and at Langtjern, 43% and 40% less SO_4* are removed during the winter than during autumn. The small difference between winter and autumn at Birkenes was expected, because much of the winter-precipitation normally comes as rain at this site. For the two other sites, winter-precipitation almost always comes as snow. Thus, snow seems to be about 40% less effective than rain in removal of chemical compounds from air, at least as far as sulphur-compounds are concerned. The longer and more stable winter-conditions at Storgama and Langtjern compared with Birkenes, might therefore, per se, contribute to a lower annual influxes of chemical compounds at these sites compared with at Birkenes.

Table 5.17 The relationships between average intenisty of rain (x in mm per day of precipitation) and average influxes of SO_4 (y in meq/m² per day of precipitation) at Birkenes, Storgama and Langtjern based on annual weighted averages, and weigthed averages during the winter-period (1 December - 28 February) and autumn-period (1 August - 31 October) from 1980-1991, based on linear regression analyses.*

		y = ax + b	r	p	n
Annual					
	Birkenes	y = 0.048x + 0.13	0.67	< 0.01	144
	Storgama	y = 0.050x + 0.01	0.67	< 0.01	143
	Langtjern	y = 0.047x + 0.02	0.69	< 0.01	141
Winter					
	Birkenes	y = 0.044x + 0.07	0.67	< 0.01	36
	Storgama	y = 0.026x + 0.03	0.58	< 0.01	36
	Langtjern	y = 0.031x + 0.00	0.79	< 0.01	35
Autumn					
	Birkenes	y = 0.052x + 0.06	0.70	< 0.01	36
	Storgama	y = 0.050x + 0.01	0.73	< 0.01	36
	Langtjern	y = 0.057x - 0.05	0.79	< 0.01	36

The relationship between dry- and wet-deposition.

Ice formed from water vapour high up in the atmosphere is the source of all kind of wet-deposition. Whether the precipitation comes as rain, snow, sleet or hail depends primarely on the air-temperature of the atmospheric strata through which the precipitation passes on the way to the ground. When the ice-particles are large enough, they starts falling to the ground, and the amount of chemical compounds that will dissolve depends on the quality and quantity of both water (the chemical solvent) and the chemical compounds present in the air. Thus, relationships between concentration of dry and wet-deposition compounds should be expected. Concerning the nitrogen and sulphur-compounds (Figure 5.31), the most significant correlation was found between SO_4^{2-} in wet and dry-deposition. Based on the regression line, a concentration of SO_4^{2-} in air of 1 μg S/m^3, should averagely give a concentration of SO_4^{2-} in wet-deposition of about 50 μeq/L (0.8 mg S/L). For nitrogen, the most significant correlation was found for the oxidized nitrogen compounds, i.e. between the concentration of $\Sigma HNO_3,NO_3^-$ in air and NO_3^- of wet-deposition (Figure 5.31). Based on the regression line, a concentration of $\Sigma HNO_3,NO_3^-$ in air of 1 μg N/m^3, should give an average concentration of NO_3^- in wet-deposition of about 100 μeq/L (1.4 mg N/L). A less significant correlation was found between the concentration of $\Sigma NH_3,NH_4^+$ in air and NH_4^+ in wet-deposition (Figure 5.31), but based on the regression line, a concentration of $\Sigma NH_3,NH_4^+$ in air of 1 μg N/m^3, should give an average concentration of NH_4^+ in wet-deposition of about 40 μeq/L (0.6 mg N/L). It is at least to good reasons for this: A) The much lower gradient or correlation-coefficient for the reduced nitrogen compounds, may indicate variable degree of NH_4-oxidation, which is further supported by the very high gradient between dry and wet of NO_x-compounds compared with dry and wet of $SO_4{}^{2-}$ (Figure 5.31); B) The reduced nitrogen compounds ($\Sigma NH_3,NH_4^+$) is generally less soluble compared with the oxidized nitrogen compounds ($\Sigma HNO_3,NO_3^-$). The dry-deposition/wet-deposition ratio of reduced nitrogen compounds are close to the ratio found for sulphate, which indicates that ammonium is relatively closely associated with sulphate, and that these particles or fractions are generally less water-soluble compared with the oxidized nitrogen fractions.

Origin of ions in precipitation.

Chemical compounds in precipitation (i.e. particles and gases) originate from a variety of natural sources, including oceanic spray, terrestrial dust, volcanic emmissions, and from natural microbial degradation of organic material. In addition combustion of fossil fuels, chemical industry and agricultural activities emit large amounts of gases and particles into the atmosphere. How particles and ionic materials find their way into a precipitation collector is an important enigma. The solubility of atmospheric gases, from either natural or anthropogenic origins, in atmospheric water is obvious, but the origin of such non-volatile constituents as Ca, Mg, Na, and K in precipitation is not so obvious. The dispersion of sea salts as NaCl, MgCl and $MgSO_4$, in atmospheric aerosols is one fairly well-known process (Junge, 1963; MacIntyre, 1974). Nevertheless, only a part of Ca and K in precipitation can be reasonable attributed to marine sources, and the "excess" is customarily assigned to unknown terrestrial sources. Concerning the strong acid anions, primarely sulphate and nitate, and the potential surface water acidifying cation, ammonium, a continuous discussion is going on to which extent these ions originate from anthropogenic and/or natural sources. To estimate the natural contribution of sulphate, nitrate and ammonium in wet-deposition at Birkenes,

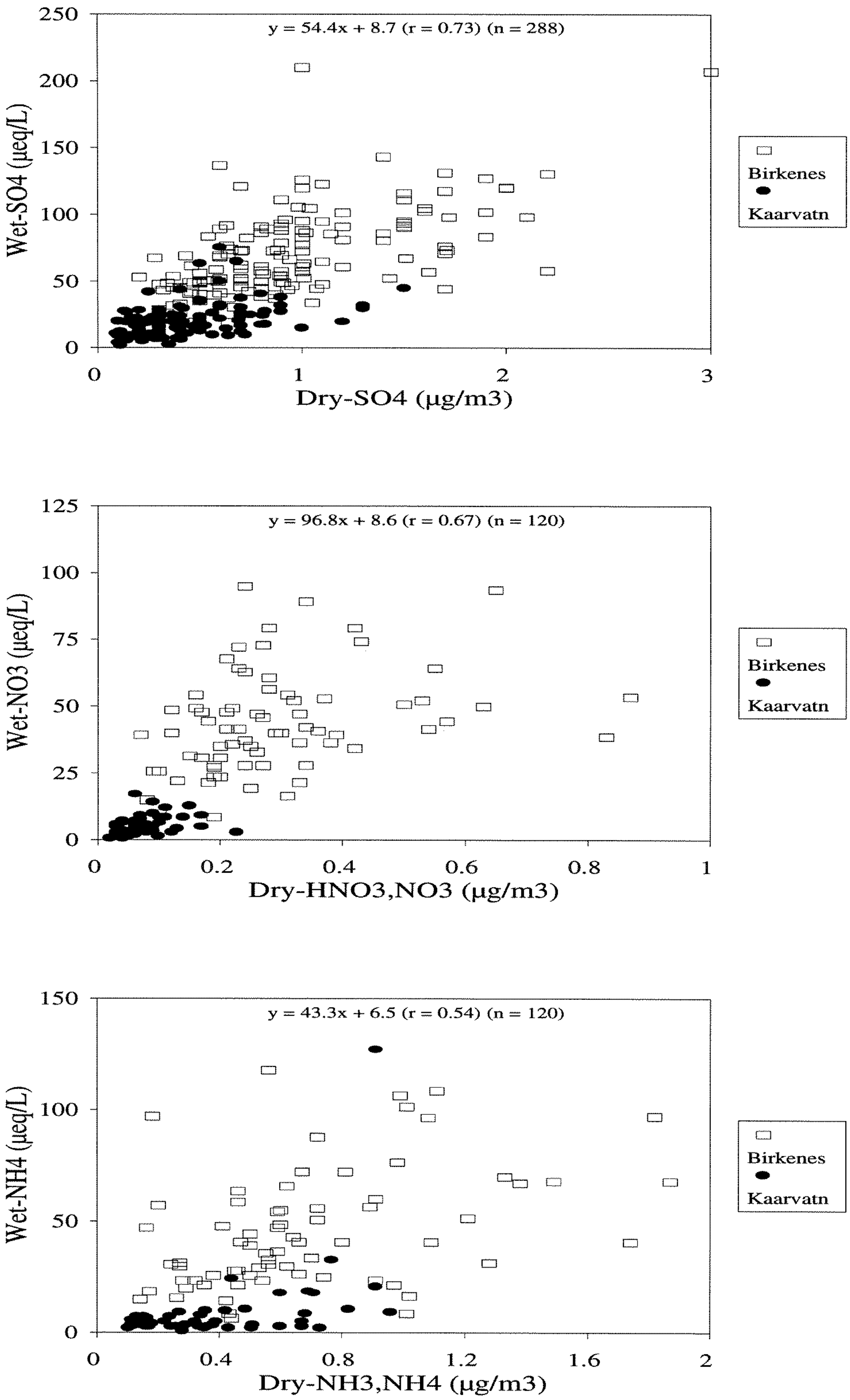


Figure 5.31 The concentration of sulphur and nitrogen compounds in air in relation to the concentration in wet-deposition. The data are monthly weighted averages from Birkenes and Kaarvatn. The SO_4 data is from 1980-1991, while nitrogen data is from 1986-1991 (at Birkenes) or 1988-1991 (at Kaarvatn).

Table 5.18 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 normalized to an annual input of water of 1000 mm/m².* *Thus, normalized concentration is $[SO_{4normalized}]$ = $[SO_{4measured}]$ * [Annual measured precipitation (mm)/1000 mm].*

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

[1] *Marine SO_4 = 0.103 * [Cl^-]*

[2] *Natural SO_4* = [SO_4 *] at Kaarvatn*

Storgama and Langtjern, the concentration of these compounds in wet-deposition at Kaarvatn is assumed to represent the natural background concentrations in Norway. By this assumption, the anthropogenic pool will probably be somewhat underestimated as long as there are good indications of anthropogenic influence also at Kaarvatn.

By this assumption, averagely 64% of SO_4^{2-} in wet-deposition at Birkenes originates from anthropogenic sources, while 27% originates from natural non-marine sources, i.e. from natural oxidation of organic and inorganic sulphide-compounds. The remaining 9% of SO_4^{2-} arises from marine sources, i.e. oceanic spray (Table 5.18). At Storgama, averagely 49% of SO_4^{2-} in wet-deposition originates from anthropogenic sources, while about 47% originates from natural non-marine sources and 4% from marine sources. At Langtjern, averagely 41% of SO_4^{2-} originates from anthropogenic sources, while 56% and 2% arise from natural non-marine and marine sources, respectively. At Kaarvatn, averagely 67% of SO_4^{2-} arise from natural non-marine sources of sulphur, while the remaining 33% arise from marine sources.

Concerning wet-deposition of NH_4^+ and NO_3^-, averagely 77% of NO_3^- and 70% of NH_4^+ at Birkenes originate from anthropogenic sources (Table 5.19), while the remaining 23% of NO_3^- and 30% of NH_4^+ originate from natural sources. At Storgama, 63% of NO_3^- and 47% of NH_4^+ averagely originate from anthropogenic sources, while 37% of NO_3^- and 53% of NH_4^+ arise from natural sources. At Langtjern, averagely 56% of NO_3^- and 53% of NH_4^+ originate from anthropogenic sources, while 44% of NO_3^- and 47% of NH_4^+ arise from natural sources.

Anthropogenic NH_4^+ primarily arises from agricultural manuring, while anthropogenic NO_3^- primarily is an oxidation-product from combustion of oil and gasoline. Naturally, the major source of NH_4^+ is from microbial degradation of organic matter, while NO_3^- primarily arises from biochemical and chemical oxidation of NH_4^+/NH_3, both over seas and continents, where NO_3^- is the most oxidized nitrogen form (+5).

Table 5.19 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 normalized to an annual input of water of 1000 mm/m^2*. Thus, normalized concentration is* $[NO_{3normalized}] = [NO_{3measured}] * [\text{Annual measured precipitation(mm)}/1000\ \text{mm}]$.

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

5.5 Runoff chemistry

Annual weighted concentrations

As for the wet-deposition chemistry, Birkenes contains far the highest concentration of chemical dissolved compounds in runoff water. The annual weighted mean concentration of ΣCations,Anions at Birkenes is 566 ± 36 μeq/L (Table 5.21). To obtain charge balance, the excess of cations (Table 5.21) should be balanced by a certain amount of anions which are assumed to be anions of dissolved humic acids (A^-). The concentration of A^- can be directly estimated as the difference between measured ΣCations and ΣAnions. Thus, ΣCations,Anions in runoff at Birkenes should be 586 μeq/L. This is 232 μeq/L higher than the ΣCations,Anions of wet-deposition at the same site (Table 5.2). The far higher total concentration of ions in runoff-water is the exclusion of dry-deposition, and the fact that the concentration increases in runoff water as a directly effect of evapotranspiration. The effect of evapotranspiration will be accounted when annual weighted fluxes are evaluated later in this chapter. One may estimate the dry-deposition of chloride and sulphate by assuming both anions being concervative, i.e. efflux = influx. Doing so, the annual weighted mean concentrations of chloride and sulphate in dry-deposition at Birkenes should be 41 μeq/L and 29 μeq/L, respectively. This dry-deposition concentrations (70 μeq/L) should correspondingly be accompanied by equal amounts of cations, which means that averagely 140 μeq/L should enter the Birkenes catchment as dry-deposition compounds of chlorine and sulphur. Thus, the total concentration of ions in precipitation at Birkenes (Σwet+dry) should be 494 μeq/L, which means that the difference between ΣCations,Anions in runoff and precipitation (wet+dry) at Birkenes should be 92 μeq/L. In this simple calculation, aluminium is estimated to be Al^{3+}, which means that the equivalent concentration of ions in runoff is somewhat overestimated. Estimates on average charge of aluminium will be discussed later. By charge balance calculations, 27 ± 14 μeq/L should averagely be present as organic anions (A^-) in runoff-water at Birkenes. Because the average weighted concentration of total organic carbon at Birkenes is 4.9 ± 0.9 mgC/L, the average net charge of organics should be 5.5 μeq of negative charges/mg C.

The annual weighted mean concentration of ΣCations,Anions in runoff at Storgama is 268 ± 34 μeq/L (Table 5.21). Assuming charge balance, the concentration of ΣCations,Anions should be 278 μeq/L. This is 50 μeq/L higher than ΣCations,Anions of wet-deposition (Table 5.2). By estimating dry-deposition of chlorine and sulphur as described above, the annual weighted mean concentrations of chlorine and sulphur in dry-deposition at Storgama should be 7 μeq/L and 4 μeq/L, which together with the accompanying cations should contribute by 22 μeq/L. Thus, the annual average concentration of ions in precipitation at Storgama should be 250 μeq/L. The difference between ΣCations,Anions in runoff and precipitation at Storgama should be 28 μeq/L, before evapotranspiration and average charge of aluminium are accounted for. The average concentration of organic anions is calculated to be 15 ± 8 μeq/L, which means that the average net charge of organics at Storgama is 3.7 μeq of negative charges/mg C.

Table 5.21 Annual weighted maximum, minimum and annual weighted mean values of runoff (mm/m²) and concentrations of dissolved substances (µeq/L) in runoff from the catchments during the monitoring periods.

Period		**Birkenes 1974-1991**	**Storgama 1974-1991**	**Langtjern 1974-1991**	**Kaarvatn 1979-1991**
	max	*1865*	*1620*	*1138*	*2352*
Runoff	**mean**	**1169 ± 288**	**947 ± 287**	**614 ± 186**	**1856 ± 306**
	min	*517*	*308*	*308*	*1331*
	max	*31*	*42*	*21*	*0.9*
H^+	**mean**	**24 ± 4**	**31 ± 5**	**17 ± 3**	**0.7 ± 0.1**
	min	*18*	*13*	*1*	*0.6*
	max	*56*	*22*	*28*	*2.5*
Al^{3+}	**mean**	**49 ± 3**	**18 ± 1**	**21 ± 3**	**2.1 ± 0.2**
	min	*16*	*16*	*2*	*1.9*
	max	*77*	*60*	*81*	*31*
Ca^{2+}	**mean**	**62 ± 8**	**39 ± 8**	**61 ± 9**	**29 ± 2**
	min	*48*	*30*	*47*	*26*
	max	*41*	*19*	*25*	*20*
Mg^{2+}	**mean**	**34 ± 4**	**13 ± 3**	**18 ± 3**	**17 ± 2**
	min	*29*	*10*	*14*	*14*
	max	*136*	*51*	*35*	*71*
Na^+	**mean**	**119 ± 10**	**35 ± 7**	**25 ± 4**	**58 ± 7**
	min	*106*	*25*	*20*	*49*
	max	*10*	*9*	*6*	*4*
K^+	**mean**	**6.1 ± 1.8**	**3.2 ± 1.9**	**3.4 ± 1.0**	**3.5 ± 0.2**
	min	*3.6*	*1.5*	*2.4*	*3.2*
	max	*155*	*103*	*99*	*22*
SO_4^{2-}	**mean**	**131 ± 15**	**78 ± 12**	**75 ± 12**	**20 ± 1**
	min	*104*	*64*	*55*	*17*
	max	*163*	*49*	*23*	*89*
Cl^-	**mean**	**127 ± 18**	**35 ± 6**	**19 ± 3**	**62 ± 13**
	min	*100*	*22*	*13*	*46*
	max	*15*	*17*	*3*	*2*
NO_3^-	**mean**	**9.0 ± 3.1**	**10 ± 3**	**2.0 ± 0.5**	**1.4 ± 0.2**
	min	*4.5*	*5.8*	*1.5*	*1.1*
	max	*0*	*0*	*0*	*29*
HCO_3^-	**mean**	**0**	**0**	**0**	**22 ± 4**
	min	*0*	*0*	*0*	*15*
	max	*5.5*	*5.1*	*9.1*	*1.1*
TOC	**mean**	**4.9 ± 0.4**	**4.1 ± 0.5**	**8.8 ± 0.4**	**1.0 ± 0.1**
(mg C/L)	*min*	*4.5*	*3.6*	*8.0*	*0.8*
	max	*456*	*283*	*274*	*165*
Ionic strength	**mean**	**419 ± 29**	**211 ± 27**	**215 ± 28**	**142 ± 12**
(µmol/L)	*min*	*365*	*179*	*173*	*121*
ΣCations	**mean**	**293 ± 20**	**139 ± 20**	**146 ± 16**	**109 ± 9**
ΣAnions	**mean**	**267 ± 20**	**123 ± 15**	**96 ± 14**	**105 ± 12**
ΣCat + ΣAn	**mean**	**566 ± 35**	**268 ± 34**	**242 ± 33**	**214 ± 22**
ΣCat - ΣAn	**mean**	**27 ± 14**	**15 ± 8**	**50 ± 8**	**4 ± 5**

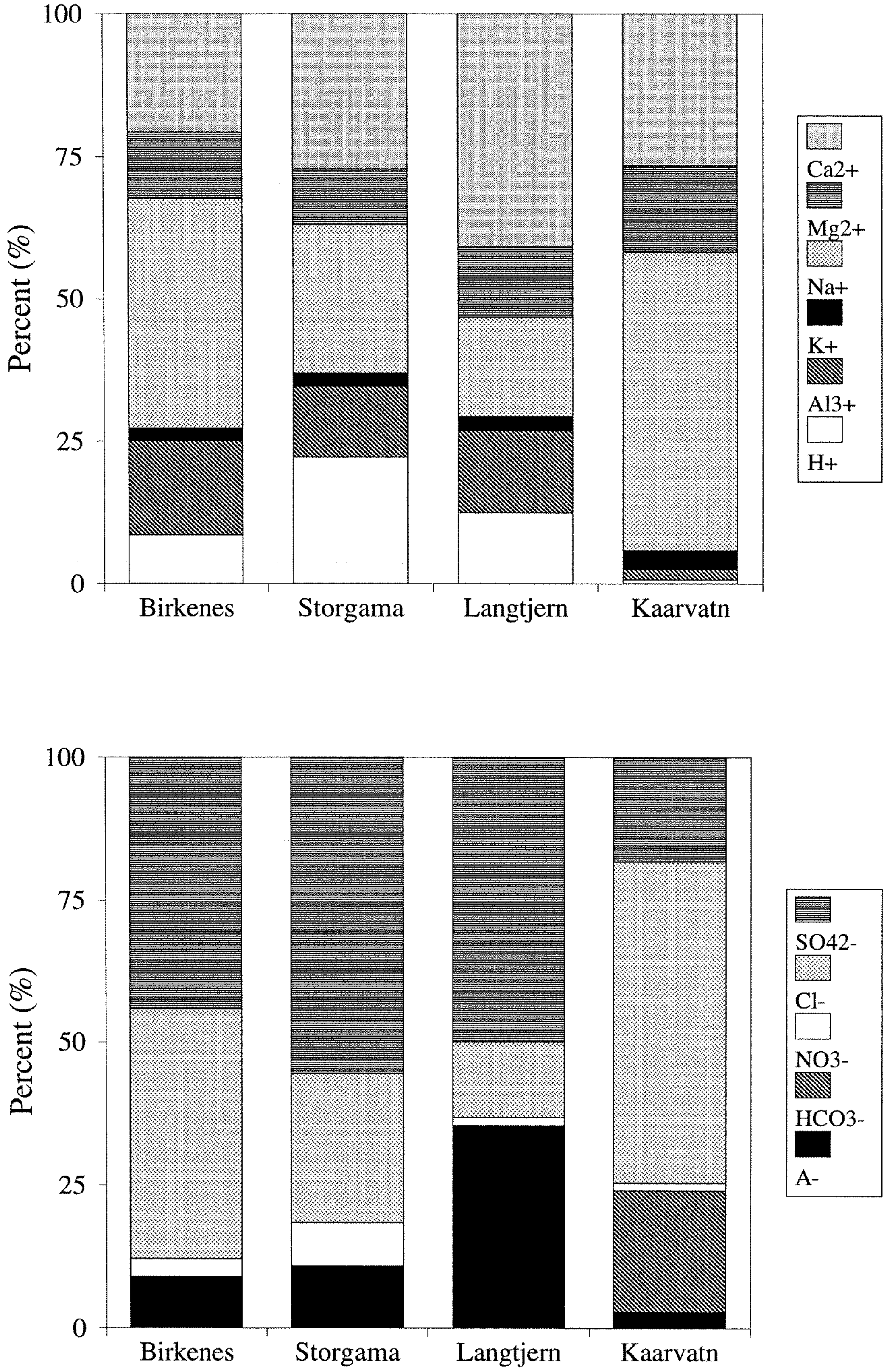


Figure 5.32 The percentage distribution of major cations and anions in runoff water from the four catchments based on annual weighted averages (µeq/L) for the monitoring periods.

Annual weighted mean concentration of ΣCations,Anions in runoff at Langtjern is 242 ± 33 μeq/L (Table 5.21). Assuming charge balance, the total concentration of ions should be 292 μeq/L. This is 78 μeq/L higher than in wet-deposition (Table 5.2). Estimating dry deposition of chloride and sulphate as described above, the annual weighted concentrations of chloride and sulphate in dry-deposition at Langtjern should be 1 μeq/L and -8 μeq/L. This means that sulphate to some extent is retained in the Langtjern catchment. By first account for the dry-deposition of chlorine (the positive value) and omitt the sulphate retention in the catchment (the neagtive value), the difference between ΣCations,Anions in runoff and precipitation is 77 μeq/L. By further account for the sulphate retention, and assume this retention to arise from reduction of sulphate into H_2S, 12 μeq/L of ions (8 μeq H^+/L and 4 μeq S^-/L) should be retained by this process. This means that without any sulphate retention within the catchment, the difference between ΣCations,Anions in runoff and precipitation at Langtjern should increase from 77 μeq/L to 89 μeq/L. This is probably a minium estimate, but this can not be confirmed since dry-deposition concentrations of sulphate can not be estimated by mass balance because total output of sulphate < total input of sulphate. As for the other sites, evapotranspiration and average charge of aluminium are not accounted for. The average concentration of organic anions at Langtjern is calculated to be 50 ± 8 μeq/L, which means an average net charge of organics of 5.7 μeq of negative charges/mg C. The higher pH in the runoff water at Langtjern compared with the runoff-water at Birkenes and Storgama, might be one of the main reasons for the higher net charge of organic anions at Langtjern. Higher pH should imply a relatively less degree of protonated organic acids, assuming an uniform chemical composition of the humic material present at the three sites.

The annual weighted mean concentration of ΣCations,Anions in runoff water from the Kaarvatn catchment is 215 ± 22 μeq/L (Table 5.21). This is only 26 μeq/L higher than in wet deposition (Table 5.2). Estimates of dry deposition as described above, can not be conducted at this site, because, as mentioned earlier, the weather-station at Kaarvatn is unrepresentative for the weather-condition in the whole catchment. By charge balance calculation of runoff water, the average concentration of organic anions is 4 ± 5 μeq/l, which means an average net charge of 4 μeq of negative charges/mg C. If the quality of the organic material is the same at all four sites, the net charge of the organic material at Kaarvatn seems far too low, because the pH in at Kaarvatn normally is > 6.0. This means that the organic acids present at Kaarvant should be far less protonated compared with the other three sites. A far a higher net charge should therefore be expected at Kaarvatn. Therefore, the humic material at Kaarvatn seems to be qualitatively different from the other three sites, which further may indicate that the quality of dissolved organic matter at the other sites may be different too. However, a far better accordance exists between net charge and pH at the three southernmost sites.

Based on annual weighted concentration averages, H^+, NH_4^+, and Na^+ are the predominant cations in wet-deposition at Birkenes. In runoff water at Birkenes, only Na^+ has strengthened its percentage contribution, while the relative contribution from H^+ is significanlty reduced, and NH_4^+ is more or less eliminated. In runoff water at Birkenes, sodium averagely constitutes 40 ± 2% of the total cationic pool, followed by Ca^{2+}, aluminium (estimated Al^{3+}) and Mg^{2+}, which constitute 21 ± 2%, 17 ± 1% and 12 ± 1%, respectively. The contribution from H^+ is only 8 ± 1%, while K^+ constitutes the remaining 2 ± 1% of the cationic pool (Figure 5.32). The H^+-concentration in runoff-water is reduced by 55 ± 9% compared with the concentration of H^+ in wet-deposition at Birkenes. While NO_3^- averagely constitutes 25 ± 3% of the anionic pool in wet-deposition at Birkenes, this ion only constitutes 3 ± 1% of the total anionic pool in runoff water (ΣAnions = $\Sigma SO_4^{2-}, Cl^-, NO_3^-$, and A^-). Because the major ionic nitrogen compounds (ammonium and nitrate) are about totally retained within the catchment, primarily due to biological uptake by vegetation and bacteria, the anionic pool is totally dominated by SO_4^{2-} and Cl^- , which both constitute 44 ± 5% of the pool. The remaining anions, 9 ± 5%, should represent organic anions (A^-), estimated from the charge balance calculations (Figure 5.32).

At Storgama, three cations predominate in the runoff water, Ca^{2+} which constitutes 27 ± 3%, and Na^+ and H^+, which contribute by 26 ± 3% and 22 ± 3%, respectively. Aluminium (Al^{3+}) and Mg^{2+} constitute 13 ± 1% and 10 ± 1% of the total cationic pool, while the remaining 2 ± 1% is K^+. As for the other three sites ammonium (and nitrate) is more or less removed from water by vegetation uptake. At Storgama the H^+-concentration in runoff-water is reduced by 38 ± 11% compared with the concentration of H^+ in wet-deposition. This reduction of protons is 30% less than the correspondant reduction at Birkenes. The SO_4^{2-} is the dominating anion in runoff water from the Storgama catchment, and constitutes 56 ± 5% of of the anionic pool, while Cl^-, A^-, and NO_3^- contribute by 26 ± 5%, 11 ± 5% and 8 ± 2%, respectively.

At Langtjern, Ca^{2+} is the dominating cation and constitutes 41 ± 2% of the cationic pool, while Na^+, Al^{3+}, Mg^{2+}, H^+, and K^+ contribute by 18 ± 1%, 14 ± 2%, 12 ± 1%, 12 ± 3% and 2 ± 0.5%, respectively. As for the other sites ammonium and nitrate are more or less retained within the catchment due to biological uptake by vegetation. At Langtjern the H^+-concentration in runoff-water is reduced by 57 ± 10% compared with the H^+-concentration in wet-deposition. This reduction is similar to that found at Birkenes. Compared with the other three sites, SO_4^{2-} undoubtedly constitutes the highest percentage contribution of inorganic anions at Langtjern. This is primarily because the Langtjern catchment is located long distance inland, and therfore low seasalt influenced (Cl^-). However, because runoff water from the Langtjern catchment is highly influenced by organic humic material (A^-), the SO_4^{2-} contributes by only 50 ± 4% to total anionic pool, while A^- contributes by 35 ± 5%. The remaining anions are Cl^- and NO_3^- ,which contribute by 13 ± 2% and 1 ± 0.2%, respectively.

As a natural consequence of the high seasalt influence at Kaarvatn, Na^+ is the dominating cation in runoff, as it also was in the precipitation. At Kaarvatn, Na^+ constitutes 52 ± 2% of the cationic pool, while while Ca^{2+} is the second most important cation with a percentage contribution of 27 ± 2%. Magnesium contributes by 15 ± 1%, while K^+ contributes by 3 ± 0.3% to the total cation pool at Kaarvatn. Ammonium and nitrogen are also more or less totally retained within the Kaarvatn catchment. Because Kaarvatn only receives small amounts of acid-precipitation, the geochemical prosesses within the catchment easily neutralize/buffer the strong acids both from precipitation and that eventually produced within the catchment. Thus, the H^+-concentration in runoff-water is reduced by 94 ± 2% compared with the H^+-concentration in precipitation. High amounts of bicarbonate ions (HCO_3^-) produced from weathering reactions are therefore not transformed into carbonic acid, but still present as HCO_3^- in runoff-water (pH > 6.0). Due to the high seasalt influence, the anionic pool is, of course, totally dominated by chloride ions, which averagely contribute by 56 ± 6%. The second most prevailing anion is bicarbonate (HCO_3^-) which constitutes 21 ± 5%, while the remaining anions contribute by 18 ± 1% (SO_4^{2-}), 3 ± 4% (A^-) and 1 ± 0.3% (NO_3^-).

As presented in Chapter 5.1, the chemistry of precipitation is more or less a solution of NaCl, NH_4NO_3 and H_2SO_4 in different proportion, primarily dependent on distance inland from sea (NaCl) and distance and position in relation to industrial and agricultural areas (NH_4NO_3 and

H_2SO_4). As the rain water percolates through the catchment, the nitrogen compounds from precipitation (NH_4^+ and NO_3^-) are about totally retained by the vegetation within the catchment. In contrast, Na^+ and Cl^- are more or less concervative ions, which means that within a certain time period (i.e. during water-year), the effluxes of these ions are about equal to their influxes. As shown in Table 5.22, the Na/Cl- ratio is somewhat higher in runoff compared with that present in precipitation (Table 5.1). This means that geochemical prosesses within the cathment feed the percolating water with some sodium. The highest relative increase in the Na/Cl-ratio of runoff-water compared with that of precipitation is observed at Langtjern, where the Na/Cl-ratio in runoff-water is a factor 1.67 higher than in precipitation (compare Table 5.1 and Table 5.22). A higher Na/Cl-ratio in runoff-water is also found at Storgama, where the ratio was a factor 1.29 higher. For the two most coastnear and precipitation-rich sites, Birkenes and Kaarvatn, no significant higher Na/Cl-ratio is present in runoff. These results demonstrates that sodium might be a relatively important product of weathering/cationexchange reactions in some catchments, in addition to the more common base cations, calcium and magnesium.

Since calcium normally is the most significant cation dissolved from geochemical weathering reactions, the largest change in the base-cation/chloride-ratios should be expected for Ca. This was also observed. At Birkenes, the annual average Ca/Cl-ratio of runoff-water was a factor 2.4 higher compared with that of precipitation, while at Kaarvatn, Storgama and Langtjern the Ca/Cl-ratios were a factor 3.4, 2.8 and 3.5 higher in runoff compared precipitation. Correspondingly, the Mg/Cl-ratios in runoff-water from Birkenes, Kaarvatn, Storgama and

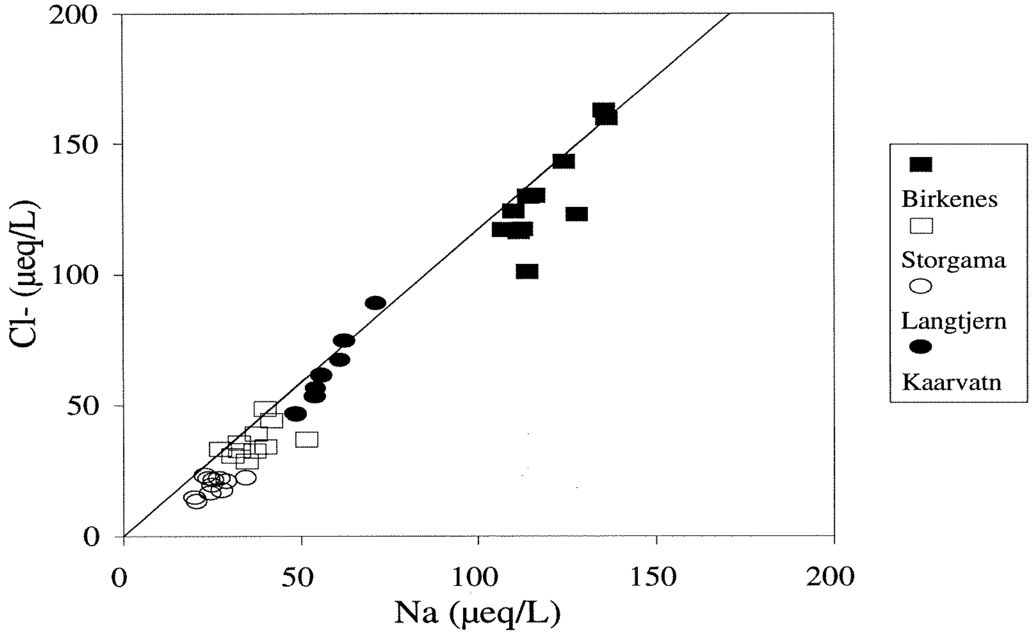


Figure 5.33 The sodium/chloride ratio in runoff at the different catchments, based on annual weighted averages during the respective monitoring periods. Continuous line represents the Na/Cl ratio of seawater.

Langtjern were a factor 1.3, 1.4, 1.7 and 2.8 higher than in precipitation. For the K/Cl ratio, it was the other way around, i.e. the ratio in precipitation was generally higher than in runoff. Because potassium normally is present in lower concentration compared with the other major base cations, this should be expected, as potassium also is an essential elements for growth of vegetation, similar to calcium and magnesium. Thus, biological uptake of base cations normally affects the K/Cl-ratio more than it effects the other base-cation/chloride ratios, where geochemical processes (Ca,Mg) and seasalt influence (Na) almost always overshadow the effect of biological uptake. The K/Cl-ratios in precipitation at Birkenes, Storgama and Langtjern were a factor 2.0, 1.4 and 2.2 higher compared with runoff. At Kaarvatn, the K/Cl ratio in precipitation was a factor 0.7 lower than in runoff, but as mentioned earlier, the weather-station at Kaarvatn is very unrepresentative for the weather condition in the whole catchment. Thus, hydrochemical relations between input and output of chemical compounds are more much more difficult to reveal.

It is the most precipitation-poor catchments, Storgama and Langtjern, which generally exhibit the largest changes in base-cation/chloride-ratios between precipitation and runoff. This possibly rely on the fact that these sites are located far from the sea, and thus receive the lowest inputs of seasalts. Thus, an equal (in equivalent) contribution of base-cations from geochemical prosesses at all four sites, consequently will give the largest changes in base-cation/chloride ratios in runoff from catchments receiving the lowest chloride loadings.

Besides the nearly total retention of the atmospheric inputs of nitrogen compounds within the catchment, the most important difference between precipitation and runoff chemistry is the fate of strong acids, primarely sulphuric acid, as long as the strong acid anion, sulphate, is present in excess. Thus, no significant net retention of sulphate occurs. Under such circumstances sulphate, as chloride, will behave like a concervative ion, i.e. output ≈ input within a relative short time period (like within a water-year). At that state, the total sulphate pool in precipitation may act as mobile anions equal to chloride. In contrast to chloride, having sodium as the predominant counterion, sulphate primarily originates from sulphuric acid in precipitation, which means that H^+-ions are the original, predominant counterion. The fate of H^+-ions within the catchment is therefor important for the chemistry of runoff. How each catchment handles the pool of H^+-ions depends not only on the concentration and/or flux of H^+ in precipitation, but also the quality and quantity of protonconsuming and protonproducing processes within the catchment as well as residence time of water. The most important proton-consuming processes are the acid-neutralization reactions, primarily the geochemical weathering/dissolution reactions of base cation containing material. This is illustrated by the following equation where $CaCO_3$ represents an acid-neutralizing geological basecation-mineral:

$$\boxed{H^+ \quad + \quad CaCO_3 \quad \rightarrow \quad Ca^{2+} \quad + \quad HCO_3^-}$$

In natural soil- or surface-water systems, these reaction are not reversible. At Kaarvatn, an about total neutralization of free protons occurs within the catchment. This catchment receives only minor amounts of acid precipitation, and only minor amounts of strong acids is assumed to be produced within the catchment. Thus, bicarbonate (HCO_3^-) will be present in runoff, which confirm the pool of H^+-ions being almost totally eliminated. Under such conditions, only minor amounts of dissolved aluminium are able to be present in runoff water, and the water is a bicarbonate-buffered system with a water-pH normally > 6.0 ($H^+ < 1$ µeq/L).

At higher strong acids loadings or if significant strong acid-producing processes are taking place within the catchment, the neutralizing capacity of the catchment will much more critical for chemistry of runoff. If neutralization of H^+-ions by basecation-reactions is too low to significantly neutralize the H^+-pool, the remainig H^+-ions will immediately protonate the bicarbonate pool from base cation dissolution, and carbonic acid is formed:

$$\boxed{H^+ \quad + \quad HCO_3^- \quad \leftrightarrow \quad H_2CO_3}$$

Under such condition, minor or no bicarbonate is present and the pH of the water is normally < 5 ($H^+ > 10$ µeq/L). This reaction is reversible, but because the amount of carbonic acid dissolved in water depends on the partialpressure of CO_2 in the surrounding air, inorganic carbon is able to leave the system as free CO_2 gas to reestablish the equilibrium. However, this process is relatively inert, which means that oversaturation of CO_2 in water often will occur in acid systems.

When all bicarbonate from weathering reactions is transformed into carbonic acid and CO_2, the water-pH is no longer controlled/buffered by the inorganic carbon, weak-acid system. At that stage pH < 5, and the chemical conditions for aluminium dissolution by weathering reactions are no present. As for dissolution of base cations, the dissolution of aluminium is also proton-consuming processes, which means that aluminium no acts as pH-buffer in the water:

$$\boxed{3H^+ \quad + \quad Al(OH)_3(H_2O)_3 \quad \leftrightarrow \quad Al(H_2O)_6^{3+}}$$

To which extent aluminium will dissolve depends very much on the concentration of strong acid (the activity of H^+), but the kinetics constraints of weathering/dissolution reactions will also play a significant role. Thus, both quality and quantity of the geological material present, as well as the residence time of water will also be highly important for the chemiistry of runoff-water. In contrast to the proton neutralizing base cation reactions, the dissolution reactions of aluminium are not proton-comsuming processes. When aluminium dissolves from solid material, H^+-ions enter into OH-groups in the coordinate-position of the aluminium molecules, but are not neutralized. Thus, if pH increases again, which often happens when water percolates further down through a soil column, solid aluminium will be formed again and H^+-ions will return into solution again. In such a case, aluminium has only transported acidity deeper down in the soil column.

In addition to weathering/dissolution reactions, ion-exchange reactions are important soil-water processes. Ion-exchange reactions are reversible reactions where ions (cations or anions) compete for a fixed number of exchange sites, and where the exchanger exhibits low to

Table 5.22 Annual weighted concentration ratios (μeq/L) of base-cation/chloride in relation to the correspondant ratios of seawater, and annual weighted concentration ratios of ***A****:* $[H^+]/[SO_4^*]$*;* ***B****:* $[\Sigma Ca^*, Mg^*, Na^*]/[SO_4^*]$*;* ***C****:* $[Al^{n+}]/[SO_4^*]$*; and* ***D****:* $[\Sigma A,B,C]/[SO_4^*]$ *in runoff-water from the four catchments. While the base-cation/chloride ratios rely on annual weighted means during the whole monitoring periods. The other ratios rely on annual weighted means from 1986/87 to 1990/91, the period during which aluminium-speciation analyses have been carried out at all sites.*

Locality	Distance from sea (km)	Ca/Cl	Mg/Cl	Na/Cl	K/Cl	A	B	C	D
Seawater		0.037	0.195	0.856	0.018				
Kaarvatn	0	0.48	0.27	0.94	0.06	0.06	2.58	0.05	2.69
Birkenes	25	0.48	0.27	0.93	0.05	0.24	0.57	0.29	1.10
Storgama	105	1.11	0.40	1.03	0.10	0.46	0.60	0.16	1.22
Langtjern	265	3.13	0.94	1.35	0.18	0.32	1.22	0.15	1.69

moderate preference for one cation/anion species compared to another (Bolt, 1979). This preference is further reduced when the temperature is low (Boyd, 1970) which means that under natural soil water temperatures (normally between 0-20°C), the preference for one cation/anion species compared with another is very low. This means that the concentration of dissolved ions is often more important than the qualitatity of ions (i.e. like their charge/size ratios). In the organic soil horizion, cation-exchange reactions will predominate (Mulder et al., 1990), because organic humic material is basically a complex, acid cation-exchange resin. Mineral soil is dominated by clay minerals which primarily act as an anion-exchange resin, where anion exchange takes part on the edge-surfaces of mineral structures. On the planar sheets of clay minerals, cation exchange reactions to some extend take part. The reversibility of cation-exchange reactions, means that H^+-ions are able to exchange for base-cations on negatively charged sites, and vice versa.

The fate of free protons on their way through a catchment is of course varying from site to site. By evaluating sulphuric acid as the only important strong acid source present in the four monitored catchments, and by also assuming the sulphate ions being concervative, i.e. efflux ≈ influx, the concentration of non-marine sulphate (SO_4^*) should indicate the quantity of H^+-ions from precipitation which are able to take part in the soil-water reactions. If SO_4^* expresses the strong acid level, the concentration of SO_4^* in runoff water should primarily be balanced with the sum of non-marine basecations, aluminium and the remaining pool of free protons ($\Sigma Ca^*, Mg^*, Na^*, Al^{n+}, H^+$). At Birkenes, but also at Storgama, the concentration of non-marine sulphate balance very well with $\Sigma Ca^*, Mg^*, Na^*, Al^{n+}, H^+$. This means that the ratio $[SO_4^*]/[\Sigma Ca^*, Mg^*, Na^*, Al^{n+}, H^+]$ is close to 1. Thus, at Birkenes and Storgama, sulphuric acid is undoubtedly the predominant acid (Figure 5.34, Table 5.22). While approximately the same $SO_4^*/\Sigma Ca^*, Mg^*, Na^*$ ratio exists at Birkenes and Storgama, the SO_4^*/Al^{n+} ratio is much higher at Birkenes compared with at Storgama (Table 5.22). It is reasonable to assume that catchment-specific differences best can explain this difference. Less and thinner soil cover, which means less reaction surfaces, larger areas with bare rock, which most likely cause shorter residence time of water at Storgama compared with at Birkenes is major catchment-specific differences. Thus, because dissolution of aluminium and probably also cation-exchange reactions with aluminium most likely are more inert processes compared

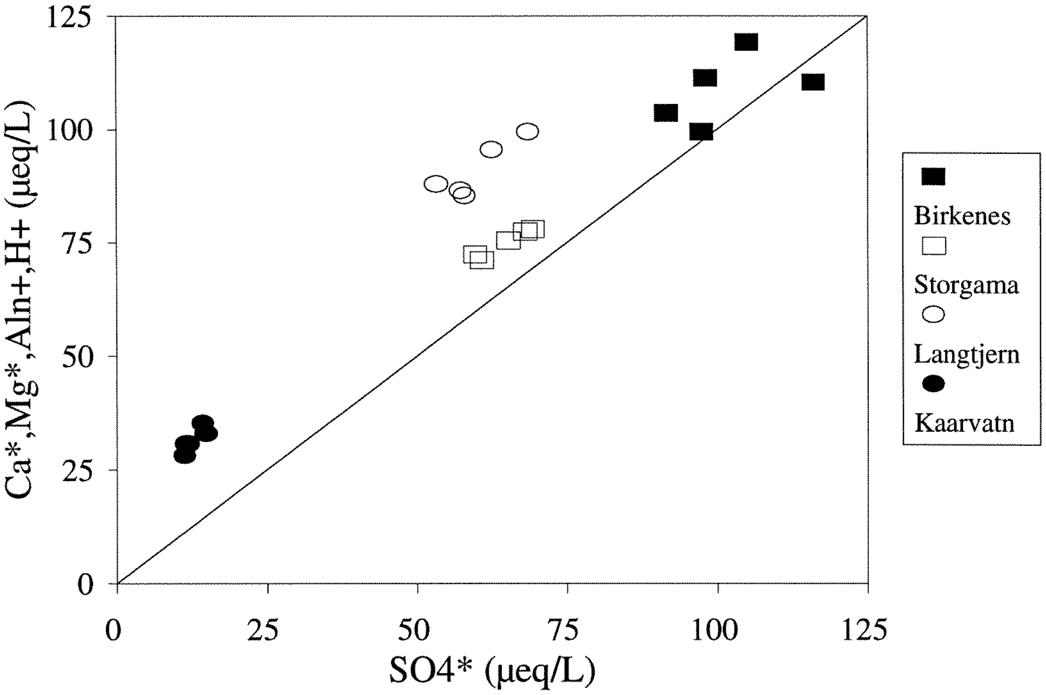


Figure 5.34 The [SO_4^*]/[$\Sigma Ca^*, Mg^*, Al^{n+}, H^+$] ratio in runoff water from the different catchments, based on annual weighted averages during the monitoring period where aluminium-speciation analyses has been performed at all sites, i.e. from 1986 to 1991. Continuous line represents the 1/1 line.

with the corresponding base cation reactions, the runoff-water from Storgama contains less aluminium and consequently more H^+-ions (lower pH) compared with the runoff-water from Birkenes.

At the two other catchments, sulphuric acid is less important for the runoff-water chemistry, at Langtjern primarily due to the high influence from humic acids, at Kaarvatn primarily due to the small amount of sulphuric acid in the system. The effects of sulphuric acid and other acids and/or acidifying processes will be discussed more firmly later.

At Birkenes, Storgama, and Kaarvatn, the annual weighted concentration means of ΣCations in runoff are not significantly different (< ± one standard deviation of mean) from the correspondant ΣAnions (Table 5.21). At Langtjern, however, ΣCations is significantly higher than ΣAnions. Not only at Langtjern, but also for the other three catchments, it is a general trend that ΣCations to some extent exceeds ΣAnions. There might be several reason for this, but the major explanation is the organic anions, which are not included in the charge balance based on measured chemical compounds (Table 5.21. The runoff-water at Birkenes and Storgama contains intermediate amounts of organic dissolved substances (4-5 mg C/L), but since the water-pH is relatively low at both sites, a lot of the negatively charged organic sites are supposed to be protonated. Thus, the influence from organic anions on the charge balance should be relatively small. At Kaarvatn, the concentration of organic dissolved compounds in

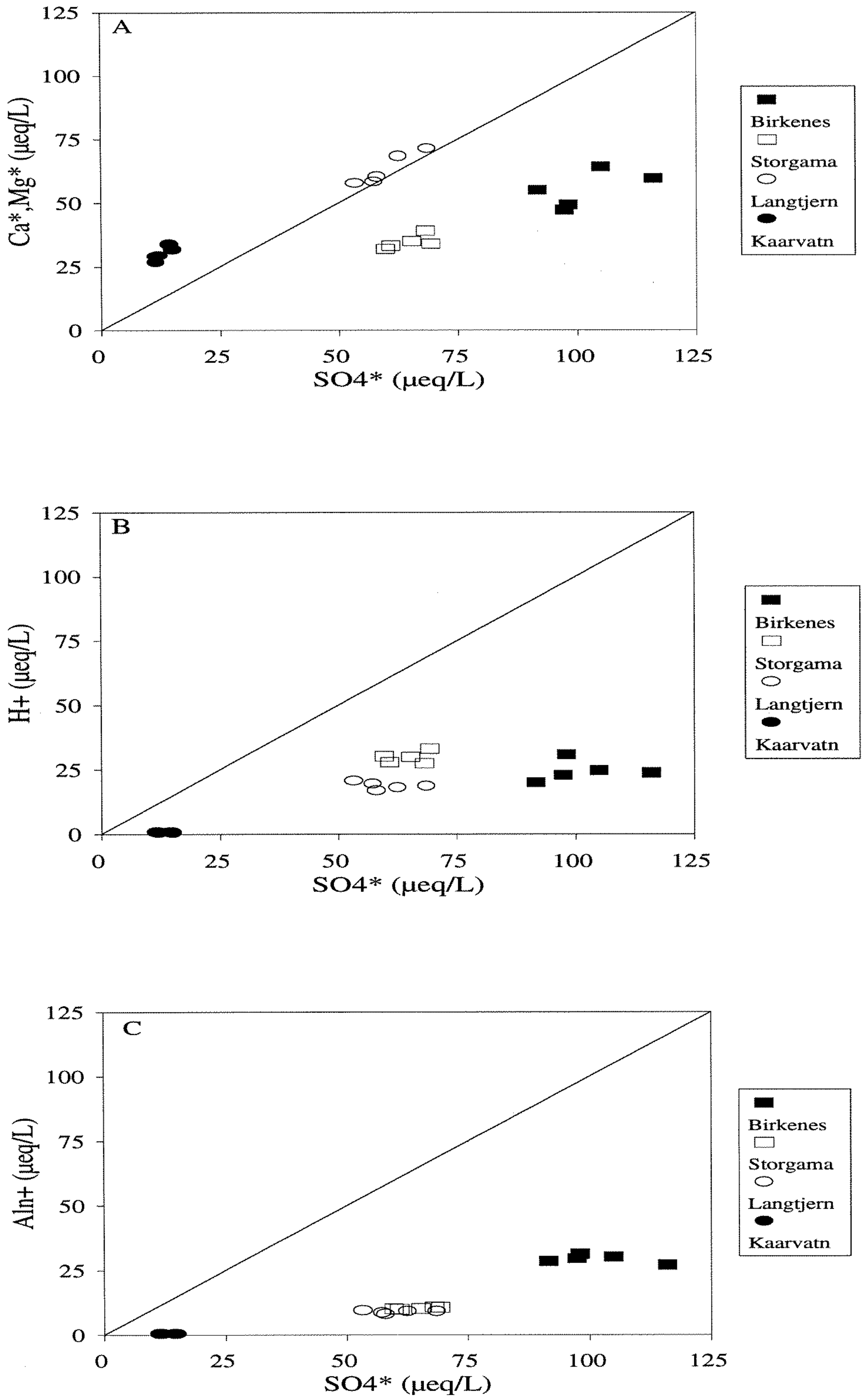


*Figure 5.35 The $[SO_4^*]/[\Sigma Ca^*,Mg^*]$ ratio (**A**), $[SO_4^*]/[H^+]$ ratio (**B**), and the$[SO_4^*]/[Al^{n+}]$ ratio (**C**) in runoff water from the different catchments, based on annual weighted averages during the monitoring period where aluminium-speciation analyses has been performed at all sites, i.e. from 1986 to 1991. Continuous line represents the 1/1 line.*

runoff-water is very low (1 mg C/L). Despite the high runoff-pH at Kaarvatn (pH normally > 6), which indicates that the organic weak-acid anions are basically unprotonated and therefore "well prepared" for cation-complexation, the concentration of organic anions seems too low to have any significant effect on the charge balance. At Langtjern, however, the concentration of organic dissolved substances is high (8.8 mg C/L). The relatively low pH in the runoff from this catchment indicates that organic anions to some extent should be protonated, but due to the large excess of cations in the charge balance, substantial amounts of the dissolved organic material are either still carrying negative charges, or the negatively charged sites are "neutralized" by cations other than protons, most likely base cations and aluminium. Exclusion of negatively charged sites of organics, will of course lead to an excess of cations in charge balance calculations. Concerning negatively charged sites which are "neutralized" by cationic metals, it is much more complicated to evaluate how this metal-organic complexes affect the charge balance. Because analysis of cations often is more or less total concentration analyses, it means that cations complexed to organic material will be incorporated. Therefore, a somewhat too high equivalent concentration of cations will be measured, since cations complexed to organic material are given their total monomeric inorganic charge, i.e. $Ca^{2+} = 2$ and and $Al^{3+} = 3$. This problem will of course increase by increasing amounts of organics present, and thereby amplify the cation-excess in humic rich runoff water.

Annual weighted effluxes

As for inputs (influxes) of chemical compounds, the outputs (effluxes) depend to a certain degree on the concentrations of ions present, but fluxes are far more dependent on the amount of water, the transporting medium, than the concentrations of ions per se. Since the highest concentrations of chemical compounds in runoff normally is present at Birkenes, and because Birkenes is the second most precipitation and runoff-rich site, the highest effluxes of chemical compounds undobtedly occurs at this site (Table 5.23). Compared with Kaarvatn, the most precipitation/runoff-rich, but least air-polluted site, the total annual average concentration of dissolved compounds in runoff at Birkenes is 2.6 times higher than at Kaarvatn, while the effluxes are only 2.0 times higher at Birkenes than at Kaarvatn.

Total annual average output of chemical compounds at Birkenes (ΣCations,Anions) is 685 ± 181 meq/m² (Table 5.23). If assuming charge balance which means that the efflux of cations = efflux of anions, the excess of cations should be balanced by anions, anions which are interpreted to represent the flux of negatively charged organic compounds, i.e. A^-. By adding organic anions to obtain an absolute charge balance, the total annual efflux of ions should be 710 meq/m² at Birkenes. This is 160 meq/m² higher than the total annual influx of chemical dissolved compounds by wet-deposition. However, by incorporating dry-deposition and assume both chloride and sulphate being concervative ions, the annual efflux of both anions should be equal to the total annual influx, i.e. Efflux - Influx by wet-deposition = Influx by dry-deposition. By also assume that all the dry-deposited sulphur leaves the catchment as sulphate by runoff, another 55 meq/m² of sulphur and 59 meq/m² of chlorine yearly enter the catchment as dry-deposited compounds. Together with an equal amount of counterions, this means that 228 meq/m² annually enters the Birkenes catchment as dry-deposited chlorine and sulphate. By neglecting NO_2-gas and assuming ammonium in dry-deposition to be the major counterion for sulphate-particles in air, the total annual influx of chemical compounds at Birkenes should be 778 meq/m². By this calculation, total annual effluxes of ions are

Table 5.23 Annual weighted maximium, minimum, and mean effluxes of water (mm/m^2) and chemical dissolved substances (meq/m^2) in runoff from the catchments during the respective monitoring periods.

Period		**Birkenes 1974-1991**	**Storgama 1974-1991**	**Langtjern 1974-1991**	**Kaarvatn 1979-1991**
	max	*1865*	*1620*	*1138*	*2352*
Runoff	**mean**	**1169 ± 288**	**947 ± 287**	**614 ± 186**	**1856 ± 306**
	min	*517*	*308*	*308*	*1331*
	max	*51*	*47*	*23*	*2.4*
H^+	**mean**	**36 ± 10**	**30 ± 9**	**12 ± 4**	**1.7 ± 0.4**
	min	*18*	*16*	*5*	*1.1*
	max	*92*	*24*	*20*	*5.5*
Al^{3+}	**mean**	**64 ± 17**	**15 ± 4**	**12 ± 4**	**4.4 ± 0.7**
	min	*34*	*8*	*6*	*3.2*
	max	*90*	*46*	*49*	*52*
Ca^{2+}	**mean**	**67 ± 15**	**32 ± 9**	**34 ± 9**	**40 ± 6**
	min	*38*	*20*	*21*	*29*
	max	*56*	*18*	*15*	*38*
Mg^{2+}	**mean**	**41 ± 10**	**12 ± 4**	**10 ± 3**	**27 ± 6**
	min	*23*	*7*	*7*	*19*
	max	*217*	*49*	*22*	*139*
Na^+	**mean**	**144 ± 36**	**30 ± 9**	**15 ± 4**	**98 ± 23**
	min	*77*	*16*	*8*	*67*
	max	*15*	*11*	*5*	*7*
K^+	**mean**	**7.6 ± 3.9**	**3.4 ± 2.6**	**2.5 ± 1.0**	**5.8 ± 1.0**
	min	*2.5*	*1.3*	*1.4*	*4.1*
	max	*229*	*99*	*64*	*39*
SO_4^{2-}	**mean**	**163 ± 43**	**69 ± 21**	**46 ± 13**	**31 ± 6**
	min	*99*	*40*	*24*	*22*
	max	*244*	*65*	*15*	*168*
Cl^-	**mean**	**155 ± 47**	**31 ± 11**	**11 ± 2**	**107 ± 31**
	min	*82*	*17*	*6*	*69*
	max	*20*	*19*	*3*	*3*
NO_3^-	**mean**	**11 ± 5**	**11 ± 5**	**2.0 ± 0.6**	**2.0 ± 0.4**
	min	*4.2*	*3.7*	*0.7*	*1.4*
	max	*0*	*0*	*0*	*35*
HCO_3^-	**mean**	**0**	**0**	**0**	**27 ± 5**
	min	*0*	*0*	*0*	*17*
	max	*9.7*	*7.3*	*9.3*	*2.2*
TOC	**mean**	**6.3 ± 1.7**	**3.9 ± 1.6**	**6.2 ± 2.1**	**2.0 ± 0.2**
(g C /m^{2}yr)	*min*	*4.2*	*2.4*	*3.7*	*1.8*
ΣCations	**mean**	**355 ± 96**	**124 ± 39**	**86 ± 26**	**175 ± 37**
ΣAnions	**mean**	**330 ± 87**	**112 ± 36**	**56 ± 17**	**165 ± 40**
ΣCat + ΣAn	**mean**	**685 ± 181**	**236 ± 74**	**143 ± 42**	**340 ± 77**
ΣCat - ΣAn	**mean**	**29 ± 19**	**11 ± 9**	**30 ± 13**	**10 ± 6**

averagely 68 meq/m² lower than the total annual influxes. This means that total annual ionic effluxes at Birkenes are averagely 9% lower than the corresponding influxes.

Total annual average output of ions at Storgama (ΣCations,Anions) is 236 ± 74 meq/m² (Table 5.23). Assuming charge balance, total annual ionic efflux should be 248 meq/m², which is 12 meq/m² lower than the corresponding annual influx of ions by wet-deposition (260 meq/m²). By incorporating dry-deposition of chloride and sulphate as decribed above, another 6 meq/m² and 7 meq/m² of chloride and sulphur averagely enter the Storgama catchment by dry-deposition during a water-year. Together with an equal amount of counterions, annually 26 meq/m² enters the catchment as dry-deposited compounds of chloride and sulphur. Ommiting NO_2-gas and assuming ammonium in dry-deposition being the major counterion for sulphate-particles in air, the total annual ionic influx should be 286 meq/m². By this calculation, the total annual effluxes of ions are averagely 38 meq/m² lower than the corresponding ionic influxes. This means that total ionic effluxes at Storgama are averagely 13% lower than the corresponding influxes.

Total annual average output of ions at Langtjern is 143 ± 42 meq/m² (Table 5.23). Assuming charge balance, total annual efflux of ions should be 172 meq/m², which is 4 meq/m² lower than the average annual ionic influx by wet-deposition (176 meq/m²). By incorporating dry-deposition of chloride as described above, annually another 2 meq/m² should enter the catchment by dry-deposition. Together with an equal amount of counterions, 4 meq/m² of chlorine-containing compounds enters the catchment as dry-deposition during a water-year. Because sulphate to some extent, is retained in the catchment, sulphate is no longer a fully concervative ion. Thus, the dry-deposition fluxes of sulphur present in Table 5.11 have to be used when total annual influxes of sulphur are estimated at this site. By adding the annual weighted dry-deposition fluxes to the corresponding wet-deposition fluxes for the three years where bot dry- and wet-deposition have been measured at Langtjern, the annual wet-deposition flux of sulphur has to be multiplied by a factor 1.19 ± 0.04 to obtain the total annual influx of sulphur to this catchment. By applying this factor on the average annual mean influx at Langtjern during the monitoring period (Table 5.3), the total annual influx of sulphur should averagely be 56 meq/m², which means that the annual average influx of sulphur by dry-deposition should be 9 meq/m². Together with an equal amount of counterions, 18 meq/m² of sulphate-containing compounds annually enters the catchment by dry-deposition. By ommitting NO_2-gas and assuming ammonium in dry-depositon being the major counterion for sulphate-particles in air, the annual average influx of ions at Langtjern is 198 meq/m². By this calculation, the total annual effluxes of ions are averagely 26 meq/m² lower than the corresponding influxes. This means that total annual ionic effluxes at Langtjern averagely are 13% lower than the corresponding influxes, identical with that also found at Storgama.

Total annual average output of ions at Kaarvatn is 340 ± 77 meq/m² (Table 5.23). Assuming charge balance, the total ionic efflux of should averagely be 350 meq/m², which means that only Birkenes exhibits a higher efflux of ions. Because the weather-station at Kaarvatn is very urepresentative for the weather condition for the catchment, both as far as the amount of rain and its chemical composition are concern, it is impossible to make any further comparison between total influxes and effluxes of ions at this site.

The generally lower annual average ionic effluxes compared with influxes, is probably even more enhanced by the fact that aluminium is assumed to be Al^{3+} in the calculation present above. By the aluminium-speciation programme (ALCHEMI Version-4.0) the average charge of aluminium was calculated to be 1.80 ± 0.02, 1.76 ± 0.03, 1.39 ± 0.03 and 0.90 ± 0.03 in the runoff water from Birkenes, Storgama, Langtjern, and Kaarvatn.

While the major annual in inputs of cations (meq/m^2) at the different catchments was H^+, NH_4^+ or Na^+, it is only Na^+ which further consolidate its position as a dominating cation in runoff water. The input of NH_4^+ is almost totally retained due to biological uptake by vegation, while H^+ is substantially reduced due to neutralization/cation-exchange reactions, which consequently implies elevation of base cation fluxes, primarily Ca^{2+} and Mg^{2+}. For the three most acidified catchments, it also implies substantial effluxes of dissolved aluminium species. As for ammonium, the effluxes of nitrate is very low at all sites due to biological uptake of nitrogen by vegetation. At Kaarvatn, chloride further consolidate its position as the dominating anion, while at Birkenes and Storgama, this is the case for both chloride and sulphate. At Langtjern, the percentage contribution of sulphate and chloride to the total anionic efflux is almost equal to their contribution in wet-deposition (chloride) or somewhat lower (sulphate). This is due to the high effluxes of negatively charged organic substances (A^-) feeded into the water from the catchment. At Langtjern (A^-) averagely constitutes 34 ± 7% of the total annual efflux of anions, while organic anions constitute < 10% of total annual anion effluxes at the other sites.

There are only minor changes in the percentage distribution of cations and anions if comparing concentrations and fluxes. However, it is a tendency in the runoff-water at all sites, that the percentage cation-contribution of protons is higher when fluxes instead of concentrations are evaluated, while the opposite tendency is present for calcium.

The effect of runoff on the ionic concentrations and fluxes

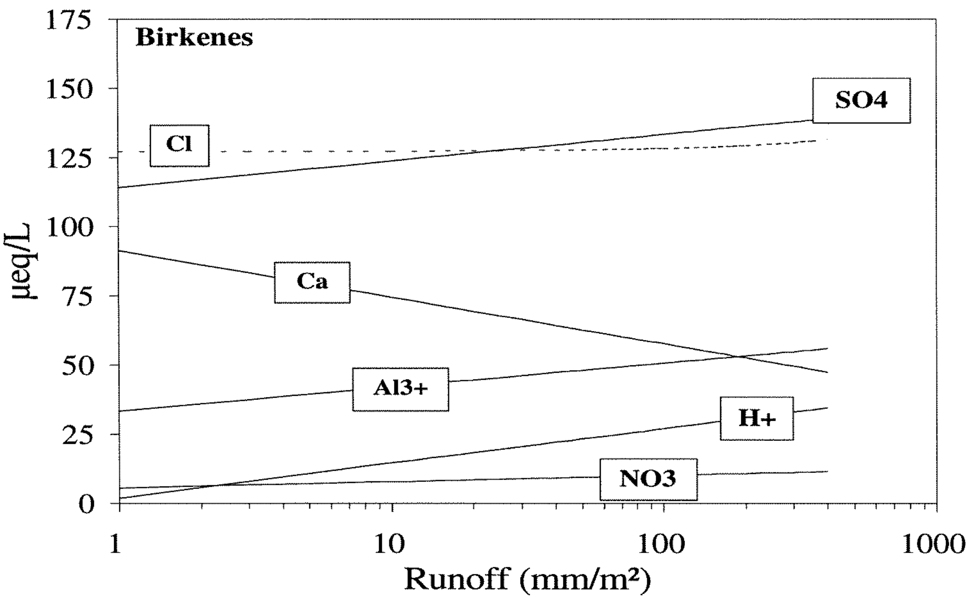
In general, the percentage concentration distribution of ions are somewhat different from the the corresponding percentage ionic flux distribution. This rely on the fact that the various ions exhibit a somewhat different concentration change with respect to changes in runoff. Simple linear regression analyses between monthly weighted runoff (mm/m^2) and monthly weighted concentrations or fluxes of ions may relatively well illustrate these effects (See Appendix A). Most ions exhibit a logaritmic concentration changes (se Appendix A) with respect to changes in runoff, and monthly weighted concentration averages express these relationships far better than if the corresponding annual weighted data are used. Only a few types of ions exhibit no significant correlation ($p < 0.05$) with runoff, and some ions exhibit a linear change in concentration by change in runoff. Concerning fluxes, yearly data are in good agreement with the corresponding monthly flux/runoff relationships (See Appendix B). A linear change in the fluxes of ions with respect to runoff seem to exist for all ions and at all sites.

Based on monthly weighted concentration averages, the major trends at all catchments are a decrease in non-marine basecations ($\Sigma Ca^*, Mg^*$) and an increase in the concentrations of H^+ (pH-decrease) by increasing runoff. As a consequence, the acid neutralizing capacity (ANC) is decreasing by increasing runoff at all sites (Table 5.24). A corresponding trend is earlier described by several scientists (e.g. Skartveit, 1980).

At Birkenes, the H^+ concentration exhibits a logaritmic increase by increasing runoff. Based on the regression analyses, the monthly weighted H^+ concentration increases by 12.6 µeq/L during a monthly increase in runoff from 10 to 100 mm/m^2, i.e. from 14.6 µeq/L (pH = 4.83) to 27.2 µeq/L (pH = 4.56). Correspondingly the concentration of ΣCa*,Mg* decreases by 18.7 µeq/L, i.e. from 80.4 µeq/L at a monthly runoff of 10 mm/m² to 61.7 µeq/L at 100 mm/m² (y = -18.7(log x) + 99.1; r = -0.56; n = 170). By the same increase in runoff, the monthly weighted concentration of Al^{3+} increases by 8.7 µeq/L. If accounts for the fact that the average charge of aluminium at Birkenes is calculated to be 1.8 ($Al^{1.8+}$), the increase in aluminium is 5.2 µeq/L. Thus, the average monthly decrease in concentration of ΣCa*,Mg*, i.e. 18.7 µeq/L, during a monthly increase in runoff from 10 to 100 mm/m², is almost totally compensated by an equivalent increase in the concentration of H^+ (12.6 µeq/L) and aluminium (5.2 µeq/L), i.e 17.8 µeq/L. For the remaining cat- and anions, it is only SO_4^{2-} (or SO_4*) and NO_3^-, which exhibit a weak, but significant relationships ($p < 0.05$) with respect to runoff (Figure 5.36). The monthly weighted concentration of SO_4^{2-} or the corresponding concentration of non-marine sulphate (SO_4*), increase by averagely 9.6 µeq/L and 9.4 µeq/L during an increase in monthly runoff from 10 to 100 mm/m². The corresponding increase in nitrate is 2.3 µeq/L. Concerning the concentration of total organic carbon (TOC), it is a significant logaritmic decrease in the concentration by averagely 1.15 mg C/L, during a monthly increase in runoff 10 to 100 mm/m².

At Birkenes it is no significant change in the total concentration of dissolved chemical compounds (ΣCations,Anions) by change i runoff. Concerning charge balance (ΣCations-Anions), it significantly decreases by averagely 10.2 µeq/L, during a monthly increase in runoff from 10 to 100 mm/m², i.e. from at cation exess of 33.6 µeq/L (at 10 mm/mm²) to 23.4 µeq/L (at 100 mm/m²). Assuming the excess of cations expressing the concentration of organic anions (A^-) in runoff, the decrease in the concentration of A^- decreases by increasing runoff is equal to the change in charge balance. Despite there is no significant change in the total concentration of ions (ΣCations,Anions) by increasing runoff, it is, however, a significant change in the chemical composition of runoff water, because it is a significant decrease in the acid neutralizing capacity (ANC) by increasing runoff. At Birkenes, the monthly weighted ANC-value decreases by approximately 33.4 µeq/L during a monthly increase in runoff from 10 to 100 mm/m² (Figure 5.38), i.e. from -21.1 µeq/L (at 10 mm/m²) to -54.5 µeq/L (at 100 mm/m²).

As at the other sites, the H^+ concentration in runoff at Storgama exhibits a logaritmic increase by increasing runoff. Based on the regression analysis, the monthly weighted concentration average of H^+ increases by 5.4 µeq/L during a monthly increase in runoff from 10 to 100 mm/m², i.e. from 26.5 µeq/L (pH = 4.58) to 31.9 µeq/L (pH = 4.50). Correspondingly, the concentration of ΣCa*,Mg* decreases, i.e. from averagely 48.8 µeq/L at a monthly runoff of 10 mm/m² to 39.4 µeq/L at 100 mm/m² (y = -9.4(log x) + 58.2; r = -0.33; n = 181). During the corresponding increase in monthly runoff, the concentration of Al^{3+} decreases (not significant) by 0.2 µeq/L, i.e, from 18.7 µeq/L to 17.5 µeq/L. Because the the average charge of aluminium is calculated to be 1.76, the decrease is from 11.0 µeq/L at a monthly runoff of 10 mm/m², to 10.3 µeq/L at a monthly runoff of 100 mm/m². For the remaining major cat- and anions, the concentrations of nitrate and potassium are both increasing by increasing runoff, while the concentration of sodium and chloride are both decreasing. During a monthly increase in runoff from 10 to 100 mm/m², the monthly weighted concentration of nitrate increases from 8.7 µeq/L to 10.2 µeq/L, while the concentration of potassium increases from 2.9 µeq/L to 3.3 µeq/L. Concerning the concentration of sodium and chloride, it is a decrease by increasing runoff, i.e. for sodium from a monthly average of 38.9 µeq/L (at 10 mm/m²) to 31.9 µeq/L (at 100 mm/m²), and for chloride from 36.6 µeq/L to 34.2 µeq/L (Figure 5.36).



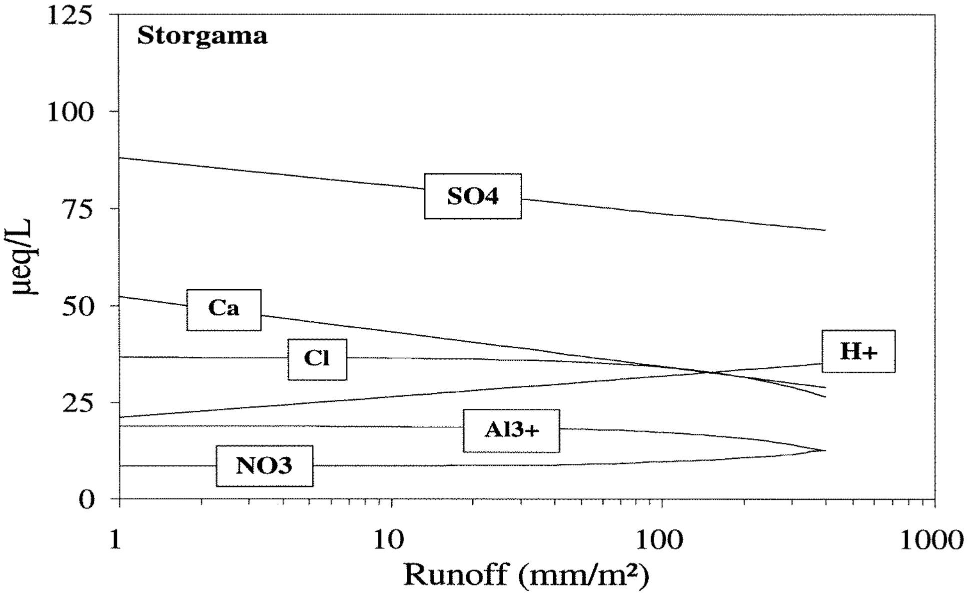
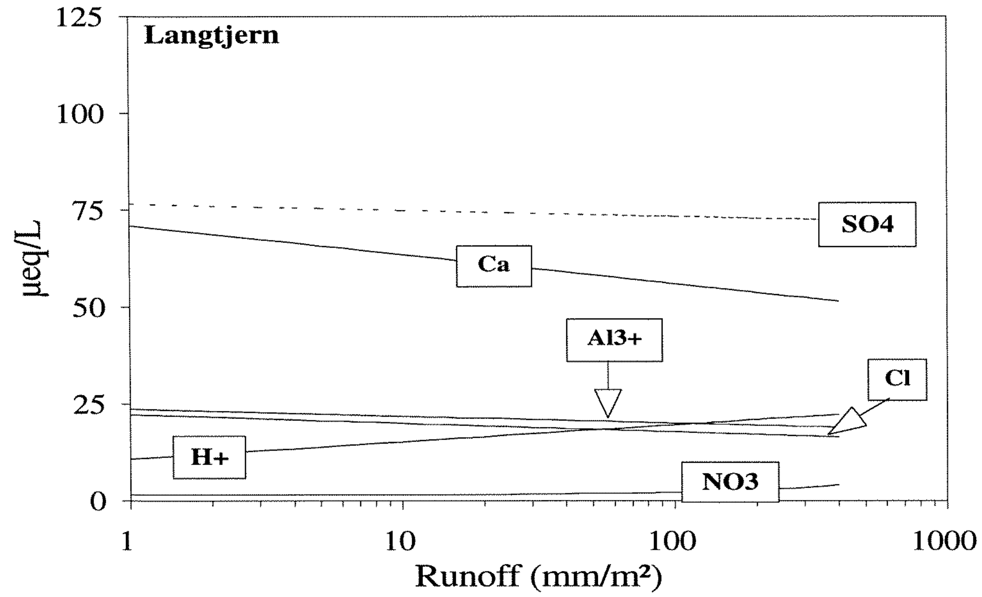


Figure 5.36 The relationships between monthly runoff (mm/m²) and monthly weighted concentrations of major chemical, dissolved species in runoff (µeq/L) at Birkenes and Storgama during the monitoring period. The relationships rely on linear regression analyses. The regression lines are ***Birkenes****: $[H^+]$: $y = 12.6(\log x) + 2.0$; $[Al^{3+}]$: $y = 8.7(\log x) + 33.4$; $[Ca^{2+}]$: $y = -16.9(\log x) + 91.4$; ; $[Cl^-]$: $y = 0.011x + 127.2$; $[NO_3^-]$: $y = 2.3(\log x) + 5.6$; $[SO_4^{2-}]$: $y = 9.6(\log x) + 114.1$.* ***Storgama****: $[H^+]$: $y = 5.4(\log x) + 21.1$; $[Al^{3+}]$: $y = -0.016x + 18.9$; $[Ca^{2+}]$: $y = -8.9(\log x) + 52.2$; $[Cl^-]$: $y = -0.026x + 36.8$; $[NO_3^-]$: $y = 0.016x + 8.6$; $[SO_4^{2-}]$: $y = -7.1(\log x) + 88.0$. Continuous line indicates a significant relationship ($p < 0.05$), while a dotted line indicates no significance, i.e. $p > 0.05$. More details from the regression analyses are present in Appendix A.*



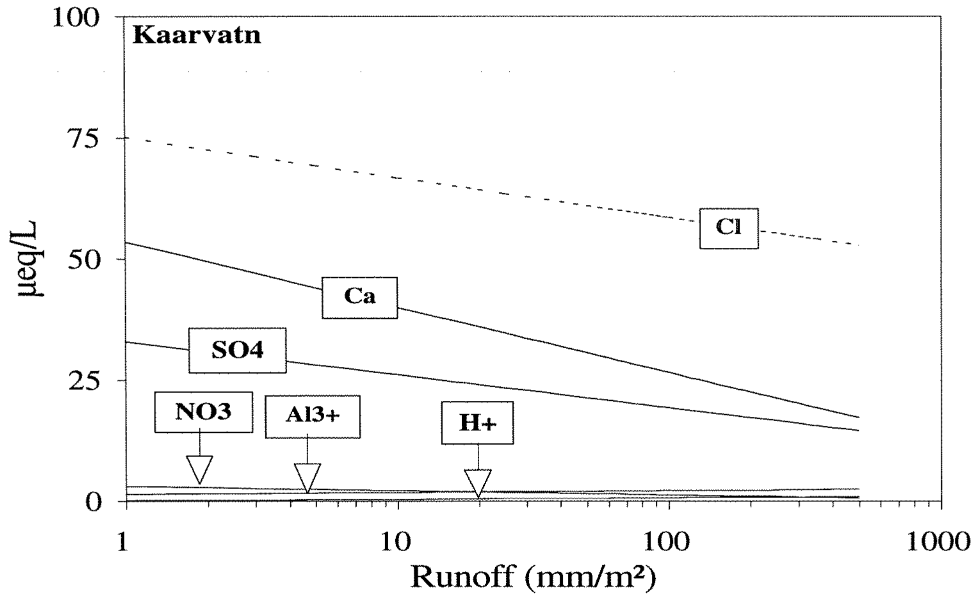


*Figure 5.37 The relationships between monthly runoff (mm/m²) and monthly weighted concentrations of major chemical, dissolved species in runoff (µeq/L) at Langtjern and Kaarvatn during the monitoring period. The relationships rely on linear regression analyses. The regression lines are **Langtjern**: $[H^+]$: $y = 4.4(\log x) + 10.7$; $[Al^{3+}]$: $y = -1.8(\log x) + 23.6$; $[Ca^{2+}]$: $y = -7.5(\log x) + 71.0$; $[Cl^-]$: $y = -2.2(\log x) + 22.3$; $[NO_3^-]$: $y = 0.006x + 1.6$; $[SO_4^{2-}]$: $y = -1.6(\log x) + 76.6$. **Kaarvatn** $[H^+]$: $y = 0.32(\log x) + 0.10$; $[Al^{3+}]$: $y = 0.37(\log x) + 1.4$; $[Ca^{2+}]$: $y = -13.4(\log x) + 53.5$; $[Cl^-]$: $y = -8.2(\log x) + 75.0$; $[NO_3^-]$: $y = -0.85(\log x) + 3.0$; $[SO_4^{2-}]$: $y = -6.8(\log x) + 32.9$. Continuous line indicates a significant relationship ($p < 0.05$), while a dotted line indicates no significance, i.e. $p > 0.05$. More details from the regression analyses are present in Appendix A.*

Table 5.24 The degree of concentration changes (positive/negative correlation) with respect to amount of runoff, based on monthly weighted averages. The table is based on the linear regressions presented in Appendix A.

Ion	**Correlation**							
H^+	positive	Birkenes	>>	Storgama	>>	Langtjern	>>	Kaarvatn
Ca^{2+}	negative	Birkenes	>	Kaarvatn	>>	Storgama	>	Langtjern
Mg^{2+}	negative	Kaarvatn	>>	Langtjern	>	Birkenes*	>	Storgama
$\Sigma Ca^*, Mg^*$	negative	Birkenes	>	Kaarvatn	>>	Storgama	>	Langtjern
Na^+	negative	Kaarvatn	>>	Storgama	>>	Langtjern	>>	Birkenes*
K^+	positive	Langtjern	>	Storgama				
K^+	negative	Kaarvatn	>>	Birkenes*				
Al^{3+}	negative	Langtjern	>	Storgama				
Al^{3+}	positive	Birkenes	>>	Kaarvatn				
Cl^-	negative	Kaarvatn*	>>	Langtjern	>>	Storgama		
Cl^-	positive	Birkenes*						
NO_3^-	positive	Birkenes	>>	Storgama	>>	Langtjern		
NO_3^-	negative	Kaarvatn						
SO_4^{2-}	negative	Storgama	=	Kaarvatn	>>	Langtjern*		
SO_4^{2-}	positive	Birkenes						
SO_4^*	negative	Storgama	=	Kaarvatn	>>	Langtjern*		
SO_4^*	positive	Birkenes						
HCO_3^-	negative	Kaarvatn						
TOC	positive	Storgama*	>>	Kaarvatn*				
TOC	negative	Birkenes	>>	Langtjern*				
ANC	negative	Birkenes	>>	Kaarvatn	>>	Storgama	>	Langtjern

= : Difference < 5% compared with the foregoing site.
> : Difference > 5% compared with the foregoing site.
>> : Difference > 25% compared with the foregoing site.
* : not statistical significant, i.e. $p > 0.05$.

Totally, it is a weak but significant logaritmic decrease in the monthly weighted concentration of ions (ΣCations,Anions) at Storgama, i.e. from 271 μeq/L to 249 μeq/L during a monthly runoff increase from 10 to 100 mm/m². Accordingly, it is an almost significant logaritmic decrease in the charge balance, which means that the difference between cations and anions decreases from 17.7 μeq/L down to 13.7 μeq/L during the corresponding monthly increase in runoff. As at the other sites, the ANC is decreasing at Storgama by increasing runoff, i.e. from -26.6 μeq/L to -34.7 μeq/L during a monthly increase in discharge from 10 to 100 mm/m² (Figure 5.38). Concerning the concentration of total organic carbon (TOC), there is a weak but not significant increase in the concentration by increasing volume of discharge.

Also at Langtjern, the H^+-concentration increases by increasing runoff, i.e. from amonthly weighted averages of 15.1 µeq/L (pH = 4.82) at a monthly runoff of 10 mm/m² to 19.6 µeq/L (pH = 4.71) at 100 mm/m² (Figure 5.37). During a corresponding runoff increase, the concentration of $\Sigma Ca^*, Mg^*$ is decreasing from 77.7 µeq/L to 69.0 µeq/L ($y = -8.7(\log x) + 86.4$; $r = -0.32$, $n=187$). As at Storgama, the concentration of aluminium is generally decreasing by increasing runoff at Langtjern. Based on calculated average charge of aluminium, the decrease is from 10.1 µeq/L to 8.3 µeq/L during a monthly increase in runoff from 10 to 100 mm/m². In contrast to the other three catchments, there is no significant change in the concentration of sulphate by change in runoff at Langtjern, even though it is a weak tendency of decreasing concentration. For the remaining chemical dissolved species, it is only the concentration of total organic carbon (TOC), which exhibits no significant correlation with runoff. Both the concentration of sodium and chloride are decreasing by increasing runoff. Based on the regression analyses, the monthly weighted concentration of sodium decreases from 26.2 µeq/L at a monthly runoff of 10 mm/m² to 24.1 µeq/L at 100 mm/m². Correspondingly, the concentration of chloride decreases from 20.1 µeq/L to 17.8 µeq/L. As at Storgama, it is a linear increase in the concentration of both potassium and nitrate by increasing runoff at Langtjern. For potassium, the monthly weighted concentration increases from 3.1 µeq/L to 3.7 µeq/L during a monthly runoff increase from 10 to 100 mm/m², while the concentration of nitrate correspondingly increases from 1.6 µeq/L to 2.2 µeq/L. Both the total concentration of ions (ΣCations+Anions) and the charge balance (ΣCations-Anions) are decreasing by increasing runoff. Based on the regression analyses, the monthly weighted concentration of ΣCations+Anions is decreases from 244 µeq/L at a monthly runoff of 10 mm/m² to 231 µeq/L at 100 mm/m², while the ΣCations-Anions correspondingly decreases from 51.7 µeq/L to 46.8 µeq/L. The far higher cation-excess at Langtjern compared with the other sites, relies on the high concentration of humic material present in the runoff water at Langtjern. This cation excess is assumed to directly express the amount of negatively charged sites present on organic material in runoff. Also at Langtjern, it is a decrease in the monthly weighted ANC-value by increasing runoff, i.e. from 14.7 µeq/L at a monthly runoff of 10 mm/m² to 7.0 µeq/L at 100 mm/m²mth. The positive ANC-value normally present at Langtjern, despite the low pH and the relatively high concentration of aluminium, is because of the high concentration of humic material present.

At Kaarvatn the H^+ concentration also increases by increasing runoff, from a monthly average of 0.94 µeq/L (pH = 6.03) at a monthly runoff of 10 mm/m² to 1.26 µeq/L (pH = 5.90) at 100 mm/m² (Figure 5.37). Correspondingly, the concentration of HCO_3^- is decreasing, i.e. from 36.5 µeq/L (at 10 mm/m²) to 20.4 µeq/L (at 100 mm/m²). Accordingly, the concentration of $\Sigma Ca^*, Mg^*$ decreases from a monthly weighted average of 43.9 µeq/L to 28.6 µeq/L ($y = -15.3(\log x) + 59.2$; $r = 0.81$; $n = 132$). As at Birkenes, the monthly weighted concentration of aluminium is increasing by increasing runoff, from 1.8 µeq/L at a monthly runoff of 10 mm/mm² to 2.1 µeq/L at 100 mm/m². By account for the average charge of aluminium, the increase is from 0.54 µeq/L to 0.63 µeq/L. The concentration of aluminium in runoff at Kaarvatn is, however, very low compared with that present at Birkenes. For all other major dissolved constituents in runoff water at Kaarvatn, except for chloride and TOC, a significant decrease is observed by increasing amount of runoff. Based on the regression analyses, the monthly weighted concentration of nitrate decreases from 2.2 µeq/L at monthly runoff of 10 mm/m² to 1.30 µeq/L at 100 mm/m², while the concentration of sulphate correspondingly decreases from 26.1 µeq/L to 19.3 µeq/L. Accordingly, the concentration of sodium and potassium decrease from 64.3 µeq/L and 4.1 µeq/L at a monthly runoff of 10 mm/m² to 54.4

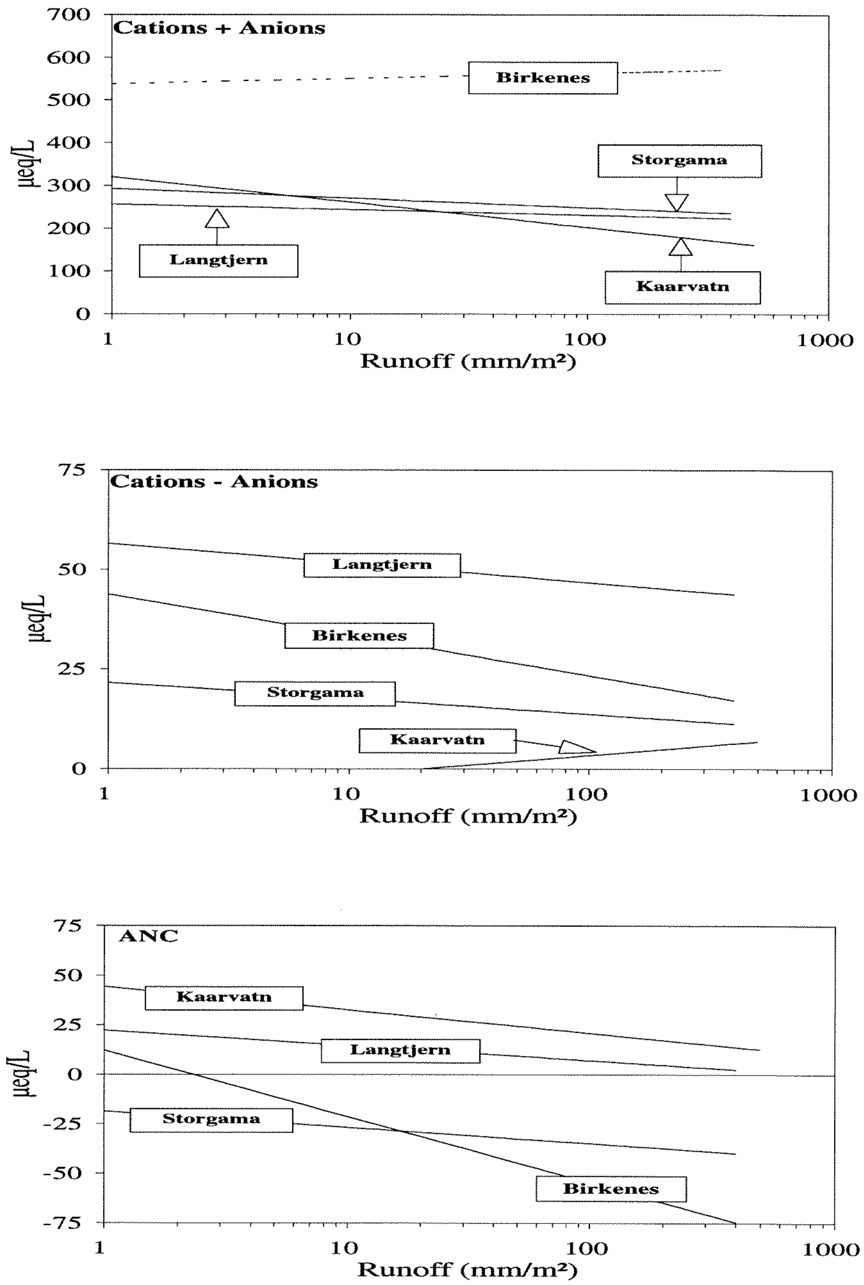
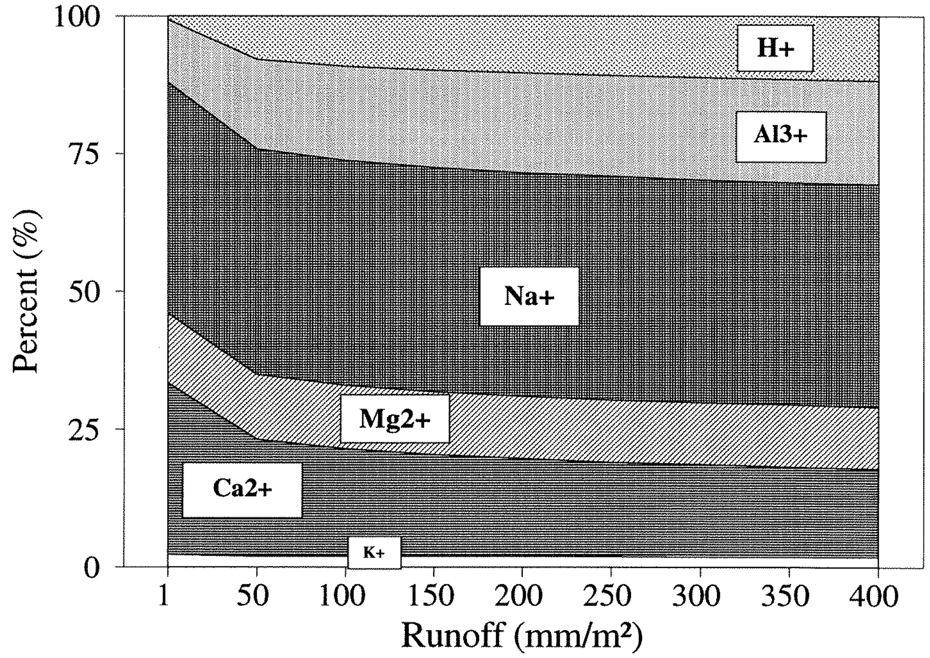


Figure 5.38 The relationships between monthly inputs of water (mm) and monthly weighted concentrations of ΣCations,Anions, ΣCations-Anions and ANC (µeq/L) in runoff-water from the four cachments during the respective monitoring periods. ***Birkenes*** *(n=158): ΣCations+Anions = 12.8(log x) + 537 (r = 0.09); ΣCations-Anions = -10.2(log x) + 43.8 (r = -0.27); ANC = -33.4(log x) +12.3 (r = -0.67).* ***Storgama*** *(n=182): ΣCations+Anions = -22.2(log x) + 293 (r = -0.18); ΣCations-Anions = -4.0(log x) + 21.7 (r = -0.14); ANC = -8.1(log x) -18.5 (r = -0.32).* ***Langtjern*** *(n=186): ΣCations+Anions = -13.0(log x) + 257 (r = -0.17); ΣCations-Anions = -4.9(log x) + 56.6 (r = -0.22); ANC = -7.7(log x) + 22.4 (r = -0.34).* ***Kaarvatn*** *(n=132): ΣCations+Anions = -59.1(log x) + 321 (r = -0.44); ΣCations-Anions = 4.9(log x) -6.5 (r = 0.32); ANC = -11.8(log x) + 44.6 (r = -0.62). Continuous line indicates a significant relationship ($p < 0.05$), while a dotted line indicates no significance, i.e. $p > 0.05$.*



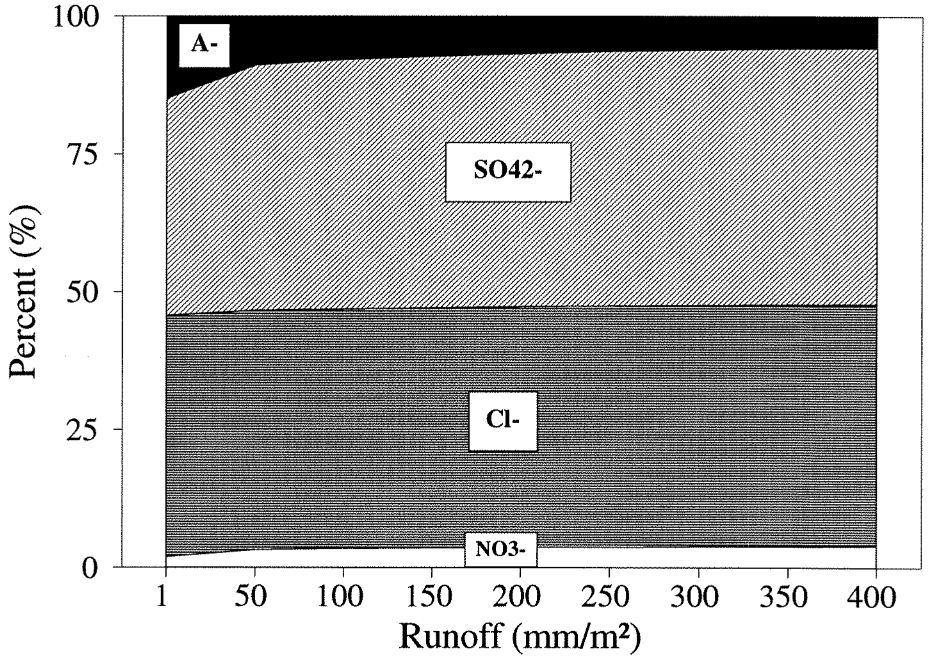


Figure 5.39 The percentage change in the distribution of inorganic cations and anions with respect to change in runoff at Birkenes, based on monthly weighted average values. The changes are based on the regression lines presented in Appendix A.

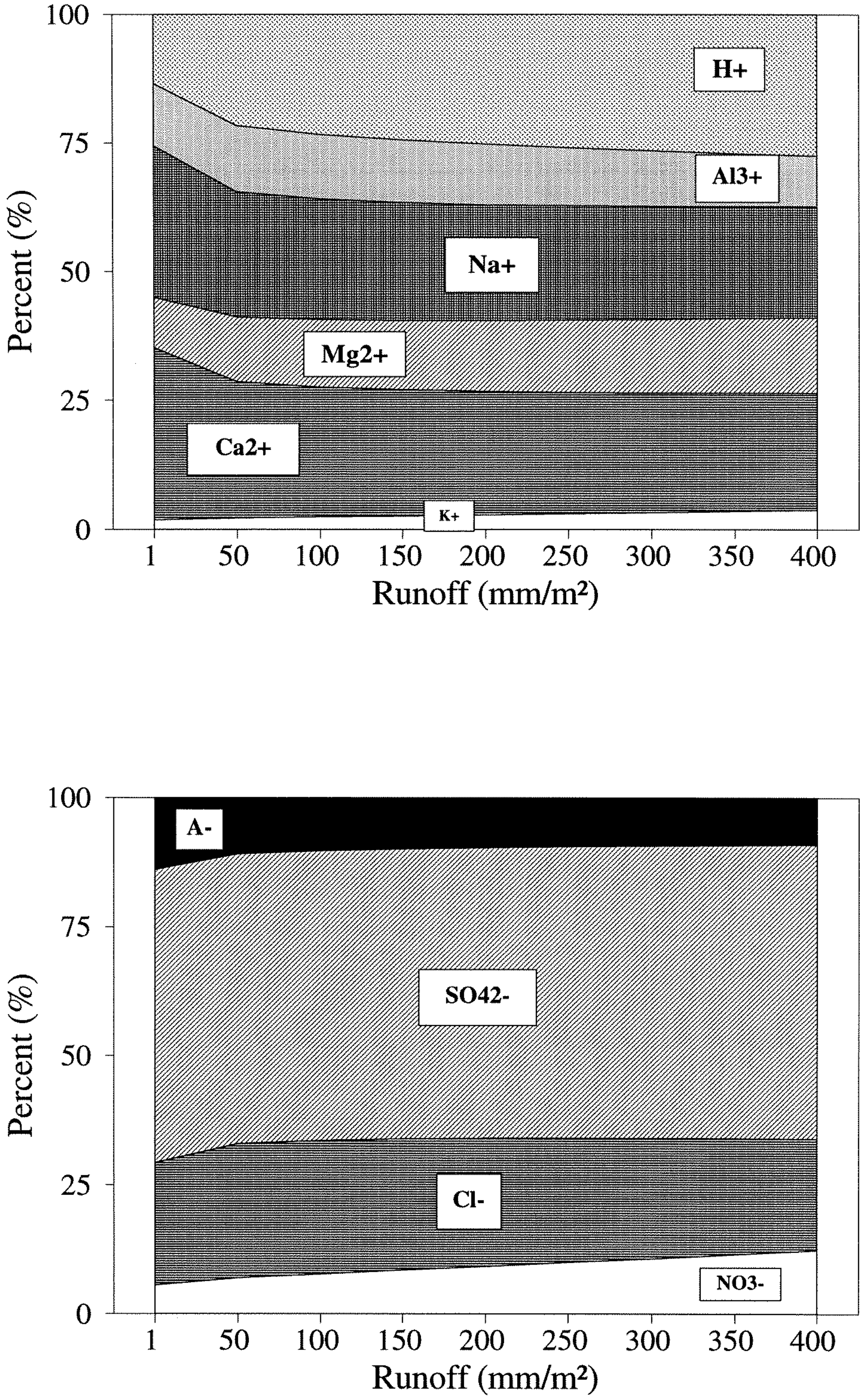


Figure 5.40 The percentage change in the distribution of inorganic cations and anions with respect to change in runoff at Storgama, based on monthly weighted average values. The changes are based on the regression lines presented in Appendix A.

