

Seasalt Effects on the Acid Neutralizing Capacity of Streamwaters in Southern Norway

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Input of neutral salt, primarily NaCl, from sea spray is an important factor for short-term acidification of surface water, primarily in already acidified areas, because Na may substitute for H⁺ and cationic aluminium by cation-exchange reactions in the soil. By evaluating the variation of non-marine sodium (Na^{*}) separately it is possible to estimate the major effect of seasalt episodes on the neutralizing capacity (ANC) of stream water. At four long-term monitored Norwegian catchments, the Na^{*} in stream water on average explained $28 \pm 4\%$ of the monthly variations of ANC in stream water at Birkenes, and $27 \pm 3\%$, $20 \pm 2\%$ and $56 \pm 5\%$ of the correspondent variations at Storgama, Langtjern and Kaarvatn, during the respective monitoring periods. The remaining variations in acid neutralizing capacity are explained by the difference between non-marine base cations ($\Sigma\text{Ca}^*, \text{Mg}^*, \text{K}^*$) and non-marine sulphate (SO₄^{*}) and NO₃. This paper also indicates that seasalt episodes are probably of greater importance for the periodic variations in ANC of stream water than commonly recognized. During the last years, extreme seasalt episodes have occurred in southern Norway, and more frequently at winter-time, which means that seasalt inputs have played a more important role for the short-term variations of ANC in stream water the last years. This tendency is also strengthened by the fact that there has been a significant decline in the input of acidic sulphur compounds and non-marine base cations in stream water during the last 10-15 years. Because the decline in soil-derived base cations in stream water is somewhat lower than the correspondent decline of sulphate, a slowly improving ANC of stream water should be expected on long-term basis. Seasalt episodes of the same magnitude as those present during the last years, will therefore most likely cause less extreme water-chemical conditions in the years to come. Because the seasalt effect seems to be a short-term effect, there is no reason to claim that these effects may cause long-term acidification, a conclusion earlier drawn from several correspondent studies.

Introduction

When a solution of neutral salts is percolating through a soil column, it may alter the pH of the soil solution, primarily due to ion exchange processes. It may either cause a retention or release of H^+ depending of the soil pH, the bonding energy of the salt cations or anions, the salt content of the soil, and the salt concentrations of the solution (Wicklander 1975; Rosenqvist 1978; Seip and Tollan 1978) This process is relevant to surface water acidification, because a certain amount of cations in seasalts, primarily Na, may exchange for other cations in the soil. In acid soils, significant amounts of the exchanged cations will be the acid cations H^+ and ΣAl^{n+} (Wicklander 1975; Skartveit 1980; Reuss and Johnson 1985; Hindar *et al.* 1994; Lydersen 1995). Thus, the pH and alkalinity of both soil solution and surface water will be affected. An idea of the seasalt effect is obtained by evaluating the concentration of Na relative to Cl. When the equivalent ratio of Na/Cl is less than that of sea water, the concentration of non-marine Na is negative, which indicates that cation-exchange reactions have occurred.

Several cases of episodic acidification of stream water have been reported from coastal regions of Norway (Skartveit 1980; Mulder *et al.* 1990; Hindar *et al.* 1994; Lydersen 1995) and eastern United States (Kahl *et al.* 1985; Sullivan *et al.* 1988). Particularly during autumn rainstorms, when seasalt enriched precipitation is percolating acidic soils, the acidification of surface water coincided with retention of Na ions. Although episodic acidification of surface water due to NaCl deposition may occur, there is so far little support for the neutral sea salt effect being an important long-term acidifying process (Seip 1980; Sullivan *et al.* 1988). Because short-term acidification of streams and lakes often is the main cause of fish kill and other undesirable biological effects (Schofield 1977; Muniz and Leivestad 1980; Harvey and Whelpdale 1986), seasalt episodes might play an important role concerning fish kill in surface waters (Hindar *et al.* 1994).

During the last decade, relatively warm winters have occurred in southern and south-western Norway. Warm winters in large part of this region mean heavy rain episodes where the low pressures enter this part of Norway by strong western/south-western winds up to hurricane strength. Thus, the low pressures have passed over large ocean areas, and large amounts of seasalts (primarily NaCl) have therefore been transferred into the atmosphere, and transported long distance inland. At the Birkenes catchment, situated in southernmost Norway, the most extreme concentrations of acute toxic Al-forms in stream water are most frequently related to seasalt episodes during these winters (Lydersen 1995). Because the precipitation primarily falls as rain during these winters, simultaneously with a highly water-saturated catchment, it leaves the catchment relatively fast through the uppermost soil layers. In January 1993, a hurricane resulted in an extreme seasalt event, and the extreme surface water-chemistry that followed caused fish-mortality over large coastnear areas of south-western Norway (Hindar *et al.* 1994).

In this paper, the effects of short-term variations in seasalt input on the acid neutralizing capacity of stream waters (ANC) are focused on, and related to the ANC variations caused by inputs of strong acids, *i.e.* sulphuric and nitric acid.

Material and Methods

The Norwegian Monitoring Programme

The precipitation and runoff water chemistry from 4 Norwegian catchments, Birkenes, Storgama, Langtjern and Kaarvatn, are 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. 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. At Birkenes, Storgama and Langtjern, continuous monitoring data are available back to 1974/75, while at Kaarvatn, continuous data series are available from 1979/80 and on.

Description of the Catchments

The Birkenes catchment is situated southernmost Norway, about 30 km north of Kristiansand in the county of Aust-Agder (Fig. 1). The catchment area is 0.41 km². Altitude in the catchment ranges from 200-300 m and the average catchment gradient is 1:6. The granitic geology (biotite-granite) is overlain by a thin layer of soil (mean depth < 20 cm). Approximately 80% of the soil is characterized as podzol and peaty podzol, low in pH and base-saturation. The forest is basically Norwegian spruce and pine with some birch. The field vegetation basically consists of various species of heather (SFT 1980).

The Storgama catchment is situated 35 km north of the Birkenes catchment, approximately 50 km inland, in the county of Telemark (Fig. 1). The catchment area is 0.6 km². Altitude 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 basically of pine, birch and heather species (SFT 1980).

The Langtjern catchment is situated about 100 km north-west of Oslo, in the inland of the county of Buskerud (Fig. 1). The catchment area is 4.8 km². Altitude in the catchment ranges from 510-750 m. The geology is basically biotite-gneiss and

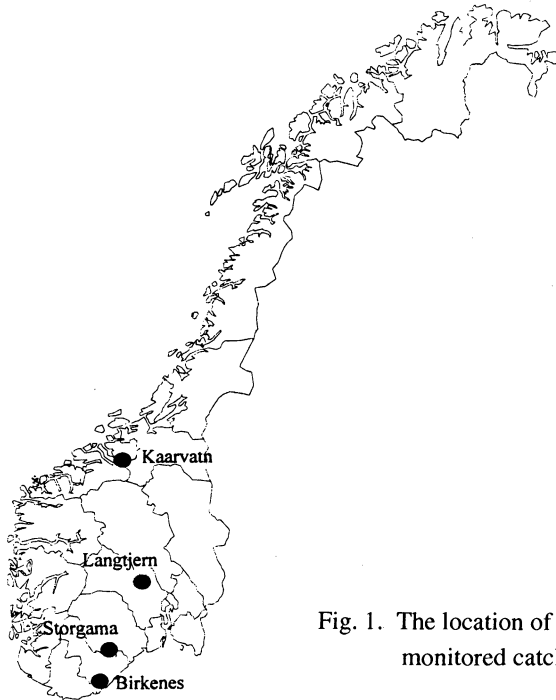


Fig. 1. The location of the four long-term monitored catchments in Norway.