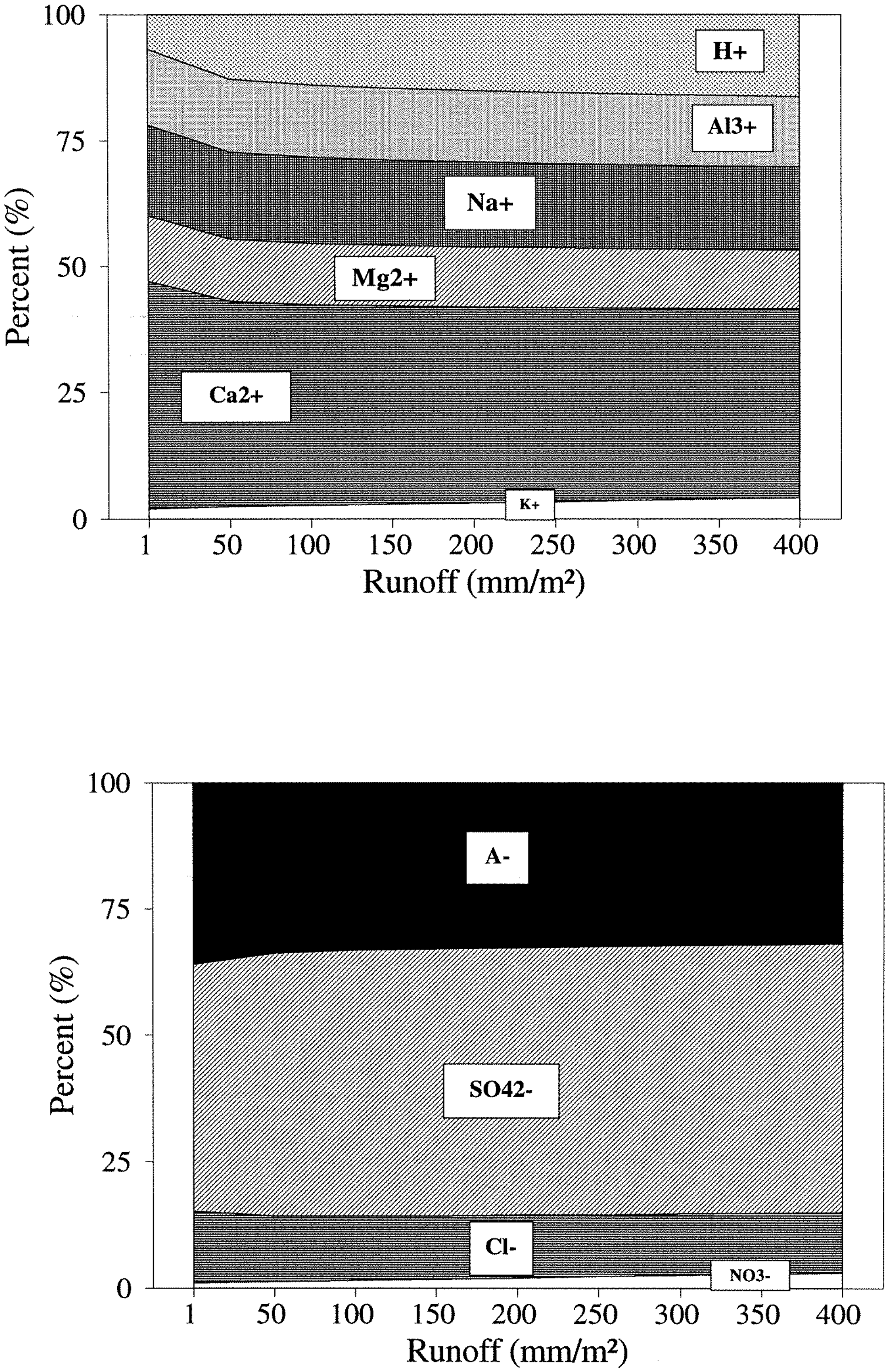
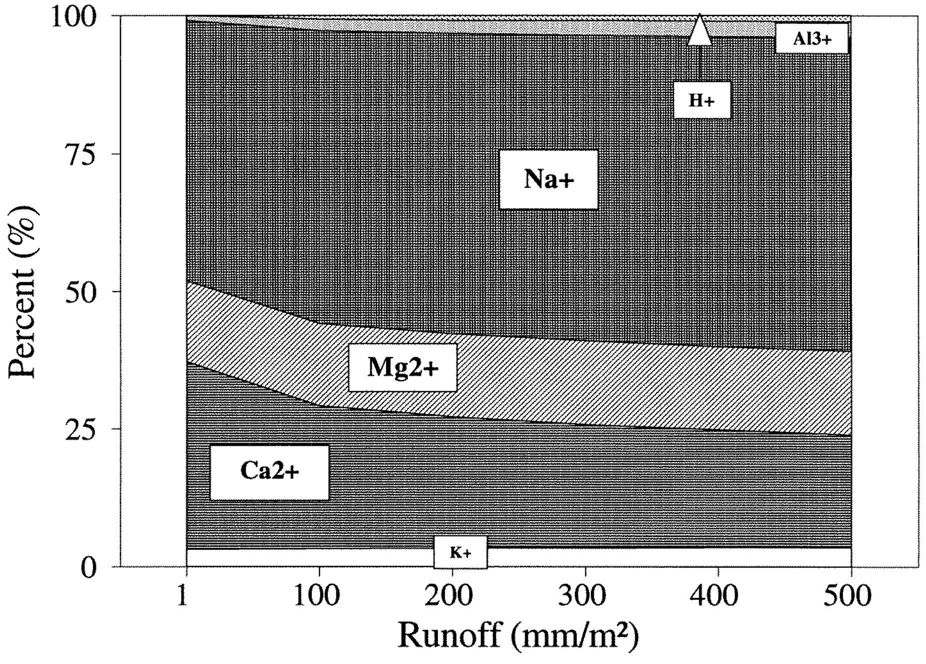


Figure 5.41 The percentage change in the distribution of inorganic cations and anions with respect to change in runoff at Langtjern, based on monthly weighted average values. The changes are based on the regression lines presented in Appendix A.



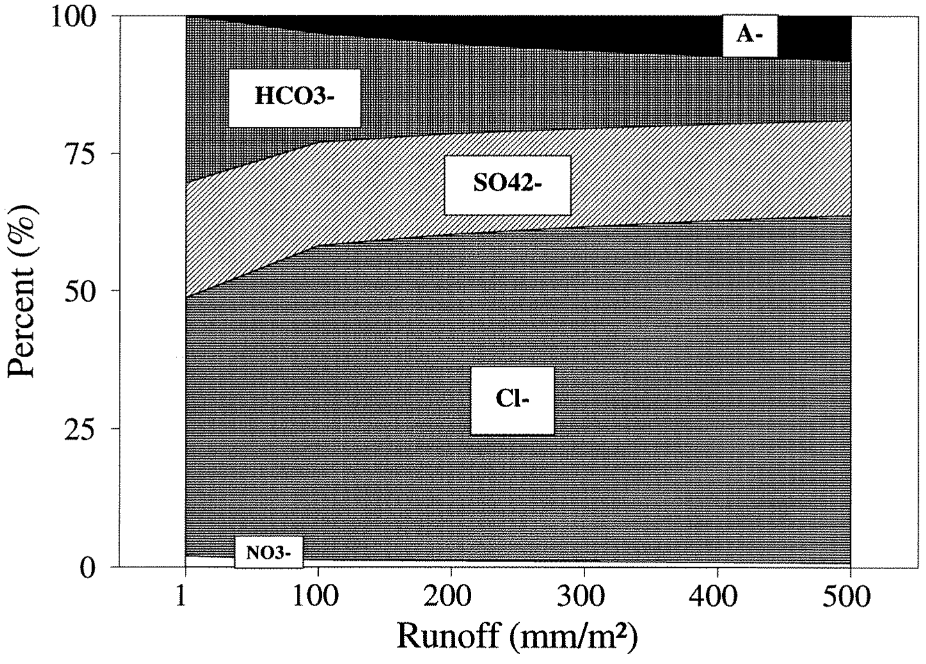


Figure 5.42 The percentage change in the distribution of inorganic cations and anions with respect to change in runoff at Kaarvatn, based on monthly weighted average values. The changes are based on the regression lines presented in Appendix A.

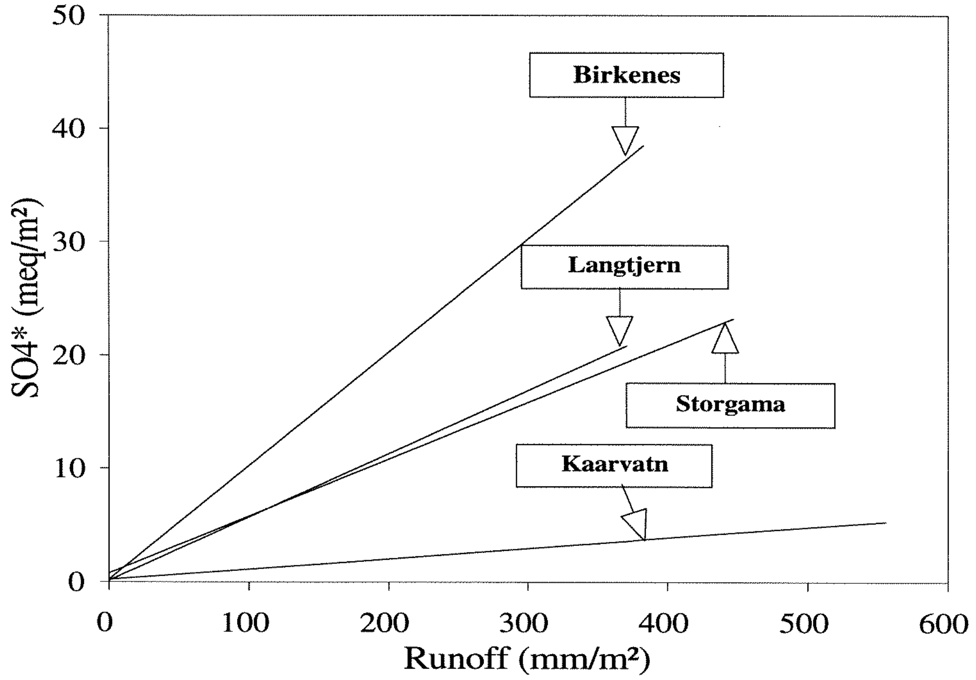
μeq/L and 3.4 μeq/L at 100 mm/m². Even though no significant relationship seems to excists between the concentration of chloride and runoff at Kaarvatn, it tends to decrease by the same order as for sodium, while TOC tends to increase by increasing runoff. At Kaarvatn, the total monthly average concentration of ions (ΣCations,Anions) decrease, i.e. from 262 μeq/L at a monthly runoff of 10 mm/m² to 203 μeq/L at 100 mm/m². Unlike the other sites, it is an increase in the charge balance (ΣCations-Anions), i.e. from -1.6 μeq/L (which means an anion-excess) at a monthly runoff of 10 mm/m² to 3.3 μeq/L at 100 mm/m². But,as at the other sites, the ANC at Kaarvatn is decreasing by increasing runoff i.e. from 32.8 μeq/L at a monthly runoff of 10 mm/m² to to 21.0 μeq/L at 100 mm/m².

While the Kaarvatn catchment generally exhibits the most statistically significant relationships between the concentrations of ions and runoff (highest correlation coefficients), the most severe deterioration in the water quality by increasing runoff, undoubtedly, occurs at Birkenes. Thus catchment exhibits the highest increases in the concentration of H^+ and Al^{3+}, and the largest decrease in the concentration of non-marine divalente basecations ΣCa*,Mg*) by increasing runoff (Table 5.24). Thus, the most severe detoration of the water quality by increasing runoff occurs at Birkenes, assuming the detoration primarily being related to concentrations of the biological harmful compounds, H^+ and aluminium.

Despite the concentration of most ions exhibit a negative correlation by increasing runoff, there is overall positive linear relationships between changes in ionic fluxes and water fluxes (se Appendix B). It is only the flux of aluminium at Storgama which exhibits a negative, but not significant correlation. However, by estimating an average charge of aluminium at Storgama, the flux of Al^{n+} also exhibits a significant linear relationship by increasing runoff.

Based on the regression analysis, it is a linear increase in the monthly weighted flux of non-marine sulphate (SO_4*) at Birkenes from 1.2 meq/mm² at a monthly runoff of 10 mm/m² to 10.2 meq/m² at a runoff of 100 mm/m². During a corresponding runoff increase, the monthly flux of SO_4* increases at Storgama, Langtjern and Kaarvatn from 1.3 meq/m², 0.7 meq/m² and 0.3 meq/m² at a monthly runoff of 10 mm/m² to 5.8 meq/m², 5.7 meq/m² and 1.2 meq/m² at 100 mm/m², respectively (Figure 5.43). Concerning the flux of non-marine base cations (ΣCa*,Mg,Na*), it is an increase from 1.1 meq/m² (Birkenes), 1.1 meq/m² (Storgama), 1.0 meq/m² (Langtjern) and 1.0 meq/m² (Kaarvatn) at a monthly runoff of 10 mm/m² to 5.2 meq/m² (Birkenes), 3.1 meq/m² (Storgama), 6.4 meq/m² (Langtjern), and 2.8 meq/m² (Kaarvatn) at a runoff of 100 mm/m² (Figure 5.43). Correspondingly the monthly weighted fluxes of Al^{n+} increase from 0.34 meq/m² (Birkenes), 0.25 meq/m² (Storgama), 0.11 meq/m² (Langtjern) and 0.009 meq/m² (Kaarvatn) at a monthly runoff of 10 mm/m² to 3.2 meq/m² (Birkenes), 0.90 meq/m² (Storgama), 0.83 meq/m² (Langtjern), and 0.06 meq/m² (Kaarvatn) at monthly runoff of 100 mm/m² (Figure 5.44). Concerning the flux of H^+-ions, it increases from 0.09 meq/m² (Birkenes), 0.54 meq/m² (Storgama), 0.16 meq/m² (Langtjern) and ≈ 0 meq/m² (Kaarvatn) at a monthly runoff of 10 mm/m² to 2.8 meq/m² (Birkenes), 3.0 meq/m² (Storgama), 2.0 meq/m² (Langtjern), and 0.08 meq/m² (Kaarvatn) at a monthly runoff of 100 mm/m² (Figure 5.44).

For the most "typically acid constituents", non-marine sulphate, aluminium and the concentration of H^+-ions, Birkenes exhibits the highest increase in these effluxes by increasing amount of runoff, while Langtjern, the most humic influenced site, exhibits the highest increase in the efflux of non-marine base cations by increasing runoff (Figure 5.43 and 5.44).



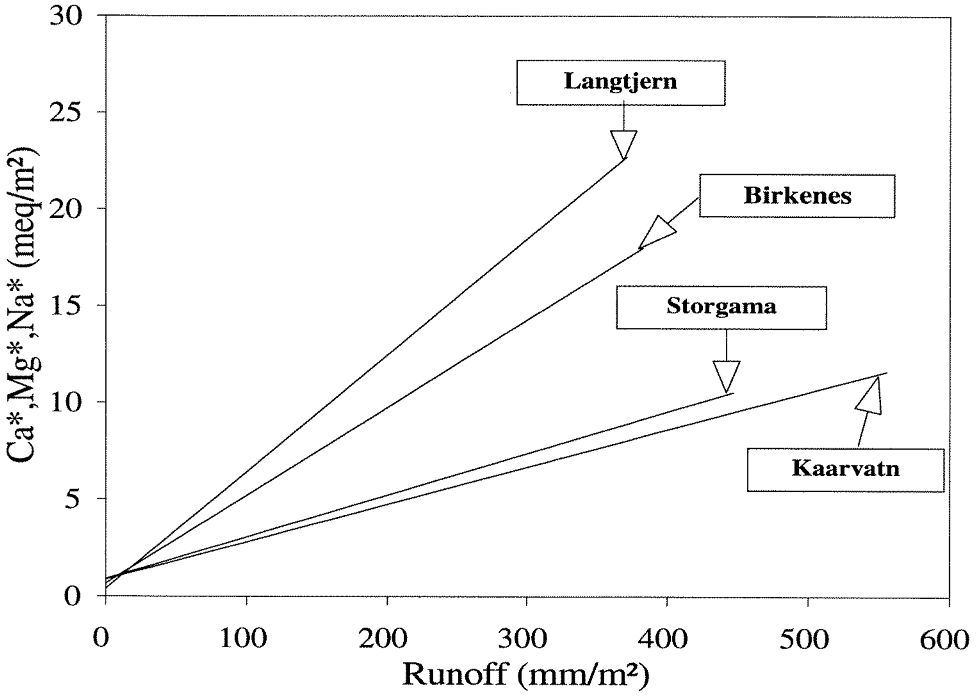


Figure 5.43 The relationships between monthly runoff and monthly fluxes of non-marine sulphate (SO_4) and non-marine base-cations (ΣCa*,Mg*,Na*) at Birkenes, Storgama, Langtjern and Kaarvatn from 1986-1991 (n=72). The relationships rely on linear regression analyses. The regression lines are:* ***SO_4**** *: Birkenes: $y = 0.10x + 0.20$ ($r = 0.97$); Storgama: $y = 0.05x + 0.78$ ($r = 0.93$); Langtjern: $y = 0.06x + 0.11$ ($r = 0.97$); Kaarvatn: $y = 0.009x + 0.24$ ($r = 0.94$).* ***ΣCa*,Mg*,Na**** *: Birkenes: $y = 0.045x + 0.67$ ($r = 0.77$); Storgama: $y = 0.022 + 0.92$ ($r = 0.93$); Langtjern: $y = 0.060x + 0.39$ ($r = 0.96$); Kaarvatn: $y = 0.019x + 0.86$ ($r = 0.91$). Continuous line indicates a significant relationship ($p < 0.05$), while a dotted line indicates no significance, i.e. $p > 0.05$.*

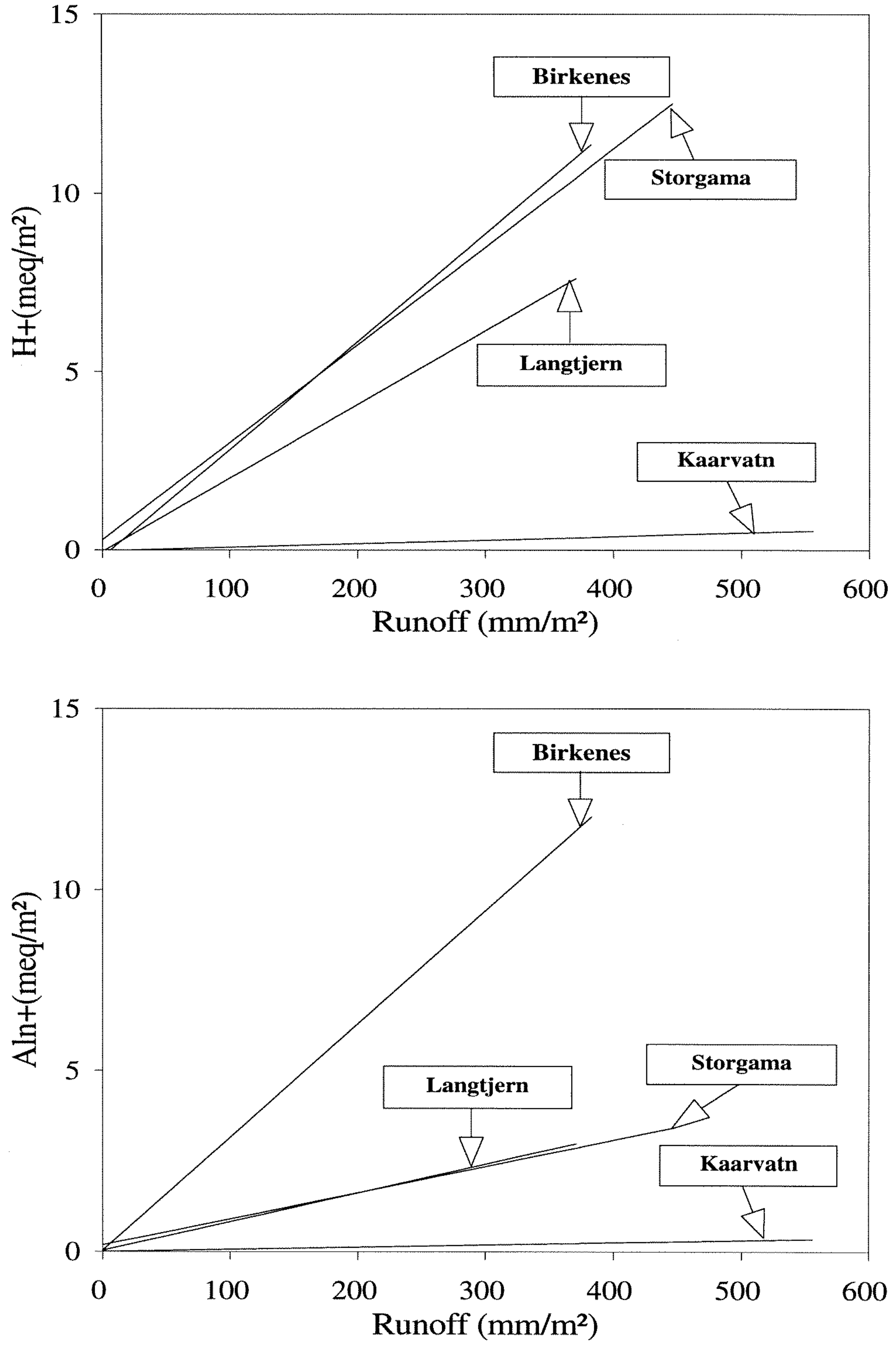


Figure 5.44 The relationships between monthly runoff and monthly fluxes of H^+ and aluminium (ΣAl^{n+}) at Birkenes, Storgama, Langtjern and Kaarvatn from 1986-1991 (n=72). The relationships rely on linear regression analyses. The regression lines are: H^+ : Birkenes: $y = 0.030x - 0.21$ ($r = 0.89$); Storgama: $y = 0.027x + 0.27$ ($r = 0.92$); Langtjern: $y = 0.021x - 0.05$ ($r = 0.97$); Kaarvatn: $y = 0.001x - 0.02$ ($r = 0.94$). ΣAl^{n+} : Birkenes: $y = 0.031x + 0.039$ ($r = 0.90$); Storgama: $y = 0.007x + 0.176$ ($r = 0.88$); Langtjern: $y = 0.008x + 0.034$ ($r = 0.98$); Kaarvatn: $y = 0.0006x + 0.0026$ ($r = 0.96$). Continuous line indicates a significant relationship ($p < 0.05$), while a dotted line indicates no significance, i.e. $p > 0.05$.

Table 5.25 The degree of changes in the ionic fluxes (positive/negative correlation) with respect to change in runoff,, based on monthly weighted averages. The table is based on the linear regressions presented in Appendix B.

Runoff **Ion**	Annual **Correlation**	Kaarvatn	>>	Birkenes	>	Storgama	>>	Langtjern
H^+	positive	Birkenes	>	Storgama	>>	Langtjern	>>	Kaarvatn
Ca^{2+}	positive	Birkenes	>	Langtjern	>>	Storgama	>>	Langtjern
Mg^{2+}	positive	Birkenes	>>	Langtjern	>	Kaarvatn	>	Storgama
$\Sigma Ca^*, Mg^*$	positive	Langtjern	>	Birkenes	>>	Storgama	=	Kaarvatn
Na^+	positive	Birkenes	>>	Kaarvatn	>>	Storgama	>	Langtjern
K^+	positive	Birkenes	>	Storgama	=	Langtjern	>>	Kaarvatn
Al^{3+}	positive	Birkenes	>>	Langtjern	>>	Kaarvatn		
Al^{3+}	negative	Storgama*						
Cl^-	positive	Birkenes	>>	Kaarvatn	>>	Storgama	>>	Langtjern
NO_3^-	positive	Storgama	>>	Birkenes	>>	Langtjern	>>	Kaarvatn
SO_4^{2-}	positive	Birkenes	>>	Langtjern	>	Storgama	>>	Kaarvatn
SO_4^*	positive	Birkenes	>>	Langtjern	>	Storgama	>>	Kaarvatn
HCO_3^-	positive	Kaarvatn						
TOC	positive	Langtjern	>>	Birkenes	>	Storgama	>>	Kaarvatn
ANC	negative	Birkenes	>>	Storgama				
ANC	positive	Kaarvatn	>>	Langtjern*				

= : Difference < 5% compared with the foregoing site.
> : Difference > 5% compared with the foregoing site.
>> : Difference > 25% compared with the foregoing site.
* : not statistical significant, i.e. p > 0.05.

The piston effect

In wet-deposition at Birkenes, a significant negative correlation was found between the amount of precipitation and the concentration of SO_4^{2-}, while the concentration of chloride exhibits a corresponding positive correlation (see Figure 5.3). In runoff, no significant realtionship was found between the concentration of chloride and the amount of runoff. It is probably several reasons for this. One reason is probably the winter-climate. Also at Birkenes, the winter temperature is most often < 0°C, which implies that much of the precipitation during the winter accumulates in the catchment as snow. During springmelt, it is well known that most of the accumulated ions in the snowpack, leave the catchment during the initial snow-melt, while the hydrological maximum occurs later. In other words, the highest concentrations of several ions during spring normally occur during the initial period of snow-melt, when the volume of discharge starts to increase. In Birkenes, this is the case for sulphate, but not for chloride which on monthly weighted basis, decreases systematically with increasing volume of discharge (Figure 5.45). This may indicate that chloride is a more mobile anion than sulphate, and thus, the concentration of chloride is more sensitive to variation in runoff. In other words, the ability of chloride to be temporarily retained in the catchment is less than compared with sulphate. Due to the higher retention properties (lower mobilty) of sulphate, the concentration of this ion is less runoff dependent than chloride. Sulphate is primarily adsorbed in the mineral soil horizion which is a common phenomenon especially in forest soils (e.g. Johnson and Cole, 1977; Reuss, 1980), a soil-type which is present in large parts of the Birkenes catchment. This means that a higher pool of sulphate is able to be temporarily retained in the catchment compared to chloride. During a highflow-period parts of this pool may redissolve and consequently reduce the concentration-variations which are expected to occur by changes in runoff. At the initial winter period, the stored pool of sulphate implies a somewhat higher efflux of sulphate compared with influx (wet and dry-depositon). Accordingly, the influx of chloride (Figure 5.49) is far higher than the efflux of chloride during the same period, even though the annual weighted fluxes of chloride and sulphate is approximately the same during the comparable period (1988-1991), i.e. 93 meq S/m² and 100 meq Cl/m² in wet-deposition, and 152 meq S/m² and 159 meq Cl/m² in runoff. Due to the different mobility between chloride and sulphate, the fluxes of sulphate is far more positively correlated with runoff compared with chloride (Figure 5.50).

The residence time of water may differ a lot both from catchment to catchment, or during a year at one single catchment. Thus, runoff during an initial hydrological high-flow period is often "old water" which has been kept in the catchment for a relatively long time, and pressed out by the very new water entering the catchment by the last rain or by snow that melts. This effect is often called the piston-effect, a phenomenon which is earlier described by several authors (e.g. Johannessen et al., 1980). The main effect of the piston effect is very high concentration of most ions during the very beginning (first hours/days) of a comming high-flow period, and occurs primarily during the initial phase of springmelt or autumn storms. Because the piston effect only lasts for a relatively short time period (days or even hours), the piston effect can not be fully quantified by monthly average concentrations, but monthly data can, however, to some extent reveal the effect.

During the last 10 years, the initial spring-melt at Birkenes normally occurs in March. The runoff this month is averagely a factor 1.36 higher compared with the previous month. Simultaneously, the monthly weighted average concentration of sulphate in March averagely increases by a factor 1.11 compared with the previous month, while chloride correspondingly decreases by a factor 1.28 (Figure 5.45). If chloride is very mobile, it primarily follows the water through the catchment, with no significant delay, and that most of the ions from the snow pack enters the runoff during the initial spring-melt, the decreasing concentration of chloride by increasing runoff is a dilution effect only. The small difference in the relative increase in runoff from February to March compared with the relative decrease in the concentration of chloride during the same period, indicates that the decline in chloride during this period is primarily due to dilution. Concerning sulphate the average weighted concentration in precipitation (ΣWet+Dry) in March at Birkenes is still lower than the corresponding concentration in runoff. Thus, the concentration increase of sulphate in runoff can not be explained by a higher concentration in precipitation than in runoff within the same period. Thus, at least for sulphate, the piston effect is revealed even by use of monthly weighted concentration averages at Birkenes.

The initial spring-melt at Storgama normally occurs in April. The runoff this month is averagely a factor 4.05 higher than the previous month (Figure 5.46). Simultaneously, it is a decrease in the monthly average concentration of both sulphate and chloride by a factor 1.05 and 1.18, respectively. Due to a more distinct and powerfull springmelt and less soil present in this catchment compared with at Birkenes, it is more difficult to reveal the piston effect at Storgama by use of monthly weighted averages. Nevertheless, the lower relative decrease in the concentration of sulphate compared with chloride by increasing runoff during springmelt, indicates a lower mobility of sulphate compared with chloride.

At Langtjern, the initial spring-melt normally occurs in April. This month the runoff is averagely a factor 6.44 higher than the previous month. Simultaneously, the monthly average concentration of sulphate increases by a factor 1.01 compared with the month before, while chloride correspondingly decreases by a factor 1.22 (Figure 5.47). Using the same dry-deposition estimates as applied at Birkenes, the concentration of sulphate in precipitation (ΣWet+Dry) may not, under any circumstances, be responsible for the maintenance or even a weak increase in the sulphate concentration in runoff during the initial period of spring melt. Despite the very distinct and powerfull springmelt which normally occurs at Langtjern, the piston effect of sulphate is to some extent also revealed at this site, by use of monthly weighted averages.

At Kaarvatn, the initial spring-melt normally occurs in April. Monthly runoff this month is averagely a factor 4.07 higher compared with the previous month. Simultaneously, the concentration of both sulphate and chloride increase by a factor 1.11 and 1.51, respectively (Figure 5.48). Because the initial spring-melt at Kaarvatn seems to occur somewhat later in April compared with at both Storgama and Langtjern, the dilution period (high-flow period) that follows normally occurs in May at Kaarvatn. Thus, the piston-effect is better revealed by monthly weighted averages at Kaarvatn compared with the two other sites. At Kaarvatn the piston-effect is revealed for both chloride and sulphate during springmelt, more enhanced for chloride than for sulphate. This probably relies on the fact that Kaarvatn is located close to the sea (high seasalt input), and does only receive low amounts of non-marine sulphate. Thus, the input of chloride is far higher than for sulphate. The net accumulation of ions within a normally deep snowpack during the winter at Kaarvatn (see Chapter: Hydrology), may therefore cause a more distinct piston effect for chloride than for sulphate during the initial springmelt at Kaarvatn.

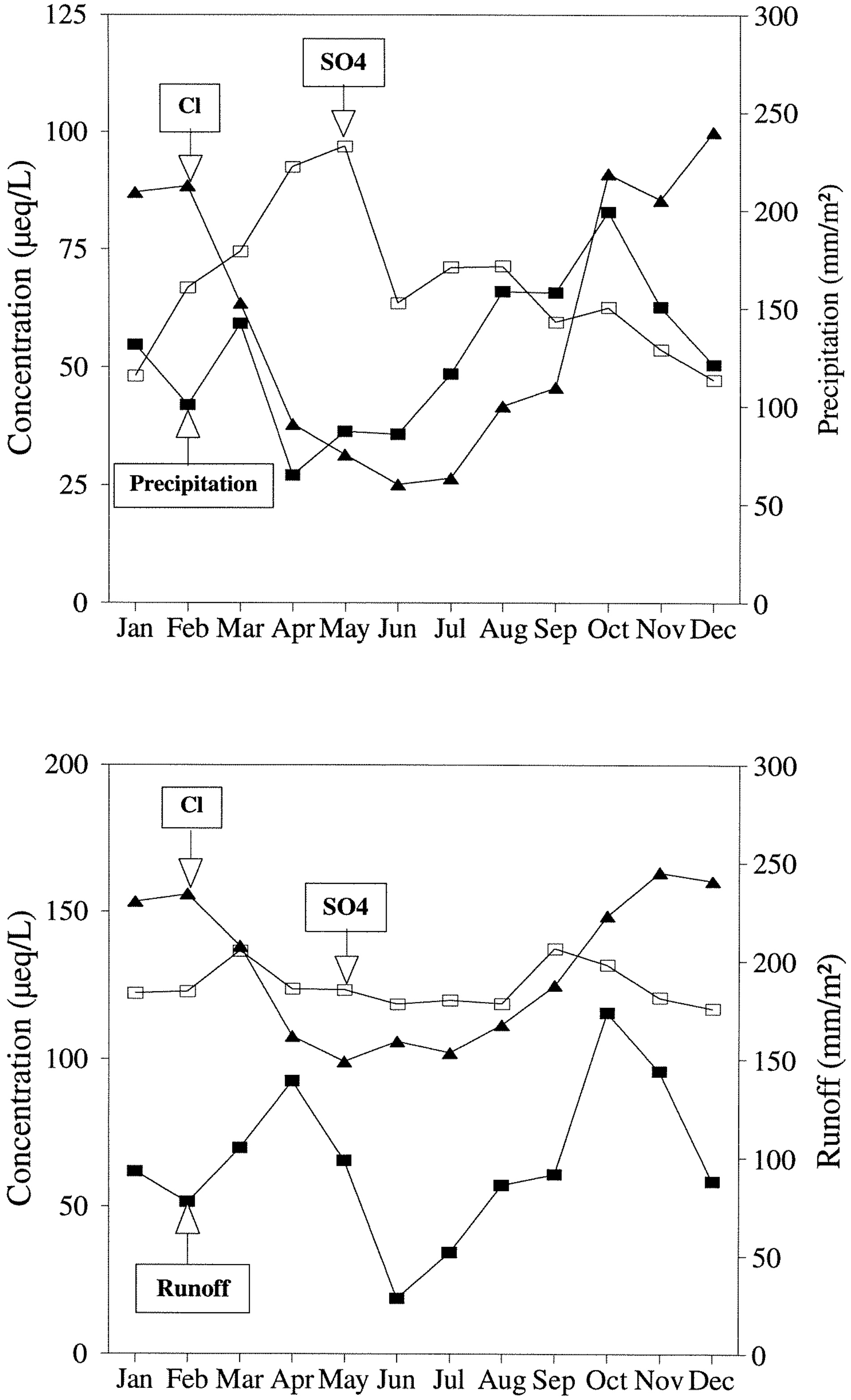


Figure 5.45 Monthly inputs and outputs of water, and monthly weighted concentration means of chloride and sulphate in precipitation and runoff at Birkenes during 1981-1991, the period during which all catchments have been analysed with respect to both chloride and sulphate in both wet-deposition and runoff.

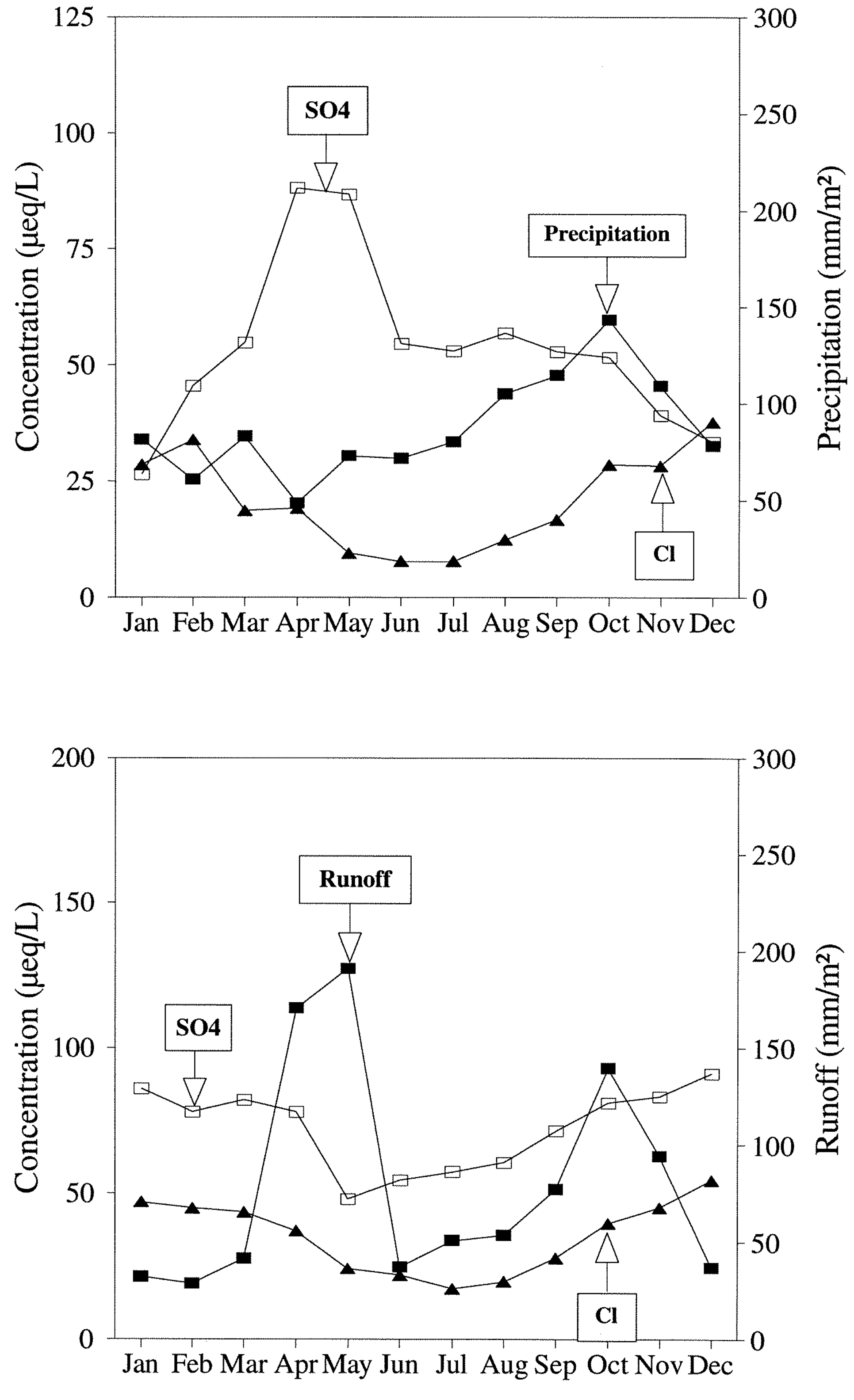
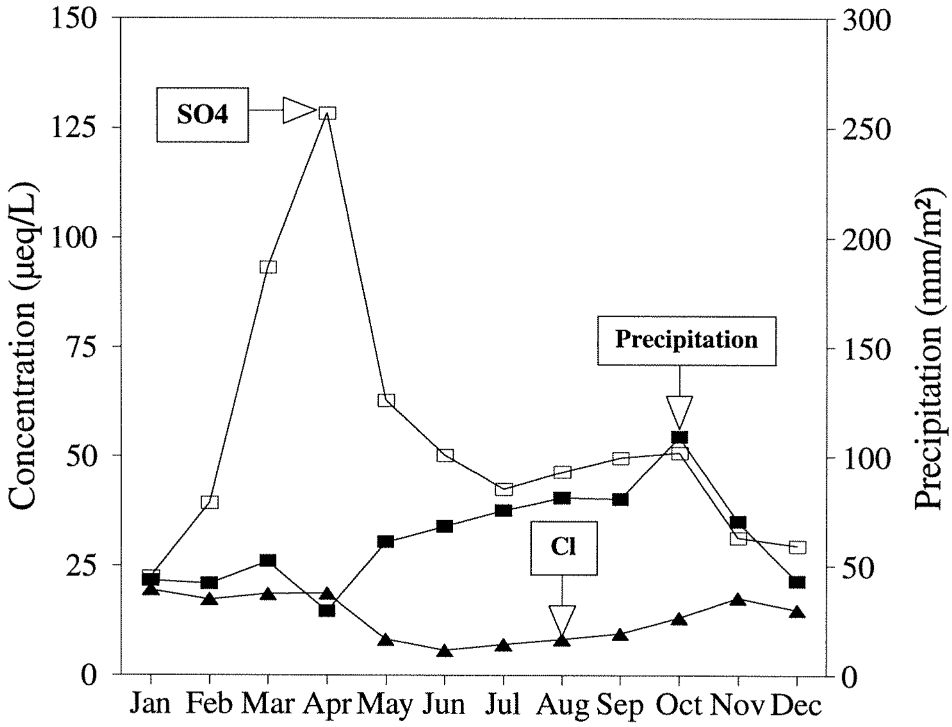


Figure 5.46 Monthly inputs and outputs of water, and monthly weighted concentration means of chloride and sulphate in precipitation and runoff at Storgama during 1981-1991, the period during which all catchments have been analysed with respect to both chloride and sulphate in both wet-deposition and runoff.



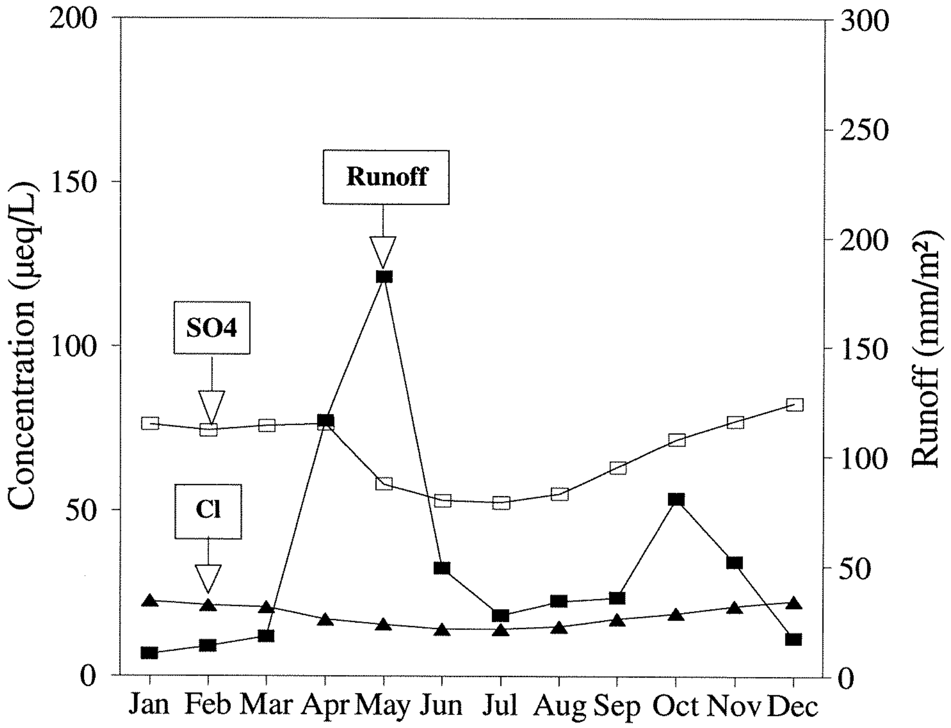
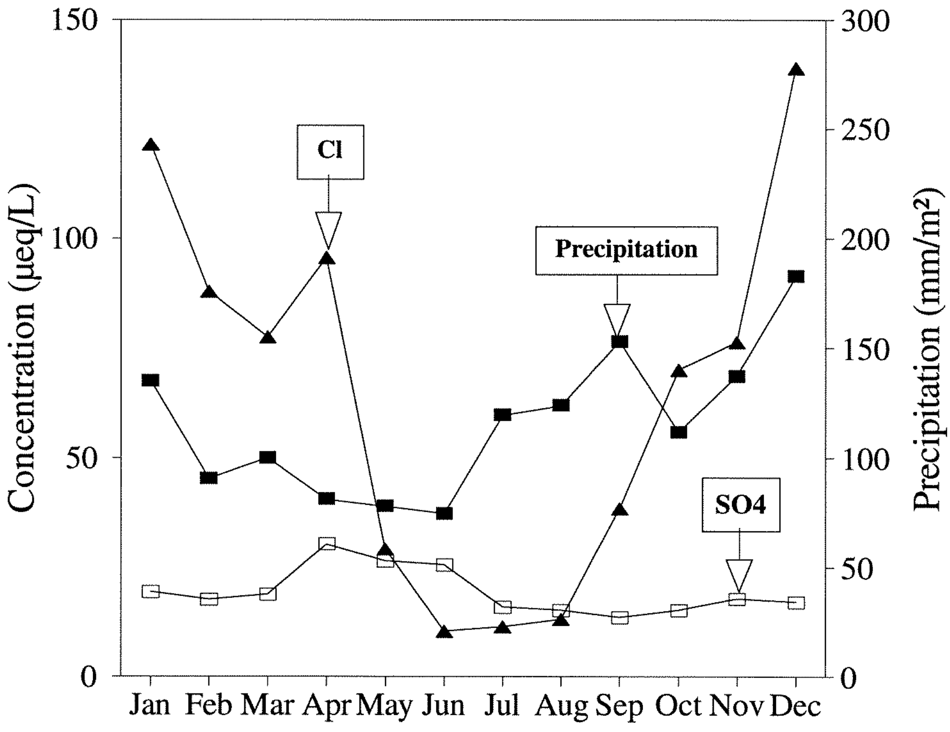


Figure 5.47 Monthly inputs and outputs of water, and monthly weighted concentration means of chloride and sulphate in precipitation and runoff at Langtjern during 1981-1991, the period during which all catchments have been analysed with respect to both chloride and sulphate in both wet-deposition and runoff.



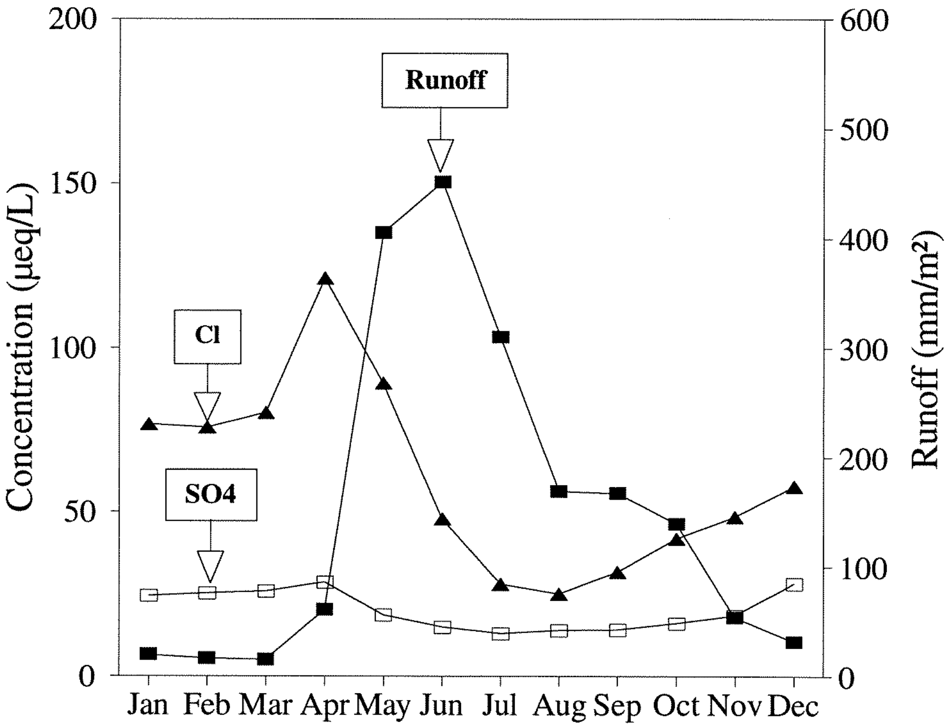
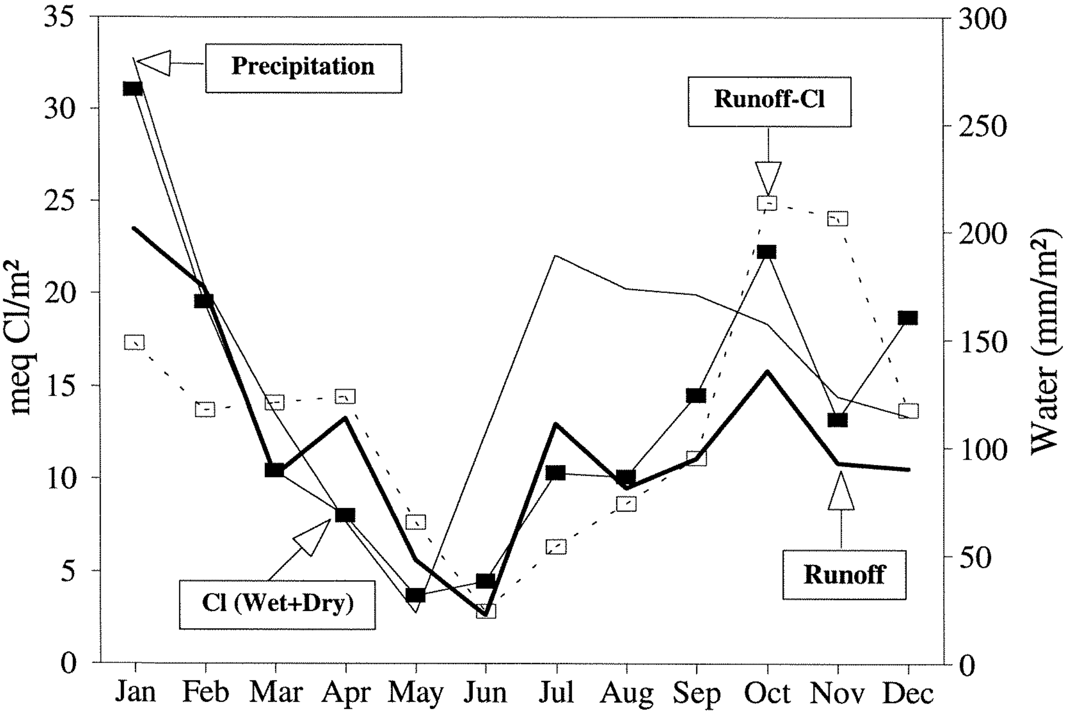


Figure 5.48 Monthly inputs and outputs of water, and monthly weighted concentration means of chloride and sulphate in precipitation and runoff at Kaarvatn during 1981-1991, the period during which all catchments have been analysed with respect to both chloride and sulphate in both wet-deposition and runoff.



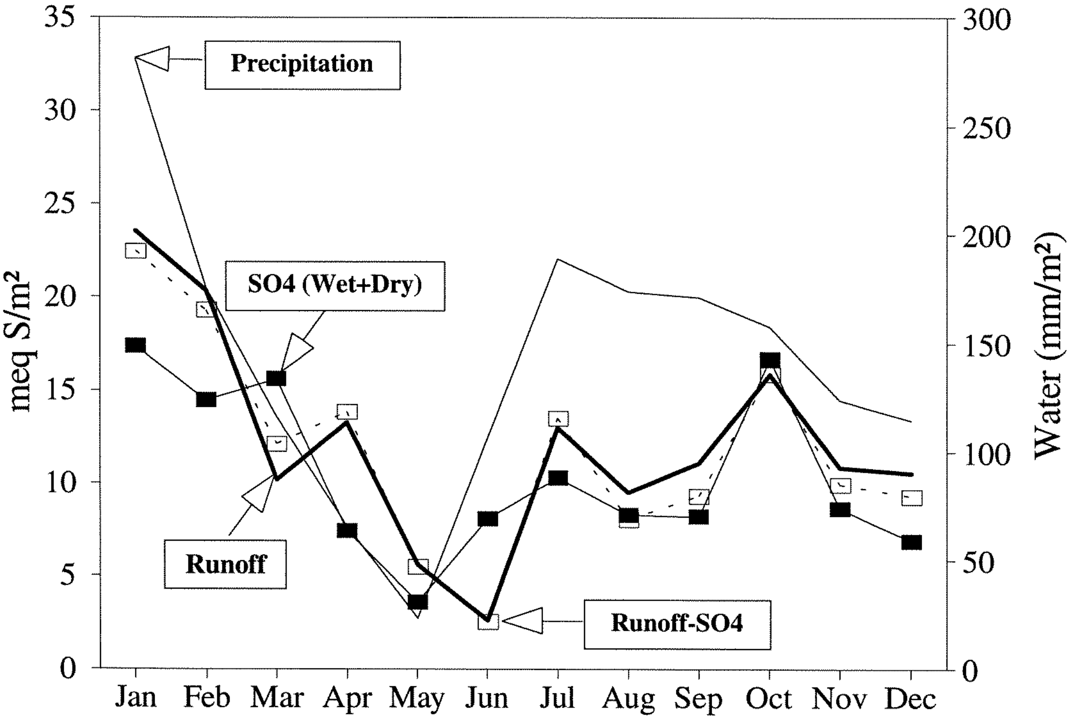
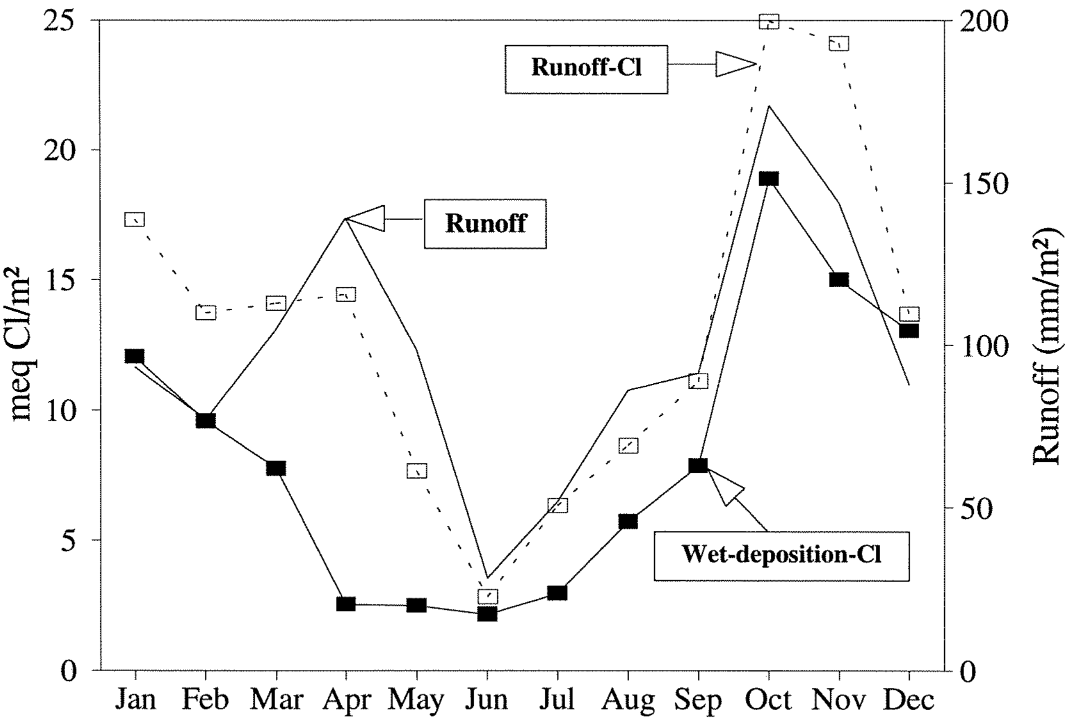


Figure 5.49 Monthly weighted influxes and effluxes of water, chloride and sulphate at Birkenes from 1988-1991, the period during which both wet- and dry-deposition of both sulphur and chloride have been measured.



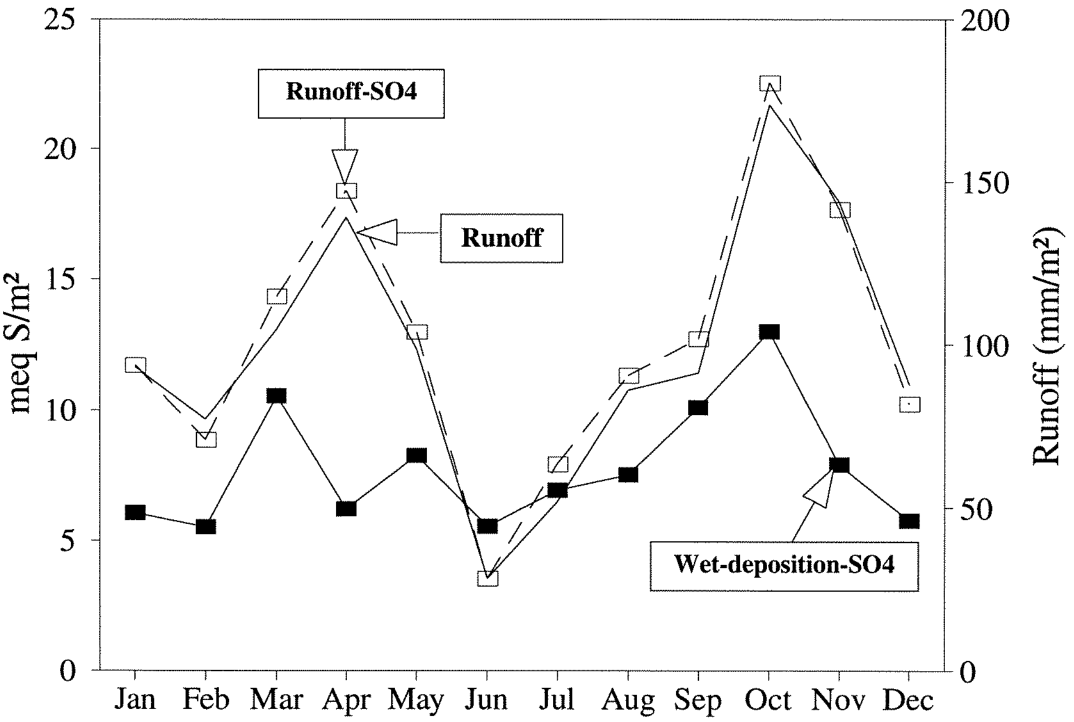


Figure 5.50 Monthly weighted influxes and effluxes of water, chloride and sulphate, at Birkenes from 1981-1991, the period during which all catchments have been analysed with respect to chloride and sulphate in runoff, but only wet-deposition in precipitation.

Especially for sulphate, which is a less mobile ion than chloride, the retention or release of this ion is probably of great importance in many catchments. The monthly flux of sulphate at the forested watershed ecosystems of the Hubbard Brook Experimental Forest shows an accumulation of sulphate during summer, followed by a later release (Likens et al., 1977). The same trend was also revealed by the input-output-budgets at Birkenes (Christophersen and Wright, 1980a,1980b). They also assumed that all sulphate of atmospheric origin which accumulates in the upper soil horizon remains water soluble and that the concentration in this reservoir is proportional to the total amount of water soluble sulphate. Johnson and Henderson (1979) further assumed that this water soluble reservoir of sulphate present in the upper soil horizion is responsible for the high autumn concentration in runoff during stormflow. This tendency is also present at the four long-term monitored catchments in Norway.

5.6 Sulphuric acid and other acidfying compounds

In most areas of Norway and Scandinavia, sulphuric acid is the most frequent cause of soil and surface water acidification. Sulphuric acid may often enter the catchment as acid rain, but may also be produced by biogeochemical processes in catchment. Normally, substantial parts of the sulphuric acid is neutralized within the catchment by dissolution of base cations, or buffered by protonation of weak, organic acid anions. Catchments with low base-saturation and low contents of humic acids, are often unable to neutralize high amounts of strong acids, and aluminium will start to leak out from the soil, often in relatively high concentrations. How each catchment neutralizes (primarily by base cation dissolution) or buffers (primarily by aluminium dissolution, cationexchange, and weak acid buffering) the strong acids is essential for the runoff pH. Because substantial amounts of free protons are "consumed" by these processes, the concentration of the more or less concervative strong acid anion, SO_4^{2-}, is used to estimate the original amount of strong acids, assuming non-marine sulphate (SO_4*) representing the total amount of strong acid anions. Thus, the concentration of Σ(Ca*,Mg*,Na*, ΣAl^{n+}, H^+) should be almost equal to the concentration of SO_4*.

Table 5.26 The mean concentrations of H^+, ΣAl^{n+}, ΣCa,Mg*,Na* and SO_4* in runoff from the four catchments, and the percentage amount of Σ(Ca*,Mg*,Na*,ΣAl^{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,*

Site	*A* H^+ µeq/L	*B* ΣAl^{n+} µeq/L	*C* ΣCa*,Mg*,Na* µeq/L	*D* *A+B+C* µeq/L	*E* SO_4* µeq/L	*F* *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 Birkenes, averagely 89% of the $\Sigma(Ca^*,Mg^*,Na^*, \Sigma Al^{n+}, H^+)$ can be explained by sulphuric acid during the period 1986-1991 (Table 5.26), and about 79% of the free protons (H^+) present in the catchment are consumed in various biogeochemical processes. About 67% of the proton consumtion is from dissolution of basecations, while the remaining 33% is from dissolution of aluminium. At Birkenes, about 10% of the concentration of $\Sigma(Ca^*,Mg^*,Na^*, \Sigma Al^{n+}, H^+)$ can not be explained by sulphuric acid. The most likely explanation to this, is the presence of weak organic acids and the increasing leakage of nitrate (See Chapter 6). If all and equal amounts of ammonium and nitrate are directly taken up by plants, and no chemical processes have changed the ratio between the two compounds, the two nitrogen sources will not cause any acidification. At Birkenes, these conditions have changed during the last years, and nitrate has start to leak out from the catchment more and more. At Birkenes, there is a significant decrease in the sulphuric acid explanatory acidification from 1986 to 1991. A simple linear regression analysis, based on monthly weighted averages, shows a decrease in the sulphuric acid explanatory acidification, from 99% in 1986 to 82% in 1991. This means that other acidifying compounds, primarily nitrate, are increasing. The nitrate which is not taken up by the catchment will act as mobile strong acid anions equal with sulphate. At Birkenes, the increase in seasalt input during the last years may also contribute to the acidification, but this is probably a more short-term effect. Even though the four catchments all exhibit a significant decrease in the concentration of sulphuric acid during the same period, there are no significant changes in the sulphuric acid explanatory acidification during 1986-1991 neither at Storgama, Langtjern nor Kaarvatn.

At Storgama, averagely 82% of the concentration of $\Sigma(Ca^*,Mg^*,Na^*, \Sigma Al^{n+}, H^+)$ can be explained by sulphuric acid during the period 1986-1991 (Table 5.26), and about 63% of the free protons (H^+) present in the catchment are consumed in various biogeochemical processes. About 79% of the proton consumtion is from dissolution of base cations, while the remaining 21% is from dissolution of aluminium. At Storgama, about 20% of the $\Sigma(Ca^*,Mg^*,Na^*, \Sigma Al^{n+}, H^+)$ can not be explained by sulphuric acid. Because it is no significant change in the nitrogen chemistry, about 20% of the concentration of $\Sigma(Ca^*,Mg^*,Na^*, \Sigma Al^{n+}, H^+)$ might be explained by organic acids and by the increase in seasalt input which has been registrated during the last years. Even though the concentrations of strong acids at Storgama are much lower compared with at Birkenes, the neutralization/buffering against strong acids is much lower in the Storgama catchment. This should also be expected, because large parts of the Storgama catchment consists of bare rock or shallow soil.

At Langtjern, averagely 59% of the concentration of $\Sigma(Ca^*,Mg^*,Na^*, \Sigma Al^{n+}, H^+)$ can be explained by sulphuric acid during the period 1986-1991 (Table 5.26), and about 83% of the free protons (H^+) present in the catchment acid are consumed in various biogeochemical processes. About 89% of the proton consumtion is from dissolution of base cations, while the remaining 11% is from dissolution of aluminium. At Langtjern, about 40% of the $\Sigma(Ca^*,Mg^*,Na^*, \Sigma Al^{n+}, H^+)$ can normally not be explained by sulphuric acid. Because it is no significant change in the nitrogen chemistry and the input of seasalt is extremely low in this typically inland catchment, the remaining 40% of the concentration of $\Sigma(Ca^*,Mg^*,Na^*, \Sigma Al^{n+}, H^+)$ might be due to organic acids. The runoff at Langtjern is highly influenced by organic acids (humic substances), and it is well known that these acids may significantly affect mineral weathering (e.g. Inoue and Wada, 1971; Huang and Keller, 1972; Boyle et al., 1974; Johnson et al., 1981; Lundström, 1990), and cation leaking from soils (Reuss, 1980; Mollitor and Raynal, 1982; Krug and Isaacson, 1984). Thus, nearly 40% of base cations and aluminium leakage from the Langtjern catchment is caused by weak organic acids, while the remaing 60% is due to strong inorganic acids. To which extend the organic acids are responsible for the pH of the runoff-water at Langtjern is difficult to evaluate, but if so, the pH of the runoff-water at Langtjern should indicate the average pK-value of the organic acids present.

At Kaarvatn, only 37% of concentration of $\Sigma(Ca^*,Mg^*,Na^*, \Sigma Al^{n+}, H^+)$ can averagely be explained by sulphuric acid during the period 1986-1991 (Table 5.26), and about 98% of the free protons (H^+) present in the catchment are consumed in various biogeochemical processes. About 98% of the proton consumtion is from dissolution of base cations, while the remaining 2% is from dissolution of aluminium. At Kaarvatn, more than 60% of the concentration of $\Sigma(Ca^*,Mg^*,Na^*, \Sigma Al^{n+}, H^+)$ can not be explained by sulphuric acid. Because the influence from sulphuric acid is relatively low at Kaarvatn, base-cation dissolution processes do neutralize the strong acids totally. The 60% of the concentration of $\Sigma(Ca^*,Mg^*,Na^*, \Sigma Al^{n+}, H^+)$ at Kaarvatn which can not be explained by strong acids, is most likely caused by the weak inorganic carbonic acid, but also to some extent due to high seasalt influence during the last years and weak organic acids. The vital role of water as transporting agent, chemical solvent and catalyst itself, should not be forgotten or underestimated in a catchment like Kaarvatn which only receives minor amounts of strong acids.

Seasonal changes.

The total fluxes or concentrations of the major non-marine base cations $\Sigma Ca^*,Mg^*,Na^*$ (BC^*), ΣAl^{n+}(Al) and H^+ (H), i.e. ΣBC^*,Al,H, which can be explained by sulphuric acid (SO_4^*) do to some extent exhibit seasonal variations. At Birkenes, the seasonal variations are relatively small (Figure 5.51). Based on mean-values made up from monthly weighted averages from 1986 -1991, the concentration of sulphuric acid explains between 78% (in August) upto 96% (in November) of the concentration of ΣBC^*,Al,H at Birkenes. The lowest percentage contribution from BC^* to the ΣBC^*,Al,H normally occurs in November (29%), at the same time as the relative contributions from both H^+ and ΣAl^{n+} are at the highest (Figure 5.52). The highest percent contribution BC^* (67%) to the ΣBC^*,Al,H normally occurs in June, but is also higher than 60% in May, July and August, periods when the contributions from ΣAl^{n+} and H^+ are at the lowest. The highest concentration of non-marine sulphate (SO_4^*) in the runoff water at Birkenes normally occurs in March (114 μeq/L) and October (110 μeg/L), During these two months, the H^+-concentration is at the highest too (March: 28 μeq/L; October: 36 μeq/L). The highest concentration of ΣAl^{n+} normally occurs in March (37 μeq/L), while the highest concentration during autumn normally occurs in November (36 μeq/L). The highest concentration of seasalts do also occur during Februar/March (166/140 μeq/L) and October/November (177/165 μeq/L).

Based on mean-values made up from monthly weighted averages from 1986 -1991, sulphuric acid can explain between 77% (in April) and 98% (in May) of ΣBC^*,Al,H at Storgama. The lowest relative contribution from BC^* to the ΣBC^*AlH, normally occurs in October (42%) and November (43%), when the relative contributions from H^+ and ΣAl^{n+} both are at the highest (Figure 5.54). The highest percent contribution from BC^* to the ΣBC^*AlH normally occurs in March (57%), but is higher than 50%, during the low-flow periods during winter (1 January to 31 March) and summer (1 June to 31 August). At the low-flow period during the winter, the percent contribution from H^+ to the BC* is at the lowest (30-34%), while the percent contribution from ΣAl^{n+} is still relatively high (13-14%). At the low-flow period during the summer, the percent contributions from ΣAl^{n+} is at the lowest (10-12%), but also the contribution from H^+ is low (36-38%). The highest concentration of non-marine sulphate (SO_4*) in runoff at Storgama normally occurs in December (84 μeq/L). During this month, the highest concentrations of both CB* (52 μeq/L) and ΣAl^{n+} (17 μeq/L) normally occur. The H^+-concentration is also very high (38 μeq/L) during December, but a somewhat lower concentration is normally present one month earlier, in November. The highest concentrations of seasalts do normally occur during the same period (1 November to 31 December).

Based on mean-values made up from monthly weighted averages from 1986 -1991, sulphuric acid can explain from 54% (in April) to 66% (in May) of ΣBC*,Al,H at Langtjern. The lowest relative contribution from BC* to the ΣBC*,Al,H normally occurs in May (69%) and November (69%), when the relative contributions from H^+ and ΣAl^{n+} are at the highest (Figure 5.56). The highest percent contribution from BC* to the ΣBC*,Al,H, normally occurs during the low flow-period during summer (77-78%), i.e. 1 June to 31 August, but the contribition from BC* to the ΣBC*,Al,H is normally higher than 70%, except in May during springmelt (69%) and in November (69%). The highest concentration of non-marine sulphate (SO_4*) in runoff at Langtjern normally occurs in December (72 μeq/L). During this month, also the highest concentrations of both H^+ (25 μeq/L) and ΣAl^{n+} (11 μeq/L) normally occur, but the concentration of BC* is also very high (84 μeq/L). A somewhat higher concentration of BC* does normally occur in January (85 μeq/L). Also at Langtjern, the concentrations of seasalts are normally at the highest during the winter, even though the catchment is situated long distance inland from the coast.

Based on mean-values made up from monthly weighted averages from 1986 -1991, sulphuric acid can explain between 32% (in January) and 57% (in April) of ΣBC*,Al,H at Kaarvatn. The lowest relative contribution from BC* to the ΣBC*,Al,H normally occurs in April (88%) and May (90%), when the relative contributions from H^+ and ΣAl^{n+} are at the highest (Figure 5.58). The highest percent contribution from BC* to the ΣBC,*Al,H normally occurs in February (98%), but is higher than 95% most of the year, except during the springmelt period from 1 April to 30 June, when the contribution from BC* is somewhat lower (88-92%). At the low-flow period during the winter, the percent contribution from H^+ and ΣAl^{n+} to the ΣBC*,Al,H is at the lowest (1-2% each). The highest concentration of non-marine sulphate (SO_4*) in runoff at Kaarvatn normally occurs in December (19 μeq/L). During this month, the concentrations of BC* (39 μeq/L), ΣAl^{n+} (0.6 μeq/L) and H^+ (0.6 μeq/L), all is nearly at their yearly weighted concentration averages. The highest concentrations of seasalts in runoff do normally occur during the winter and early spring, normally at the highest in April (114.4 μeq/L), which is the initial month of springmelt.

The concentration of SO_4* in runoff seems to be most important for the concentration levels of ΣBC*,Al,H in runoff, while temporary changes in TOC and seasalts seems more important for the seasonal, more short-term changes in the concentrations of these compounds. At Birkenes, there is a significant positive correlation between the non-sulphuric-acid explanatory concentration of ΣBC*,Al,H and TOC ($y = 0.069x + 4.26$; $r = 0.51$; $n = 70$). This can be illustrated very well during August 1991 (Figure 5.59), when only 40% of ΣBC*,Al,H was sulphuric-acid explainable, and the concentration of total organic carbon (TOC) was very

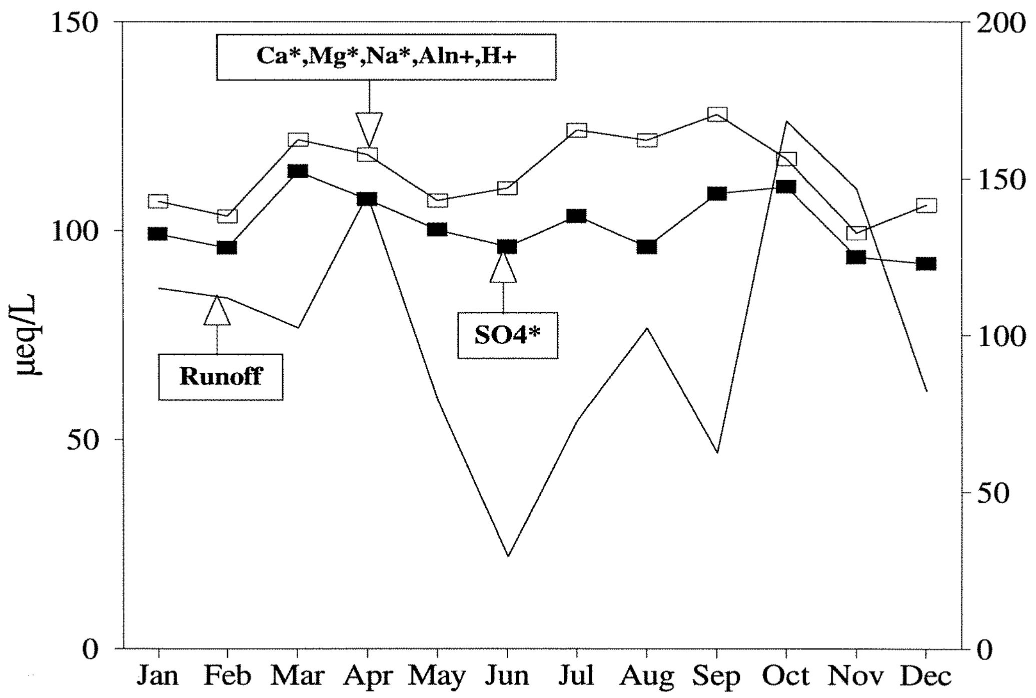


Figure 5.51 Seasonal variations in runoff and concentrations of non-marine sulphate (SO_4) and Σ(Ca*,Mg*,Na*, ΣAl^{n+}, H^+) at Birkenes based on monthly weighted averages from 1986-1991.*

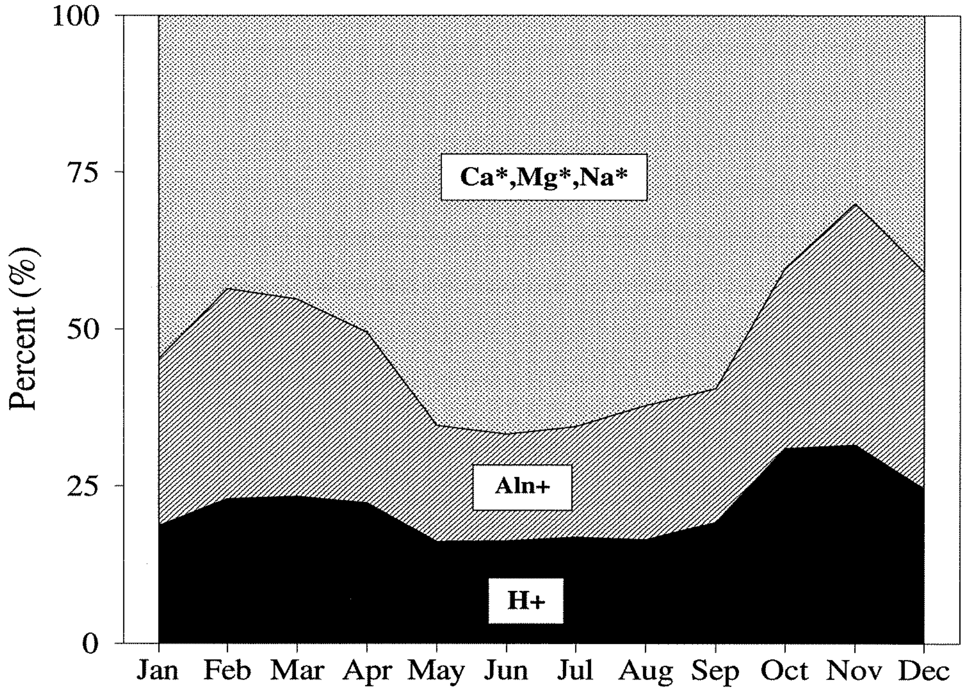


Figure 5.52 Seasonal variations in percentage contribution from ΣCa,Mg*,Na*, ΣAl^{n+}, and H^+ to the Σ(Ca*,Mg*,Na*, ΣAl^{n+}, H^+) at Birkenes based on monthly weighted averages from 1986-1991.*

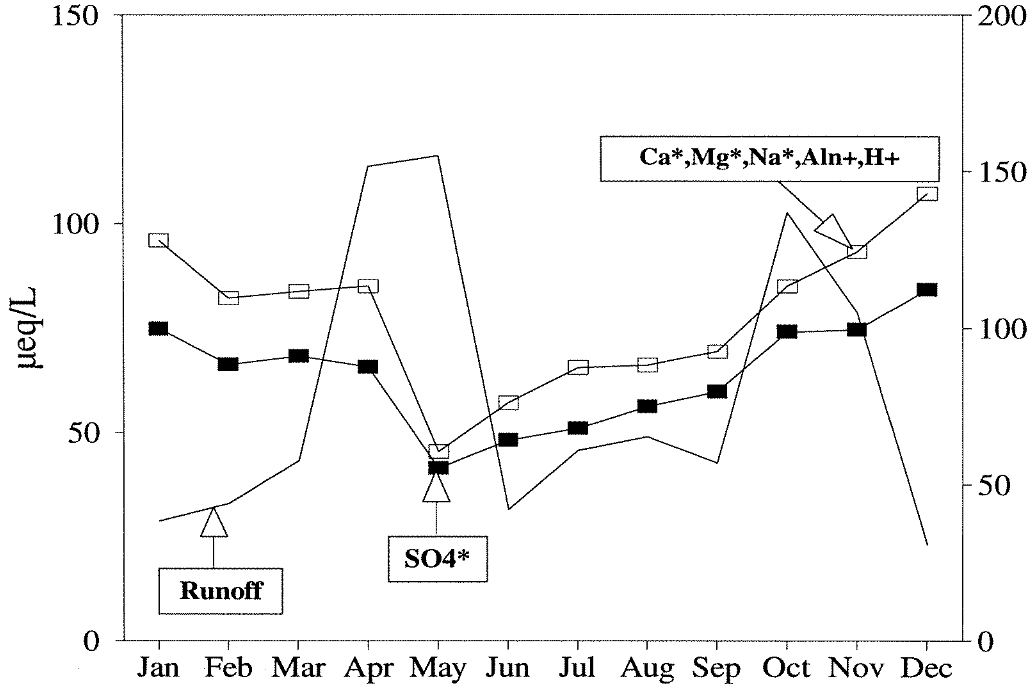


Figure 5.53 Seasonal variations in runoff and concentrations of non-marine sulphate (SO_4) and Σ(Ca*,Mg*,Na*, ΣAl^{n+}, H^+) at Storgama based on monthly weighted averages from 1986-1991.*

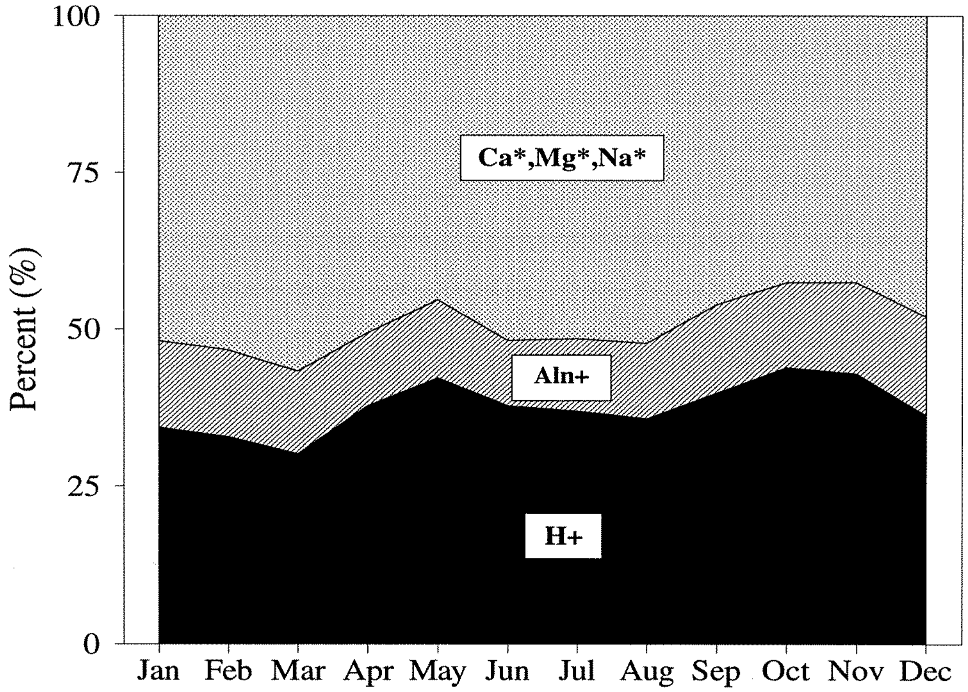


Figure 5.54 Seasonal variations in percentage contribution from ΣCa,Mg*,Na*, ΣAl^{n+}, and H^+ to the Σ(Ca*,Mg*,Na*, ΣAl^{n+}, H^+) at Storgama based on monthly weighted averages from 1986-1991.*

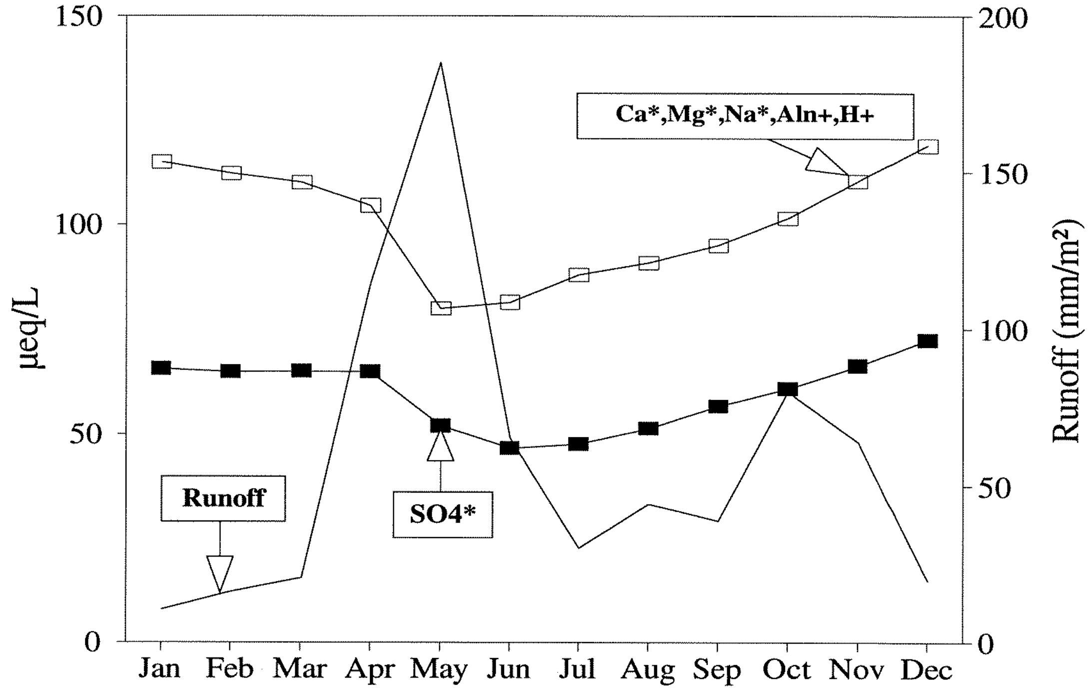


Figure 5.55 Seasonal variations in runoff and concentrations of non-marine sulphate (SO_4) and Σ(Ca*,Mg*,Na*, ΣAl^{n+}, H^+) at Langtjern based on monthly weighted averages from 1986-1991.*

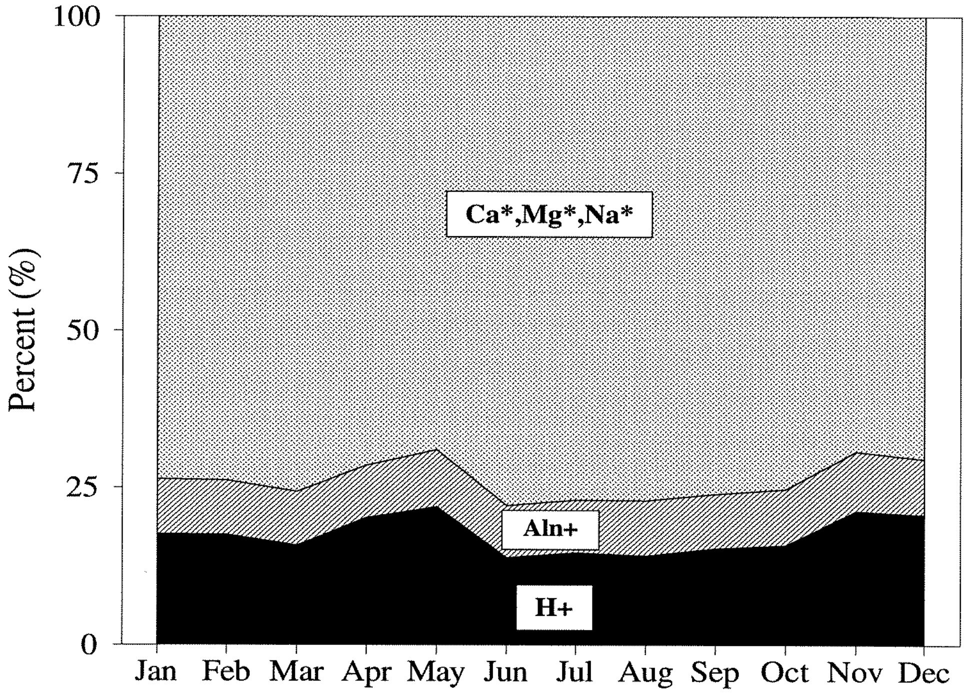


Figure 5.56 Seasonal variations in percentage contribution from ΣCa,Mg*,Na*, ΣAl^{n+}, and H^+ to the Σ(Ca*,Mg*,Na*, ΣAl^{n+}, H^+) at Langtjern based on monthly weighted averages from 1986-1991.*

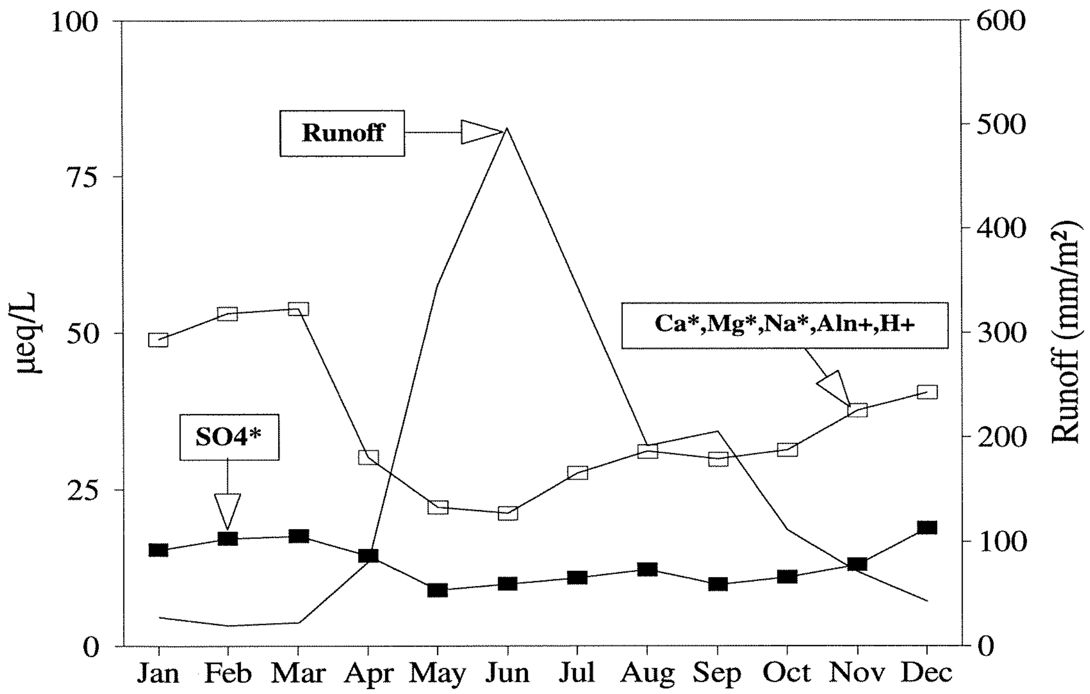


Figure 5.57 Seasonal variations in runoff and concentrations of non-marine sulphate (SO_4) and $\Sigma(Ca^*,Mg^*,Na^*, \Sigma Al^{n+}, H^+)$ at Kaarvatn based on monthly weighted averages from 1986-1991.*

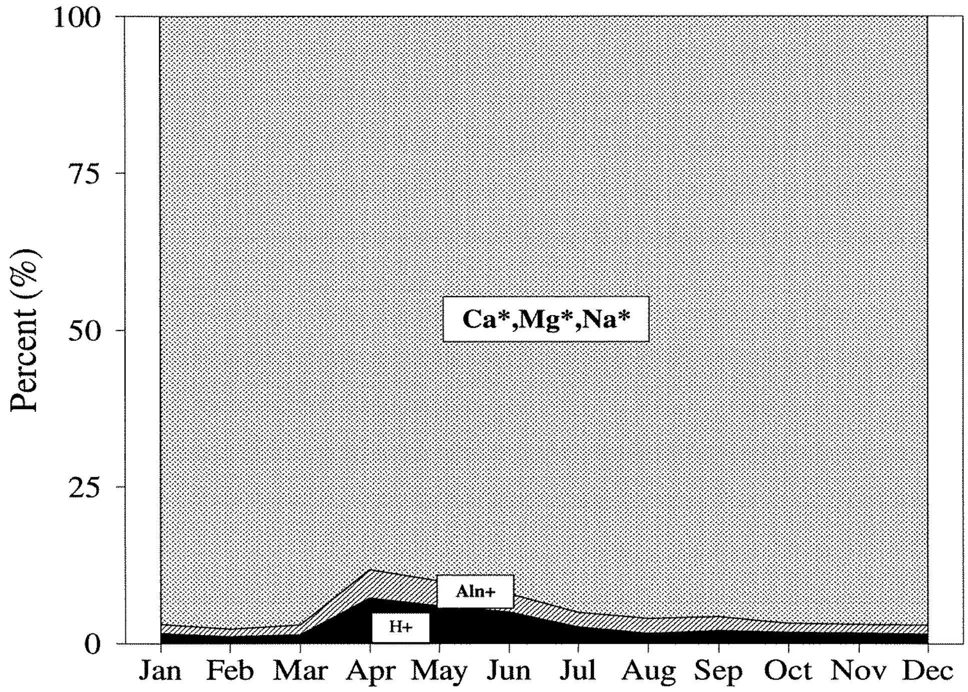
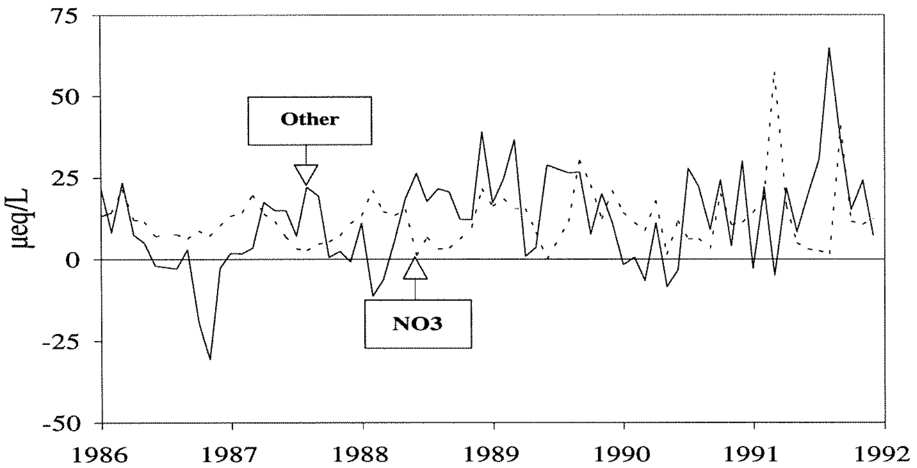
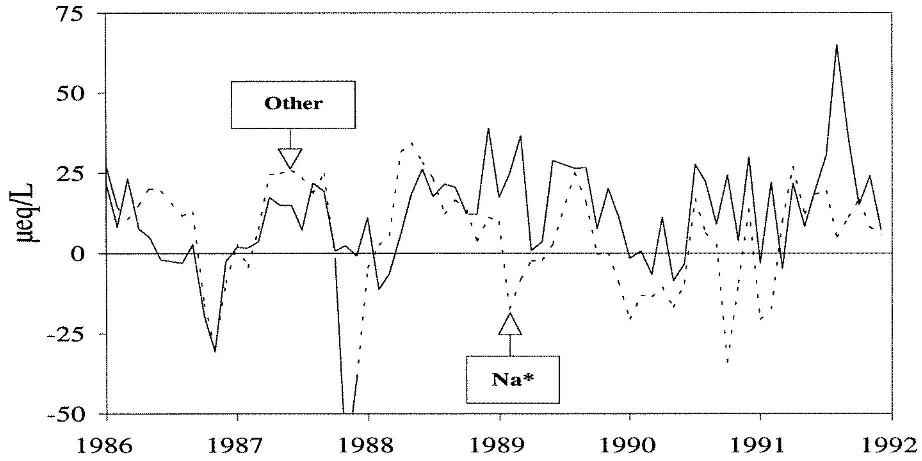


Figure 5.58 Seasonal variations in percentage contribution from $\Sigma Ca^*,Mg^*,Na^*$, ΣAl^{n+}, and H^+ to the $\Sigma(Ca^*,Mg^*,Na^*, \Sigma Al^{n+}, H^+)$ at Kaarvatn based on monthly weighted averages from 1986-1991.





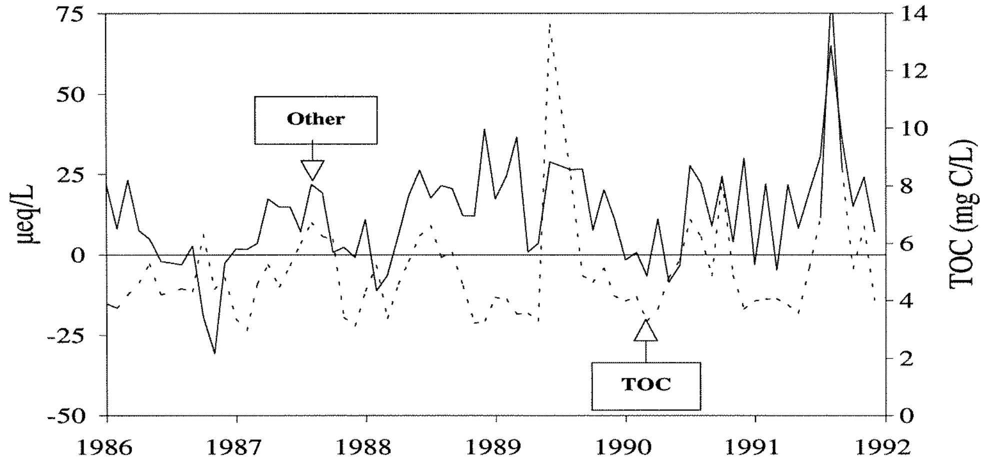


Figure 5.59 Monthly weighted concentrations of non-sulphuric-acid explanatory concentration of ΣBC,Al,H (named Other), and the concentration of nitrate, non-marine sodium (Na*), and total organic carbon (TOC) at Birkenes from 1986 to 1991.*

high (13 mg C/L). There is also a significant positive correlation between non-sulphuric-acid explanatory concentration of ΣBC*,Al,H and non-marine sodium (Na*) (y = 0.46x - 0.89; r = 0.38; n = 70), but because Na* is present in both the x- and y-value, the interpretation of this relationship is far-fetched. Nevertheless, this relationship is of interest to illustrate seasalt events, like in March 1989, when 30% of ΣBC*,Al,H was non-sulphuric-acid explainable, and the concentration of Na* was negative (≈ -20 µeq/L). Negative concentrations of non-marine sodium means that sodium has cation-exchanged, most likely with H^+ and cationic aluminium present on negatively charged sites of organic acids.

At Langtjern, the most organic influenced catchment, there is a significant positive correlation between non-sulphuric-acid explainable concentration of ΣBC*,Al,H and the concentration of TOC (Figure 5.60), i.e. y = 0.10x + 4.56 (r = 0.69; n = 72). This illustrates the importance of TOC for the concentration of ΣBC*,Al,H in runoff at this site.

At Kaarvatn, there is also a positive correlation between non-sulphuric-acid explainable concentration of ΣBC*,Al,H and the concentration of Na* (y = 0.54x -8.04; r = 0.62; n = 72). Because it is also a negative correlation between non-sulphuric-acid explainable concentration of ΣBC*,Al,H and runoff at Kaarvatn (y = -7.6x + 334; r = 0.57; n = 72), it means that residence time of water is very important for the dissolution of non-marine base cations from this catchment. However, as in Birkenes during the winter 1989, an increase in the concentration of non-sulphuric-acid explainable ΣBC*,Al,H occurred simultaneously with a negative concentration of non-marine sodium (Figure 5.61), which indicates acidification of the catchment due to cationexchange by sodium which primarily enters the catchment as a neutral seasalt (NaCl).

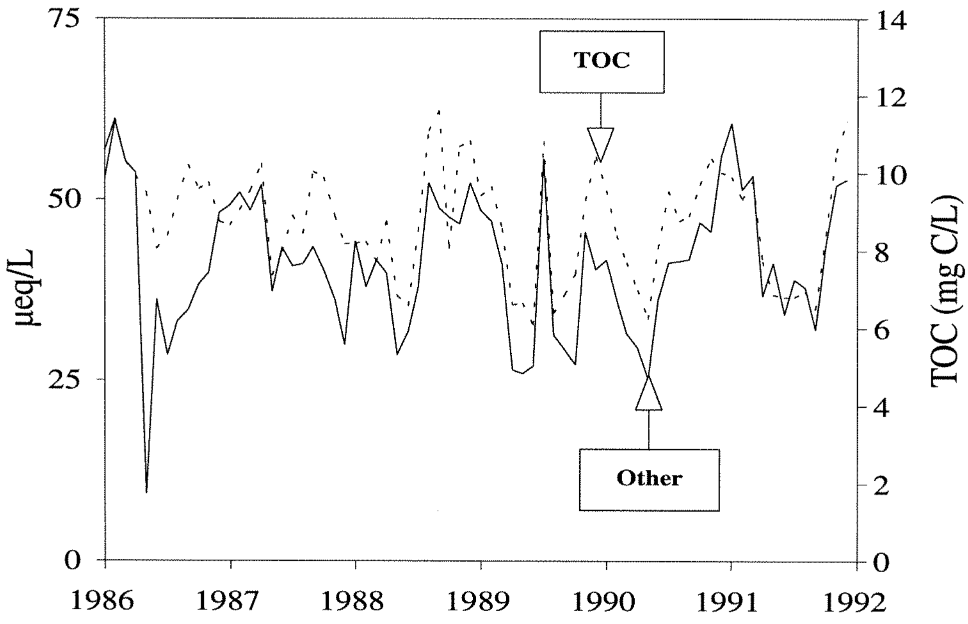


Figure 5.60 Monthly weighted concentrations of non-sulphuric-acid explanatory concentration of ΣBC,Al,H (named Other), and the concentration of total organic carbon (TOC) at Langtjern from 1986 to 1991.*

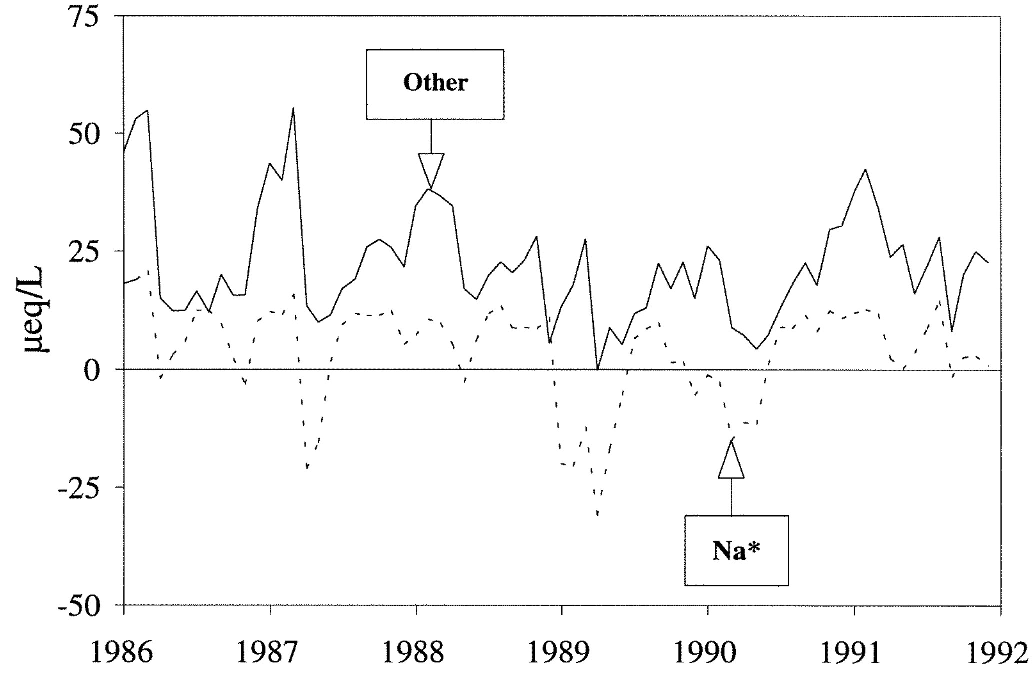
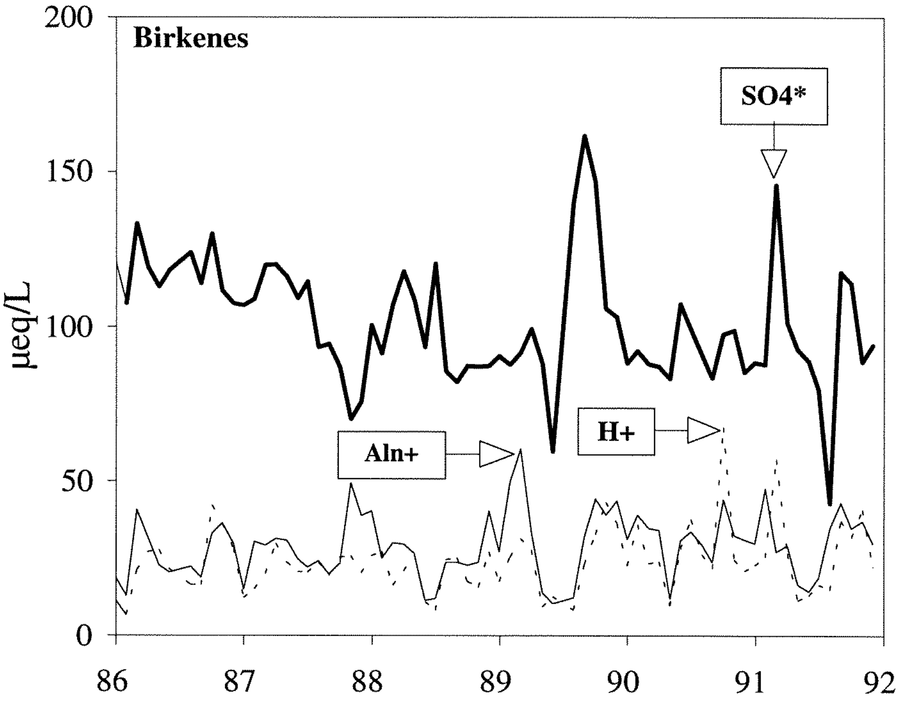


Figure 5.61 Monthly weighted concentrations of non-sulphuric-acid explanatory concentration of ΣBC,Al,H (named Other), and the concentration of non-marine sodium, Na* at Kaarvatn from 1986 to 1991.*

Seasalt episodes

In coastnear sites, seasalt episodes occur no and then. During the last years, there has been several very mild winters in Southern-Norway. Typically, for these winters are heavy rain episodes, which enters this part of Norway from west/south-west, often accompanied by strong winds up to hurricane strength. Thus, the low pressures have passed over large ocean areas, and large amounts of seasalts (primarily NaCl) are therefore able to dissolved in the atmospheric water or transported by winds long distance inland as particles and aerosols. Despite the monthly mean air temperature during the mild winters often is > 0°C, the ground is almost always more or less frozen. Thus, the precipitation will leave the catchment relatively fast through the upper humic-rich soil horizion. The short residence time of water is documented by the fact that there was a statistical significant correlation between the concentration of ΣAl^{n+} in streamwater and the concentration of chloride (and non-marine sodium, Na*) in both streamwater and precipiation at Birkenes during mild winters, while no corresponding precipitation/streamwater relationships were not present during cold years. During cold winters, the precipitation normally enters the catchment as snow, and does not leave the catchment until the initial spring melt occurs.



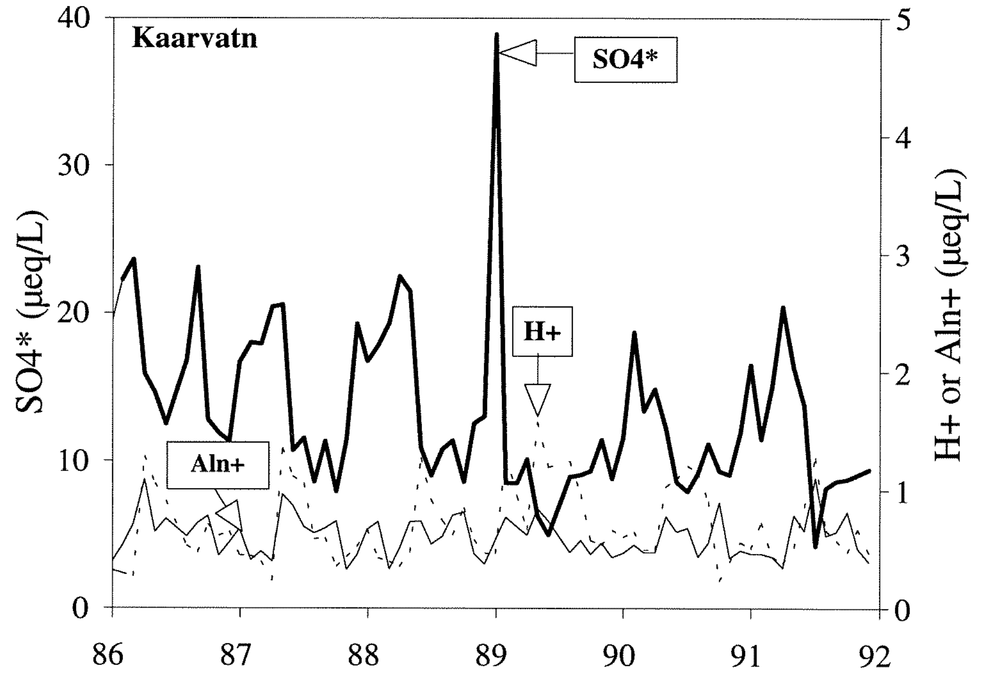


Figure 5.62 Monthly weighted average concentrations of non-marine sulphate (SO_4), H^+ and ΣAl^{n+} at Birkenes and Kaarvatn during 1986-1991.*

Table 5.27 Annual mean water-fluxes and annual weighted mean concentrations of major chemical compounds in runoff at Birkenes during two cold (1986, 1987) and two warm (1989, 1990) years.

	Water-flux			**Streamwater chemistry**								
	Influx	Efflux	Evap.	H^+	Ca^{2+}	Mg^{2+}	Na^+	ΣAl^{n+}	Cl^-	SO_4^{2-}	NO_3^-	TOC
	mm/m²yr			µeq/L								mg/L
Cold	1653	1268	385	23.2	57.5	32.7	109	26.2	119	131	10.9	4.6
	1616	1382	234	21.5	54.2	31.1	110	28.3	124	114	9.4	4.8
Warm	1279	894	385	24.4	64.6	36.1	129	33.3	149	122	15.6	5.4
	1893	1272	621	28.6	56.1	31.4	138	31.4	170	109	10.2	5.0

It is primarily the catchments at Birkenes and Kaarvatn which periodically receive high amounts of seasalts. At both sites, significant linear correlation exist between the concentration of non-marine sulphate (SO_4*) and the concentration of non-marine base cations (ΣCa*,Mg*), but no significant correlations exist between SO_4* and ΣAl^{n+}. Undobtedly, sulphuric acid is the main source of aluminium leakage in most acidified areas, and the concentration of sulphuric acid is therefore decisive for the aluminium concentration level present. However, especially in the acidified coastnear Birkenes catchment, the concentration of seasalts is more essential for the seasonal or short-term fluctuations in the aluminium concentration of streamwater than sulphate. Because aluminium is the most frequent toxic element present in acidified surface waters, it is essential that the most significant difference between cold and warm years in coastnear areas of southern Norway, is the input of NaCl during the winter. Primarily in the Birkenes catchment which is continuously exposed to high amounts of acid rain, substantial amounts of negatively charged organic sites are protonated or complexed with cationic aluminium. Thus, when seasalt episodes occur during the winter when much water leaves the catchment realtively fast through surface and subsurface runoff, substantial cation-exchange reactions may take place in the upper organic soil horizion, where primarily sodium will exchange for H^+ and cationic aluminium.

An idea of the amount of sodium which are involved in such cation-exchange reactions is obtained by estimating the amount of non-marine sodium in streamwater (Na*). When negative Na* values occurs (see Figure 5.63 to 5.66), sodium has been temporarily retained in the catchment. In Southern-Norway seasalt episodes also occur at heavy rainfall at autumn, before the ground is frozen. This is well documented at Birkenes. The monthly weighted mean concentration of chloride during November 1987 was 253 µeq/L, while the highest weakly weighted mean concentration of chloride and Na* during this month was 302 µeq/L and -87 µeq/L. The negative value of Na*, indicates that substantial amounts of sodium was temporarily retained in the catchment due to cation-exchange reactions within the catchment. The highest weakly weighted mean concentrations of H^+ and inorganic monomeric aluminium (labile aluminium = LAL) during this episode were 49 µeq/L (pH = 4.31) and 756 µg Al/L. The highest weakly mean concentration of LAL (807 µeq/L) was, however, measured during a seasalt episode in February/March 1989, when the the highest weakly concentrations of H^+ and Na* were 35 µeq/L (pH = 4.45) and -29 µeq/L.

The time of the year at which seasalt episodes occur is essential for the runoff chemistry at both Birkenes and Kaarvatn. Seasalt episodes during the winter do normally cause the most

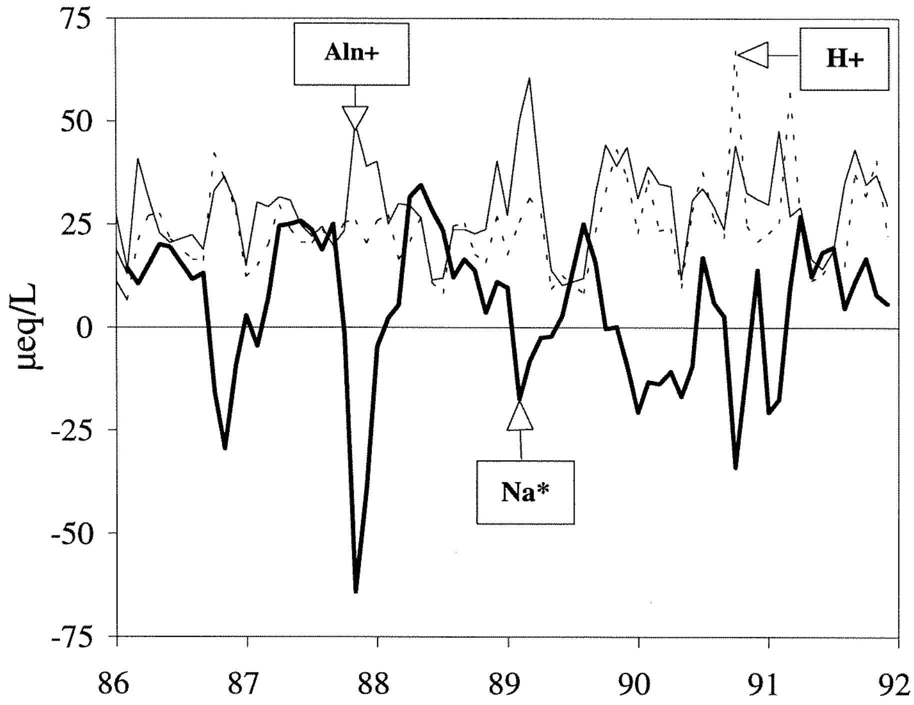


Figure 5.63 Monthly weighted average concentrations of non-marine sodium (Na), H^+ and ΣAl^{n+} in runoff water at Birkenes during 1986-1991.*

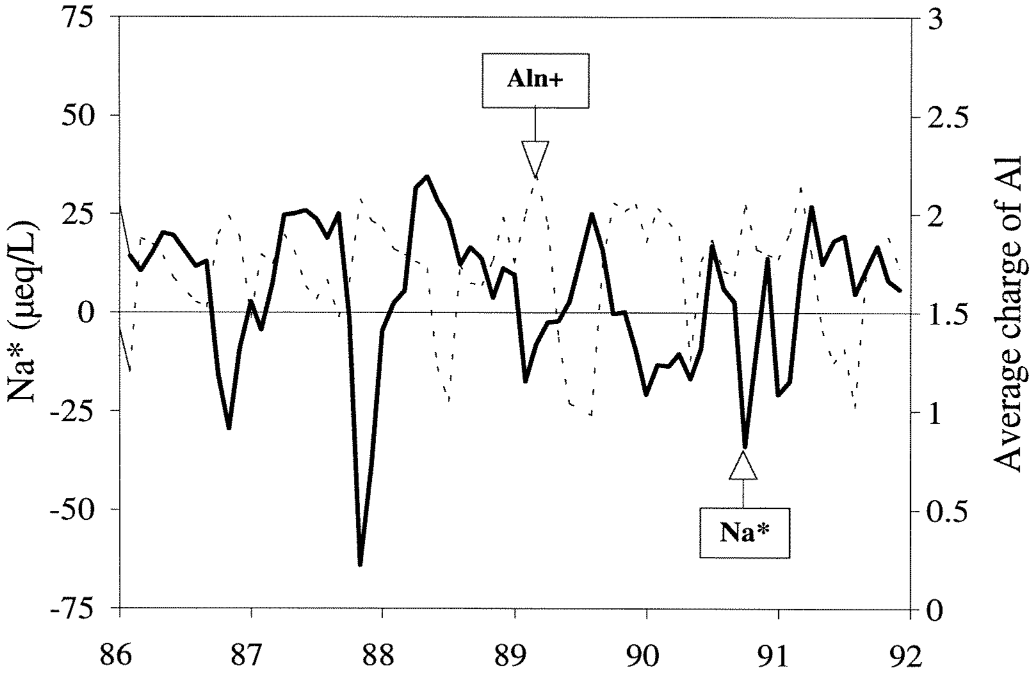


Figure 5.64 Monthly weighted average concentrations of non-marine sodium (Na) and the average charge of dissolved aluminium ions in runoff water at Birkenes during 1986-1991.*

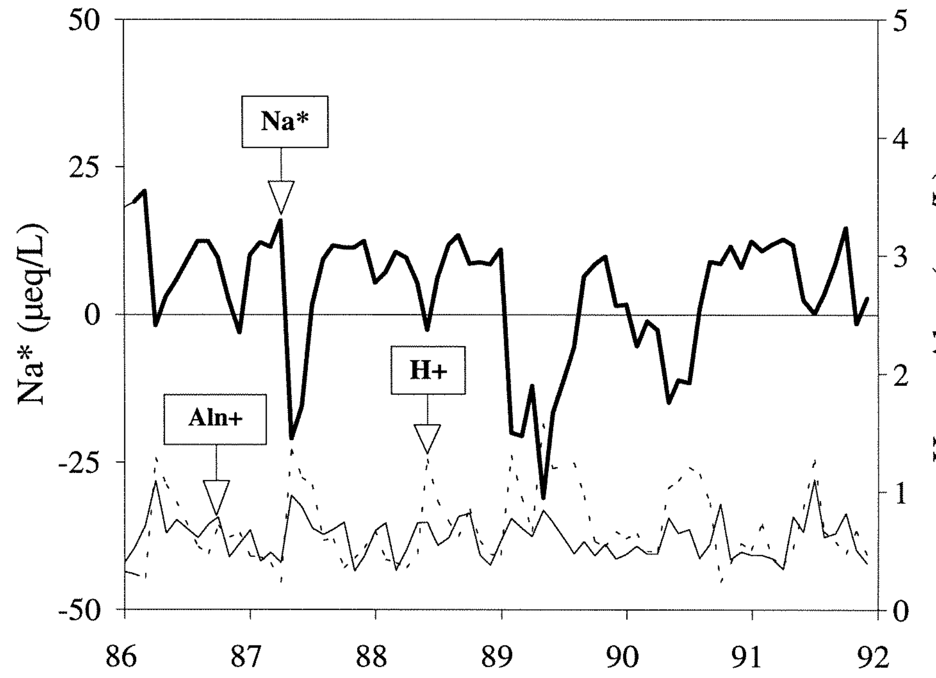


Figure 5.65 Monthly weighted averages concentrations of non-marine sodium (Na), H^+ and ΣAl^{n+} in runoff water at Kaarvatn during 1986-1991.*

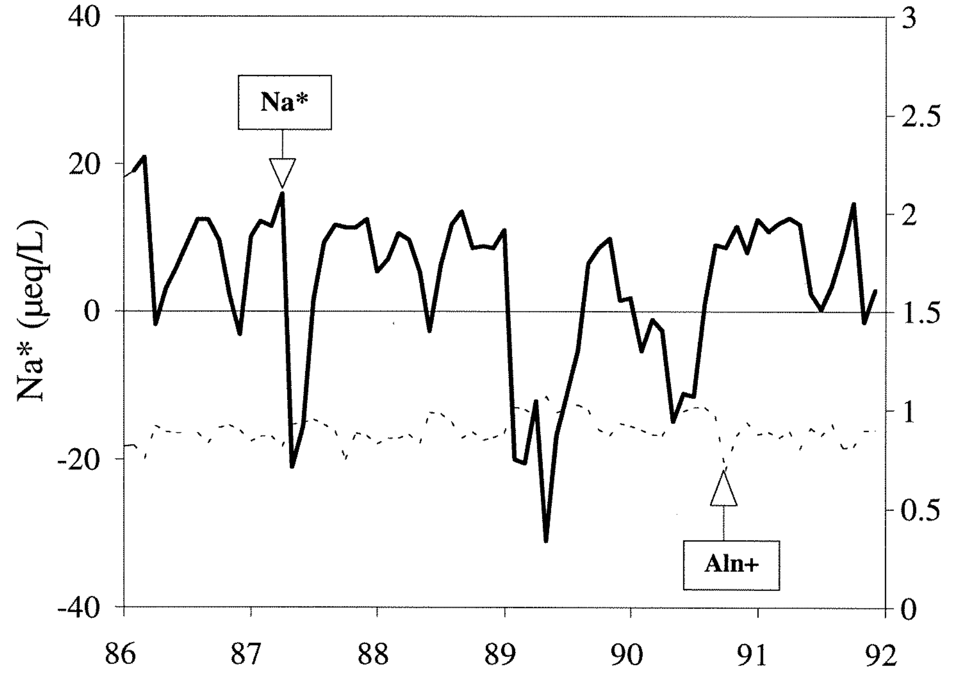


Figure 5.66 Monthly weighted average concentrations of non-marine sodium (Na) and the average charge of dissolved aluminium ions in runoff water at Kaarvatn during 1986-1991.*

severe chemical conditions as far as H^+ and aluminium are concerned. As described earlier, when lowpressures accompanied by strong winds and large amounts of precipitation enters the catchments as rain during the winter, the water is able to leave the catchments relatively fast as surface and subsurface discharge. Thus, this water will primarily flow through the upper organic-rich soil layer, where sodium will cationexchange for aluminium and H^+. Of cause this is aslo the case at seasalt events during autumn, but in these cases, more water is able to penetrate deeper into the inorganic soil layers. Thus, much of the dissolved aluminium and H^+-ions from the cationexchange reactions higher up in the organic humic layer, are able to be retained in the catchment again by variuos neutralization/ precipitation reactions.

If one of the main effect of global warming is warmer winters with stronger and more frequent seasalt episodes, it may have negative consequences for the surface water chemistry in acidified coastnear areas of Southern-Norway, due to the elevated aluminium concentration associated with such episodes(see Table 5.27).

Corresponding effects of seasalt episodes on runoff water chemistry are well documented earlier (e.g. the (Sullivan et al., 1988) and also specific at Birkenes (e.g. Mulder et al, 1990; Mulder et al, 1991).

Total organic carbon

Production of organic acids, such as citric, tartaric, tannic and oxalic acids by biological activity within the soil zone, is undoubtedly of great importance for the weathering and thereby important for the runoff water chemistry of most catchments. Unfortunately, the quantitative effects that these organic acids exert are difficult to assess from the data available. However, it is possible to estimate a total average charge of the organic humic acids by assuming charge balance, and interprete the total changes in the average charge (AC) of these compounds. AC of organic acids is estimated as [AC]: [ΣCations] - [ΣAnions], when the average charge of Al (ΣAl^{n+}) is incorporated in the [ΣCations]. For this purpose the ALCHEMI-speciation programme (Schecher and Driscoll, 1987, 1988) was used. The difference between ΣCations ($[H^+]+[Ca^{2+}]+[Mg^{2+}]+[Na^+]+[K^+]+[\Sigma Al^{n+}]$) and ΣAnions ($[SO_4^{2-}]+[Cl^-]+[NO_3^-]+[HCO_3^-]$) is then the AC of organics. By further evaluating the AC of organics in relation to the measured concentration of total organic carbon (TOC) in runoff, it is possible to estimate the average net charge (NC) of the dissolved organic pool, i.e. NC = AC/TOC (unit: μeq of charges/mg C). Because AC: ΣCations - ΣAnions, positive values means that there is a total net of negative charges present on the organic complexes, while negative values means that a net of postive charges are present. Based on monthly weighted averages from 1986-1991, Storgama and Langtjern normally exhibit positive AC-values of organics during the whole year. Monthly negative AC-values are only present at Birkenes during January, February and March and at Kaarvatn during May, November and December. Negative AC-values are no and then also recorded at Storgama, primarily during autumn and winter months, while negative AC-values is so far never recorded at Langtjern, the most humic-influenced runoff water. Despite negative AC- or NC-values means a positive net charge on the organic complexes, unprotonated negative sites (like $[RCOO]^-$, with AC = -1) may, however, very well be present, but the majority of organic sites exhibit a net of positive charges, i.e. $Al^{3+} + [RCOO]^- = [RCOOAl]^{2+}$ (AC = +2). Thus, the total charge of organics will be positive.

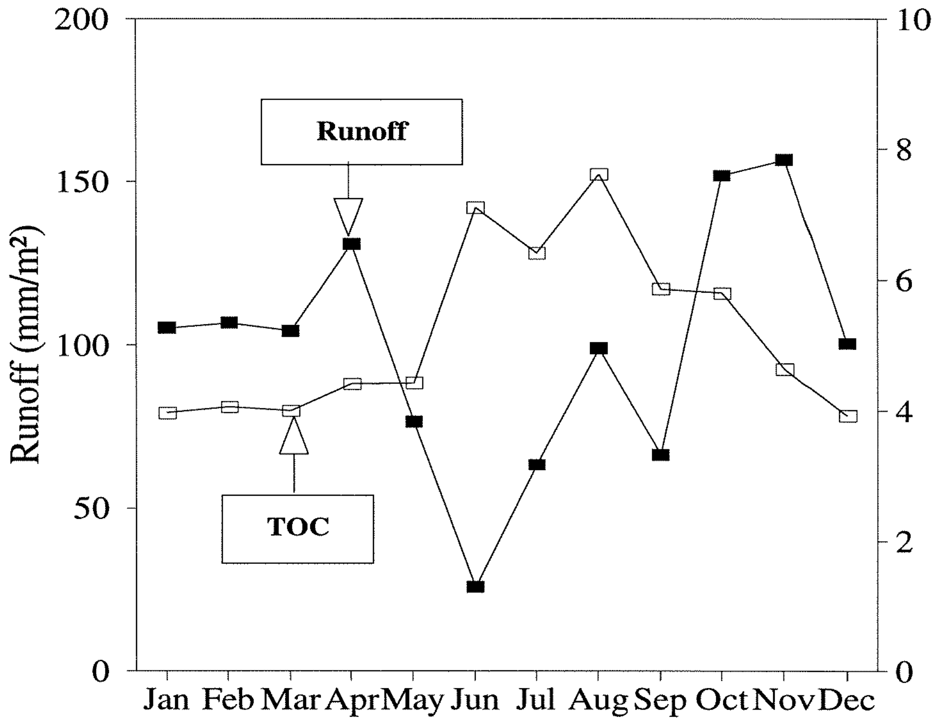


Figure 5.67 Monthly runoff means and monthly weighted concentration means of total organic carbon (TOC) at Birkenes, based on monthly weighted averages from 1986-1991.

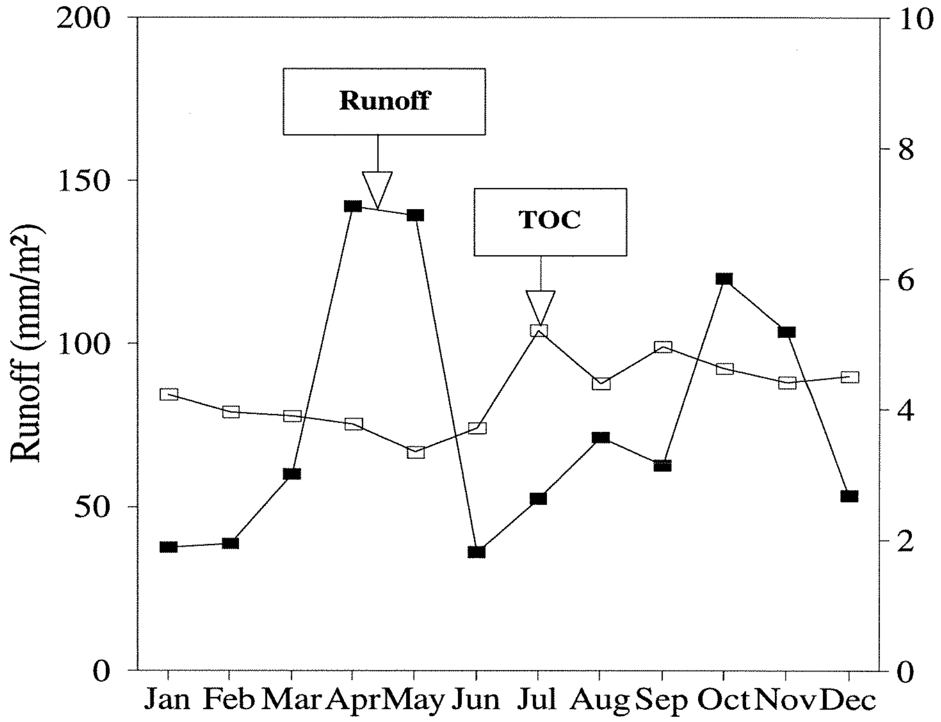


Figure 5.68 Monthly runoff means and monthly weighted concentration means of total organic carbon (TOC) at Storgama, based on monthly weighted averages from 1986-1991.

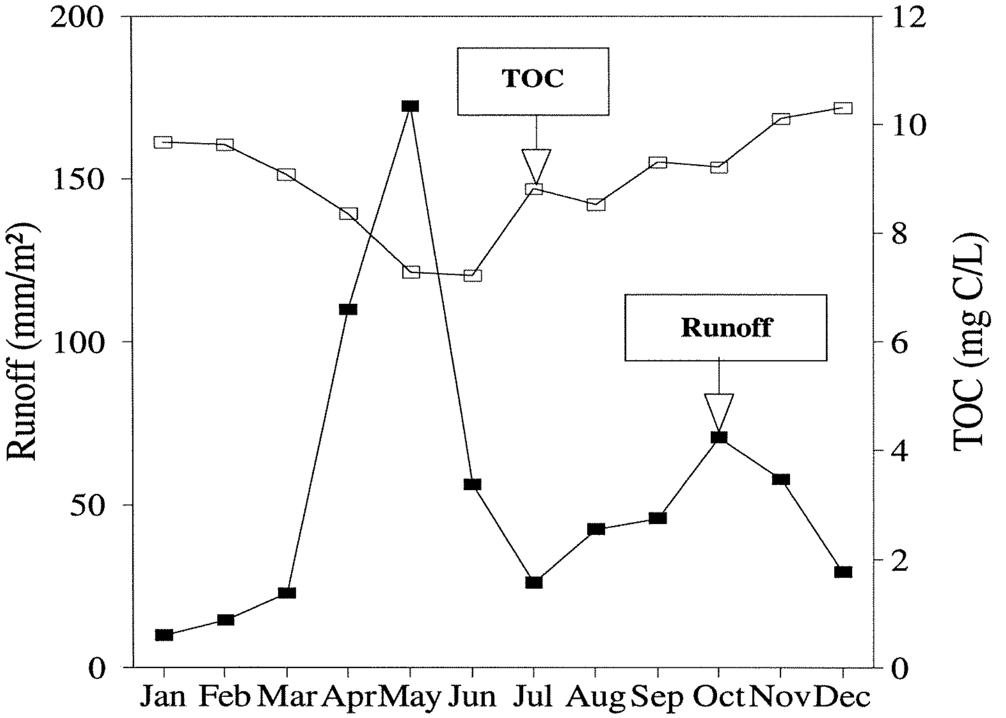


Figure 5.69 Monthly runoff means and monthly weighted concentration means of total organic carbon (TOC) at Langtjern, based on monthly weighted averages from 1986-1991.

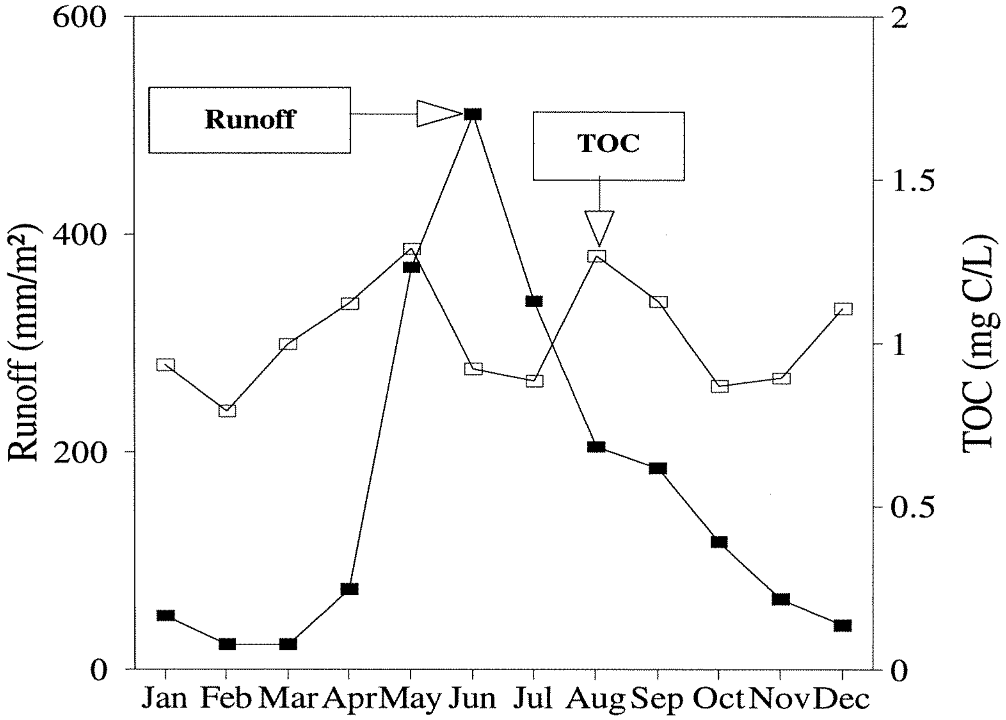


Figure 5.70 Monthly runoff means and monthly weighted concentration means of total organic carbon (TOC) at Kaarvatn, based on monthly weighted averages from 1986-1991.

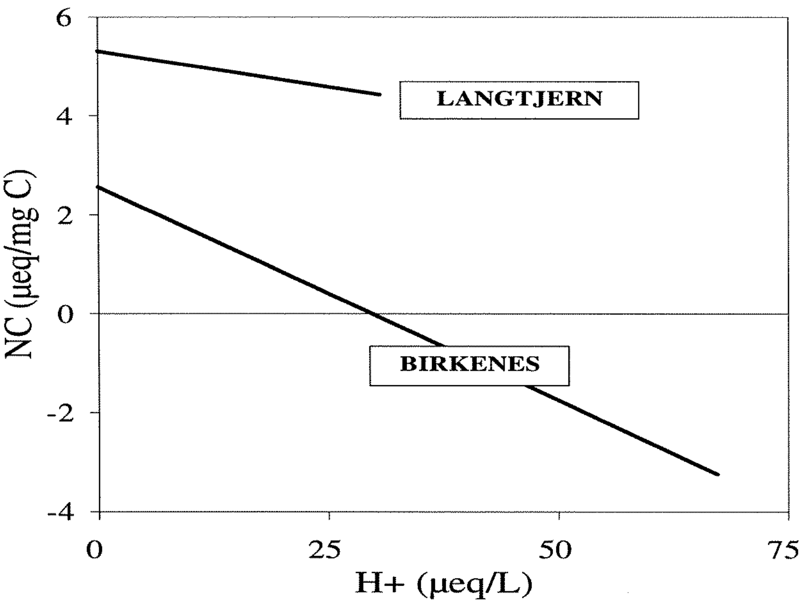


Figure 5.71 The relationship between concentration of H^+ and NC (µeq of charges/ mg C) of organic compounds present in runoff water at Birkenes and Langtjern. The relationships rely on simple linear regression analyses by using monthy weighted means from 1986-1991. Birkenes: y = -0.086x + 2.56 (r = -0.28) (n = 70); Langtjern: y = -0.029x + 5.31 (r = -0.24) (n = 72). Positive NC-values mean net negative charges on organics.

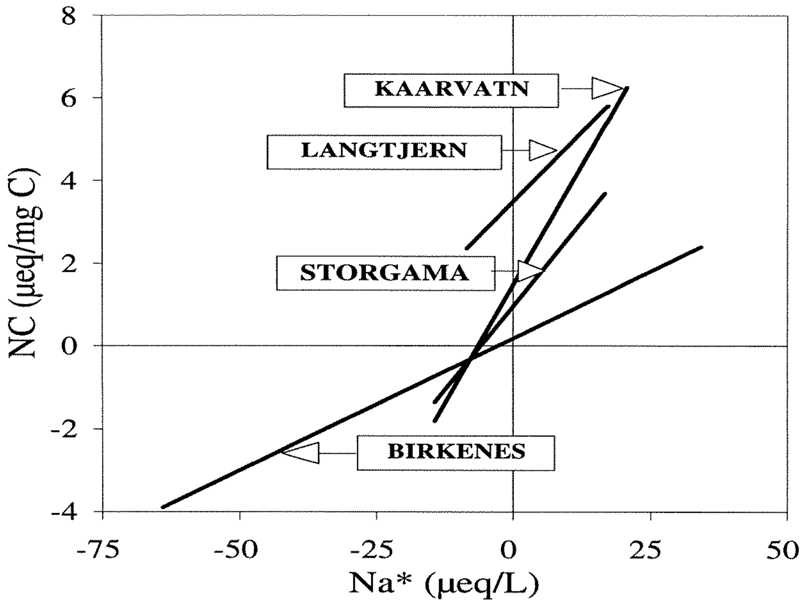


Figure 5.72 The relationship between concentration of non-marine sodium (Na) and NC (µeq of charges/ mg C) of organic compounds present in runoff water at the four catchments. The relationships rely on simple linear regression analyses by using monthy weighted means from 1986-1991. Birkenes: y = 0.063x + 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-values mean net negative charges on organics.*

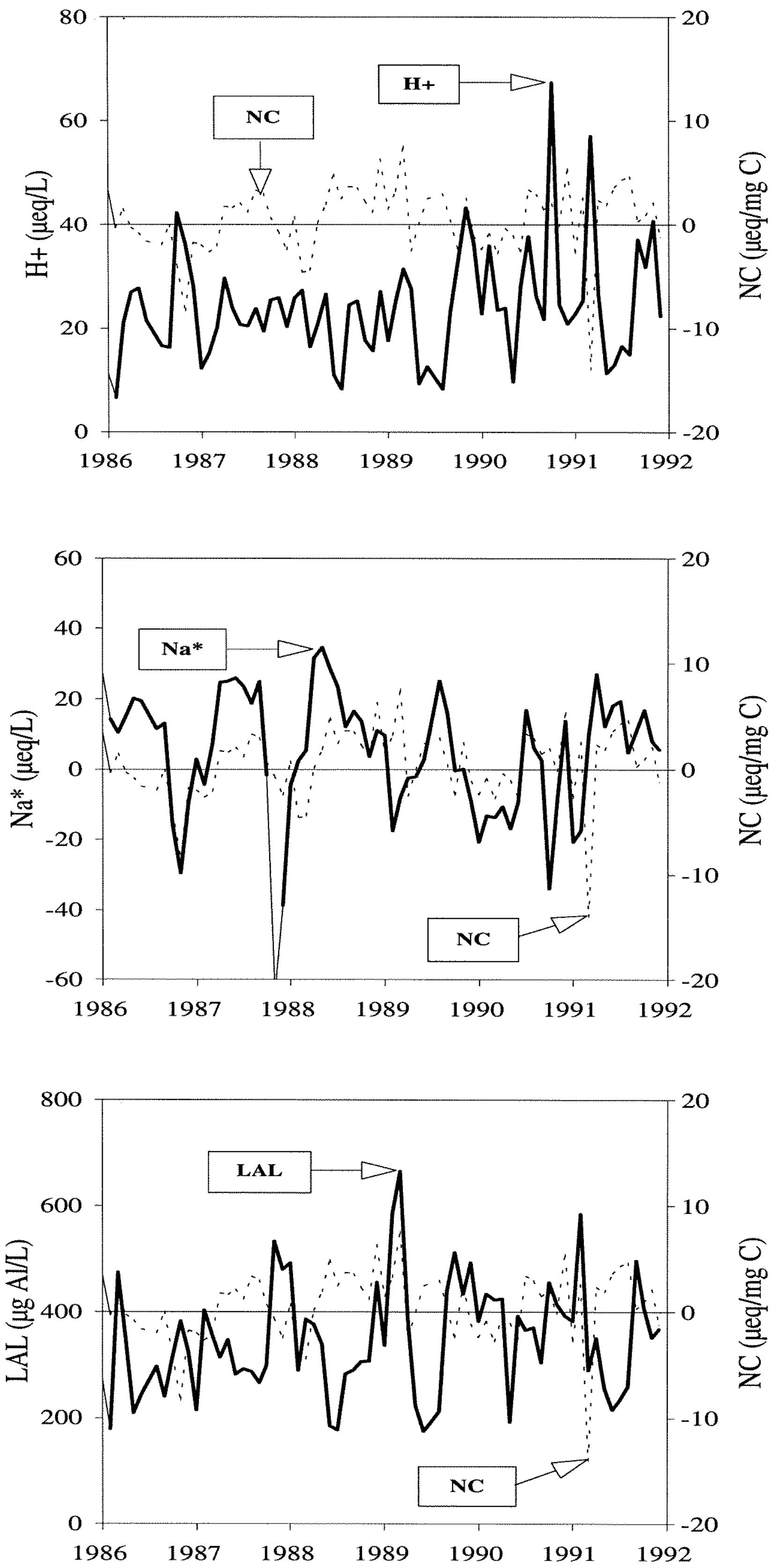


Figure 5.73 Monthly variations in the NC (μeq of charges/mg C) of organic compounds and the concentration of H^+, non-marine sodium (Na), and labile aluminium (LAL) at Birkenes during 1986-1991. Positive NC-values mean net negative charges on organics.*

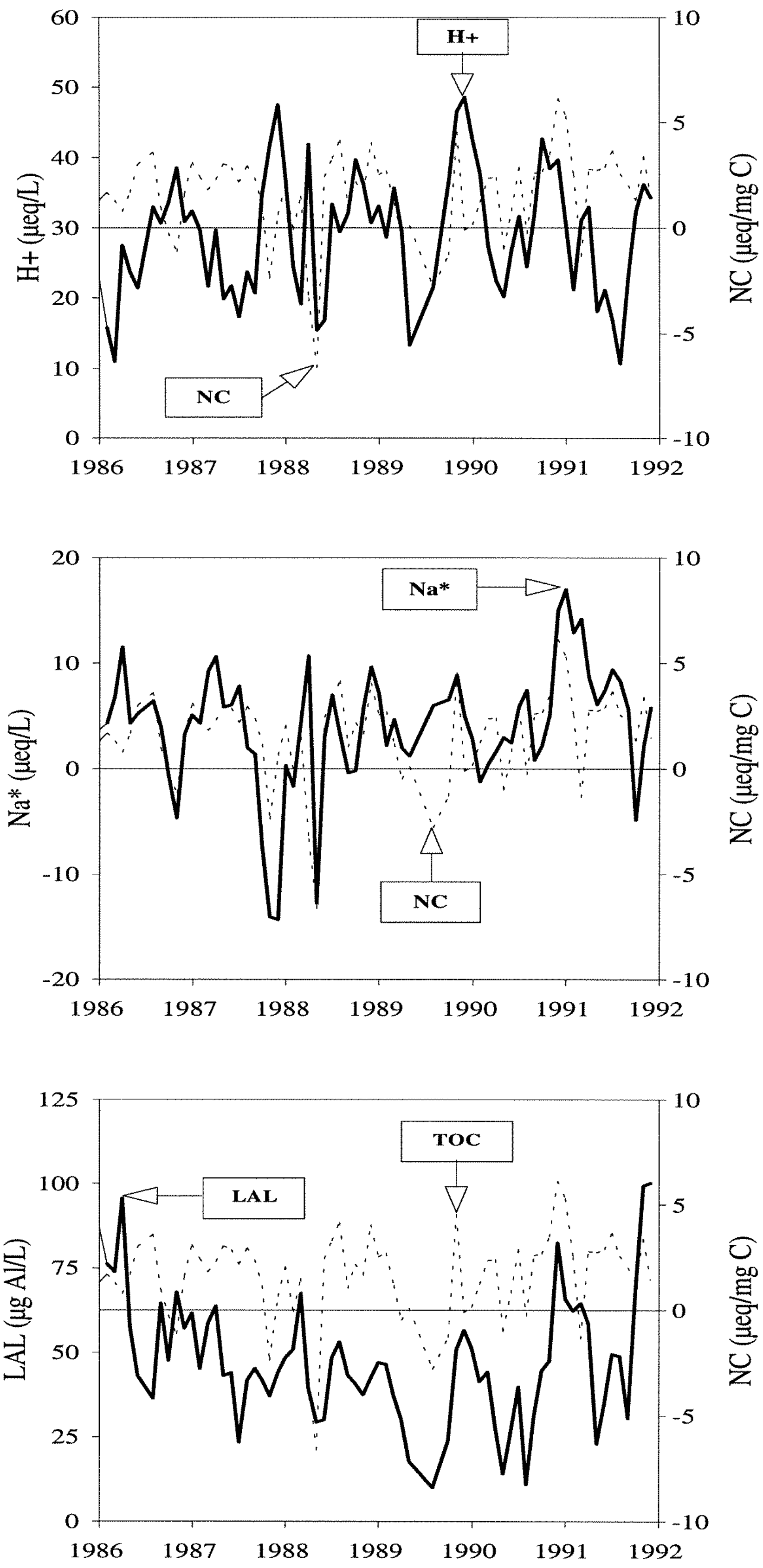


Figure 5.74 Monthly variations in the NC (µeq of charges/mg C) of organic compounds and the concentration of H+, non-marine sodium (Na), and labile aluminium (LAL) at Storgamas during 1986-1991. Positive NC-values mean net negative charges on organics.*

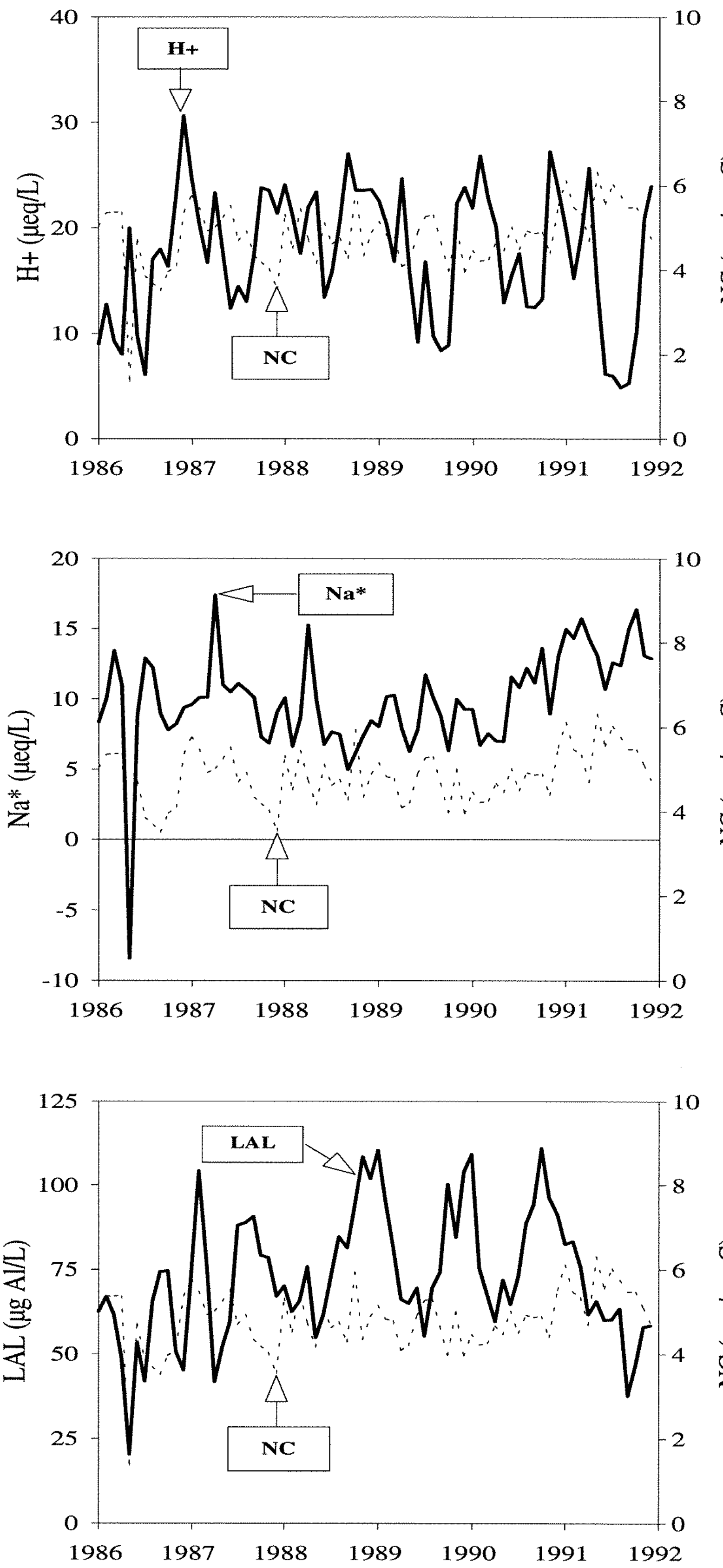


Figure 5.75 Monthly variations in the NC (µeq of charges/mg C) of organic compounds and the concentration of H^+, non-marine sodium (Na), and labile aluminium (LAL) at Langtjern during 1986-1991. Positive NC-values mean net negative charges on organics.*

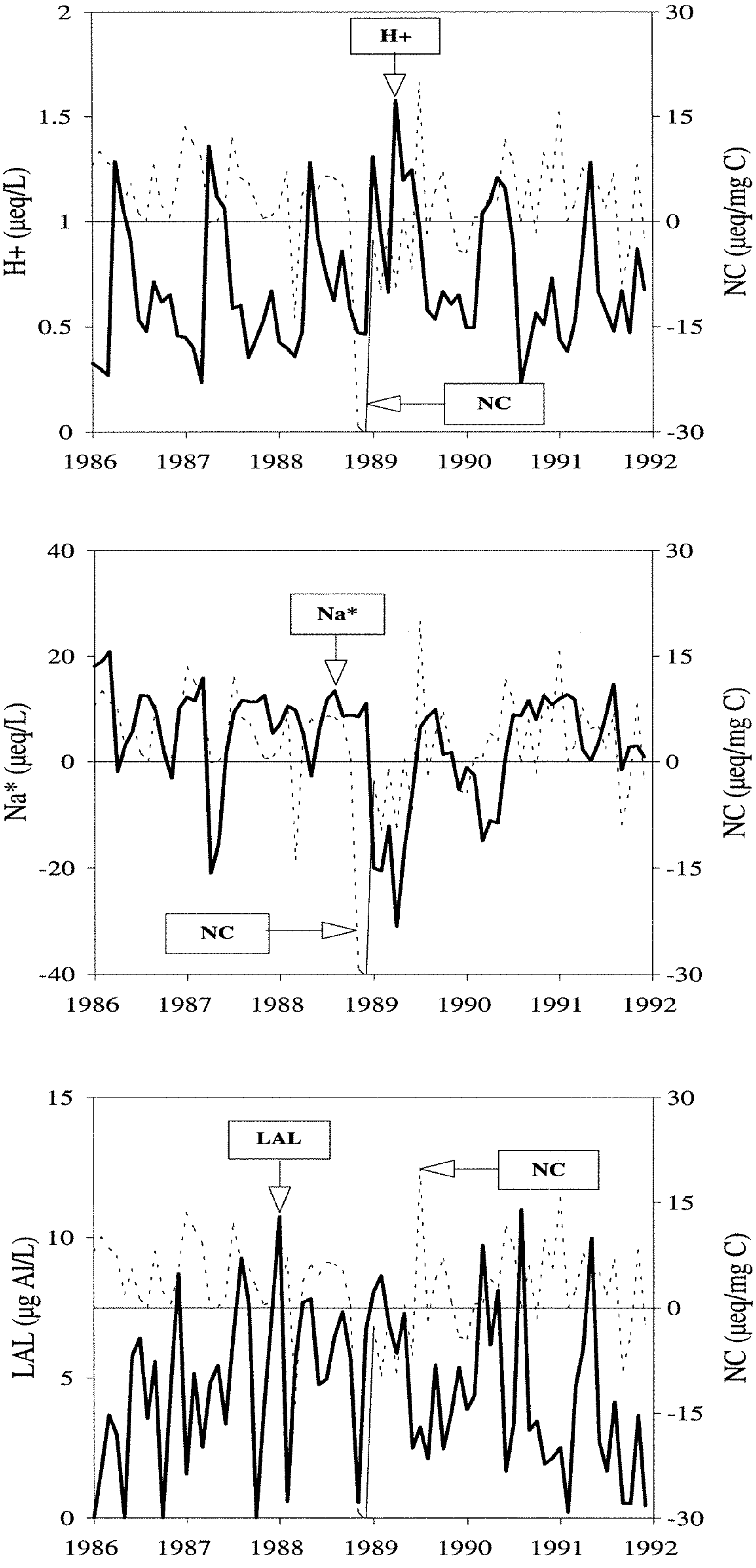


Figure 5.76 Monthly variations in the NC (μeq of charges /mg C) of organic compounds and the concentration of H^+, non-marine sodium (Na), and labile aluminium (LAL) at Kaarvatn during 1986-1991. Positive NC-values mean net negative charges on organics.*

There are no significant correlation between monthly runoff and monthly average concentration of total organic carbon (TOC) at any of the four catchments (Figure 5.67..5.70), but the highest TOC-concentrations normally occur at low-flow at late summer.

Only in runoff at Birkenes and Langtjern a significant negative correlation was found between H^+ concentration and NC of organics (Figure 5.71). Simply evaluated, this means that when the H^+-concentration increases, negative organic sites are protonated so that the total NC of organics decreases. Despite the pH of rainwater does not deviate very much between the two sites, the average H^+-concentration in runoff is lower and the variation in H^+-concentration smaller at Langtjern compared with runoff water at Birkenes. This is due to factors as lower inputs of rain (longer residence time of water) and seasalts, and higher pH-buffering from organic acids at Langtjern compared with at Birkenes. The fact that no significant correlation was found between H^+ and NC of organics at Storgama and Kaarvatn might have several causes. At both sites, especially at Storgama, substantial amount of precipitation falls on bare rock, which means that a lot of chemical reactions have already taken place before the water enters the patchy humic areas present. At Kaarvatn, the pH of rainwater is fairly high, the pH-buffering capacity of the catchment is good, and the concentration of total organic compounds in runoff water is very low. Thus, no significant H^+/NC relationship should therefore be expected at this site, because of the combination of low organic content and the fact that pH in runoff water is almost the same all the year.
At all sites there are a significant positive correlation between non-marine sodium (Na*) and NC of organic compounds in the runoff (Figure 5.72). This means that a decrease in sodium-ions in relation to chloride ions often is a confirmation of cation-exchange. Sodium may either occupy exposed negative organic sites present, or cation-exchange for H^+ or other cations already complexed to organic anions. If sodium substitutes for H^+ on organics, it means that soil-water pH will decrease. But because the weak organic acids are pH-buffers, they are able to take up H^+-ions again. This, in addition to the pH-buffering of Al-dissolution processes, means that a smaller or no pH decrease often is measured in the runoff water.

Only at Langtjern, there is a positive correlation between ΣCa*,Mg* and NC of organic compounds in runoff water. This may have an hydrological explanation, because Langtjern is the only site which also exhibits a negative correlation between runoff and NC of organics.

At all catchments, the major part of calcium and magnesium originates from weathering reactions within the catchments. Based on monthly weighted averages during 1986-1991, 63 ± 10%, 80 ± 7%, 94 ± 2% and 70 ± 10% of the ΣCa,Mg originates from non-marine sources (ΣCa*,Mg*) at Birkenes, Storgama, Langtjern and Kaarvatn, respectively. This comfirms that calcium and magnesium primarily originates from weathering reactions within the catchments. The major source of sodium, on the other hand, is from rainwater. During the same period (1986-1991), the mean contributions from sodium to the total amount of base cations in wet-deposition at the four sites are 63 ± 14% (Birkenes), 53 ± 16% (Storgama), 39 ± 15% (Langtjern), and 66 ± 12% (Kaarvatn).

At all sites, no correlation was found between the NC of organic complexes and the concentration of inorganic aluminium (LAL) or ΣAl^{n+}. This lack of correlation, and the lack of correlation between divalente base cations and NC of organic compounds (except at Langtjern) may rely on several factors:

1) Except for NH_4^+-ions, which are taken up relatively fast by the vegetation, the predominant cations in precipitation at all sites are H^+-ions and Na^+-ions. Because most of the organic compounds are present in the uppermost soil-horizion, the majority of rainwater has to pass through this layer on its way to rivers and lakes. The H^+- and Na^+-ions may therefore very well be the most important cations, as far as the chemical influence on the quality of organic compounds is concern. When water penetrate further down into more inorganic soil layers, or when water from these deeper layer is pressed up into the uppermost organic soil horizion, divalente base cations and aluminium may substitute for H^+ and Na^+, but due to the lack of correlation between base-cation or aluminium and NC of organics, these cation-exchange processes seem to have minor effect on the NC of organic substances.

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

3) Similar to the organic acids, aluminium itself acts as a pH-buffer, where H^+-ions are taken up or released dependent on the pH of solution. Thus, a pH change affects both the average charge of organic acids and aluminium.

4) The negative correlation between NC of organics and H^+ concentration in the two most TOC-rich runoff waters, Langtjern and Kaarvatn, may indicate that humic acids to a certain degree is influencing on the pH of runoff-water, when the concentration of TOC is relatively high.

5.7 The acid neutralizing capacity (ANC)

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

$$ANC = [Ca^{2+}]+[Mg^{2+}]+[Na^+]+[K^+] - [SO_4^{2-}]+[Cl^-]+[NO_3^-]$$

Basically, ANC is a collective term for the concentration of organic anions (A^-), alkalinity (as HCO_3^-) in relation to the concentration of H^+, and aluminium (ΣAl^{n+}), i.e. $ANC = ([A^-] + [HCO_3^-]) - ([H^+] + [\Sigma Al^{n+}])$. 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^-) is high like at Langtjern. When negative ANC-values occur, aluminium is able to enters into solution in relatively high concentrations, and pH is normally < 5.0 (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 tend to 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 (Schecher and Driscoll, 1987, 1988).

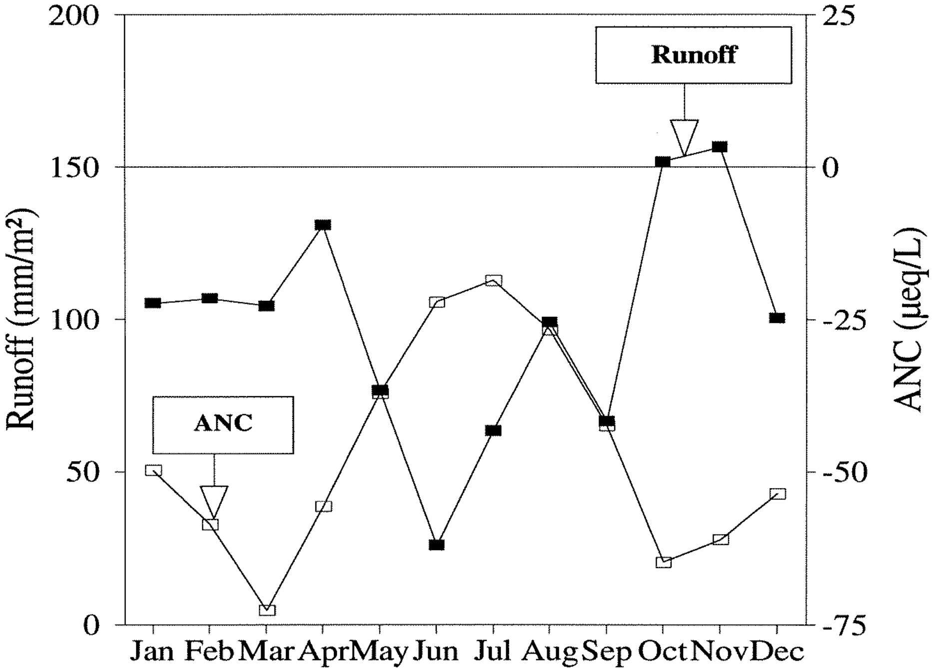


Figure 5.77 Monthly runoff-means and mean acid neutralizing capacity (ANC) in runoff at Birkenes, based on monthly weighted averages during 1986-1991.

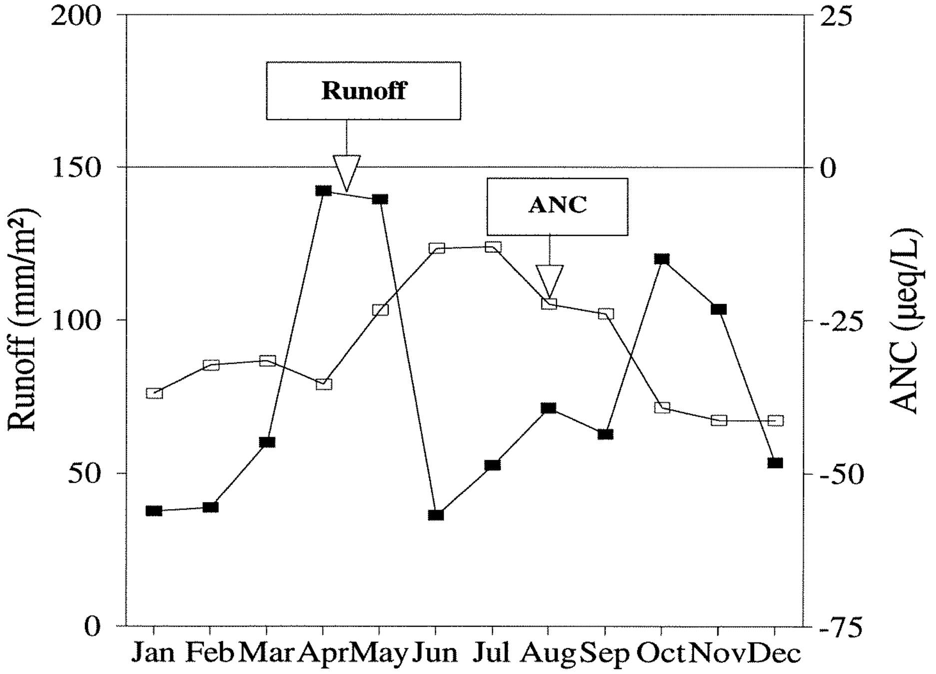


Figure 5.78 Monthly runoff-means and mean acid neutralizing capacity (ANC) in runoff at Storgama, based on monthly weighted averages during 1986-1991.

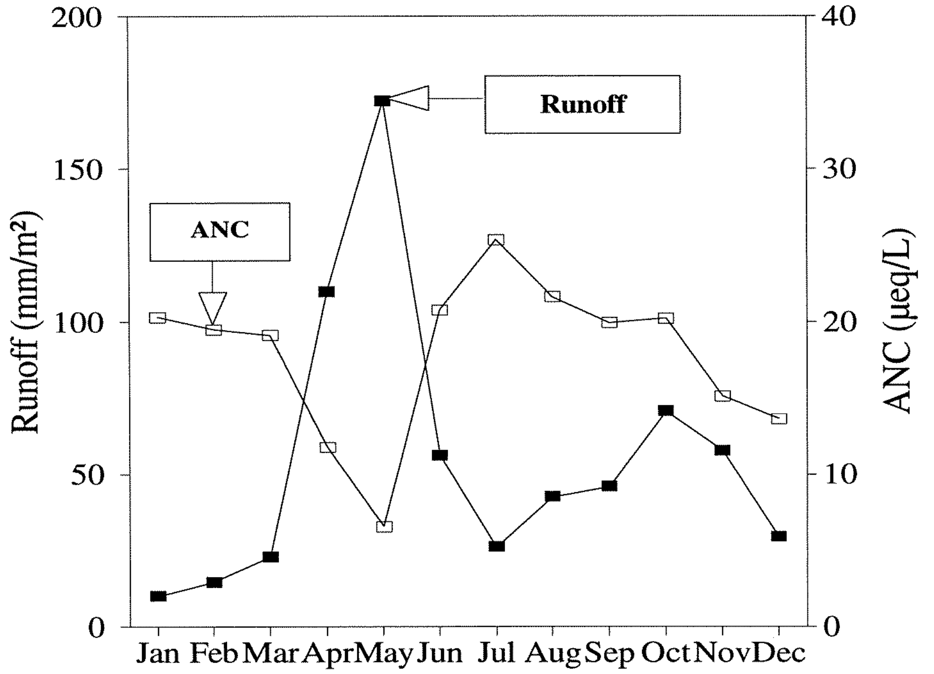


Figure 5.79 Monthly runoff-means and mean acid neutralizing capacity (ANC) in runoff at Langtjern, based on monthly weighted averages during 1986-1991.

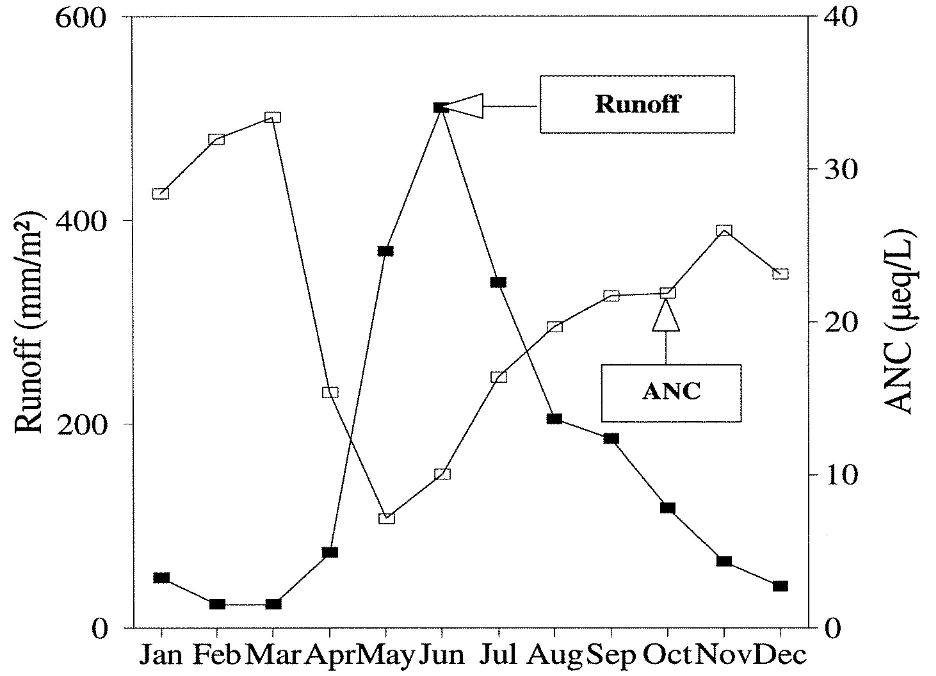


Figure 5.80 Monthly runoff-means and mean acid neutralizing capacity (ANC) in runoff at Kaarvatn, based on monthly weighted averages during 1986-1991.

In extremely acidified areas or during very acidic episodes, the average charge of organics may be positive, which means that the amount of positive charges from base cations, cationic aluminium, and H^+ associated with organic complexes are higher than the amount of negative charges present on the organic complexes. Positive net charge in the organic complexes may very well occur, i.e. $Al^{3+} + [RCOO]^- = [RCOOAl]^{2+}$ (AC = +2). Despite a positive net charge of organic complexes, unprotonated negative sites (e.g. $[RCOO]^-$, with AC = -1) may, however, very well be present, but other organic sites may then have a relatively higher positive net charge. This will cause a total excess of positive charges on organic complexes compared with the amount of negative organic sites present . Under such conditions, the use of $[A^-]$ to express the average charge of organic complexes may be somewhat misleading, because the total net charge of organics than is positive, not negative.

The mean ANC-values, based on monthly weighted averages from 1986-1991, are -49 ± 28 µeq/L (Birkenes), -33 ± 14 µeq/L (Storgama), 16 ± 10 µeq/L (Langtjern) and 22 ± 12 µeq/L (Kaarvatn).

The acid neutralizing capacity (ANC) is normally at the highest during the low-flow period during summer (Figure 5.77..5.80). There is a significant negative correlation between runoff and ANC at Birkenes, Langtjern and Kaarvatn, most significant at Kaarvatn (Figure 5.81). Also at Storgama a negative relationship exists, but it is not significant at this site. This means that the residence time of water is very important for the ANC of the catchments.

At all sites, there are a positive significant correlation between the concentration of organic anions and ANC (Figure 5.82). 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 means that more organic anions will complex with H^+ and cationic aluminum. Especially at Birkenes, but also at Kaarvatn and Storgama, negative values of A^- occur no and then, which indicates a total net positive charge of organic complexes. Also seasalt episodes may lead to negative A^--values, when sodium is complexed to negative organic sites and/or substitutes for H^+ and aluminium on organic sites.

All four catchments exhibit negative correlations between ANC and the concentration of aluminium (ΣAl^{n+}) in runoff water, but at Langtjern the correlation is not significant (Figure 5.83). Due to the high concentration of dissolved organic carbon present in runoff water at Langtjern, ANC-variations in runoff water tend to have minor influence on the aluminium chemistry. The most significant negative correlation between ANC and ΣAl^{n+} is present at Storgama (r = -0.70) and Birkenes (r = -0.65)

At all catchments, there are significant negative correlations between the concentration of chloride and ANC in runoff (Figure 5.83), most significant at Storgama (r = -0,74) and Birkenes (-0.48). Correspondingly there are significant positive correlations between ANC and the concentration of non-marine sodium (Na*) in runoff water at all four sites. This means that when the Na*-value is decreasing, more sodium is temporarily retained in the catchment due to cation-exchange. This further leads to an increase in concentration of H^+ and/or ΣAl^{n+} in solution, which means that ANC is decreasing. The most significant correlations between Na* and ANC are present at Kaarvatn (r = 0.65) and at Langtjern (r = 0.57).

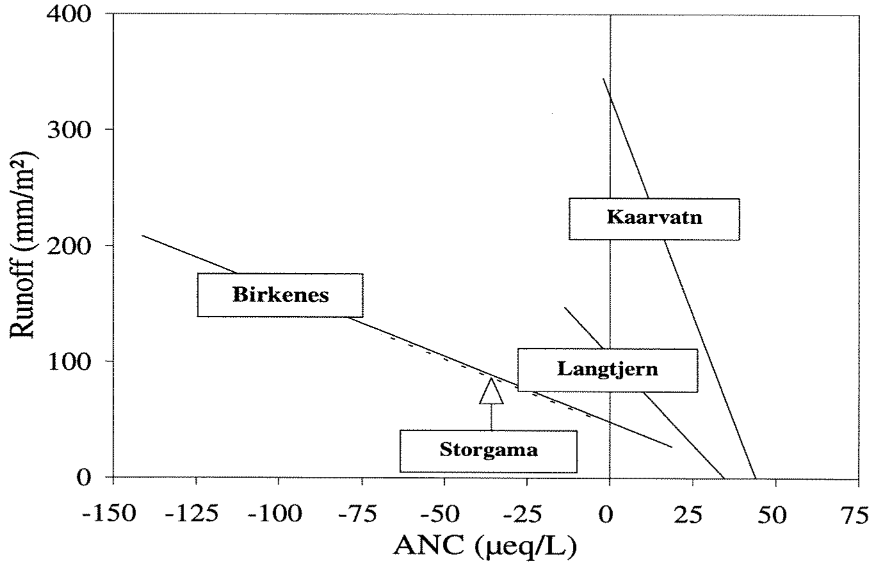


Figure 5.81 The relationships between acid neutralizing capacity (ANC) and runoff, based on monthly weighted averages from 1986-1991. The correlations are based on linear regression analyses, and the correlations are assumed to be significant when $p < 0.05$. Continuous line means $p < 0.05$, dotted line means $p > 0.05$. The regression lines are: Birkenes: $y = -1.15x + 48.7$ ($r = -0.39$) ($p < 0.01$); Storgama: $y = -1.12x + 46.7$ ($r = -0.18$) ($p > 0.05$); Langtjern: $y = -3.06x + 106.1$ ($r = -0.42$) ($p < 0.01$); Kaarvatn: $y = -7.51x + 329.3$ ($r = -0.57$) ($p < 0.01$).

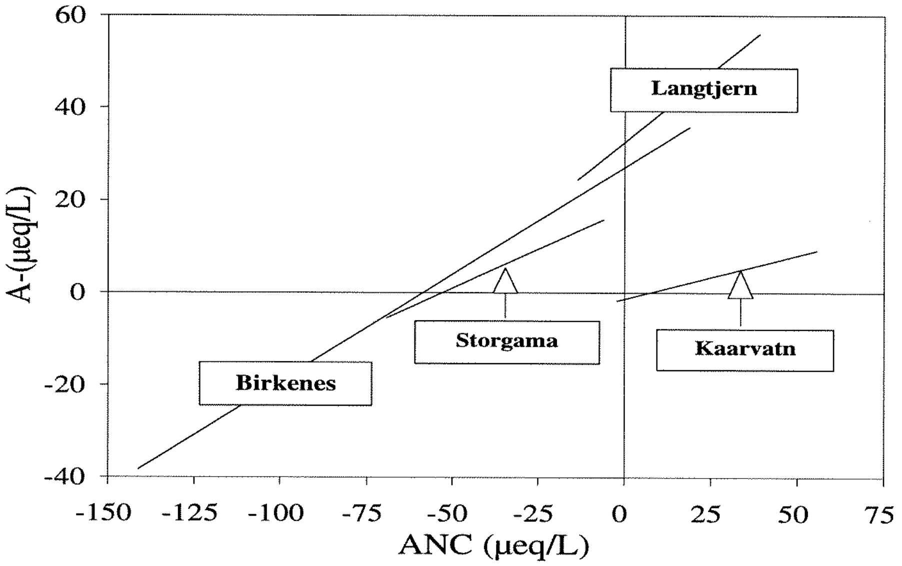


Figure 5.82 The relationships between acid neutralizing capacity (ANC) and concentration of organic anions (A^-), based on monthly weighted averages from 1986-1991. The correlations are based on linear regression analyses, and the correlations are assumed to be significant when $p < 0.05$. Continuous 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: $y = 0.19x - 1.44$ ($r = 0.33$) ($p < 0.01$).

At all catchments, significant negative correlations was found between ANC and the concentration of H^+ in runoff water (Figure 5.84), most significant at Birkenes (r = -0.78) and Storgama (r = -0.78). Concerning concentration of non-marine sulphate (SO_4*) and ANC, significant negative correlations exist at Birkenes, Storgama and Langtjern, while at Kaarvatn a significant positive correlation is present (Figure 5.84). This means that when the concentration of SO_4* increases, the ANC at Kaarvatn also increases. At Kaarvatn this is primarily due to the fact that there is a significant negative correlation between monthly runoff and the monthly weighted average concentration of SO_4*. This means that the highest concentration of SO_4* normally is present at low runoff. Because SO_4* primarily expresses the concentration of sulphuric acid, this means that a long residence time of water within the catchment causes an increase in the acid neutralizing capacity (ANC) of the catchment, but it also indicates that the sulphuric acid to some extent may act as a catalyst in the weathering/dissolution reactions whith base cations in this weakly acidified catchment.

At Birkenes, Langtjern and Kaarvatn, there are significant positive correlations between ANC and the concentration of non-marine base cations, i.e. ΣCa*,Mg* (Figure 5.84), most significant at Kaarvatn (r = 0.66). This means that the acid neutralizing capacity (ANC) is high when the concentration of base cations is high, which also should be expected. At Storgama, however, a significant negative correlation exists between ANC and the concentration of ΣCa*,Mg* in runoff water (r = -0.51). This means that the concentration of non-marine base cations increases when the acid neutralizing capacity is decreasing, which sounds like a water-chemical paradox. As expected there is a very significant positive correlation between the concentration of non-marine sulphate (SO_4*) and ΣCa*,Mg* in runoff water at Storgama (Figure 5.85). But compared with the other sites which exhibit a negative correlation between the concentrations of ΣCa*,Mg* and H^+ in runoff water, there is also a significant positive correlation between the concentrations of ΣCa*,Mg* and H^+ in runoff water at Storgama (Figure 5.86). This means that when the concentration of the typical acid neutralizing compounds as ΣCa*,Mg* is increasing, there is simultaneously a paradoxial increase in the concentration of H^+. At Storgama, the lowest ANC-values normally occur from October to January, more or less undependent of volume of discharge. Out of the14 most negative monthly weighted ANC-values at Storgama during 1986-1991, 12 occured from 1 October until 31 January. Simultaneously the highest monthly weighted concentrations of SO_4* and ΣCa*,Mg* occured. There is far from any significant correlation between the concentration of H^+ in rain water and the concentration of H^+ in runoff water (Figure 5.87). Despite the high concentration of H^+ normally present in precipitation during autumn, often is accompanied by high concentration of H^+ in runoff water a month or two later, the significant positive correlation between the concentrations of H^+ and ΣCa*,Mg* in runoff water can not only be explained by a piston effect. The most reasonable explanation to the paradox, is that sulphuric acid has to be formed within the catchment. The catchment consists of exposed granite (22%), rankers and shallow podzols (49%) and about 19 % has a peat cover > 30 cm in depth (Christophersen et al. , 1984). This means that the catchment is very drought-sensitive, and the condition for oxidation of sulphides should be relatively good. Typically, the most extreme water-chemical condition was recorded in November 1989. Earlier this year, no runoff was recorded neither in June, July nor in September. Three months during a year with no runoff water has never been recorded neither earlier nor later. The monthly weighted concentrations of H^+, ΣCa*,Mg*, and SO_4* in November 1989 were 49 μeq/L, 63 μeq/L and 118 μeq/L, respectively.

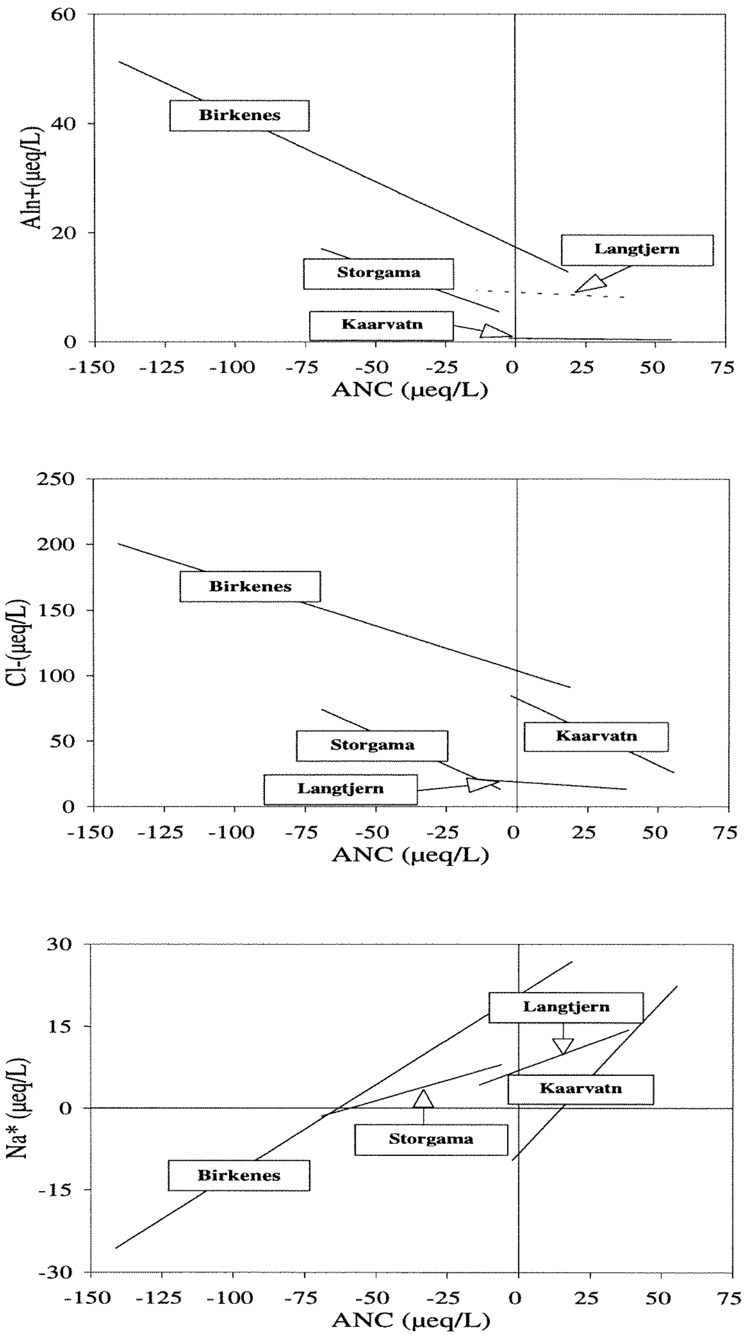


Figure 5.83 The relationships between acid neutralizing capacity (ANC) and the concentration of aluminium (ΣAl^{n+}), chloride (Cl^-) and non-marine sodium (Na) in runoff water, based on monthly weighted averages from 1986-1991. The correlations are based on linear regression analyses, and the correlations 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:* ***ΣAl^{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: $y = 0.55x - 8.31$ ($r = 0.65$) ($p < 0.01$).*

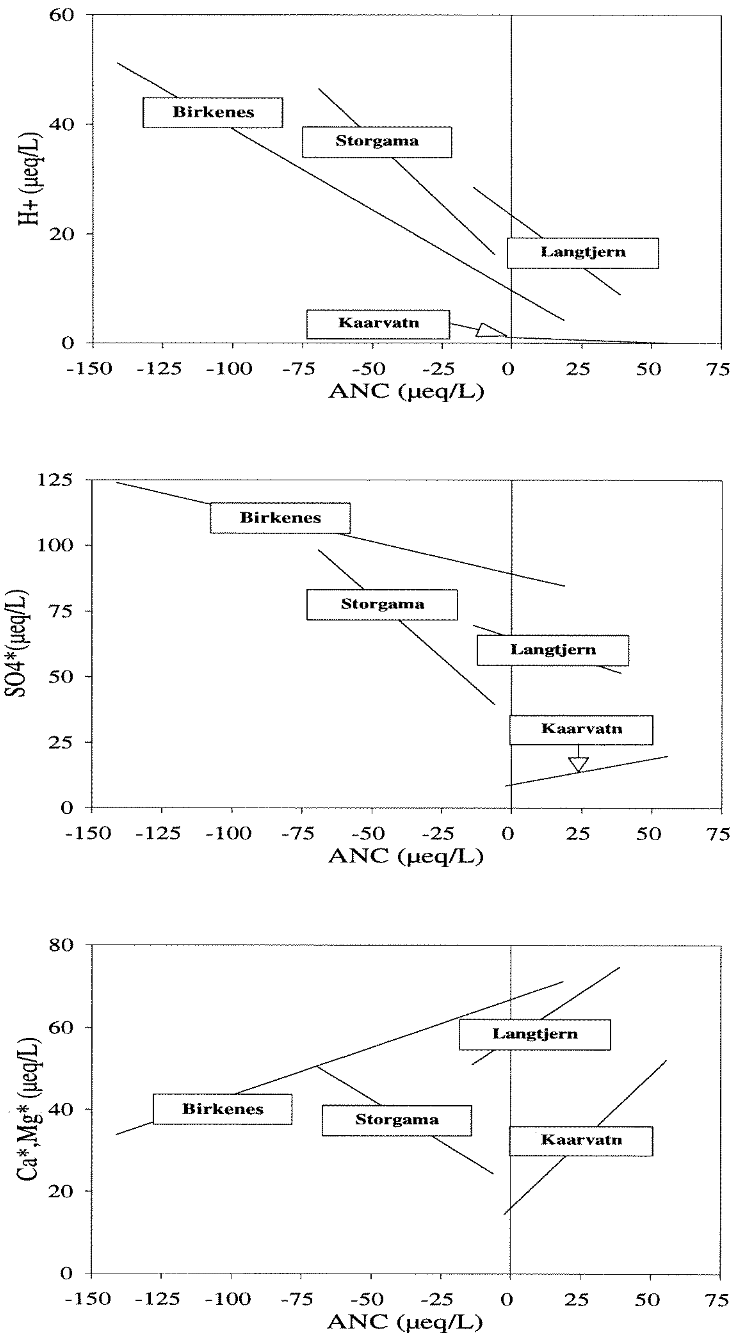


Figure 5.84 The relationships between acid neutralizing capacity (ANC) and the concentration of H^+, non-marine sulphate (SO_4) and non-marine base cations (ΣCa*,Mg*) in runoff water, based on monthly weighted averages from 1986-1991. The correlations are based on linear regression analyses, and the 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:* ***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: $y = 0.20x + 8.84$ ($r = 0.43$) ($p < 0.01$).* ***ΣCa*,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: $y = 0.65x + 16.0$ ($r = 0.66$) ($p < 0.01$).*

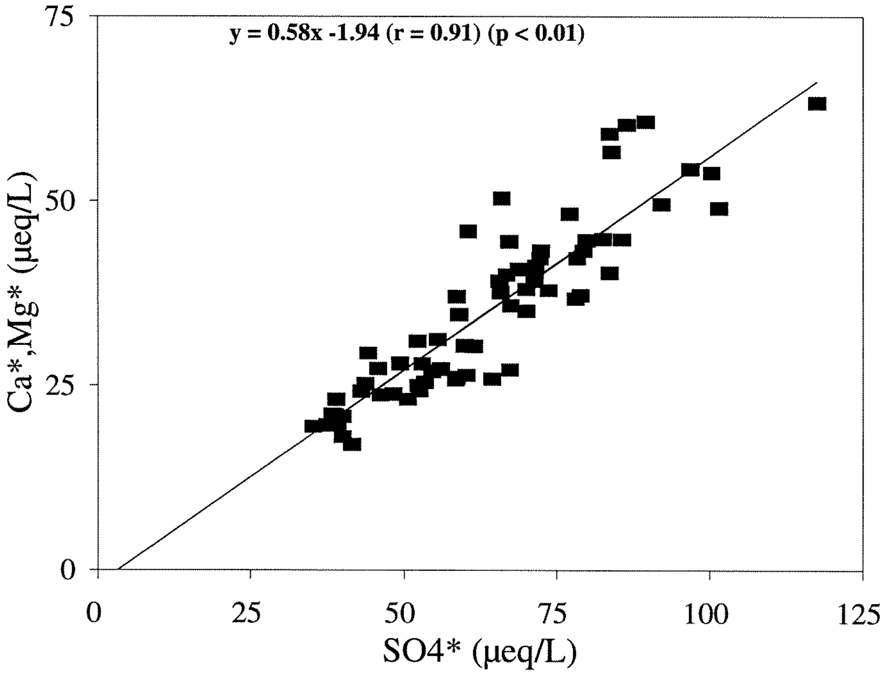


Figure 5.85 The correlation between monthly weighted concentrations of non-marine sulphate (SO₄) and non-marine base cations (ΣCa*,Mg*) in runoff water at Storgama during 1986-1991.*

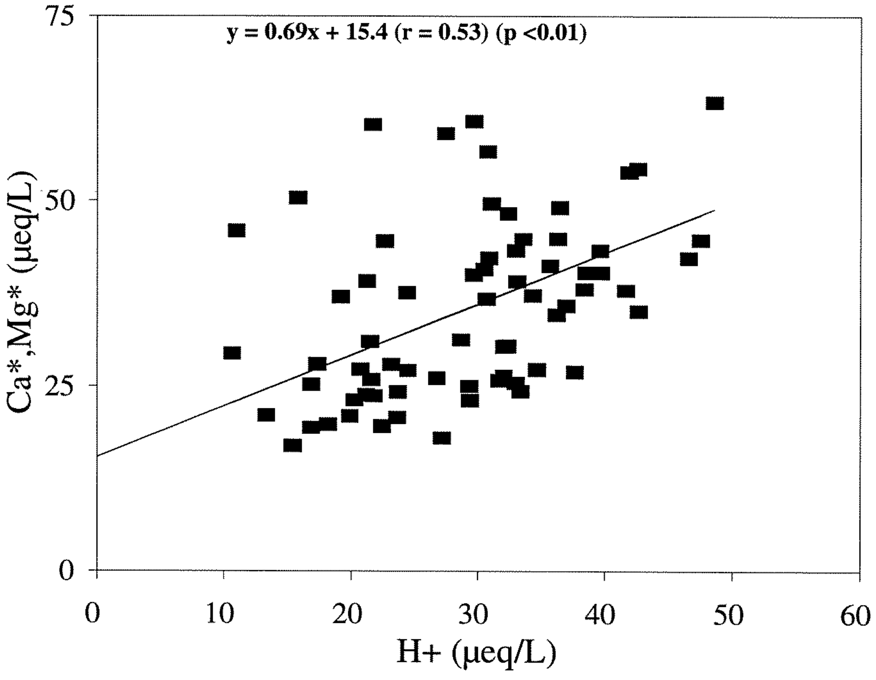


Figure 5.86 The correlation between monthly weighted concentrations of H^+ and non-marine base cations (ΣCa,Mg*) in runoff water at Storgama during 1986-1991.*

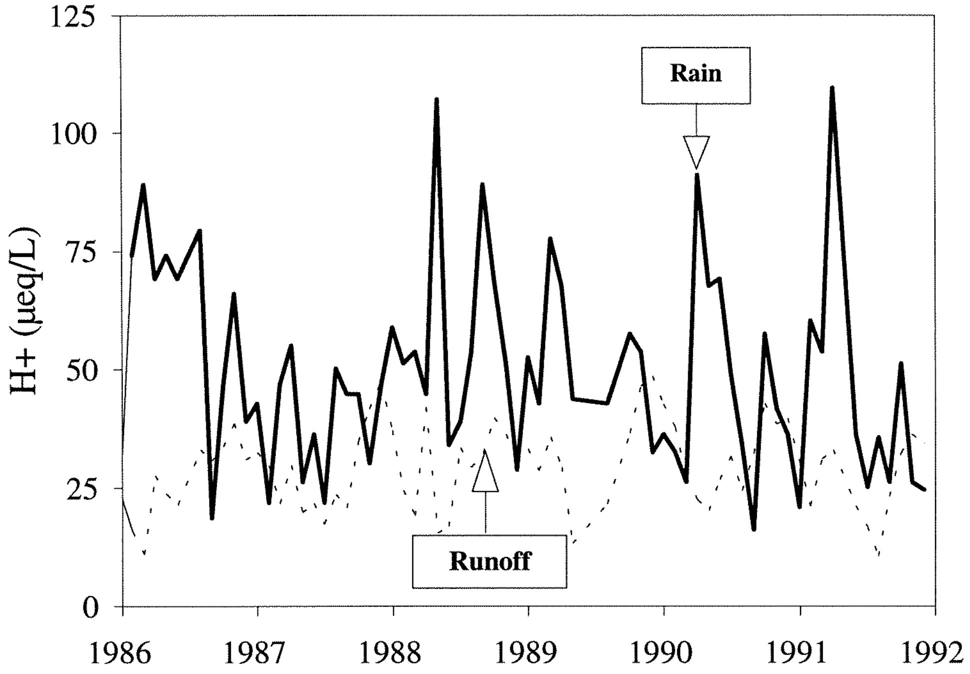


Figure 5.87 Monthly changes in the concentrations of H^+ in rain and runoff water from the Storgama catchment during 1986-1991.

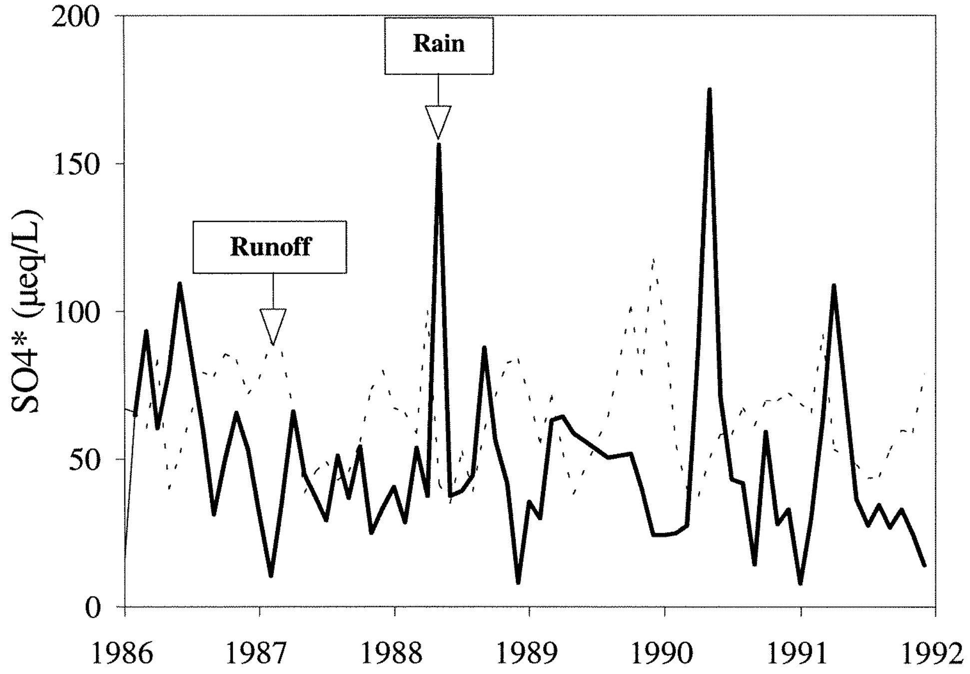


Figure 5.88 Monthly changes in the concentrations of non-marine sulphate (SO_4) in rain and runoff water from the Storgama catchment during 1986-1991.*

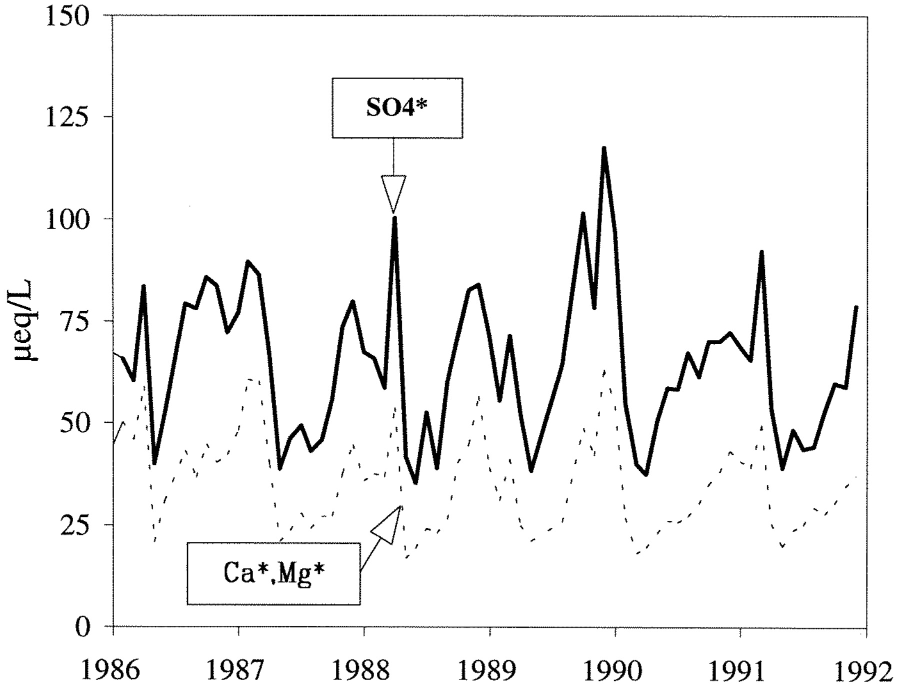


Figure 5.89 Monthly changes in the concentrations of non-marine sulphate (SO_4) and non-marine base cations (ΣCa*,Mg*) in runoff water from the Storgama catchment during 1986-1991.*

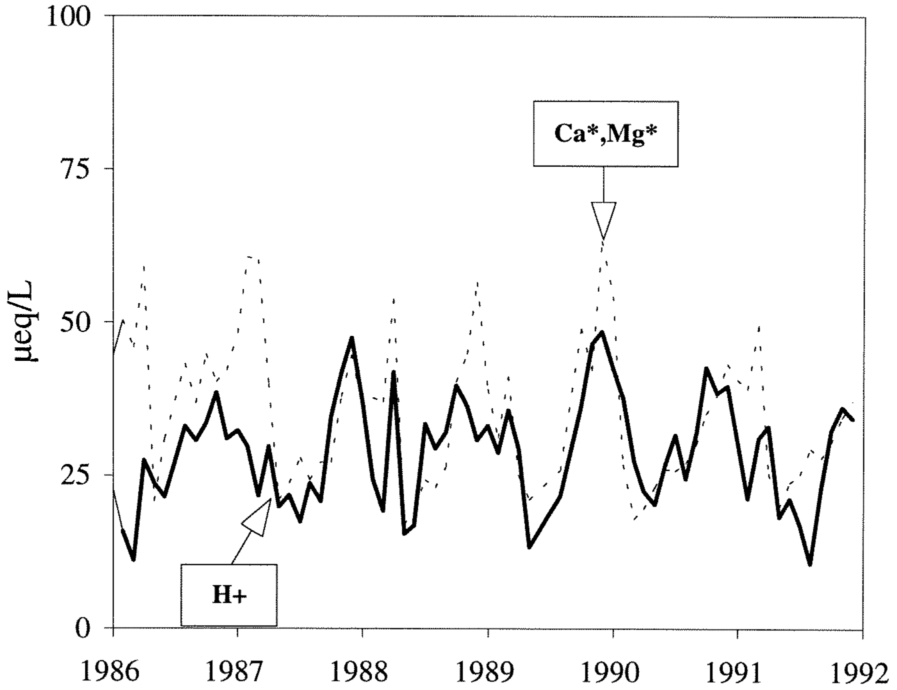


Figure 5.90 Monthly changes in the concentrations of H^+ and non-marine base cations (ΣCa,Mg*) in runoff water from the Storgama catchment during 1986-1991.*

The ANC-value was estimated to - 69 μeq/L. All four observations are the most extreme monthly weighted values recorded at Storgama during the period 1986-1991.

Almost every autumn it is a period when the concentration of H^+ and SO_4^* in runoff-water exceeds that correpondingly present in rain-water (Figure 5.87, 5.88). Thus, the main reason for the significant positive correlation between the concentration of H^+ and $\Sigma Ca^*,Mg^*$ is the sulphid-oxidation which takes place within the catchment during drought-periods. Because of the low acid neutralizing capacity of the catchment both H^+ and $\Sigma Ca^*,Mg^*$ is able to increase simultaneously. The source of the sulphide being oxidized, is most likely sulphate from the atmosphere which earlier has been reduced to sulphides.

Variations in the concentration of H^+ and organic anions (A^-) cause the most statistical significant changes in ANC in runoff at Birkenes and Langtjern. At Storgama the variation in the concentration of H^+ and SO_4^* are the most significant, while at Kaarvatn it is the variation in the concentrations of H^+ and alkalinity (HCO_3^-) which exhibit the strongest correlations with ANC.

5.8 Aluminium

To obtain high concentration of aluminium in runoff water, the acid neutralizing 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.

The monthly weighted mean concentration of total reactive aluminium (RAL) at Birkenes (from 1986-1991) is 454 ± 34 μg Al/L, and averagely 78% of the total aluminium (RAL) is present as labile aluminium (LAL), the fraction which primarily contains the inorganic, acute toxic aluminium forms (Table 5.28). The diffrence between RAl and LAL is defined as non-labile Al (ILAL) and basically contains the non-acute toxic, organic Al-complexes. Monthly weighted averages charge of aluminium (ΣAl^{n+}) at Birkenes is 29.6 ± 1.4 μeq/L, which gives an average charge of each Al-ion of +1.80.

The monthly weighted mean concentration of RAL at Storgama is 164 ± 8 μg Al/L, and averagely 70% of RAL is present as LAL (Table 5.28). The total average charge of aluminium (ΣAl^{n+}) at Storgama is 10.6 ± 0.4 μeq/L, which gives an average charge of each Al-ion of +1.76.

The monthly weighted mean concentration of RAL at Langtjern is 175 ± 9 μg Al/L, and averagely 42% of RAL is present as LAL (Table 5.28). The total average charge of aluminium (ΣAl^{n+}) at Langtjern is 8.9 ± 0.5 μeq/L, which gives an average charge of each Al-ion of +1.39.

The high acid neutralizing capacity (ANC) in runoff water at Kaarvatn means that only minor amounts of aluminium is able to leak out from the catchment. Thus, the monthly weighted mean concentration of RAL is low (18.2 ± 0.7 μg Al/L) and only 25% of RAL is averagely present as LAL (Table 5.28). The total average charge of aluminium (ΣAl^{n+}) at Kaarvatn is 0.62 ± 0.03 μeq/L, which gives an average charge of each Al-ion of +0.90.

At Birkenes, the highest concentration of LAL normally occurs during autumn and early spring, while the highest concentration of non-labile aluminium (ILAL), predominantly organic Al-forms, occurs during August. While the concentration of LAL is decreasing during the springmelt period and remains low during the summer, the concetration of ILAL remains more or less at the same level during the corresponding period, but a certain higher ILAL concentration may often occur at late summer. At Birkenes, no significant correlation was found between monthly runoff and monthly weighted concentrations of RAL, LAL or ILAL (Table 5.29) from 1986-1991, but for the whole monitoring period (1974 -1991), there is a significant positive correlation between monthly weighted concentration of RAL and monthly runoff. No Al-speciation has been conducted before 1985/86 at any of the sites.

At Storgama, the concentration of LAL is more or less continuously increasing from May to December. At December the maximum value normally occurs, but LAL remains high until next springmelt. The concentration of ILAL does not exhibit large seasonal fluctuation, but the highest concentration normally occurs during autumn and winter. At Storgama, a significant negative correlation was present between monthly runoff and monthly weighted concentrations of both RAL and LAL(Table 5.29), which means that the concentration of RAL and LAL are decreasing by increasing volume of discharge.

At Langjern, the concentrations of both LAL and ILAL are more or less continuously increasing from May until a maximum occurs once during the winter and remain relatively high until springmelt. During springmelt the concentrations both LAL and ILAL are at the lowest (Figure 5.96). As at Storgama, there is a significant negative correlation between monthly runoff and monthly weighted concentrations of both RAL and LAL at Langtjern (Table 5.29), which means that the concentration of RAL and LAL are decreasing by increasing volume of discharge.

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 µg AL/L (Figure 5.98). At Kaarvatn as in Birkenes, there was no significant correlation between monthly runoff and monthly weighted concentrations of RAL, LAL or ILAL (Figure 5.97) during 1986-1991, but, as at Birkenes, when the whole monitoring period (1980-1991) was analysed, there was a postive correlation between monthly weighted concentrations of RAL and monthly runoff.

Based on the ALCHEMI-speciation programme (Schecher and Driscoll, 1987,1988), the predominant inorganic dissolved aluminium-species at Birkenes are: $Al^{3+} > AlF^{2+} > AlH_3SiO_4^{2+}$, while the corresponding order of predominance at Storgama and Langtjern is: $AlF^{2+} > Al^{3+} > AlF_2^{+}$. At Kaarvatn the concentrations of dissolved inorganic Al-species are very low (Table 5.28).

At all sites, there are several factors which exhibit significant correlations with the concentration of aluminium (Table 5.29), i.e. ILAL, LAL and RAL (RAL = ILAL+LAL). Based on monthly weighted averages, the three most significant factors for the concentration of LAL at the coastnear Birkenes catchment are the concentration of $Cl^- > Na^* > H^+$, positive correlation concerning Cl^- and H^+ and negative for Na^*. Correspondingly at Kaarvatn, the other coastnear catchment, the concentrations of Cl^- and Na^* are the most important factors as far as the concentration of labile aluminium is concern. At both sites there are no significant correlation between monthly weighted concentration of SO_4^* and LAL, which

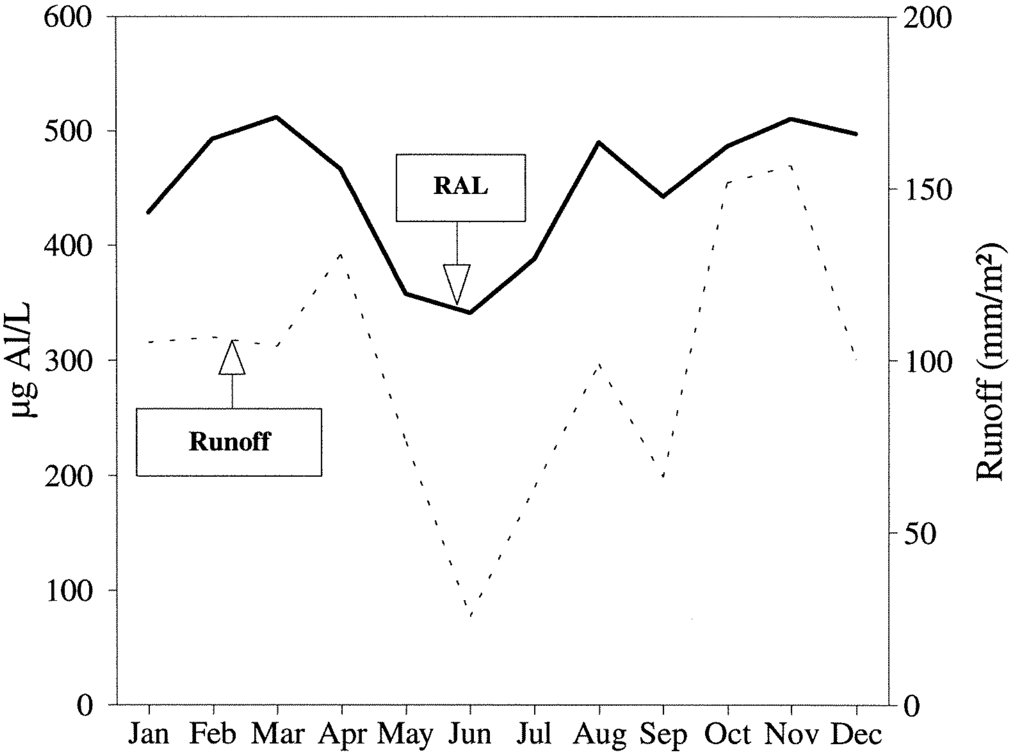


Figure 5.91 Monthly runoff-means and monthly mean concentrations of reactive aluminium (RAL) at Birkenes, based on monthly weighted averages from 1986-1991.