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 as field vegetation (SFT 1980).

The Kaarvatn catchment is situated in the north-western part of Southern-Norway in the county of Moere and Romsdal (Fig. 1). The catchment area is 25 km². Altitude in the catchment range from 200-1,375 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. This catchment is relatively unaffected by polluted rain, *i.e.* the compounds of rain are basically of marine origin (SFT 1980).

Physico-chemical Analysis

Wet and dry-deposition samples are analysed by The Norwegian Institute for Air Research (NILU), while stream water samples are analysed by The Norwegian Institute for Water Research (NIVA).

Ca, Mg and Na were analysed by Induced Coupled Plasma atomic-emission spectrometry (ICP), while K was analysed by Atomic Absorption Spectroscopy (AAS). SO₄²⁻ and Cl⁻ were measured by ion chromatography (IC), while NO₃⁻ was measured colourimetrically (Norwegian Standard NS 4745).

Water Year and Estimates of Precipitation

To optimize the relationship between annual inputs and outputs of chemical compounds, the calendar year is 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 dependent 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 stream flow had been examined, the water-year at Birkenes and Langtjern begins on 1 June and ends 31 May, while at Storgama and Kaarvatn it starts on 1 September and ends at 31 August.

Even though precipitation and stream flow have been monitored accurately, the 4 weather stations do not necessarily represent the precipitation input to the catchments. At Kaarvatn, even though the weather station is located at the outlet of the catchment, the measured runoff is much higher than the measured precipitation input. The significant upward correction for the precipitation at Kaarvatn is due to the fact that the catchment is mountainous, whereas the rain gage is located at the low-elevation outlet. Table 1 presents the linear regressions between measured, P_m , and estimated, P_e , input of water for the respective water years (in mm), based on annual input data from the monitoring period up to 1990/91 (SFT 1992).

Table 1 - The linear regressions between measured, P_m , and estimated, P_e , input of water for the respective water years (in mm), based on annual input data from the four catchments during the monitoring period up to 1991/92 (SFT 1992)

Birkenes	$P_e = 1.13P_m - 155$	$r^2 = 0.96$
Storgama	$P_e = 1.06P_m + 103$	$r^2 = 0.95$
Langtjern	$P_e = 1.10P_m + 55$	$r^2 = 0.74$
Kaarvatn	$P_e = 1.05P_m + 728$	$r^2 = 0.86$

Definition of Terms

In runoff water, only minor amounts of ammonium and hydroxide are present, and can therefore be omitted in the ANC-calculations, as well as the concentration of bicarbonate, if the runoff water pH < 5. Omitting charge indications, we have on an equivalent basis the following relations (for negligible NH_4, HCO_3 and OH)

$$\text{Electric neutrality: } 0 = (Ca+Mg+Na+K+H+Al) - (SO_4+Cl+NO_3+A) \tag{1}$$

The acid neutralizing capacity (ANC) of runoff-water is defined as

$$ANC = (Ca+Mg+Na+K) - (SO_4+NO_3+Cl) \tag{2}$$

Thus, the ANC of acidified water primarily expresses the $\Sigma(\text{H}^+) + (\Sigma\text{Al}^{n+}) - (\text{A}^-)$, *i.e.*

$$\text{Eq. (2)} - \text{Eq. (1)} = \text{ANC} = (\text{A}) - (\text{H} + \text{Al}) \quad (3)$$

(A) is an expression for the amount of organic anions. Assuming that all the major ions incorporated in the charge balance equation are measured, the amount of (A-) ($\mu\text{eq/l}$) can be estimated, so that charge balance is obtained. The concentration of Al is in the expression the sum of positively charged Al-ions (ΣAl^{n+}), which can be estimated by the ALCHEMI-speciation programme (Schecher and Driscoll 1987, 1988).

Of the strong acid anions, Cl^- is the most mobile, usually following water through the ecosystem from precipitation to runoff, *i.e.* influx of Cl^- = efflux of chloride. In general, the major source of Cl^- is from pH-neutral seasalts. The equivalent relationships between Cl^- and base cations (Ca, Mg, Na and K) and sulphate derived from sea water are therefore used to estimate the non-marine contribution of these ions in rain and surface water. The *non-marine* supplies of base cations are always marked with asterisk, and the equivalent correction equations are

$$[\text{Ca}^{2+}]^* = [\text{Ca}^{2+}] - 0.037 [\text{Cl}^-] \quad (4)$$

$$[\text{Mg}^{2+}]^* = [\text{Mg}^{2+}] - 0.195 [\text{Cl}^-] \quad (5)$$

$$[\text{Na}^+]^* = [\text{Na}^+] - 0.856 [\text{Cl}^-] \quad (6)$$

$$[\text{K}^+]^* = [\text{K}^+] - 0.018 [\text{Cl}^-] \quad (7)$$

$$[\text{SO}_4]_* = [\text{SO}_4] - 0.103 [\text{Cl}^-] \quad (8)$$

In this paper the seasalt contributions, estimated on the basis of chloride, are taken out of the ANC calculation and defined as ANC*

$$\text{ANC}^* = (\text{Ca}^* + \text{Mg}^* + \text{Na}^* + \text{K}^*) - (\text{SO}_4^* + \text{NO}_3) \quad (9)$$

Because the organic humic material to a large extent, acts as a complex acid cation exchange resin, cation-exchange reactions will predominate in the upper organic soil horizon (Mulder *et al.* 1990). This means that base-cations and other cationic metals are able to compete with H^+ -ions for a fixed number of exchange sites, depending on factors as charge/size ratio and concentration. However, ion-exchange reactions are reversible reactions, and the exchanger exhibits low to moderate preference for one cation species compared with another (Bolt 1979), a preference that is further reduced when the temperature is low (Boyd 1970), as in soil and surface water. This means that the concentration of a cation often is more important than the type of cation concerning the possibility of taking part in ion exchange reactions. Because the concentration of marine Mg is significantly lower than Na, and the terrestrial derived Mg is much larger than the marine part, this paper primarily focuses on Na^* when evaluating the major impacts of seasalts on the ANC of surface water. Thus, Na^* and the $\text{ANC}^* - \text{Na}^*$ indicate to which extent seasalts and more terrestrial derived processes affect the acid neutralizing capacity (ANC*) in runoff water at four long termed monitored catchments in Norway.

Seasalts and Acidification

Table 2 - The annual output of Na (meq/m²yr), and the average percentage (%) contribution of Na from wet-deposition, dry-deposition and from weathering and other soil processes. The averages are only based on those water-years where both precipitation and runoff data are available, and the inputs of wet-deposition are based on estimated precipitation amounts

	Output-Na meq/m ² yr	Wet-deposition %	Dry-deposition %	Soil-Na %
Birkenes	138.4	58.6	35.8	5.6
Storgama	32.7	67.0	19.3	13.7
Langtjern	14.7	48.8	6.3	44.9
Kaarvatn	102.7		96.4	3.6

Results and Discussions

During the periods 1974/75-1991/92, on average 138.4 meq Na/m² left the Birkenes catchment by runoff every year (Table 2). By assuming no storage of Cl within the catchment during the period, and that chloride totally derives from marine sources and enters the catchments as a seasalt with the same equivalent Na/Cl-ratio as in sea water, on average 94.4% of the Na in runoff-water at Birkenes originates from seasalts, as wet-deposition (58.6%) and dry-deposition (35.8%). The remaining 5.6% of Na may therefore originate from weathering processes, but also to a certain degree from terrestrial airborne dust. Correspondingly, annually 32.7 meq Na/m² has left the Storgama catchment by runoff water during the periods 1975/76-1991/92, and on average 86.3% of Na originates from seasalts, as wet-deposition (67.0%) and dry-deposition (19.3%). The remaining 13.7% of Na derives from soil. At Langtjern, 14.7 meq Na/m² left the catchment by runoff-water every year during the period 1974/75-1991/92, and on average 55.1% of Na originates from seasalts, as wet-deposition (48.8%) and dry-deposition (6.3%), while the remaining 44.9% of Na derives from soil. At Kaarvatn, 102.7 meq Na/m² has annually left the catchment by runoff-water during the period 1980/81-1992/93, and on average 96.4% of the Na originates from seasalts, as wet- and dry-deposition (Table 2). Because the weather station at Kaarvatn is not very representative for the weather-conditions of the whole catchment, the Σ Wet-Na, Dry-Na is calculated on the basis of chloride in runoff. At the other stations wet-deposition fluxes of Na are calculated by use of measured concentrations and annual precipitation estimates (see Material and Methods). The difference between marine effluxes of Na and the wet-deposition marine influx estimates is assumed to be the annual marine dry-deposition fluxes.

As expected, the highest influxes of seasalts were found in the well-forested, coastnear Birkenes catchment, while the lowest influxes were recorded at Langtjern, the most typical inland site (Table 2, Fig. 2). It was only minor changes in the Na/Cl

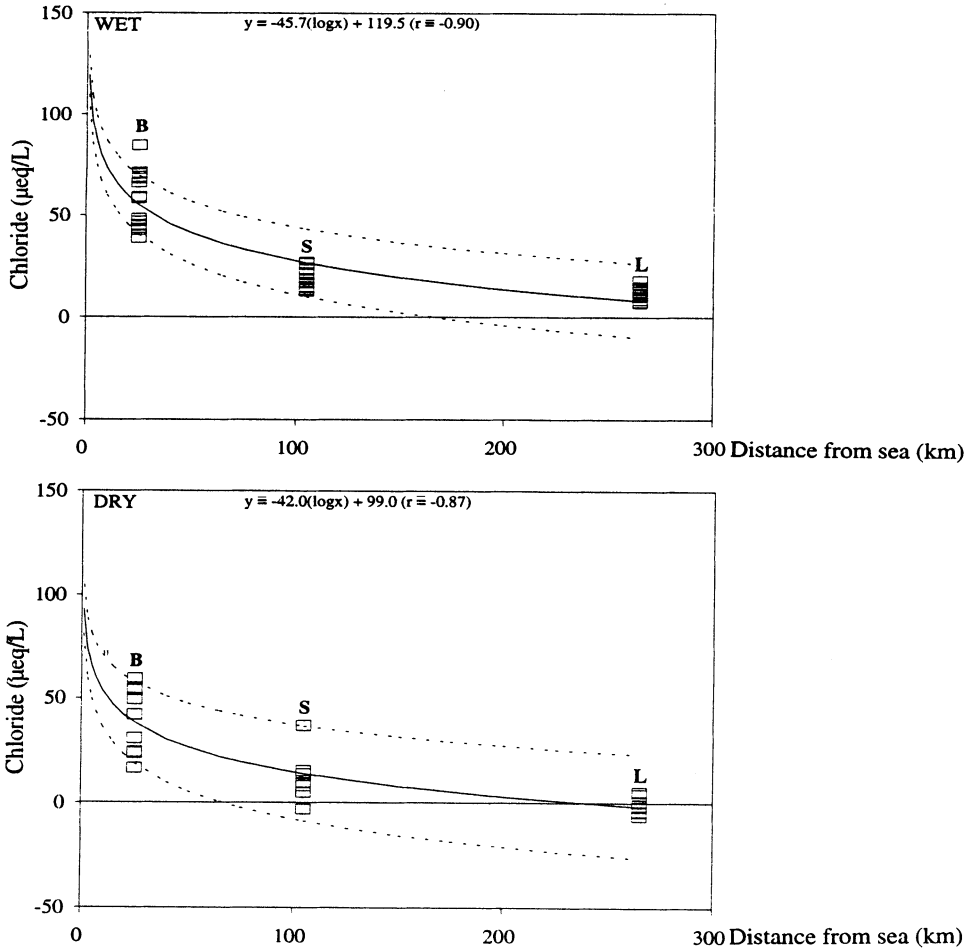


Fig. 2. The runoff water concentration of Cl from wet- and dry-deposition plotted *versus* distance from the coast, based on annual weighted concentration averages. Dry-deposition of chloride is based on mass-balance calculations, *i.e.* annual $\text{Cl}_{\text{efflux}} = \text{Cl}_{\text{influx}}$. The dotted lines indicate \pm one std. deviation of mean.

ratio regarding distance from the coast, which indicates that sea water is the major source of Na and Cl to the catchments (Sullivan *et al.* 1988). While the expected Na/Cl ratio of sea water is about 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 , respectively.

Even though almost 50% of Na in runoff at Langtjern derives from soil, for practical reasons, the ANC* is also split in two parts at this site, *i.e.* ANC*-Na* and Na*. At all four sites, more Na leaves the catchment by runoff compared with that entering the catchment by wet- and dry-deposition on the basis of annual fluxes (Figs. 3 and 4).