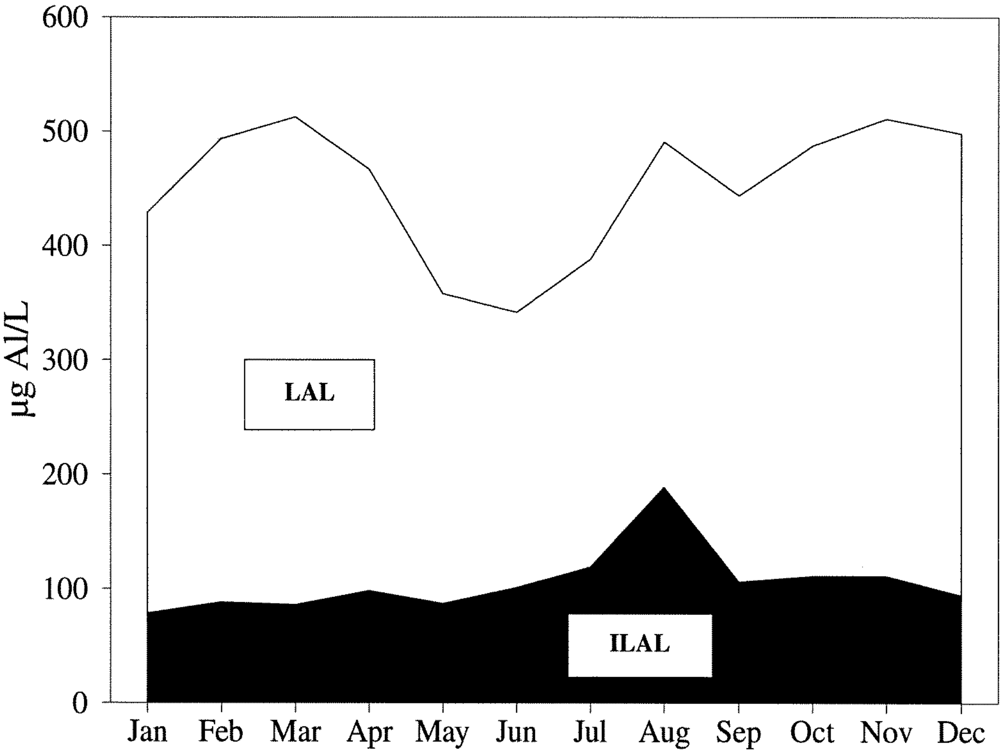


Figure 5.92 Monthly mean concentrations of non-labile (ILAL) and labile (LAL) aluminium at Birkenes, based on monthly weighted averages from 1986-1991. RAL = LAL + ILAL.

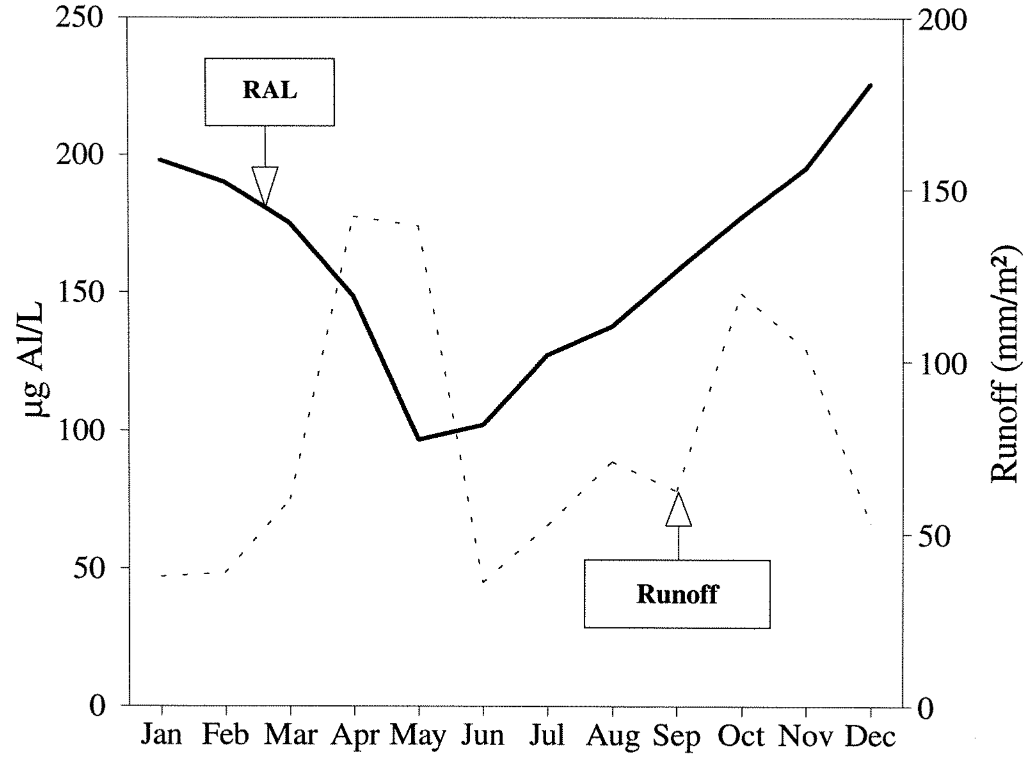


Figure 5.93 Monthly runoff-means and monthly mean concentrations of reactive aluminium (RAL) at Storgama, based on monthly weighted averages from 1986-1991.

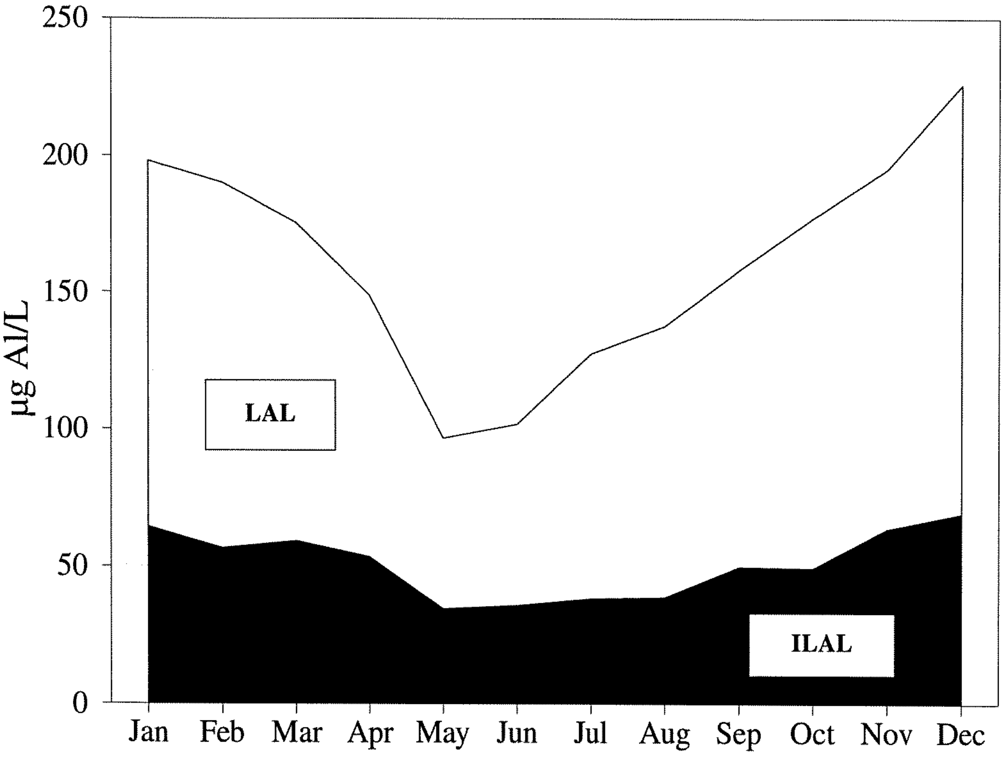


Figure 5.94 Monthly mean concentrations of non-labile (ILAL) and labile (LAL) aluminium at Storgama, based on monthly weighted averages from 1986-1991. RAL = LAL + ILAL.

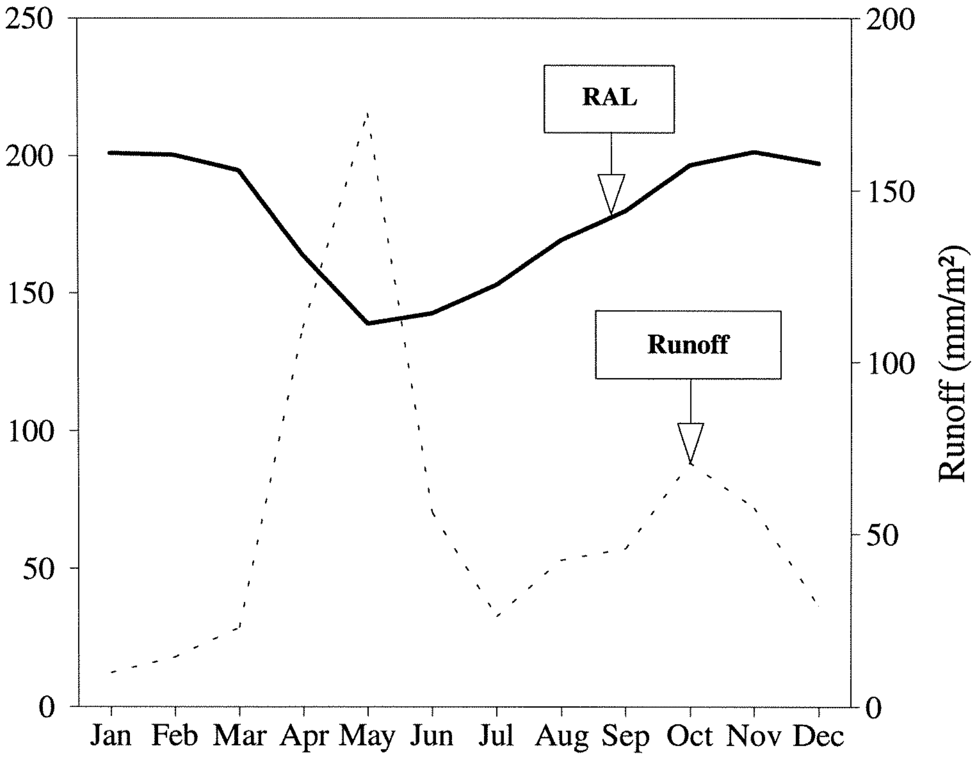


Figure 5.95 Monthly runoff-means and monthly mean concentrations of reactive aluminium (RAL) at Langtjern, based on monthly weighted averages from 1986-1991.

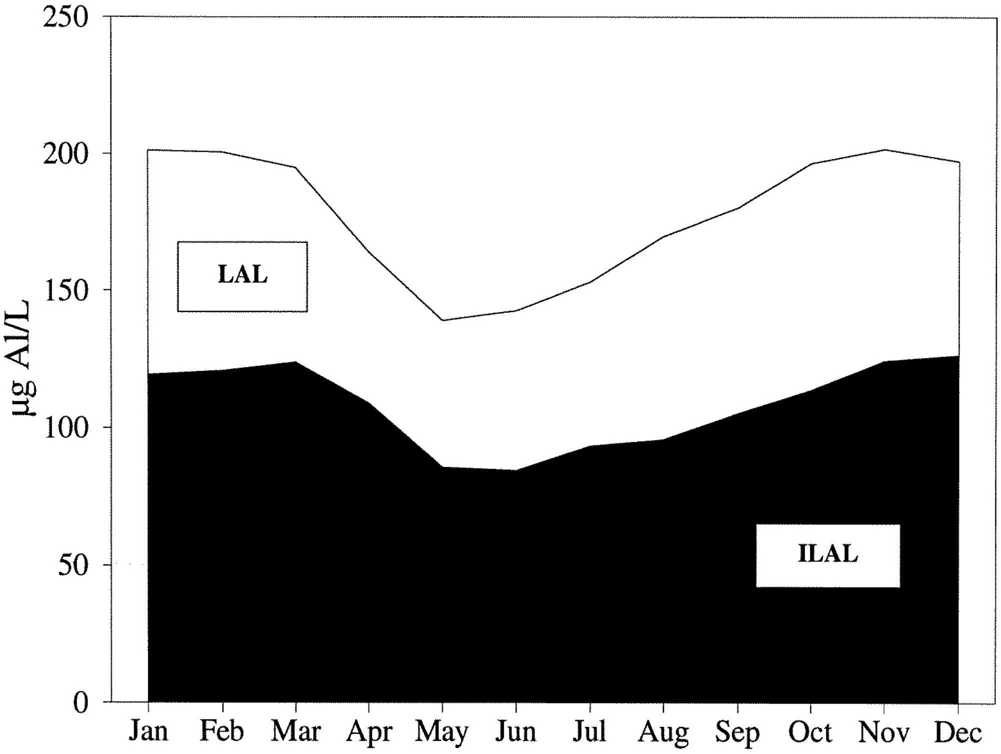


Figure 5.96 Monthly mean concentrations of non-labile (ILAL) and labile (LAL) aluminium at Langtjern, based on monthly weighted averages from 1986-1991. RAL = LAL + ILAL.

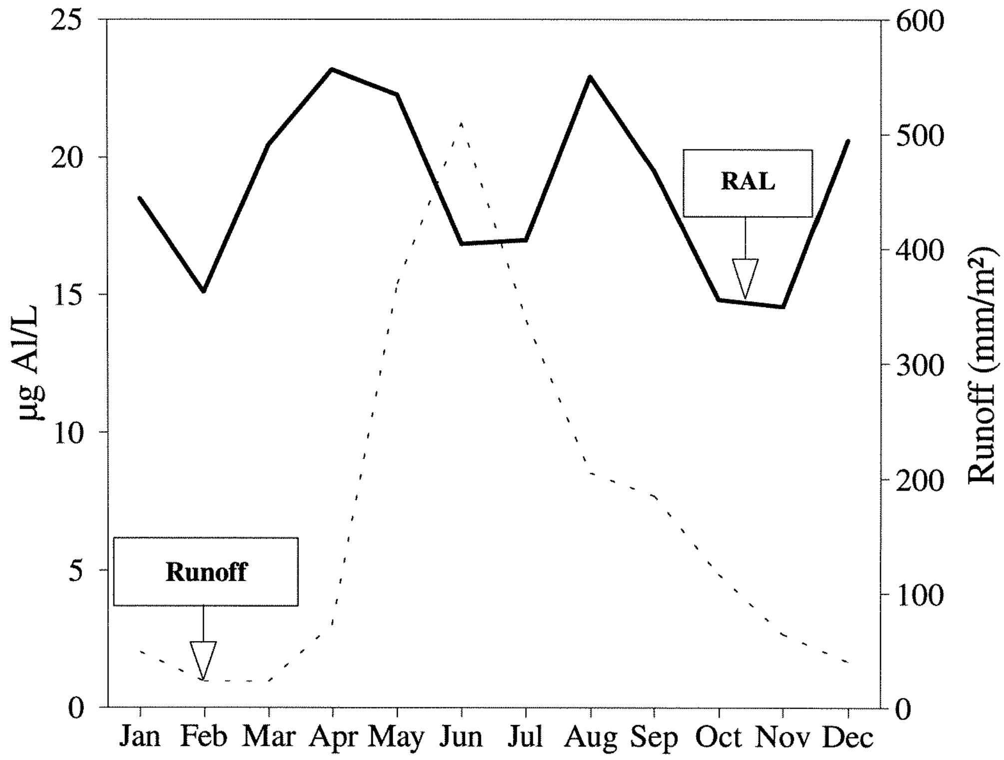


Figure 5.97 Monthly runoff-means and monthly mean concentrations of reactive aluminium (RAL) at Kaarvatn, based on monthly weighted averages from 1986-1991.

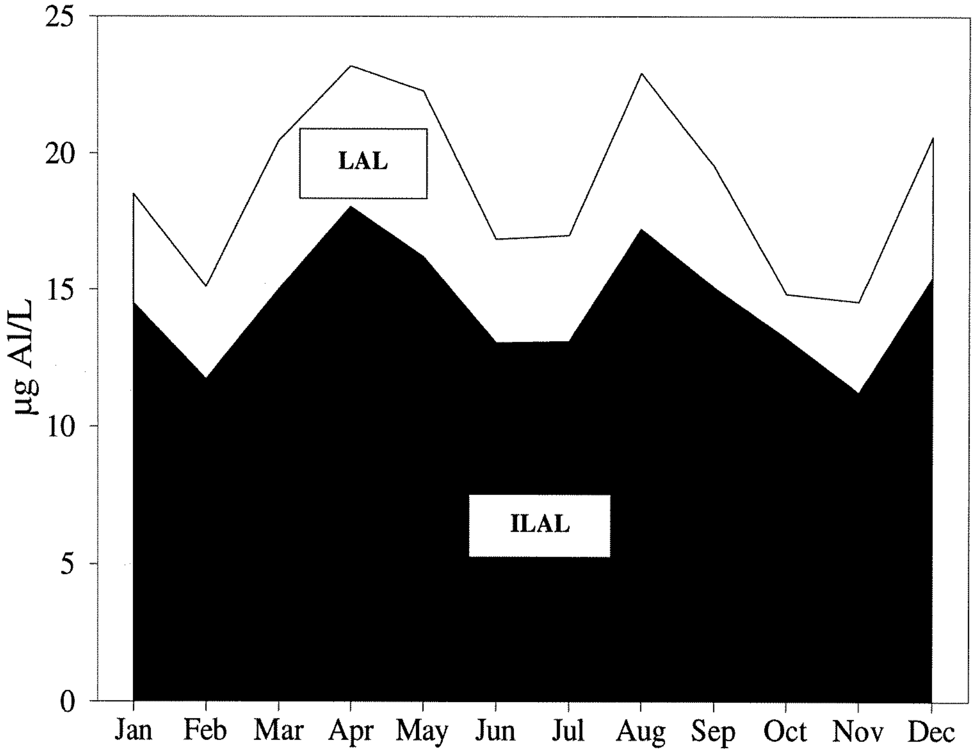


Figure 5.98 Monthly mean concentrations of non-labile (ILAL) and labile (LAL) aluminium at Kaarvatn, based on monthly weighted averages from 1986-1991. RAL = LAL + ILAL.

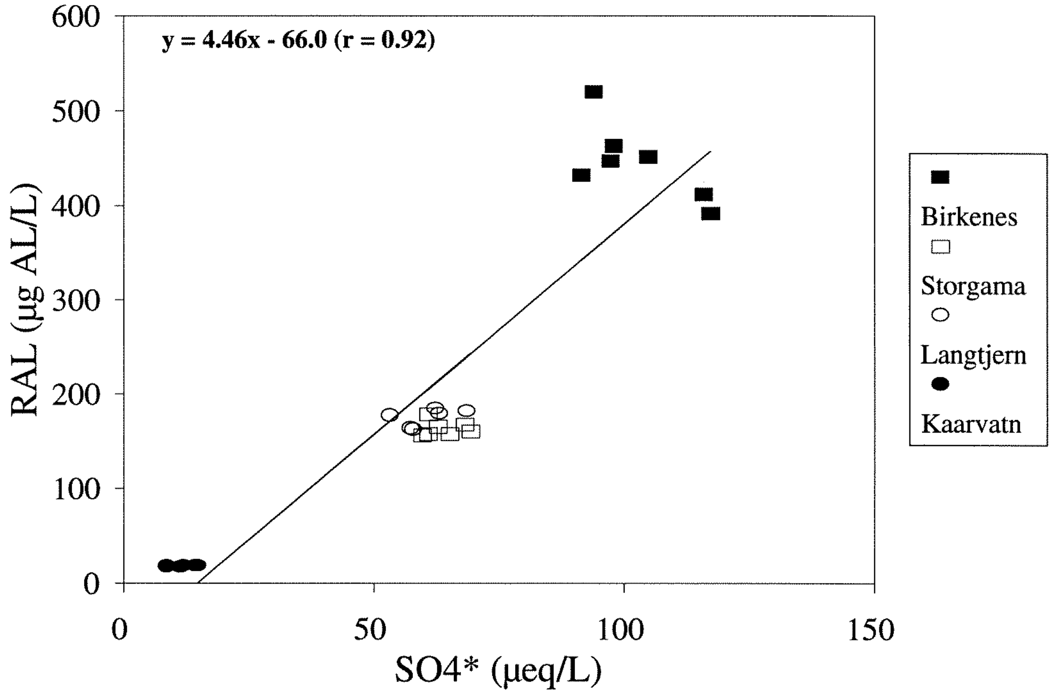


Figure 5.99 The relationship between annual weighted concentrations averages of non-marine sulphate (SO4) and total reactive aluminium (RAL) in runoff water from the four catchments from 1986-1991.*

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 SO_4* is undoubtedly decesive for the level of aluminium present in runoff water (Figure 5.99), but in coastnear 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 corresponding concentrations of SO_4* and ΣCa*,Mg*, with chloride as the third most significant (Table 5.29). The fact that there are positive correlations between LAL and both SO_4* and ΣCa*,Mg*, must be due to the sulphide oxidation in the catchment (See chapter 5.7). Also in the runoff water at Storgama, a high positive correlation was present between the concentration of Cl^- and LAL, which indicates that seasalt episodes may play an important role even for the aluminium chemistry at Storgama. The negative correlation between Na* and LAL at both Birkenes and Kaarvatn, is however, not present at Storgama. This may rely on the very positive base cation (ΣCa*,Mg*)/aluminium correlation present, which also means that the concentration Na* most likely increases during sulphide oxidation in the catchment. Thus, in the soil-poor, draught sensitive Storgama catchment, sulphide oxidation processes within the catchment seems to overshaddow the seasalt-effect. As described earlier, tha major seasalt effect is that sodium from precipitation is retained in the catchment due to cation-exchange, so that the concentration of Na* is decreasing or even negative values occur.

Table 5.28 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 SiO_2/L *and 100* $\mu g\ F^-/L$. *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:* $Al^{3+} + A^{3-} = Al(A)$ $(pK = 8.38)$ *and* $Al^{3+} + HA^{2-} = Al(HA)^+$ $(pK = 13.1)$. *The constants are identical with those present in the ALCHEMI-version 4.0 (Schecher and Driscoll, 1987,1988).*

Al-species	*unit*	**Birkenes**	**Storgama**	**Langtjern**	**Kaarvatn**
RAL	µg Al/L	454 ± 34	164 ± 8	175 ± 9	18.2 ± 0.7
ILAL	"	100 ± 34	48 ± 11	103 ± 15	13.6 ± 1.4
LAL	"	354 ± 22	116 ± 7	73 ± 11	4.6 ± 1.1
ΣAl^{n+} (tot.)	µeq/L	29.6 ± 1.4	10.6 ± 0.4	8.9 ± 0.5	0.62 ± 0.03
Al^{3+}	µeq/L	13.6 ± 1.1	2.5 ± 0.2	1.25 ± 0.2	
$Al(OH)^{2+}$	"	0.9 ± 0.1	0.11 ± 0.01	0.11 ± 0.01	0.01 ± 0.001
$Al(OH)_2^+$	"				0.03 ± 0.01
AlF^{2+}	"	7.9 ± 0.3	5.7 ± 0.1	4.7 ± 0.4	0.11 ± 0.01
AlF_2^+	"		0.7 ± 0.01	0.8 ± 0.02	0.12 ± 0.01
$AlOHF^+$	"	0.7 ± 0.1	0.4 ± 0.03	0.6 ± 0.05	0.29 ± 0.02
$AlSO4^+$	"	0.2 ± 0.02			
$AlH_3SiO_4^{2+}$	"	3.6 ± 0.2	0.6 ± 0.06	0.5 ± 0.03	0.04 ± 0.002
ΣAl^{n+}(inorg.)	"	27.0 ± 1.2	10.0 ± 0.3	7.9 ± 0.5	0.6 ± 0.02
$Al(organic)^0$	µmol/L	2.2 ± 0.5	0.35 ± 0.10	1.1 ± 0.22	0.09 ± 0.02
$Al(H\text{-}organic)^+$	"	2.7 ± 0.6	0.55 ± 0.13	1.0 ± 0.11	0.004 ± 0.001
ΣAl^{n+}(org.)	µeq/L	2.7 ± 0.6	0.55 ± 0.13	1.0 ± 0.11	0.004 ± 0.001

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 desicive 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 total organic carbon and runoff, but on the other hand, it is a weak but significant negative correlation between runoff and charge density of organics (See: "Total organic carbon" in chapter 5.6). Despite there are no quantitative significant changes in TOC due to change in runoff, this means that there is a qualitative change in the TOC, since the amount of negative charges on organic complexes are decreasing by increasing runoff.

At all catchments, the most significant factors for the chemistry of non-labile aluminium (ILAL) are the concentration and charge of dissolved organic carbon (Table 5.29), At all four sites, positive correlations were present between the monthly weighted concentration of ILAL and the monthly weighted TOC-concentration or average charge (A^-) of dissolved organic carbon. This should be expected, because ILAL primarily expresses the concentrations of organic-aluminium complexes present in solution. At Langtjern, however, the concentration of $\Sigma Ca^*,Mg^*$ is a somewhat more significant factor than TOC, concerning the concentration of ILAL. The positive correlation between $\Sigma Ca^*,Mg^*$ and ILAL at Langtjern may rely on at least two factors:

A) There is a positive significant correlation between the concentration of $\Sigma Ca^*,Mg^*$ and the concentration of TOC or organic anions (A^-).

B) There is a positive significant correlation between the concentration of TOC and the concentration H^+ in runoff water.

Thus, the high amount of organic acids in runoff water at Langtjern is important, not only for the aluminium chemistry, but also for the base cation chemistry, and probably also for the pH of runoff water at this site.

By the ALCHEMI-speciation programme, it is possible to estimate the concentration of organic aluminium (ILAL), by feeding the programme with measured concentrations for total reactive aluminium (RAL) and major chemical dissolved compounds, including TOC. By use of the organic constants given by the programme (see the text of Table 5.28), the concentration of ILAL can be calculated. Despite the constants are empirical constants and of cause somewhat speculative, they are at least constant. This means that the relative changes between measured ILAL and calculated ILAL in the runoff water at the four sites may give useful information about qualitative differences in the dissolved organic pools. At Birkenes, the programme seems to overestimate the concentrations of ILAL, while an underestimation of ILAL seems to be the case at the other sites (Figure 5.100).

Accordingly, the opposite should be the case concerning the concentration of LAL, because RAL = ILAL + LAL. The reason why the concentration of ILAL is somewhat overestimated at Birkenes, should thoretically rely on at least two factors:

A: The dissociation constants of the triprotic acid in the programme should be higher at Birkenes site compared with the other sites.

B: The complex-constants between aluminium and the organic triprotic acid given by the programme should be lower at Birkenes compared with the other sites.

Since the dissociation constants already is high in the ALCHEMI-programme high, it is more likely that the complex-constants between aluminium and the triprotic acids at Birkenes should be lower than those given by the programme. Accordingly the complex-constants for the organic acids should be somewhat higher than those present in the ALCHEMI-programme at the three other catchments.

The fact that there seems to be general lower organic-complexing constants for aluminium at Birkenes compared with the other sites, is an important observation, especially in light of the fact that qualitative changes in the functional-groups of organic substances seems to occur during acidification, i.e. a decrease in the carboxylic-acidity and an increase in phenolic acidity by acidification (Malcom and Gjessing, 1993). Thus, the lowest organic Al-complexing-constants should be expected at Birkenes, because phenolic-groups normally are weaker than carboxylic-groups with respect to complexing strength. In addition the molecular weight of dissolved organic carbon seems to increase when pH is lowered (Shaw et al., 1993).

This may also lead to a reduction in the complexing capacity, because the concentration of negative sites/ mg C most likely decrease when the organic complexes are increasing in size.

Table 5.29 The parameters in runoff water which exhibit significant correlations with aluminium, based on linear regression analyses. The linear regressions are based on monthly weighted concentrations averages from 1986-1991, and the relationships are assumed to be significant when $p < 0.05$. The correlation coefficients (r) are in brackets and a negative value means negative correlation.

Al-fraction	**Cathment**		**Degree of significance**
RAL (n =70)	BIRKENES	:	Cl[0.46] > H^+[0.43] > Na^*[-0.41] > NO_3[0.28]
RAL (n = 68)	STORGAMA	:	$\Sigma Ca^*,Mg^*$[0.85] = SO_4^*[0.85] > Cl[0.68] > H^+[0.62] > NO_3[0.28] > TOC [0.36] > Runoff[-0.28]
RAL (n = 72)	LANGTJERN	:	TOC[0.79] > A^-[0.75] = $\Sigma Ca^*,Mg^*$[0.75] > SO_4^*[0.40] > Runoff[-0.33] > Na^*[0.25] > H^+[0.23]
RAL (n = 72)	KAARVATN	:	TOC[0.77] > H^+[0.25]
LAL (n =70)	BIRKENES	:	Cl[0.55] > Na^*[-0.51] > H^+[0.49] > NO_3[0.43] > TOC[-0.31] > $\Sigma Ca^*,Mg^*$[-0.23]
LAL (n = 68)	STORGAMA	:	SO_4^*[0.85] > $\Sigma Ca^*,Mg^*$[0.78] > Cl[0.70] > H^+[0.64] > NO_3[0.49] > Runoff[-0.31]
LAL (n = 72)	LANGTJERN	:	Runoff[-0.34] > A^-[0.29] > TOC[0.28] > H^+[0.24]
LAL (n = 72)	KAARVATN	:	Cl[0.33] > Na^*[-0.30] > TOC[0.27] > H^+[0.23]
ILAL (n =70)	BIRKENES	:	TOC[0.69] > A^-[0.49] > SO_4^*[-0.28]
ILAL (n = 68)	STORGAMA	:	TOC[0.61] > $\Sigma Ca^*,Mg^*$[0.44] > A^-[0.31] > NO_3[0.28] > SO_4^*[0.27]
ILAL (n = 72)	LANGTJERN	:	$\Sigma Ca^*,Mg^*$[0.73] > TOC[0.72] > A^-[0.67] > SO_4^*[0.36] > Na^*[0.29]
ILAL (n = 72)	KAARVATN	:	TOC[0.81] > A^-[0.26]

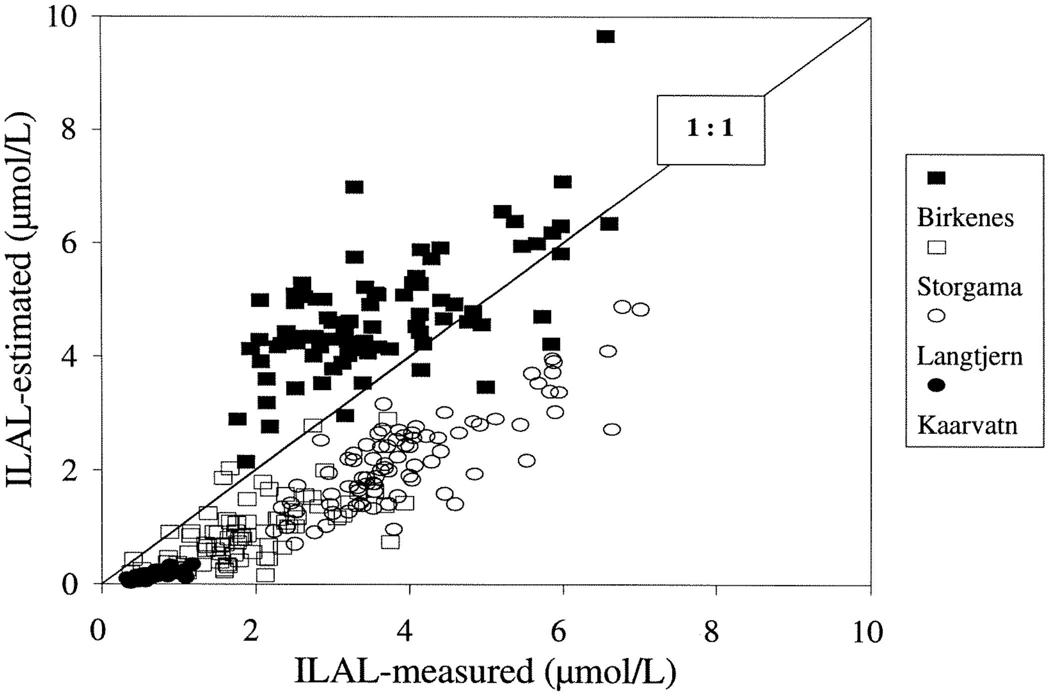


Figure 5.100 The relationship between measured and calculated (by the ALCHEMI-specitation programme) concentration of non-labile aluminium (LAL) at the four catchments, based on monthly weighted averages during 1986-1991. Birkenes: y = (1.11 ± 0.03)x (r = 0.79); Storgama: y = (0.48 ± 0.02)x (r = 0.64); Langtjern: y = (0.56 ± 0.01)x (r = 0.82); Kaarvatn: y = (0.20 ± 0.007)x (r = 0.80).

6. TIME TRENDS IN PRECIPITATION AND RUNOFF CHEMISTRY

The relationships between concentrations and fluxes of chemical compounds and input or output of water presented in Appendix A and B, rely on annual and monthly weighted averages from the beginning of the monitoring period up to 1991. During the preparation of this book, also data fra 1992 are available. Thus, the time trends analyses presented in this chapter also incorporate these data. Because there are minor differences in the concentration changes by time between water-year and calendar-year, calendar-year is used for time trend analyses of concentrations, while water-year is used for time trends analyses of fluxes. The time trend analyses are based on simple linear regression analyses. By large, time trends based on annual weighted averages are in good agreement wiht the trends obtained from monthly weighted averages. Thus, monthly weighted data will be used for time trends analysis of concentration changes, while annual (water-year) weighted data will be used for the trend analyses of fluxes.

It is primarily the chemical compounds which exhibit significant changes during the monitoring periods which are basically focused on in this chapter. In addition to time trends obtained from raw-data ($y = (\delta y_1/\delta t)t + b$), the effect of water input/output on the concentrations and fluxes of chemical compounds is evaluated. While the concentration of ions normallly exhibit a logaritmic change due to change in input or output of water [$\delta y/\delta \log(q)$], the fluxes of ions normally exhibit a linear change [$\delta y/\delta q$] with respect to change in input/output of water.

In contrast to a multiple regression analysis, where different relationships are subtracted, the effect of input/output of water on the concentration/flux of an ions is in this chapter added to the time trend equation obtained from raw-data only:

$$\mathbf{Y = (\delta y_1/\delta t)t + [\delta y_1/\delta \log(q)]\log(q)}$$

where

Y = the concentration of ion of interest.

$\delta y_1/\delta t$ = linear regression coefficient for the time trend based on raw data.

$\delta y_1/\delta \log(q)$= the linear regression coefficient, which express the water-dependant concentration changes.

If no significant hydrological time trend has occured during the actual time period, the linear regression coefficient (slope) based on raw data ($\delta y_1/\delta t$) should be identical to the linear regression coefficient obtained after the water dependent regression coefficient ($\delta y_1/\delta \log(q)$ is added to the equation, i.e. $\delta y_1/\delta t = \delta y_2/\delta t$. When the water dependent concentration change is added to the time trend equation based on raw-data, the least hydrological "sensitive" ions will more or less follow the time-trend line obtained from raw-data, which means that the standard deviation of the correlation coefficient ($\delta y_2/\delta t$) will be small.

At Birkenes, Storgama and Langtjern, there are no significant changes in the amount of precipitation or runoff during the monitoring period. Thus, the time trends obtained from raw-data ($\delta y_1/\delta t$) should be almost identical with the time trend obtained after the influence of water is added to the equation ($\delta y_2/\delta t$). At Kaarvatn there is a tendency of increasing input and output of water during the monitoring period (1980-1992), but the increase is not very significant, and for practical reasons not accounted for. The regression coefficient only obtained from raw-data ($\delta y_1/\delta t$) may therefore differ to some extent from the regression coefficient obtained after the influence of water is added to the equation.

Time trends obtained from both raw-data and calculated data (after addition of the water dependent concentration change) are present in the tables, while the time trends for each chemical compound present in the figures are presented twice, one presenting the average weighted raw-data only, while the second figures presents the time trends after the water dependant relationship is added, and the linear regression line obtained from the corrected data [$Y = (\delta y_1/\delta t)t + [\delta y_1/\delta \log(q)]\log(q)$].

The time trend lines in the figures with corrected data, are the linear regression equation obtained from raw data only, while the scattering of data in these figures only visualize the influence of water-on the concentration of each chemical compounds, i.e. large scattering means high water dependence and vise versa.

6.1 Precipitation

Time trends in concentration of dry-deposited compounds

It is only the weather stations at Birkenes and Kaarvatn were sufficient dry-deposition data exist, so that time trend analyses can be run. Measurements on SO_2-gas and SO_4-particles have been conducted since 1978 at Birkenes, and back to 1980 at Kaarvatn, while nitrogen compounds in dry-deposition have been measured since 1986 at Birkenes and from 1988 and on at Kaarvatn.

Based on the linear regression analysis (see Table 6.1), the concentration of SO_2-gas in the air at Birkenes has decreased from a monthly weighted average of 1.33 ± 0.78 µg S/m^3 at the beginning of 1978 to a monthly weighted average of 0.25 ± 0.15 µg S/m^3 at the end of 1992 (Figure 6.1), which means a 81% reduction during 1978-1992. Accordingly, while the monthly weighted average of SO_4-particles in air at the beginning of 1978 was 1.31 ± 0.41 µg S/m^3, the monthly weighted average at the end of 1992 was 0.61 ± 0.15 µg S/m^3 (Figure 6.2), which is a reduction by 53% from 1978 to 1992. The total monthly weighted average sulphur in dry deposition at the beginning of 1978 was 2.63 ± 1.09 µg S/m^3. At the end of 1992 it has decreased by 67%, down to an average of 0.86 ± 0.30 µg S/m^3 (Figure 6.3).

At Kaarvatn, the concentration of SO_2-gas in the air has decreased from a monthly weighted average of 0.52 ± 0.35 µg S/m^3 at the beginning of 1980, to an average of 0.10 ± 0.13 µg S/m^3 at the end of 1992 (Figure 6.4), which means a 81% reduction during 1980-1992. Accordingly, while the monthly weighted average of SO_4-particles in air at the beginning of 1980 was 0.53 ± 0.25 µg S/m^3, the average concentration at the end of 1992 was 0.27 ± 0.13 µg S/m^3 (Figure 6.5), which is a reduction by 49% from 1980 to 1992. The total monthly weighted average of total sulphur in dry deposition at the beginning of 1980 was 1.05 ± 0.48 µg S/m^3. At the end of 1992 it has decreased by 64% down to an average of 0.38 ± 0.13 µg S/m^3 at the end of 1992 (Figure 6.6).

The decline in SO_2-gas and SO_4-particles is relative significant at both Birkenes and Kaarvatn, and the percentage decline of sulphur in dry-deposition is about equal at Kaarvatn and Birkenes.

The major dry-deposition compounds of nitrogen in air are NO_2-gas and NH_4-particles. Based on the linear regression analysis (see Table 6.1), the concentration of NO_2-gas at Birkenes has decreased from a monthly weighted average of 1.29 ± 0.52 µg N/m^3 at the beginning of 1986 to an average of 0.77 ± 0.21 µg N/m^3 at the end of 1992 (Figure 6.7), which means a 40% reduction from 1986-1992. Accordingly, while the monthly weighted average of NH_4-particles in air at the beginning of 1986 was 0.63 ± 0.35 µg N/m^3, the average concentration at the end of 1992 was 0.59 ± 0.14 µg N/m^3 (Figure 6.8), which is a reduction by 6% from 1986 to 1992. The total monthly weighted average of oxidized and reduced nitrogen compounds in dry deposition ($\Sigma NO_2, HNO_3$, NO_3, NH_4, NH_3) at the beginning of 1986 was 2.32 ± 0.76 µg N/m^3. At the end of 1992 it has decreased by 30% down to an average of 1.63 ± 0.28 µg N/m^3 at the end of 1992 (Figure 6.9).

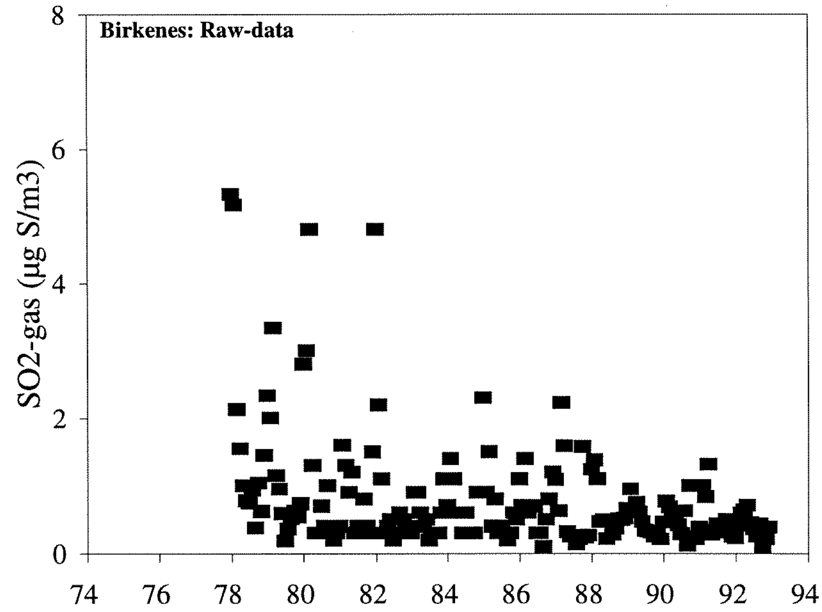
At Kaarvatn, the concentration of NO_2-gas in the air has decreased from a monthly weighted average of 0.56 ± 0.16 µg N/m^3 and the beginning of 1988 to an average of 0.14 ± 0.05 µg N/m^3 at the end of 1992 (Figure 6.10), which means a 75% reduction during 1988-1992.

Accordingly, while the monthly weighted average of NH_4-particles in air at the beginning of 1988 was 0.40 ± 0.24 μg N/m^3, the average concentration at the end of 1992 was 0.33 ± 0.10 μg N/m^3 (Figure 6.11), which is a reduction by 18% from 1988 to 1992. The total monthly weighted average of oxidized and reduced nitrogen compounds in dry deposition at the beginning of 1988 was 1.08 ± 0.31 μg N/m^3. At the end of 1992 it has decreased by 49% down to an average of 0.55 ± 0.15 μg N/m^3 at the end of 1992 (Figure 6.12).

The declines in NO_2-gas and total nitrogen in air are significant (if assuming $p < 0.05$ as criteria of significance) at both Birkenes and Kaarvatn, most significant at Kaarvatn, while the concentration of NH_4-particles in air has been more or less unchanged during the same periods, i.e. during 1986-1992 at Birkenes and 1988-1992 at Kaarvatn.

Table 6.1 Time trends in the concentration (μg/m^3) of sulphur and nitrogen compounds in dry-deposition, at Birkenes and Kaarvatn, based on raw data [$y(t) = (\delta y_1/\delta t)t + b_1$] and time trends after the water dependent concentration changes [$\delta y_1/\delta log(q)$] are accounted for, i.e. [$Y(t) = (\delta y_1/\delta t)t + [\delta y_1/\delta log(q)]log(q)] + b_2$]. The constant b_2 is fitted so $b_2=b_1$. (: $p < 0.05$, **: $p < 0.01$).*

		Raw-data			**Water dependance**		**Corrected data**	
	Period	**$\delta y_1/\delta t$**	**b_1**	**r_1**	**$\delta y/\delta log(q)$**	**r_q**	**$\delta y_2/\delta t$**	**r_2**
Birkenes								
SO_2-gas	1978-1992	-0.07 ± 0.01	1.33 ± 0.78	-0.37**	-0.02 ± 0.16	-0.01	-0.07 ± 0.00	-1.00**
SO_4-part.	1978-1992	-0.05 ± 0.01	1.31 ± 0.41	-0.42**	-0.12 ± 0.09	-0.10	-0.05 ± 0.00	-0.97**
ΣDry-S	1978-1992	-0.12 ± 0.02	2.63 ± 1.09	-0.43**	-0.06 ± 0.23	-0.02	-0.12 ± 0.00	-1.00**
NO_2-gas	1986-1992	-0.07 ± 0.03	1.29 ± 0.52	-0.28**	0.39 ± 0.14	0.30**	-0.08 ± 0.01	-0.71**
NH_4-part.	1986-1992	-0.01 ± 0.02	0.63 ± 0.35	-0.04	-0.09 ± 0.09	-0.11	-0.00 ± 0.00	-0.22*
ΣDry-N	1986-1992	-0.10 ± 0.04	2.32 ± 0.76	-0.25*	0.36 ± 0.21	-0.19	-0.10 ± 0.01	-0.82**
Kaarvatn								
SO_2-gas	1980-1992	-0.03 ± 0.01	0.52 ± 0.35	-0.33**	-0.21 ± 0.09	-0.19*	-0.04 ± 0.00	-0.89**
SO_4-part.	1980-1992	-0.02 ± 0.01	0.53 ± 0.25	-0.28**	-0.45 ± 0.05	-0.57**	-0.03 ± 0.00	-0.58**
ΣDry-S	1980-1992	-0.05 ± 0.01	1.05 ± 0.48	-0.38**	-0.66 ± 0.11	-0.42**	-0.06 ± 0.00	-0.74**
NO_2-gas	1988-1992	-0.08 ± 0.01	0.56 ± 0.16	-0.61**	-0.16 ± 0.09	-0.23	-0.09 ± 0.00	-0.94**
NH_4-part.	1988-1992	-0.01 ± 0.02	0.40 ± 0.24	-0.08	-2.60 ± 0.10	-0.32*	-0.02 ± 0.01	-0.37**
ΣDry-N	1988-1992	-0.11 ± 0.03	1.08 ± 0.31	-0.45**	-0.49 ± 0.14	-0.41**	-0.12 ± 0.01	-0.78**



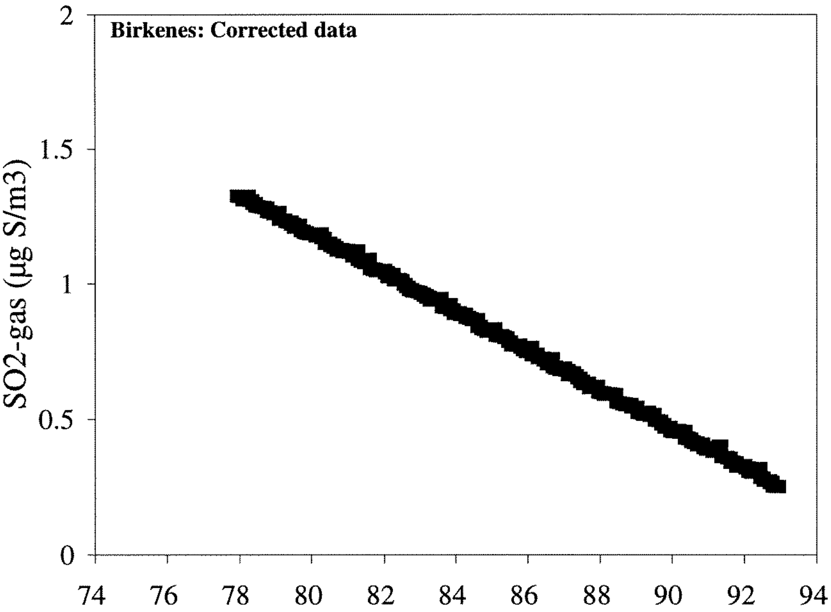
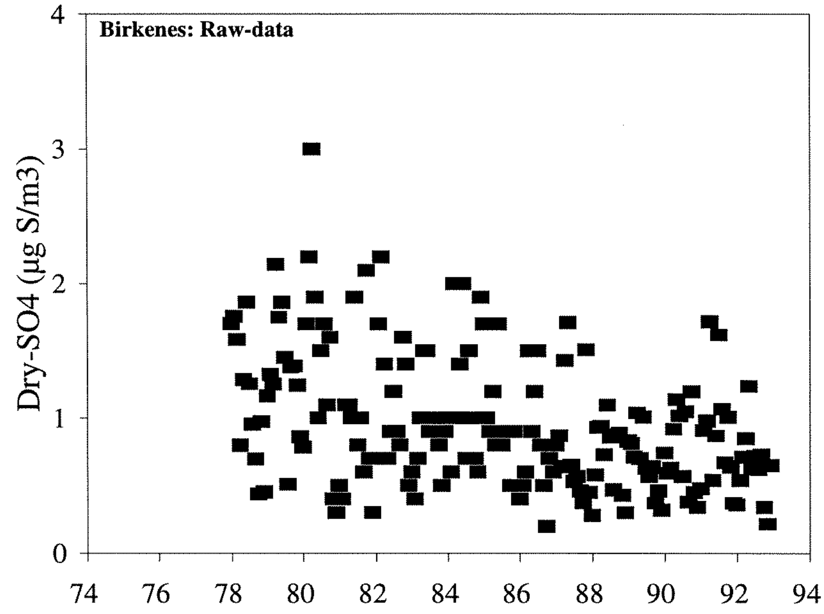


Figure 6.1 The monthly weighted concentration of SO_2-gas in air (µg S/m^3) at Birkenes from 1978-1992, present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualizes the influence of water on the concentration of each chemical compounds, i.e. large scattering means high water dependence and vise versa. The linear regression equations are present in Table 6.1. Continuous line means that the linear regression is significant, i.e. $p < 0.05$*, while a dottet line means no significance,* $p > 0.05$.



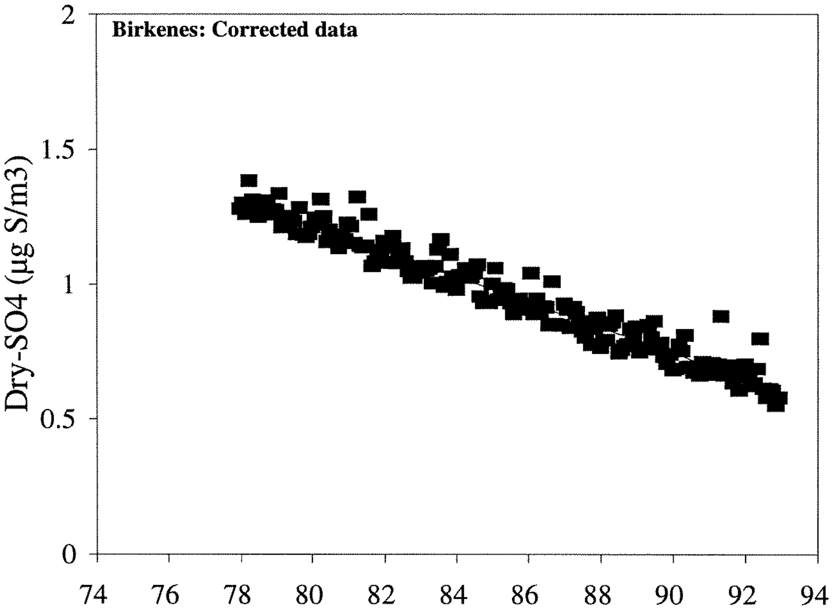
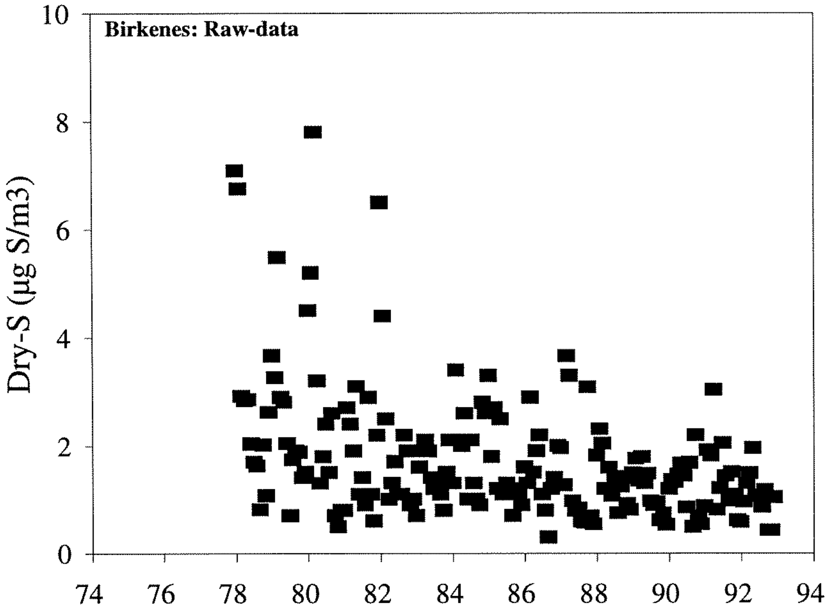


Figure 6.2 The monthly weighted concentration of SO_4-particles in air (µg S/m^3) at Birkenes from 1978-1992, present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualizes the influence of water on the concentration of each chemical compounds, i.e. large scattering means high water dependence and vise versa. The linear regression equations are present in Table 6.1. Continuous line means that the linear regression is significant, i.e. $p < 0.05$, while a dottet line means no significance, $p > 0.05$.



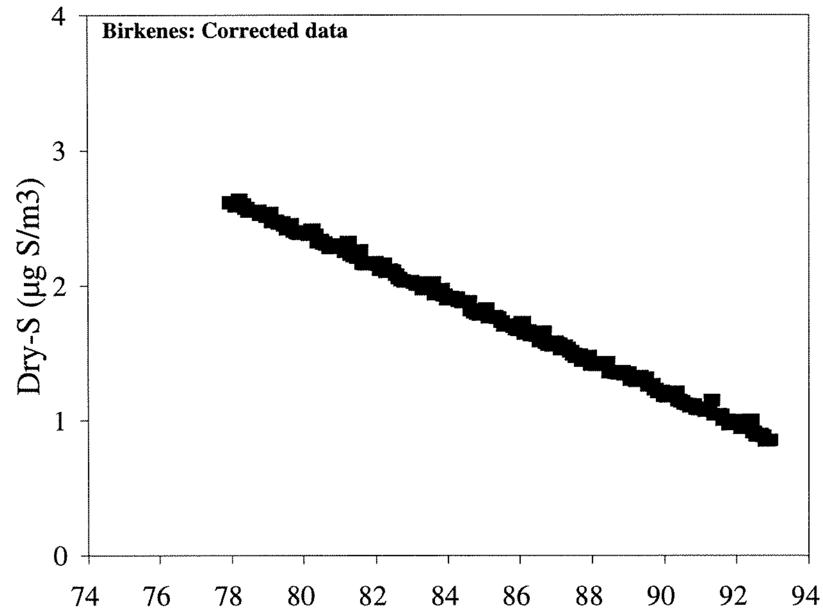
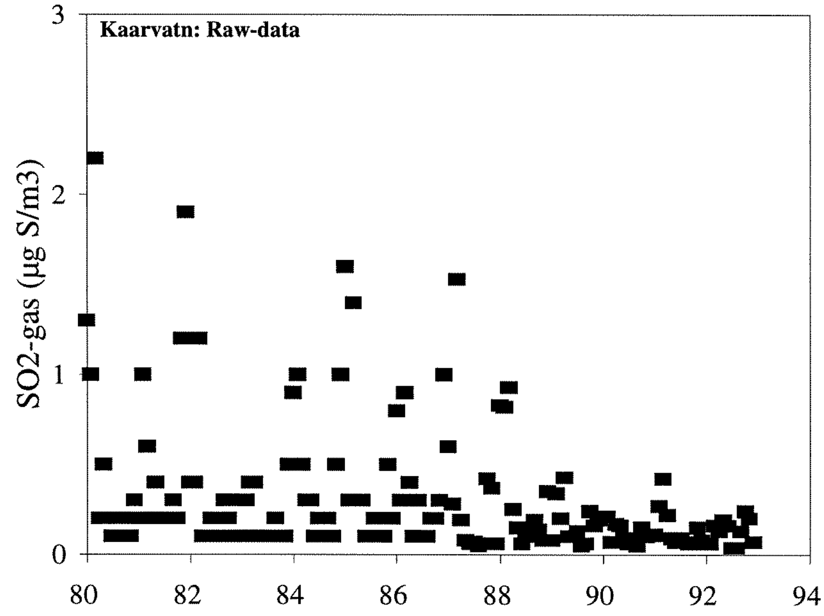


Figure 6.3 The monthly weighted concentration of sulphur in air (µg S/m^3) at Birkenes from 1978-1992, present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualizes the influence of water on the concentration of each chemical compounds, i.e. large scattering means high water dependence and vise versa. The linear regression equations are present in Table 6.1. Continuous line means that the linear regression is significant, i.e. $p < 0.05$, *while a dottet line means no significance,* $p > 0.05$.



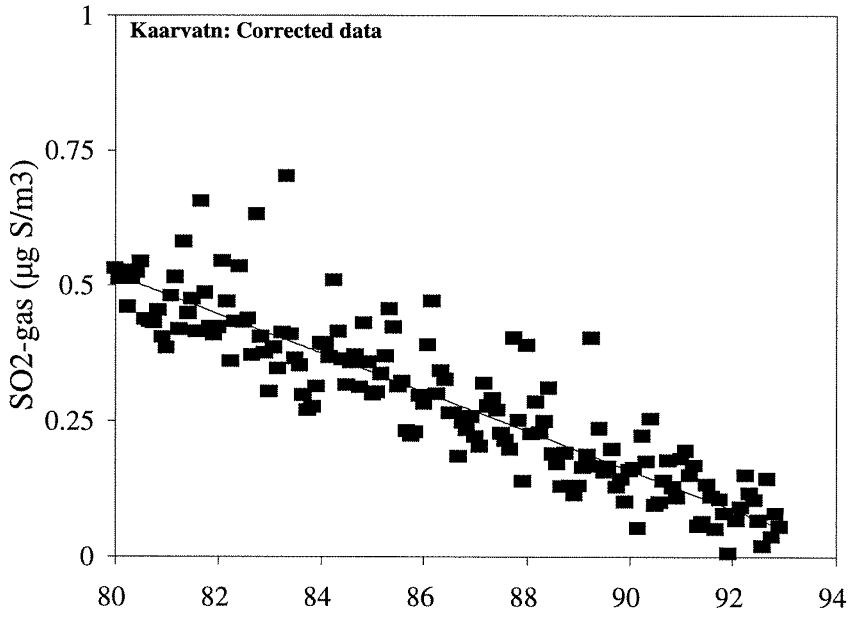
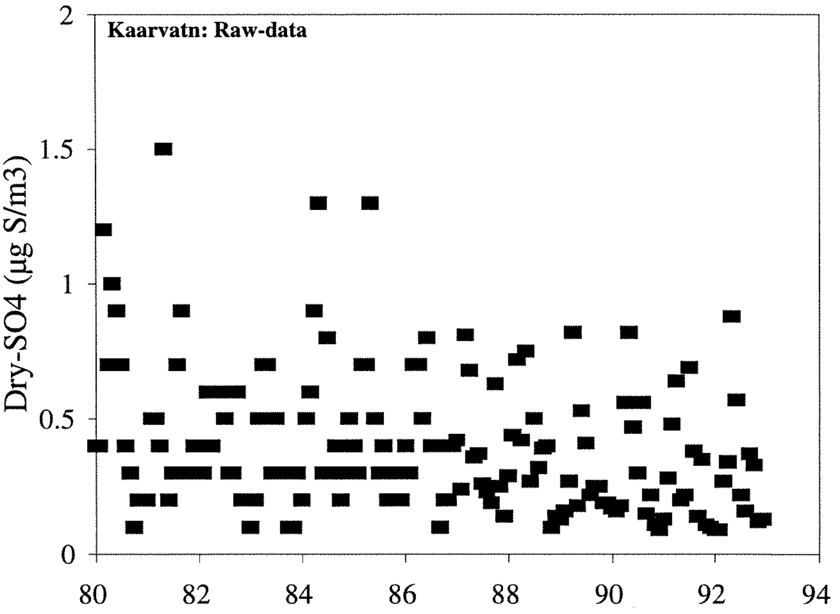


Figure 6.4 The monthly weighted concentration of SO_2-gas in air (µg S/m^3) at Kaarvatn from 1980-1992, present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualizes the influence of water on the concentration of each chemical compounds, i.e. large scattering means high water dependence and vise versa. The linear regression equations are present in Table 6.1. Continuous line means that the linear regression is significant, i.e. $p < 0.05$, while a dottet line means no significance, $p > 0.05$.



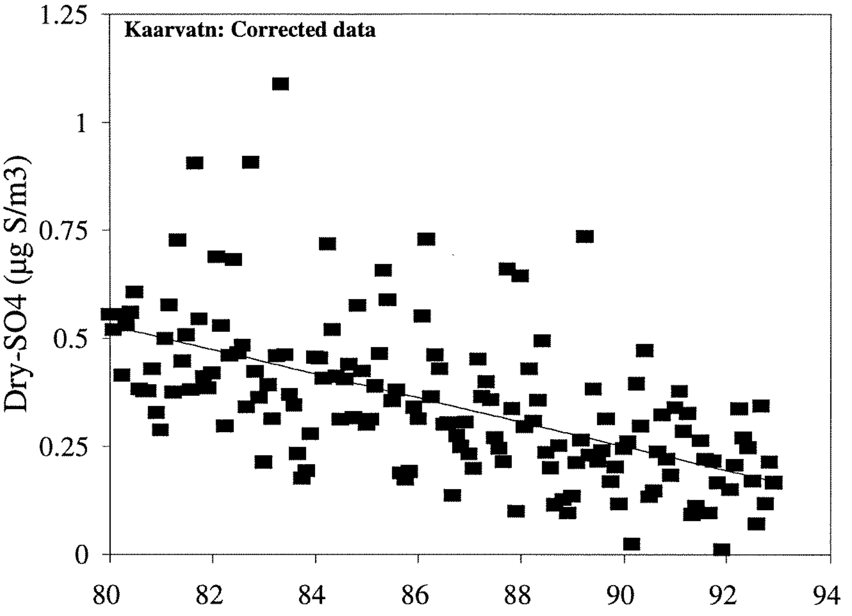
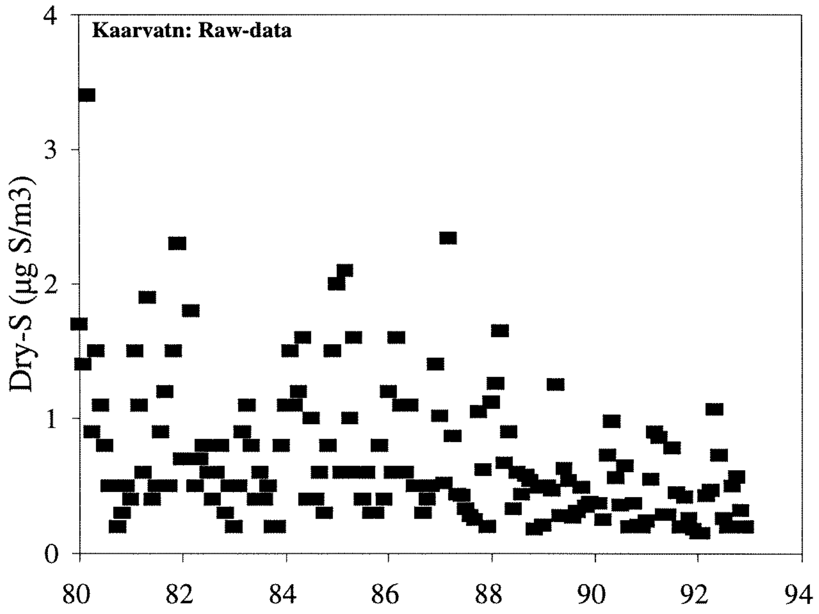


Figure 6.5 The monthly weighted concentration of SO_4*-particles in air (*$\mu g\ S/m^3$*) at Kaarvatn from 1980-1992, present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualizes the influence of water on the concentration of each chemical compounds, i.e. large scattering means high water dependence and vise versa. The linear regression equations are present in Table 6.1. Continuous line means that the linear regression is significant, i.e.* $p < 0.05$*, while a dottet line means no significance,* $p > 0.05$*.*



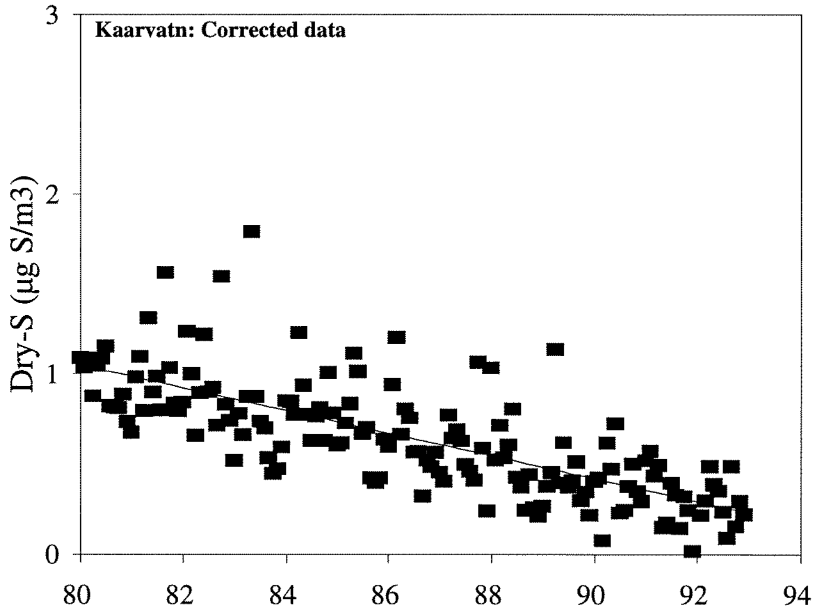
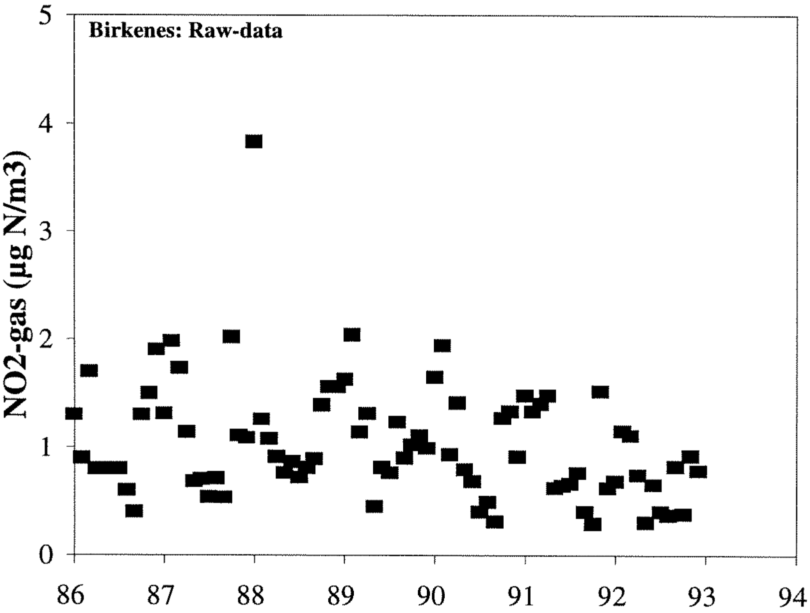


Figure 6.6 The monthly weighted concentration of sulphur in air (µg S/m^3*) at Kaarvatn from 1980-1992, present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualizes the influence of water on the concentration of each chemical compounds, i.e. large scattering means high water dependence and vise versa. The linear regression equations are present in Table 6.1. Continuous line means that the linear regression is significant, i.e.* $p < 0.05$*, while a dottet line means no significance,* $p > 0.05$*.*



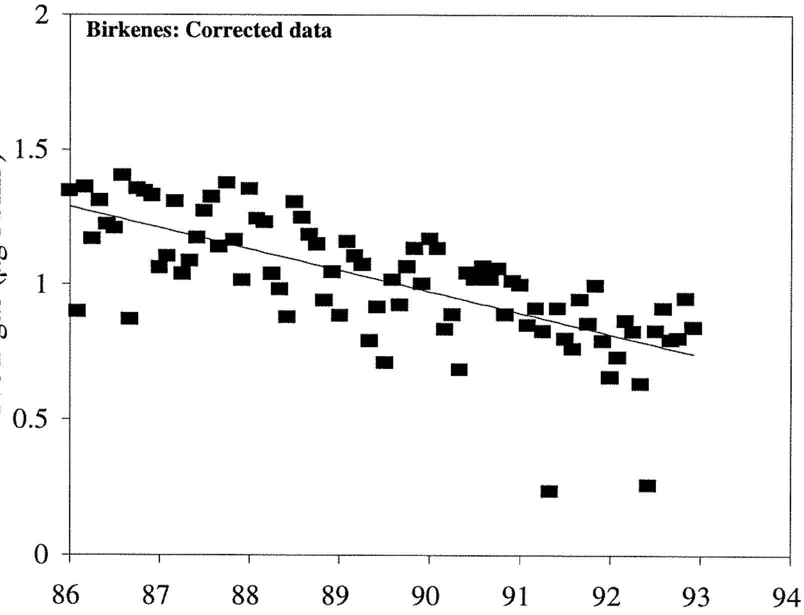
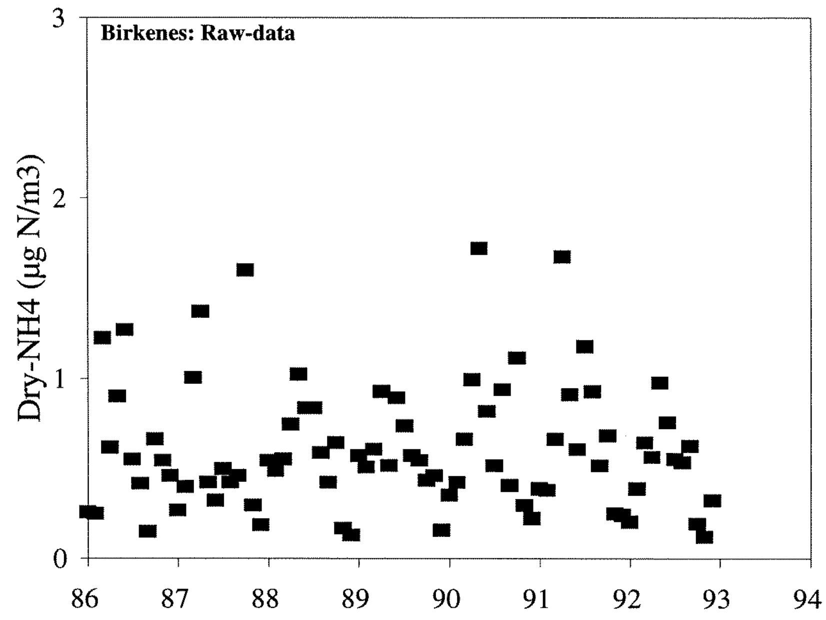


Figure 6.7 The monthly weighted concentration of NO_2-gas in air (µg N/m^3) at Birkenes from 1986-1992, present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualizes the influence of water on the concentration of each chemical compounds, i.e. large scattering means high water dependence and vise versa. The linear regression equations are present in Table 6.1. Continuous line means that the linear regression is significant, i.e. $p < 0.05$, while a dottet line means no significance, $p > 0.05$.



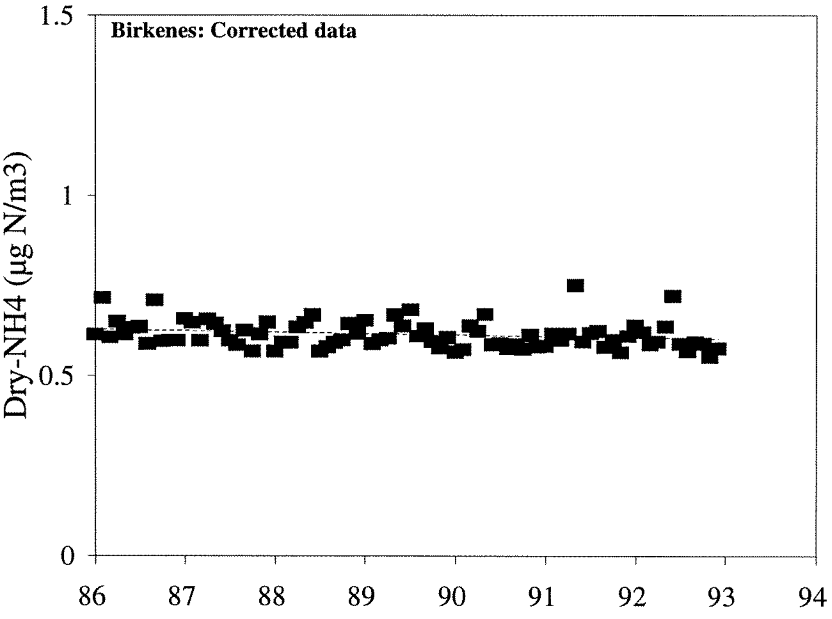


Figure 6.8 The monthly weighted concentration of NH4-particles in air (μg N/m³) at Birkenes from 1986-1992, present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualizes the influence of water on the concentration of each chemical compounds, i.e. large scattering means high water dependence and vise versa. The linear regression equations are present in Table 6.1. Continuous line means that the linear regression is significant, i.e. $p < 0.05$, while a dottet line means no significance, $p > 0.05$.

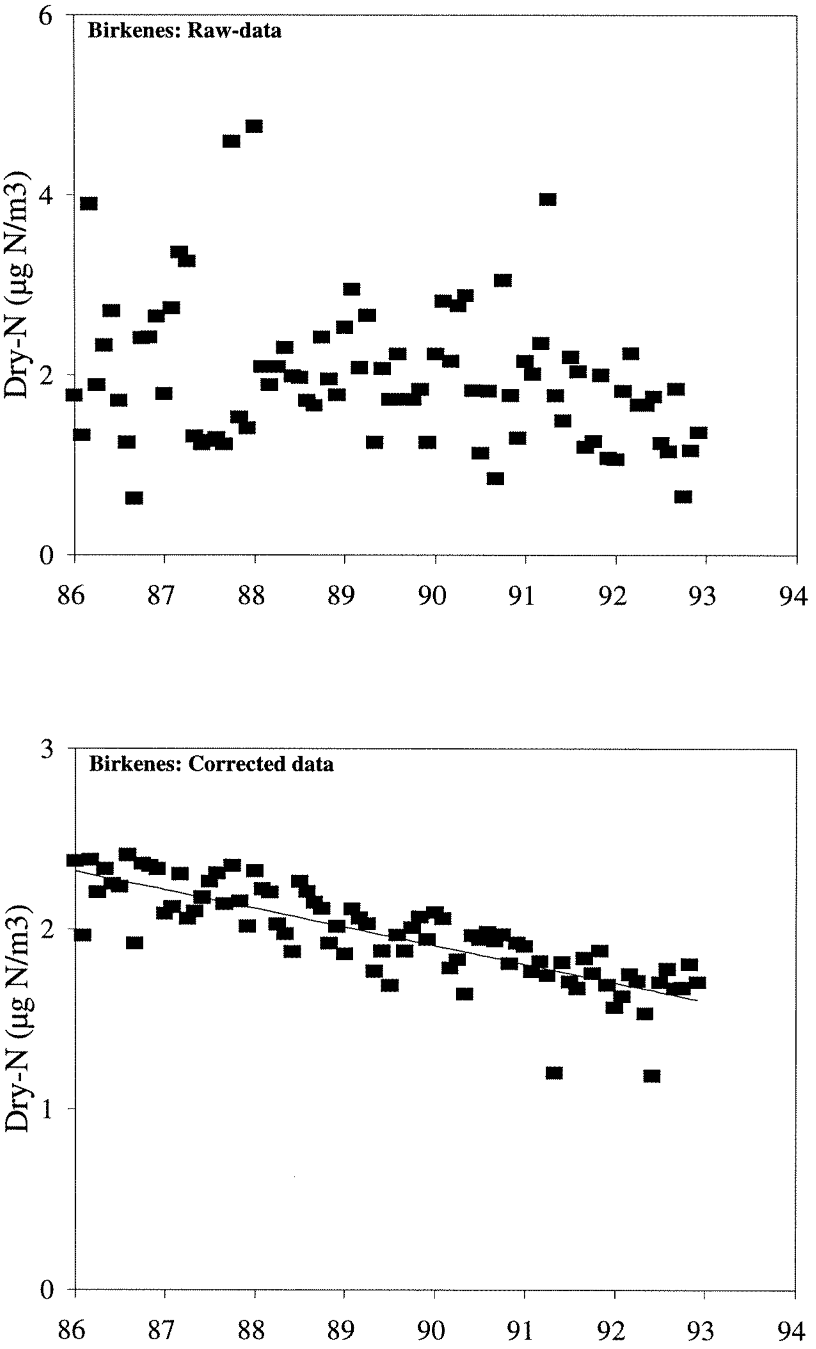
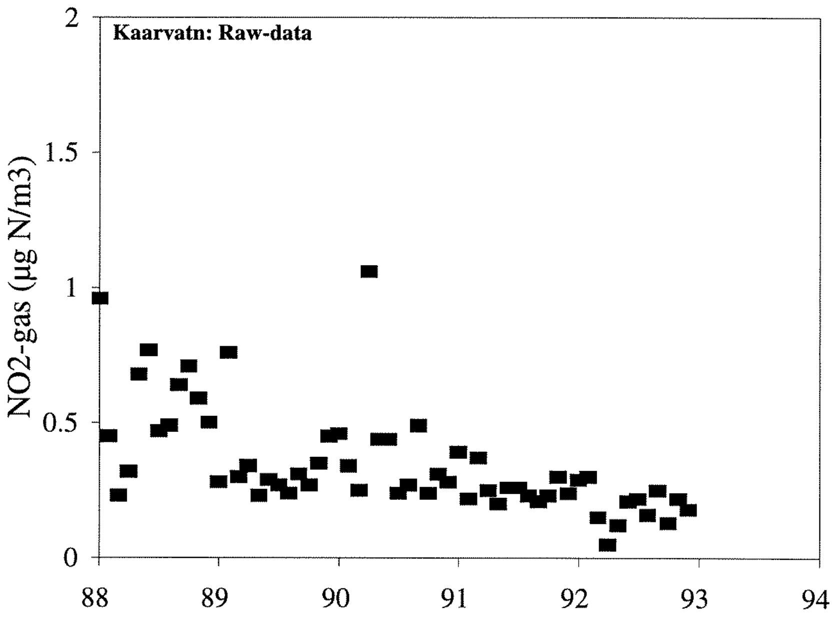


Figure 6.9 The monthly weighted concentration of oxidized and reduced nitrogen compounds in air (μg N/m^3) at Birkenes from 1986-1992, present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualizes the influence of water on the concentration of each chemical compounds, i.e. large scattering means high water dependence and vise versa. The linear regression equations are present in Table 6.1. Continuous line means that the linear regression is significant, i.e. $p < 0.05$, while a dottet line means no significance, $p > 0.05$.



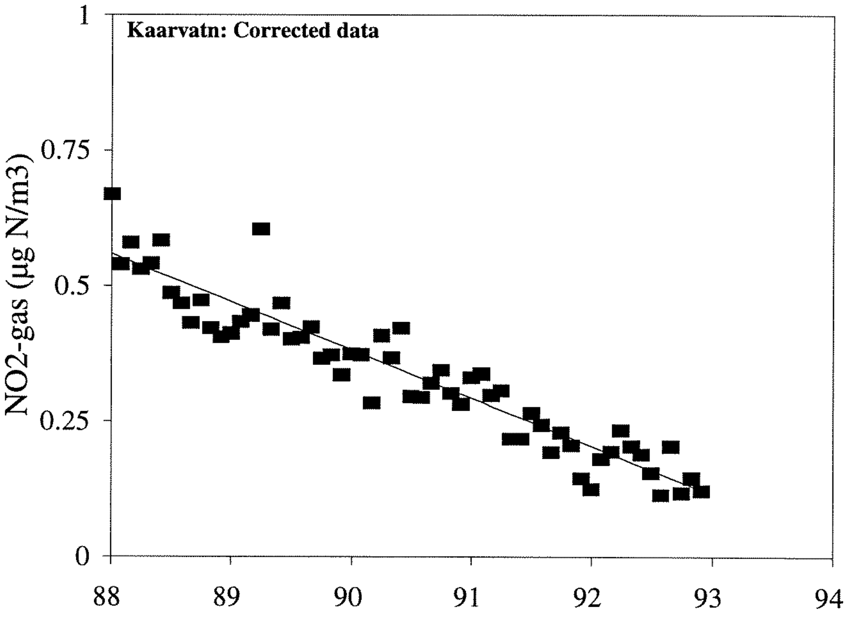
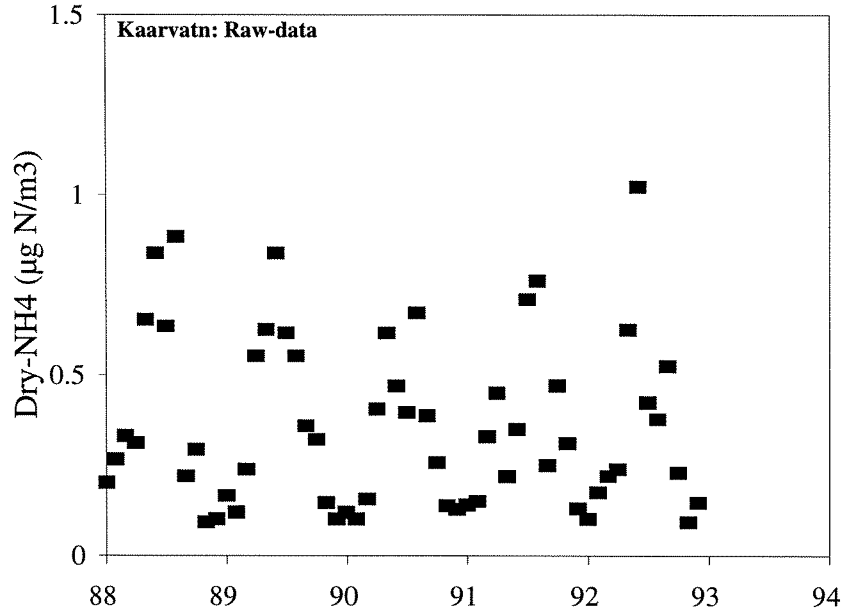


Figure 6.10 The monthly weighted concentration of NO_2-gas in air (µg N/m^3) at Kaarvatn from 1988-1992, present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualizes the influence of water on the concentration of each chemical compounds, i.e. large scattering means high water dependence and vise versa. The linear regression equations are present in Table 6.1. Continuous line means that the linear regression is significant, i.e. $p < 0.05$, while a dottet line means no significance, $p > 0.05$.



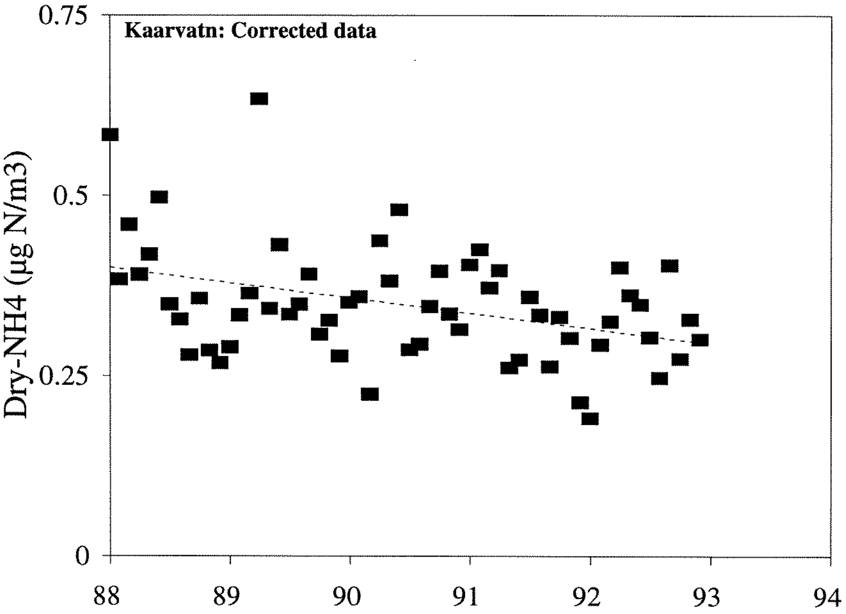
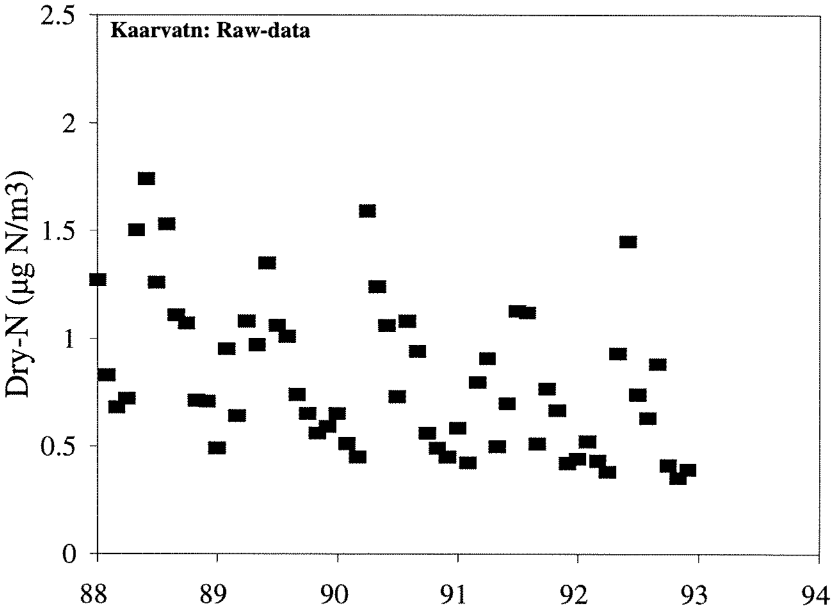


Figure 6.11 The monthly weighted concentration of NH_4-particles in air (μg N/m^3) at Kaarvatn from 1988-1992, present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualizes the influence of water on the concentration of each chemical compounds, i.e. large scattering means high water dependence and vise versa. The linear regression equations are present in Table 6.1. Continuous line means that the linear regression is significant, i.e. $p < 0.05$, while a dottet line means no significance, $p > 0.05$.



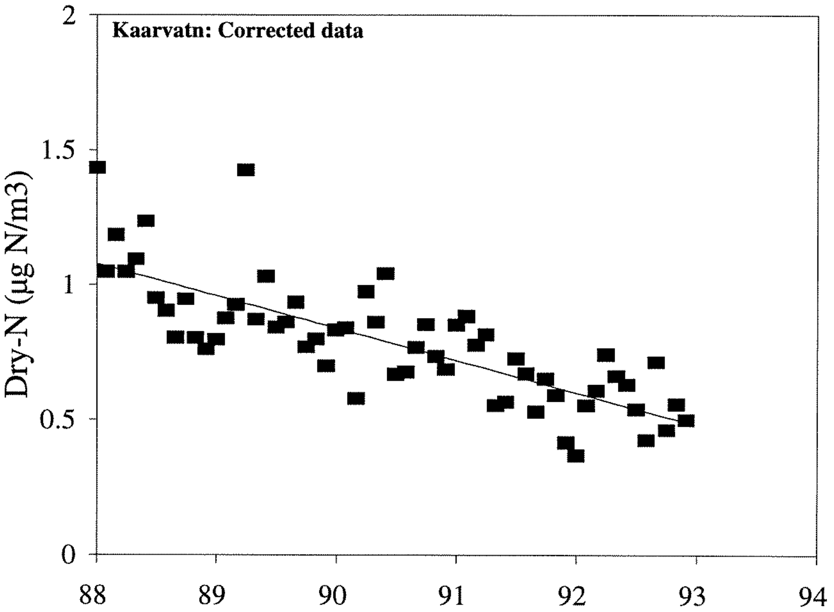
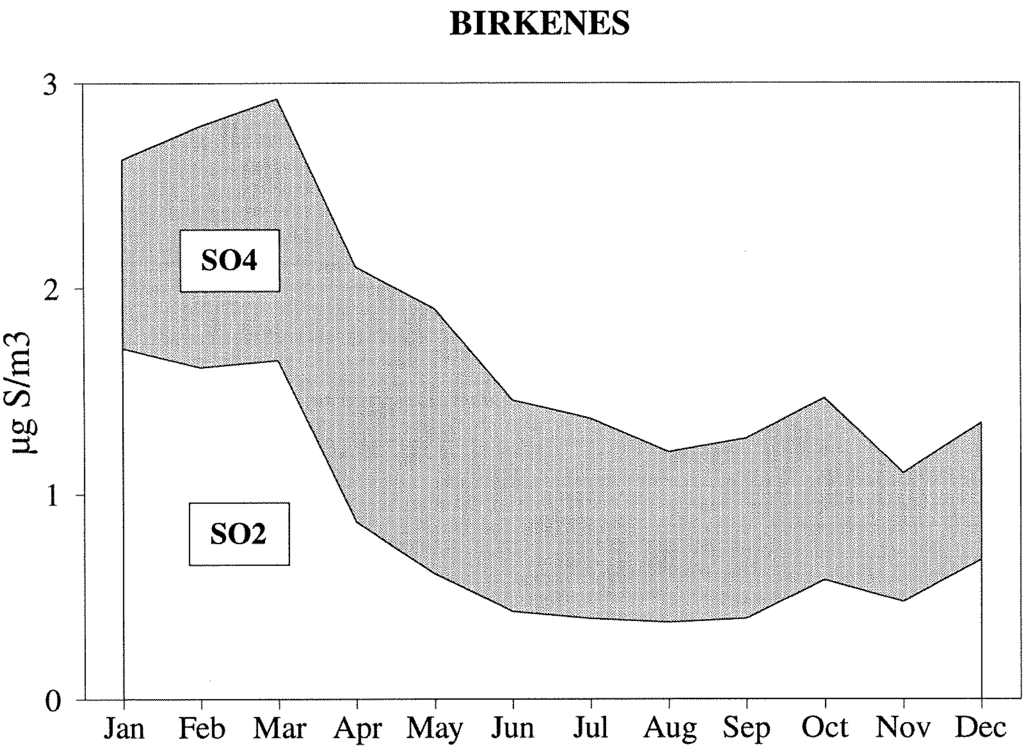


Figure 6.12 The monthly weighted concentration of oxidized and reduced nitrogen compounds in air (µg N/m^3) at Kaarvatn from 1988-1992, present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualizes the influence of water on the concentration of each chemical compounds, i.e. large scattering means high water dependence and vise versa. The linear regression equations are present in Table 6.1. Continuous line means that the linear regression is significant, i.e. $p < 0.05$, *while a dottet line means no significance,* $p > 0.05$.

As described above, the scattering of data in the figures based on corrected data, visualizes the degree of water-influence on the concentration of chemical compounds, i.e. large scattering means high water influence and vise versa. As well illustrated in Table 6.1 (and Figure 6.1 to 6.3, and Figure 6.7 to 6.9), the amount of precipitation has minor influence on the concentration of sulphur and nitrogen compounds in dry-deposition at Birkenes. Generally the concentration of sulphur in air exhibits a very weak decrease by increasing inputs of water. It is only the concentration of NO_2 in air which exhibits a positive but also significant correlation with amount of preciptation. This may rely on several factors. One possible explanation is that high inputs of water often is associated with thunder and lightening, an atmospheric activity which forms nitrogen oxides from molecular N_2 and O_2. If so, an increase in NO_2 by increasing amount of precipitation should also be expected at Kaarvatn, but at this site the concentration of NO_2-gas generally decreases by increasing amount of precipitation.

Another explanation is that the NO_2-gas in the air at Birkenes to a large extent derives from England and Central Europe. The strongest low-pressures normally enters southern Norway from these areas (south and southwestern winds). Strong low pressures are often associated with strong winds and heavy rainfall, which means that they moves very fast from England and Central Europe to southernmost Norway, which of cause reduce the posibility of gases to. dilute. The third and probably most likely explanation is that the highest concentrations of NO_2-gas normally occur during autumn and winter, when the vegetation growth has terminated and the anthropogenic produced NO_2-gas is at the highest (Figure 6.14). During the same period, the input of water at Birkenes is at the highest (Figure 4.3). Thus, the increase in the concentration of NO_2-gas by increasing amount of precipitation only relies on these concurrence of events.

At Kaarvatn the concentration of sulphur compounds in dry-deposition is far more dependant on the amount of precipitation. This is most enhanced for the concentration of SO_4-particles, which illustrates the influence of SO_4-particles from seaspray more than anthropogenic pollution (Figure 6.19). The concentration of NH_4-particles in air is also relatively water-dependant. But, while the concentration of NH_4-particles at Birkenes is at the highest during initial growth period, when the fields are fertilized and the influence from natural break-down processes of organic material are at the highest, it continuous to increase during the whole summer at Kaarvatn. This may rely on several factors. The lowest amounts of precipitation normally occur during the summer. During the same period, the influence from local animal husbandry (grazing) is at the higest, which implies high local concentration of NH_4 in air. The strong seasonal regularity (Figure 6.10) in the NH_4-concentration in dry-deposition at Kaarvatn may therefore indicate local influence from animal husbandry.



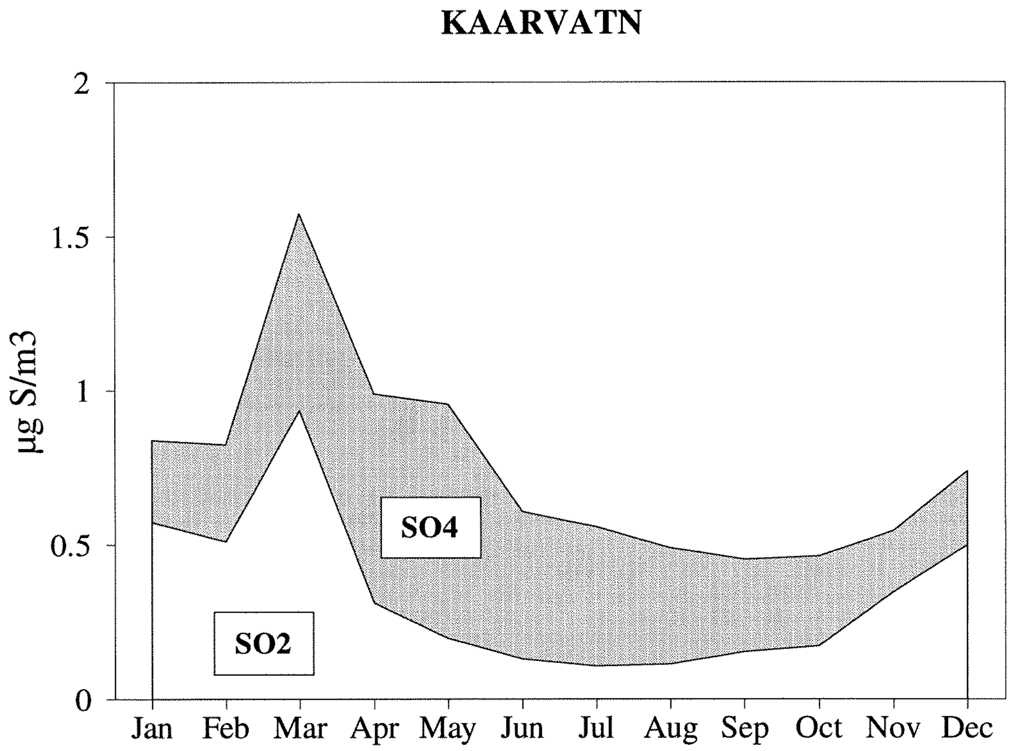
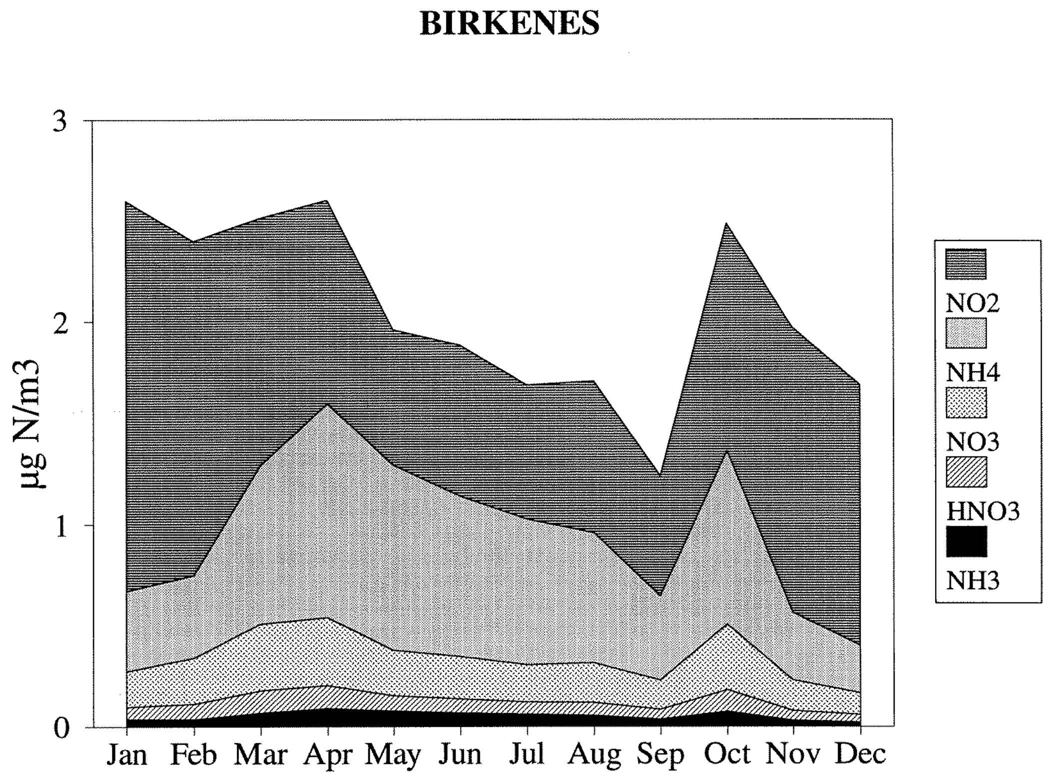


Figure 6.13 The monthly weighted concentration averages of SO_2-gas and SO_4-particles in dry-deposition at Birkenes and Kaarvatn.



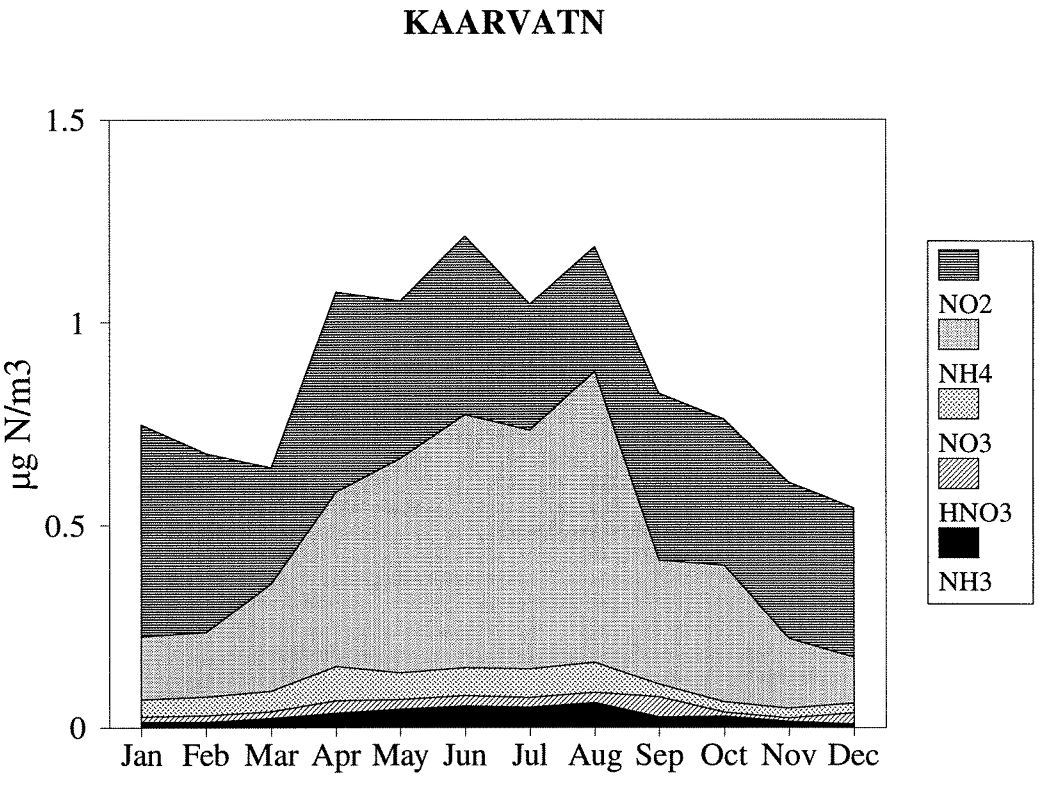


Figure 6.14 The monthly weighted concentration averages of reduced and oxidized nitrogen compounds in dry-deposition at Birkenes and Kaarvatn.

Time trends in fluxes of dry-deposited compounds

While a linear/linear relationship best describes the the effects of water changes on the fluxes of chemical compounds in wet-deposition and runoff, a correspondant half-logaritmic relationship better explain changes in fluxes of chemical compounds in dry-deposition, i.e. the influx of a chemical compound in dry-deposition normally exhibits a logaritmic decrease by increasing input of water.

Based on linear regression analysis (see Table 6.2), the monthly weighted deposition average of SO_2-gas (mg S/m^2) at Birkenes has decreased from an average of 8.67 ± 5.34 mg S/m^2 at the beginning of 1978 to 3.44 ± 1.35 mg S/m^2 at the end of 1992 (Figure 6.15), which means a 60% reduction during 1978-1992. Accordingly, while the average monthly influx of SO_4-particles at the beginning of 1978 was 13.7 ± 7.59 mg S/m^2, the average influx at the end of 1992 was 7.10 ± 1.95 mg S/m^2 (Figure 6.16), which is a 48% reduction from 1978 to 1992. The total average monthly influx of sulphur in dry-deposition was 22.8 ± 12.2 mg S/m^2 at the beginning of 1978. At the end of 1992, the average monthly influx has decreased by 57% to an average of 9.76 ± 3.15 mg S/m^2 (Figure 6.17).

At Kaarvatn, the monthly weighted deposition of SO_2-gas (mg S/m^{2}mth) has decreased from an average of 3.14 ± 1.68 mg S/m^2 at the beginning of 1980 to 0.98 ± 0.52 mg S/m^2 at the end of 1992 (Figure 6.18), which means a 69% reduction during 1980-1992. Accordingly, while the monthly average influx of SO_4-particles at the beginning of 1980 was 6.08 ± 4.43 mg S/m^2, the average influx at the end of 1992 was 3.27 ± 1.17 mg S/m^2 (Figure 6.19), which is a 46% reduction from 1980 to 1992. While the monthly average influx of total sulphur in dry deposition at the beginning of 1980 was 9.22 ± 5.74 mg S/m^2, the influx has decreased by 54% at the end of 1992 down to an average of 4.24 ± 1.56 mg S/m^2 (Figure 6.20).

As for the concentration of SO_2-gas and SO_4-particles, the correspondent fluxes are significantly reduced at both Birkenes and Kaarvatn, The percentage decline is about the same at the two sites. Because the anthropogenic emmissions of sulphur compounds in Europe started to decline about 1978-1980, a significant reduction in sulphur compounds in air should also be expected.

Based on linear regression analysis (see Table 6.2), the monthly deposition of NO_2-gas at Birkenes has decreased from an average 7.66 ± 4.10 mg N/m^2 at the beginning of 1986 to an average of 5.49 ± 1.54 mg N/m^2 at the end of 1992 (Figure 6.21), which means a 28% reduction during 1986-1992. Accordingly, while the average monthly deposition of NH_4-particles at the beginning of 1986 was 6.72 ± 6.14 mg N/m^2, the average deposition at the end of 1992 was 7.54 ± 2.31 mg N/m^2 (Figure 6.22), which is an increase by 12% from 1986 to 1992. The total average weighted monthly influx of nitrogen in dry deposition (ΣNO_2,HNO_3, NO_3, NH_4,NH_3) at the beginning of 1986 was 22.0 ± 13.5 mg N/m^2. At the end of 1992, the average monthly influx has decreased by 15% down to an average of 18.6 ± 5.11 mg N/m^2(Figure 6.23).

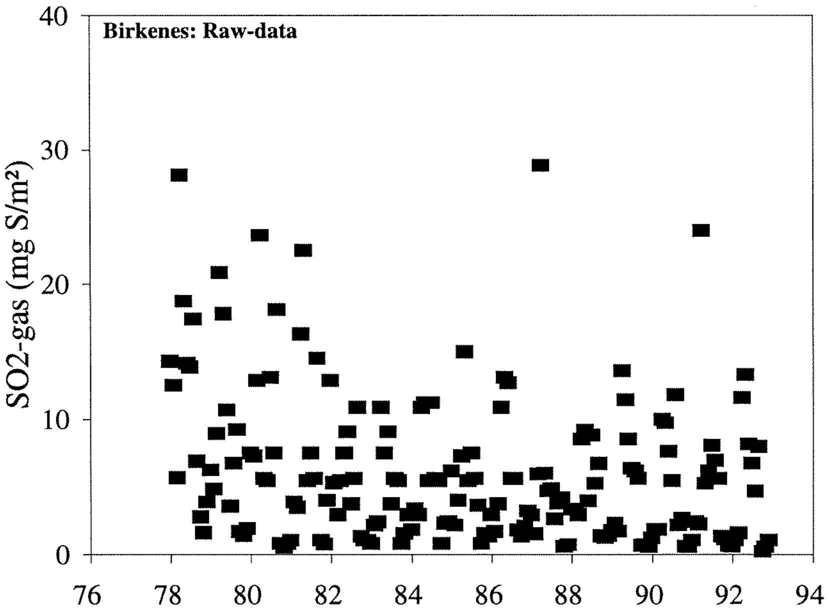
At Kaarvatn, the deposition of NO_2-gas has decreased from a monthly weighted average of 4.34 ± 2.54 mg N/m^2 at the beginning of 1988 to an average of 1.12 ± 1.15 mg N/m^2 at the end of 1992 (Figure 6.24), which means a 74% reduction during the period. Accordingly, while the average monthly input of NH_4-particles was 5.21 ± 4.46 mg N/m^2 at the beginning of 1988, the average monthly input at the end of 1992 was 4.23 ± 2.00 mg N/m² (Figure 6.25), which is a reduction of 19%.

The total average monthly influx of oxidized and reduced nitrogen compounds in dry deposition was 12.5 ± 7.92 mg N/m² at the beginning of 1988. At the end of 1992 the monthly input has decreased by 46% down to an average of 6.72 ± 3.55 mg N/m² (Figure 6.26).

Only the decline in input of NO_2-gas at Kaarvatn is significant (if assuming $p < 0.05$ as criteria of significance) during the monitoring period (1988-1992). The remaining nitrogen compounds in dry-deposition at both Birkenes and Kaarvatn exhibit no significant trends during the monitoring periods, i.e. from 1986-1992 at Birkenes, and from 1988-1992 at Kaarvatn.

Table 6.2 Annual time trends in fluxes (mg/m²) of sulphur and nitrogen compounds in dry-deposition, at Birkenes and Kaarvatn, based on raw data $[y(t) = (\delta y_1/\delta t)t + b_1]$ *and time trends after the water dependent concentration changes* $[\delta y_1/\delta \log(q)]$ *are accounted for, i.e.* $[Y(t) = (\delta y_1/\delta t)t + [\delta y_1/\delta \log(q)]\log(q)] + b_2]$. *The constant* b_2 *is fitted so* $b_2 = b_1$. *(*:* $p < 0.05$, ***:* $p < 0.01$*).*

		Raw-data			**Water dependance**		**Corrected data**	
	Period	$\delta y_1/\delta t$	b_1	r_1	$\delta y/\delta \log(q)$	r_q	$\delta y_2/\delta t$	r_2
Birkenes								
SO_2-gas	1978-1992	-0.35 ± 0.09	8.67 ± 5.34	-0.27**	-3.21 ± 1.03	-0.23**	-0.36 ± 0.02	-0.78**
SO_4-part.	1978-1992	-0.44 ± 0.13	13.7 ± 7.59	-0.25**	-1.30 ± 1.49	-0.07	-0.45 ± 0.01	-0.97**
ΣDry-S	1978-1992	-0.87 ± 0.21	22.8 ± 12.2	-0.29**	-6.19 ± 2.39	-0.19	-0.89 ± 0.04	-0.85**
NO_2-gas	1986-1992	-0.31 ± 0.22	7.66 ± 4.10	-0.15	-1.52 ± 1.09	-0.15	-0.29 ± 0.03	-0.69**
NH_4-part.	1986-1992	0.12 ± 0.33	6.72 ± 6.14	0.04	-4.17 ± 1.56	-0.28**	-0.17 ± 0.09	-0.20
ΣDry-N	1986-1992	-0.49 ± 0.73	22.0 ± 13.5	-0.07	-6.40 ± 3.51	-0.20	-0.41 ± 0.14	-0.30**
Kaarvatn								
SO_2-gas	1980-1992	-0.16 ± 0.04	3.14 ± 1.68	-0.35**	-2.03 ± 0.40	-0.37**	-0.15 ± 0.01	-0.65**
SO_4-part.	1980-1992	-0.22 ± 0.09	6.08 ± 4.43	-0.18*	-6.21 ± 0.97	-0.46**	-0.32 ± 0.04	-0.52**
ΣDry-S	1980-1992	-0.38 ± 0.12	9.22 ± 5.74	-0.24**	-8.24 ± 1.27	-0.46**	-0.53 ± 0.06	-0.59**
NO_2-gas	1988-1992	-0.65 ± 0.23	4.34 ± 2.54	-0.35**	-2.60 ± 1.18	-0.28*	-0.73 ± 0.07	-0.82**
NH_4-part.	1988-1992	-0.20 ± 0.40	5.21 ± 4.46	-0.06	-4.27 ± 1.95	-0.28*	-0.32 ± 0.11	-0.36**
ΣDry-N	1988-1992	-1.16 ± 0.71	12.5 ± 7.92	-0.21	-8.06 ± 3.51	-0.29*	-1.39 ± 0.21	-0.66**



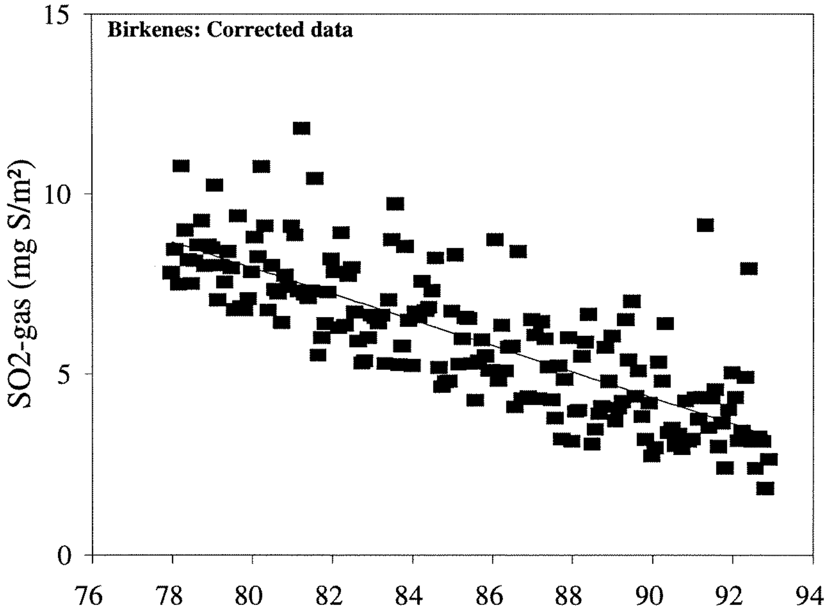


Figure 6.15 The monthly weighted influx of SO_2-gas (mg S/m^2) at Birkenes from 1978-1992, present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualizes the influence of water on the flux of each chemical compounds, i.e. large scattering means high water dependence and vise versa. The linear regression equations are present in Table 6.2. Continuous line means that the linear regression is significant, i.e. $p < 0.05$, while a dottet line means no significance, $p > 0.05$.

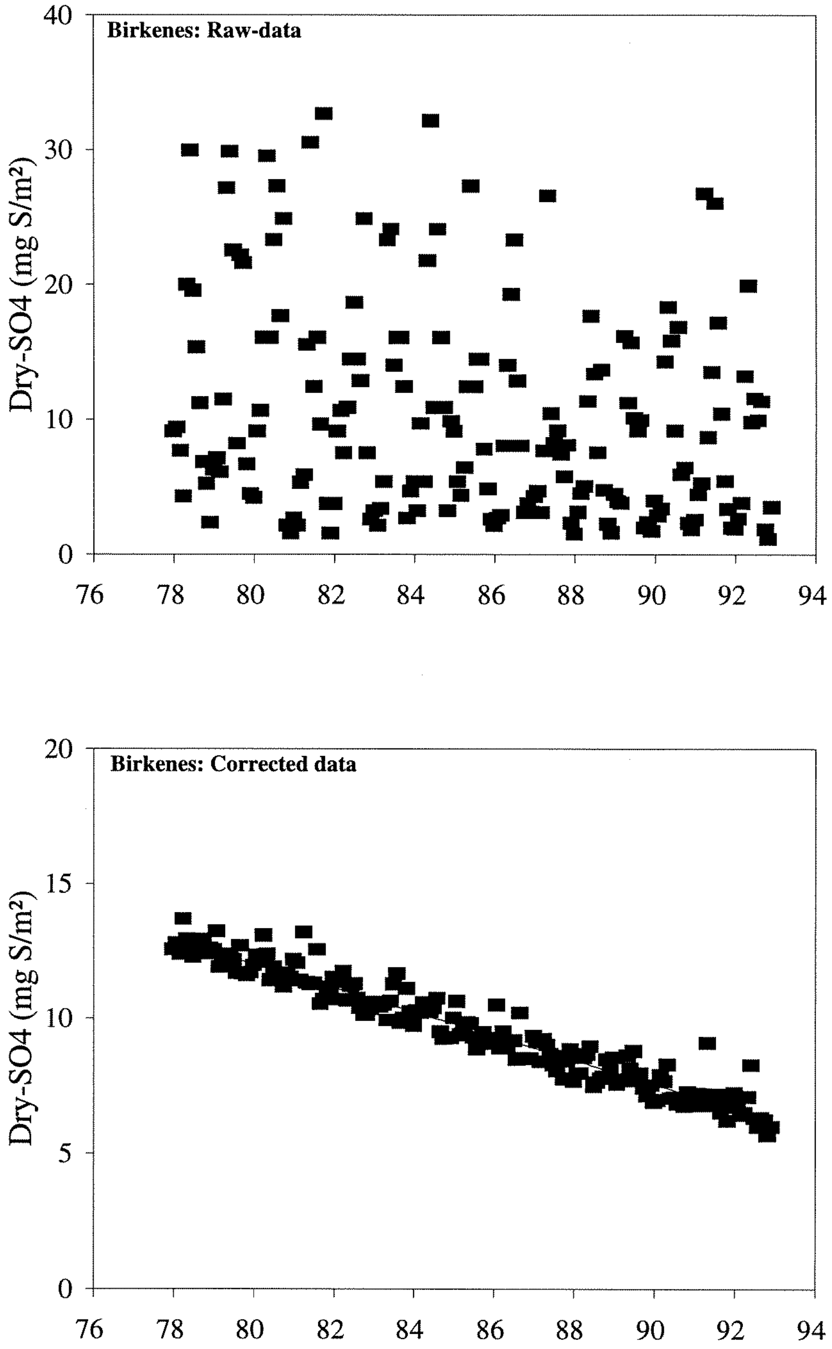
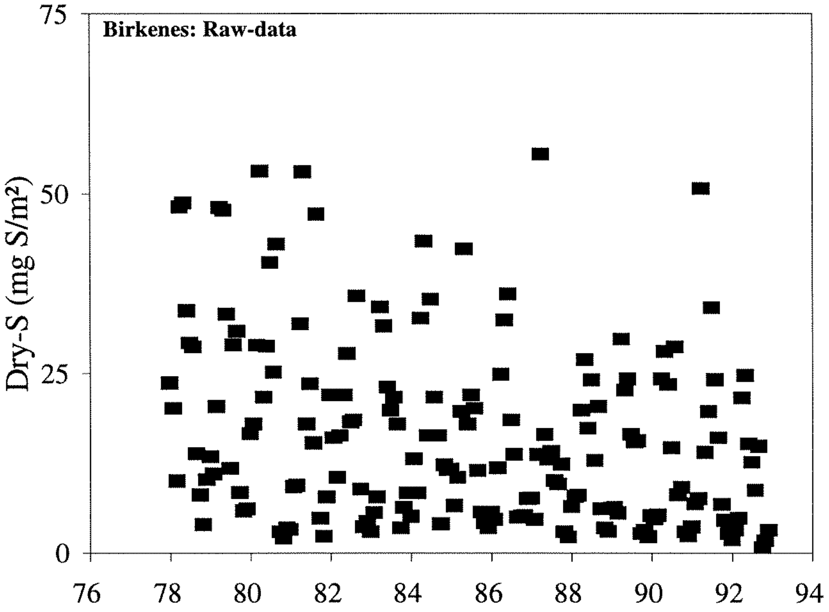


Figure 6.16 The monthly weighted influx of SO_4-particles (mg S/m^2) at Birkenes from 1978-1992, present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualizes the influence of water on the flux of each chemical compounds, i.e. large scattering means high water dependence and vise versa. The linear regression equations are present in Table 6.2. Continuous line means that the linear regression is significant, i.e. $p < 0.05$, while a dottet line means no significance, $p > 0.05$.



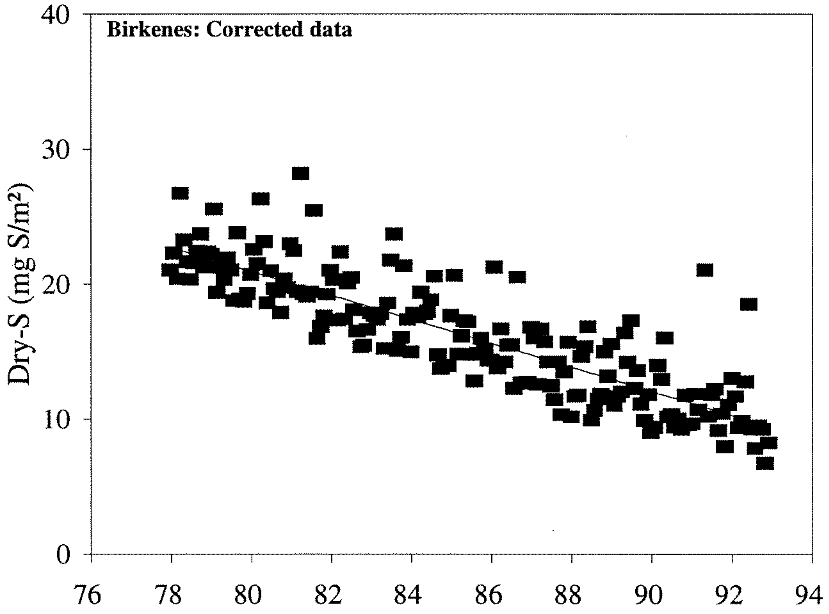
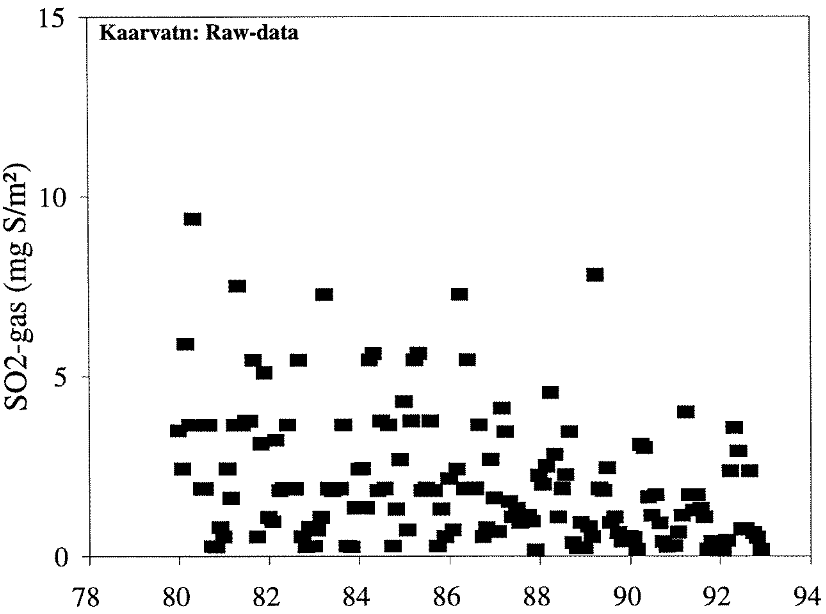


Figure 6.17 The monthly weighted influx of sulphur in dry-deposition (mg S/m²) at Birkenes from 1978-1992, present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualizes the influence of water on the flux of each chemical compounds, i.e. large scattering means high water dependence and vise versa. The linear regression equations are present in Table 6.2. Continuous line means that the linear regression is significant, i.e. $p < 0.05$, while a dottet line means no significance, $p > 0.05$.



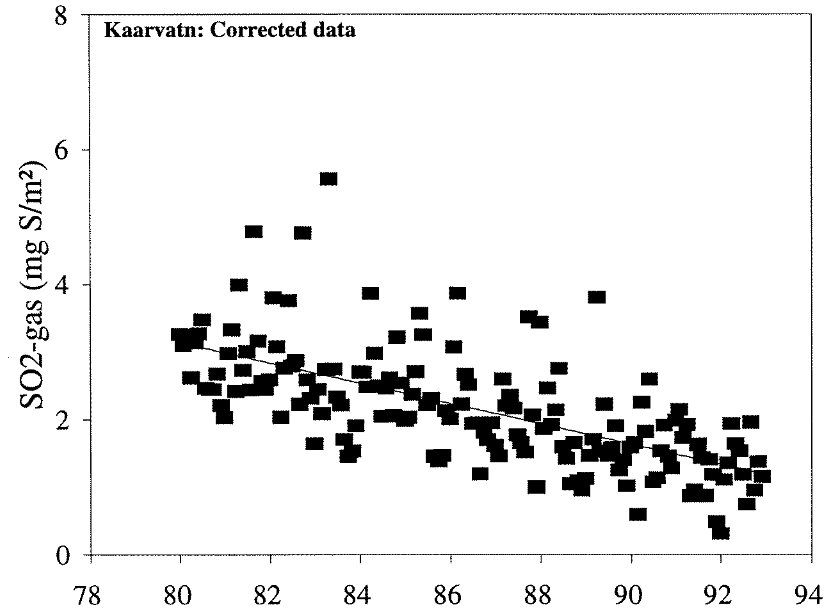
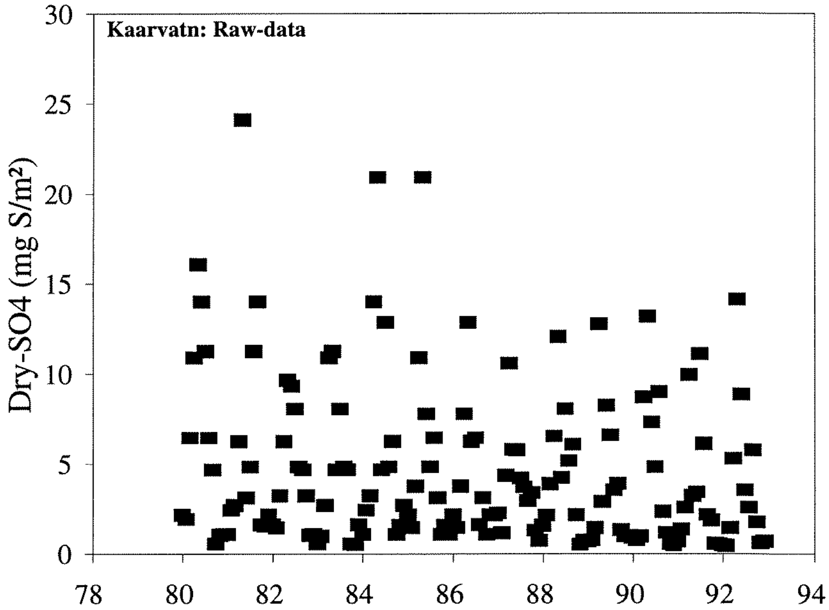


Figure 6.18 The monthly weighted influx of SO_2-gas (mg S/m^2) at Kaarvatn from 1980-1992, present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualizes the influence of water on the flux of each chemical compounds, i.e. large scattering means high water dependence and vise versa. The linear regression equations are present in Table 6.2. Continuous line means that the linear regression is significant, i.e. $p < 0.05$, while a dottet line means no significance, $p > 0.05$.



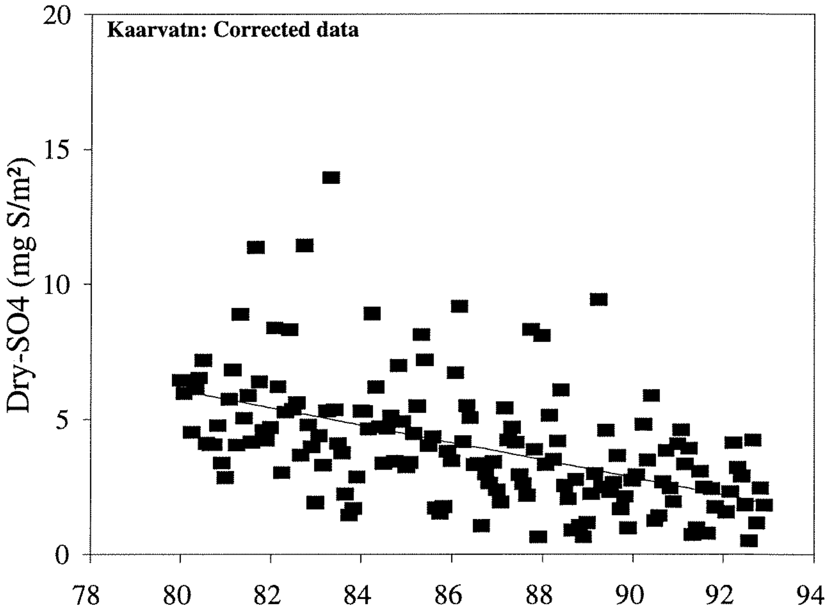
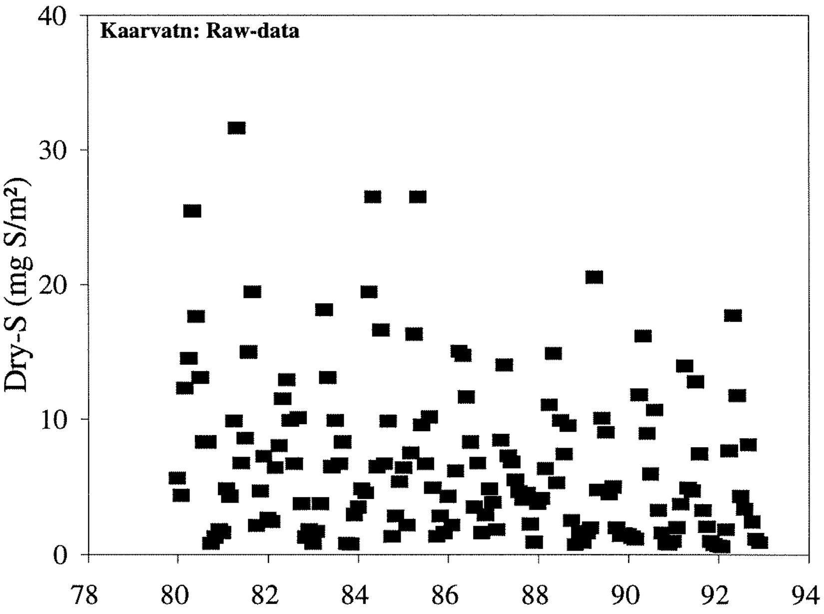


Figure 6.19 The monthly weighted influx of SO_4-particles (mg S/m^2) at Kaarvatn from 1980-1992, present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualizes the influence of water on the flux of each chemical compounds, i.e. large scattering means high water dependence and vise versa. The linear regression equations are present in Table 6.2. Continuous line means that the linear regression is significant, i.e. $p < 0.05$, while a dottet line means no significance, $p > 0.05$.



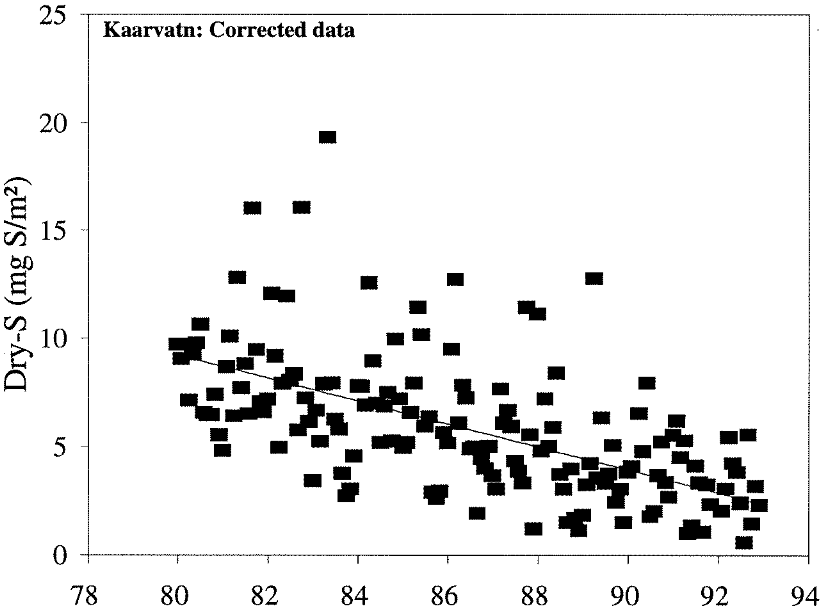
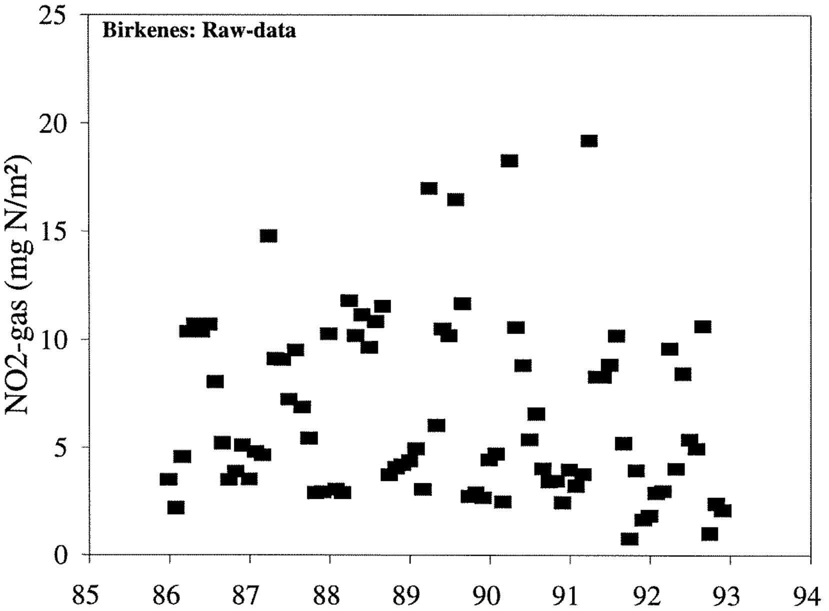


Figure 6.20 The monthly weighted influx of sulphur in dry-deposition (mg S/m²) at Kaarvatn from 1980-1992, present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualizes the influence of water on the flux of each chemical compounds, i.e. large scattering means high water dependence and vise versa. The linear regression equations are present in Table 6.2. Continuous line means that the linear regression is significant, i.e. $p < 0.05$, while a dottet line means no significance, $p > 0.05$.



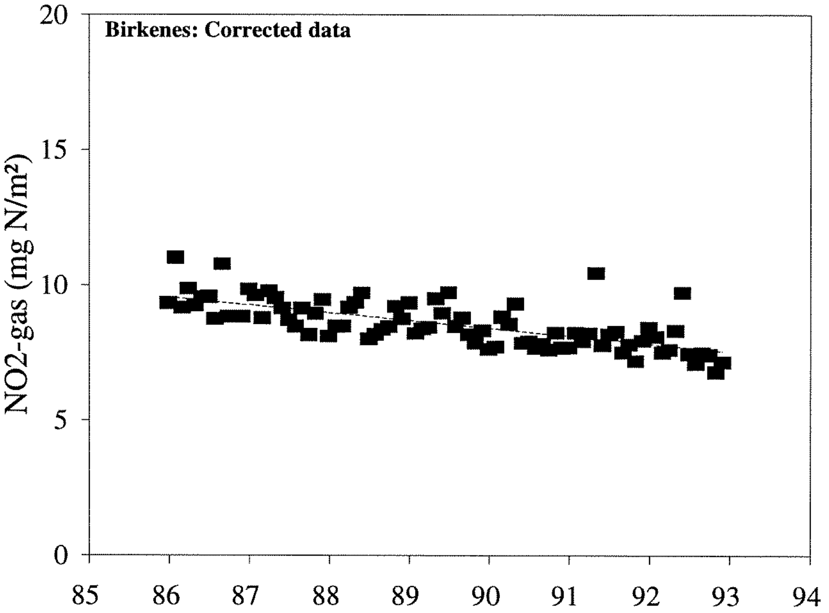
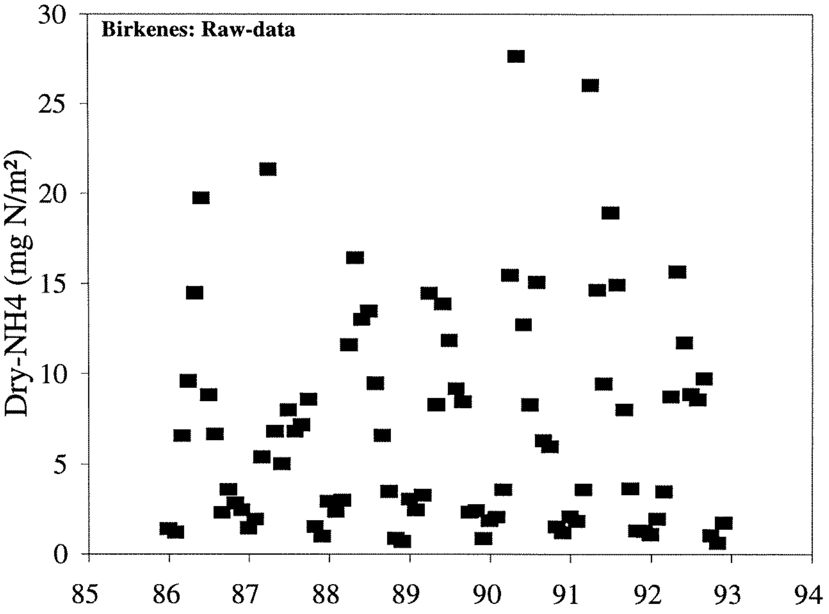


Figure 6.21 The monthly weighted influx of NO_2*-gas (mg N/m*^{2}*) at Birkenes from 1986-1992, present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualizes the influence of water on the flux of each chemical compounds, i.e. large scattering means high water dependence and vise versa. The linear regression equations are present in Table 6.2. Continuous line means that the linear regression is significant, i.e.* $p < 0.05$*, while a dottet line means no significance,* $p > 0.05$*.*



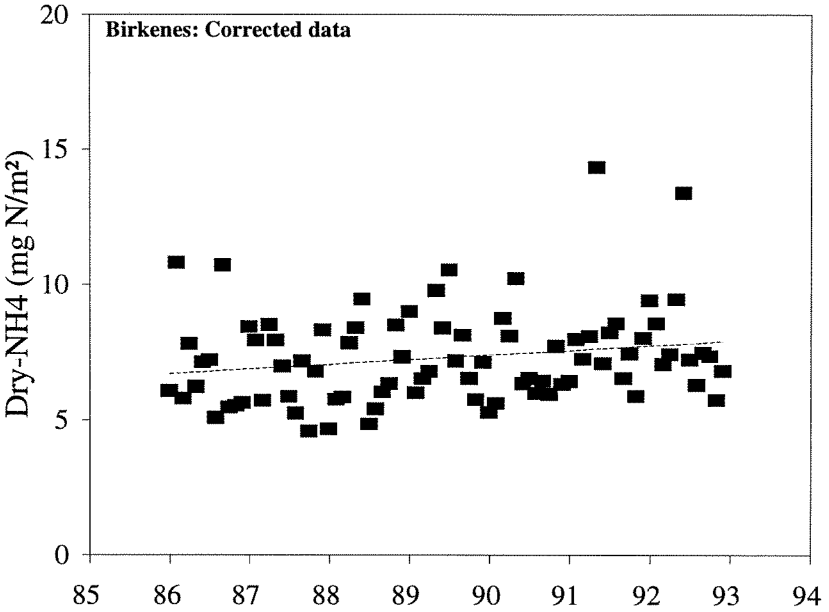
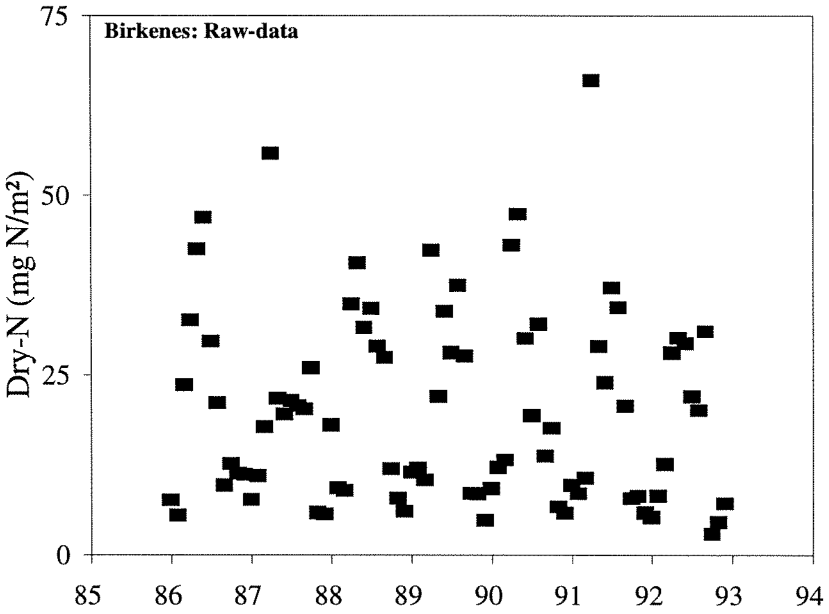


Figure 6.22 The monthly weighted influx of NH_4-particles (mg N/m^2) at Birkenes from 1986-1992, present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualizes the influence of water on the flux of each chemical compounds, i.e. large scattering means high water dependence and vise versa. The linear regression equations are present in Table 6.2. Continuous line means that the linear regression is significant, i.e. $p < 0.05$, while a dottet line means no significance, $p > 0.05$.



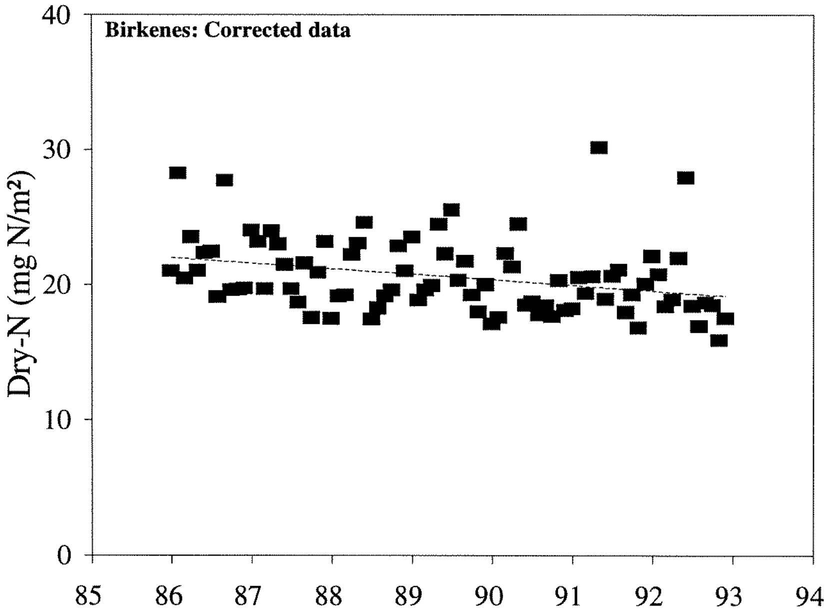


Figure 6.23 The monthly weighted influx of oxidized and reduced nitrogen in dry-deposition (mg N/m²) at Birkenes from 1986-1992, present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualizes the influence of water on the flux of each chemical compounds, i.e. large scattering means high water dependence and vise versa. The linear regression equations are present in Table 6.2. Continuous line means that the linear regression is significant, i.e. p < 0.05, while a dottet line means no significance, p > 0.05.

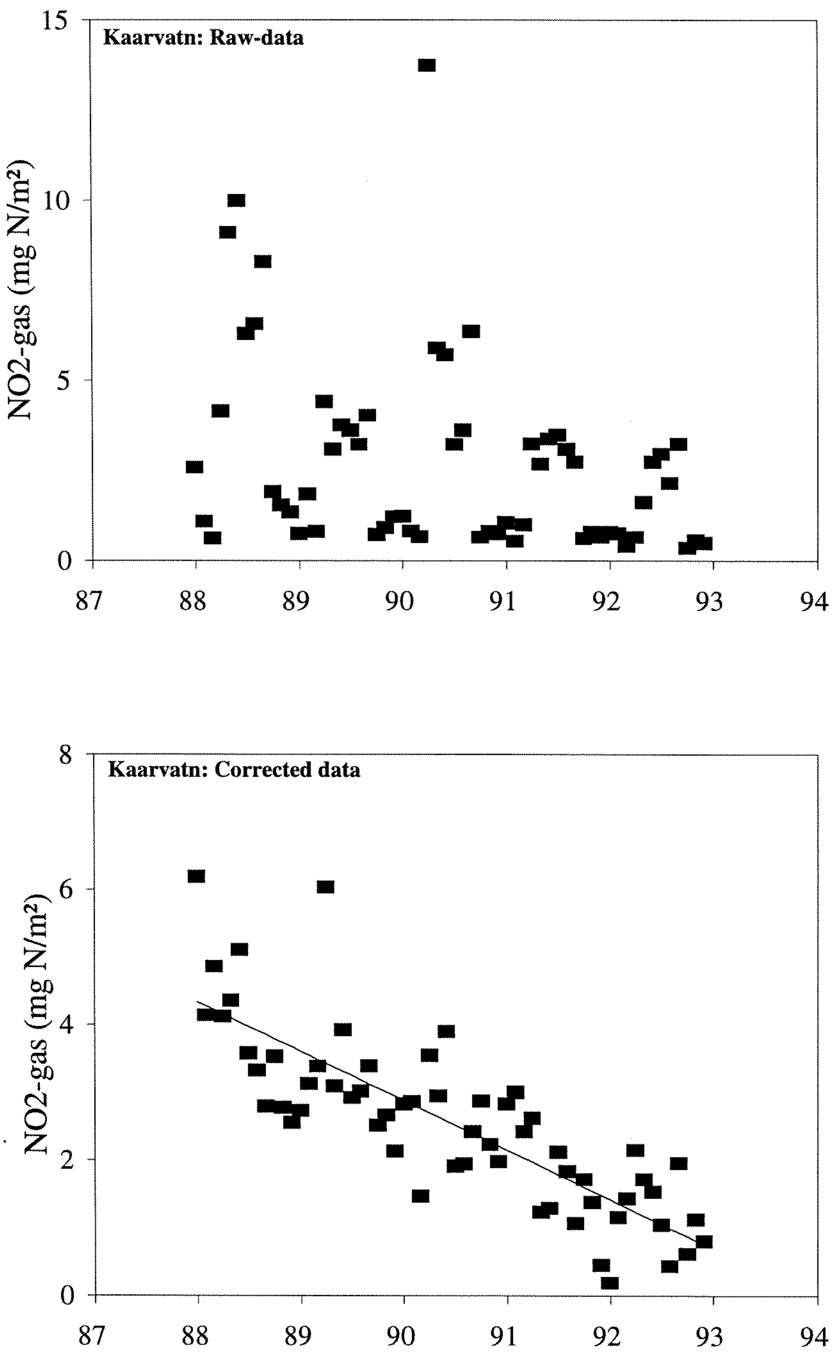
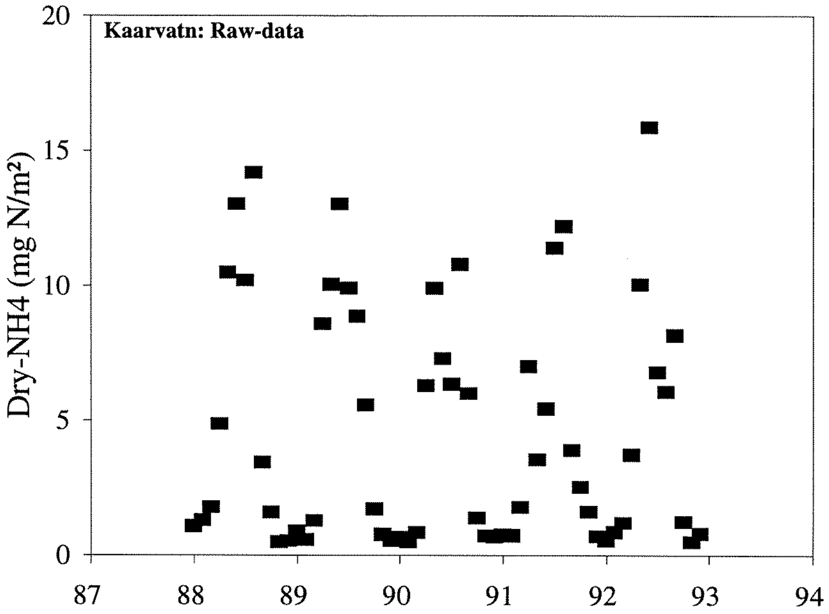


Figure 6.24 The monthly weighted influx of NO_2*-gas (mg N/m*^{2}*) at Kaarvatn from 1988-1992, present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualizes the influence of water on the flux of each chemical compounds, i.e. large scattering means high water dependence and vise versa. The linear regression equations are present in Table 6.2. Continuous line means that the linear regression is significant, i.e.* $p < 0.05$*, while a dottet line means no significance,* $p > 0.05$*.*



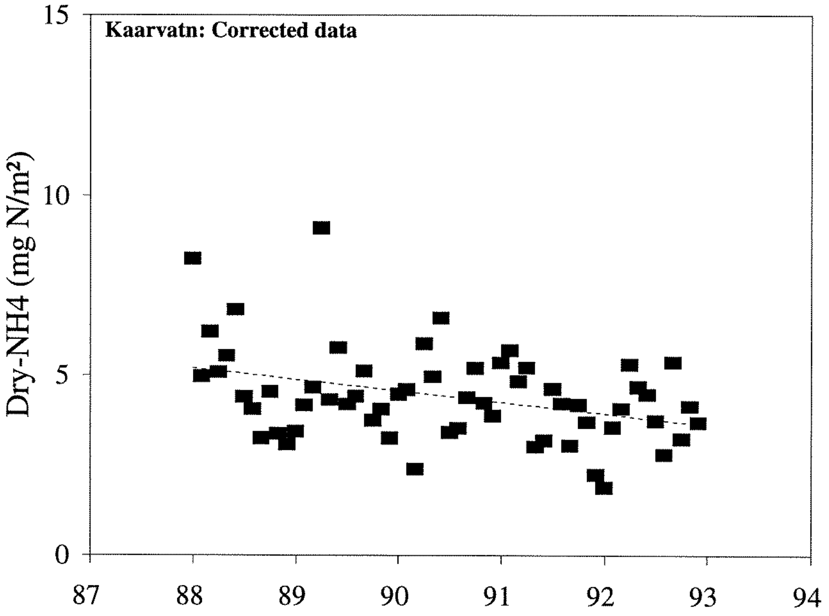
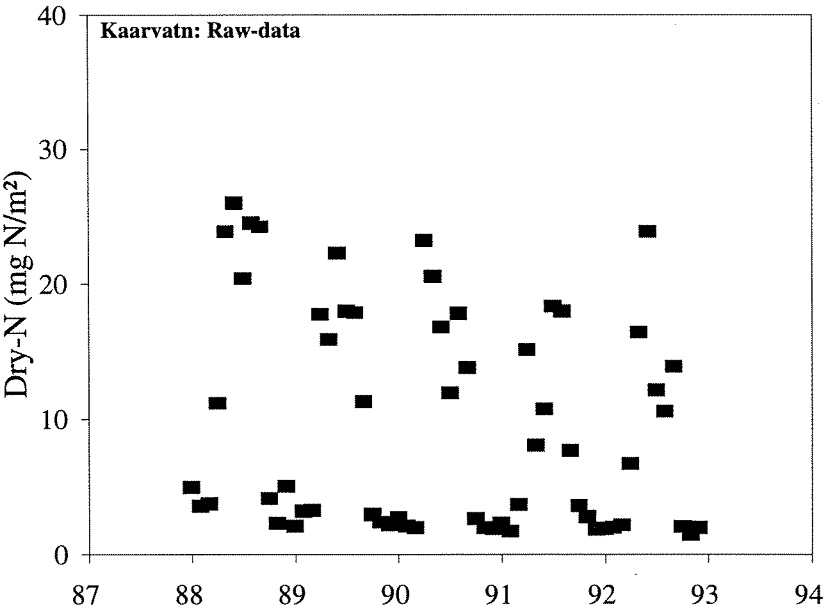


Figure 6.25 The monthly weighted influx of NH_4-particles (mg N/m^2) at Kaarvatn from 1988-1992, present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualizes the influence of water on the flux of each chemical compounds, i.e. large scattering means high water dependence and vise versa. The linear regression equations are present in Table 6.2. Continuous line means that the linear regression is significant, i.e. $p < 0.05$, while a dottet line means no significance, $p > 0.05$.



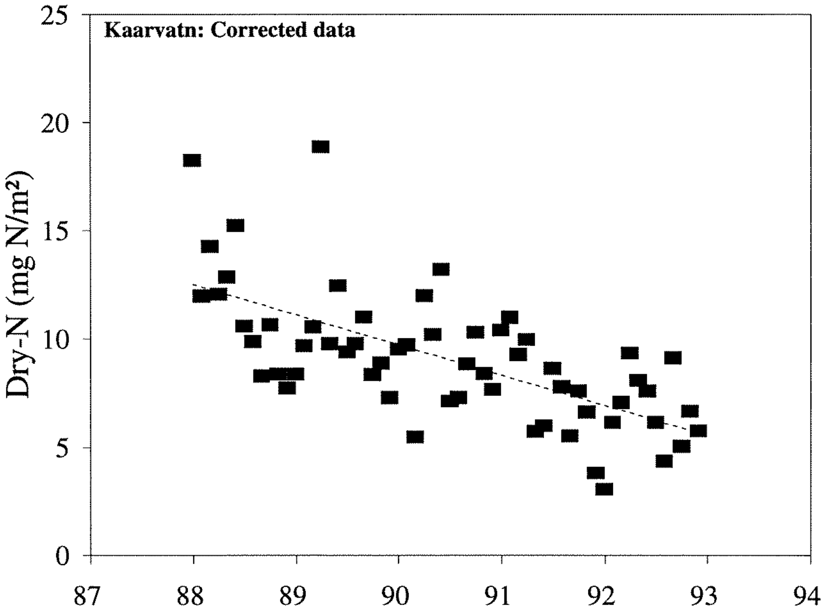
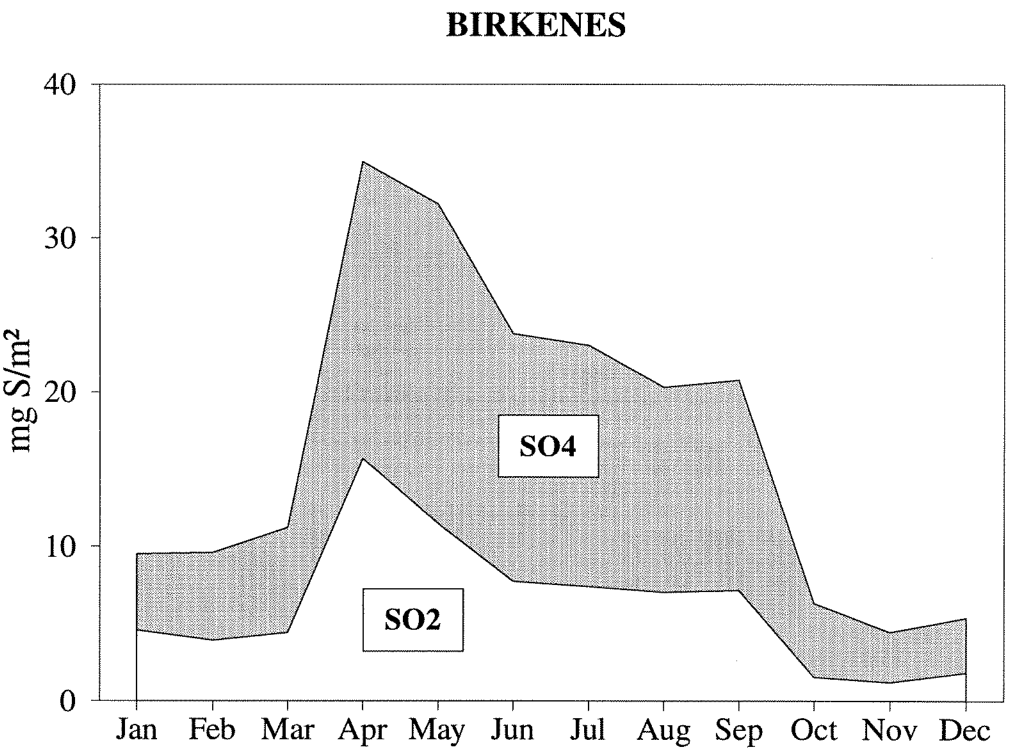


Figure 6.26 The monthly weighted influx of oxidized and reduced nitrogen in dry-deposition (mg N/m²) at Kaarvatn from 1988-1992, present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualizes the influence of water on the flux of each chemical compounds, i.e. large scattering means high water dependence and vise versa. The linear regression equations are present in Table 6.2. Continuous line means that the linear regression is significant, i.e. p < 0.05, while a dottet line means no significance, p > 0.05.



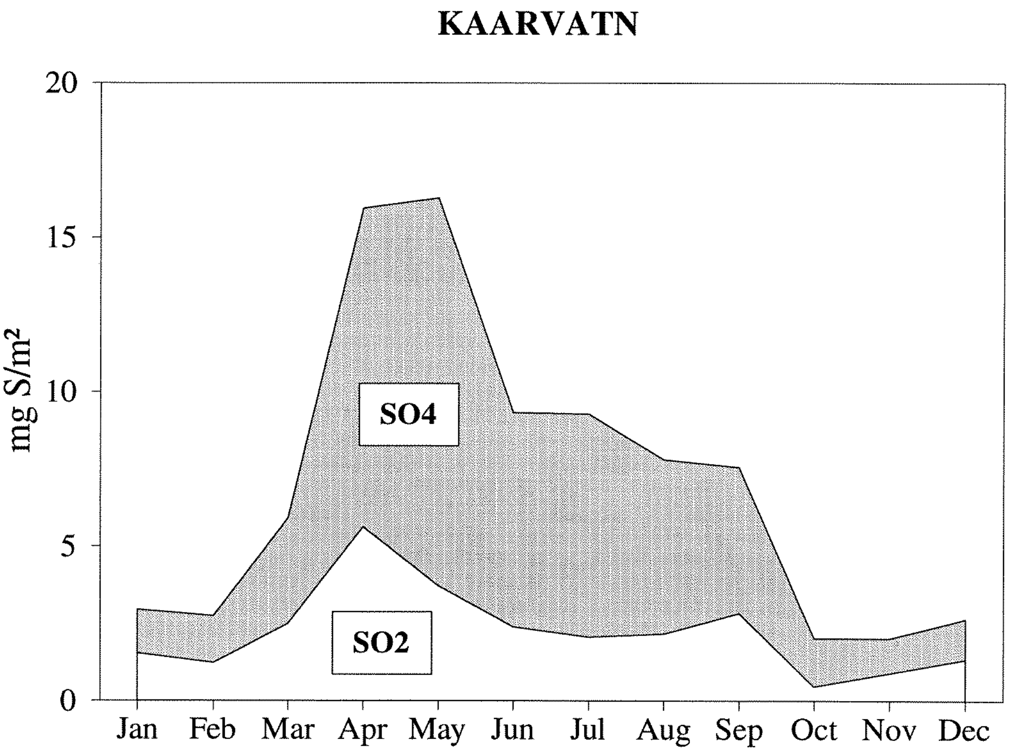
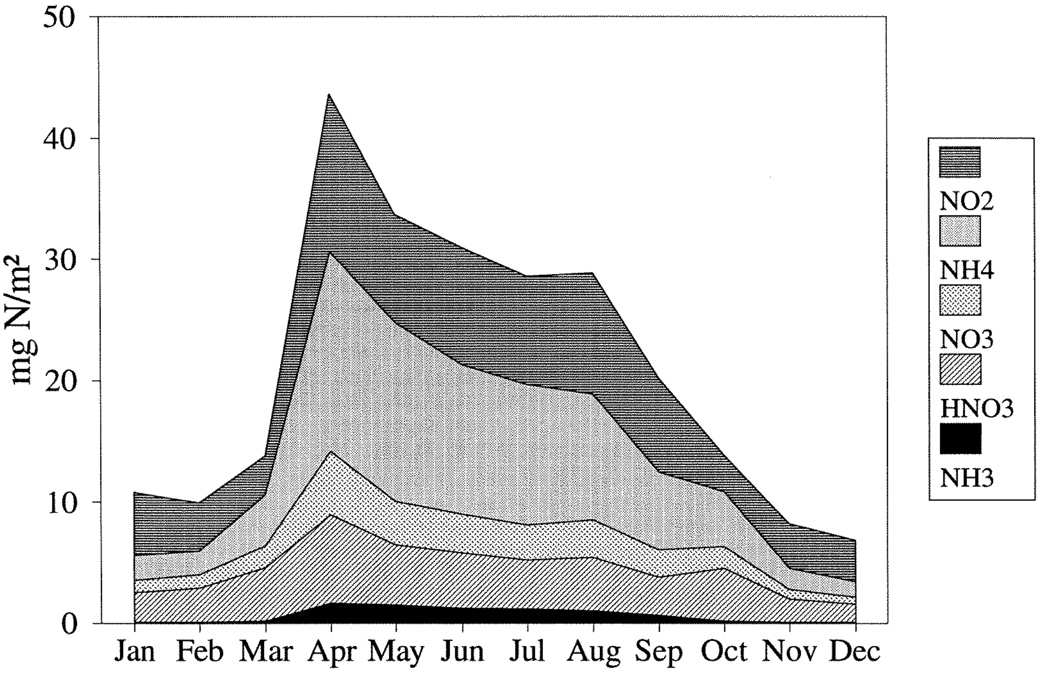
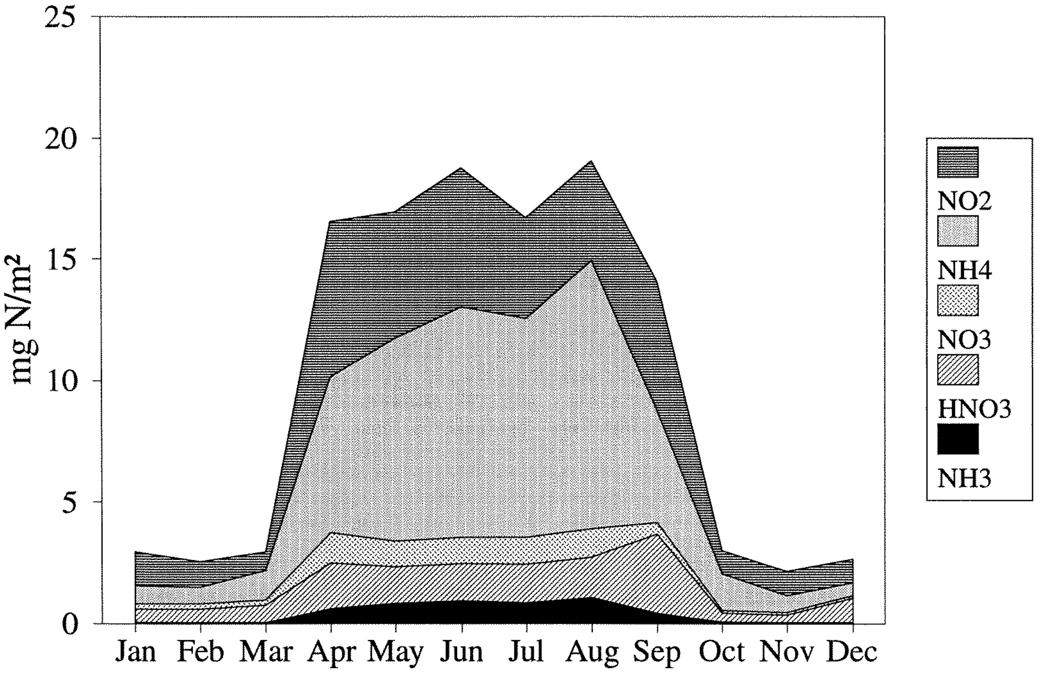


Figure 6.27 The monthly weighted input averages of SO_2-gas and SO_4-particles in dry-deposition at Birkenes and Kaarvatn.



BIRKENES



KAARVATN

Figure 6.28 The monthly weighted input averages of reduced and oxidized nitrogen compounds in dry-deposition at Birkenes and Kaarvatn.

Time trends in concentration of chemical compounds in wet-deposition

The only significant trends in the chemistry of wet-deposition are the reductions in sulphate and H^+-concentration during the monitoring period, which primarily means that the concentration of sulphuric acid has declined at all sites. This is in accordance with the reduction in sulphur emmission in Europe from the end of the 70-thies.

Based on the linear regressions made up from monthly weighted raw-data (Table 6.3), the monthly average concentration of sulphate at Birkenes at the beginning of 1974 was 86.1 ± 33.9 µeq/L. At the end of 1992, the monthly concentration has decreased by 27%, down to an average of 62.7 ± 7.80 µeq/L. Because the concentration of chloride has been measured at Birkenes and Storgama only since 1977, the estimates of non-marine sulphate (SO_4*) is also from 1977, since SO_4* = SO_4 -0.103*Cl. The monthly average concentration of SO_4* at the beginning of 1977 was 83.0 ± 33.8 µeq/L. At the end of 1992, the monthly average concentration of SO_4* has decreased to 52.8 ± 8.48 µeq/L, a decrease by 36% since the beginning of 1977. This decrease is much lower than the decrease in the concentration of sulphur in dry-deposition during 1978-1992 (67%). At Birkenes, the average monthly concentration of H^+ in wet-deposition at the beginning of 1974 was 71.2 ± 24.2 µeq/L (pH=4.15). At the end of 1992, the concentration has decreased by 33%, down to a monthly average of 47.6 ± 5.70 µeq/L (pH=4.32) at the end of 1992.

The average monthly concentration of sulphate at Storgama at the beginning of 1974 was 68.2 ± 32.3 µeq/L (Table 6.3). At the end of 1992, the concentration has decreased by 34% down to 44.8 ± 7.60 µeq/L. The monthly average concentration of SO_4* at the beginning of 1977 was 62.5 ± 30.5 µeq/L. At the end of 1992, the monthly concentration of SO_4* has decreased to averagely 43.1 ± 8.00 µeq/L, a decrease by 31% since the beginning of 1977. At Storgama, the average monthly concentration of H^+ in wet-deposition at the beginning of 1974 was 60.7 ± 22.7 µeq/L (pH=4.22). At the end of 1992, the concentration has decreased by 26%, down to a monthly average of 44.8 ± 5.32 µeq/L (pH=4.32) at the end of 1992.

The average monthly concentration of sulphate at Langtjern at the beginning of 1974 was 77.0 ± 51.7 µeq/L (Table 6.3). At the end of 1992, the monthly average concentration has decreased by 47% down to 40.7 ± 12.0 µeq/L. Due to lack of chloride data from 1974, the concentration of SO_4* is from 1975 and on. At the beginning of 1975 the monthly concentration of SO_4* was 78.8 ± 51.8 µeq/L. At the end of 1992, the monthly concentration of SO_4* has decreased to average of 36.9 ± 12.2 µeq/L, a decrease by 53% since the beginning of 1975. At Langtjern, the average monthly concentration of H^+ in wet-deposition at the beginning of 1974 was 64.8 ± 34.3 µeq/L (pH=4.19). At the end of 1992, the concentration has decreased by 58%, down to a monthly average of 27.4 ± 7.98 µeq/L (pH=4.56) at the end of 1992.

The monthly average concentration of sulphate at Kaarvatn at the beginning of 1980 was 25.6 ± 10.6 µeq/L. At the end of 1992, the concentration has decreased by 44% down to a monthly average of 14.4 ± 2.99 µeq/L. The monthly average concentration of SO_4* at the beginning of 1980 was 19.8 ± 10.8 µeq/L. At the end of 1992, the monthly concentration of SO_4* has decreased to 7.6 ± 2.99 µeq/L, a decrease by 62% since the beginning of 1980. This percentage decrease is in accordance with the reduction in the concentration of sulphur in dry-deposition (64%). The average monthly concentration of H^+ in wet-deposition at Kaarvatn at the beginning of 1980 was 15.0 ± 7.34 µeq/L (pH=4.82). At the end of 1992, the

Table 6.3 Time trends in the concentration (µeq/L) of major chemical compounds in wet-deposition at the four catchments, based on monthly weighted raw data $[y(t) = (\delta y_1/\delta t)t + b_1]$ *and time trends after the water dependent concentration changes* $[\delta y_1/\delta \log(q)]$ *are accounted for, i.e.* $[Y(t) = (\delta y_1/\delta t)t + [\delta y_1/\delta \log(q)]\log(q)] + b_2]$*. The constant* b_2 *is fitted so* $b_2 = b_1$*. (*:* $p < 0.05$*, **:* $p < 0.01$*).*

		Raw-data			**Water dependance**		**Corrected data**	
	Period	$\delta y_1/\delta t$	b_1	r_1	$\delta y/\delta \log(q)$	r_q	$\delta y_2/\delta t$	r_2
Birkenes								
H^+	1974-1992	-1.24 ± 0.30	71.2 ± 24.2	-0.27**	-10.9 ± 4.27	-0.17*	-1.25 ± 0.05	-0.85**
Ca	1974-1992	-0.06 ± 0.12	11.9 ± 10.1	-0.03	-12.9 ± 1.52	-0.49**	-0.08 ± 0.06	-0.09
NH_4	1974-1992	-0.02 ± 0.34	45.6 ± 28.0	-0.00	-24.8 ± 4.53	-0.34**	-0.05 ± 0.12	-0.03
NO_3	1974-1992	0.16 ± 0.25	40.8 ± 20.6	0.04	-10.2 ± 3.50	-0.19**	0.14 ± 0.05	0.19**
Cl	1977-1992	1.02 ± 0.64	46.1 ± 40.9	0.12	0.12 ± 0.04	0.24**	1.14 ± 0.16	0.47**
SO_4	1974-1992	-1.23 ± 0.41	86.1 ± 33.9	-0.20**	-36.3 ± 5.14	-0.43**	-1.35 ± 0.18	-0.45**
SO_4*	1977-1992	-1.89 ± 0.53	83.0 ± 33.8	-0.25**	-39.7 ± 5.86	-0.44**	-1.91 ± 0.24	-0.50**
Storgama								
H^+	1974-1992	-0.83 ± 0.28	60.7 ± 22.7	-0.20**	-8.69 ± 4.15	-0.14*	-0.87 ± 0.04	-0.82**
Ca	1974-1992	-0.20 ± 0.09	9.54 ± 7.13	-0.15*	-8.77 ± 1.16	-0.46**	-0.23 ± 0.04	-0.36**
NH_4	1974-1992	-0.25 ± 0.32	35.2 ± 25.9	-0.05	-19.0 ± 4.53	-0.28**	-0.33 ± 0.09	-0.24**
NO_3	1974-1992	0.02 ± 0.23	32.6 ± 18.6	0.00	-9.75 ± 3.31	-0.20**	-0.02 ± 0.05	-0.03
Cl	1977-1992	0.48 ± 0.26	14.1 ± 15.8	0.14	0.01 ± 0.02	0.05	0.50 ± 0.01	0.94**
SO_4	1974-1992	-1.23 ± 0.40	68.2 ± 32.3	-0.21**	-25.4 ± 5.42	-0.31**	-1.28 ± 0.13	-0.57**
SO_4*	1977-1992	-1.21 ± 0.50	62.5 ± 30.5	-0.18*	-24.9 ± 6.06	-0.30**	-1.17 ± 0.15	-0.50**
Langtjern								
H^+	1974-1992	-1.97 ± 0.42	64.8 ± 34.3	-0.30**	-5.57 ± 6.43	-0.06	-2.00 ± 0.03	-0.98**
Ca	1974-1992	-0.33 ± 0.17	13.6 ± 13.9	-0.13*	-12.2 ± 2.37	-0.33**	-0.28 ± 0.10	-0.19**
NH_4	1974-1992	0.56 ± 0.46	35.2 ± 37.3	0.08	-33.9 ± 6.30	-0.34**	0.41 ± 0.16	0.17*
NO_3	1974-1992	-0.19 ± 0.36	36.3 ± 29.4	-0.04	-21.2 ± 5.07	-0.27**	-0.28 ± 0.10	-0.19**
Cl	1975-1992	0.01 ± 0.16	12.6 ± 11.8	0.00	-10.0 ± 2.02	-0.33**	-0.07 ± 0.05	-0.09
SO_4	1974-1992	-1.91 ± 0.63	77.0 ± 51.7	-0.20**	-27.9 ± 9.18	-0.20**	-2.01 ± 0.13	-0.72**
SO_4*	1975-1992	-2.33 ± 0.68	78.8 ± 51.8	-0.23**	-27.8 ± 9.40	-0.20**	-2.50 ± 0.14	-0.78**
Kaarvatn								
H^+	1980-1992	-0.50 ± 0.16	15.0 ± 7.34	-0.25**	-10.7 ± 1.62	-0.47**	-0.68 ± 0.07	-0.59**
Ca	1980-1992	-0.32 ± 0.16	9.54 ± 7.30	-0.17*	-5.74 ± 1.73	-0.26**	-0.42 ± 0.04	-0.65**
NH_4	1980-1992	-0.17 ± 0.28	10.7 ± 13.3	-0.05	-11.7 ± 3.10	-0.29**	-0.38 ± 0.08	-0.35**
NO_3	1980-1992	-0.13 ± 0.11	7.32 ± 4.96	-0.10	-9.02 ± 0.96	-0.60**	-0.28 ± 0.06	-0.34**
Cl	1980-1992	0.61 ± 1.23	57.2 ± 57.6	0.04	0.29 ± 0.06	0.35**	1.65 ± 0.42	0.30**
SO_4	1980-1992	-0.86 ± 0.23	25.6 ± 10.6	-0.29**	-13.9 ± 2.44	-0.42**	-1.10 ± 0.10	-0.68**
SO_4*	1980-1992	-0.94 ± 0.23	19.8 ± 10.8	-0.31**	-19.2 ± 2.28	-0.56**	-1.27 ± 0.13	-0.60**

concentration has decreased by 43% down to a monthly average of 8.51 ± 2.08 µeq/L (pH=5.07) at the end of 1992.

Because of the almost identical equivalent decrease in the concentration of both H^+ and SO_4 in wet-deposition at the four catchment, the decline is primarily a consequence of reduced concentration of sulphuric acid in precipitation. The percentage decrease in the concentration of SO_4^* from 1974-1992 at Birkenes, Storgama and Langtjern is 36%, 31% and 53%, while the percentage decrease from 1980-1992 at Kaarvatn was 62%. Thus, it seems to be a geographical gradient concerning the reduction of sulphur with respect to distance from the main sulphur emmission sites in England and Central Europe. The Kaarvatn catchment, which is located most far away from the central emmission sites exhibits the highest percentage reduction in sulphur, while the Birkenes catchment, which is nearest located to the central emmission areas, exhibits the lowest percentage decline in sulphate.

Even though, it was a decrease in concentration of NO_2 in dry-deposition at Birkenes from 1986-1992, and at Kaarvatn from 1988-1992, the concentration of NO_3 in wet-deposition exhibits no significant change neither at Birkenes from 1974-1992 nor at Kaarvatn from 1980-1992. Thus, the decline in NO_2 in dry-deposition during the last years at the two sites is probably not a "real" tendency, but within normal fluctuation due to factors as varying winter-climate ect.

How much variations in the amount of precipitation per se affects the concentration of various ions in precipitation differ from catchment to catchment. This is illustrated Table 5.4. Even though the 1992 data are not incorporated in this table, the rank is the same even after the 1992 data are incorporated.

As well illustrated in the figures (Figure 6.29...6.36), the concentration of sulphate in wet-deposition is more sensitive with respect to changes in amount of precipiation than the concentration of H^+ (i.e. large scatter in the figures with corrected data), especially at the three most air-polluted sites. In addition, the influence of precipiation on the the concentration of H^+ in wet-deposition seems to decrease by distance inland from Birkenes towards Langtjern, which may rely on the fact that the fluctuation in monthly precipitation is larger at the most coastnear sites. Why the concentration of H^+ is less "water-sensitive" than sulphate is, however, more difficult to explain.

At all four catchments, the highest concentration of ions in wet-deposition normally occur during the winter and early spring (Figure 6.37..6.40). At Birkenes (Figure 6.37), the highest concentrations (> 400 µeq/L) normally occur in December, February, March and April, while the highest concentrations at Storgama (> 250 µeq/L) occur within the period Februray-May (Figure 6.38). At Langtjern (Figure 6.39), the highest concentration undoubtedly occurs in April (> 500 µeq/L), but the concentrations in March and May are also relatively high (≈ 300 µeq/L). The extreme concentration in wet-deposition in April at Langtjern, is probably due to a combination of minor precipitation and high influence from soil dust due to agricultural activities and very wind exposed ground at that time. The weather station at Langtjern is located on farmer-land, and the consequences of this are discussed earlier. The highest concentrations of ions in wet-deposition at Kaarvatn (Figure 6.40) do normally occur during the winter, highest in December (> 300 µeq/L), but high concentrations do also often occur in April. High ionic concentrations in wet-deposition in April are common at all sites. The primary reasons for this are the same as described at Langtjern.

At all sites, the percentage contribution from seasalts are at the highest during the winter. Based on monthly weighted averages, Na and Mg contribute by 60-70% and 10-15% to the total amount of cations during the winter (November-February) at Kaarvatn, while Cl contributes by 75-85% to the total anionic pool during the same period. At the second most seasalt influenced site, Birkenes, Na and Mg contribute by 30-45% and 8-9% to the total cationic pool during the winter, while Cl at the same time contributes by 40-50% to the anionic pool. At Storgama, Na, Mg and Cl correspondingly contribute by 20-30% (Na), 6-7% (Mg) and 30-35% (Cl) during the winter period. At Langtjern, the most typical inland site, Na and Mg contribute by 14-15% and 4-5% to the total cationic pool during the winter, while Cl constitutes 18-20% of the total anionic pool during the correspondent period.

By large, NH_4 and NO_3 in wet-deposition, exhibit their highest percentage contributions during spring and early summer. During this period, NH_4 constitutes 30-40% of the total cationic pool, while NO_3 contributes by 20-40% to the total anionic pool at the four sites. Because the more typically soil derived ions, Ca and K, also exhibit their highest percentage contribution during the same period, it confirm the high influence from terrestrial/agricultural sources at that time of the year.

At all sites, the highest percentage contribution from H^+ and SO_4 normally occur during late spring, and continue at a high level until early autumn. During this period, H^+ contributes by 40-45%, $\approx$ 50%, 45-50%, and 25-30% to the total cationic pool in wet-deposition at Birkenes, Storgama, Langtjern, and Kaarvatn, respectively, while the correspondant contributions of SO_4 to the total anionic pool is 50-55% at Birkenes, 60-65% at Storgama, 60-70% at Langtjern, and 45-60% at Kaarvatn.

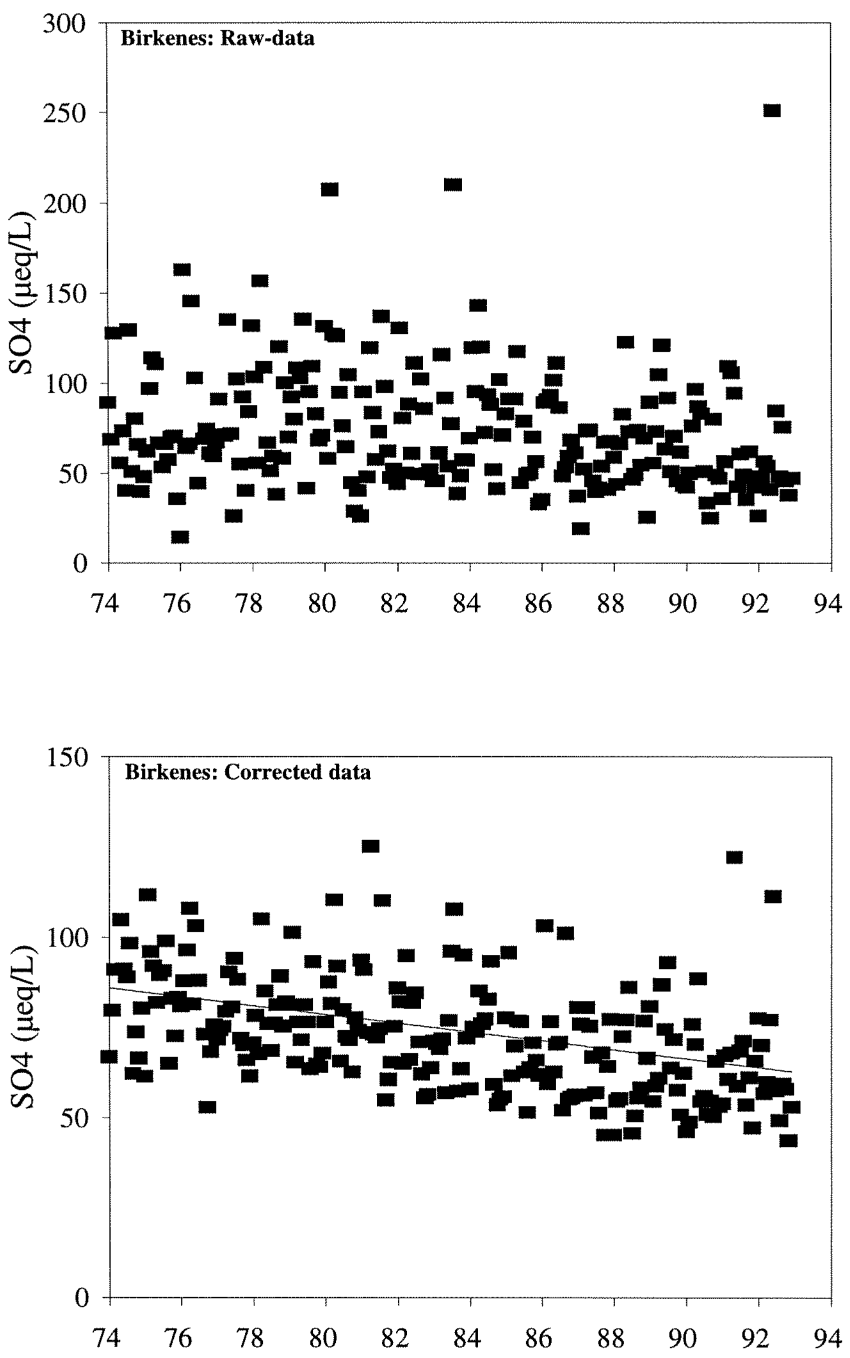
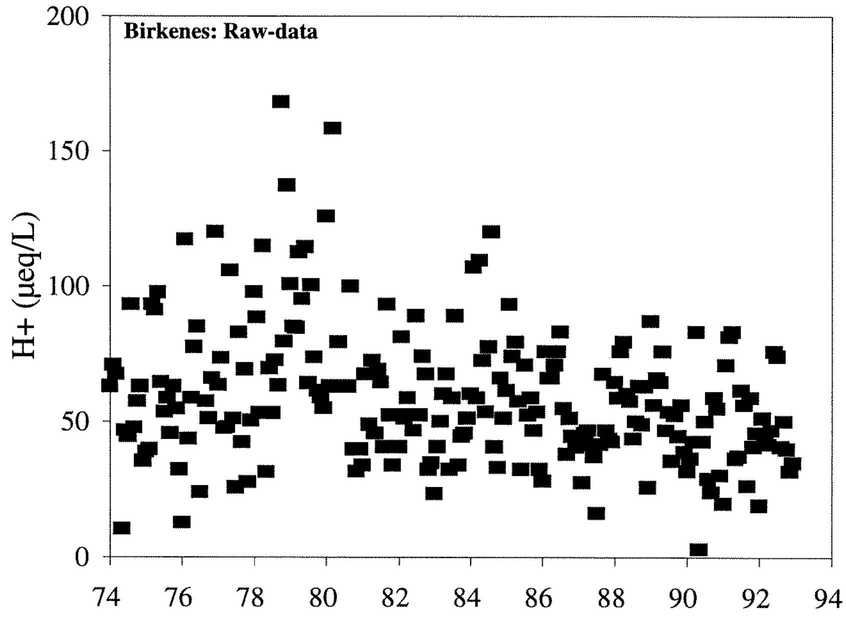


Figure 6.29 The monthly weighted concentration of SO_4 in wet-deposition (µeq/L) at Birkenes from 1974-1992, present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualizes the influence of water on the concentration/flux of each chemical compounds, i.e. large scattering means high water dependence and vise versa. The linear regression equations are present in Table 6.3. Continuous line means that the linear regression is significant, i.e. $p < 0.05$, while a dottet line means no significance, $p > 0.05$.



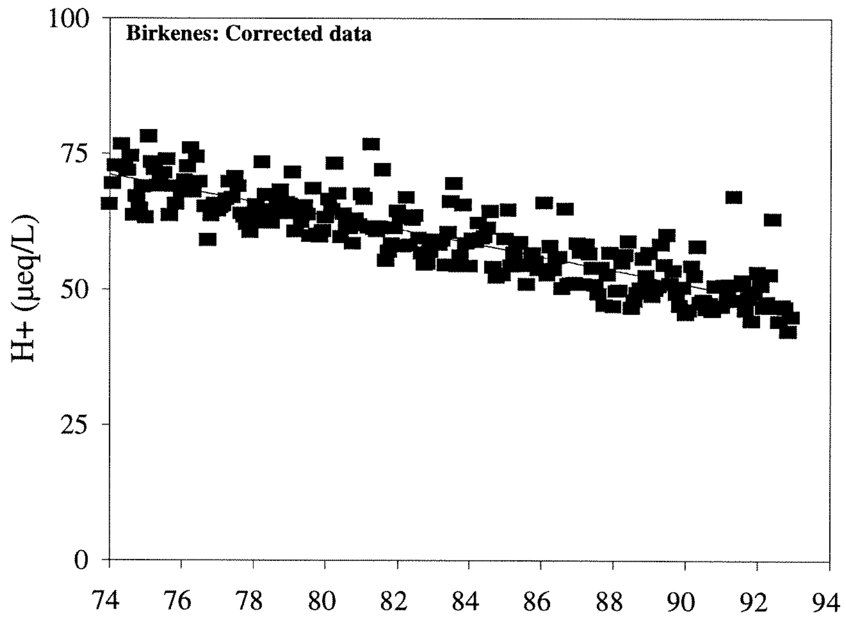
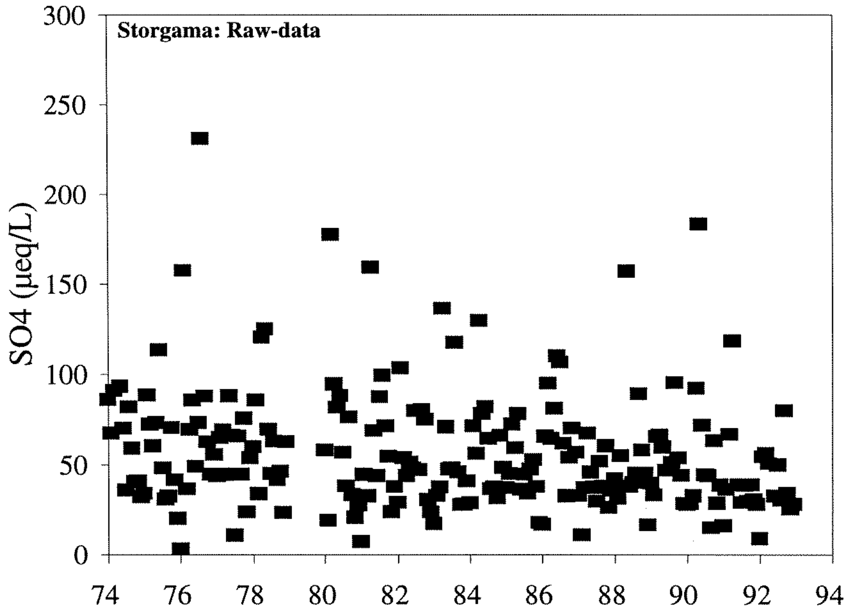


Figure 6.30 The monthly weighted concentration of H+ in wet-deposition (µeq/L) at Birkenes from 1974-1992, present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualizes the influence of water on the concentration/flux of each chemical compounds, i.e. large scattering means high water dependence and vise versa. The linear regression equations are present in Table 6.3. Continuous line means that the linear regression is significant, i.e. $p < 0.05$, while a dottet line means no significance, $p > 0.05$.



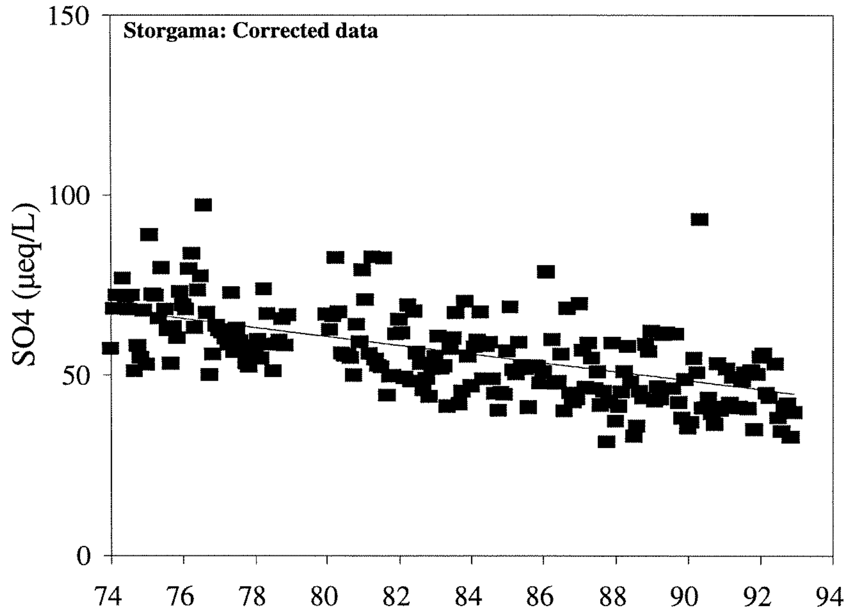
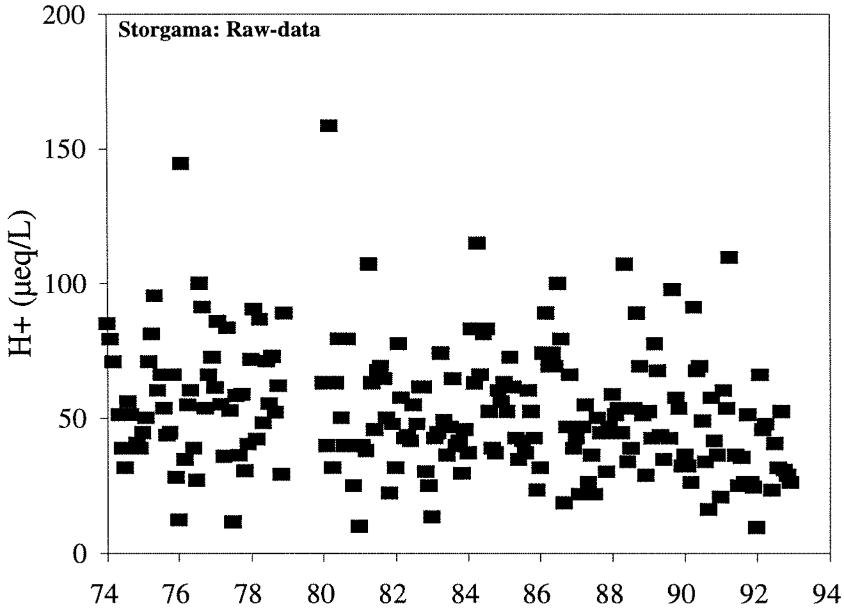


Figure 6.31 The monthly weighted concentration of SO_4 in wet-deposition (µeq/L) at Storgama from 1974-1992, present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualizes the influence of water on the concentration/flux of each chemical compounds, i.e. large scattering means high water dependence and vise versa. The linear regression equations are present in Table 6.3. Continuous line means that the linear regression is significant, i.e. $p < 0.05$, while a dottet line means no significance, $p > 0.05$.



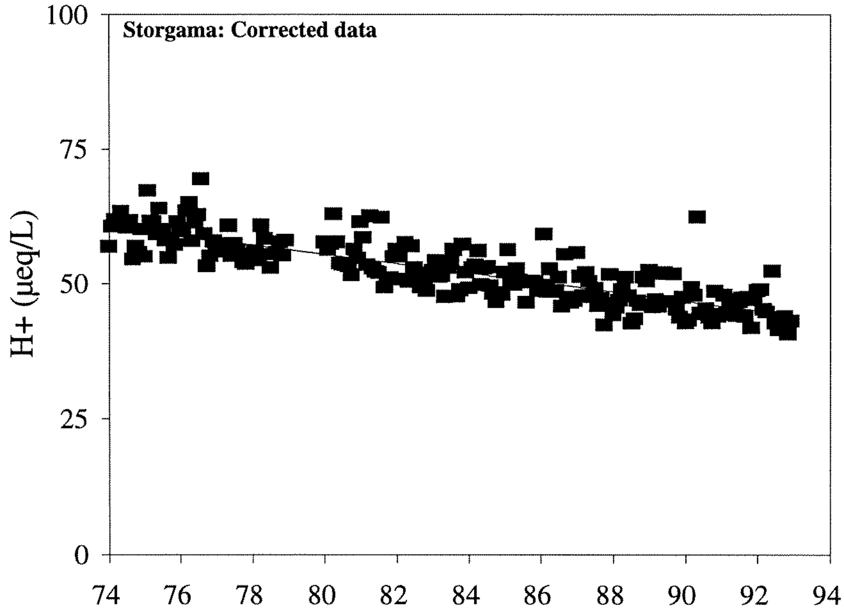
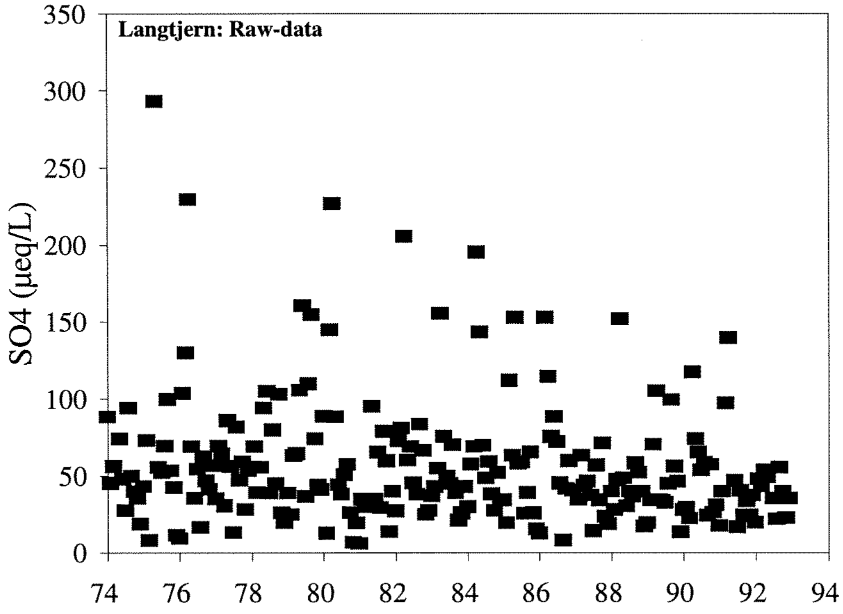


Figure 6.32 The monthly weighted concentration of H+ in wet-deposition (μeq/L) at Storgama from 1974-1992, present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualizes the influence of water on the concentration/flux of each chemical compounds, i.e. large scattering means high water dependence and vise versa. The linear regression equations are present in Table 6.3. Continuous line means that the linear regression is significant, i.e. $p < 0.05$, while a dottet line means no significance, $p > 0.05$.



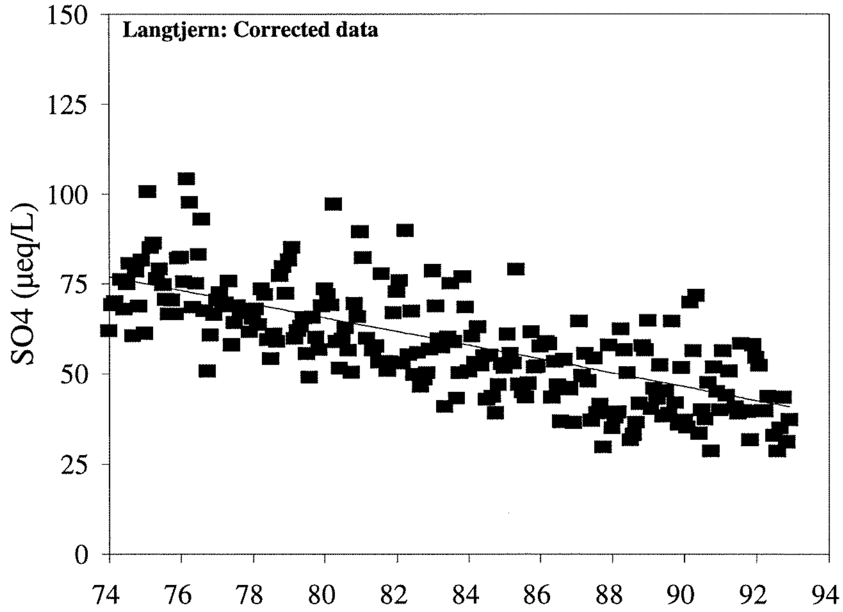
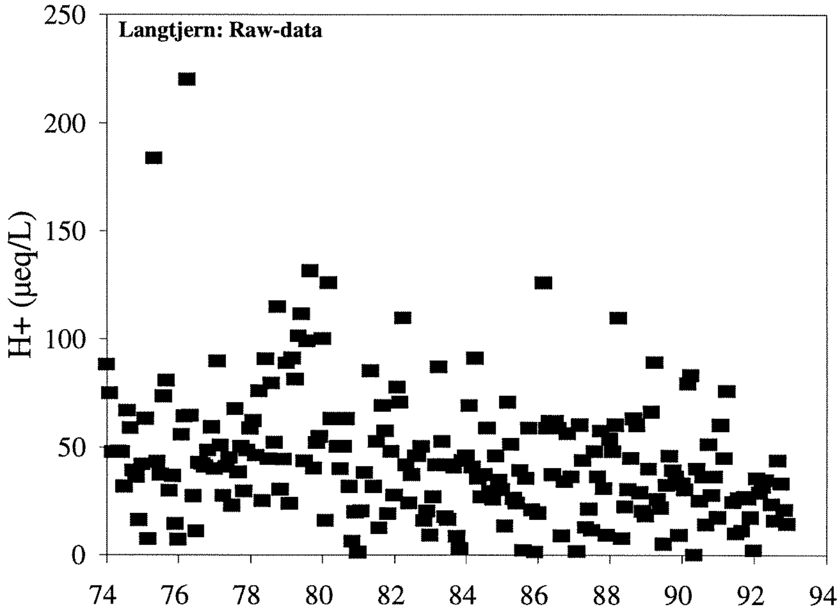


Figure 6.33 The monthly weighted concentration of SO_4 *in wet-deposition (µeq/L) at Langtjern from 1974-1992, present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualizes the influence of water on the concentration/flux of each chemical compounds, i.e. large scattering means high water dependence and vise versa. The linear regression equations are present in Table 6.3. Continuous line means that the linear regression is significant, i.e.* $p < 0.05$*, while a dottet line means no significance,* $p > 0.05$*.*



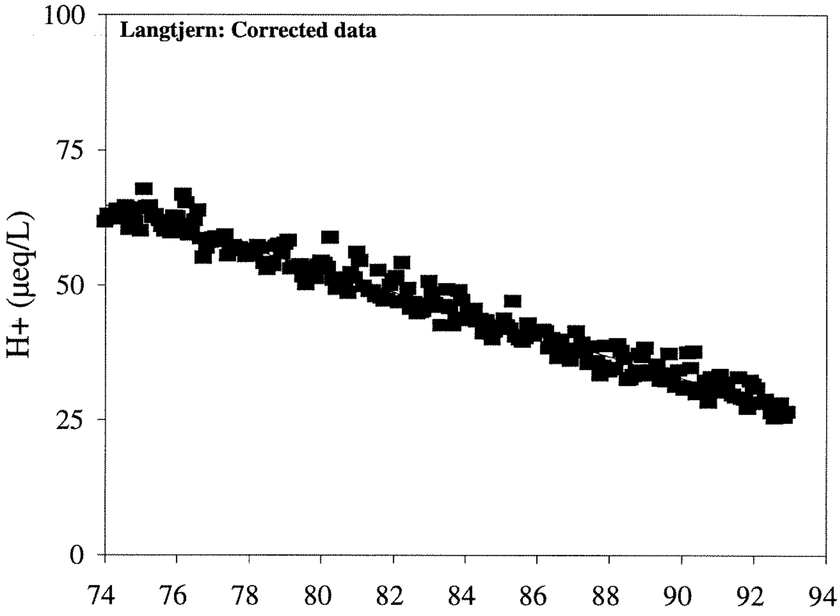
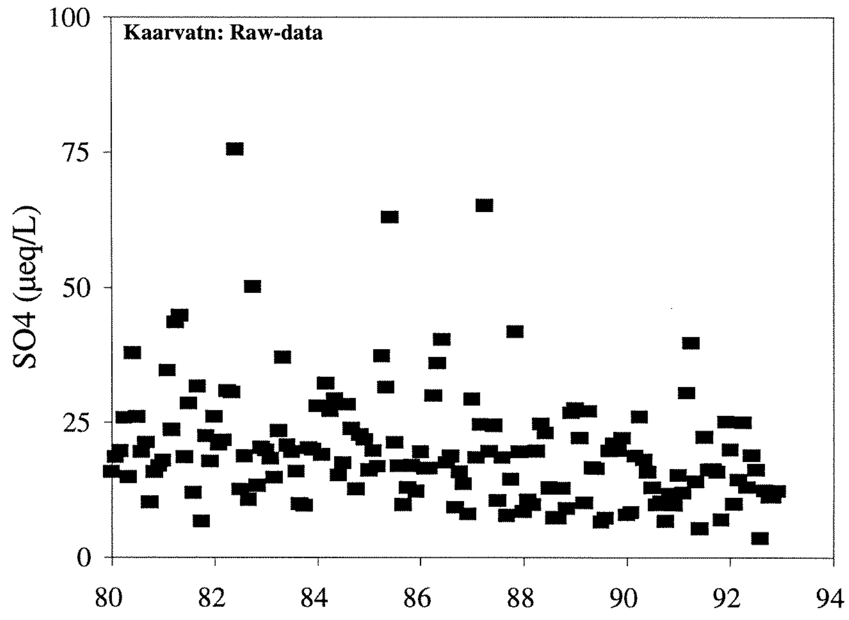


Figure 6.34 The monthly weighted concentration of H+ in wet-deposition (µeq/L) at Langtjern from 1974-1992, present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualizes the influence of water on the concentration/flux of each chemical compounds, i.e. large scattering means high water dependence and vise versa. The linear regression equations are present in Table 6.3. Continuous line means that the linear regression is significant, i.e. $p < 0.05$*, while a dottet line means no significance,* $p > 0.05$.