Seasalts and Acidification

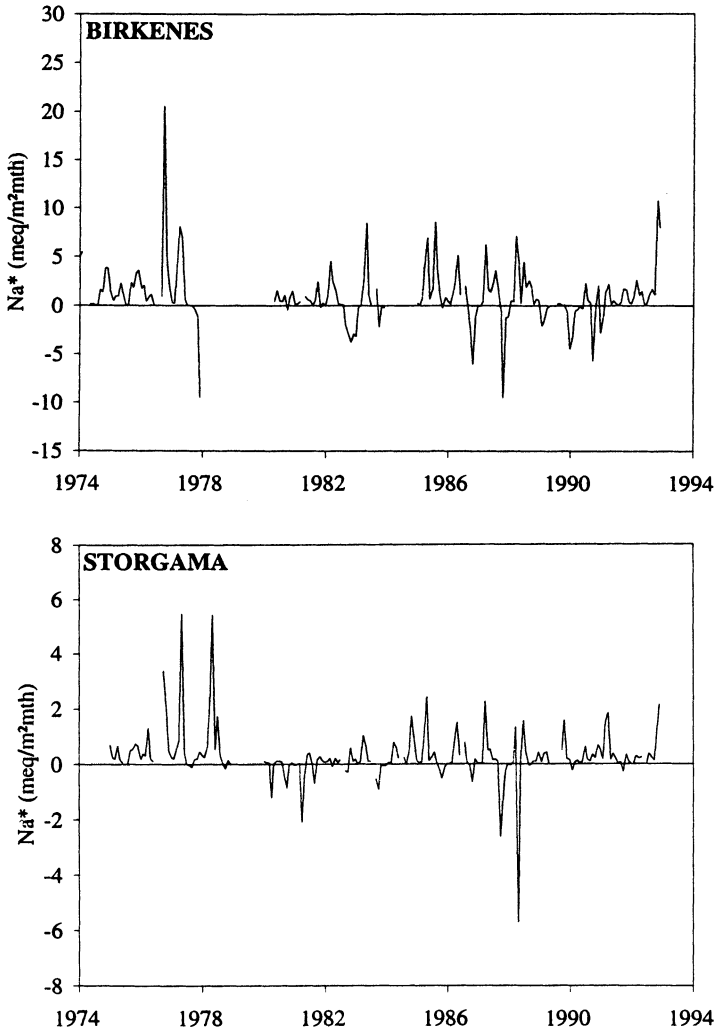


Fig. 3. Monthly fluxes of non-marine Na (Na^+) in runoff-water at Birkenes and Storgama. For the total monitoring period, 7.7 meq/m² (5.6%), 4.5 meq/m² (13.7%) of Na in runoff have annually derived from non-marine sources at Birkenes, Storgama, respectively.

During the period 1974-1993, $\text{ANC}^* - \text{Na}^+$ explained $72 \pm 4\%$ of the monthly variations in ANC^* of stream water at Birkenes, while the remaining $28 \pm 4\%$ was explained by Na^+ , since $\text{ANC}^* \equiv \text{ANC}^* - \text{Na}^+ + \text{Na}^+$. Correspondingly, $\text{ANC}^* - \text{Na}^+$ explained $67 \pm 6\%$ of the monthly variations in ANC^* , while the remaining $33 \pm 6\%$ was explained by Na^+ in runoff water at Birkenes during the period 1985-1993.

At Storgama, $\text{ANC}^* - \text{Na}^+$ explained $73 \pm 3\%$ of the monthly variations in ANC^*

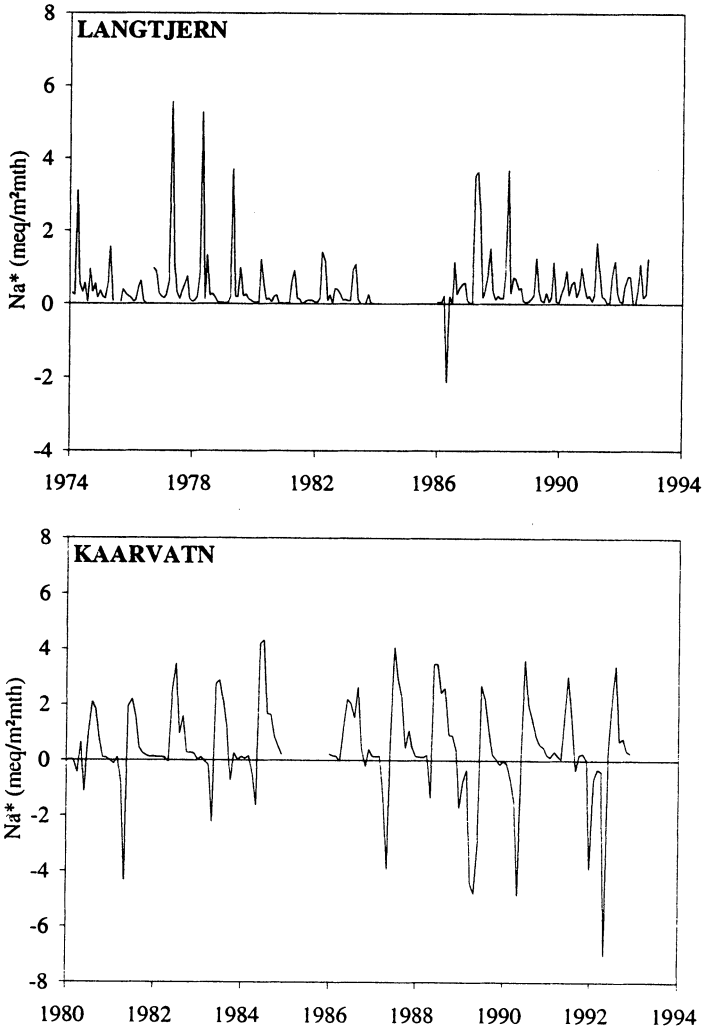


Fig. 4. Monthly fluxes of non-marine Na (Na^*) in runoff-water at Langtjern and Kaarvatn. For the total monitoring period, 6.6 meq/m^2 (44.9%) and 3.7 meq/m^2 (3.6%) of Na in runoff have annually derived from non-marine sources at Langtjern and Kaarvatn, respectively.

of stream water, while the remaining $27 \pm 3\%$ was explained by Na^* during the period 1975-1993. During the period 1985-1993, $\text{ANC}^* - \text{Na}^*$ explained $86 \pm 4\%$ of the monthly variations in ANC^* , while the remaining $14 \pm 5\%$ was explained by Na^* .

At Langtjern, $\text{ANC}^* - \text{Na}^*$ explained $80 \pm 2\%$ of the monthly variations in ANC^* of stream water, while the remaining $20 \pm 2\%$ was explained by Na^* . For the period 1985-1993, $\text{ANC}^* - \text{Na}^*$ explained $82 \pm 3\%$ of the monthly variations in ANC^* ,

while the remaining $18 \pm 3\%$ was explained by Na^* .

At Kaarvatn, ANC^*-Na^* explained $44 \pm 5\%$ of the monthly variations in ANC^* of stream water, while the remaining $56 \pm 5\%$ was explained by Na^* during the period 1980-1993. For the period 1985-1993, ANC^*-Na^* explained $40 \pm 7\%$ of the monthly variations in ANC^* , while the remaining $60 \pm 7\%$ was explained by Na^* .