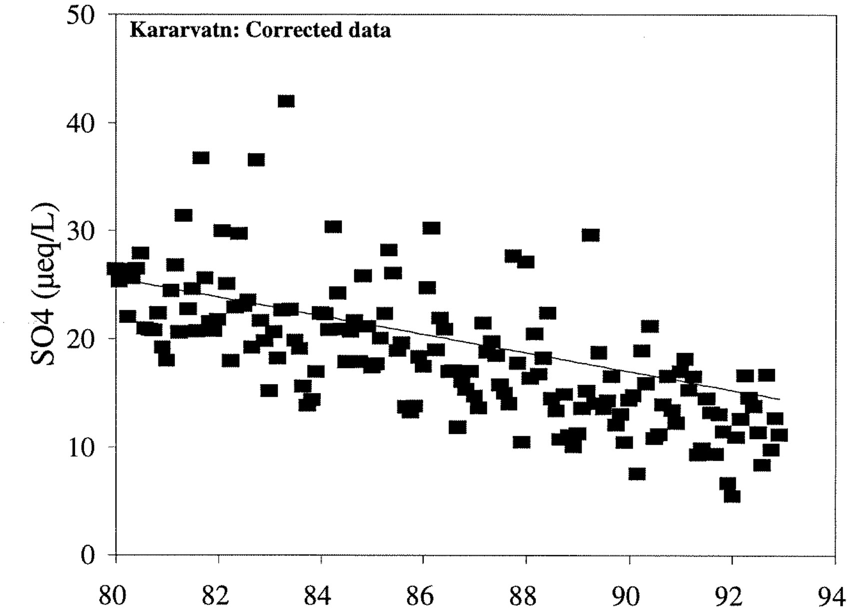
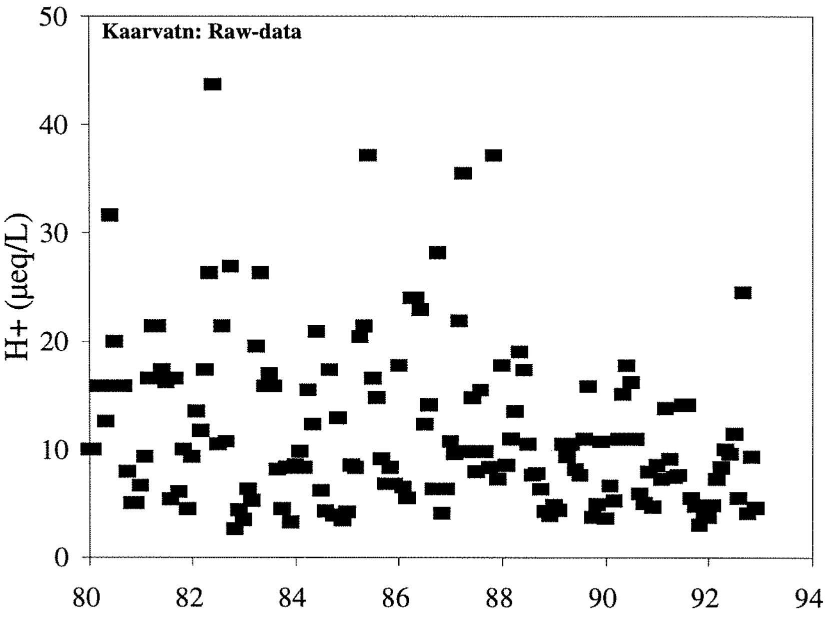


Figure 6.35 The monthly weighted concentration of SO_4 *in wet-deposition (μeq/L) at Kaarvatn from 1980-1992, present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualizes the influence of water on the concentration/flux of each chemical compounds, i.e. large scattering means high water dependence and vise versa. The linear regression equations are present in Table 6.3. Continuous line means that the linear regression is significant, i.e.* $p < 0.05$*, while a dottet line means no significance,* $p > 0.05$*.*



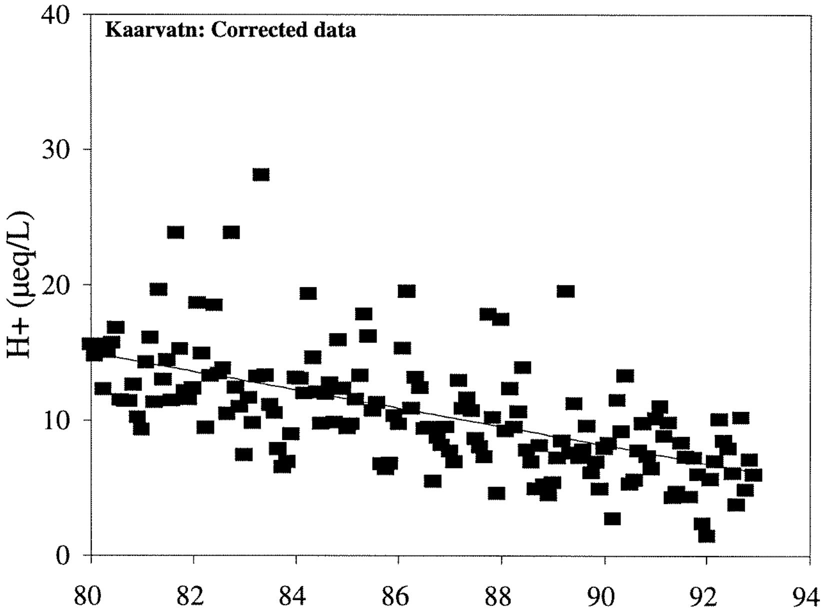
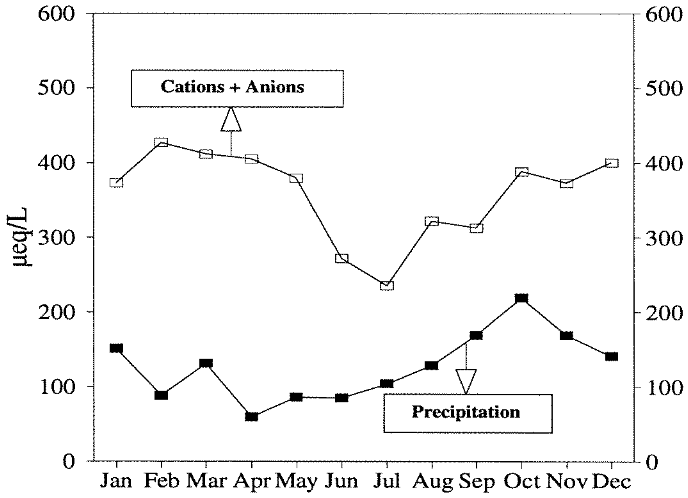
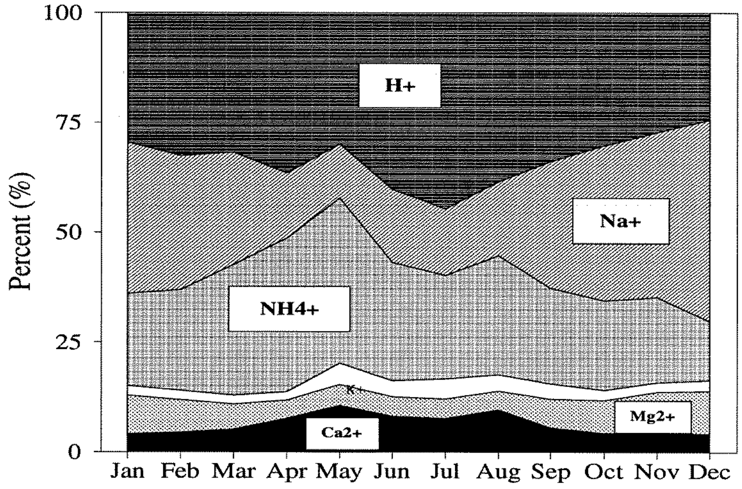


Figure 6.36 The monthly weighted concentration of H+ in wet-deposition (μeq/L) at Kaarvatn from 1980-1992, present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualizes the influence of water on the concentration/flux of each chemical compounds, i.e. large scattering means high water dependence and vise versa. The linear regression equations are present in Table 6.3. Continuous line means that the linear regression is significant, i.e. $p < 0.05$, while a dottet line means no significance, $p > 0.05$.





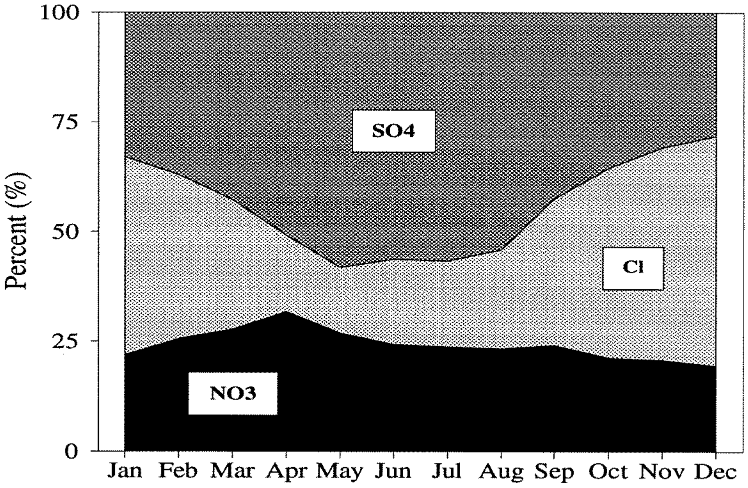


Figure 6.37 The monthly mean ionic concentration, amount of precipitation, and the average percentage distribution of cations and anions in precipitation during a year at Birkenes, based on monthly weighted averages from 1974-1992.

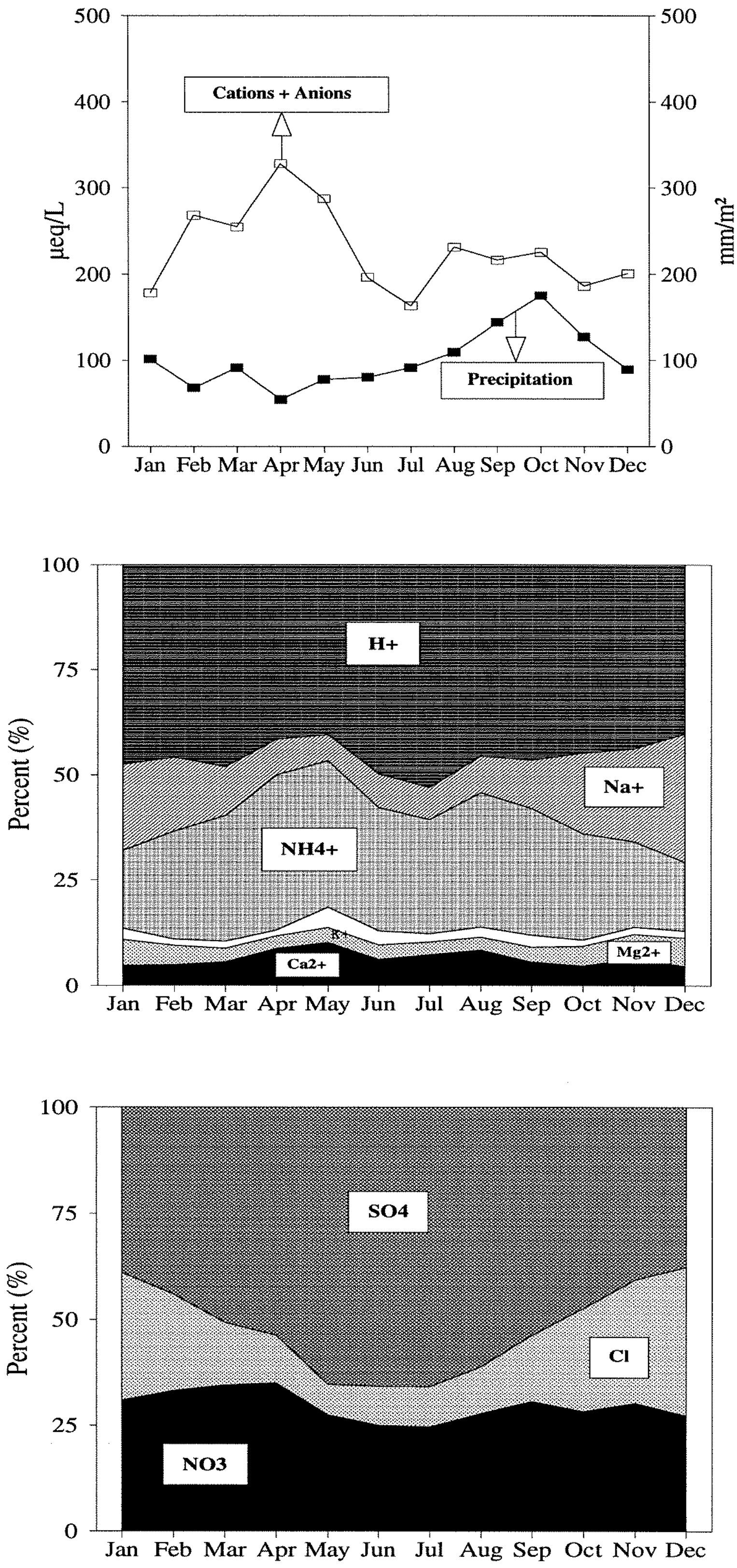


Figure 6.38 The monthly mean ionic concentration, amount of precipitation, and the average percentage distribution of cations and anions in precipitation during a year at Storgama, based on monthly weighted averages from 1974-1992.

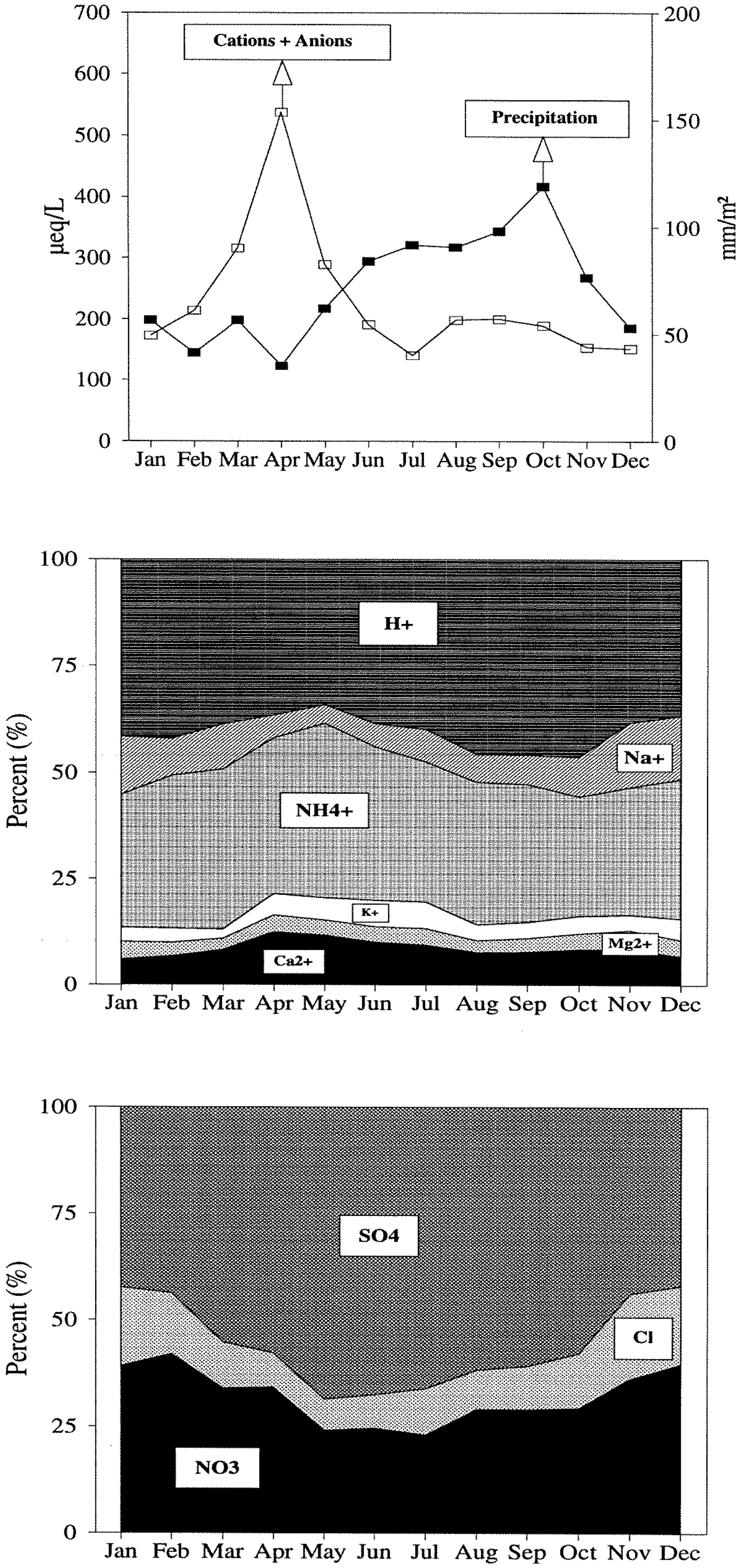


Figure 6.39 The monthly mean ionic concentration, amount of precipitation, and the average percentage distribution of cations and anions in precipitation during a year at Langtjern, based on monthly weighted averages from 1974-1992.

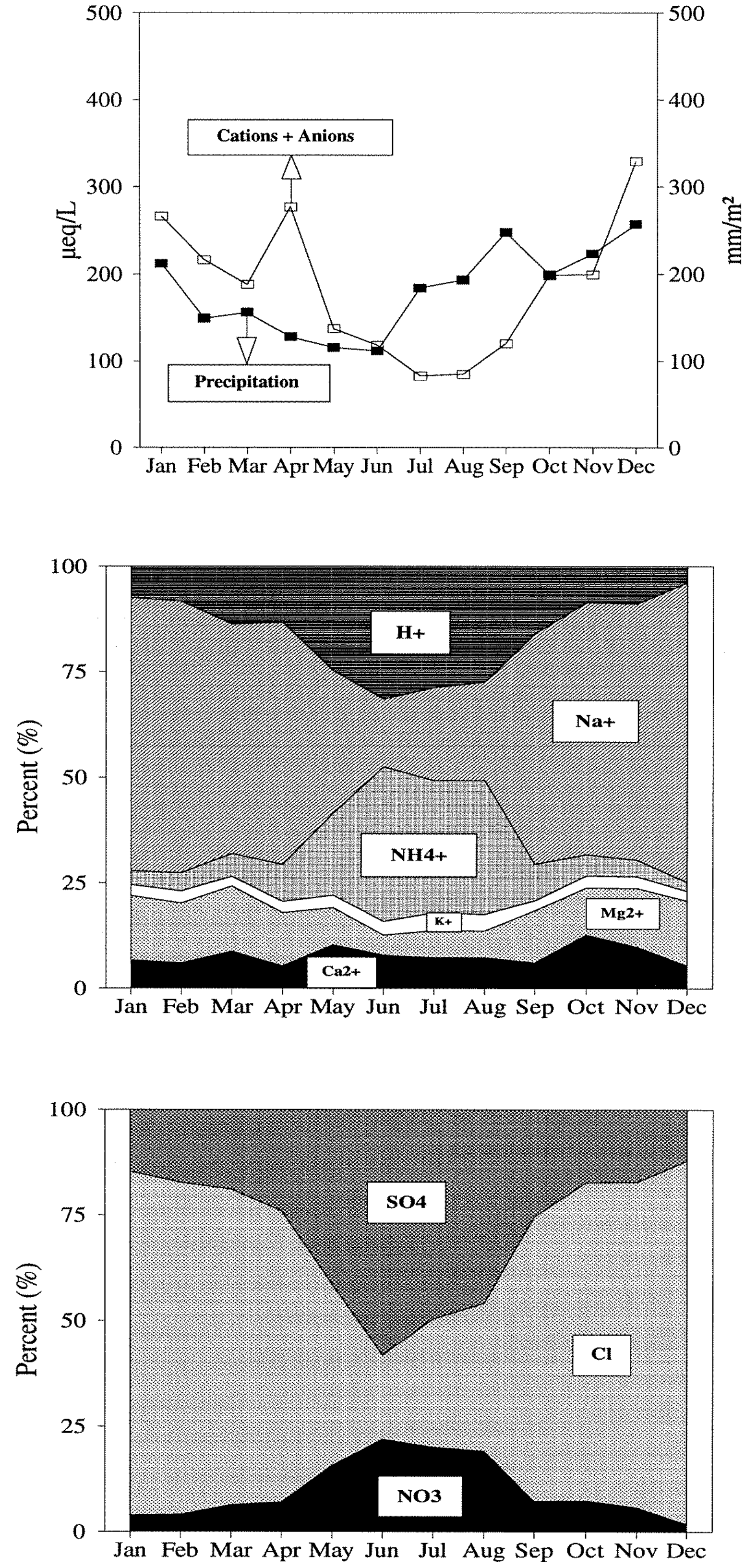


Figure 6.40 The monthly mean ionic concentration, amount of precipitation, and the average percentage distribution of cations and anions in precipitation during a year at Kaarvatn, based on monthly weighted averages from 1980-1992.

Time trends in fluxes of chemical compounds in wet-deposition

The only significant trends ($p < 0.05$) in wet-deposition fluxes of major ions during the monitoring periods are the reduction in SO_4* at Birkenes, Storgama and Kaarvatn, and the flux of H^+ at Kaarvatn. The tendency of increasing amount of precipitation at Langtjern during the period is probably the main reason why a significant reduction in SO_4* was not found at this site. The large increase in annual precipitation at Kaarvatn from 1980-1992, also explain why the decreases in fluxes of both sulphate and H^+ were most significant at this site. This is not a contradiction, because the three most airpolluted sites exhibit an increase in the annual fluxes of sulphate and H^+ by increasing inputs of water, while the opposite relation was found at Kaarvatn, the least air-polluted site.

Based on the linear regressions made up from annual weighted raw-data fluxes (Table 6.4), the annual average influx of sulphate at Birkenes for the water-year 1974/75 was 111.2 ± 19.8 meq S/m^2. In 1991/92, the annual average influx was lowered by 23%, down to an average of 85.3 ± 16.2 meq S/m^2. Because the concentration of chloride has only been measured at Birkenes back to 1977, the estimates of non-marine sulphate (SO_4*) is also available from that time and on, since SO_4* is calculated as: $SO_4^* = SO_4 - 0.103^*Cl$. The annual weigted influx of SO_4* in 1991/92 was 68.3 ± 15.2 meq S/m^2, which is a 36% decrease compared with the water-year 1977/78. The percent decrease in <u>influx</u> of sulphur is almost similar to the percentage decrease in <u>concentration</u> of sulphur during the corresponding period. At Birkenes, the annual average wet-deposition influx of H^+ in 1974/75 was 95.6 ± 19.0 meq/m^2. In 1991/92, the annual average influx was 72.6 ± 15.5 meq/m^2, which is a decrease in the annual influx of H^+-ions by 24% from 1974/75 to 1991/92.

Based on annual weighted raw-data fluxes (Table 6.4), the average annual influx of sulphate at Storgama in 1974/75 was 58.4 ± 14.1 meq S/m^2. In 1991/92, the annual average influx was lowered by 21%, down to an average annual influx of 46.0 ± 12.1 meq S/m^2. Because the concentration of chloride has been measured at Storgama only since 1977, the estimates of SO_4* are from 1977/78. The average annual influx of SO_4* for 1977/78 was 61.9 ± 12.9 meq S/m^2. The annual weighted influx of SO_4* in 1991/92 was 38.7 ± 11.9 meq S/m^2, which is a 37% decrease compared with the water year 1977/78. The percent decrease in influx of sulphur is close to the percentage reduction in the concentration of sulphur in wet-deposition during the corresponding. At Storgama, the annual average wet-deposition influx of H^+ in 1974/75 was 66.1 ± 14.5 meq/m^2. In 1991/92, the annual average influx was 53.3 ± 12.4 meq/m^2, which means a decline in the annual influx of H^+-ions by 19% from 1974/75 to 1991/92.

Based on the linear regressions made up from annual weighted raw-data fluxes (Table 6.4), the annual average influx of sulphate at Langtern in 1974/75 was 41.3 ± 10.7 meq S/m^2. In 1991/92, the annual average influx was lowered by 14%, down to an average annual influx of 35.4 ± 8.64 meq S/m^2. Due to lack of chloride data from 1974, the concentration of SO_4* at Langtjern is from 1975/76. The average annual influx of SO_4* for 1975/76 was 41.8 ± 10.8 meq S/m^2, while the annual weigted influx was lowered by 20%, down to 33.6 ± 9.01 meq S/m^2 in 1991/92. Due to a tendency of increasing amount of precipitation during the period of recording, the percentage reduction in wet-deposition influx of sulphate is lower than the percentage reduction in the concentration of sulphate in wet-deposition at Langtjern during the corresponding period. At Langtjern, the annual average influx of H^+ as wet-deposition in 1974/75 was 43.6 ± 12.6 meq/m^2. In 1991/92, the annual average influx was 31.9 ± 10.8

Table 6.4 Time trends in annual fluxes of major chemical compounds (meq/m^2*) in wet-deposition at the four catchments, based on annual (water-year) weighted raw data fluxes* $[y(t) = (\delta y_1/\delta t)t + b_1]$ *and time trends after the water dependent flux changes* $[\delta y_1/\delta q$ *in meq/mm] are accounted for, i.e.* $[Y(t) = (\delta y_1/\delta t)t + (\delta y_1/\delta q)q + b_2]$*. The constant* b_2 *is fitted so* $b_2=b_1$*. (**: $p < 0.05$, **: $p < 0.01$*).*

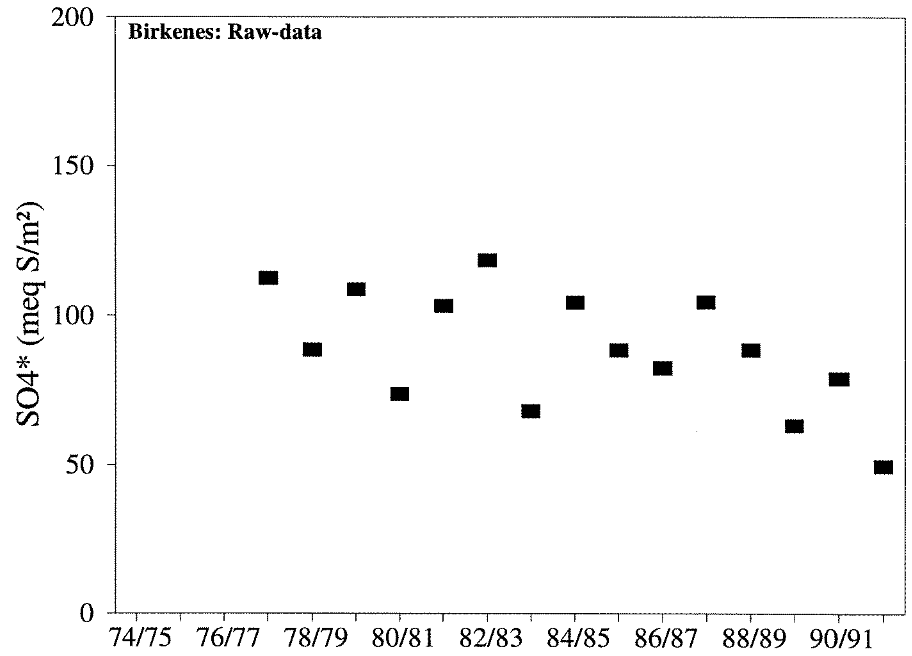
		Raw-data			**Water dependance**		**Corrected data**	
	Period	**$\delta y_1/\delta t$**	**b_1**	**r_1**	**$\delta y/\delta q$**	**r_q**	**$\delta y_2/\delta t$**	**r_2**
Birkenes								
Water(mm)	74/75-91/92	7.5 ± 13.7	1447 ± 301	0.14				
H^+	74/75-91/92	-1.28 ± 0.86	95.6 ± 19.0	-0.35	0.044 ± 0.013	0.66**	-0.95 ± 0.60	-0.37
Ca	74/75-91/92	-0.11 ± 0.15	14.9 ± 3.21	-0.18	0.006 ± 0.002	0.56*	-0.06 ± 0.08	-0.19
NH_4	74/75-91/92	0.12 ± 0.73	59.9 ± 16.0	0.04	0.044 ± 0.007	0.84**	0.45 ± 0.61	0.18
NO_3	74/75-91/92	0.30 ± 0.66	56.7 ± 14.5	0.11	0.041 ± 0.006	0.86**	0.61 ± 0.56	0.26
Cl	77/78-91/92	2.00 ± 1.78	77.3 ± 29.8	0.30	0.066 ± 0.022	0.64**	2.85 ± 1.16	0.56*
SO_4	74/75-91/92	-1.44 ± 0.90	111.2 ± 19.8	-0.37	0.050 ± 0.012	0.71**	-1.06 ± 0.68	-0.36
SO_4*	77/78-91/92	-2.55 ± 1.01	106.5 ± 16.9	-0.57*	0.041 ± 0.015	0.60**	-2.02 ± 0.73	-0.61*
Storgama								
Water(mm)	74/75-91/92	-0.9 ± 13.6	1200 ± 288	0.02				
H^+	74/75-91/92	-0.71 ± 0.69	66.1 ± 14.5	-0.27	0.045 ± 0.007	0.87**	-0.75 ± 0.62	-0.31
Ca	74/75-91/92	-0.14 ± 0.12	8.64 ± 2.56	-0.29	0. 007 ± 0.002	0.73**	-0.15 ± 0.09	-0.39
NH_4	74/75-91/92	-0.06 ± 0.49	35.3 ± 10.5	-0.03	0.027 ± 0.006	0.75**	-0.09 ± 0.37	-0.06
NO_3	74/75-91/92	0.26 ± 0.47	34.3 ± 10.0	0.14	0.029 ± 0.005	0.83**	0.23 ± 0.40	0.15
Cl	77/78-91/92	0.47 ± 0.53	20.0 ± 7.64	0.26	0.018 ± 0.006	0.69**	0.22 ± 0.37	0.18
SO_4	74/75-91/92	-0.69 ± 0.67	58.4 ± 14.1	-0.27	0.045 ± 0.008	0.87**	-0.73 ± 0.61	-0.30
SO_4*	77/78-91/92	-1.55 ± 0.79	61.9 ± 12.9	-0.50*	0.043 ± 0.008	0.85**	-1.98 ± 0.77	-0.61*
Langtjern								
Water(mm)	74/75-91/92	7.8 ± 7.6	786 ± 167	0.25				
H^+	74/75-91/92	-0.65 ± 0.57	43.6 ± 12.6	-0.27	0.048 ± 0.015	0.63**	-0.28 ± 0.36	-0.19
Ca	74/75-91/92	-0.04 ± 0.13	7.15 ± 2.88	-0.07	0.006 ± 0.004	0.33	0.01 ± 0.04	0.03
NH_4	74/75-91/92	0.82 ± 0.43	21.5 ± 9.46	0.43	0.036 ± 0.012	0.59**	1.10 ± 0.27	0.71**
NO_3	74/75-91/92	0.38 ± 0.29	21.7 ± 6.48	0.30	0.032 ± 0.006	0.83**	0.63 ± 0.25	0.53*
Cl	75/76-91/92	0.19 ± 0.09	7.08 ± 1.88	0.47	0.005 ± 0.003	0.38	0.22 ± 0.04	0.82**
SO_4	74/75-91/92	-0.33 ± 0.48	41.3 ± 10.7	-0.16	0.041 ± 0.012	0.65**	-0.01 ± 0.31	-0.01
SO_4*	75/76-91/92	-0.48 ± 0.53	41.8 ± 10.8	-0.23	0.040 ± 0.012	0.64**	-0.18 ± 0.34	-0.13
Kaarvatn								
Water(mm)	80/81-91/92	52.8 ± 22.9	1933 ± 274	0.59*				
H^+	80/81-91/92	-0.25 ± 0.34	22.9 ± 4.06	-0.23	-0.002 ± 0.004	-0.17	-0.37 ± 0.05	-0.92**
Ca	80/81-91/92	-0.40 ± 0.37	17.3 ± 4.42	-0.32	0.001 ± 0.004	0.07	-0.35 ± 0.02	-0.98**
NH_4	80/81-91/92	-0.06 ± 0.34	16.7 ± 4.04	-0.05	0.002 ± 0.004	0.20	0.07 ± 0.05	0.36
NO_3	80/81-91/92	-0.01 ± 0.12	10.8 ± 1.39	-0.02	-0.001 ± 0.001	-0.15	-0.04 ± 0.01	-0.66*
Cl	80/81-91/92	4.11 ± 4.89	136.1 ± 58.5	0.26	0.142 ± 0.034	0.80**	11.6 ± 3.26	0.75**
SO_4	80/81-91/92	0.09 ± 0.37	24.9 ± 4.48	0.07*	0.010 ± 0.003	0.78**	0.64 ± 0.24	0.65*
SO_4*	80/81-91/92	-0.49 ± 0.22	17.2 ± 2.64	-0.58*	-0.003 ± 0.003	-0.36	-0.65 ± 0.07	-0.95**

meq/m², which is a decrease in the annual influx of H^+-ions by 27% from 1974/75 to 1991/92.

Based on the linear regressions made up from annual weighted raw-data fluxes (Table 6.4), the annual average influx of sulphate at Kaarvatn in 1980/81 was 24.9 ± 4.48 meq S/m². In 1991/92, the annual average influx exhibits a minor increase by 4%, to an average annual influx of 26.0 ± 4.44 meq S/m². The weak increase in total influx of sulphate is most likely a result of an increasing influence of seasalt during the period. The average annual influx of SO_4^* for 1980/81 was 17.2 ± 2.64 meq S/m². In 1991/92, the annual weigted influx was lowered by 34%, down to 11.3 ± 2.64 meq S/m². At Kaarvatn, the annual average influx of H^+ as wet-deposition in 1980/81 was 22.9 ± 4.06 meq/m². In 1991/92, the annual average influx was 19.9 ± 4.08 meq/m², which is a decrease in the annual influx of H^+-ions by 13% from 1980/81 to 1991/92.

The variation in monthly contributions of major ions in wet-deposition are present in Figure 6.37 to 6.40. The high deposition velocities during the summer-period (1 April to 30 September) are almost totally responsible for the very high influx of dry-deposition compounds during this period compared with the remaining 6 months winter-period (Figure 6.27 and 6.28). Except the high influxes of sulphur and nitrogen compounds in wet-deposition during March and/or April when the amounts of precipitation are relatively low at all sites, the highest influxes of sulphur and nitrogen compounds (Figure 6.49..6.52), as well as other major ions, are at the highest when the catchments also receive the highest inputs of water. This should also be expected because of the high correlation which generally exists between influx of ions and influx of water (See Table 6.4). Thus, the monthly differences between influxes of chemical compounds in dry- and wet-deposition may exhibit large seasonal variations.

Despite the small differences in the concentrations of sulphur and nitrogen compounds in wet-deposition between the three most "air-polluted" sites, Birkenes, Storgama and Langtjern, the differences in fluxes between the sites are, however, very large. This, of cause, primarily relies on the large difference in annual precipitation between the sites. At Kaarvatn, however, which undoubtedly receives the highest inputs of water, the influxes of sulphur and nitrogen are far the lowest. This is primarily because this catchment is well "protected" from heavily air-polluted areas.



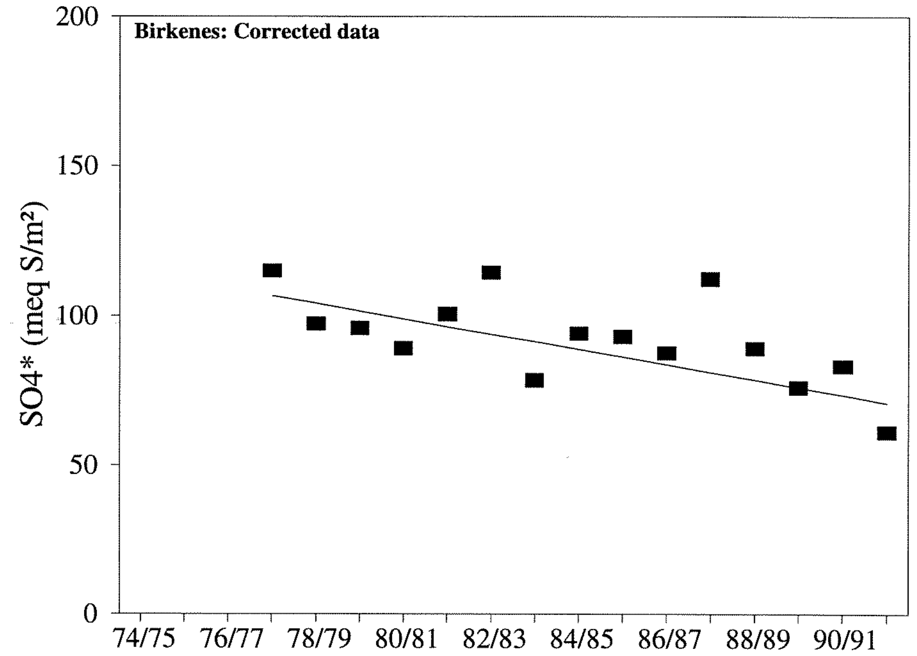


Figure 6.41 Annual weighted influxes of SO_4 in wet-deposition (meq S/m²) at Birkenes from 1974/75-1991/92, present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualizes the influence of water on the concentration/flux of each chemical compounds, i.e. large scattering means high water dependence and vise versa. The linear regression equations are present in Table 6.4. Continuous line means that the linear regression is significant, i.e. $p < 0.05$, while a dottet line means no significance, $p > 0.05$.*

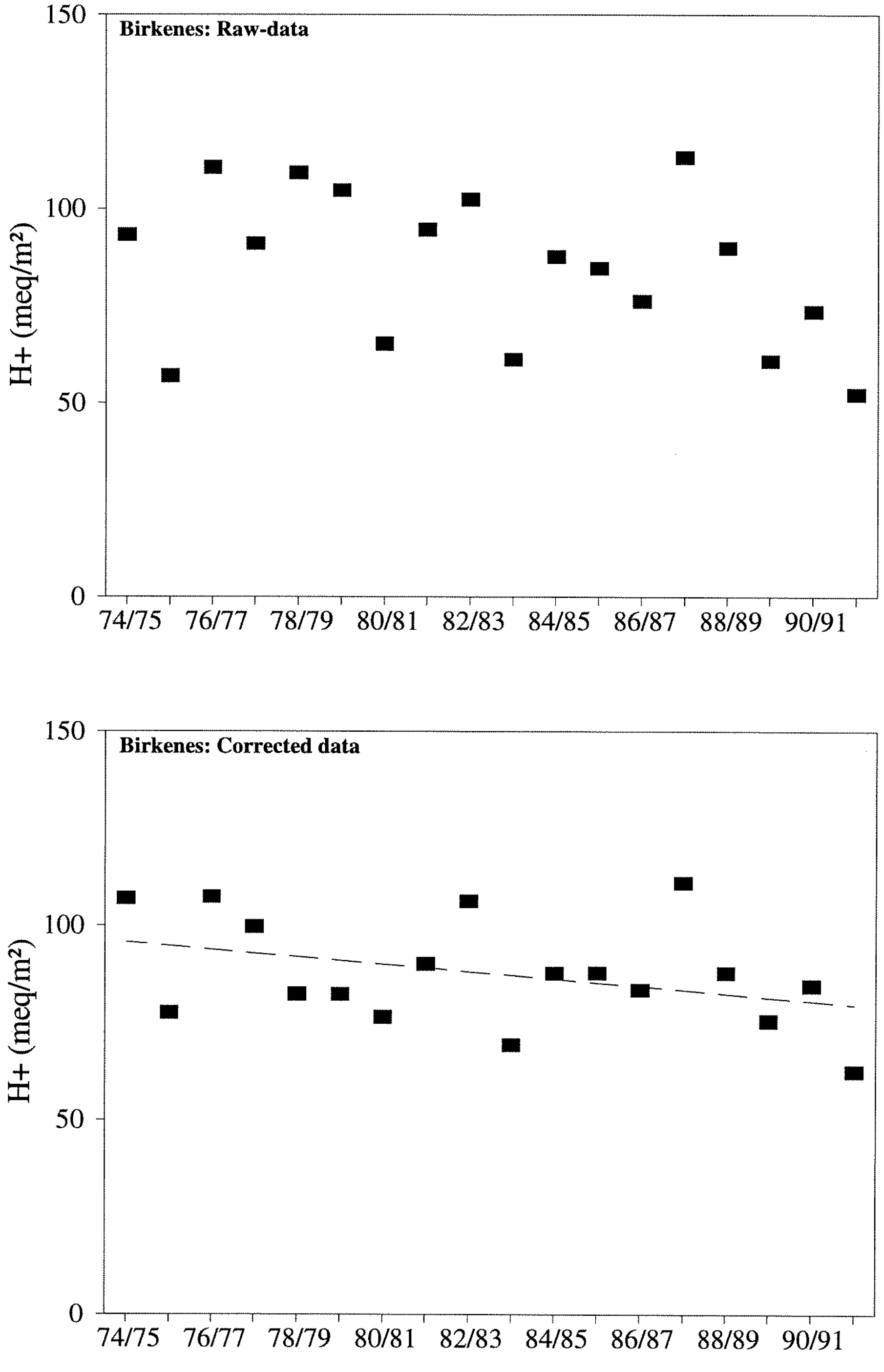


Figure 6.42 Annual weighted influxes of H^+ *in wet-deposition (meq/*m^2*) at Birkenes from 1974/75-1991/92, present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualizes the influence of water on the concentration/flux of each chemical compounds, i.e. large scattering means high water dependence and vise versa. The linear regression equations are present in Table 6.4. Continuous line means that the linear regression is significant, i.e.* $p < 0.05$*, while a dottet line means no significance,* $p > 0.05$*.*

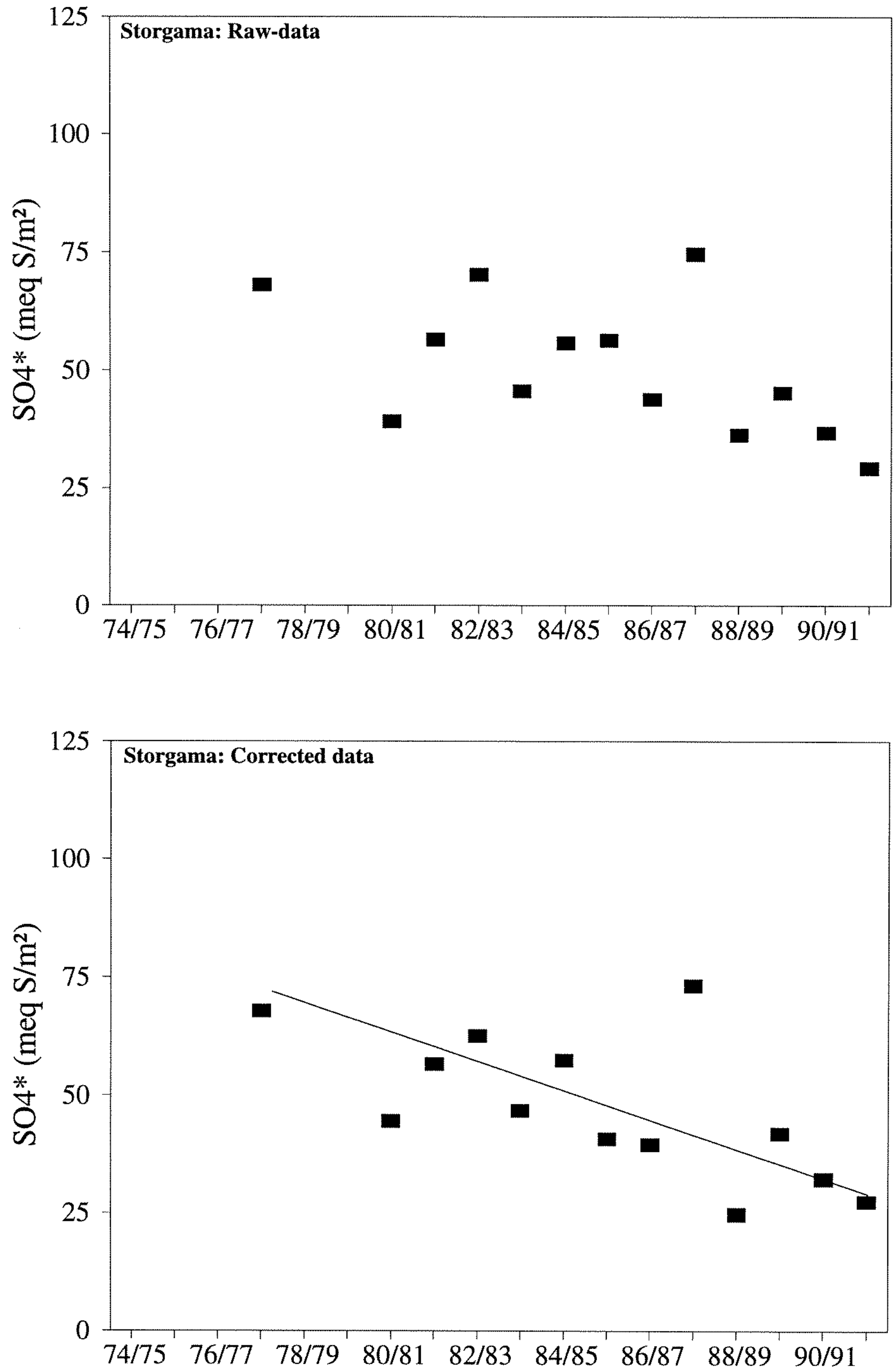
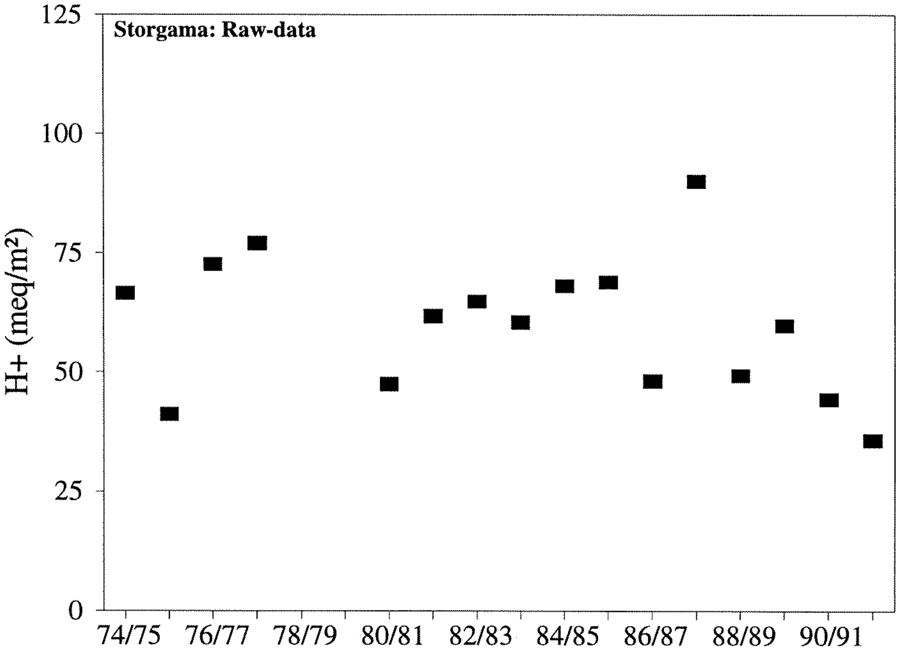


Figure 6.43 Annual weighted influxes of SO_4 wet-deposition (meq S/m^2) at Storgama from 1974/75-1991/92, present as raw-data and corrected data. The figure made on corrected data means that changes of fluxes due to change in inputs of water are added to the time trend equation made up from raw-data only. Thus, large scatter from the calculated trend line (in the figure based on calculated data) means that the influx is highly water dependant. The linear regression equations are present in Table 6.4. Continuous line means that the linear regression is significant, i.e. $p < 0.05$, while a dottet line means no significance, $p > 0.05$.*



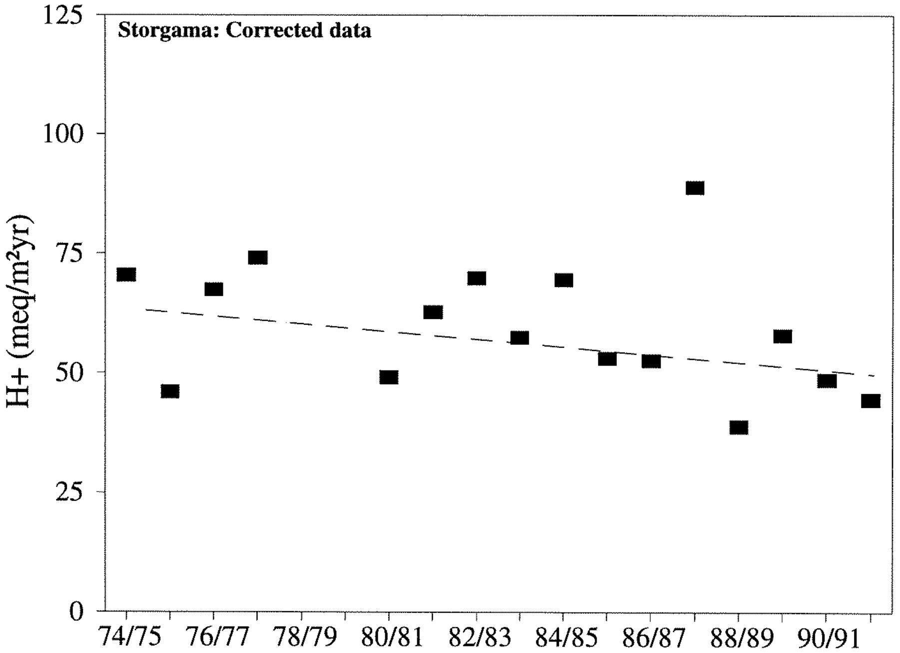
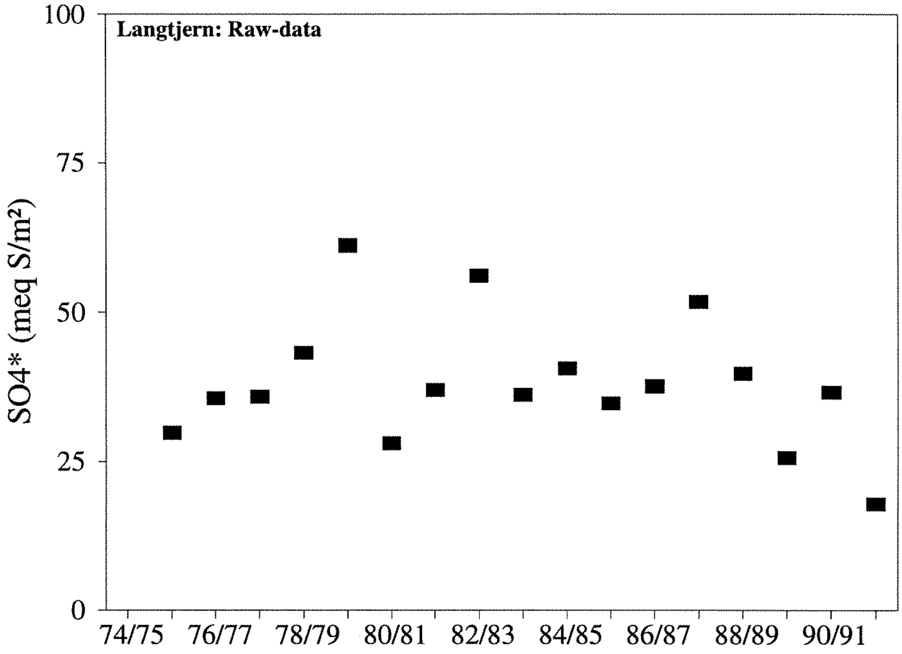


Figure 6.44 Annual weighted influxes of H^+ in wet-deposition (meq/m^2) at Storgama from 1974/75-1991/92, present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualizes the influence of water on the concentration/flux of each chemical compounds, i.e. large scattering means high water dependence and vise versa. The linear regression equations are present in Table 6.4. Continuous line means that the linear regression is significant, i.e. $p < 0.05$, while a dottet line means no significance, $p > 0.05$.



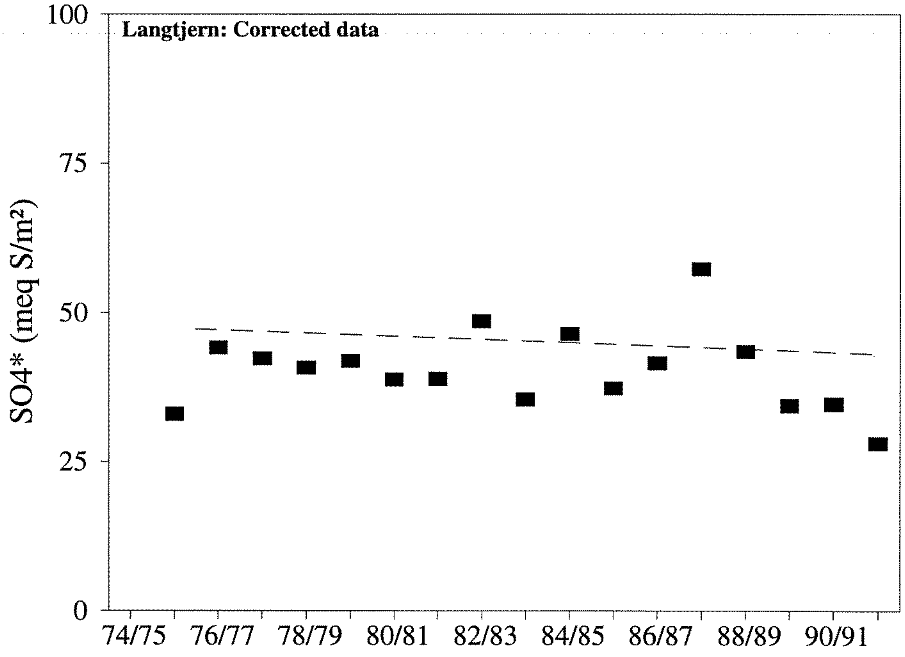
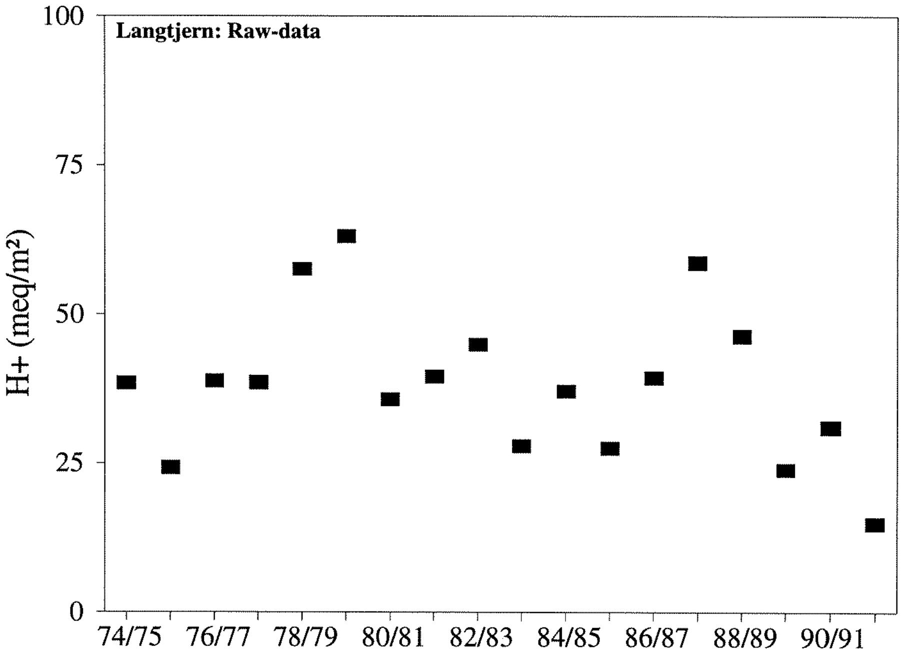


Figure 6.45 Annual weighted influxes of SO_4 wet-deposition (meq S/m^2) at Langtjern from 1974/75-1991/92, present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualizes the influence of water on the concentration/flux of each chemical compounds, i.e. large scattering means high water dependence and vise versa. The linear regression equations are present in Table 6.4. Continuous line means that the linear regression is significant, i.e. $p < 0.05$, while a dottet line means no significance, $p > 0.05$.*



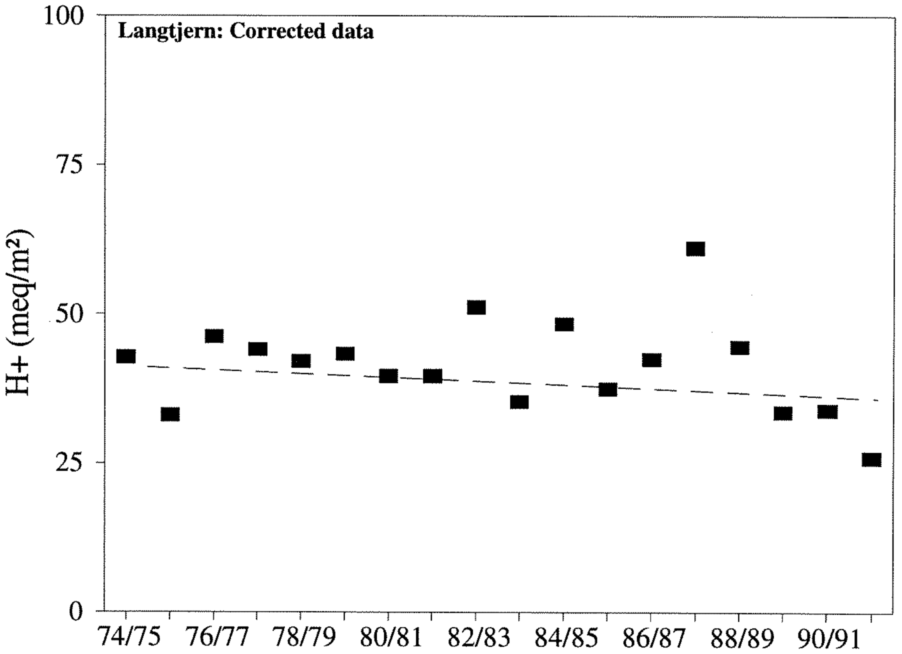
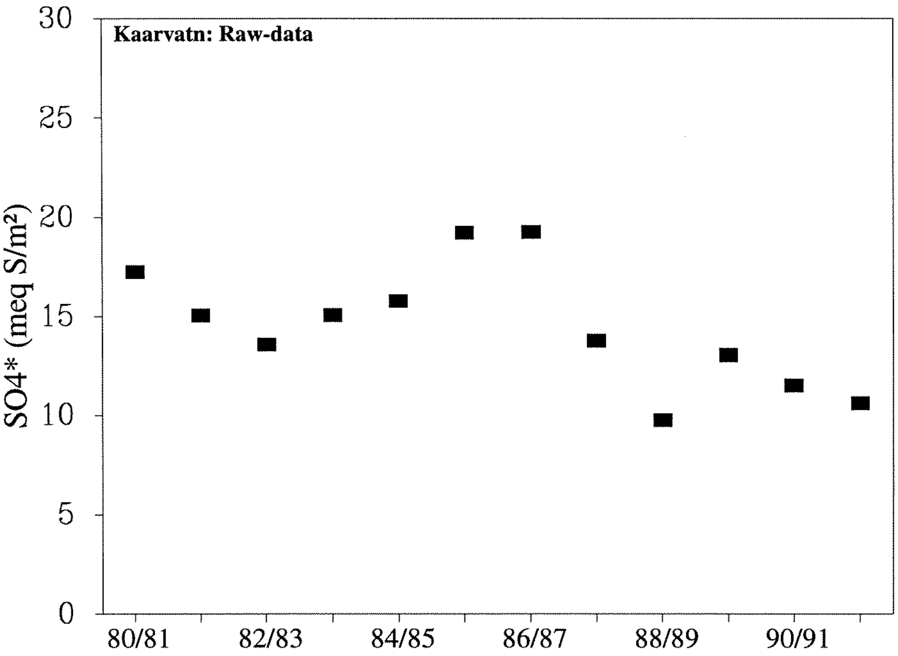


Figure 6.46 Annual weighted influxes of H^+ in wet-deposition (meq/m^2) at Langtjern from 1974/75-1991/92, present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualizes the influence of water on the concentration/flux of each chemical compounds, i.e. large scattering means high water dependence and vise versa. The linear regression equations are present in Table 6.4. Continuous line means that the linear regression is significant, i.e. $p < 0.05$, while a dottet line means no significance, $p > 0.05$.



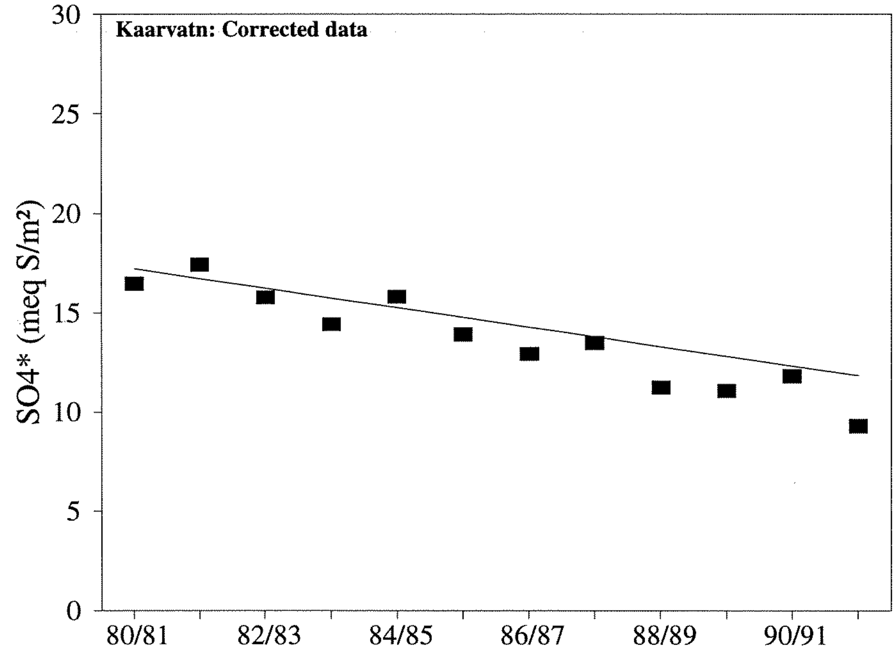
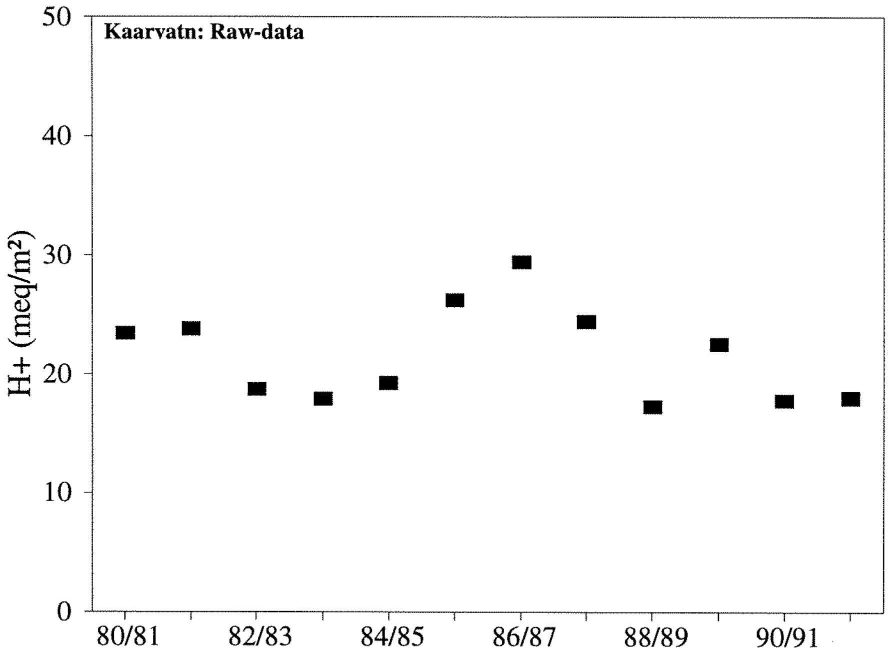


Figure 6.47 Annual weighted influxes of SO_4 in wet-deposition (meq S/m^2) at Kaarvatn from 1980/81-1991/92, present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualizes the influence of water on the concentration/flux of each chemical compounds, i.e. large scattering means high water dependence and vise versa. The linear regression equations are present in Table 6.4. Continuous line means that the linear regression is significant, i.e. $p < 0.05$, while a dottet line means no significance, $p > 0.05$.*



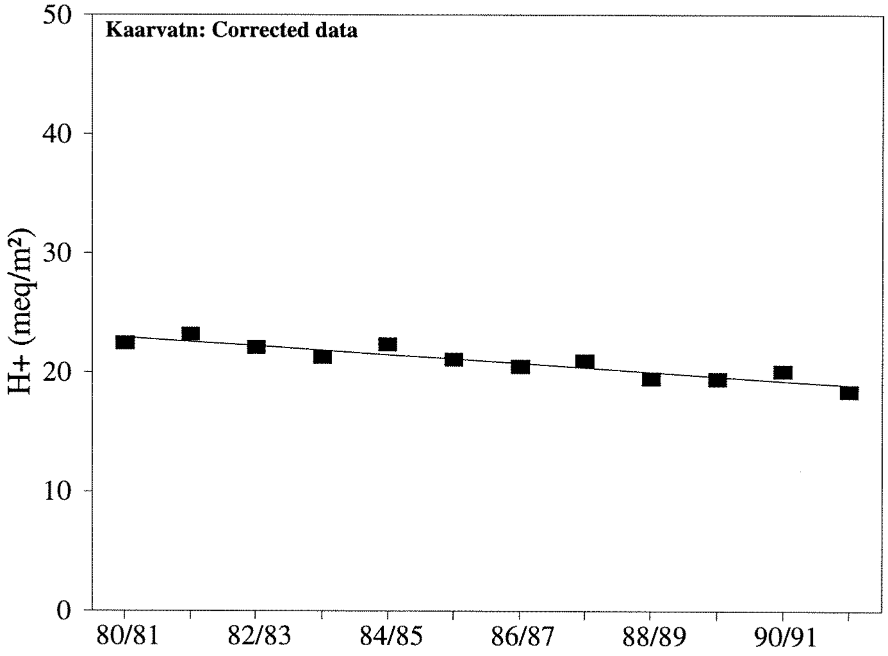


Figure 6.48 Annual weighted influxes of H^+ *in wet-deposition (meq/*m^2*) at Kaarvatn from 1980/81-1991/92, present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualizes the influence of water on the concentration/flux of each chemical compounds, i.e. large scattering means high water dependence and vise versa. The linear regression equations are present in Table 6.4. Continuous line means that the linear regression is significant, i.e.* $p < 0.05$*, while a dottet line means no significance,* $p > 0.05$*.*

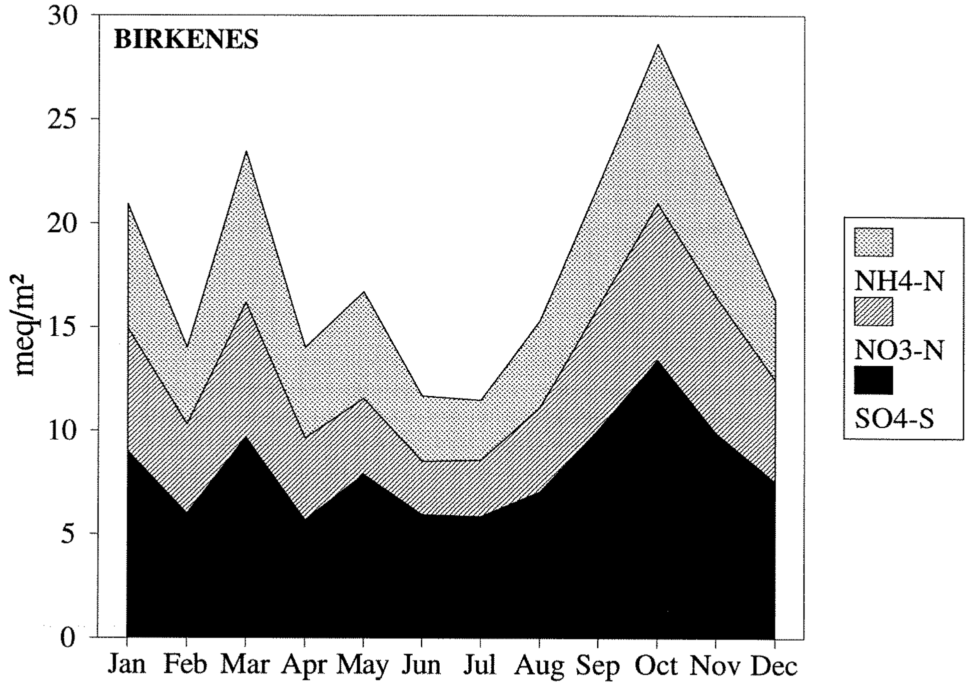


Figure 6.49 Monthly mean influxes of SO_4^{2-}, NO_3^- and NH_4^+ as wet-deposition at Birkenes, obtained from monthly weighted averages from 1974-1992.

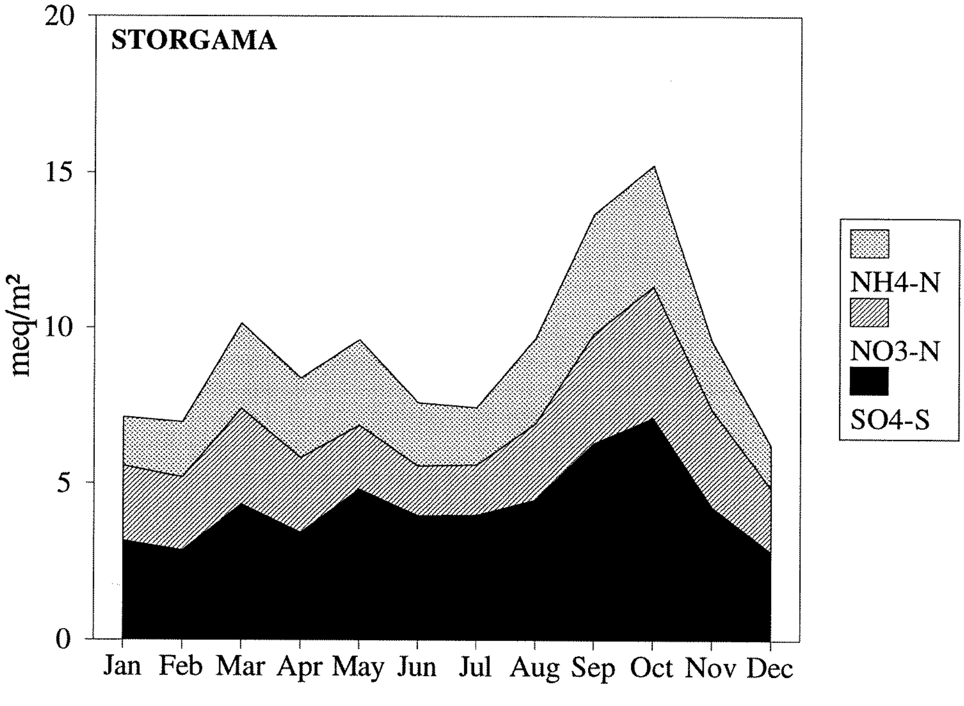


Figure 6.50 Monthly mean influxes of SO_4^{2-}, NO_3^- and NH_4^+ as wet-deposition at Storgama, obtained from monthly weighted averages from 1974-1992.

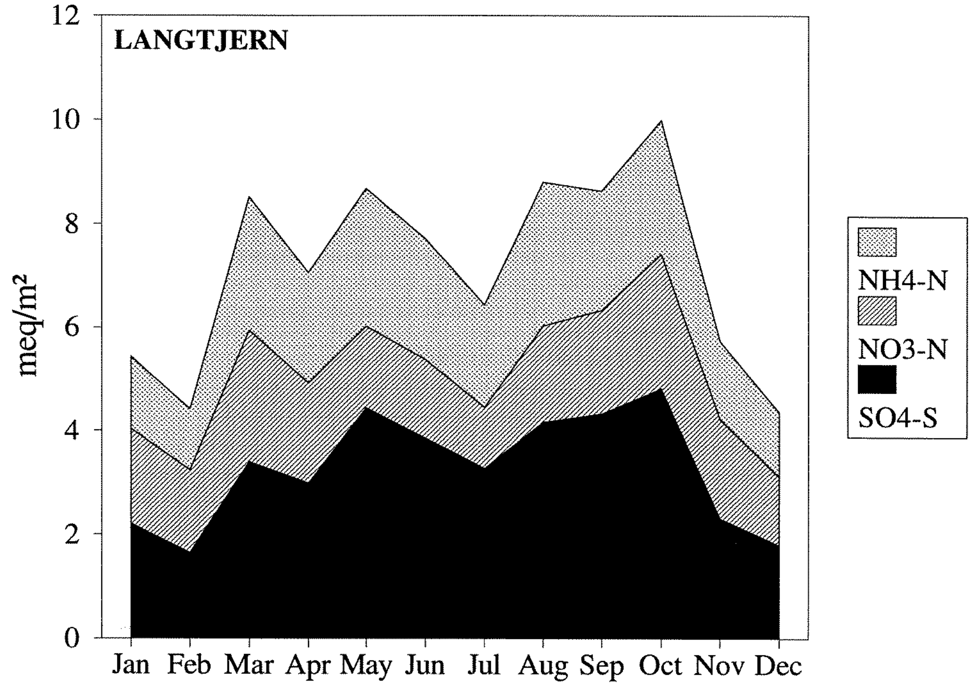


Figure 6.51 Monthly mean influxes of SO_4^{2-}, NO_3^- and NH_4^+ as wet-deposition at Langtjern, obtained from monthly weighted averages from 1974-1992.

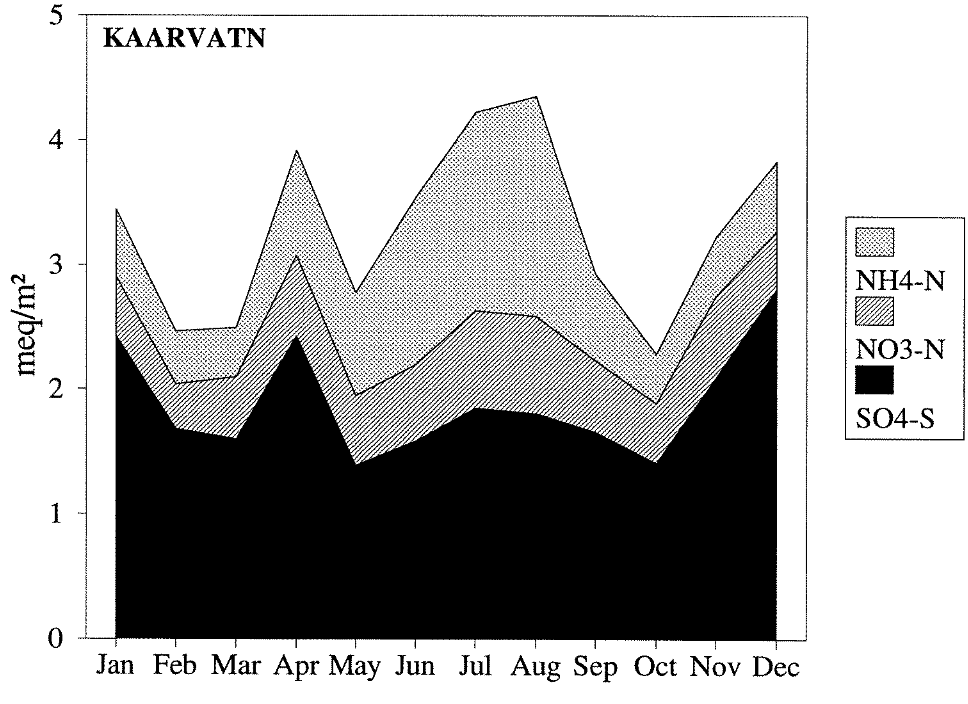


Figure 6.52 Monthly mean influxes of SO_4^{2-}, NO_3^- and NH_4^+ as wet-deposition at Kaarvatn, obtained from monthly weighted averages from 1980-1992.

6.1 Runoff

Time trends in concentration of chemical compounds

Like in wet- and dry-deposition, the most distinct time trend in the runoff-water chemistry at the four catchments is the decrease in non-marine sulphate (SO_4*) during the monitoring periods (Table 6.5 and 6.6). At Birkenes, Storgama, Langtjern and Kaarvatn, the concentration of SO_4* in runoff-water has decreased by averagely 31%, 32%, 35% and 34%, respectively. The corresponding decreases in wet-deposition during the almost identical time periods were 36% (Birkenes), 31% (Storgama), 53% (Langtjern), and 62% (Kaarvatn). The primary reason for the decreases in SO_4* at all sites are the reduction in sulphur emmision in Europe during the last 15 years. The corresponding percentage decreases in the concentration of ΣCa*,Mg* during the monitoring periods were 44% (Birkenes), 42% (Storgama), 28% (Langtjern) and 13% (Kaarvatn). The decrease in the concentration of SO_4*, however, is almost equal to the decrease in the concentrations of base cations, ΣCa*,Mg*.

Because the amount of total organic carbon (TOC) was not analysed before 1985, time trends of this parameter is left out in the further presentation. However, at the four catchments, no significant changes in the concentration of TOC in runoff-water were found during the period 1985-1992.

Based on the linear regressions made up from monthly weighted raw-data (Table 6.5), the average monthly concentrations of sulphate in runoff water at Birkenes at the beginning of 1974 was 151 ± 19.4 μeq/L. At the end of 1992, the monthly concentration has decreased by averagely 27%, down to 111 ± 4.8 μeq/L. By estimating "the real" amount of sulphur in dry-deposition as the difference between the total concentration of sulphate in runoff water and that of wet-deposition, dry-deposition averagely constituted 43% of total input of sulphur at the beginning of 1974, and 46% at the end of 1992. At the beginning of 1974, the average monthly concentration of SO_4* in runoff water at Birkenes was 139 ± 19.4 μeg/L, which means that SO_4* constituted 92% of total dissolved sulphur in runoff at the beginning of 1974. At the end of 1992, the monthly concentration of SO_4* has decreased by averagely 31%, down to a monthly weighted average of 96 ± 4.8 μeq/L, and SO_4* no constituted 87% of total dissolved inorganic sulphur. At the beginning of 1974, the average monthly concentration of ΣCa*,Mg* in runoff water at Birkenes was 86 ± 17.4 μeq/L, while at the end of 1992 the average concentration was 48 ± 4.2 μeq/L. This is a 44% decrease during the 19 years period from 1974-1992. While the concentration of SO_4* in runoff has decreased by averagely 43 μeg/L during the period 1974-1992, the concentration of ΣCa*,Mg* has correspondingly decreased by averagely 38 μeg/L. During the monitoring period, there has also been a certain increase in the concentration of seasalt (Na and Cl) and nitrate in runoff-water from Birkenes, most distinct for nitrate (Table 6.5).

Based on the linear regressions made up from monthly weighted raw-data (Table 6.5), the average concentrations of sulphate in runoff water at Storgama at the beginning of 1974 was 90 ± 20.3 μeq/L. At the end of 1992, the monthly concentration has decreased by averagely 30%, down to 63 ± 5.5 μeq/L. While dry-deposition averagely constituted 24% of total input of sulphur at the beginning of 1974, it contributed by averagely 29% at the end of 1992. At the beginning of 1974, the average monthly concentration of SO_4* in runoff water at Storgama was 87 ± 19.4 μeg/L, which means that SO_4* contributed with 97% of total dissolved sulphur in runoff at the beginning of 1974. At the end of 1992, the monthly concentration of SO_4* has decreased by averagely 32%, down to a monthly weighted average of 59 ± 5.3 µeq/L, and SO_4* contributed with 93% of total dissolved inorganic sulphur in runoff. At the beginning of 1974, the average monthly concentration of ΣCa*,Mg* in runoff water at Storgama was 59 ± 13.9 µeq/L, while at the end of 1992 the average concentration was 34 ± 3.8 µeq/L. This is a 42% decrease during the period 1974-1992. While the concentration of SO_4* in runoff has decreased by averagely 28 µeg/L during the period 1974-1992, the concentration of ΣCa*,Mg* has correspondingly decreased by averagely 25 µeg/L. As at Birkenes, there has also been a tendency of increasing concentration of seasalt (Na and Cl) during the monitoring period at Storgama, while there is a tendency of decreasing concentration of nitrate in runoff-water, which is the opposite of what observed at Birkenes. The most site specific time-trend at Storgama, is the decrease in K during the monitoring period. During the period the average monthly concentration of K has decreased by 81%, from 5.62 ± 2.45 µeq/L at the beginning of 1974, to 1.06 ± 0.57 µeq/L at the end of 1992 (Table 6.5). Because there also is a tendency of decreasing concentration of nitrate, it inicates a significant vegetation growth, or a deforestation within the catchment soon before or at the time of which the monitoring started (1974/75). This is however, still not confirmed.

Based on the linear regressions made up from monthly weighted raw-data (Table 6.6), the monthly average concentrations of sulphate in runoff water at Langtjern at the beginning of 1974 was 89 ± 14.5 µeq/L. At the end of 1992, the monthly concentration has decreased by averagely 35%, down to 58 ± 4.4 µeq/L. While dry-deposition averagely constituted 14% of total input of sulphur at the beginning of 1974, it contributed with averagely 23% at the end of 1992. At the beginning of 1974, the average monthly concentration of SO_4* in runoff water at Langtjern was 87 ± 14.2 µeg/L, which means that SO_4* contributed with 98% of total dissolved sulphur in runoff at the beginning of 1974. At the end of 1992, the concentration of SO_4* has decreased by 35%, down to a monthly weighted average of 56 ± 3.4 µeq/L, and SO_4* contributed by 97% of total dissolved inorganic sulphur in runoff. At the the beginning of 1974, the average monthly concentration of ΣCa*,Mg* in runoff water at Langtjern was 89 ± 14.2 µeq/L, while at the end of 1992 the monthly average was 63 ± 3.2 µeq/L. This is a 28% decrease during the 19 years period from 1974-1992. While the concentration of SO_4* in runoff has decreased by averagely 31 µeg/L during the period 1974-1992, the concentration of ΣCa*,Mg* has correspondingly decreased by averagely 26 µeg/L. At Langtjern, there has been a weak tendency of decreasing concentration of all base cations and strong acid anions, as well as a decrease in the concentration of total aluminium, during the monitoring period (Table 6.6.). The most site specific trend at Langtjern, is the decrease in total aluminium during the period of recording. During the period the monthly concentration of total Al (estimated as Al^{3+}) has decreased by averagely 17%, from 23.3 ± 4.64 µeq/L at the beginning of 1974, to 19.3 ± 1.14 µeq/L at the end of 1992 (Table 6.6).

Based on the linear regressions made up from monthly weighted raw data (Table 6.6), the monthly average concentrations of sulphate in runoff water at Kaarvatn at the beginning of 1980 was 22 ± 6.5 µeq/L. At the end of 1992, the monthly concentration has decreased by averagely 20%, down to 18 ± 1.8 µeq/L. Because the weather station at Kaarvatn is very unrepresentative for the weather conditions for the whole catchment, estimates of dry-deposition can not be calculated the same way as at the three other sites. At the beginning of 1980, the average monthly concentration of SO_4* in runoff water at Kaarvatn was 16 ± 4.9 µeg/L, which means that SO_4* contributed with 74% of total dissolved sulphur in runoff at the beginning of 1980. At the end of 1992, the average concentration of SO_4* has decreased by 34%, down to a monthly weighted average of 11 ± 1.4 µeq/L, and SO_4* contributed with 61%

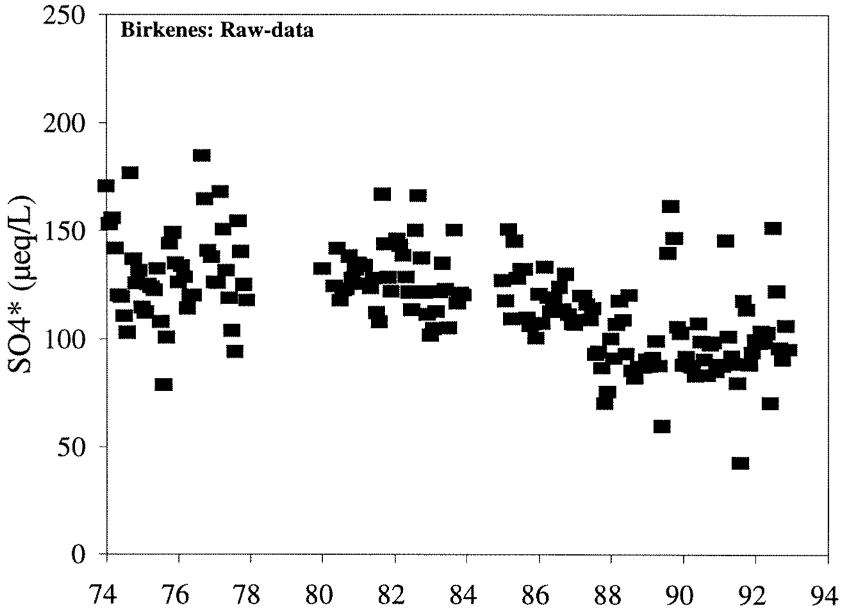
of total dissolved sulphur in runoff. At the the beginning of 1980, the average monthly concentration of ΣCa*,Mg* in runoff water at Kaarvatn was 39 ± 13.9 µeq/L, while at the end of 1992 the average concentration was 34 ± 3.9 µeq/L. This is a 13% decrease during the 13 years period from 1980-1992, but the decrease is not statistically significant (assuming $p < 0.05$ as criteria for significance). While the concentration of SO_4* in runoff has decreased by averagely 5.6 µeg/L during the period 1974-1992, the concentration of ΣCa*,Mg* has correspondingly decreased by averagely 5.1 µeg/L. Also at Kaarvatn, there is a weak tendency of increasing influence from seasalts on the runoff-water chemistry, which is slightly confirmed by the weak increase in Na, Mg and Cl from 1980 to 1992.

Table 6.5 Time trends in the concentration (µeq/L) of major chemical compounds in runoff water from Birkenes and Storgama, based on monthly weighted raw data $[y(t) = (\delta y_1/\delta t)t + b_1]$ *and time trends after the water dependent concentration changes* $[\delta y_1/\delta \log(q)]$ *are accounted for, i.e.* $[Y(t) = (\delta y_1/\delta t)t + [\delta y_1/\delta \log(q)]\log(q)] + b_2]$. *The constant* b_2 *is fitted so* $b_2=b_1$. *(*:* $p < 0.05$, ***:* $p < 0.01$*).*

		Raw-data			Water dependance		Corrected data	
	Period	**$\delta y_1/\delta t$**	**b_1**	**r_1**	**$\delta y/\delta \log(q)$**	**r_q**	**$\delta y_2/\delta t$**	**r_2**
Birkenes								
H^+	1974-1992	0.17 ± 0.15	22.2 ± 11.5	0.08	12.4 ± 1.05	0.66**	0.29 ± 0.10	0.22**
Ca	1974-1992	-1.10 ± 0.20	72.7 ± 15.3	-0.39**	-17.0 ± 1.56	-0.63**	-1.27 ± 0.13	-0.58**
Mg	1974-1992	-0.57 ± 0.07	39.8 ± 5.85	-0.50**	-1.54 ± 0.81	-0.14	-0.59 ± 0.01	-0.96**
ΣCa*,Mg*	1974-1992	-2.01 ± 0.22	85.9 ± 17.4	-0.56**	-18.7 ± 2.14	-0.54**	-2.20 ± 0.15	-0.75**
K	1974-1992	0.03 ± 0.04	5.38 ± 2.86	0.12	-0.55 ± 0.35	-0.12	0.03 ± 0.00	0.43*
Na	1974-1992	0.58 ± 0.26	116 ± 19.8	0.17*	-1.35 ± 2.43	-0.04	0.57 ± 0.01	0.97**
Al_{tot} (Al^{3+})	1975-1992	0.32 ± 0.19	45.3 ± 13.6	0.13	8.74 ± 1.66	0.38**	0.39 ± 0.07	0.38**
SO_4	1974-1992	-2.11 ± 0.25	151 ± 19.4	-0.54**	8.96 ± 2.71	0.24**	-2.02 ± 0.07	-0.91**
SO_4*	1974-1992	-2.26 ± 0.25	139 ± 19.4	-0.56**	8.90 ± 2.77	0.23**	-2.17 ± 0.07	-0.92**
NO3	1974-1992	0.45 ± 0.10	5.08 ± 7.76	0.32**	2.34 ± 0.98	0.18*	0.47 ± 0.02	0.89**
Cl	1974-1992	1.48 ± 0.43	114 ± 33.9	0.24**	0.55 ± 4.25	0.01	1.49 ± 0.00	1.00**
Storgama								
H^+	1975-1992	-0.18 ± 0.22	31.3 ± 15.7	-0.06	5.21 ± 1.66	0.22**	-0.11 ± 0.05	-0.17*
Ca	1975-1992	-0.87 ± 0.16	46.2 ± 11.3	-0.37**	-8.19 ± 1.66	-0.34**	-0.89 ± 0.06	-0.74**
Mg	1975-1992	-0.32 ± 0.06	16.4 ± 4.34	-0.36**	-1.56 ± 0.66	-0.17*	-0.33 ± 0.01	-0.91**
ΣCa*,Mg*	1975-1992	-1.29 ± 0.20	58.6 ± 13.9	-0.43**	-9.05 ± 2.13	-0.30**	-1.32 ± 0.07	-0.83**
K	1975-1992	-0.24 ± 0.03	5.62 ± 2.45	-0.46**	0.01 ± 0.30	0.00	-0.24 ± 0.01	-1.00**
Na	1975-1992	0.13 ± 0.21	33.9 ± 15.3	0.04	-7.01 ± 1.58	-0.31**	0.05 ± 0.06	0.05
Al_{tot} (Al^{3+})	1975-1992	0.11 ± 0.08	16.6 ± 5.42	0.11	-1.15 ± 0.58	-0.14	0.10 ± 0.01	0.56**
SO_4	1975-1992	-1.42 ± 0.29	90.3 ± 20.3	-0.34**	-6.89 ± 3.08	0.16*	-1.44 ± 0.05	-0.90**
SO_4*	1975-1992	-1.49 ± 0.28	87.4 ± 19.4	-0.37**	-6.38 ± 2.99	0.15*	-1.51 ± 0.05	-0.92**
NO3	1975-1992	-0.25 ± 0.12	12.2 ± 8.53	-0.15*	1.41 ± 0.93	0.11	-0.23 ± 0.01	-0.79**
Cl	1975-1992	0.59 ± 0.21	29.3 ± 15.1	0.20**	-3.68 ± 1.65	-0.16*	0.54 ± 0.03	0.76**

Table 6.6 Time trends in the concentration (µeq/L) of major chemical compounds in runoff water from Langtjern and Kaarvatn, based on monthly weighted raw data $[y(t) = (\delta y_1/\delta t)t + b_1]$ *and time trends after the water dependent concentration changes* $[\delta y_1/\delta log(q)]$ *are accounted for, i.e.* $[Y(t) = (\delta y_1/\delta t)t + [\delta y_1/\delta log(q)]log(q)] + b_2]$*. The constant* b_2 *is fitted so* $b_2=b_1$*. (*:* $p < 0.05$*, **:* $p < 0.01$*).*

		Raw-data			**Water dependance**		**Corrected data**	
	Period	**$\delta y_1/\delta t$**	**b_1**	**r_1**	**$\delta y/\delta log(q)$**	**r_q**	**$\delta y_2/\delta t$**	**r_2**
Langtjern								
H^+	1974-1992	0.06 ± 0.10	16.1 ± 7.90	0.04	4.52 ± 0.87	0.35**	0.05 ± 0.03	0.10
Ca	1974-1992	-1.03 ± 0.14	70.4 ± 11.5	-0.46**	-7.14 ± 1.42	-0.34**	-1.01 ± 0.05	-0.80**
Mg	1974-1992	-0.33 ± 0.04	21.2 ± 3.35	-0.50**	-1.59 ± 0.44	-0.25**	-0.33 ± 0.01	-0.89**
$\Sigma Ca^*, Mg^*$	1974-1992	-1.34 ± 0.17	88.7 ± 14.2	-0.48**	-8.43 ± 1.78	-0.32**	-1.32 ± 0.06	-0.83**
K	1974-1992	-0.04 ± 0.02	3.80 ± 1.46	-0.15*	0.36 ± 0.17	0.15*	-0.04 ± 0.00	-0.71**
Na	1974-1992	-0.09 ± 0.06	26.5 ± 5.08	-0.10	-2.17 ± 0.58	-0.26**	-0.08 ± 0.02	-0.34**
Al_{tot} (Al^{3+})	1975-1992	-0.21 ± 0.06	23.3 ± 4.64	-0.24**	-1.34 ± 0.56	-0.17*	-0.21 ± 0.01	-0.82**
SO_4	1974-1992	-1.64 ± 0.18	89.1 ± 14.5	-0.55**	-1.12 ± 2.02	-0.04	-1.64 ± 0.01	-1.00**
SO_4^*	1974-1992	-1.62 ± 0.18	86.9 ± 14.2	-0.55**	-0.91 ± 1.99	-0.03	-1.62 ± 0.01	-1.00**
NO3	1974-1992	-0.03 ± 0.02	2.14 ± 1.48	-0.12	0.58 ± 0.17	0.24**	-0.03 ± 0.00	-0.46**
Cl	1974-1992	-0.16 ± 0.06	20.9 ± 4.73	-0.20**	-2.08 ± 0.54	-0.26**	-0.16 ± 0.02	-0.59**
Kaarvatn								
H^+	1980-1992	0.01 ± 0.01	0.66 ± 0.35	0.10	0.33 ± 0.04	0.58**	0.02 ± 0.00	0.37**
Ca	1980-1992	-0.35 ± 0.24	30.8 ± 11.4	-0.12	-13.9 ± 1.02	-0.75**	-0.84 ± 0.18	-0.37**
Mg	1980-1992	0.08 ± 0.16	15.8 ± 7.51	0.04	-3.87 ± 0.96	-0.32*	-0.06 ± 0.05	-0.10
$\Sigma Ca^*, Mg^*$	1980-1992	-0.39 ± 0.30	38.6 ± 13.9	-0.11	-16.6 ± 1.27	-0.74**	-0.97 ± 0.21	-0.35**
K	1980-1992	-0.03 ± 0.02	3.69 ± 1.05	-0.11	-0.74 ± 0.13	-0.44**	-0.05 ± 0.01	-0.43**
Na	1980-1992	0.27 ± 0.55	55.3 ± 25.5	0.04	-9.92 ± 3.35	-0.24**	-0.08 ± 0.13	-0.05
Al_{tot} (Al^{3+})	1980-1992	-0.00 ± 0.02	2.12 ± 0.80	-0.01	0.32 ± 0.10	0.25**	0.01 ± 0.00	0.18*
SO_4	1980-1992	-0.35 ± 0.14	22.2 ± 6.45	-0.21*	-6.48 ± 0.71	-0.61**	-0.59 ± 0.08	-0.50**
SO_4^*	1960-1992	-0.43 ± 0.11	16.4 ± 4.93	-0.33**	-5.62 ± 0.52	-0.67**	-0.63 ± 0.07	-0.59**
NO3	1980-1992	-0.03 ± 0.02	1.63 ± 0.95	-0.13	-0.85 ± 0.11	-0.55**	-0.06 ± 0.01	-0.42**
Cl	1980-1992	0.79 ± 0.84	56.6 ± 39.3	0.08	-8.36 ± 5.27	-0.13	0.49 ± 0.11	0.36**



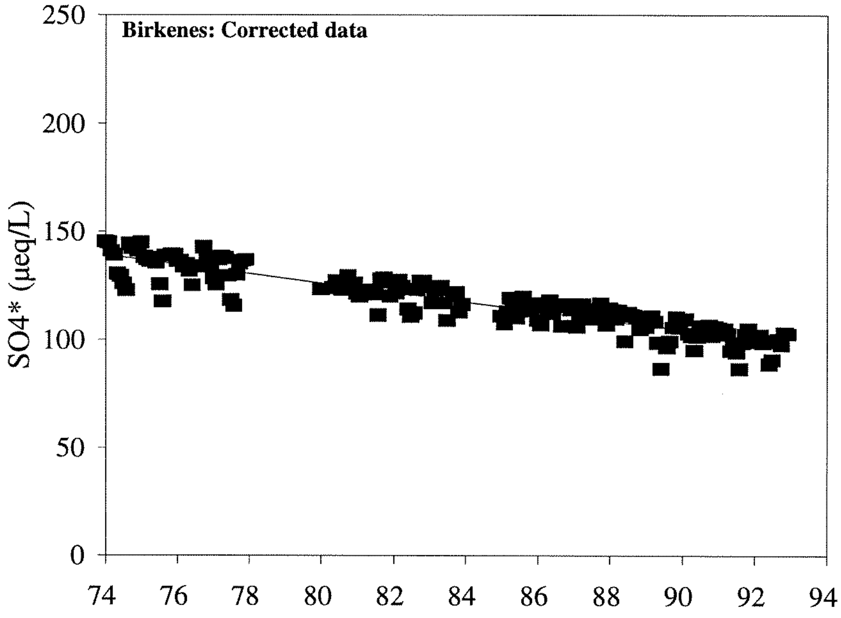
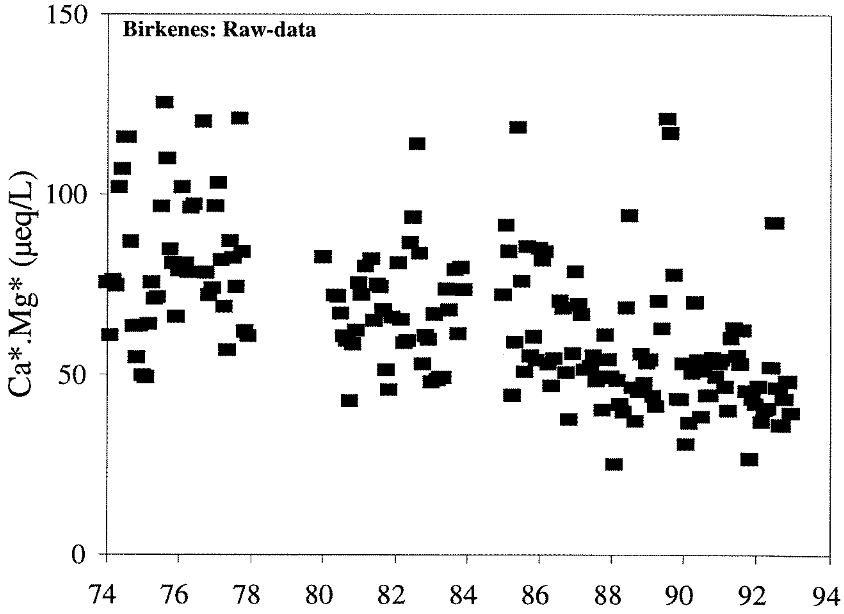


Figure 6.53 The monthly weighted concentration of SO_4 in runoff (µeq/L) at Birkenes from 1974-1992, present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualizes the influence of water on the concentration/flux of each chemical compounds, i.e. large scattering means high water dependence and vise versa. The linear regression equations are present in Table 6.5. Continuous line means that the linear regression is significant, i.e.* $p < 0.05$*, while a dottet line means no significance,* $p > 0.05$.



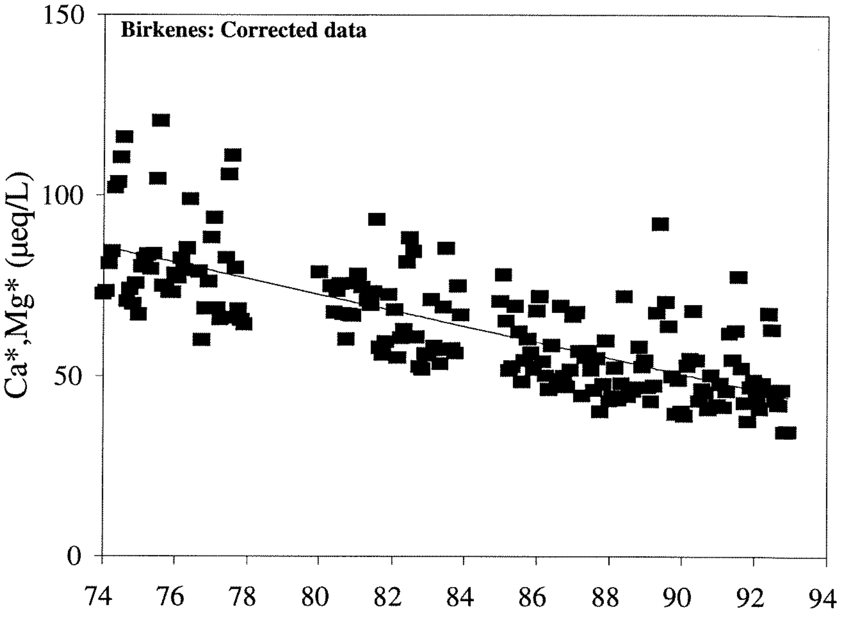
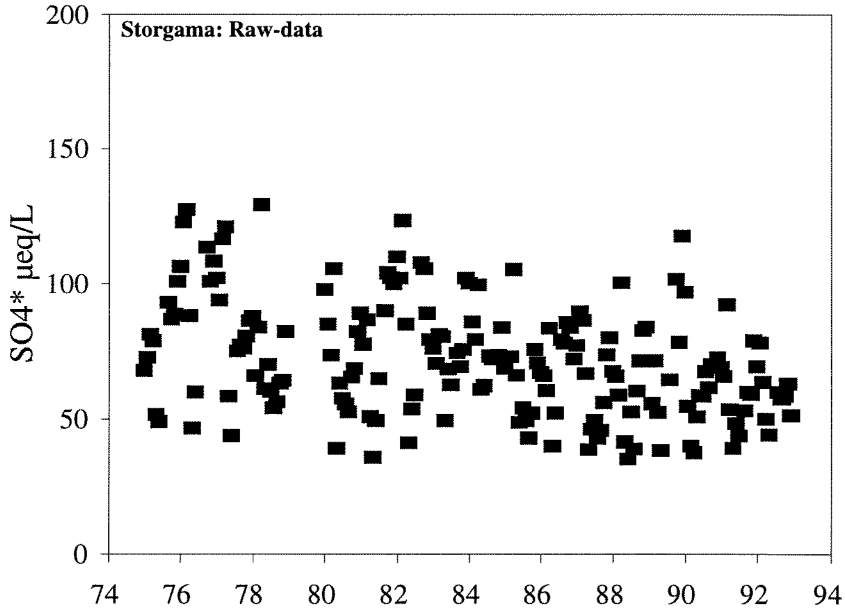


Figure 6.54 The monthly weighted concentration of $\Sigma Ca^*, Mg^*$ *in runoff (µeq/L) at Birkenes from 1974-1992, present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualizes the influence of water on the concentration/flux of each chemical compounds, i.e. large scattering means high water dependence and vise versa. The linear regression equations are present in Table 6.5. Continuous line means that the linear regression is significant, i.e.* $p < 0.05$, *while a dottet line means no significance,* $p > 0.05$.