By comparing the relative importance of ANC^*-Na^* and Na^* for the total monitoring periods with the last period from 1985-1992, ANC^* is getting somewhat less important during the last period. Accordingly, the seasalt influence and the subsequent mobility difference between Na and Cl (Na^*) is getting more important for the acid neutralizing capacity of stream water at the two most coastnear sites (Birkenes and Kaarvatn) during the last years. Why Na^* is so important for the acid neutralizing capacity in runoff-water at Langtjern is primarily due to the significant contribution of Na from weathering processes (45%) in this catchment (Table 2).

At Birkenes, the lowest monthly weighted ANC^* averages of stream water normally occur in March (Fig. 5). In this month the ANC^* mean is $-66.3 \mu\text{eq/l}$, while the mean values of ANC^*-Na^* and Na^* for the same month are $-77.3 \mu\text{eq/l}$ and $10.3 \mu\text{eq/l}$, respectively. At Storgama, the lowest monthly weighted ANC^* averages of stream water normally occur in April (Fig. 6), with a mean ANC^* -value of $-43.9 \mu\text{eq/l}$. During the same month, the mean values of ANC^*-Na^* and Na^* are $-50.2 \mu\text{eq/l}$ and $6.3 \mu\text{eq/l}$, respectively. At Langtjern, the lowest monthly weighted ANC^* averages normally occur in May (Fig. 7). In this month the mean ANC^* -value is $3.1 \mu\text{eq/l}$, while the mean values of ANC^*-Na^* and Na^* are $-5.5 \mu\text{eq/l}$ and $8.6 \mu\text{eq/l}$, respectively. At Kaarvatn, the lowest monthly weighted ANC^* averages normally occur in June (Fig. 8), with a monthly ANC^* mean of $10.9 \mu\text{eq/l}$, while the mean values of ANC^*-Na^* and Na^* for the same month are $7.7 \mu\text{eq/l}$ and $3.2 \mu\text{eq/l}$, respectively.

At Birkenes, the lowest monthly weighted averages of Na^* in stream water normally occur in November (Fig. 5), with a monthly mean of $-0.1 \mu\text{eq/l}$. The mean values of ANC^*-Na^* and ANC^* for the same month are $-61.8 \mu\text{eq/l}$ and $-61.9 \mu\text{eq/l}$, respectively. At Storgama, the lowest monthly weighted averages of Na^* normally occur in October (Fig. 6), with a mean Na^* -value of $0.2 \mu\text{eq/l}$, while the correspondent monthly means of ANC^*-Na^* and ANC^* are $-39.5 \mu\text{eq/l}$ and $-39.3 \mu\text{eq/l}$, respectively. At Langtjern, the lowest monthly weighted averages of Na^* normally occur in October (Fig. 7), with a monthly mean of $7.5 \mu\text{eq/l}$, while the correspondent monthly means of ANC^*-Na^* and ANC^* are $5.8 \mu\text{eq/l}$ and $13.2 \mu\text{eq/l}$, respectively. At Kaarvatn, the lowest monthly weighted averages of Na^* normally occur in April (Fig. 8), *i.e.* $-9.4 \mu\text{eq/l}$, while the mean values of ANC^*-Na^* and ANC^* for the same month are $25.6 \mu\text{eq/l}$ and $16.2 \mu\text{eq/l}$, respectively.

At all catchments, the lowest monthly ANC^* -values normally occur during spring melt, at Birkenes in March, at Storgama in April, at Langtjern in May, and at Kaarvatn in June. At Birkenes, Storgama and Langtjern, the lowest monthly Na^* -values normally occur during late autumn, in October and November. This is a period often

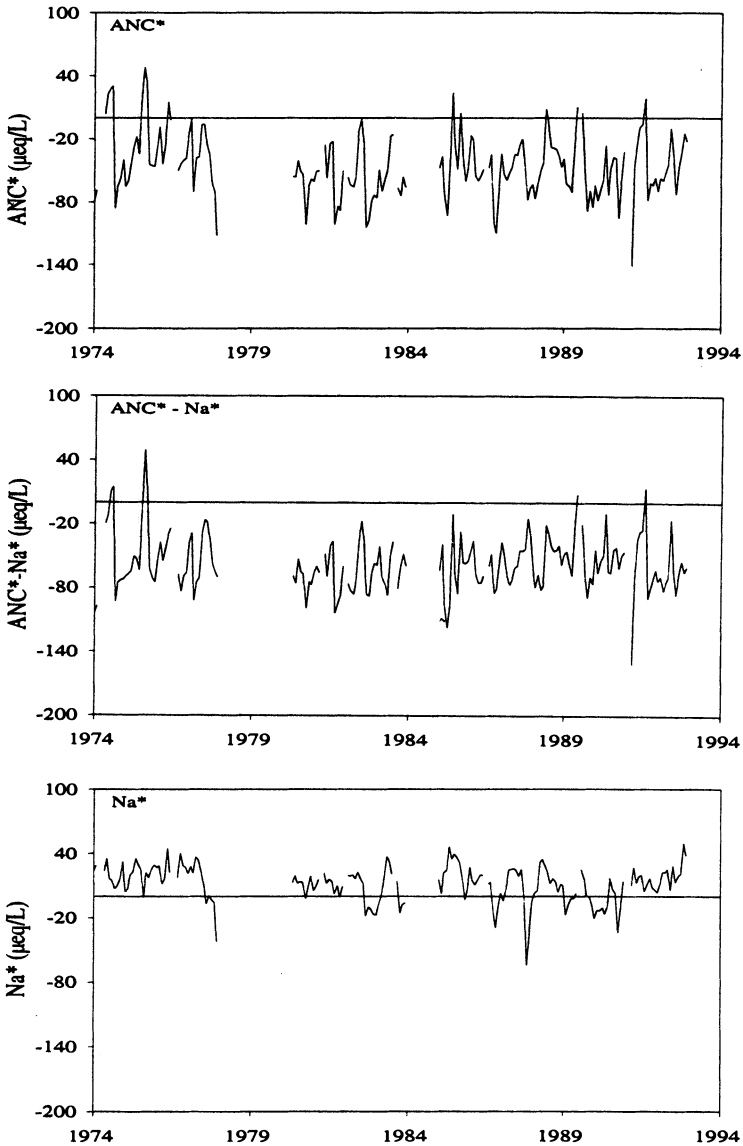


Fig. 5. Monthly weighted averages of ANC*, ANC*-Na*, and Na* in streamwater at Birkenes during the monitoring period, 1974-1993.

characterized by heavy rainfall and strong winds, and the soil is often approximately water saturated. At Kaarvatn the lowest monthly Na* values normally occur in April and May, during the initial period of spring melt. While the lowest ANC*-values at Birkenes, Storgama and Langtjern normally occur when the ANC*-Na*-values ($\Sigma\text{Ca}^*, \text{Mg}^*, \text{K}^* - \Sigma\text{SO}_4^*, \text{NO}_3$) are at the lowest, the lowest ANC*-values at Kaar-