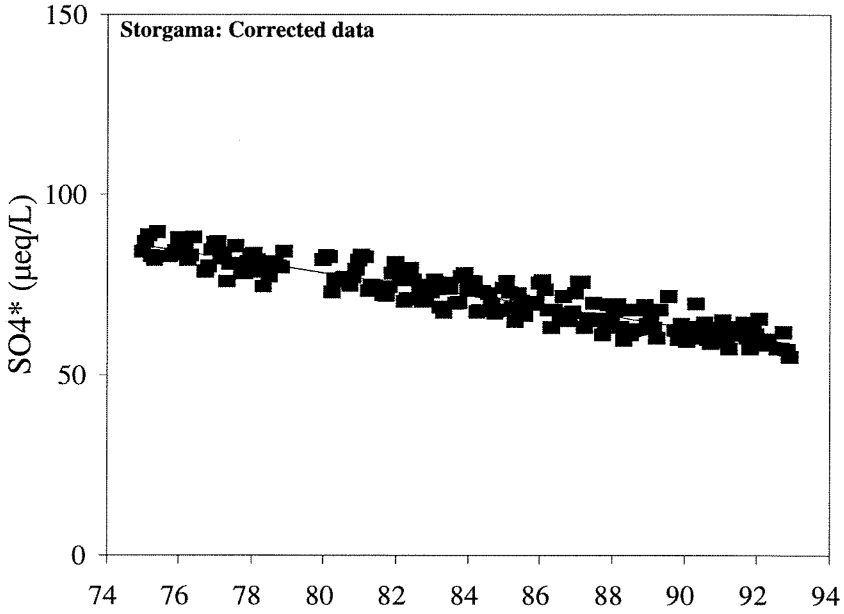
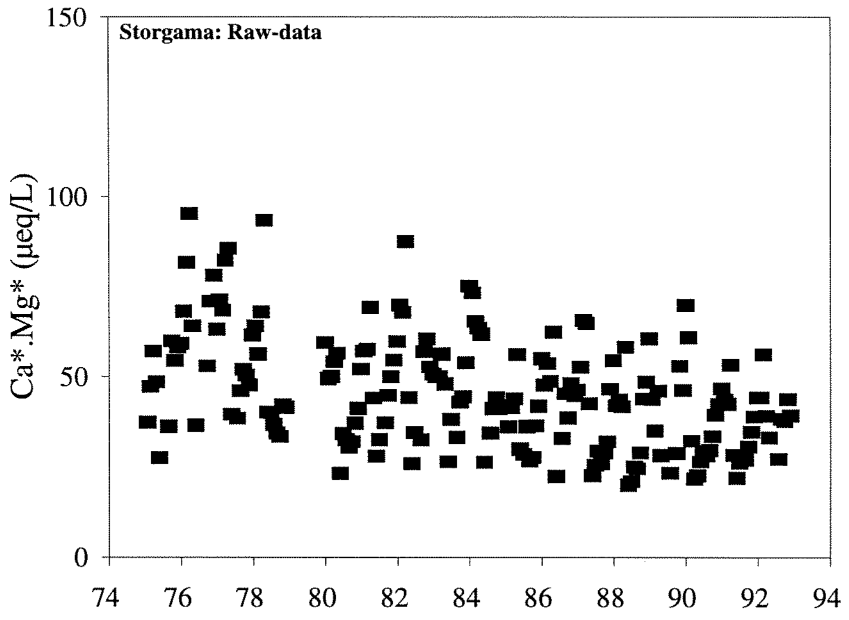


Figure 6.55 The monthly weighted concentration of SO_4 in runoff (µeq/L) at Storgama from 1974-1992, present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualizes the influence of water on the concentration/flux of each chemical compounds, i.e. large scattering means high water dependence and vise versa. The linear regression equations are present in Table 6.5. Continuous line means that the linear regression is significant, i.e. $p < 0.05$, while a dottet line means no significance, $p > 0.05$.*



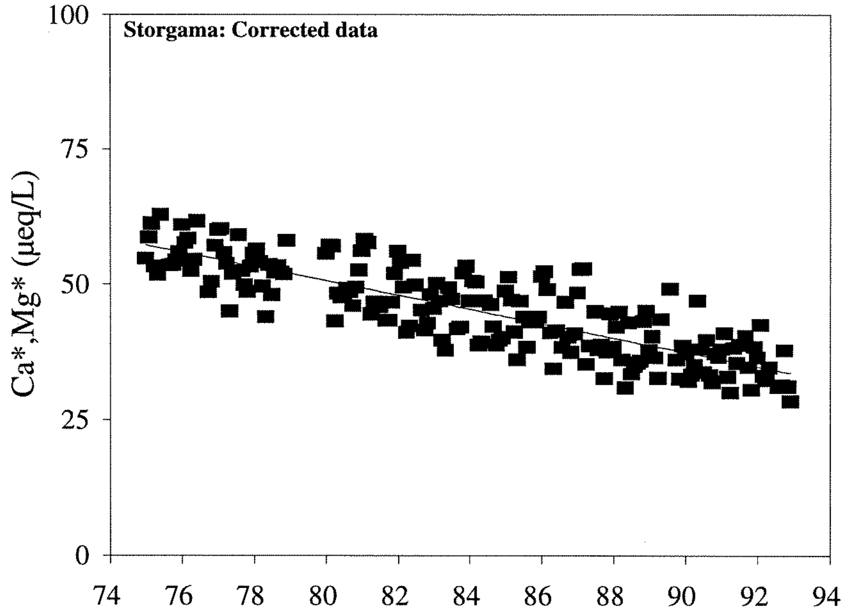
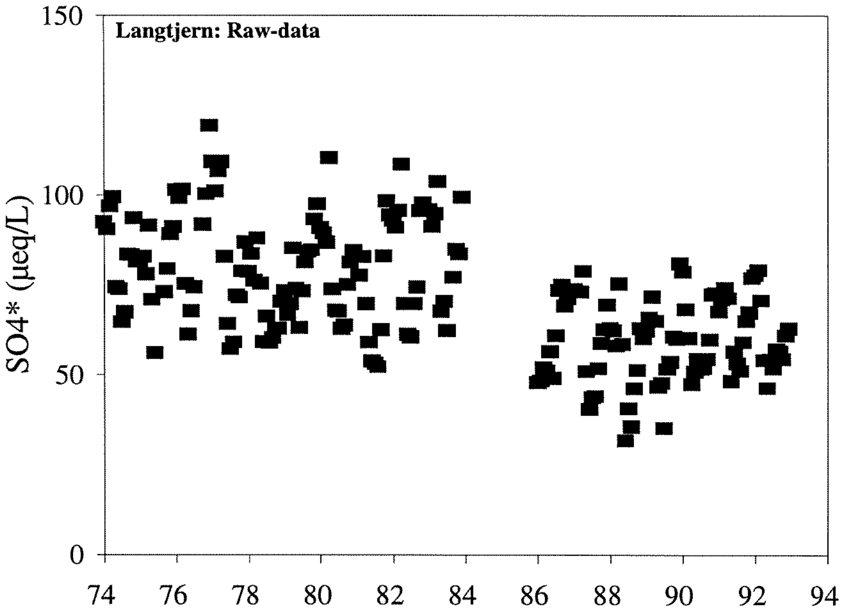


Figure 6.56 The monthly weighted concentration of ΣCa,Mg* in runoff (µeq/L) at Storgama from 1974-1992, present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualizes the influence of water on the concentration/flux of each chemical compounds, i.e. large scattering means high water dependence and vise versa. The linear regression equations are present in Table 6.5. Continuous line means that the linear regression is significant, i.e. $p < 0.05$, while a dottet line means no significance, $p > 0.05$.*



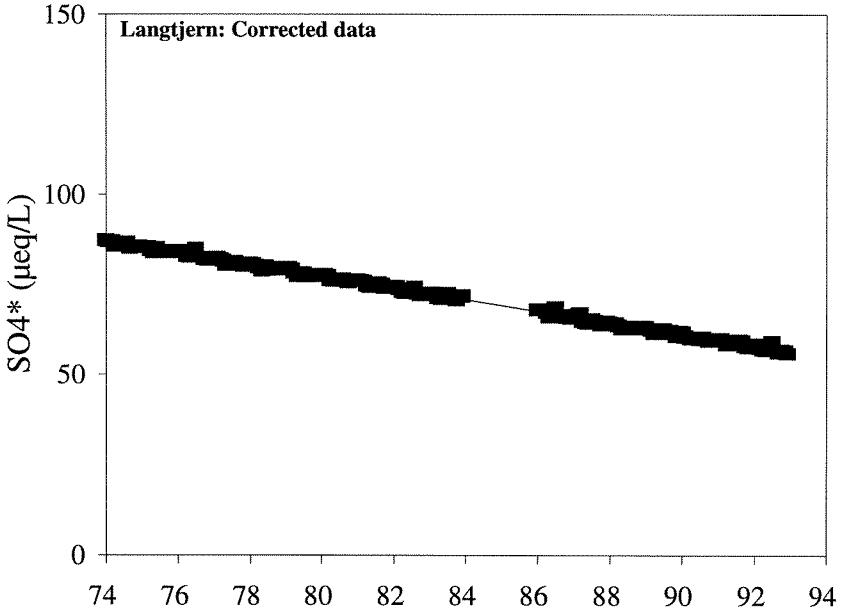
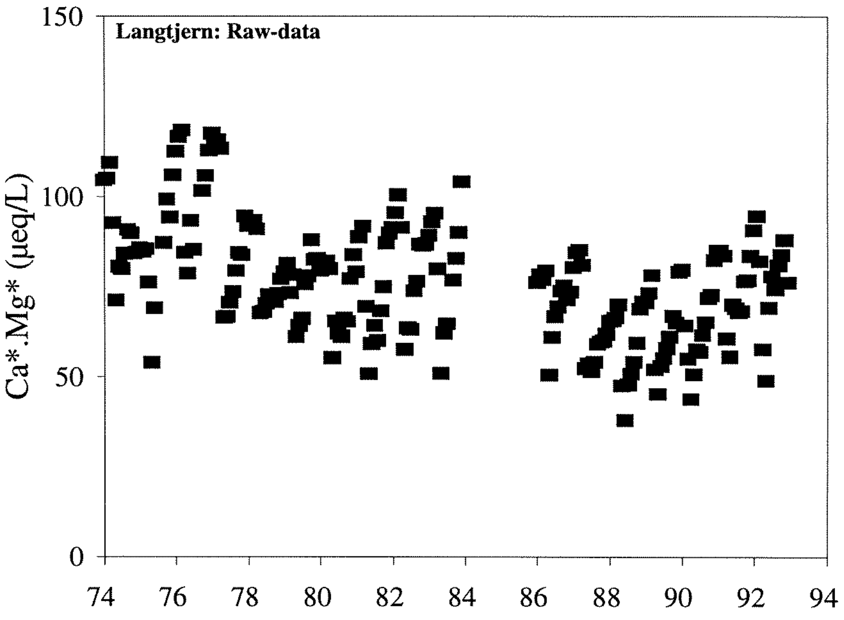


Figure 6.57 The monthly weighted concentration of SO_4 in runoff (µeq/L) at Langtjern from 1974-1992, present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualizes the influence of water on the concentration/flux of each chemical compounds, i.e. large scattering means high water dependence and vise versa. The linear regression equations are present in Table 6.6. Continuous line means that the linear regression is significant, i.e. $p < 0.05$, while a dottet line means no significance, $p > 0.05$.*



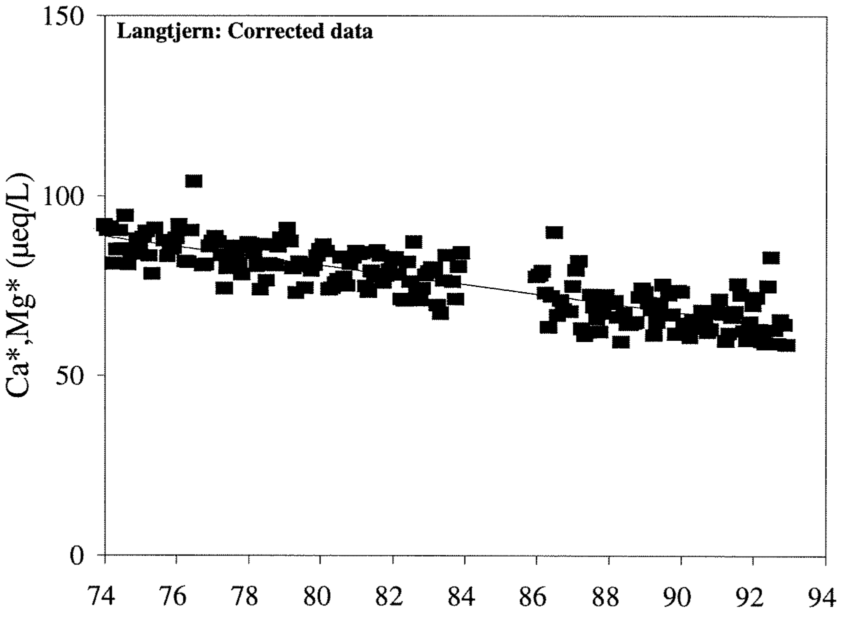
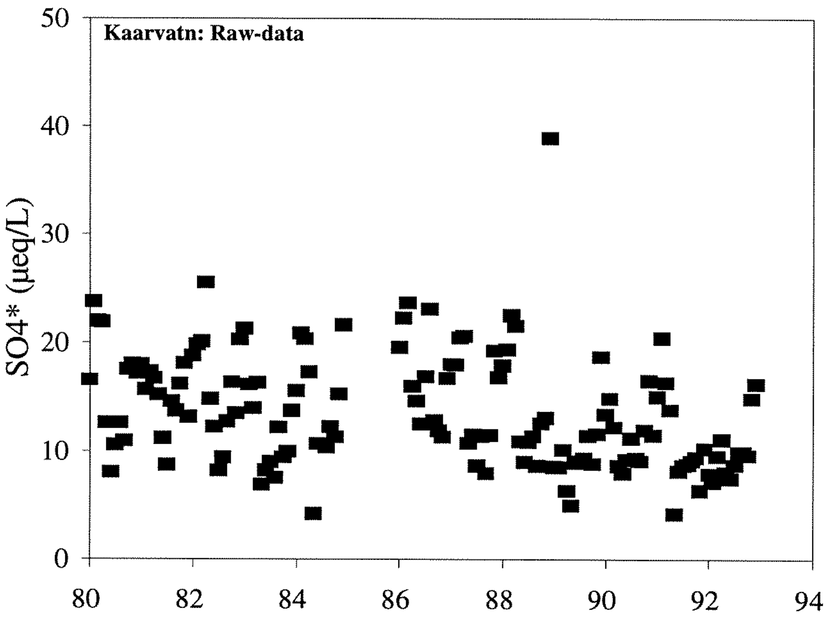


Figure 6.58 The monthly weighted concentration of $\Sigma Ca^*,Mg^*$ in runoff (µeq/L) at Langtjern from 1974-1992, present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualizes the influence of water on the concentration/flux of each chemical compounds, i.e. large scattering means high water dependence and vise versa. The linear regression equations are present in Table 6.6. Continuous line means that the linear regression is significant, i.e. $p < 0.05$, while a dottet line means no significance, $p > 0.05$.



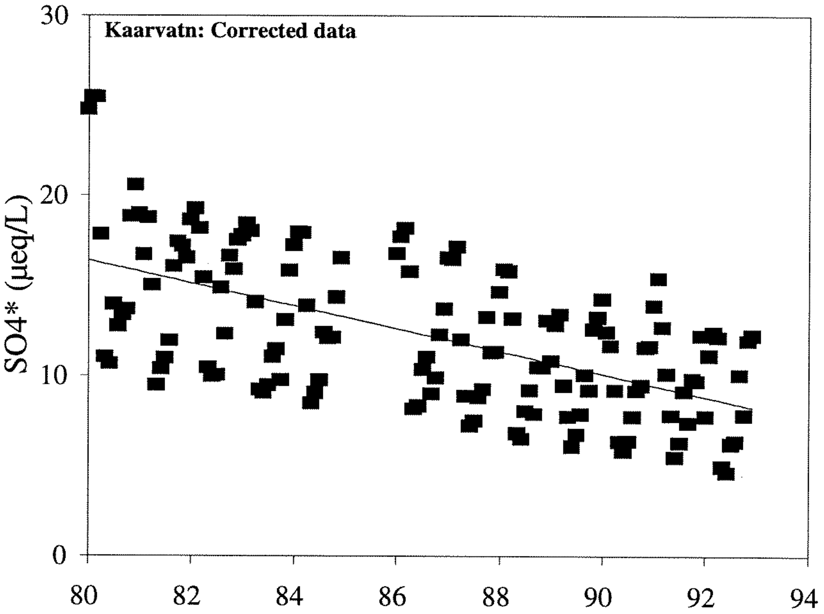
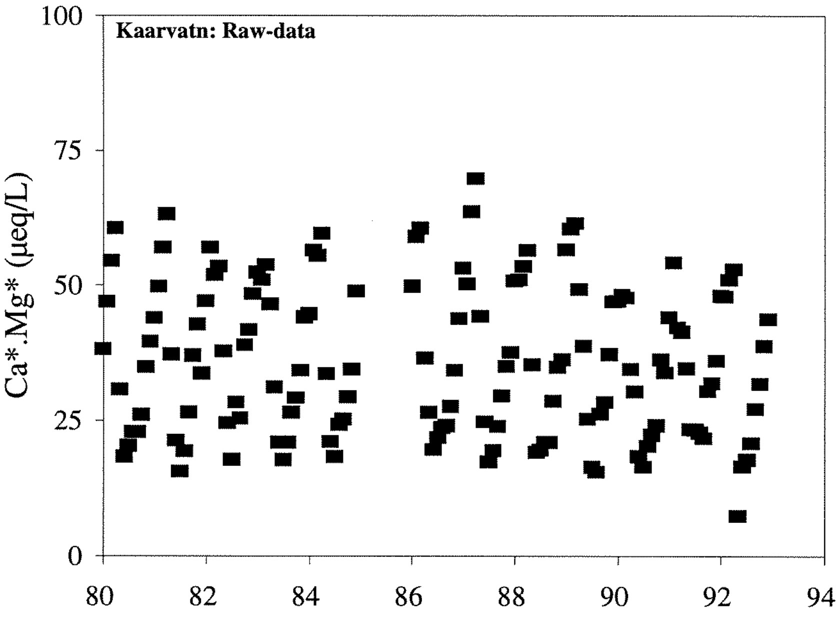


Figure 6.59 The monthly weighted concentration of SO_4 in runoff (μeq/L) at Kaarvatn from 1980-1992, present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualizes the influence of water on the concentration/flux of each chemical compounds, i.e. large scattering means high water dependence and vise versa. The linear regression equations are present in Table 6.6. Continuous line means that the linear regression is significant, i.e. $p < 0.05$, while a dottet line means no significance, $p > 0.05$.*



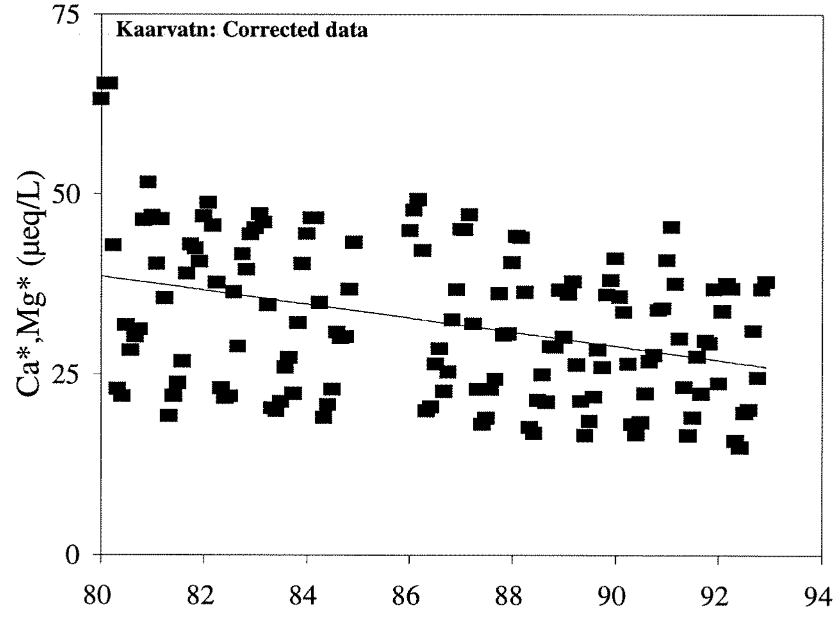


Figure 6.60 The monthly weighted concentration of ΣCa,Mg* in runoff (µeq/L) at Kaarvatn from 1980-1992, present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualizes the influence of water on the concentration/flux of each chemical compounds, i.e. large scattering means high water dependence and vise versa. The linear regression equations are present in Table 6.6. Continuous line means that the linear regression is significant, i.e. $p < 0.05$, while a dottet line means no significance, $p > 0.05$.*

If comparing the decrease in concentration of SO_4* and ΣCa*,Mg* during the monitoring periods, the decreases are slightly higher for SO_4* compared with ΣCa*,Mg* at all sites. If this tendency continues, we might expect an increase in the acid neutralizing capacity (ANC) of runoff-water in the years to come. The ANC of runoff-water will be more firmly discussed later in this chapter.

From 1974-1992, dry-deposition seems to constitute an increasing part of the total amount of sulphur which enters into the catchments. This should also be expected, as a consequence of vegetation growth. Increased amount of vegetation means increased filter-effect, which in other words means that more dry-deposition is able to be retained within the catchments (See chapter 5.2).

How much variations in amount of runoff are influencing on the concentration of various ions in runoff-water differ from catchment to catchment. This is illustrated in Table 5.24. Even though the data from 1992 are not incorporated in this table, the rank is the same even after the 1992 data was incorporated.

While the concentrations of sulphate in wet-deposition at all sites, exhibit relative large variation with respect to variations in amount of precipitation, the corresponding water-dependence are much less in runoff-water, but varies a lot from catchment to catchment. The concentration of SO_4 and SO_4* in runoff-water at Kaarvatn were the most discharge-sensitive, followed by Birkenes and Storgama, while the concentrations of SO_4 and SO_4* in runoff water at Langtjern were almost insensitive to variations in runoff (Figure 6.57). 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. This means that the residence time of water probably is much higher at this site compared with the other, and that the ability of a catchment to moderate hydrological and chemical extremes is far the best at Langtjern.

The concentrations of H^+ in runoff-water are increasing by increasing volume of discharge at all sites. Nevertheless, it is only in the runoff-water at Birkenes where a corresponding positive relationship exists concerning the concentration of SO_4 and SO_4*, while at the three other sites, the concentrations of SO_4 and SO_4* are decreasing by increasing volume of discharge. Except at Kaarvatn, the concentration of nitrate is increasing by increasing volume of discharge, while it is only at Birkenes and Kaarvatn where the concentration of total aluminium is increasing by increasing volume of discharge.

At all sites, there are a substantial decrease in the concentration of non-marine base cations (ΣCa*,Mg*) by increasing runoff, most significant at Birkenes and Kaarvatn. At all sites, the concentrations of ΣCa*,Mg* are much more dependent on variation in hydrology compared with the concentration of SO_4 and SO_4*. This should be expected, because non-marine base cations primarily derive from physico-chemical soil-water processes, while sulphate primarily enters the catchment as atmospheric dry- and wet-deposition compounds.

When the effect of hydrology is added to the regression equations made up from raw-data only, the concentration of most ions present in runoff water at Kaarvatn still exhibit very distinct seasonal patterns. Corresponding seasonal patterns are far more difficult to reveal at the three other sites.

At all four catchments, the highest concentration of ions in runoff-water normally occur within the period September to April. At Birkenes, the highest monthly weighted average concentrations of ions (≥ 600 µeq/L) do normally occur in September, October, December, January, February and March (Figure 6.61). There are, however, only minor variations in the monthly weighted concentrations of ions in runoff-water during a year at Birkenes, from an average of 612 µeq/L in September, to 490 µeq/L in May. In September, when the highest concentration of ions normally occurs, the highest monthly average concentrations of sulphate and total aluminium do also occur.

At Storgama, the highest monthly weighted average concentration of ions (≥ 300 µeq/L) is normally present in December, January and March (Figure 6.62). At Storgama, there are relatively large variations in the monthly weighted concentration of ions in runoff-water during a year, from an average of 335 µeq/L in December to about 170 µeq/L in May, June and July. In December, when the highest concentration of ions normally occurs, the highest monthly average concentrations of H^+, sulphate, total aluminium, sodium and chloride are also registrated.

At Langtjern, the highest monthly weighted average concentration of ions (≥ 250 µeq/L) is normally present from November to April, (Figure 6.63). As in the runoff water at Birkenes, there are only minor variations in the monthly weighted average concentrations of ions in runoff-water at Langtjern during a year, from an average of 282 µeq/L in December to about 200 µeq/L during May-August. In December, when the highest concentration of ions normally occurs, the highest monthly average concentrations are also recorded for H^+, sulphate, total aluminium, sodium and chloride.

At Kaarvatn, the highest monthly weighted average concentration of ions (≥ 250 µeq/L) does normally occur during January-April, (Figure 6.64). As in the runoff water at Storgama, there are relatively large variations in monthly weighted concentration averages of ions in runoff-water at Kaarvatn during a year, from an average of 346 µeq/L in April to about 120 µeq/L in June and July. In April, when the highest concentration of ions normally occurs, the highest monthly average concentrations are also recorded for sulphate, total aluminium, sodium, magnesium and chloride.

At the four catchments, the highest monthly weighted concentration averages of ions in runoff-water do occur at different time of the year, but normall within the period 1 September to 30 April. At all sites, the highest monthly weighted concentration averages of sulphate and total aluminium are normally recorded during the same month as when the total concentrations of ions are at the highest. While there are relatively small variation in the monthly average concentration of ions in runoff during a year at Birkenes and Langtjern, Storgama and Kaarvatn exhibit relatively large variations.

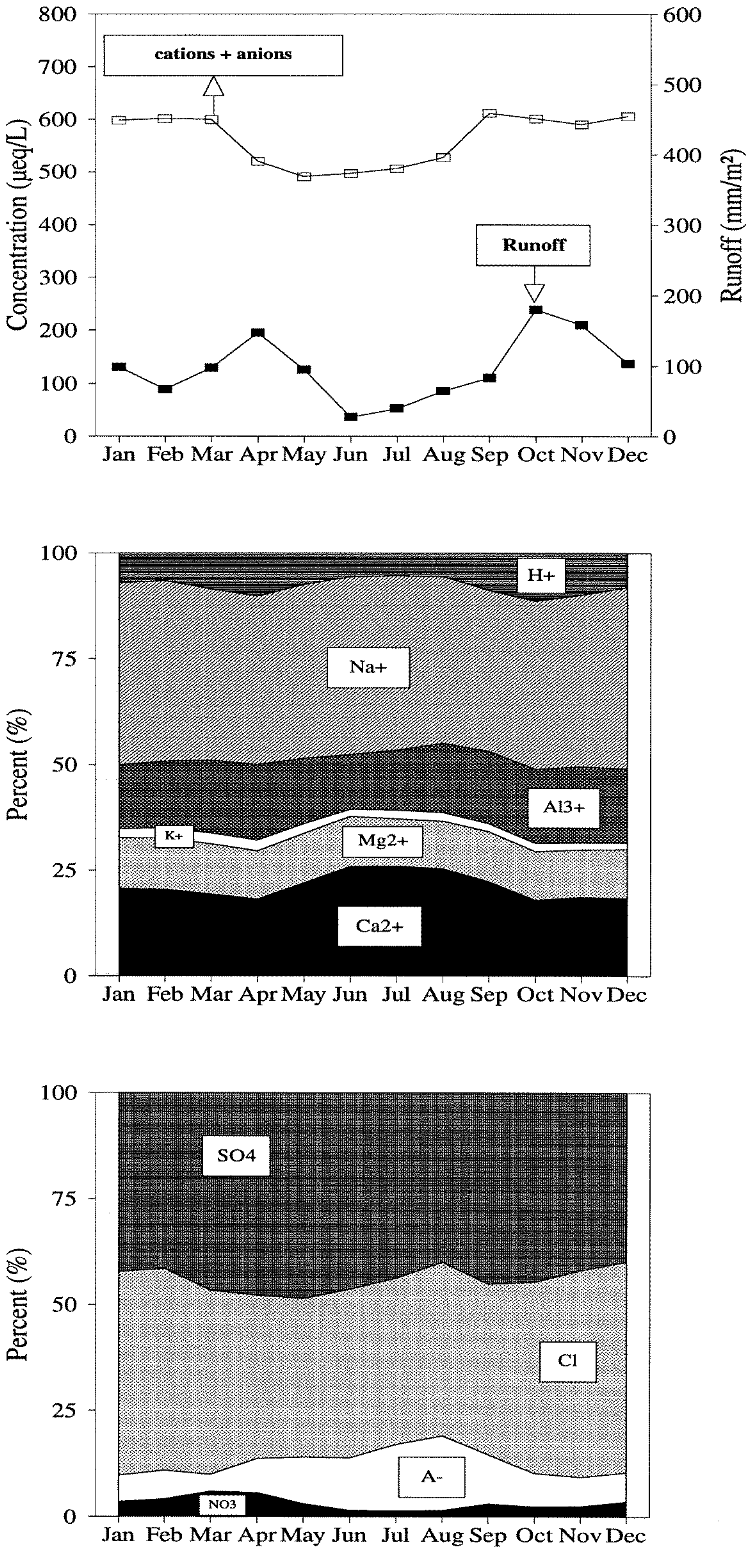


Figure 6.61 The monthly mean ionic concentration, amount of runoff, and the average percentage distribution of cations and anions in runoff during a year at Birkenes, based on monthly weighted averages from 1974-1992.

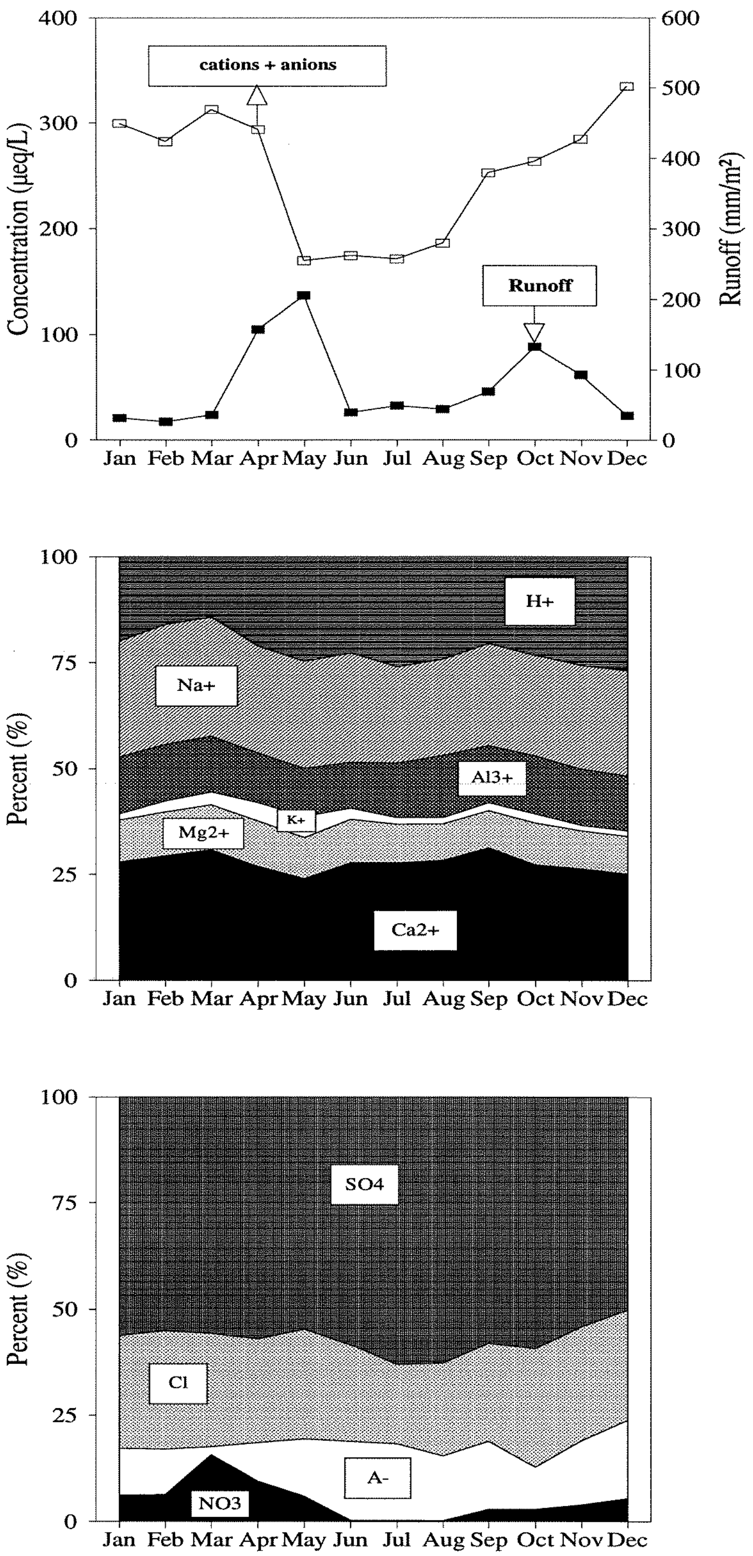


Figure 6.62 The monthly mean ionic concentration, amount of runoff, and the average percentage distribution of cations and anions in runoff during a year at Storgama, based on monthly weighted averages from 1974-1992.

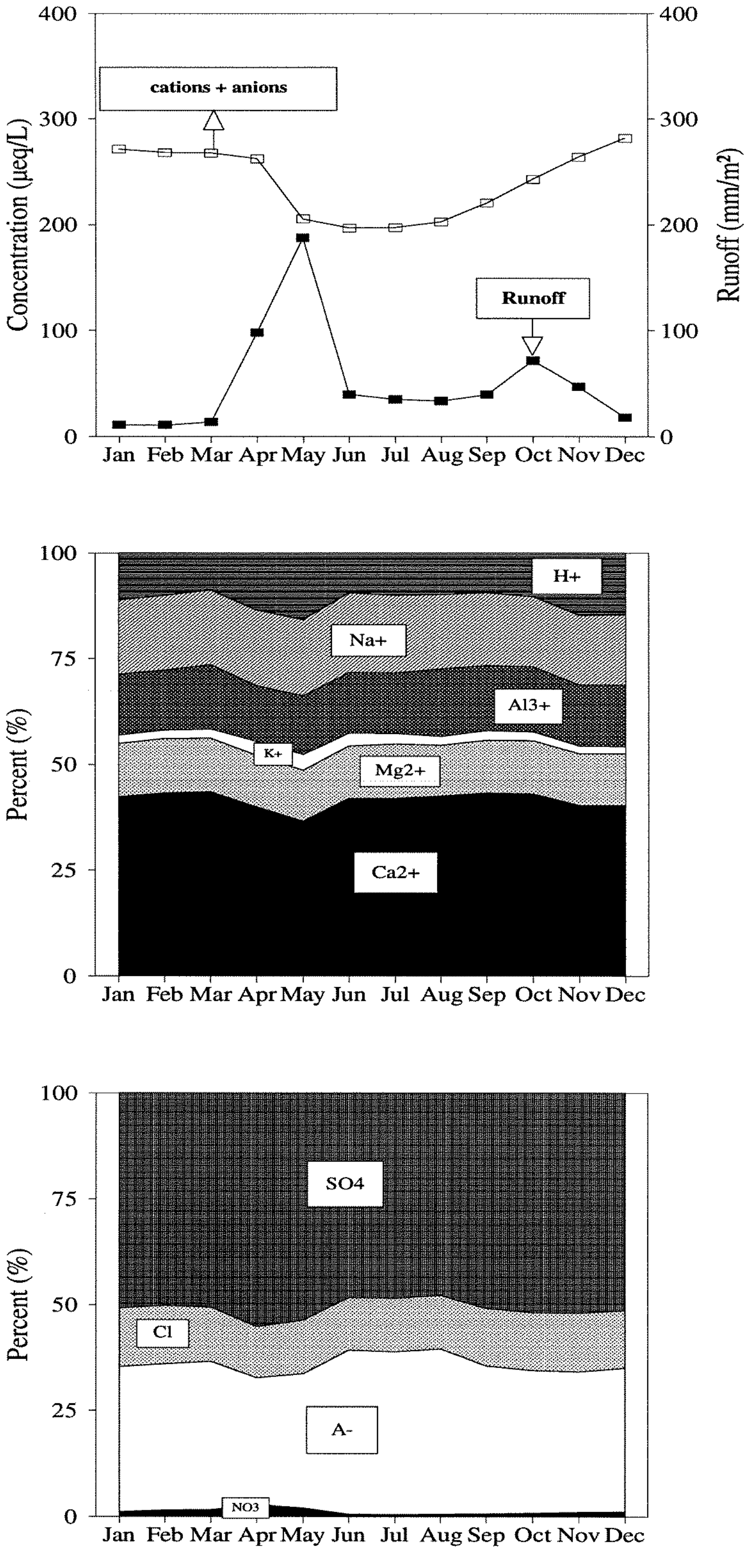


Figure 6.63 The monthly mean ionic concentration, amount of runoff, and the average percentage distribution of cations and anions in runoff during a year at Langtjern, based on monthly weighted averages from 1974-1992.

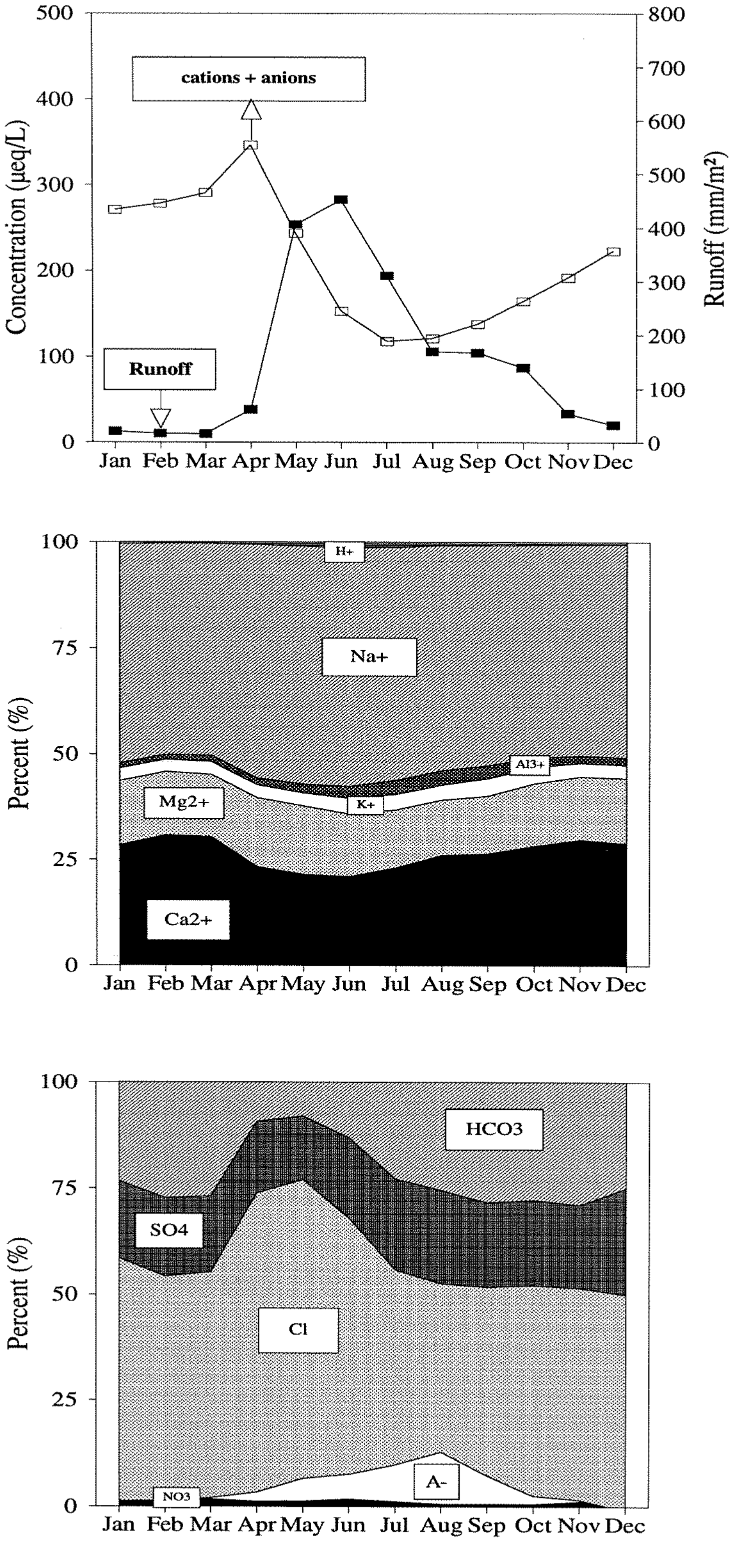


Figure 6.64 The monthly mean ionic concentration, amount of runoff, and the average percentage distribution of cations and anions in runoff during a year at Kaarvatn, based on monthly weighted averages from 1980-1992.

Time trends in fluxes of chemical compounds

The most significant time trends in output/efflux of chemical compounds at the three most acidified catchments, are the decrease in non-marine base cations (ΣCa*,Mg*) and non-marine sulphate (SO_4*). These time trends are, however, not very significant (Table 6.7 and 6.8). At Kaarvatn, the relatively large increase in annual input/output of water during the monitoring period, has more or less "compensated" for the decrease in the concentration of ΣCa*,Mg* and SO_4* (Table 6.6.), which means that no time-trends were revealed concerning the fluxes of these compounds (Table 6.8). The most significant changes in output of chemical compounds by time, are the increase in output of nitrate at Birkenes, and the decrease in potassium at Storgama from 1974/75 to 1991/92.

Based on the linear regressions made up from annual weighted raw-data fluxes (Table 6.7), the annual weighted output of sulphate at Birkenes for the water-year 1974/75 was 189 ± 44.7 meq S/m^2. In 1991/92, the annual weighted output was lowered by 33%, down to an average annual output of 127 ± 38.2 meq S/m^2. The annual weighted output of SO_4* for 1974/75 was 174 ± 41.0 meq S/m^2, while in 1991/92 the output was lowered by 37%, down to 109 ± 34.9 meq S/m^2. At Birkenes, the annual weighted output of ΣCa*,Mg* in 1974/75 was 87.9 ± 18.0 meq/m^2. In 1991/92, the output was 49.4 ± 15.3 meq/m^2, which is a decrease in the annual weighted output of ΣCa*,Mg* by 44% from 1974/75 to 1991/92. The most significant trend in the output of chemical compounds at Birkenes from 1974/75 to 1991/92 is the increase of nitrate, from an annual weighted average of 5.91 ± 3.55 meq N/m^2 in 1974/75 to 16.2 ± 3.06 meq N/m^2 in 1991/92.

Based on the linear regressions made up from annual weighted raw-data fluxes (Table 6.7), the annual weighted output of sulphate at Storgama for the water-year 1975/76 was 80.3 ± 21.8 meq S/m^2. In 1991/92, the output was lowered by 30%, down to an annual weighted output of 56.0 ± 19.6 meq S/m^2. The annual weighted output of SO_4* for 1975/76 was 77.8 ± 21.0 meq S/m^2, while in 1991/92 it was lowered by 33%, down to an annual average of 52.5 ± 18.7 meq S/m^2. At Storgama, the annual weighted output of ΣCa*,Mg* in 1975/76 was 48.2 ± 10.8 meq/m^2. In 1991/92, the annual average output was 25.1 ± 9.67 meq/m^2, which is a decrease in annual output of ΣCa*,Mg* by 48% from 1975/76 to 1991/92. The most significant trend in the output of chemical compounds at Storgama from 1975/76 to 1991/92 is the decrease of potassium by 89%, from an annual weighted average of 6.53 ± 2.13 meq/m^2 in 1975/76 to 0.75 ± 1.87 meq/m^2 in 1991/92.

Based on the linear regressions made up from annual weighted raw-data fluxes (Table 6.8), the annual weighted output of sulphate at Langtjern for the water-year 1974/75 was 50.5 ± 13.9 meq S/m^2. In 1991/92, it was lowered by 28%, down to an annual weighted average of 36.6 ± 11.5 meq S/m^2. The annual weighted output of SO_4* in 1974/75 was 49.3 ± 13.7 meq S/m^2, while in 1991/92 it was lowered by 28%, down to an annual weighted average of 35.6 ± 11.3 meq S/m^2. At Langtjern, the annual weighted output of ΣCa*,Mg* in 1974/75 was 45.0 ± 11.9 meq/m^2. In 1991/92, the annual weighted output was 36.0 ± 9.9 meq/m^2, which is a 20 % decrease from 1974/75 to 1991/92.

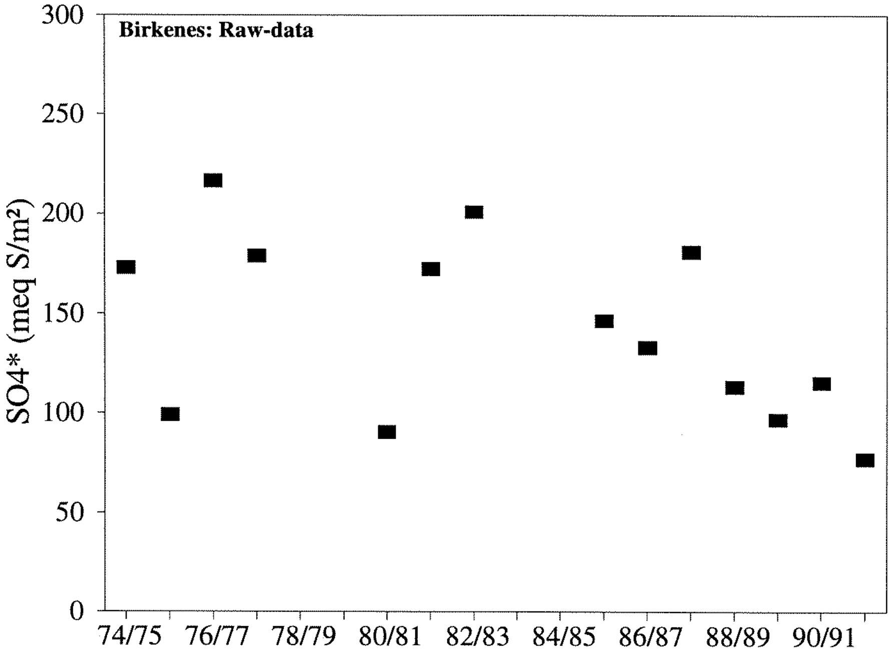
Based on the linear regressions made up from annual weighted raw-data fluxes (Table 6.8), the annual output of sulphate at Kaarvatn for the water-year 1980/81 was 30.3 ± 6.47 meq S/m^2. In 1991/92, the annual weighted output has increased by 9%, to an average annual output of 32.9 ± 6.60 meq S/m². The annual weighted output of SO_4* for 1980/81 was 20.4 ± 3.58 meq S/m², while in 1991/92 the output was lowered by 4%, down to 19.6 ± 3.60 meq S/m². At Kaarvatn, the annual weighted output of ΣCa*,Mg* in 1980/81 was 41.0 ± 6.74 meq/m². In 1991/92, the annual output was 42.6 ± 6.84 meq/m², which is a 4% increase in the annual output of ΣCa*,Mg* from 1980/81 to 1991/92. The time trends in output of chemical compounds at Kaarvatn, are highly influenced by the large increase in annual input/output of water which have occured at this site from 1980 to 1992.

Table 6.7 Time trends in annual fluxes of major chemical compounds (meq/m²yr) in runoff-water at Birkenes and Storgama, based on annual (water-year) weighted raw data fluxes [$y(t) = (\delta y_1/\delta t)t + b_1$] and time trends after the water dependent flux changes [$\delta y_1/\delta q$ in meq/mm] are accounted for, i.e. [$Y(t) = (\delta y_1/\delta t)t + (\delta y_1/\delta q)q + b_2$]. The constant b_2 is fitted so $b_2=b_1$. (: $p < 0.05$, **: $p < 0.01$).*

		Raw-data			**Water dependance**		**Corrected data**	
	Period	**$\delta y_1/\delta t$**	**b_1**	**r_1**	**$\delta y/\delta \log(q)$**	**r_q**	**$\delta y_2/\delta t$**	**r_2**
Birkenes								
Water(mm)	74/75-91/92	-2.93 ± 15.6	1221 ± 330	-0.05				
H^+	74/75-91/92	-0.30 ± 0.52	37.5 ± 11.0	-0.16	0.028 ± 0.01	0.84**	-0.38 ± 0.44	-0.24
Ca	74/75-91/92	-1.01 ± 0.77	73.6 ± 16.2	-0.36	0.048 ± 0.01	0.91**	-1.15 ± 0.75	-0.41
Mg	74/75-91/92	-0.74 ± 0.51	46.2 ± 10.8	-0.38	0.032 ± 0.005	0.89**	-0.83 ± 0.49	-0.44
ΣCa*,Mg*	74/75-91/92	-2.14 ± 0.85	87.9 ± 18.0	-0.59*	0.052 ± 0.01	0.77**	-2.29 ± 0.80	-0.63*
K	74/75-91/92	0.02 ± 0.20	7.12 ± 4.26	0.03	0.009 ± 0.003	0.73**	-0.01 ± 0.15	-0.02
Na	74/75-91/92	0.21 ± 1.84	140 ± 39.9	0.03	0.11 ± 0.01	0.91**	-0.10 ± 1.67	-0.02
Al_{tot} (Al^{3+})	75/76-91/92	-0.20 ± 1.00	64.1 ± 19.0	-0.06	0.054 ± 0.004	0.97**	-0.24 ± 0.97	-0.08
SO_4	74/75-91/92	-3.46 ± 2.12	189 ± 44.7	-0.43	0.131 ± 0.021	0.87**	-3.84 ± 2.04	-0.48
SO_4*	74/75-91/92	-3.63 ± 1.94	174 ± 41.0	-0.48	0.119 ± 0.022	0.84**	-3.98 ± 1.86	-0.53*
NO_3	74/75-91/92	0.57 ± 0.17	5.91 ± 3.55	0.70**	0.007 ± 0.004	0.44	0.55 ± 0.10	0.84**
Cl	74/75-91/92	1.67 ± 2.33	138 ± 49.3	0.20	0.12 ± 0.03	0.79**	1.32 ± 1.88	0.20
Storgama								
Water(mm)	75/76-91/92	-3.16 ± 16.4	953 ± 312	-0.05				
H^+	75/76-91/92	-0.20 ± 0.53	30.8 ± 10.1	-0.11	0.031 ± 0.003	0.96**	-0.30 ± 0.51	-0.16
Ca	75/76-91/92	-0.86 ± 0.47	39.0 ± 8.99	-0.45	0.028 ± 0.005	0.86**	-0.95 ± 0.45	-0.50
Mg	75/76-91/92	-0.36 ± 0.20	14.9 ± 3.82	-0.44	0.011 ± 0.002	0.82**	-0.39 ± 0.18	-0.51*
ΣCa*,Mg*	75/76-91/92	-1.36 ± 0.57	48.2 ± 10.8	-0.55*	0.032 ± 0.007	0.77**	-1.46 ± 0.53	-0.61*
K	75/76-91/92	-0.34 ± 0.11	6.53 ± 2.13	-0.64**	0.003 ± 0.002	0.35	-0.35 ± 0.05	-0.88**
Na	75/76-91/92	0.09 ± 0.50	28.4 ± 9.54	0.05	0.025 ± 0.005	0.82**	0.02 ± 0.41	0.01
Al_{tot} (Al^{3+})	75/76-91/92	0.10 ± 0.25	14.0 ± 4.70	0.12	0.014 ± 0.002	0.93**	0.06 ± 0.23	0.07
SO_4	75/76-91/92	-1.43 ± 1.15	80.3 ± 21.8	-0.33	0.066 ± 0.009	0.90**	-1.64 ± 1.09	-0.38
SO_4*	75/76-91/92	-1.49 ± 1.10	77.8 ± 21.0	-0.35	0.063 ± 0.009	0.89**	-1.69 ± 1.04	-0.41
NO_3	75/76-91/92	-0.35 ± 0.27	13.8 ± 5.16	-0.34	0.014 ± 0.003	0.79**	-0.39 ± 0.23	-0.43
Cl	75/76-91/92	0.62 ± 0.60	24.4 ± 11.4	0.28	0.029 ± 0.007	0.76**	0.53 ± 0.47	0.29

Table 6.8 Time trends in annual fluxes of major chemical compounds (meq/m^{2}yr) in runoff -water at Langtjern and Kaarvatn, based on annual (water-year) weighted raw data fluxes [$y(t) = (\delta y_1/\delta t)t + b_1$] and time trends after the water dependent flux changes [$\delta y_1/\delta q$ in meq/mm] are accounted for, i.e. [$Y(t) = (\delta y_1/\delta t)t + (\delta y_1/\delta q)q + b_2$]. The constant b_2 is fitted so $b_2=b_1$. (: $p < 0.05$, **: $p < 0.01$).*

		Raw-data			**Water dependance**		**Corrected data**	
	Period	**$\delta y_1/\delta t$**	**b_1**	**r_1**	**$\delta y/\delta \log(q)$**	**r_q**	**$\delta y_2/\delta t$**	**r_2**
Langtjern								
Water(mm)	74/75-91/92	3.93 ± 9.65	584 ± 210	0.11				
H^+	74/75-91/92	0.04 ± 0.21	11.8 ± 4.63	0.05	0.021 ± 0.001	0.98**	0.12 ± 0.21	0.16
Ca	74/75-91/92	-0.39 ± 0.44	36.3 ± 9.48	-0.24	0.041 ± 0.006	0.89**	-0.23 ± 0.40	-0.16
Mg	74/75-91/92	-0.14 ± 0.14	11.4 ± 2.99	-0.26	0.013 ± 0.002	0.87**	-0.09 ± 0.12	-0.19
ΣCa*,Mg*	74/75-91/92	-0.50 ± 0.55	45.0 ± 11.9	-0.25	0.052 ± 0.007	0.89**	-0.30 ± 0.50	-0.16
K	74/75-91/92	-0.04 ± 0.05	2.78 ± 1.01	-0.24	0.002 ± 0.001	0.46	-0.03 ± 0.02	-0.38
Na	74/75-91/92	-0.03 ± 0.20	15.1 ± 4.40	-0.04	0.018 ± 0.003	0.87**	0.04 ± 0.18	0.06
Al_{tot} (Al^{3+})	75/76-91/92	0.01 ± 0.21	11.8 ± 4.27	0.01	0.017 ± 0.003	0.88**	0.14 ± 0.18	0.21
SO_4	74/75-91/92	-0.77 ± 0.64	50.5 ± 13.9	-0.32	0.057 ± 0.011	0.82**	-0.54 ± 0.55	-0.26
SO_4*	74/75-91/92	-0.76 ± 0.63	49.3 ± 13.7	-0.32	0.056 ± 0.011	0.82**	-0.54 ± 0.54	-0.27
NO3	74/75-91/92	-0.02 ± 0.03	1.70 ± 0.64	-0.21	0.002 ± 0.001	0.67**	-0.01 ± 0.02	-0.19
Cl	74/75-91/92	-0.09 ± 0.11	11.2 ± 2.37	-0.21	0.009 ± 0.002	0.78**	-0.05 ± 0.09	-0.16
Kaarvatn								
Water(mm)	80/81-91/92	42.4 ± 24.5	1724 ± 290	0.52				
H^+	80/81-91/92	0.02 ± 0.04	1.68 ± 0.42	0.21	0.001 ± 0.000	0.86**	0.07 ± 0.03	0.67*
Ca	80/81-91/92	0.26 ± 0.58	38.7 ± 6.83	0.15	0.016 ± 0.005	0.78**	0.92 ± 0.39	0.64*
Mg	80/81-91/92	0.54 ± 0.51	24.7 ± 6.08	0.35	0.018 ± 0.003	0.92**	1.29 ± 0.43	0.73*
ΣCa*,Mg*	80/81-91/92	0.13 ± 0.57	41.0 ± 6.74	0.08	0.011 ± 0.006	0.57	0.61 ± 0.28	0.61
K	80/81-91/92	0.10 ± 0.09	5.38 ± 1.04	0.36	0.003 ± 0.001	0.88**	0.22 ± 0.07	0.74*
Na	80/81-91/92	1.79 ± 2.16	91.1 ± 25.6	0.28	0.067 ± 0.014	0.86**	4.66 ± 1.66	0.70*
Al_{tot} (Al^{3+})	80/81-91/92	-0.04 ± 0.06	4.64 ± 0.67	-0.24	0.001 ± 0.001	0.48	0.00 ± 0.02	0.03
SO_4	80/81-91/92	0.22 ± 0.55	30.3 ± 6.47	0.14	0.016 ± 0.004	0.81**	0.89 ± 0.38	0.63*
SO_4*	80/81-91/92	-0.07 ± 0.30	20.4 ± 3.58	-0.09	0.006 ± 0.003	0.55	0.17 ± 0.14	0.40
NO3	80/81-91/92	0.04 ± 0.04	1.78 ± 0.44	0.36	0.001 ± 0.000	0.58	0.07 ± 0.02	0.81**
Cl	80/81-91/92	2.87 ± 3.06	96.5 ± 36.2	0.31	0.095 ± 0.021	0.85**	6.91 ± 2.33	0.72*
HCO3	80/81-91/92	0.07 ± 0.47	26.9 ± 5.60	0.05	0.005 ± 0.006	0.28	0.26 ± 0.11	0.63*



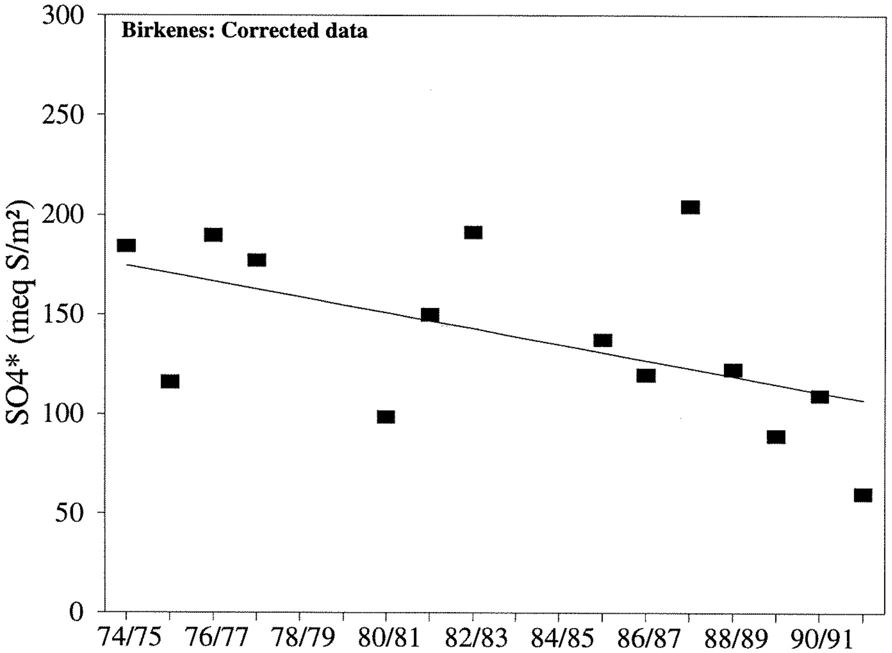
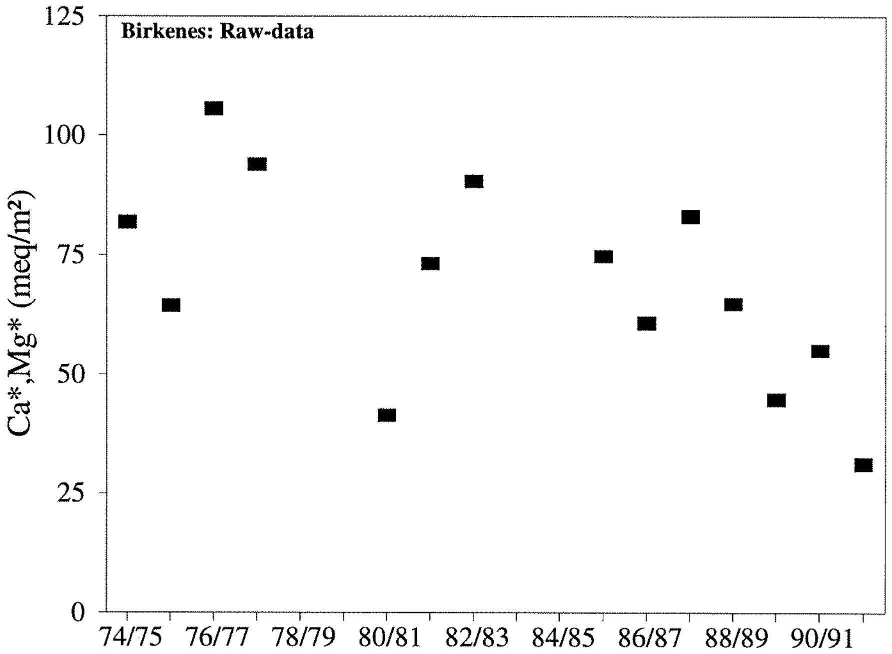


Figure 6.65 Annual weighted output of SO_4* in runoff (meq S/m^2yr) at Birkenes from 1974/75-1991/92, present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualizes the influence of water on the concentration/flux of each chemical compounds, i.e. large scattering means high water dependence and vise versa. The linear regression equations are present in Table 6.7 Continuous line means that the linear regression is significant, i.e. $p < 0.05$, while a dottet line means no significance, $p > 0.05$.



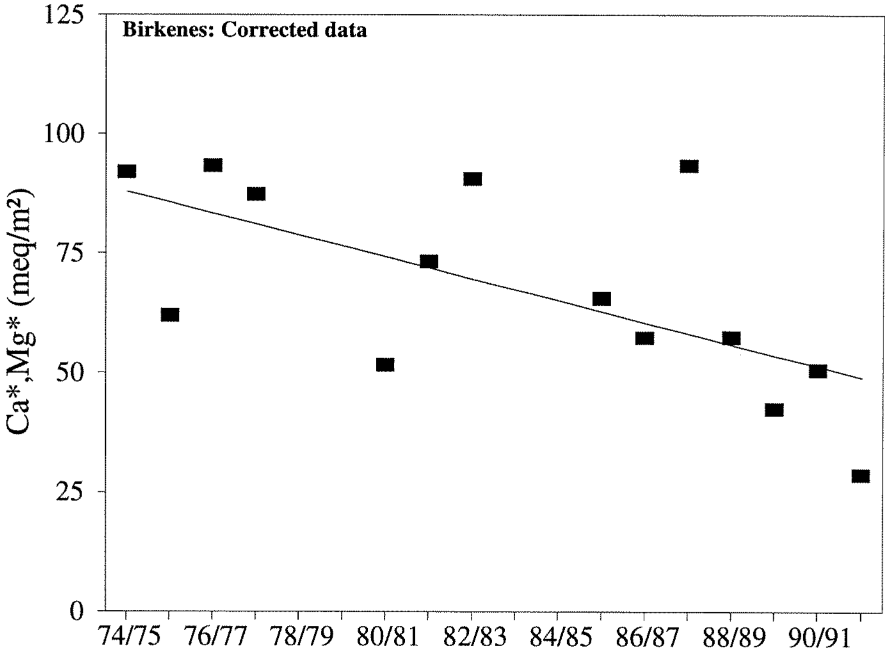
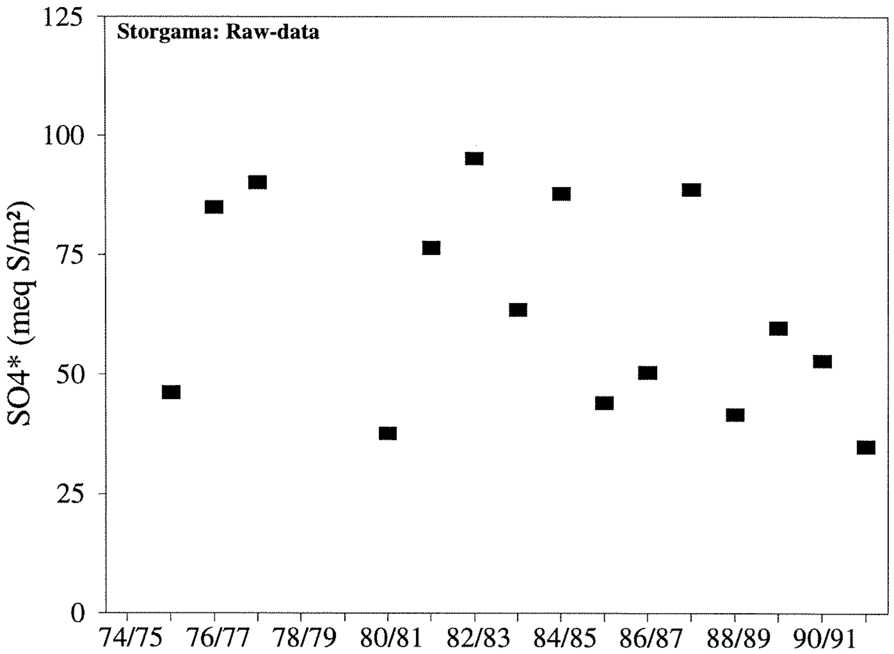


Figure 6.66 Annual weighted output of $\Sigma Ca^*, Mg^*$ *in runoff (meq/m²yr) at Birkenes from 1974/75-1991/92, present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualizes the influence of water on the concentration/flux of each chemical compounds, i.e. large scattering means high water dependence and vise versa. The linear regression equations are present in Table 6.7 Continuous line means that the linear regression is significant, i.e.* $p < 0.05$*, while a dottet line means no significance,* $p > 0.05$.



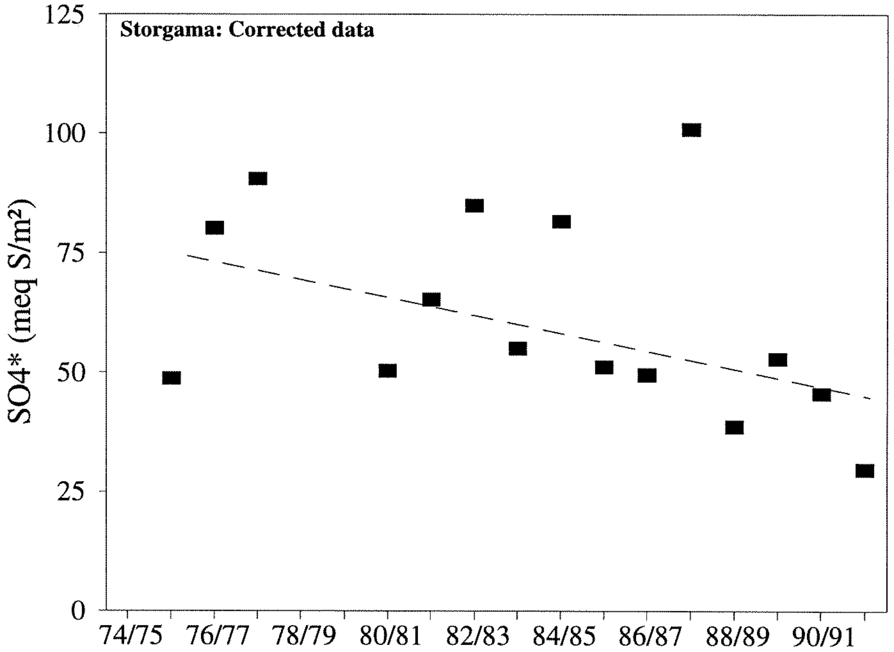
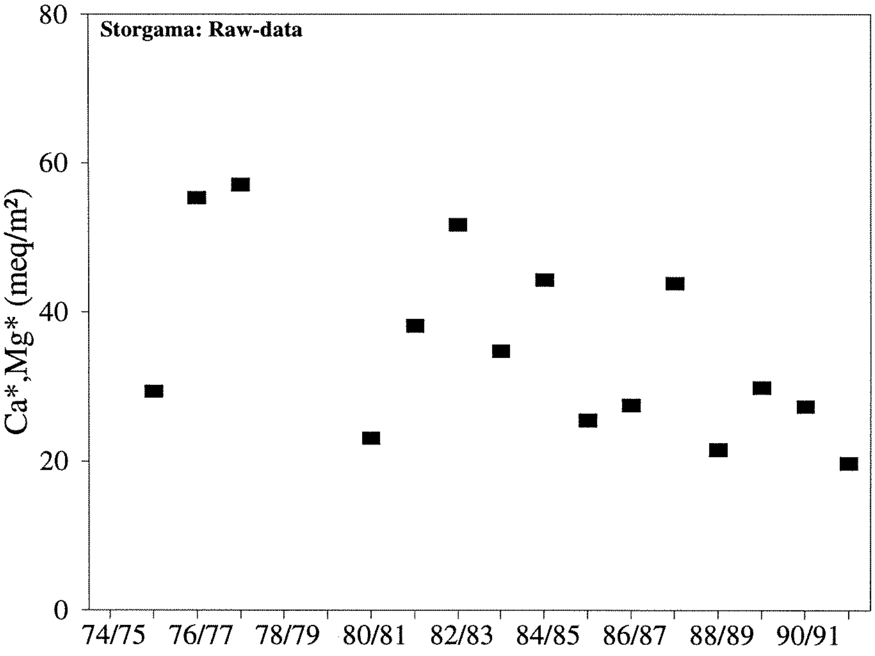


Figure 6.67 Annual weighted output of SO_4* *in runoff (meq* S/m^2yr*) at Storgama from 1974/75-1991/92, present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualizes the influence of water on the concentration/flux of each chemical compounds, i.e. large scattering means high water dependence and vise versa. The linear regression equations are present in Table 6.7 Continuous line means that the linear regression is significant, i.e.* $p < 0.05$*, while a dottet line means no significance,* $p > 0.05$*.*



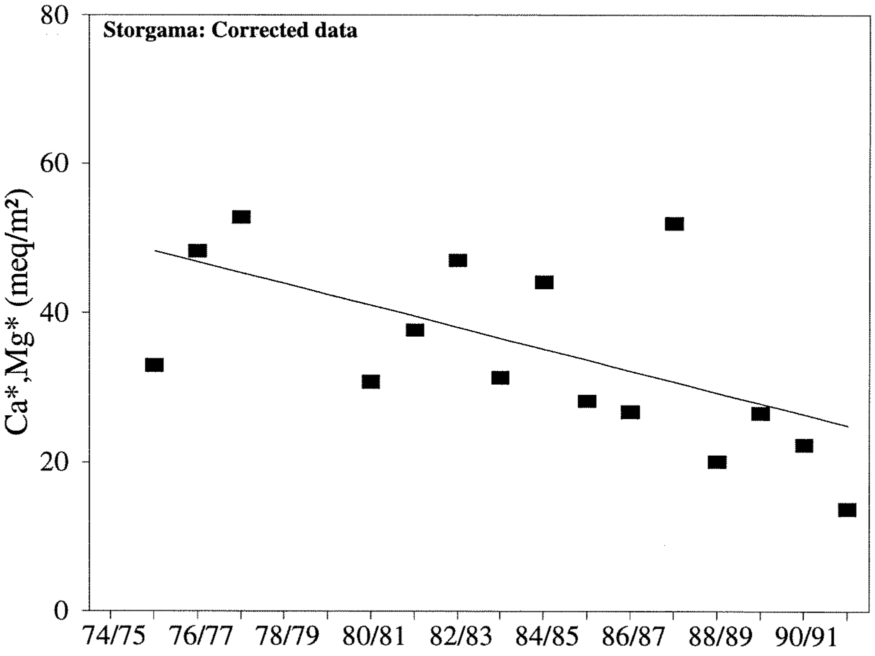


Figure 6.68 Annual weighted output of $\Sigma Ca^*, Mg^*$ *in runoff (meq/m²yr) at Storgama from 1974/75-1991/92, present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualizes the influence of water on the concentration/flux of each chemical compounds, i.e. large scattering means high water dependence and vise versa. The linear regression equations are present in Table 6.5. Continuous line means that the linear regression is significant, i.e.* $p < 0.05$*, while a dottet line means no significance,* $p > 0.05$.

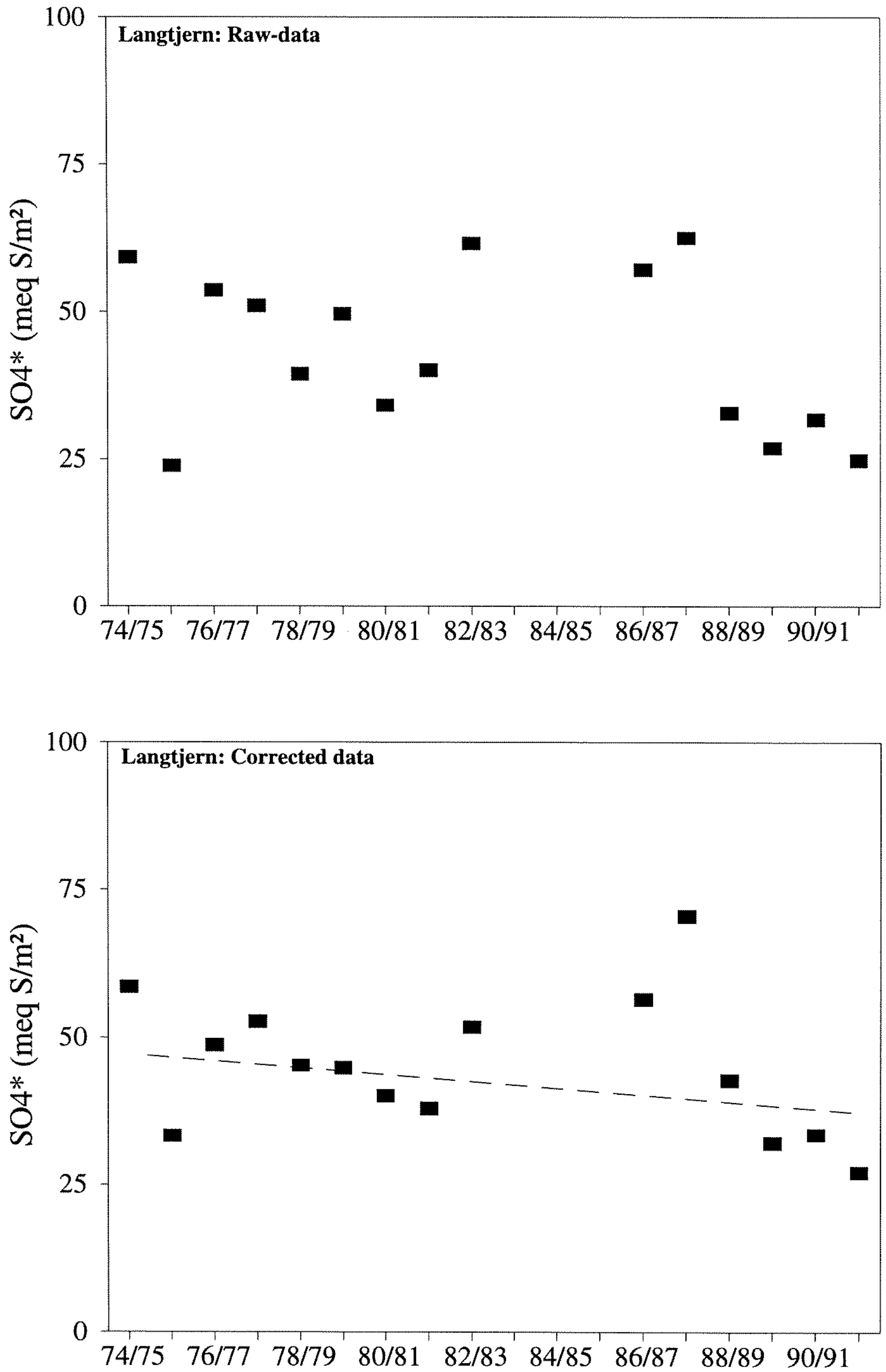


Figure 6.69 Annual weighted output of SO_4 in runoff (meq S/m^2yr) at Langtjern from 1974/75-1991/92, present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualizes the influence of water on the concentration/flux of each chemical compounds, i.e. large scattering means high water dependence and vise versa. The linear regression equations are present in Table 6.8 Continuous line means that the linear regression is significant, i.e. $p < 0.05$, while a dottet line means no significance, $p > 0.05$.*

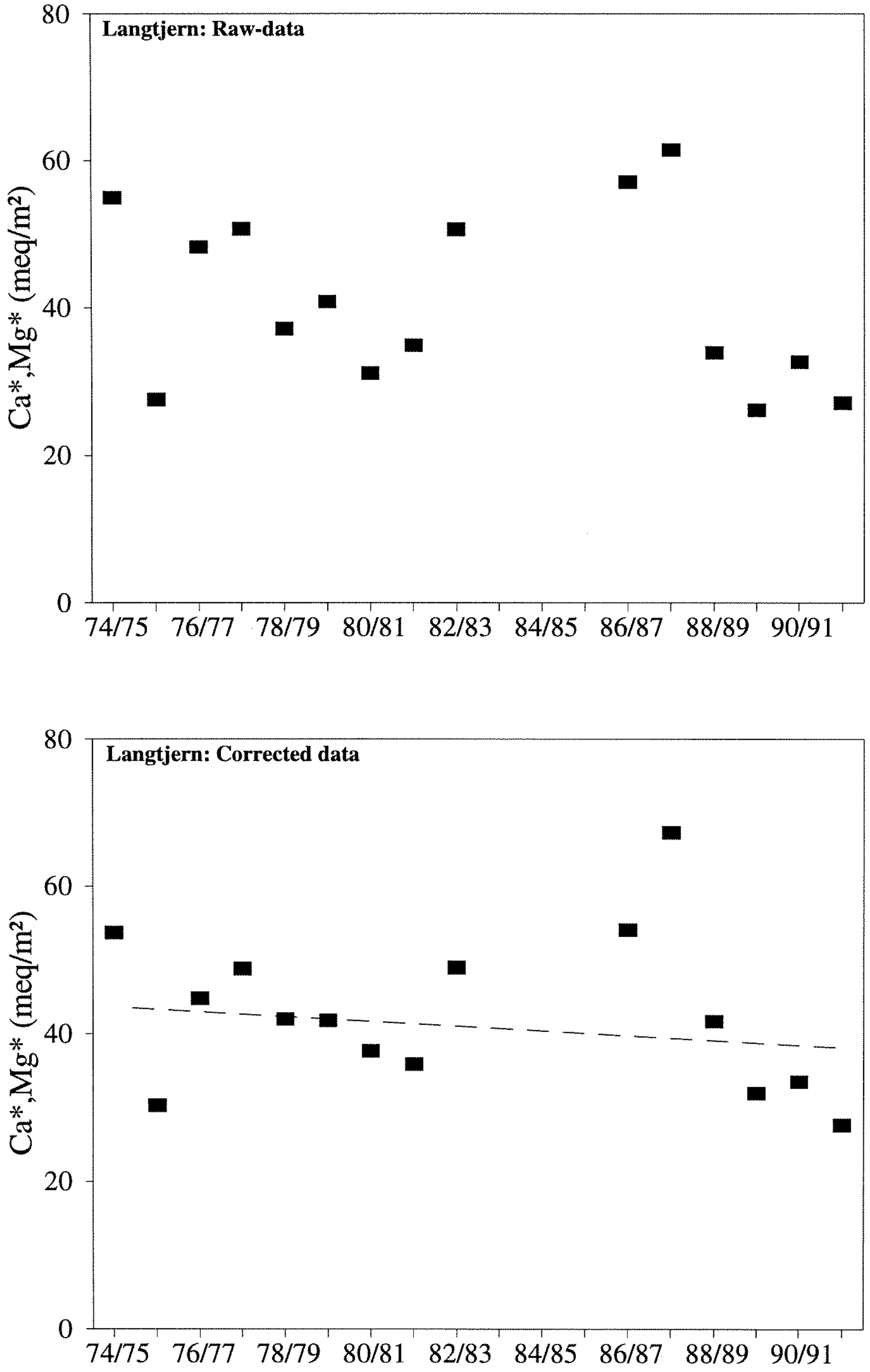


Figure 6.70 Annual weighted output of $\Sigma Ca^*, Mg^*$ in runoff (meq/m^{2}yr) at Langtjern from 1974/75-1991/92, present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualizes the influence of water on the concentration/flux of each chemical compounds, i.e. large scattering means high water dependence and vise versa. The linear regression equations are present in Table 6.8. Continuous line means that the linear regression is significant, i.e. $p < 0.05$, while a dottet line means no significance, $p > 0.05$.

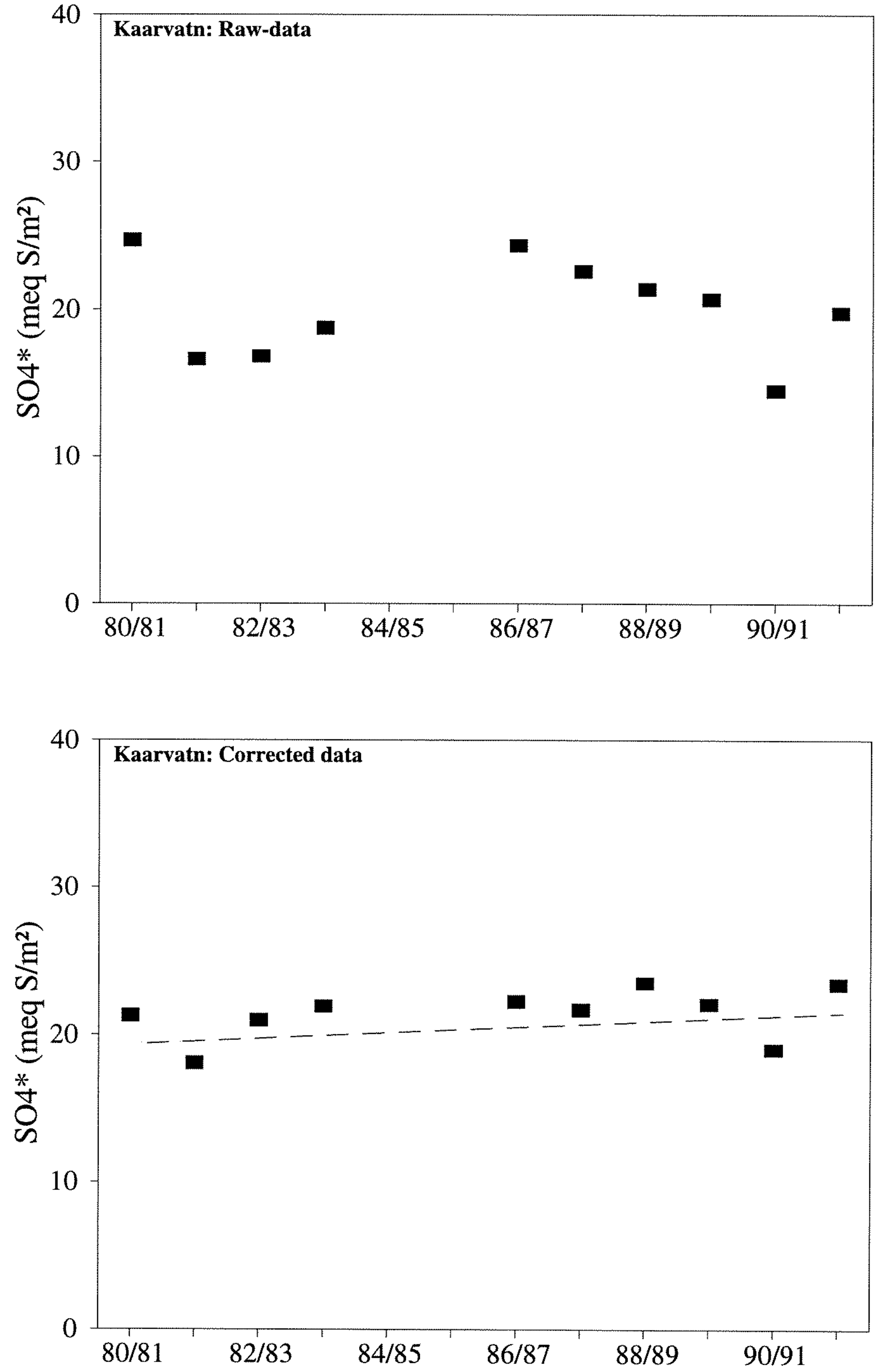
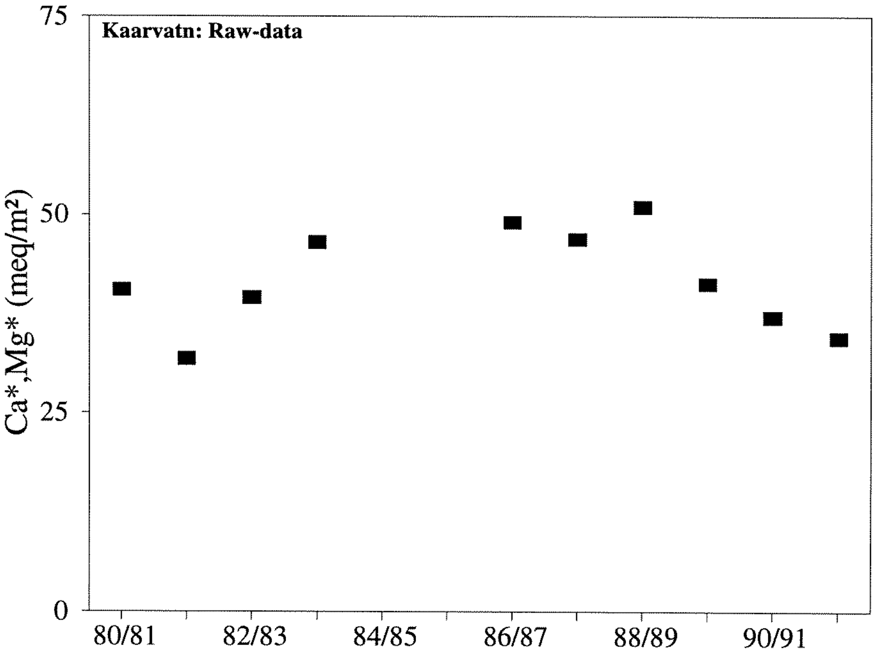


Figure 6.71 Annual weighted output of SO_4 in runoff (meq S/m^{2}yr) at Kaarvatn from 1980/81-1991/92, present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualizes the influence of water on the concentration/flux of each chemical compounds, i.e. large scattering means high water dependence and vise versa. The linear regression equations are present in Table 6.8. Continuous line means that the linear regression is significant, i.e. $p < 0.05$, while a dottet line means no significance, $p > 0.05$.*



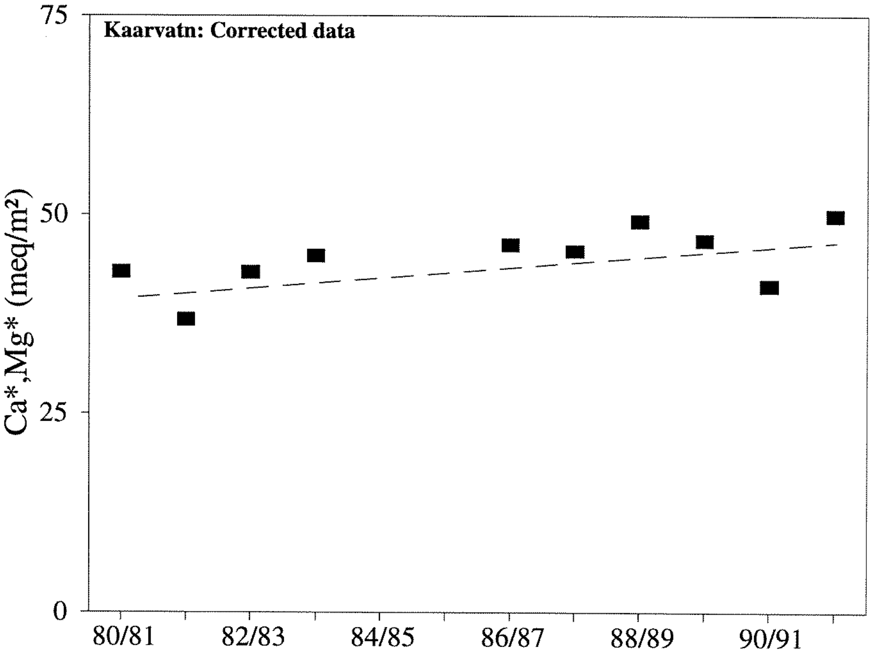


Figure 6.72 Annual weighted output of ΣCa,Mg* in runoff (meq/m²) at Kaarvatn from 1980/81-1991/92, present as raw-data and corrected data. The time trend line in the figure of corrected data, is the linear regression equation obtained from raw data only, while the scattering of data in this figure only visualizes the influence of water on the concentration/flux of each chemical compounds, i.e. large scattering means high water dependence and vise versa. The linear regression equations are present in Table 6.8. Continuous line means that the linear regression is significant, i.e. $p < 0.05$, while a dottet line means no significance, $p > 0.05$.*

By comparing time-trends made up from raw-data only, with time trends obtained by adding the effect of runoff to the linear regression obtained from raw-data, the annual outputs are very similar. Thus, by large, it means that the main cause of variation in fluxes of chemical compounds is the variation in fluxes of water. This is well illustrated in the Figures 6.65 to 6.72.

The relationships between the output of ΣCa*,Mg* and SO_4*, may relatively well discribe the acidification status of the four catchment. At Birkenes, the monthly average output of ΣCa*,Mg* is about half the monthly average of SO_4* (50 ± 5%). During June and July (Figure 6.73), the monthly output of ΣCa*,Mg* is normally about 60% compared with that of SO_4*, while during April and May, the monthly output of ΣCa*,Mg* is only 40-45% compared with the monthly output of SO_4*.

At Storgama, as at Birkenes, the monthly average output of ΣCa*,Mg* is about half the monhtly average of SO_4* (56 ± 2%). During February and March (Figure 6.74), the monthly output of ΣCa*,Mg* is about 60% compared with that of SO_4*, while during May and July, the monthly output of ΣCa*,Mg* is 50-55% compared with the monthly output of SO_4*.

At Langtjern, the monthly average output of ΣCa*,Mg* is about equal to the monthly average output of SO_4* (101 ± 7%). During June (Figure 6.75), the monthly output of ΣCa*,Mg* is normally 10-15% higher compared with the monthly output SO_4*, while during April and May, the monthly output of ΣCa*,Mg* is about 85-90% compared with the monthly output of SO_4*.

At Kaarvatn, the monthly averge output of ΣCa*,Mg* is more than twice the monthly average output of SO_4* (232 ± 54%). During January and February (Figure 6.76), the monthly output of ΣCa*,Mg* is normally more than 3 times higher compared with the monthly output SO_4*, while during July and August, the monthly output of ΣCa*,Mg* is 1.5 times higher compared with the monthly output of SO_4*.

At all catchment the relationship between is ΣCa*,Mg* and SO_4* is at the highest during low-flow periods, either during the winter or summer. This should be expected, because during low-flow periods, the residence time of water is at the highest. Thus, the interaction-time between water and soil is long, and more soil derived compounds (ΣCa*,Mg*) are therefore able to dissolve.

The relationship between ΣCa*,Mg* and SO_4* gives a relative nice acidification status of the four catchments. Most severe acidification is present at Birkenes, followed by Storgama, Langtjern and Kaarvatn. By this simple acidification index, the status at Langtjern is better than expected from pH of runoff-water, but the relatively high concentration of ΣCa*,Mg* at this site is to a certain extend a consequence of the high concentration of dissolved organic carbon, which is an important factor in weathering reactions.

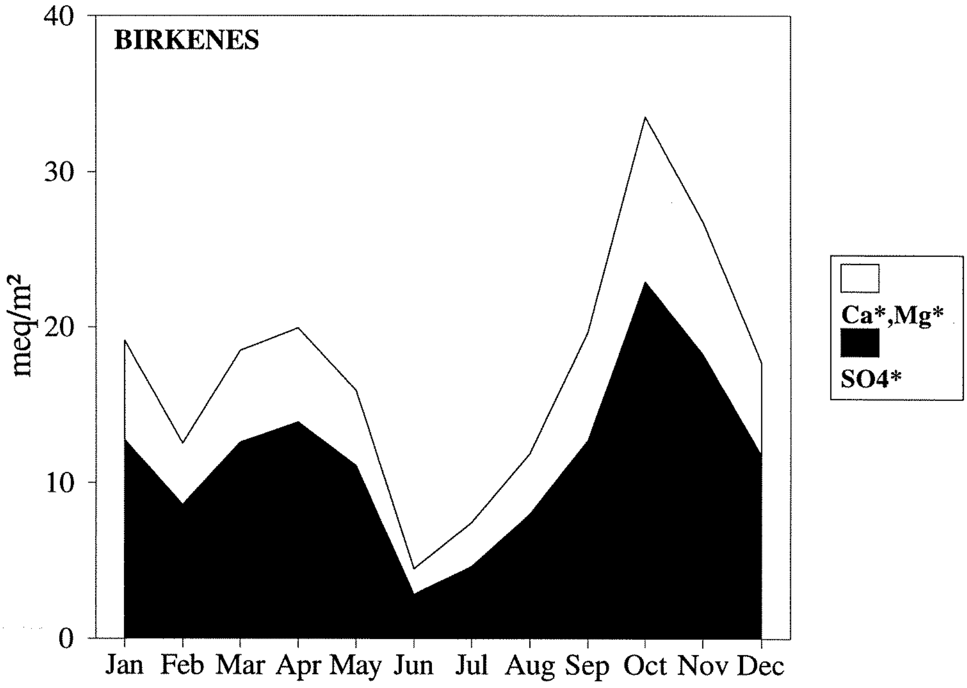


Figure 6.73 Monthly mean output of SO_4 and ΣCa*,Mg* in runoff at Birkenes, obtained from monthly weighted averages from 1974-1992.*

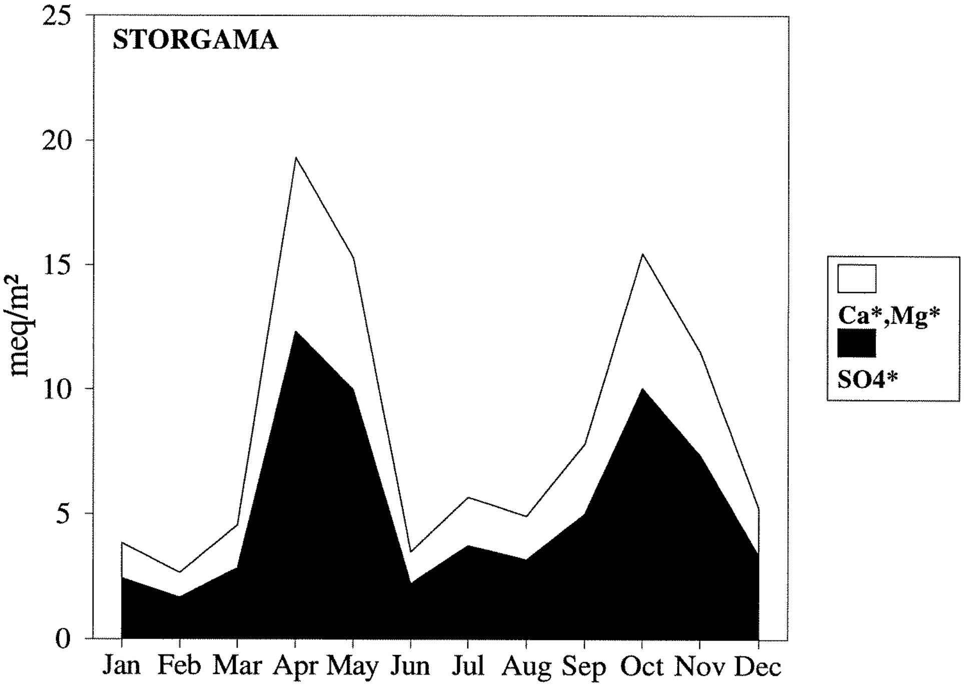


Figure 6.74 Monthly mean output of SO_4 and ΣCa*,Mg* in runoff at Storgama, obtained from monthly weighted averages from 1974-1992.*

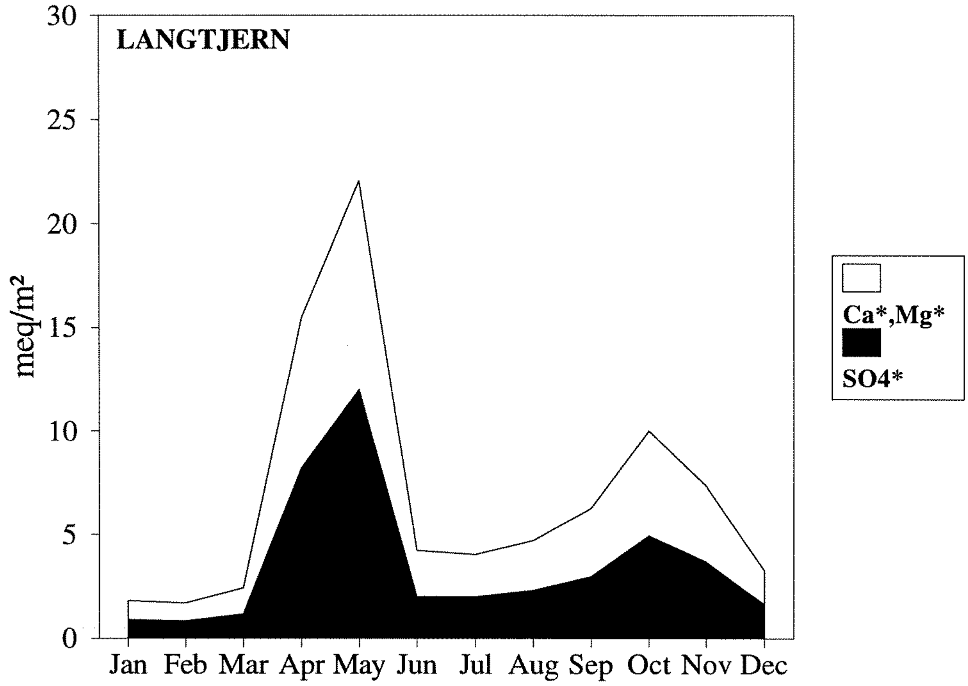


Figure 6.75 Monthly mean output of SO₄ and ΣCa*,Mg* in runoff at Langtjern, obtained from monthly weighted averages from 1974-1992.*

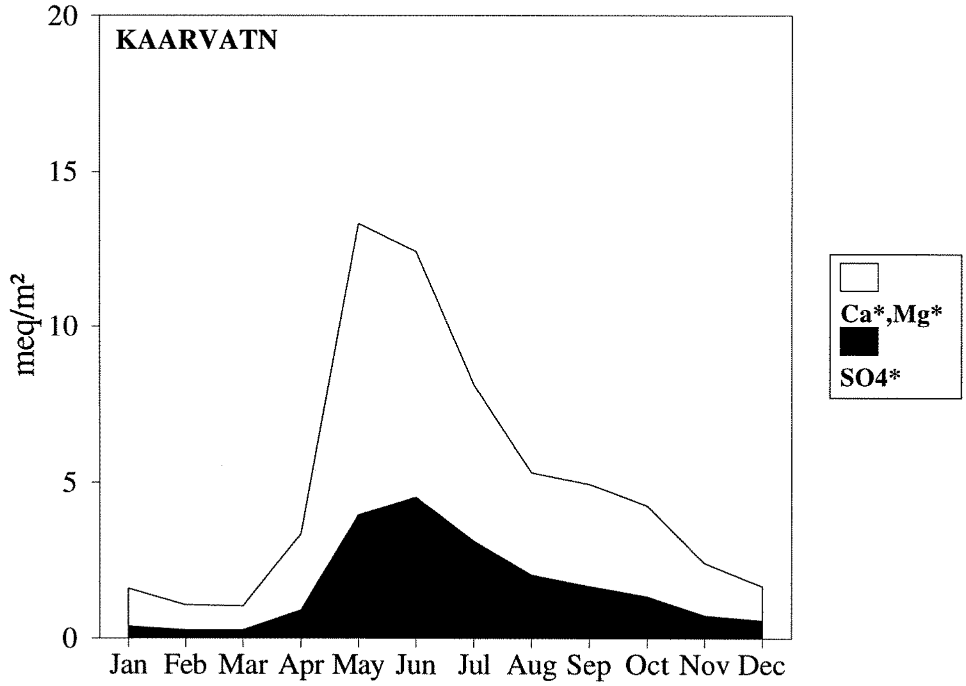


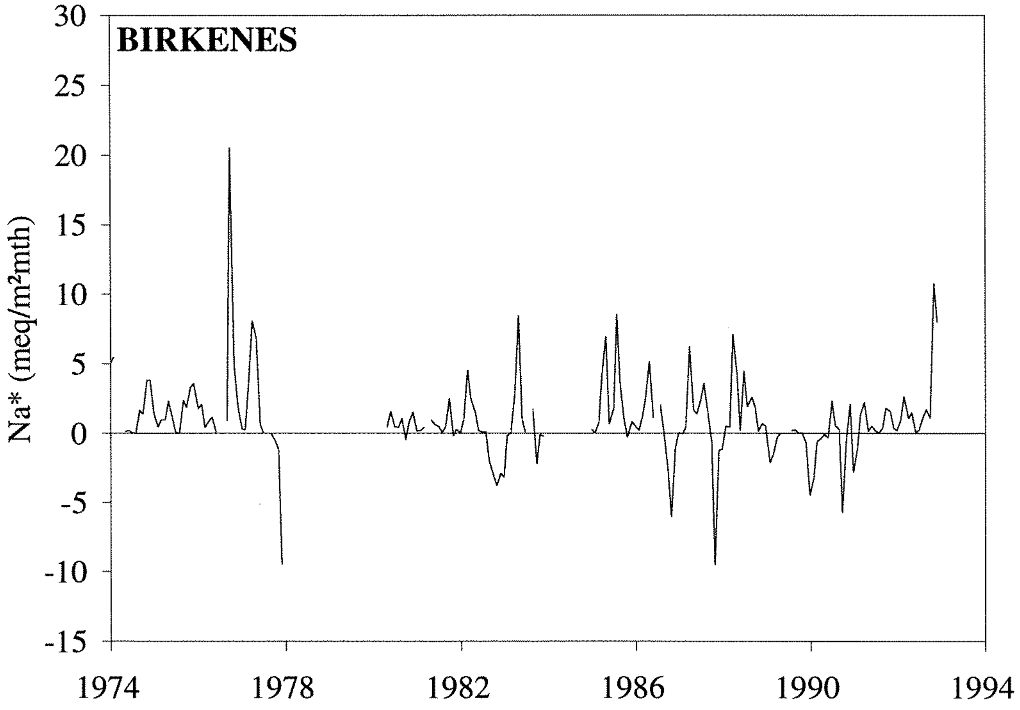
Figure 6.76 Monthly mean output of SO₄ and ΣCa*,Mg* in runoff at Kaarvatn, obtained from monthly weighted averages from 1980-1992.*

Time trends in ANC

The definition of the acid neutralizing capacity (ANC) is presented in Chapter 5. ANC of runoff-water is the difference between base cations (ΣCa,Mg,Na,K) and strong acid anions ($\Sigma SO_4, NO_3, Cl$). Because Na and Cl primarily originates from marine sources, and enters the catchment as wet- or dry-deposition, we prefer to leace out these elements from the ANC-value, and interpret the difference between Na and Cl separately. Because sodium enters the catchment as a neutral salt with chloride as the predominant anion, from the starting point, NaCl, per se, will not cause any significant changes in the acidfication status of a catchment. However, the mobility of the two ions through a catchment differ to some extent. While sodium often is temporarily retained in the catchment, chloride leaves the catchment much faster. Because sodium primarily is retained in the catchment due to cationexhange processes, where sodium often substitutes for H^+ and Al-ions, seasalt-episodes may cause water-acidification. The remaining part of the ANC-value (ANC') is the difference between ΣCa,Mg,K and $\Sigma SO_4, NO_3$. The base cations predominantly derive from soil and other terrestrial sources, while SO_4 and NO_3 primarily originate from industrial and agricultural activities. As SO_4 and to a certain degree NO_3 to a large extent express the acidification stress in a catchment, the concentrations of these ions in soil water are highly important for the amount of base cations which are able to dissolve from physico-chemical soil processes.

During the period 1974-1992, yearly an average of 134 meq/m² of sodium has left the catchment by runoff at Birkenes. By assuming no storage of chloride within the catchment during the period, and that all chloride which enters the catchment derives totally from marine sources and with the same Na/Cl-ratio as in seawater, about 92% of the sodium in runoff-water at Birkenes originates from seasalts. The remaining 8% of sodium may therefore originates from weathering processes in the soil and to some extent from terrestrial derived dust. During the period 1985-1992, averagely 141 meq/m² of sodium has left the Birkenes catchment by runoff-water every year, and 93% of the sodium originated from seasalts. At Storgama, an average of 28.5 meq/m² of sodium has left the catchment yearly by runoff during the period 1975-1992, and 88% of the sodium originated from seasalts. During the period 1985-1992, averagely 30.0 meq/m² of sodium left the catchment yearly by runoff-water, and 92% of the sodium originated from seasalts. At Langtjern, averagely 14.5 meq/m² of sodium left the catchment by runoff every year during the period 1974-1992, and 62% of the sodium originated from seasalts. During the period 1985-1992, averagely 15.1 meq/m² of sodium left the catchment yearly by runoff-water, and 60% of the sodium originated from seasalts. At Kaarvatn, averagely 94.3 meq/m² of sodium left the catchment by runoff-water every year during the period 1980-1992, and 94% of the sodium originated from seasalts. During the period 1985-1992, averagely 98.6 meq/m² of sodium left the catchment yearly by runoff-water, and 96% of the sodium originated from seasalts.

At all sites, an increased output of sodium has been recorded during the last years. At the three most coastnear sites, the increase in sodium output was primarily a result of increased inputs of seasalts as wet- and dry-deposition. At Langtjern, a significant amount of sodium undoubtedly derives from soil, but for practical reasons the ANC-values are split in two, ANC' and Na-Cl, also at this site. At all sites more sodium leaves the catchments by runoff compared with what enters the catchment by wet- and dry-deposition (Figure 6.77 and Figure 6.78).



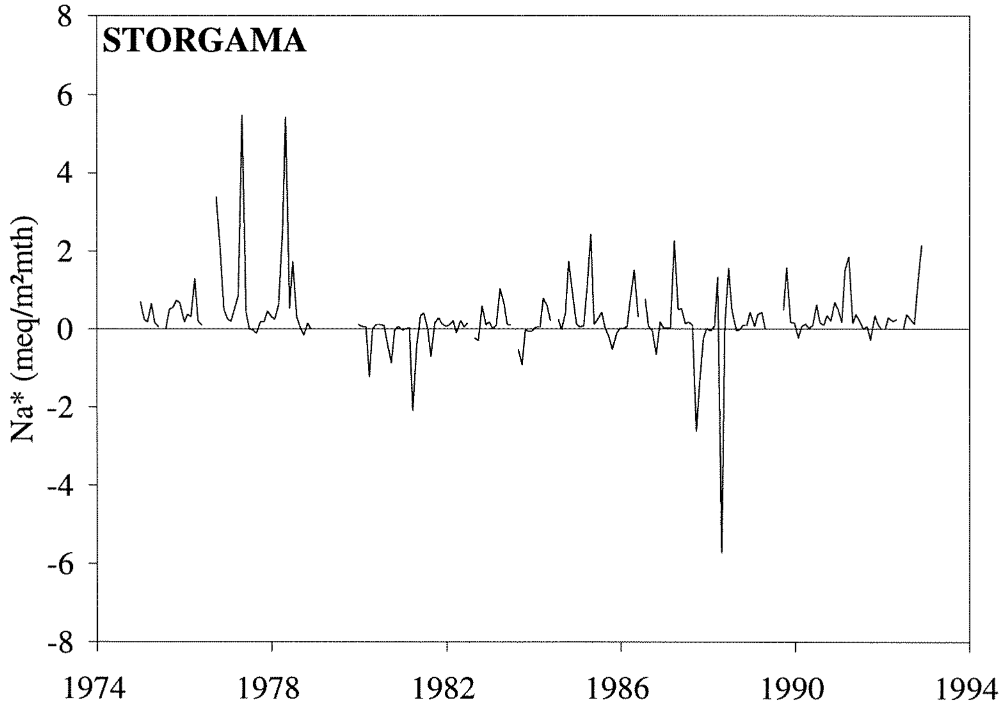
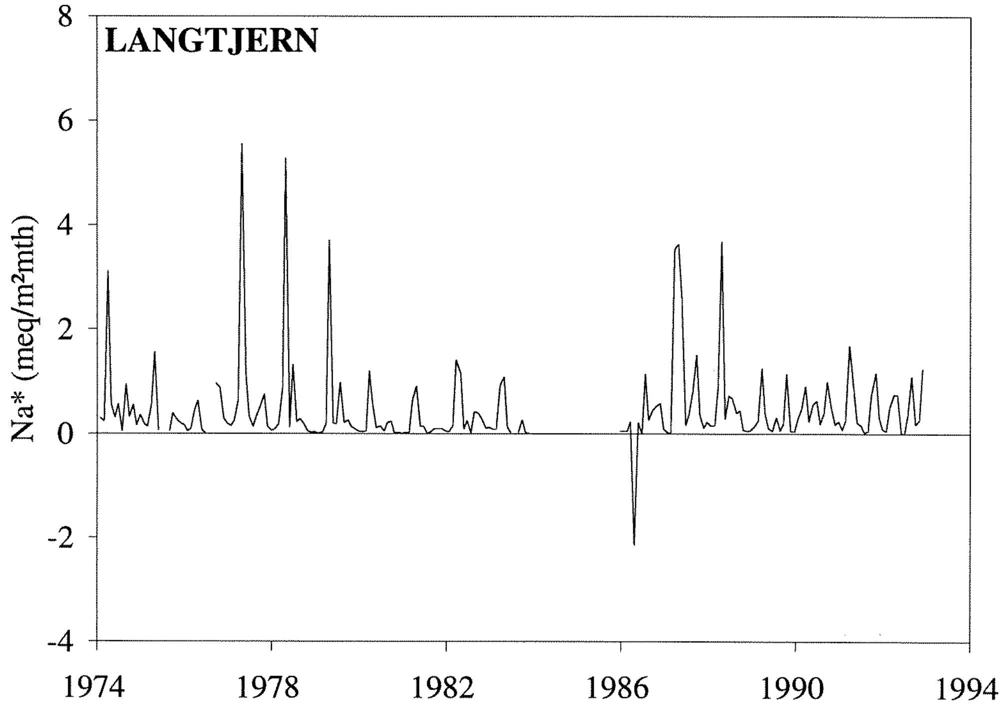


Figure 6.77 Monthly fluxes of non-marine sodium in runoff-water at Birkenes and Storgama from 1974 to 1992. By adding up the monthly fluxes for the total monitoring periods, an average of 11.3 meq/m² and 3.3 meq/m² of sodium in runoff yearly derives from non-marine sources at Birkenes and Storgama, respectively.



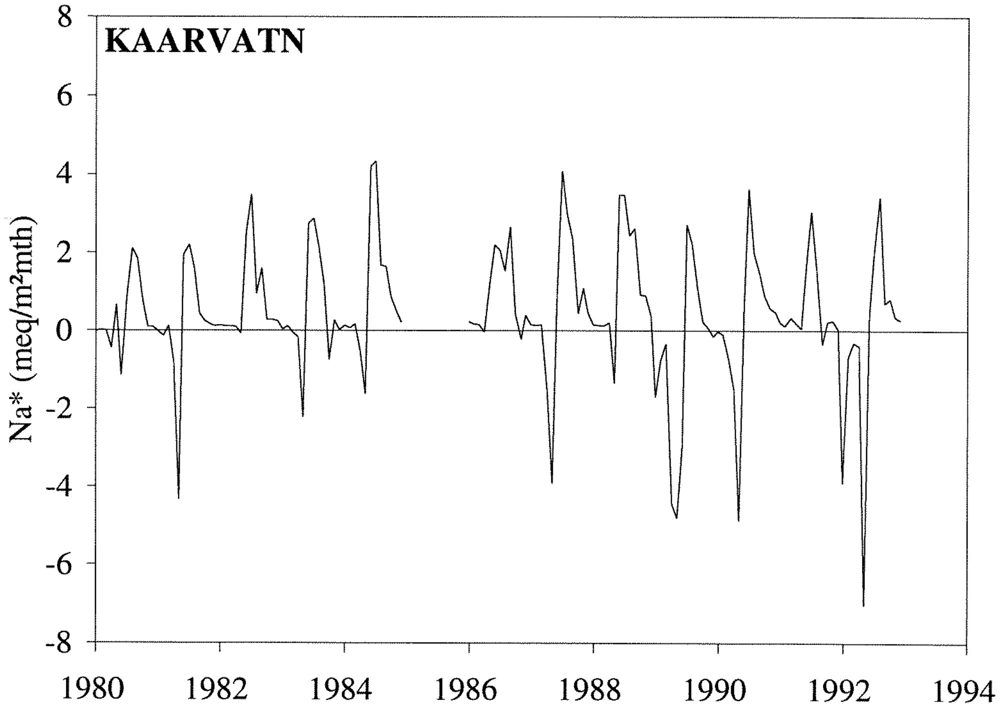


Figure 6.78 Monthly fluxes of non-marine sodium in runoff-water at Langtjern and Kaarvatn from 1974 -1992 and from 1980-1992. By adding up the monthly fluxes for the total periods, an average of 5.5 meq/m² and 5.1 meq/m² of sodium in runoff yearly derives from non-marine sources at Langtjern and Kaarvatn, respectively.

For the period 1974-1992, averagely ANC' (ΣCa,Mg,K - $\Sigma SO_4,NO_3$) was responsible for 71 ± 23% of the ANC-value at Birkenes, while Na-Cl was responsible for the remaining 29 ± 23%. During the same period, ANC' explained 65 ± 5% of the monthly variations in ANC, while the remaining 35 ± 5% was explained by Na-Cl (Figure 6.79). For the period 1985-1992, ANC' was responsible for 67 ± 24% of the ANC-value at Birkenes, while Na-Cl was responsible for the remaining 33 ± 24%. During the same period, ANC' explained 59 ± 8% of the monthly variations in ANC, while the remaining 41 ± 8% was explained by Na-Cl.

At Storgama, ANC' was responsible for 84 ± 14% of the ANC-value as an average for the period 1975-1992, while Na-Cl was responsible for the remaining 16 ± 14%. During the same period, ANC' explained 81 ± 3% of the monthly variations in ANC, while the remaining 19 ± 3% was explained by Na-Cl (Figure 6.80). For the period 1985-1992, ANC* was responsible for 86 ± 10% of the ANC-value at Storgama, while Na-Cl was responsible for the remaining 14 ± 10%. During the same period, ANC' explained 74 ± 5% of the monthly variations in ANC, while the remaining 26 ± 5% was explained by Na-Cl.

At Langtjern, ANC' was responsible for 58 ± 21% of the ANC-value as an average for the period 1974-1992, while Na-Cl was responsible for the remaining 42 ± 21%. During the same period, ANC' explained 79 ± 2% of the monthly variations in ANC, while the remaining 21 ± 2% was explained by Na-Cl (Figure 6.81). For the period 1985-1992, ANC' was responsible for 52 ± 19% of the ANC-value at Langtjern, while Na-Cl was responsible for the remaining 48 ± 19%. During the same period, ANC' explained 81 ± 3% of the monthly variations in ANC, while the remaining 19 ± 3% was explained by Na-Cl.

At Kaarvatn, ANC' was responsible for 74 ± 15% of the ANC-value as an average for the period 1980-1992, while Na-Cl was responsible for the remaining 26 ± 15%. During the same period, ANC' explained 32 ± 9% of the monthly variations in ANC, while the remaining 68 ± 9% was explained by Na-Cl (Figure 6.82). For the period 1985-1992, ANC' was responsible for 72 ± 17% of the ANC-value at Kaarvatn, while Na-Cl was responsible for the remaining 28 ± 17%. During the same period, ANC' explained 27 ± 11% of the monthly variations in ANC, while the remaining 71 ± 11% was explained by Na-Cl.

During the last years, ANC' (ΣCa,Mg,K - $\Sigma SO_4,NO_3$) is getting somewhat less important, while the amount of seasalt and the mobility difference between sodium and chloride is getting somewhat more important for the ANC in runoff at Birkenes, Storgama and Kaarvatn. The reason why Na-Cl is so important for the ANC of runoff-water at Langtjern, is primarily due to the significant contribution of Na from weathering processes in this catchment.

At Birkenes, the lowest monthly weighted average of ANC in runoff normally occurs in March (Figure 6.83). In this month the mean ANC-value is -66.7 µeq/L, and the mean values of ANC' and Na-Cl for the same month are -57.6 µeq/L and -9.1 µeq/L, respectively. At Storgama, the lowest monthly weighted average of ANC in runoff normally occurs in April (Figure 6.84), with a mean ANC-value of -43.8 µeq/L. During the same month, the mean values of ANC' and Na-Cl -44.6 µeq/L and 0.8 µeq/L, respectively. At Langtjern, the lowest monthly weighted average of ANC in runoff normally occurs in May (Figure 6.85). In this month the mean ANC-value is 3.1 µeq/L, while the mean values of ANC' and Na-Cl are -3.1 µeq/L and 6.2 µeq/L, respectively. At Kaarvatn, the lowest monthly weighted average of ANC in runoff is in May (Figure 6.86). The monthly mean of ANC in May is 9.9 µeq/L, while the mean values of ANC' and Na-Cl for the same month are 28.5 µeq/L and -18.6 µeq/L, respectively.

At Birkenes, the lowest monthly weighted average of Na-Cl in runoff normally occurs in November (Figure 6.83). In this month the mean Na-Cl is -21.2 µeq/L, and the mean values of ANC' and ANC for the same month are -40.2 µeq/L and -61.4 µeq/L, respectively. At Storgama, the lowest monthly weighted average of Na-Cl in runoff normally occurs in October (Figure 6.84), with a mean Na-Cl-value of -5.4 µeq/L. During the same month, the mean values of ANC' and ANC -33.8 µeq/L and -39.9 µeq/L, respectively. At Langtjern, the lowest monthly weighted average of Na-Cl in runoff normally occurs in November (Figure 6.85). In this month the mean Na-Cl-value is 4.4 µeq/L, while the mean values of ANC' and ANC are 3.8 µeq/L and 8.2 µeq/L, respectively. At Kaarvatn, the lowest monthly weighted average of Na-Cl in runoff normally occurs in April (Figure 6.86). The monthly mean of Na-Cl in April is -27.2 µeq/L, while the mean values of ANC' and ANC for the same month are 43.8 µeq/L and 16.6 µeq/L, respectively.

At all catchments, the lowest monthly ANC-values normally occur during springmelt, at Birkenes in March, at Storgama in April, and at Langtjern and Kaarvatn in May. At Birkenes, Storgama and Kaarvatn, the lowest monthly Na-Cl-values normally occur during late autumn, in October and November. This is a period often characterized by heavy rainfall and strong winds, and the soil is often more or less frozen. At Karvatn the lowest monthly Na-Cl-values normally occur in April, during the initial melting period. While the lowest ANC-values at Birkenes, Storgama and Langtjern normally occur when the ANC'-values ($\Sigma Ca,Mg,K$-$\Sigma SO_4,NO_3$) are at the lowest, the lowest ANC-values at Kaarvatn normally occur when the Na-Cl-values are at the lowest. Another very intersting observation at Kaarvatn is that when the Na-Cl-values normally are at the lowest, in April during the initial melting period, the ANC'-values normall are at the highest. Thus, the catchment is well protected as far as severe acid episodes are concerned.

*Table 6.9 Time trends (µeq/L per yr) from 1974-1992 (1980-1992 at Kaarvatn) in the ANC of runoff at the four catchments, based on linear regressions obtained from monthly weighted raw-data averages. * means $p < 0.05$. ** means $p < 0.01$. ANC'= $\Sigma Ca,Mg,K$ - $\Sigma SO_4,NO_3$. The remaining part of ANC is Na-Cl.*

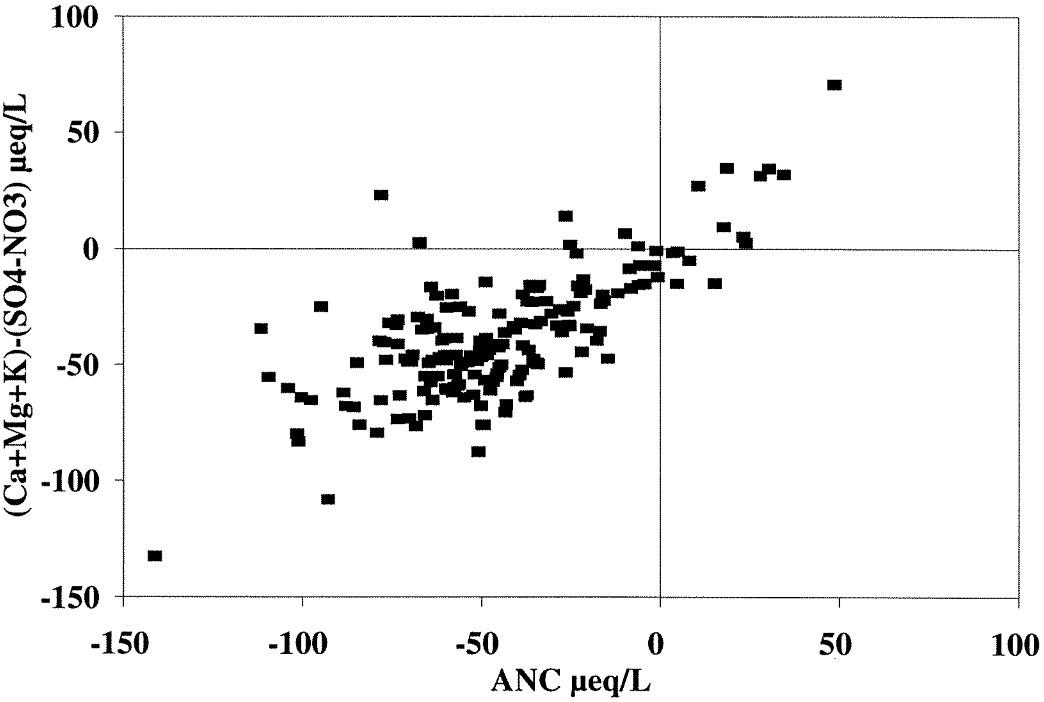
	ANC	**ANC***	**Na-Cl**
Birkenes	y = -0.97x - 35.2 r = -0.18*	y = -0.06x - 37.2 r = -0.01	y = -0.91x + 2.01 r = -0.24**
Storgama	y = -0.08x - 31.6 r = -0.03	y = 0.27x - 34.8 r = 0.10	y = -0.35x + 3.13 r = -0.24**
Langtjern	y = 0.36x + 9.63 r = 0.16*	y = 0.29x + 4.04 r = 0.15*	y = 0.08x + 5.60 r = 0.10
Kaarvatn	y = -0.44x + 25.2 r = -0.14	y = 0.08x + 26.5 r = 0.02	y = -0.51x - 1.25 r = -0.13

*Table 6.10 Time trends (μeq/L per yr) from 1985-1992 in the ANC of runoff at the four catchments, based on linear regressions obtained from monthly weighted raw-data averages. * means $p < 0.05$. ** means $p < 0.01$. ANC'= $\Sigma Ca,Mg,K - \Sigma SO_4,NO_3$. The remaining part of ANC is Na-Cl.*

	ANC	**ANC***	**Na-Cl**
Birkenes	$y = -0.22x - 46.3 \quad r = -0.02$	$y = 1.43x - 42.8 \quad r = 0.13$	$y = -1.65x - 3.58 \quad r = -0.16$
Storgama	$y = 0.69x - 34.2 \quad r = 0.11$	$y = 0.53x - 32.0 \quad r = 0.10$	$y = 0.17x - 2.19 \quad r = 0.05$
Langtjern	$y = 1.80x + 9.78 \quad r = 0.33^{**}$	$y = 1.28x + 4.34 \quad r = 0.27^{**}$	$y = 0.52x + 5.43 \quad r = 0.30^{**}$
Kaarvatn	$y = -1.44x + 27.7 \quad r = -0.23^{*}$	$y = 0.08x + 26.9 \quad r = 0.01$	$y = -1.52x + 0.82 \quad r = -0.18$

Based on the linear regression analyses (Table 6.9) there are only minor changes in the ANC of runoff at the four catchments during the periods of monitoring. At Birkenes, Storgama and Kaarvatn, there has been a weak tendency of decreasing ANC by time, while a tendency of increasing ANC is observed at Langtjern. Common to the three sites exhibiting a tendency of decreasing ANC by time, is the decrease in Na-Cl by time. Because these sites are the most coastnear sites, it means that there has been a increasing influence of seasalts during the monitoring period. During the period 1985-1992, there are a tendency of increasing ANC' in runoff-water from all four catchments, while the Na-Cl continues to decrease at the two most coastnear sites, Birkenes and Kaarvatn.

It seems to be a general tendency of a minor increase in the ANC of runoff water at all sites during the last years (Table 6.10), 1985-1992, but the decreases in Na-Cl at Birkenes and Kaarvatn are more or less owershaddowing this improvement at these sites. A decrease in Na-Cl in runoff water, means that the basesaturation of the soil is temporarily improved, because sodium is retained in the catchment. During the same period, 1985-1992, it is a tendency of a higher decline in sulphate concentration compared with the decline in base-cations of runoff-water at all sites. The fact that the base cations tend to decline with a slower rate than sulphate, means that the basecation "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 (SO4 and NO3) during the last years, may therefore be a signal of a slowly improving surface-water chemistry in Southern-Norway.



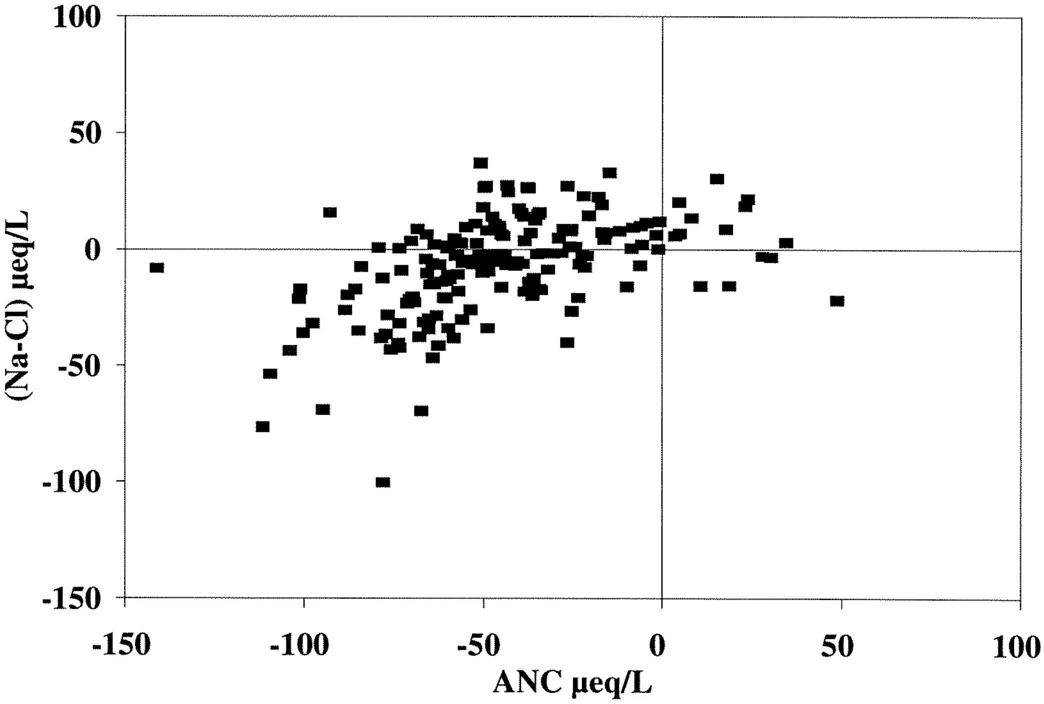


Figure 6.79 The relationships between ANC and ANC' ($\Sigma Ca,Mg,K$ - $\Sigma SO_4,NO_3$) and ANC and Na-Cl in runoff-water at Birkenes, based on monthly weighted averages from 1974-1992. The regression lines are: $y = 0.65ANC' - 8.56$ ($r = 0.73$); $y = 0.35(Na\text{-}Cl) + 8.56$ ($r = 0.50$) ($n = 180$).

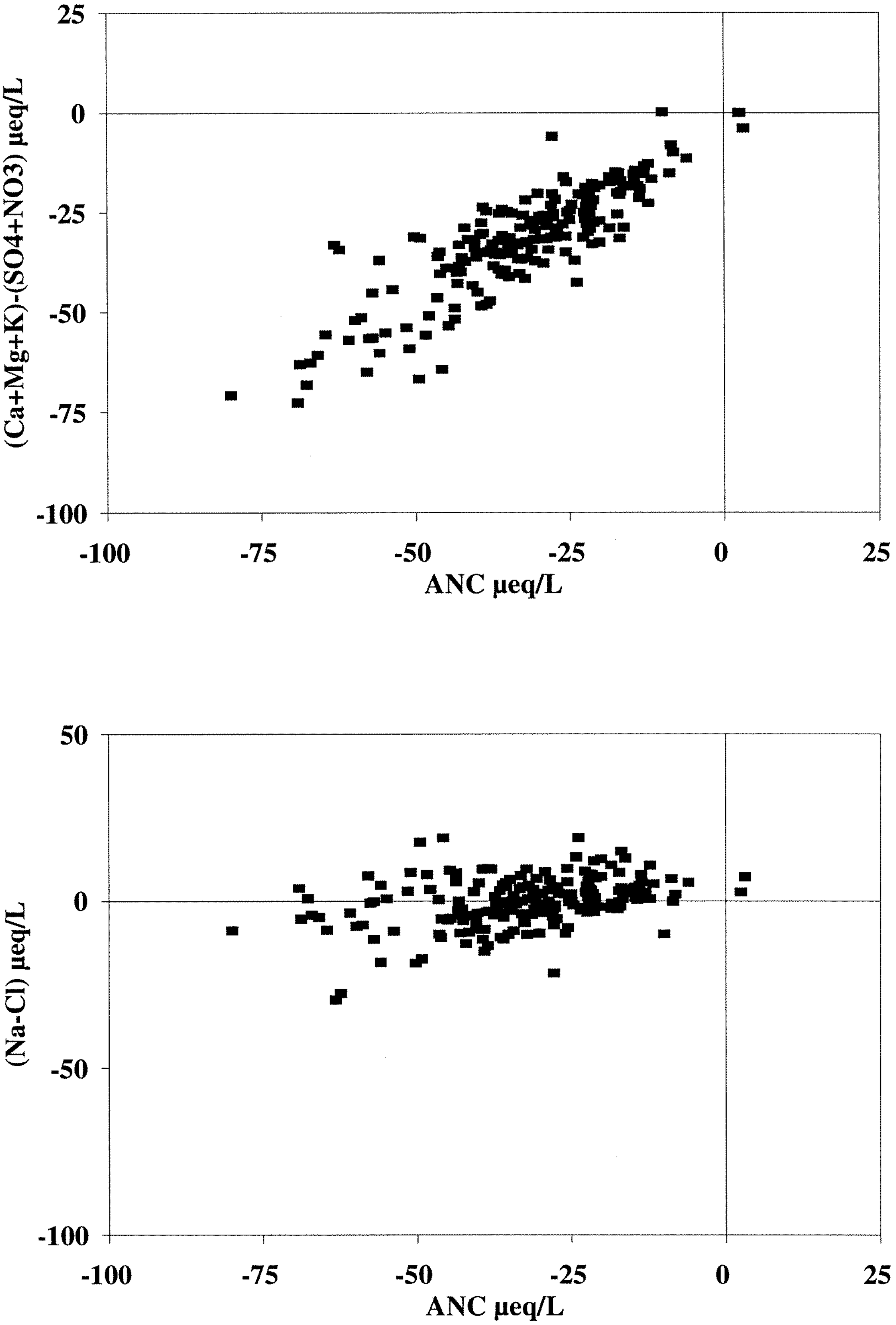


Figure 6.80 The relationships between ANC and ANC' (ΣCa,Mg,K - $\Sigma SO_4,NO_3$) and ANC and Na-Cl in runoff-water at Storgama, based on monthly weighted averages from 1975-1992. The regression lines are: $y = 0.81ANC' - 5.76$ ($r = 0.86$); $y = 0.19(Na-Cl) + 5.76$ ($r = 0.37$) ($n = 192$).

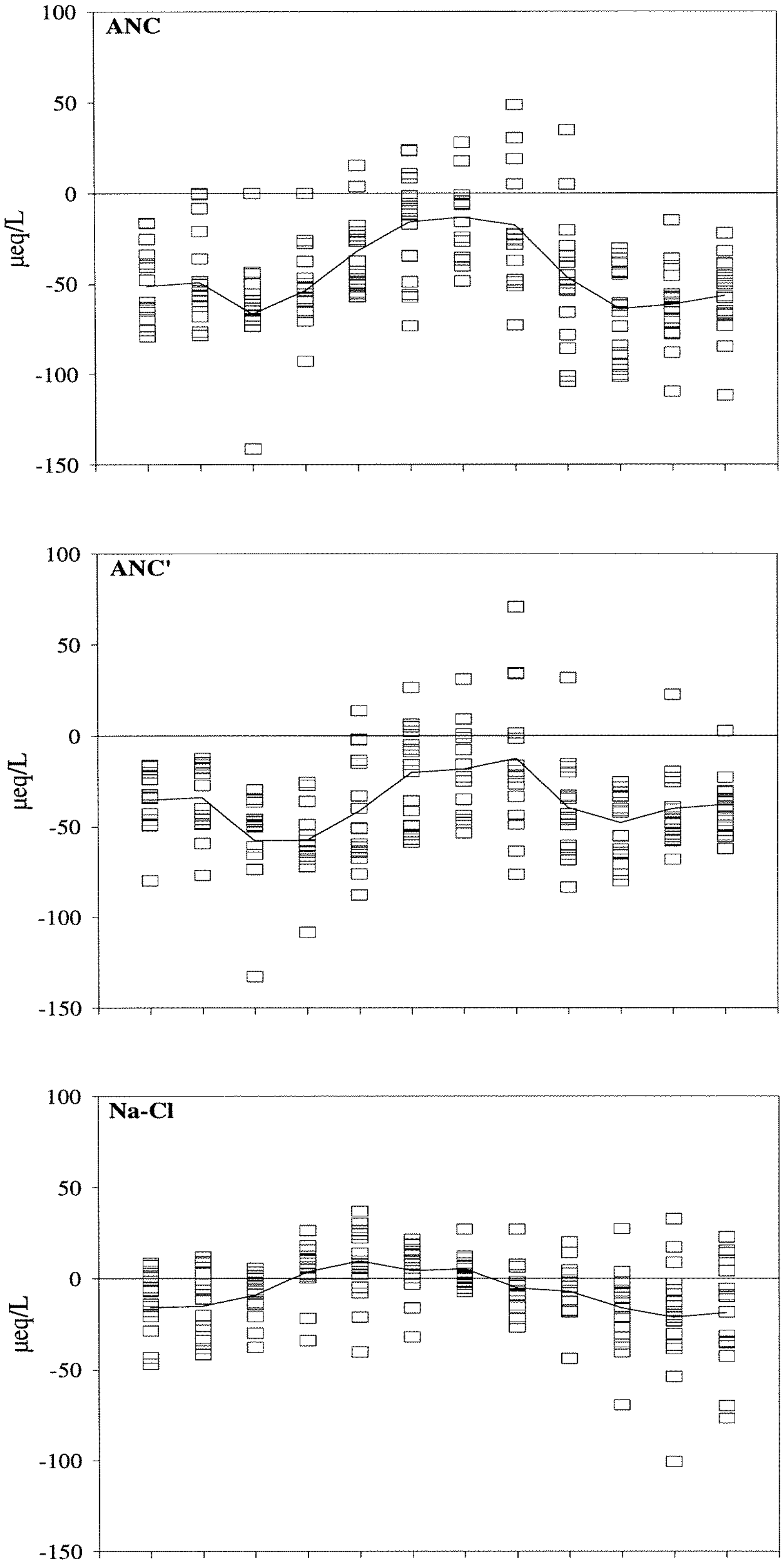
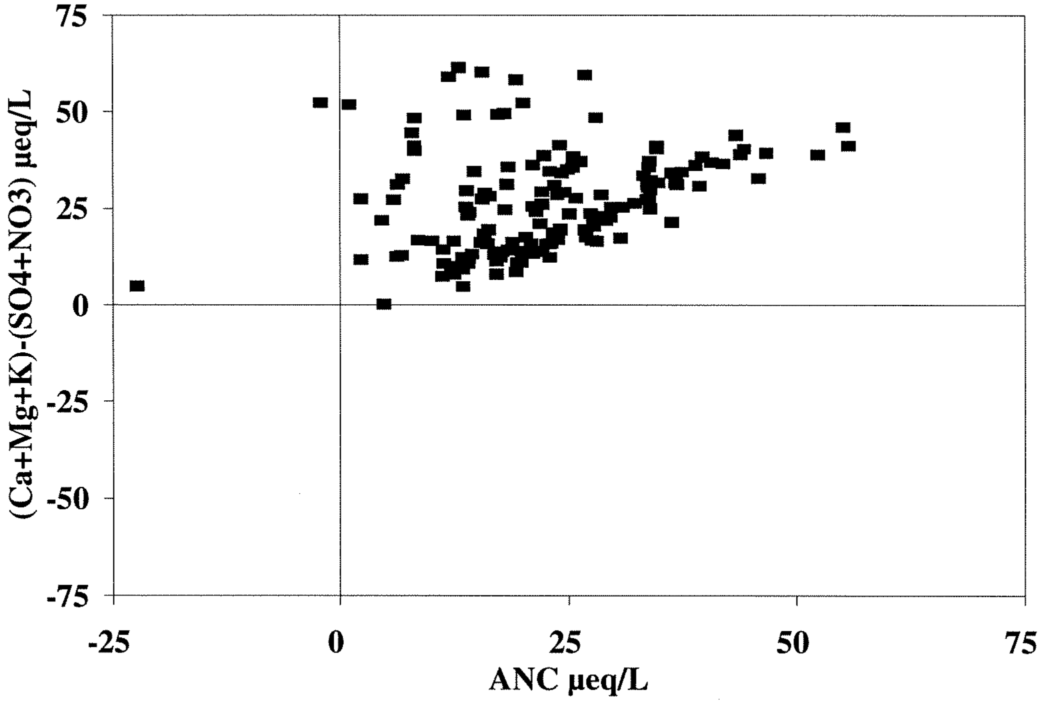


Figure 6.83 The monthly variations (from Jan to Dec) of ANC, ANC', and Na-Cl in runoff at Birkenes, based on monthly weighted concentration averages from 1974-1992. The continues line represents the monthly mean values.



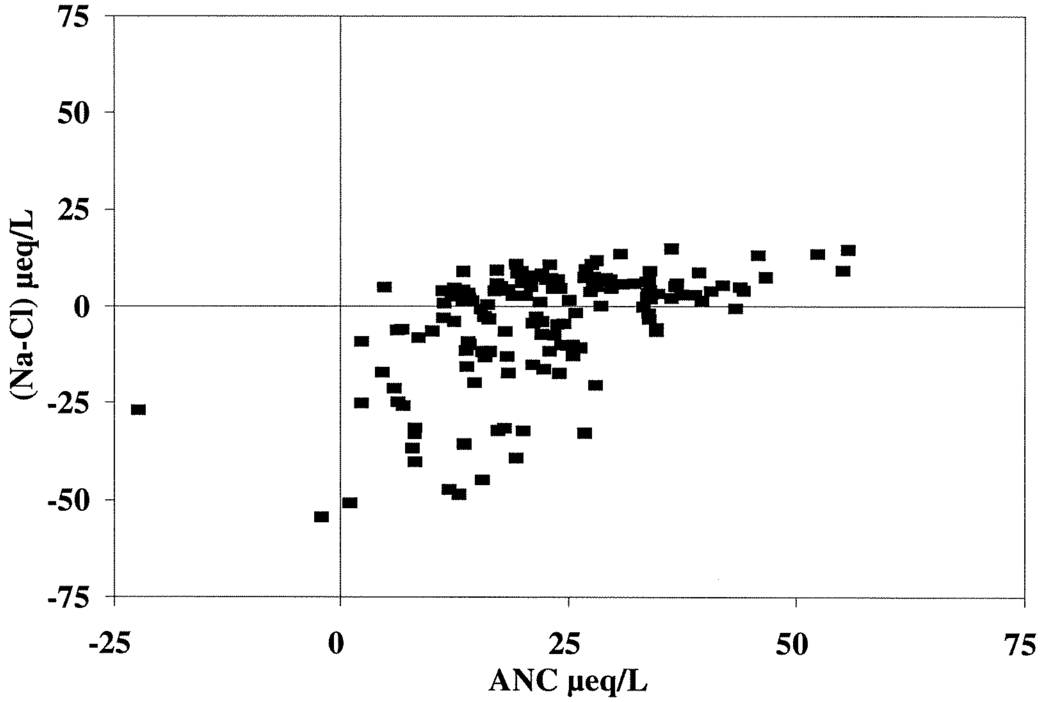
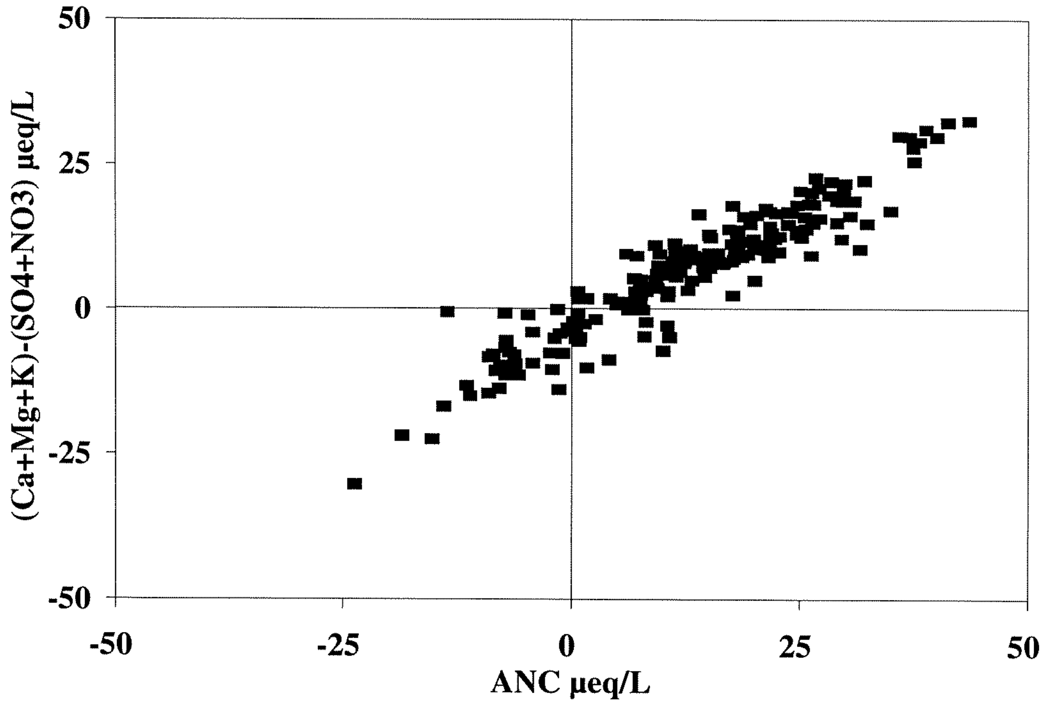


Figure 6.82 The relationships between ANC and ANC' (ΣCa,Mg,K - ΣSO$_4$,NO$_3$) and ANC and Na-Cl in runoff-water at Kaarvatn, based on monthly weighted averages from 1980-1992. The regression lines are: y = 0.32ANC' + 19.9 (r = 0.28); y = 0.68(Na-Cl) - 19.9 (r = 0.54) (n = 144).



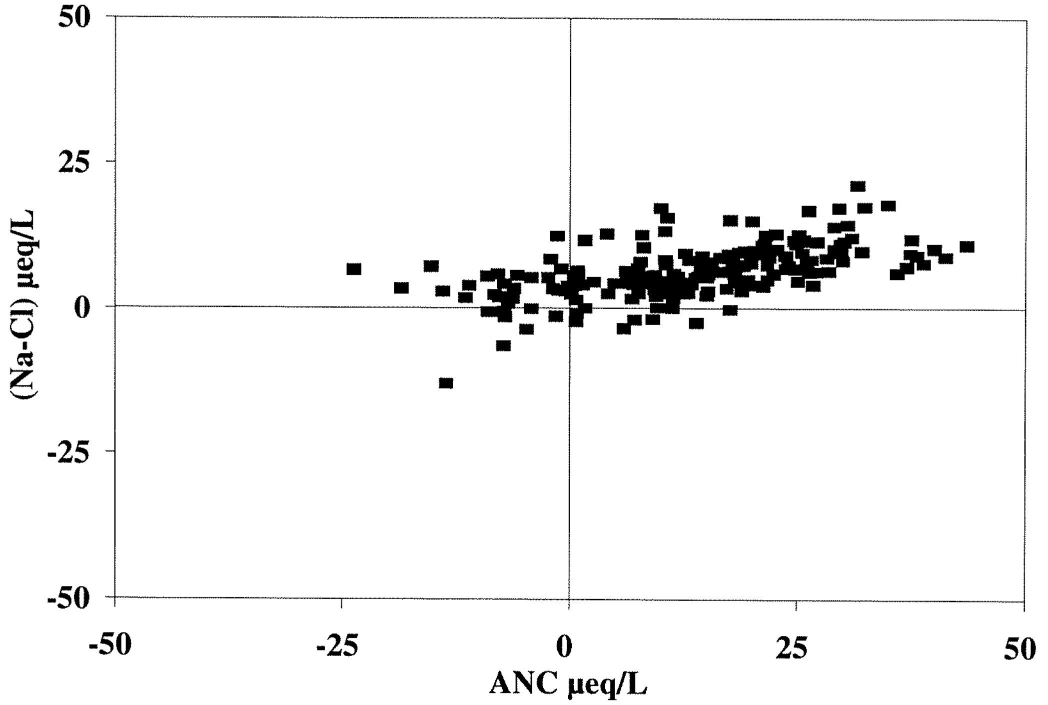


Figure 6.81 The relationships between ANC and ANC' (ΣCa,Mg,K - $\Sigma SO_4,NO_3$) and ANC and Na-Cl in runoff-water at Langtjern, based on monthly weighted averages from 1974-1992. The regression lines are: $y = 0.79ANC' - 3.57$ ($r = 0.94$); $y = 0.21(Na\text{-}Cl) + 3.57$ ($r = 0.59$) ($n = 198$).

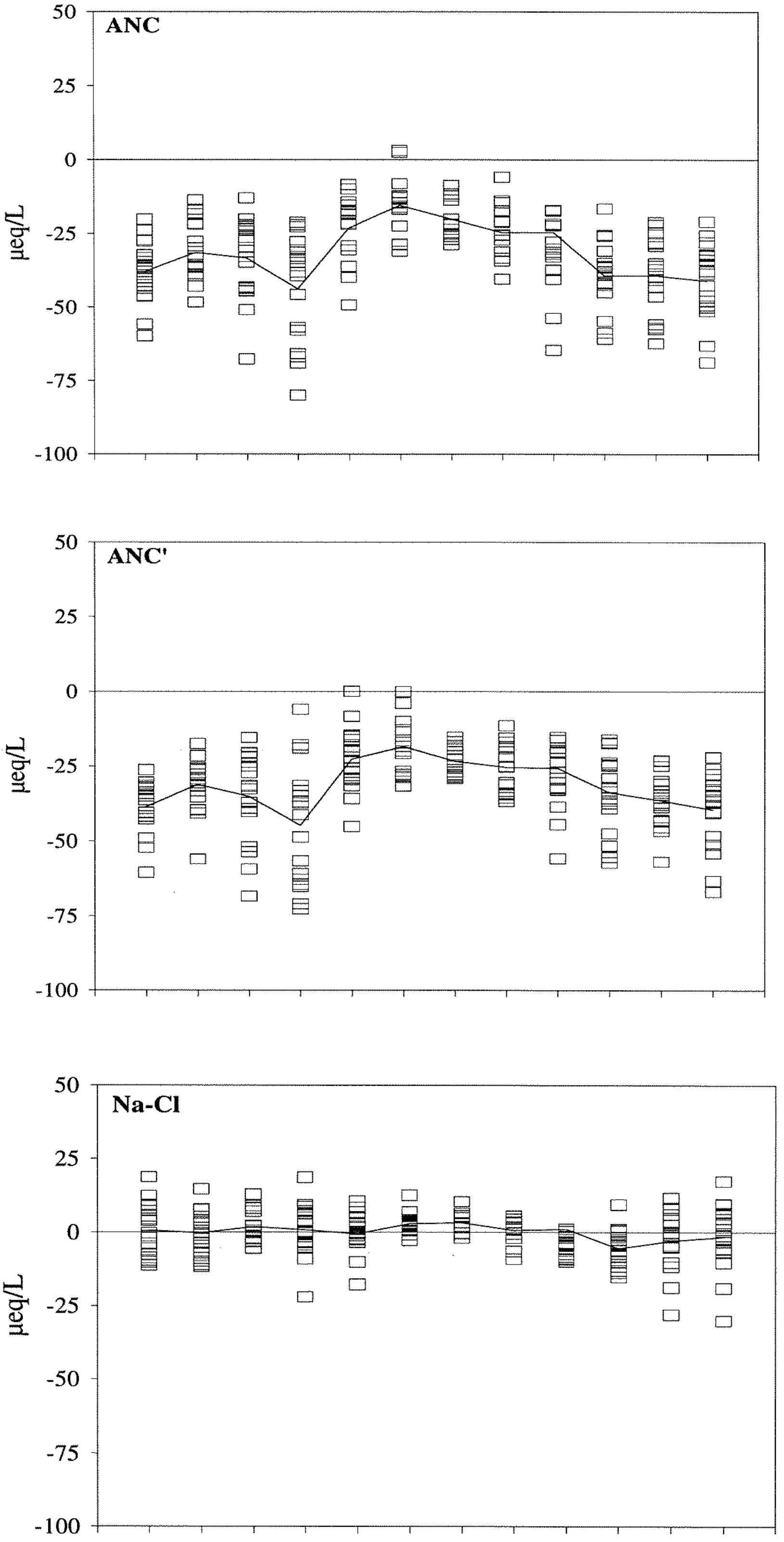


Figure 6.84 The monthly variations (from Jan to Dec) of ANC, ANC', and Na-Cl in runoff at Storgama, based on monthly weighted concentration averages from 1975-1992. The continues line represents the monthly mean values.

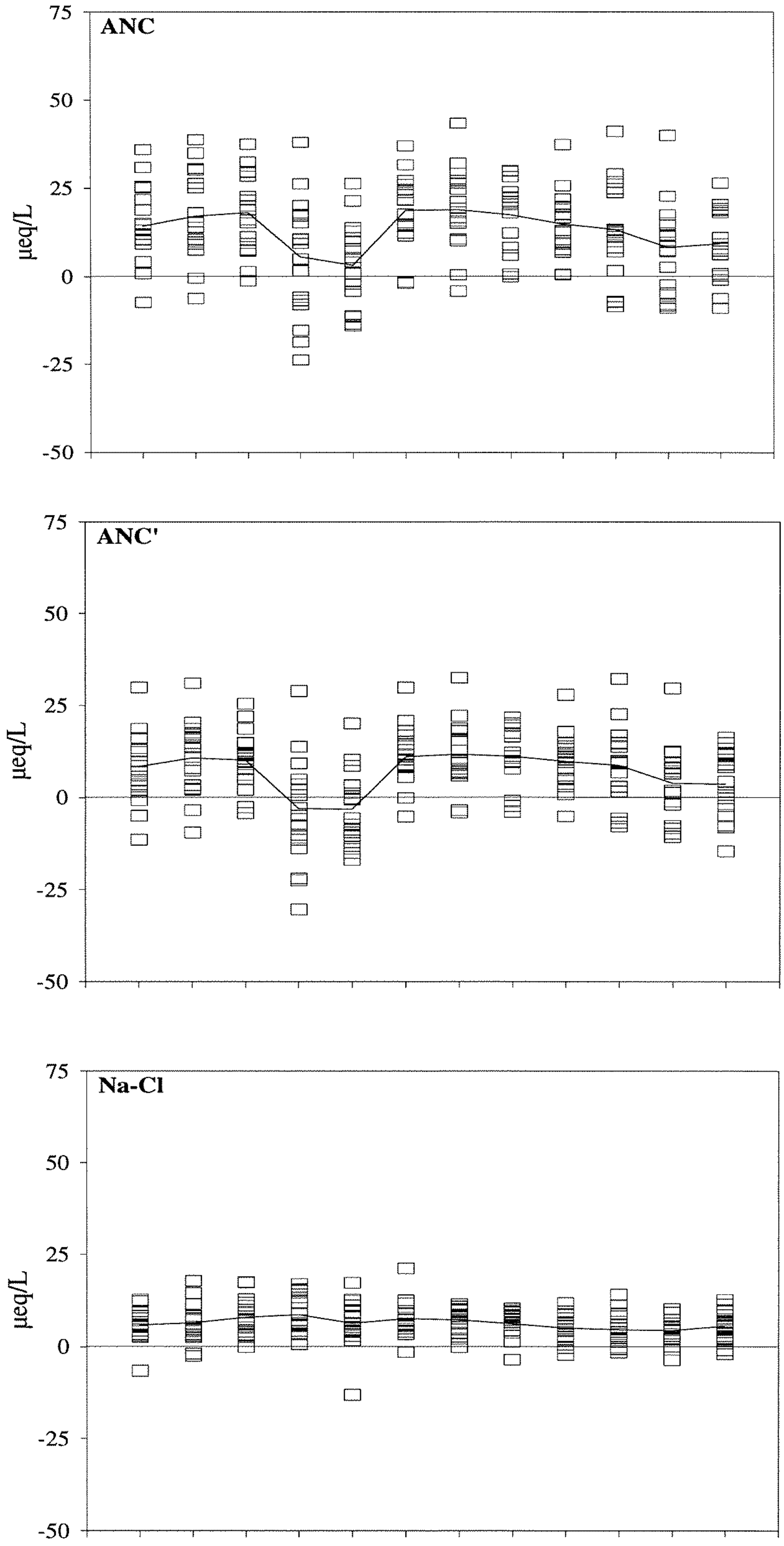


Figure 6.85 The monthly variations (from Jan to Dec) of ANC, ANC' and Na-Cl in runoff at Langtjern, based on monthly weighted concentration averages from 1974-1992. The continues line represents the monthly mean values.

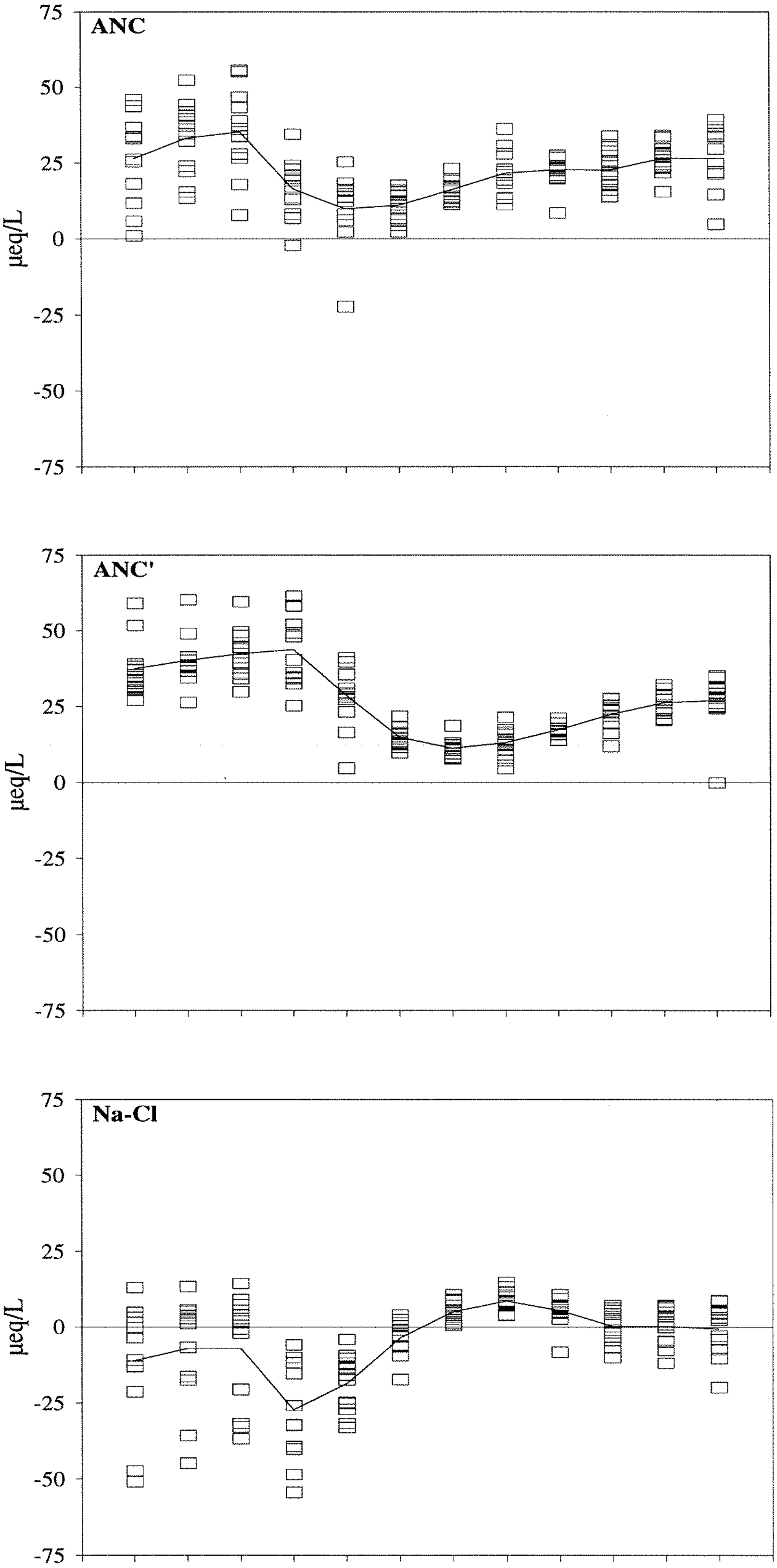


Figure 6.86 The monthly variations (from Jan to Dec) of ANC, ANC', and Na-Cl in runoff at Kaarvatn, based on monthly weighted concentration averages from 1980-1992. The continues line represents the monthly mean values.

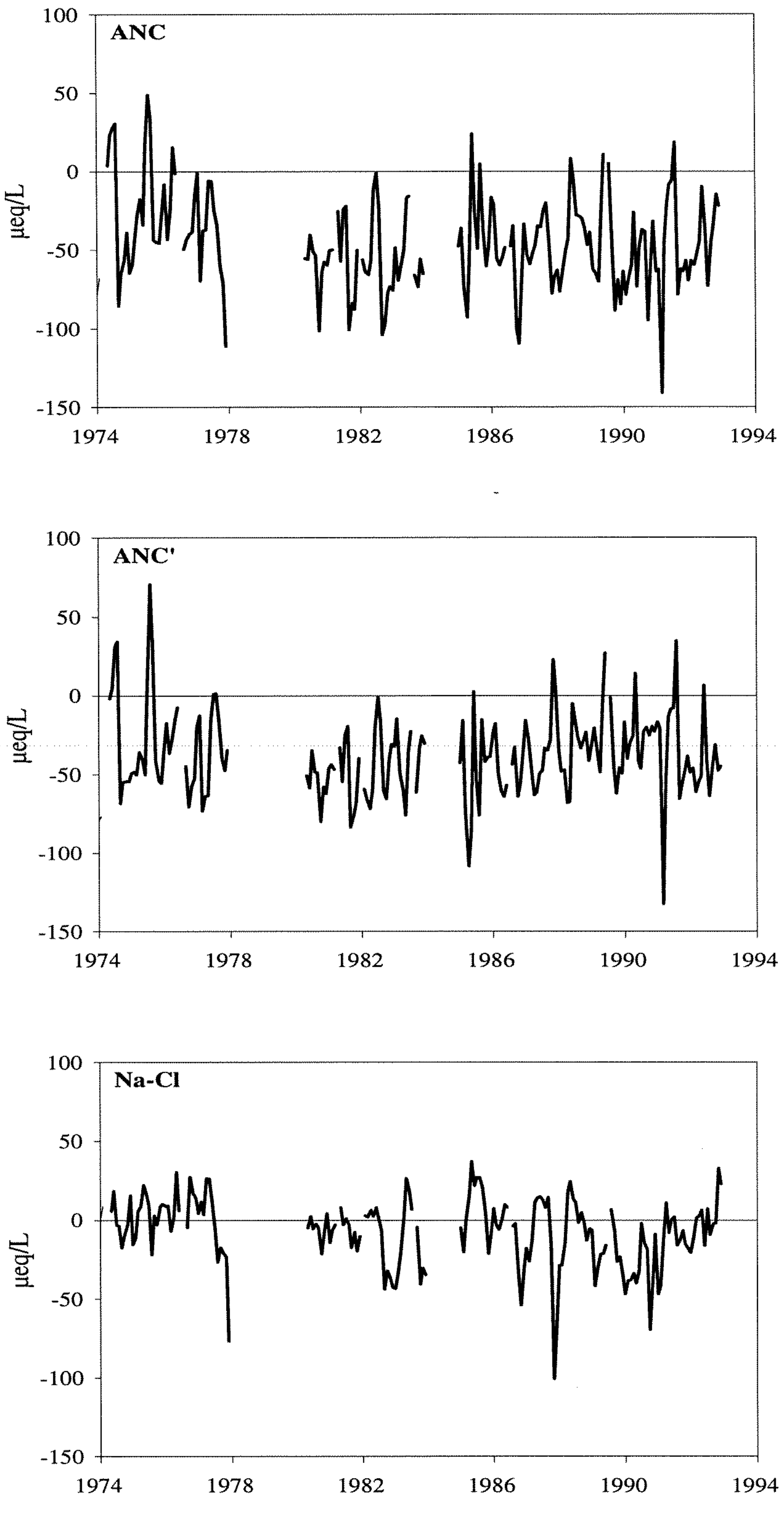
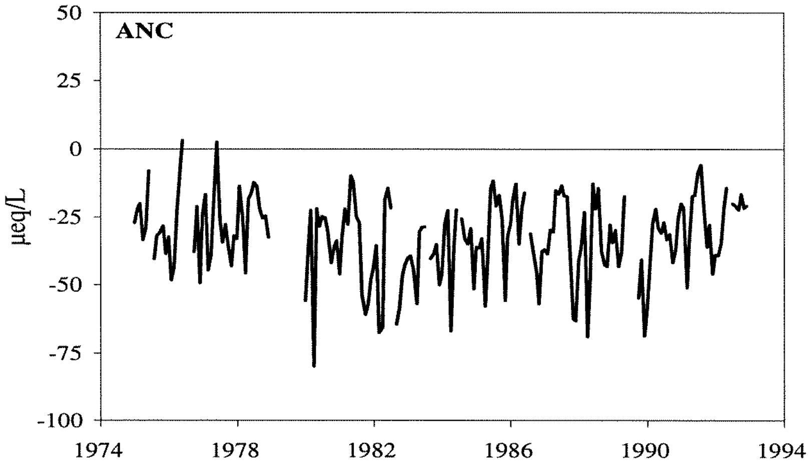
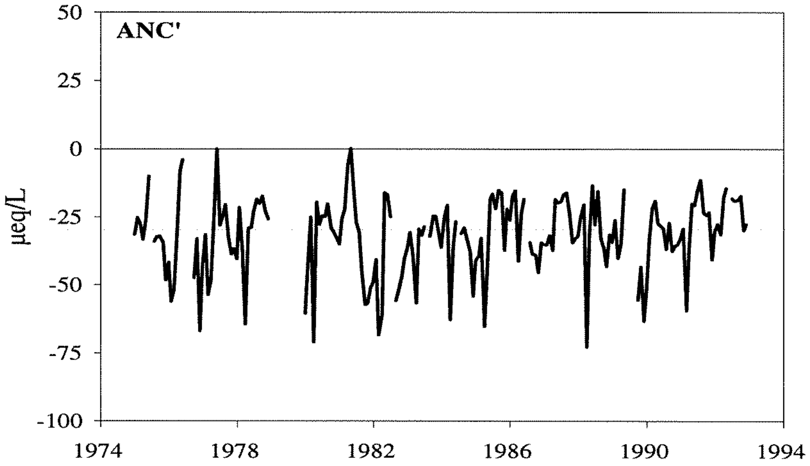


Figure 6.87 Changes in monthly weighted averages of ANC, ANC', and Na-Cl in runoff at Birkenes during the monitoring period, 1974-1992.





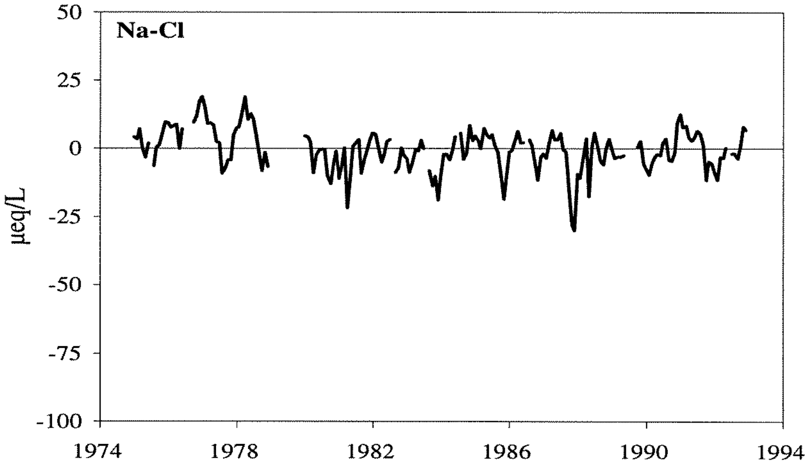


Figure 6.88 Changes in monthly weighted averages of ANC, ANC', and Na-Cl in runoff at Storgama during the monitoring period, 1975-1992.

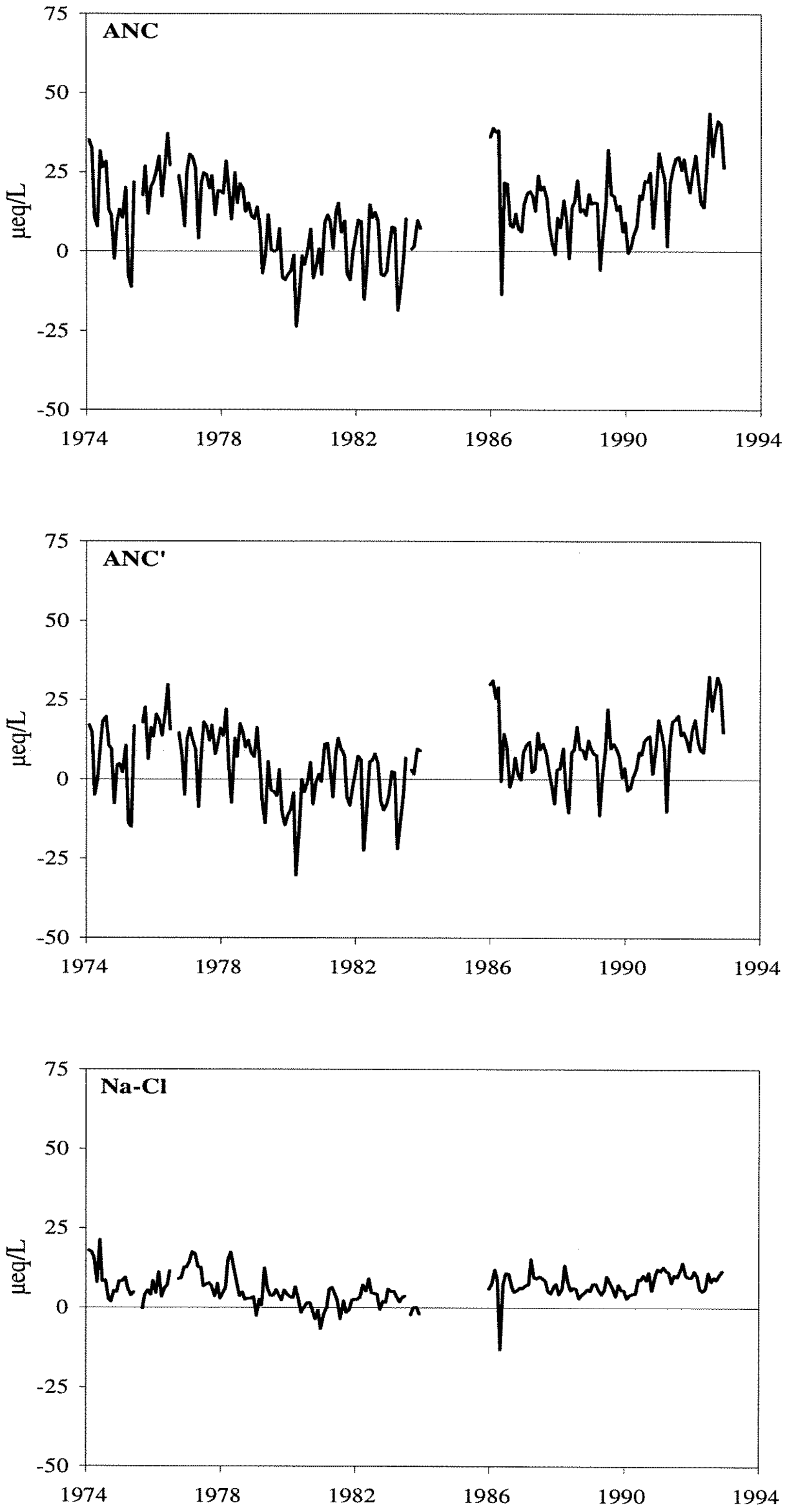


Figure 6.89 Changes in monthly weighted averages of ANC, ANC', and Na-Cl in runoff at Langtjern during the monitoring period, 1974-1992.

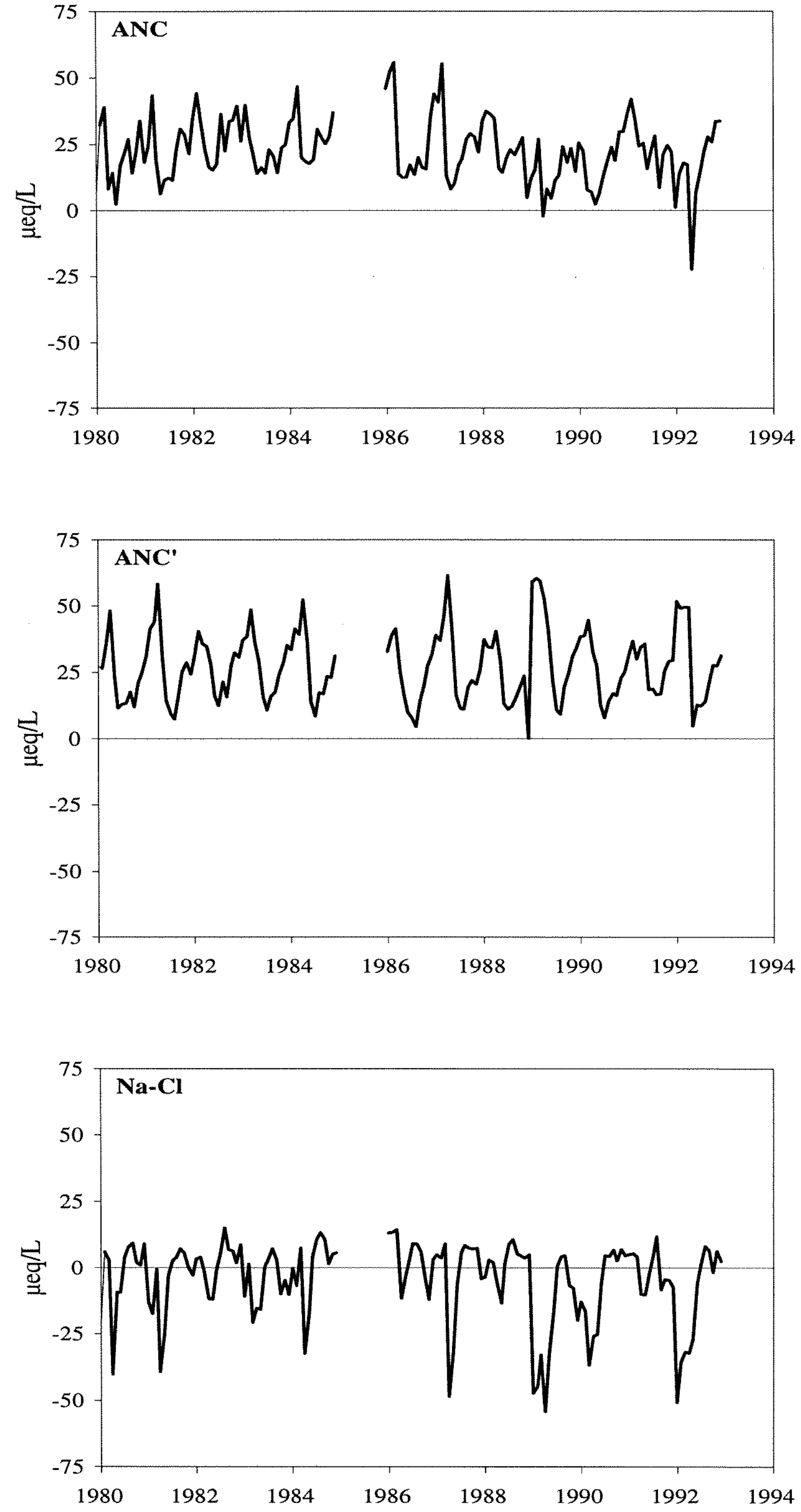


Figure 6.90 Changes in monthly weighted averages of ANC, ANC', and Na-Cl in runoff at Kaarvatn during the monitoring period, 1980-1992.

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APPENDIX

Table A-1 Annual (A) and monthly (B) relationships between preciptation/runoff (mm) and precipitation (wet-deposition)/streamwater chemistry (µeq/L) at Birkenes from 1974/75 to 1990/91, based on linear regression: $y = ax + b$; y = chemical variable; x = water (mm); a = x-coefficient; b = constant; n = no. of observations. When $p \leq 0.05$, the linear regression is assumed to be statistical significant.

	A				**B**			
Parameter	**n**	**y = ax + b**	**r**	**sign.**	**n**	**y = ax + b**	**r**	**sign.**
Hydrogen								
Input	17	y = -0.01x + 81.5	-0.31		214	y = -0.06x + 67.2	-0.20	Yes
Output	13	y = 4.41(log x) + 10.0	0.14		170	y = 12.6(log x) + 2.0	0.66	Yes
Calcium								
Input	17	y = -13.0(log x) + 52.8	-0.39		214	y = -10.7(log x) + 32.2	-0.46	Yes
Output	13	y = -26.1(log x) + 142.3	-0.36		170	y = -16.9(log x) + 91.4	-0.63	Yes
Magnesium								
Input	17	y = -0.002x + 14.6	-0.22		214	y = 0.02x + 10.0	0.19	Yes
Output	13	y = -10.7(log x) + 67.5	-0.31		170	y = -1.49(log x) + 36.9	-0.14	
Sodium								
Input	10	y = 0.003x + 44.4	0.07		144	y = 0.11x + 35.0	0.27	Yes
Output	13	y = -0.006x + 126.1	-0.18		168	y = -0.011 x + 121.6	-0.05	
Potassium								
Input	7	y = 0.91(log x) + 2.5	0.08		108	y = -5.49(log x) + 15.9	-0.56	Yes
Output	13	y = 6.06(log x) -12.6	0.37		170	y = -0.49(log x) + 6.7	-0.11	
Ammonium								
Input	17	y = 7.26(log x) + 23.0	0.08		214	y = -22.6(log x) + 90.1	-0.31	Yes
Output	a				a			
Aluminium								
Input								
Output	12	y = 13.8(log x) + 6.5	0.50		158	y = 8.66(log x)+ 33.4	0.36	Yes
Sulphate								
Input	17	y = -49.4(log x) + 232.2	-0.35		214	y = -28.9(log x) + 130.6	-0.34	Yes
Output	13	y = -13.9(log x) + 173.7	-0.10		170	y = 9.6(log x) + 114.1	0.26	Yes
Nitrate								
Input	17	y = 7.49(log x) + 18.8	0.11		214	y = -9.58(log x) + 61.2	-0.18	Yes
Output	13	y = 0.23(log x) + 8.3	0.04		170	y = 2.31(log x) + 5.6	0.17	Yes
Chloride								
Input	15	y = -0.002x + 61.5	-0.05		180	y = 0.13x + 41.9	0.25	Yes
Output	13	y = -0.002x + 128.5	-0.03		170	y = 0.01x +127.2	0.10	
TOC (mg C/L)								
Input								
Output	6*	y = -0.72(log x) + 7.1	-0.18		82	y = -1.15(log x) + 7.1	-0.33	Yes

a: less than two years of data; *: TOC measured from 1985.

Table A-2 Annual (A) and monthly (B) relationships between preciptation/runoff (mm) and precipitation (wet-deposition)/streamwater chemistry (μeq/L) at Storgama from 1974/75 to 1990/91, based on linear regression: $y = ax + b$; y = chemical variable; x = water (mm); a = x-coefficient; b = constant; n = no. of observations. When $p \leq 0.05$, the linear regression is assumed to be statistical significant.

	A				**B**			
Parameter	**n**	**y = ax + b**	**r**	**sign.**	**n**	**y = ax + b**	**r**	**sign.**
Hydrogen								
Input	15	$y = -0.0004x + 53.3$	-0.02		202	$y = -0.05x + 57.8$	-0.14	Yes
Output	14	$y = 11.5(\log x) - 3.7$	0.32		181	$y = 5.41(\log x) + 21.1$	0.22	Yes
Calcium								
Input	15	$y = 1.32(\log x) + 3.4$	0.06		202	$y = -8.00(\log x) + 22.1$	-0.44	Yes
Output	14	$y = -10.4(\log x) + 69.5$	-0.17		181	$y = -8.93(\log x) + 52.2$	-0.37	Yes
Magnesium								
Input	15	$y = -4.36(\log x) + 18.2$	-0.45		202	$y = -1.46(\log x) + 7.4$	-0.19	Yes
Output	14	$y = -1.62(\log x) + 18.3$	-0.08		181	$y = -1.31(\log x) + 15.3$	-0.18	Yes
Sodium								
Input	8	$y = -0.006x + 24.1$	0.61		131	$y = 0.02x + 14.7$	0.08	
Output	14	$y = 1.31(\log x) + 31.5$	0.03		181	$y = -7.12(\log x) + 46.1$	-0.31	Yes
Potassium								
Input	7	$y = -0.67(\log x) + 4.8$	-0.07		106	$y = -4.82(\log x) + 11.3$	-0.53	Yes
Output	14	$y = 0.0000x + 3.2$	0.01		181	$y = 0.005x + 2.8$	0.15	Yes
Ammonium								
Input	15	$y = -5.08(\log x) + 49.2$	-0.13		202	$y = -16.6(\log x) + 62.8$	-0.25	Yes
Output	a				a			
Aluminium								
Input								
Output	14	$-0.0003x\ 18.1$	-0.06		181	$y = -0.016x + 19.9$	-0.26	Yes
Sulphate								
Input	15	$y = -11.36(\log x) + 91.3$	-0.14		202	$y = -26.8(\log x) + 105.0$	-0.32	Yes
Output	14	$y = -9.43(\log x) + 105.6$	-0.10		181	$y = -7.13(\log x) + 88.0$	-0.21	Yes
Nitrate								
Input	15	$y = 1.82(\log x) + 27.4$	0.04		202	$y = -7.69(\log x) + 46.6$	-0.16	Yes
Output	14	$y = 0.003x + 7.2$	0.30		181	$y = 0.016x + 8.6$	-0.16	Yes
Chloride								
Input	12	$y = -0.009x + 30.9$	-0.54		166	$y = 0.015x + 18.3$	0.05	
Output	13	$y = 0.003x + 32.2$	0.14		181	$y = -0.026x + 36.8$	-0.15	Yes
TOC (mg C/L)								
Input								
Output	6*	$y = 0.56(\log x) + 2.5$	0.14		80	$y = 0.30(\log x) + 3.7$	0.18	

a: less than two years of data; *: TOC measured from 1985.

Table A-3 Annual (A) and monthly (B) relationships between preciptation/runoff (mm) and precipitation (wet-deposition)/streamwater chemistry (µeq/L) at Langtjern from 1974/75 to 1990/91, based on linear regression: $y = ax + b$; y = chemical variable; x = water (mm); a = x-coefficient; b = constant; n = no. of observations. When $p \leq 0.05$, the linear regression is assumed to be statistical significant.

	A				**B**			
Parameter	**n**	**$y = ax + b$**	**r**	**sign.**	**n**	**$y = ax + b$**	**r**	**sign.**
Hydrogen								
Input	17	$y = -0.028x + 71.9$	-0.32		212	$y = -0.017x + 48.2$	-0.02	
Output	14	$y = +8.78(\log x) - 7.0$	0.51		187	$y = 4.44(\log x) + 10.7$	0.33	Yes
Calcium								
Input	17	$y = -16.9(\log x) + 60.5$	-0.26		212	$y = -12.0(\log x) + 30.6$	-0.32	Yes
Output	14	$y = -28.7(\log x) + 140.3$	-0.40		187	$y = -7.51(\log x) + 71.0$	-0.34	Yes
Magnesium								
Input	17	$y = -6.29(\log x) + 22.5$	-0.35		212	$y = -3.83(\log x) + 10.4$	-0.40	Yes
Output	14	$y = -8.39(\log x) + 41.5$	-0.36		187	$y = -1.75(\log x) + 20.5$	-0.26	Yes
Sodium								
Input	10	$y = -5.37(\log x) + 25.1$	-0.14		140	$y = -6.70(\log x) + 21.0$	-0.30	Yes
Output	14	$y = -6.35(\log x) + 43.1$	-0.24		186	$y = -2.12(\log x) + 28.3$	-0.25	Yes
Potassium								
Input	9	$y = -2.76(\log x) + 12.4$	-0.26		140	$y = -0.04(\log x) + 1.8$	-0.37	Yes
Output	14	$y = -0.002x + 4.4$	-0.30		187	$y = 0.007x + 3.0$	0.31	Yes
Ammonium								
Input	17	$y = 10.2(\log x) + 12.2$	0.06		212	$y = -34.3(\log x) + 98.1$	-0.34	Yes
Output	a				a			
Aluminium								
Input								
Output	13	$y = -3.27(\log x) + 30.4$	-0.17		175	$y = -1.76(\log x) + 23.6$	-0.22	Yes
Sulphate								
Input	17	$y = -89.6(\log x) + 324.2$	-0.39		212	$y = -34.7(\log x) + 118.7$	-0.24	Yes
Output	14	$y = -24.8(\log x) + 143.9$	-0.27		187	$y = -1.63(\log x) + 76.6$	-0.05	
Nitrate								
Input	17	$y = -6.29(\log x) + 53.7$	-0.06		202	$y = -21.0(\log x) + 69.7$	-0.27	Yes
Output	14	$y = -0.0003x + 2.2$	-0.12		187	$y = 0006x + 1.6$	0.28	Yes
Chloride								
Input	16	$y = -6.18(\log x) + 30.0$	-0.16		201	$y = -8.84(\log x) + 27.0$	-0.31	Yes
Output	13	$y = -13.9(\log x) + 57.9$	-0.64		187	$y = -2.23(\log x) + 22.3$	-0.27	Yes
TOC (mg C/L)								
Input								
Output	5*	$y = 0.48(\log x) + 7.4$	0.16		72	$y = -0.25(\log x) + 9.2$	-0.11	

a: less than two years of data; *: TOC measured from 1986.

Table A-4 Annual (A) and monthly (B) relationships between preciptation/runoff (mm) and precipitation (wet-deposition)/streamwater chemistry (µeq/L) at Kaarvatn from 1980/81 to 1990/91, based on linear regression: $y = ax + b$; y = chemical variable; x = water (mm); a = x-coefficient; b = constant; n = no. of observations. When $p \leq 0.05$, the linear regression is assumed to be statistical significant.

	A				**B**			
Parameter	**n**	**y = ax + b**	**r**	**sign.**	**n**	**y = ax + b**	**r**	**sign.**
Hydrogen								
Input	11	y = -0.007x + 26.5	-0.71	Yes	156	y = -0.052x + 18.9	-0.42	Yes
Output	9	y = 0.67(log x) -1.5	0.54		132	y = 0.32(log x) + 0.10	0.62	Yes
Calcium								
Input	11	y = -19.5(log x) + 72.9	-0.40		156	y = -5.64(log x) + 18.5	-0.25	Yes
Output	9	y = 0.29(log x) + 27.8	0.01		132	y = -13.4(log x) + 53.5	-0.75	Yes
Magnesium								
Input	11	y = 0.005x + 1.96	0.45		156	y = 0.049x + 6.6	0.30	Yes
Output	9	y = 16.6(log x) -37.8	0.66	Yes	132	y = -3.81(log x) + 23.1	-0.33	Yes
Sodium								
Input	7	y = 0.018x + 13.9	0.51		120	y = 0.24x + 26.6	0.30	Yes
Output	9	y= 56.6(log x) - 127.9	0.58		132	y = -9.77(log x) + 74.1	-0.25	Yes
Potassium								
Input	7	y = -0.72(log x) + 5.1	-0.11		108	y = -0.40(log x) + 3.52	-0.08	
Output	9	y = -0.08(log x) + 3.7	-0.03		132	y = -0.73(log x) + 4.84	-0.43	Yes
Ammonium								
Input	11	y = 3.13(log x) - 0.20	0.07		156	y = -11.5(log x) + 32.2	-0.29	Yes
Output	a				a			
Aluminium								
Input								
Output	9	y = -0.11(log x) + 2.4	-0.05		132	y = 0.37(log x) + 1.4	0.29	Yes
Sulphate								
Input	11	y = -39.3(log x) + 151.1	-0.50		156	y = -15.0(log x) + 49.4	-0.43	Yes
Output	9	y = 1.39 (log x) + 15.3	0.07		132	y = -6.82(log x) + 32.9	-0.58	Yes
Nitrate								
Input	11	y = -17.8(log x) + 65.8	-0.74	Yes	156	y = -8.59(log x) + 23.4	-0.60	Yes
Output	9	y = -1.87(log x) + 7.5	-0.60		132	y = -0.85(log x) + 3.0	-0.54	Yes
Chloride								
Input	11	y = 0.031x - 7.3	0.57		156	y = 0.26x + 30.6	0.30	Yes
Output	9	y = 118.7(log x) - 326.7	0.65		132	y = -8.23(log x) + 75.0	-0.14	
Bicarbonate								
Input	a				a			
Output	9	y = -42.0(log x) + 160.2	-0.70	Yes	132	y = -16.1(log x) + 52.6	-0.80	Yes
TOC (mg C/L)								
Input								
Output	5*	y = -1.29(log x) + 5.3	-0.74		72	y = 0.09(log x) + 0.85	0.13	

a: less than two years of data; *: TOC measured from 1986.

Table B-1 Annual (A) and monthly (B) relationships between preciptation/runoff (mm/m^2 year or month) and precipitation (wet-deposition)/streamwater fluxes (meq/m^2 year or month) of dissolved chemical substances at Birkenes from 1974/75 to 1990/91, based on linear regression: $y = ax + b$; y = chemical variable; x = input or output of water ; a = x-coefficient; b = constant; n = no. of observations. When $p \leq 0.05$, the linear regression is assumed to be statistical significant.

	A				B			
Parameter	**n**	**y = ax + b**	**r**	**sign.**	**n**	**y = ax + b**	**r**	**sign.**
Hydrogen								
Input	17	$y = 0.033x + 33.8$	0.56	Yes	214	$y = 0.049x + 0.89$	0.85	Yes
Output	13	$y = 0.028x + 1.18$	0.81	Yes	170	$y = 0.036x - 0.62$	0.92	Yes
Calcium								
Input	17	$y = 0.004x + 8.66$	0.44		214	$y = 0.008x + 0.24$	0.70	Yes
Output	13	$y = 0.045x + 11.9$	0.90	Yes	170	$y = 0.050x + 0.43$	0.95	Yes
Magnesium								
Input	17	$y = 0.009x + 5.04$	0.53	Yes	214	$y = 0.015x - 0.25$	0.75	Yes
Output	13	$y = 0.030x + 4.13$	0.87	Yes	170	$y = 0.033x + 0.01$	0.96	Yes
Sodium								
Input	10	$y = 0.057x - 5.05$	0.65	Yes	144	$y = 0.071x - 2.03$	0.76	Yes
Output	13	$y = 0.114x + 3.93$	0.92	Yes	168	$y = 0.118x + 0.18$	0.96	Yes
Potassium								
Input	7	$y = 0.004x - 0.12$	0.90	Yes	108	$y = 0.004x + 0.06$	0.85	Yes
Output	13	$y = 0.009x - 3.93$	0.70	Yes	170	$y = 0.006x - 0.04$	0.79	Yes
Ammonium								
Input	17	$y = 0.036x + 5.93$	0.81	Yes	214	$y = 0.034x + 0.81$	0.75	Yes
Output	a				a			
Aluminium								
Input								
Output	12	$y = 0.055x - 3.31$	0.97	Yes	158	$y = 0.053x - 0.13$	0.97	Yes
Sulphate								
Input	17	$y = 0.043x + 35.9$	0.67	Yes	214	$y = 0.060x + 0.95$	0.85	Yes
Output	13	$y = 0.125x + 9.14$	0.85		170	$y = 0.139x - 0.51$	0.97	Yes
Nitrate								
Input	17	$y = 0.035x + 5.08$	0.82	Yes	214	$y = 0.034x + 0.67$	0.81	Yes
Output	13	$y = 0.008x + 1.37$	0.48		170	$y = 0.008x + 0.20$	0.53	Yes
Chloride								
Input	15	$y = 0.056x + 10.9$	0.57	Yes	180	$y = 0.080x - 1.99$	0.73	Yes
Output	13	$y = 0.128x - 1.22$	0.79	Yes	170	$y = 0.126x + 0.34$	0.89	Yes
TOC (g C/m^{2}time)								
Input								
Output	6*	$y = 0.006x - 1.03$	0.98	Yes	82	$y = 0.005x - 0.043$	0.94	Yes

a: less than two years of data; *: TOC measured from 1985.

Table B-2 Annual (A) and monthly (B) relationships between preciptation/runoff (mm/m^2 year or month) and precipitation (wet-deposition)/streamwater fluxes (meq/m^2 year or month) of dissolved chemical substances at Storgama from 1974/75 to 1990/91, based on linear regression: $y = ax + b$; y = chemical variable; x = input or output of water ; a = x-coefficient; b = constant; n = no. of observations. When $p \leq 0.05$, the linear regression is assumed to be statistical significant.

	A				**B**			
Parameter	**n**	**y = ax + b**	**r**	**sign.**	**n**	**y = ax + b**	**r**	**sign.**
Hydrogen								
Input	15	y = 0.041x + 3.92	0.91	Yes	202	y = 0.046x + 0.45	0.86	Yes
Output	14	y = 0.030x + 0.87	0.95	Yes	181	y = 0.030x - 0.15	0.91	Yes
Calcium								
Input	15	y = 0.006x - 0.94	0.74	Yes	202	y = 0.006x + 0.07	0.66	Yes
Output	15	y = 0.027x + 6.12	0.84	Yes	181	y = 0.028x + 0.44	0.90	Yes
Magnesium								
Input	15	y = 0.004x - 0.01	0.78	Yes	202	y = 0.006x - 0.08	0.74	Yes
Output	14	y = 0.011x + 1.64	0.80	Yes	181	y = 0.012x + 0.07	0.91	Yes
Sodium								
Input	8	y = 0.016x - 1.19	0.85	Yes	131	y = 0.023x - 0.53	0.72	Yes
Output	14	y = 0.026x + 4.89	0.82	Yes	181	y = 0.027x + 0.36	0.89	Yes
Potassium								
Input	7	y = 0.001x + 0.58	0.58		106	y = 0.002x + 0.04	0.66	Yes
Output	14	y = 0.003x + 0.72	0.31		181	y = 0.005x - 0.12	0.73	Yes
Ammonium								
Input	15	y = 0.024x + 1.80	0.78	Yes	202	y = 0.025x + 0.38	0.68	Yes
Output	a				a			
Aluminium								
Input								
Output	14	y = 0.014x + 1.54	0.93	Yes	181	y = -0.002x +1.65	-0.12	
Sulphate								
Input	15	y = 0.042x + 2.64	0.88	Yes	202	y = 0.047x + 0.41	0.81	Yes
Output	14	y = 0.064x + 7.80	0.89	Yes	181	y = 0.065x + 0.60	0.92	Yes
Nitrate								
Input	15	y = 0.027x - 0.11	0.85	Yes	202	y = 0.027x + 0.32	0.78	Yes
Output	14	y = 0.013x - 1.54	0.76	Yes	181	y = 0.015x - 0.25	0.79	Yes
Chloride								
Input	12	y = 0.018x + 0.09	0.72	Yes	166	y = 0.026x - 0.48	0.67	Yes
Output	13	y = 0.031x - 1.40	0.78	Yes	181	y = 0.028x + 0.34	0.85	Yes
TOC (g C/m^2time)								
Input								
Output	6*	y = 0.005x - 0.69	0.99	Yes	80	y = 0.004x + 0.006	0.97	Yes

a: less than two years of data; *: TOC measured from 1985.

Table B-3 Annual (A) and monthly (B) relationships between preciptation/runoff (mm/m^2 year or month) and precipitation (wet-deposition)/streamwater fluxes (meq/m^2 year or month) of dissolved chemical substances at Langtjern from 1974/75 to 1990/91, based on linear regression: $y = ax + b$; y = chemical variable; x = input or output of water ; a = x-coefficient; b = constant; n = no. of observations. When $p \leq 0.05$, the linear regression is assumed to be statistical significant.

	A				**B**			
Parameter	**n**	**$y = ax + b$**	**r**	**sign.**	**n**	**$y = ax + b$**	**r**	**sign.**
Hydrogen								
Input	17	$y = 0.038x + 1.13$	0.61	Yes	212	$y = 0.047x - 0.05$	0.80	Yes
Output	14	$y = 0.021x - 0.79$	0.98	Yes	187	$y = 0.022x - 0.12$	0.96	Yes
Calcium								
Input	17	$y = 0.004x + 2.11$	0.30		212	$y = 0.005x + 0.20$	0.47	Yes
Output	14	$y = 0.040x + 8.51$	0.89	Yes	187	$y = 0.047x + 0.39$	0.96	Yes
Magnesium								
Input	17	$y = 0.001x + 1.13$	0.36		212	$y = 0.002x - 0.07$	0.59	Yes
Output	14	$y = 0.012x + 2.67$	0.86	Yes	187	$y = 0.015x + 0.07$	0.96	Yes
Sodium								
Input	10	$y = 0.005x + 1.69$	0.58		141	$y = 0.007x + 0.09$	0.64	Yes
Output	14	$y = 0.018x + 3.54$	0.87	Yes	186	$y = 0.023x + 0.05$	0.97	Yes
Potassium								
Input	9	$y = 0.003x - 0.08$	0.86	Yes	140	$y = 0.003x + 0.05$	0.68	Yes
Output	14	$y = 0.002x + 1.01$	0.46		187	$y = 0.005x - 0.05$	0.86	Yes
Ammonium								
Input	17	$y = 0.031x + 1.98$	0.81	Yes	212	$y = 0.026x + 0.51$	0.63	Yes
Output	a				a			
Aluminium								
Input								
Output	13	$y = 0.017x + 1.56$	0.87	Yes	175	$y = 0.017x + 0.10$	0.94	Yes
Sulphate								
Input	17	$y = 0.035x + 9.80$	0.61	Yes	212	$y = 0.050x + 0.30$	0.75	Yes
Output	14	$y = 0.054x + 11.6$	0.80	Yes	187	$y = 0.070x + 0.15$	0.96	Yes
Nitrate								
Input	17	$y = 0.029x - 2.74$	0.83	Yes	201	$y = 0.024 + 0.36$	0.72	Yes
Output	14	$y = 0.002x + 0.37$	0.64	Yes	187	$y = 0.003x - 0.04$	0.78	Yes
Chloride								
Input	16	$y = 0.005x + 2.64$	0.50	Yes	201	$y = 0.007x + 0.18$	0.62	Yes
Output	13	$y = 0.009x + 5.29$	0.76	Yes	187	$y = 0.015x + 0.11$	0.92	Yes
TOC (g C/m^2time)								
Input								
Output	5*	$y = 0.008x + 0.038$	0.99	Yes	72	$y = 0.008x + 0.032$	0.98	Yes

a: less than two years of data; *: TOC measured from 1986.

Table B-4 Annual (A) and monthly (B) relationships between preciptation/runoff (mm/m^2 year or month) and precipitation (wet-deposition)/streamwater fluxes (meq/m^2 year or month) of dissolved chemical substances at Kaarvatn from 1980/81 to 1990/91, based on linear regression: $y = ax + b$; y = chemical variable; x = input or output of water ; a = x-coefficient; b = constant; n = no. of observations. When $p \leq 0.05$, the linear regression is assumed to be statistical significant.

	A				**B**			
Parameter	**n**	**y = ax + b**	**r**	**sign.**	**n**	**y = ax + b**	**r**	**sign.**
Hydrogen								
Input	11	$y = 0.003x + 7.12$	0.32		156	$y = 0.005x + 0.64$	0.89	Yes
Output	9	$y = 0.001x - 0.18$	0.82	Yes	132	$y = 0.001x - 0.03$	0.94	Yes
Calcium								
Input	11	$y = 0.003x + 2.47$	0.30		156	$y = 0.007x + 0.03$	0.61	Yes
Output	9	$y = 0.021x - 0.59$	0.95	Yes	132	$y = 0.018x + 0.44$	0.92	Yes
Magnesium								
Input	11	$y = 0.023x - 29.6$	0.81	Yes	156	$y = 0.021x - 0.82$	0.67	Yes
Output	9	$y = 0.018x + 7.17$	0.91	Yes	132	$y = 0.013x + 0.04$	0.87	Yes
Sodium								
Input	7	$y = 0.100x - 129.2$	0.84	Yes	120	$y = 0.102x - 4.42$	0.66	Yes
Output	9	$y = 0.065x - 27.1$	0.83	Yes	132	$y = 0.050x - 0.005$	0.88	Yes
Potassium								
Input	7	$y = 0.003x - 3.15$	0.92	Yes	108	$y = 0.003x - 0.05$	0.69	Yes
Output	9	$y = 0.003x + 0.21$	0.86	Yes	132	$y = 0.003x - 0.01$	0.93	Yes
Ammonium								
Input	11	$y = 0.005x - 0.92$	0.52		156	$y = 0.001x + 0.71$	0.08	
Output	a				a			
Aluminium								
Input								
Output	9	$y = 0.001x + 2.23$	0.50		132	$y = 0.002x - 0.02$	0.87	Yes
Sulphate								
Input	11	$y = 0.011x + 0.57$	0.62	Yes	156	$y = 0.012x + 0.57$	0.63	Yes
Output	9	$y = 0.017x - 0.69$	0.80	Yes	132	$y = 0.015x + 0.18$	0.93	Yes
Nitrate								
Input	11	$y = 0.001x + 4.65$	0.29		156	$y = 0.002 + 0.39$	0.31	Yes
Output	9	$y = 0.001x + 0.37$	0.55		132	$y = 0.001x - 0.01$	0.73	Yes
Chloride								
Input	11	$y = 0.121x - 166.0$	0.83	Yes	156	$y = 0.108x - 4.26$	0.66	Yes
Output	9	$y = 0.088x - 62.3$	0.81	Yes	132	$y = 0.056x - 0.29$	0.81	Yes
Bicarbonate								
Input	a				a			
Output	9	$y = 0.006x + 15.5$	0.34		132	$y = 0.009x + 0.72$	0.78	Yes
TOC (g C/m^2time)								
Input								
Output	5*	$y = 0.00018x + 1.63$	0.28		72	$y = 0.000x + 0.000018$	0.85	Yes

a: less than two years of data; *: TOC measured from 1986.

NIVA

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