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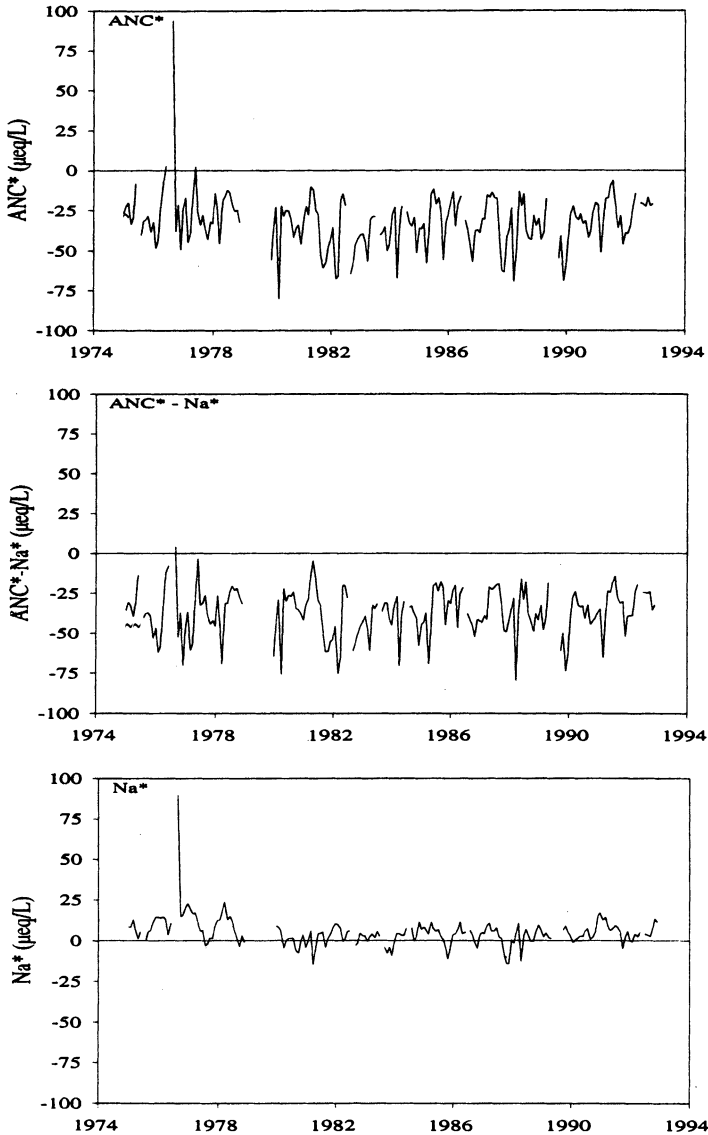


Fig. 6. Monthly weighted averages of ANC*, ANC*-Na*, and Na* in streamwater at Storgama during the monitoring period, 1975-1993.

vatn normally occur when the Na*-values are at the lowest. Another very interesting observation at Kaarvatn is that when the Na*-values normally are at the lowest, in April during the initial melting period, the ANC*-Na*-values normally are at the highest. Thus, the catchment is well protected against too severe acidic stream water episodes.

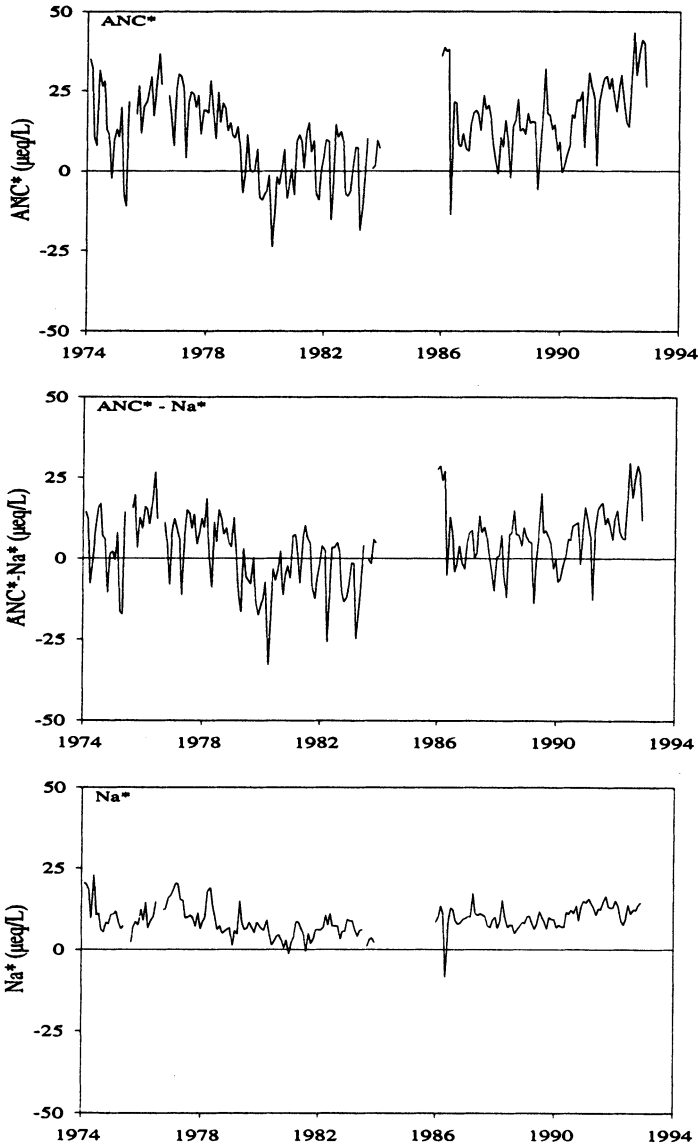


Fig. 7. Monthly weighted averages of ANC*, ANC*-Na*, and Na* in streamwater at Langtjern during the monitoring period, 1974-1993.

At the two most coastnear sites, Birkenes and Kaarvatn, the lowest recorded monthly weighted ANC*-value at Birkenes was recorded in March 1991, directly related to extreme outputs of SO₄* and NO₃ (Table 3). The lowest monthly weighted ANC*-value at Kaarvatn was recorded in May 1992, primarily related to a low Na*-value and an extreme high runoff this month (520 mm). The runoff in May

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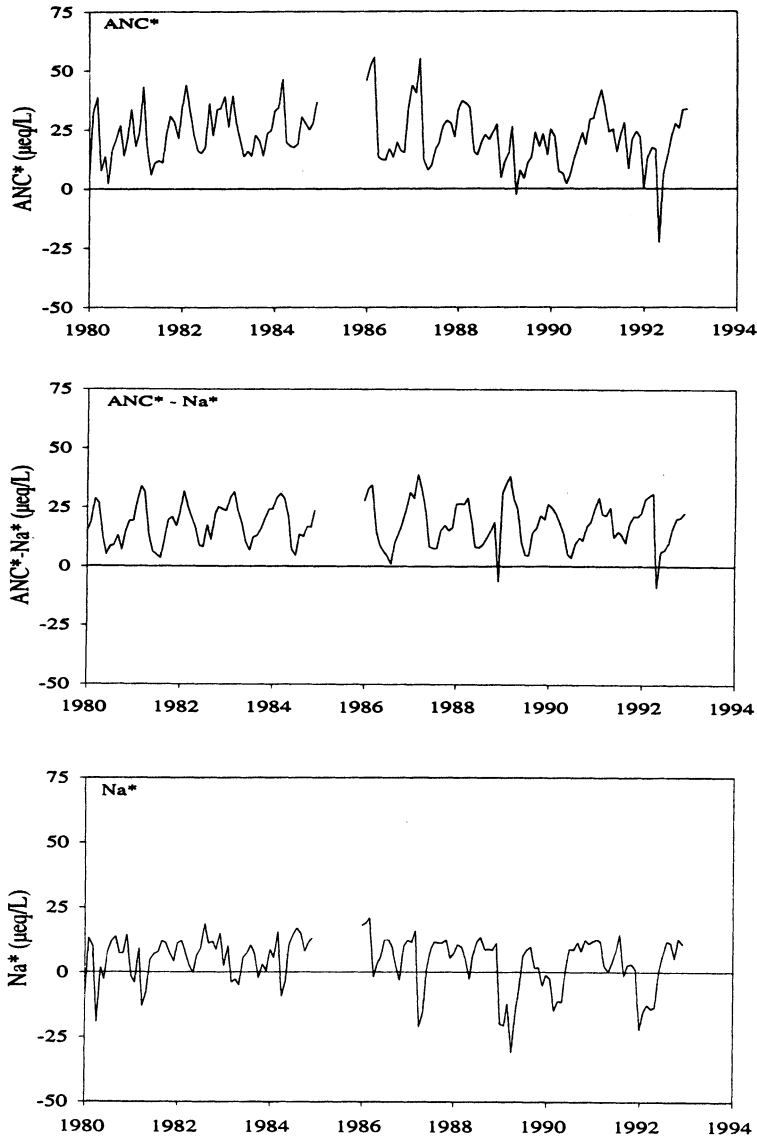


Fig. 8. Monthly weighted averages of ANC*, ANC*-Na*, and Na* in streamwater at Kaarvatn during the monitoring period, 1980-1993.

1992 was nearly 25% of total runoff from the catchment this year. 5 of the 10 lowest monthly weighted ANC*-values at Birkenes were recorded before 1985, while correspondingly 3 of the 10 lowest ANC*-values were recorded before 1985 at Kaarvatn. The lowest recorded monthly weighted Na*-value was recorded in November 1987 at Birkenes, and in April 1989 at Kaarvatn (Table 4). At Birkenes 7 of the 10

Table 3 – The monthly weighted concentrations ($\mu\text{eq/l}$) Mg^* , SO_4^* , NO_3 , ANC^*-Na^* , and Na^* for the 10 lowest monthly ANC^* -values at the two most coastnear sites during the monitoring periods, *i.e.* during 1974-1993 at Birkenes and 1980-1993 at Kaarvatn

Birkenes								
Year	Mth.	ANC^*	ANC^*-Na^*	Na^*	Ca^*	Mg^*	SO_4^*	NO_3
1991	Mar	-141.3	-151.2	9.9	45.0	1.8	145.7	57.5
1977	Dec	-112.1	-70.0	-42.1	55.3	5.6	118.0	15.5
1986	Nov	-109.9	-80.4	-29.5	38.2	-0.6	111.6	7.0
1982	Sep	-104.4	-85.9	-18.5	71.5	12.2	166.1	5.1
1980	Oct	-101.6	-99.2	-2.4	38.5	4.3	138.4	4.7
1981	Sep	-101.3	-103.5	2.3	52.8	15.3	166.8	7.4
1986	Oct	-100.6	-85.0	-15.6	43.6	7.1	129.9	8.7
1982	Oct	-97.9	-87.7	-10.2	47.4	5.6	137.4	4.0
1990	Oct	-95.4	-61.4	-33.9	45.5	-1.1	97.6	20.0
1985	Apr	-92.9	-117.3	24.4	33.3	11.1	109.3	57.9
Kaarvatn								
1992	May	-2.8	10.7	-13.5	18.5	0.3	8.0	1.8
1989	Apr	-2.6	28.4	-31.0	33.6	1.0	6.3	1.8
1992	Jan	0.4	22.5	-22.1	30.3	-0.2	7.9	0.9
1990	May	2.0	13.5	-11.5	20.7	1.2	7.9	2.4
1980	Jun	2.2	4.9	-2.7	13.1	1.2	8.0	4.6
1989	Jun	4.3	9.7	-5.4	17.0	0.9	8.9	1.0
1988	Dec	4.7	-6.4	11.1	26.7	5.8	38.9	1.7
1980	Jan	5.6	15.1	-9.6	28.8	2.1	16.5	1.4
1981	May	5.9	13.3	-7.4	25.2	1.2	15.2	0.9
1990	Jun	6.1	5.0	1.1	12.8	1.1	9.2	1.3

lowest Na^* values have been recorded after 1986, and 9 of the 10 lowest Na^* at Kaarvatn have been recorded after 1987. This indicates that seasalt episodes have been a more important factor for the surface water chemistry in coastnear sites in southern Norway during the last years. At the same time there has been a 30% decline in SO_4^* in runoff from the long-term monitored sites during the respective monitoring periods (SFT 1994). Due to this fact, seasalt episodes of the same magnitude as those displayed during the last years, most likely will cause less extreme water chemical conditions in the years to come.

Based on linear regression analyses (Table 5), there are only small changes in the ANC^* of stream water at all four catchments, but Birkenes exhibits a weak but significant decrease in ANC^* from 1974-1993, while Langtjern exhibits a weak but significant increase (Table 5). During the last period, 1985-1993, the two most coastnear sites still exhibit a decreasing trend in ANC^* , while for the more inland catchments there is a tendency of increasing ANC^* during the same period (Table 6). At Langtjern the increase in ANC^* is significant, and based on the regression

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Table 4 – The monthly weighted concentrations ($\mu\text{eq/l}$) of Ca^* , Mg^* , SO_4^* , NO_3 , ANC^* and ANC^*-Na^* , for the 10 lowest monthly Na^* -values at the two most coastnear sites during the monitoring periods, *i.e.* during 1974-1993 at Birkenes and 1980-1993 at Kaarvatn

Birkenes								
Year	Mth.	Na^*	ANC^*	ANC^*-Na^*	Ca^*	Mg^*	SO_4^*	NO_3
1987	Nov	-64.0	-78.4	-14.4	68.9	-7.8	70.3	7.2
1977	Dec	-42.1	-112.1	-70.0	55.3	5.56	118.0	15.5
1987	Dec	-38.7	-67.7	-29.0	56.4	-2.1	75.7	10.8
1990	Oct	-33.9	-95.4	-61.5	45.5	-1.1	97.6	20.0
1986	Nov	-29.5	-109.9	-80.4	38.2	-0.6	111.6	7.0
1990	Jan	-20.6	-64.2	-43.7	56.1	-3.1	88.3	14.2
1982	Sep	-18.5	-104.4	-85.9	71.5	12.2	166.1	5.1
1983	Jan	-17.5	-76.1	-58.6	46.7	1.4	101.8	5.6
1989	Feb	-17.4	-62.8	-45.4	51.6	2.7	87.8	18.4
1990	May	-16.7	-26.7	-10.0	70.6	-0.5	83.2	1.4
Kaarvatn								
1989	Apr	-31.0	-2.6	28.4	33.6	1.0	6.3	1.8
1992	Jan	-22.1	0.4	22.5	30.3	-0.2	7.9	0.9
1987	Apr	-21.0	12.4	33.4	46.4	6.3	20.6	2.1
1989	Feb	-20.5	15.0	35.5	41.2	4.1	8.5	1.6
1989	Jan	-20.0	11.3	31.3	39.0	0.6	8.5	1.3
1980	Apr	-19.3	7.7	27.0	44.6	3.0	21.9	2.2
1989	May	-16.7	7.8	24.4	25.8	2.7	5.0	1.2
1987	May	-15.4	7.8	23.2	30.8	3.3	10.7	2.3
1992	Feb	-15.4	13.1	28.5	33.4	1.9	7.1	1.8
1990	Mar	-14.9	7.4	22.3	32.5	1.6	12.2	2.0

equation ANC^* has increased by an average of $1.8 \mu\text{eq/l}$ per yr at this site from 1985-1993. Except at Kaarvatn, there is a tendency of increasing ANC^*-Na^* from 1985 to 1993 (only significant at Langtjern). The tendency of decreasing ANC^*-Na^* at Kaarvatn even during the last years is probably an effect of increased seasalt influence, which means that the non-marine (Mg^*) is very low, and that the annual amount of precipitation has been very high during the last years. The latter reduces the residence time of water and subsequently reduces the acid neutralizing capacity of the catchment. Because of the tendency of decreasing Na^* at the two most coastnear sites, especially at Kaarvatn, the ANC^* in the runoff water from these sites still exhibit decreasing trends. In addition to the tendency of increasing input of seasalts during the monitoring period, the seasalt episodes have occurred more frequently in winter-time the last years (Hindar *et al.* 1994; Lydersen 1995). This fact has largest consequences for the two most coastnear sites, Birkenes and Kaarvatn, because the winter temperature has been $> 0^\circ\text{C}$ during several of the last years. Thus, seasalt enriched precipitation more often enters the catchment by rain than by snow, which

Table 5 = Time trends ($\mu\text{eq/l}$ per yr) from 1974-1993 (1980-1993 at Kaarvatn) in the acid neutralizing capacity (ANC*), ANC*-Na* ($\Sigma\text{Ca}^*,\text{Mg}^*,\text{K}^* - \Sigma\text{SO}_4^*,\text{NO}_3$) and Na* in streamwater from the four catchments, based on linear regression analyses, by use of monthly weighted concentration averages. * means $p < 0.05$. ** means $p < 0.01$

	ANC*	ANC*-Na*	Na*
Birkenes	$y = -0.98x - 35.5$ $r = -0.18^*$	$y = -0.28x - 54.0$ $r = -0.06$	$y = -0.70x + 18.5$ $r = -0.23^{**}$
Storgama	$y = -0.26x - 29.2$ $r = -0.08$	$y = 0.12x - 38.1$ $r = 0.04$	$y = -0.38x + 8.89$ $r = -0.22^{**}$
Langtjern	$y = 0.37x + 9.57$ $r = 0.16^*$	$y = 1.14x + 2.43$ $r = 0.24^{**}$	$y = 0.06x + 8.61$ $r = 0.07$
Kaarvatn	$y = -0.39x + 24.9$ $r = -0.13$	$y = 0.02x + 18.0$ $r = 0.01$	$y = -0.40x + 6.89$ $r = -0.16$

Table 6 = Time trends ($\mu\text{eq/l}$ per yr) from 1985-1993 in the acid neutralizing capacity (ANC*), ANC*-Na* ($\Sigma\text{Ca}^*,\text{Mg}^*,\text{K}^* - \Sigma\text{SO}_4^*,\text{NO}_3$) and Na* in streamwater from the four catchments, based on linear regression analyses, by use of monthly weighted concentration averages. * means $p < 0.05$. ** means $p < 0.01$

	ANC*	ANC*-Na*	Na*
Birkenes	$y = -0.24x - 46.7$ $r = -0.02$	$y = 0.38x - 58.2$ $r = 0.03$	$y = -0.62x + 11.7$ $r = -0.08$
Storgama	$y = 0.69x - 34.3$ $r = 0.11$	$y = 0.25x - 36.5$ $r = 0.04$	$y = 0.44x - 2.23$ $r = 0.18$
Langtjern	$y = 1.80x + 9.74$ $r = 0.32^{**}$	$y = 1.14x + 2.43$ $r = 0.24^*$	$y = 0.66x + 7.30$ $r = 0.39^{**}$
Kaarvatn	$y = -1.29x + 25.7$ $r = -0.21^*$	$y = -0.21x + 18.9$ $r = -0.04$	$y = -1.08x + 6.88$ $r = -0.20$

means that precipitation is able to leave the catchment relatively fast by surface and subsurface runoff. Large amounts of Na are therefore able to cation-exchange for H⁺ and/or cationic Al in the uppermost soil horizons. Despite the tendency of increasing ANC*-Na* in runoff-water during the period 1985-1993 (Table 6), the tendency of decreasing Na* at the two most coastnear sites, Birkenes and Kaarvatn, have totally caused a weak worsening rather than an improvement of ANC* in these stream waters. A decrease in Na* in runoff water, however, means that the base saturation of the soil is temporarily improved, because sodium is retained in the catchment. At all four sites, there are tendencies of higher declines in the sulphate concentrations in runoff water compared with the correspondent declines in base-cations (SFT 1994). That the base cations tend to decline with a somewhat slower rate than sulphate, means that the base cations are »strengthening« their position *versus* sulphate. Because there are minor changes in the concentration of nitrate during the same period, this may indicate an improvement, not only for the ANC in runoff-waters, but also for the base-cation status of the soil, in the long run. The weak improvement in base cation status ($\Sigma\text{Ca}^*, \text{Mg}^*, \text{K}^*$) *versus* strong acid anions ($\Sigma\text{SO}_4^*\text{NO}_3$) during the last years, may therefore be a signal of a slowly improving surface-water chemistry in Southern-Norway. The seasalt episodes, will continue to cause severe short-term water-chemical conditions as far as the aquatic biology of acidified, coastnear areas are concerned. However, if the weak tendency of improving acid neutralizing capa-

city of surface waters continues, seasalt episodes of the same magnitude as during the last years, will probably result in less extreme water-chemical conditions in the years to come.

The presented work shows that sea-salt inputs are probably of greater importance for the periodic variations in ANC of stream water than commonly recognized. In other words seasalt episodes may be a major cause of many harmful water chemical episodes. The influence seems to be particularly strong during late autumn and winter if the temperature is too high for a long-lasting snow pack to accumulate. Three factors seem to be of major importance for periodic low ANC values of stream water: sulphate concentration, discharge (or water pathways) and sea-salt input. Since the two last factors are highly correlated, the individual importance is more difficult to establish with certainty.

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