

## Relationships between Precipitation Chemistry, Hydrology, and Runoff Acidity.

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High precipitation amounts of strongly varying ionic composition make the western parts of southern Norway well-suited for studies of certain relationships between precipitation chemistry, hydrology, and runoff acidity. Ions from sea-spray are the predominant ions in precipitation in these areas. The remaining ions are almost exclusively acidifying compounds ( $\text{H}^+$ ,  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ), negatively correlated to the sea-spray ions.

Hydrochemical observations during 5 years confirm that  $\text{Cl}^-$  and, to a considerable extent, also  $\text{SO}_4^{2-}$  move rather easily through the catchments, while  $\text{NO}_3^-$  is strongly adsorbed. The acid top soil tends to lead to acid surface runoff, while water penetrating deeper mineral soils becomes enriched in  $\text{Ca}^{2+}$  and depleted in  $\text{H}^+$ , resulting in a high correlation between runoff acidity and runoff rate. The short-term variations in runoff acidity are thus governed largely by runoff rate and by atmospheric deposits of  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ . In this particular precipitation climate this yields in fact a negative short-term correlation between precipitation acidity and runoff acidity.

A long-term acidification, indicated by declining fish populations, does probably arise from a  $\text{SO}_4^{2-}$ -increase in runoff (caused by increased atmospheric deposition), and from a change in soil properties (caused by acid precipitation, and possibly also by changed vegetation).

### Introduction

Acidification of freshwater ecosystems, with detrimental consequences to aquatic life, has during the last decades been observed in several areas in the world. Considering the pattern of acid precipitation and the bedrock in the areas, the

picture nicely supports the hypothesis that acid precipitation is the dominant source of acidification on a regional basis (Likens et al. 1979).

The pH of freshwaters is, however, a result of complex interactions between air, soils, vegetation, and all ionic components in the precipitation, and the processes involved in the acidification are not fully understood. Mohn et al. (1980) report on a statistical analysis of hydrochemical data limited to precipitation amount and concentrations of  $H^+$ ,  $Ca^{2+}$ ,  $NO_3^-$  and  $SO_4^{2-}$ . Although they found that  $H^+$  and  $SO_4^{2-}$  in small Norwegian lakes were significantly correlated *spatially* to precipitation quality, and that »precipitation quality can explain some of the observed changes in the lakes«, they conclude that the changes in  $H^+$  concentration in lakewater from year-to-year were »not significantly correlated to any one precipitation parameter.« Rosenqvist (1978) stresses the importance of runoff hydrology and claims that »the greater part of the acidity in freshwaters is the result of ion-exchange reactions in raw humus in the soil profiles of the catchment areas«, and that the buffering capacity and buffer level of the humus layers have »changed considerably during the last century due to activities such as forestry and agriculture as well as changes in animal husbandry.« From studies both in the laboratory and in the field Njøs (1978), Skartveit and Gjessing (1979), and Seip (1980) emphasize the importance of atmospheric depositions of mobile anions like  $SO_4^{2-}$  and  $Cl^-$  for the runoff acidity from catchments where the base saturation of the soils is low.

The present paper summarizes 5 years of hydrochemical observations in small pristine catchments at the western coast of Norway, where precipitation amounts are high and the ionic composition of the precipitation varies strongly, i.e., an area particularly well-suited for studying certain relationships between the ionic composition of precipitation and runoff.

## Area Descriptions

The 3 catchment areas, Botnane (3.4 km<sup>2</sup>, 180-650 m a.s.l.), the upper part of Breidvikdalen (1.8 km<sup>2</sup>, 295-695 m a.s.l.), and Dyrtdalen (3.3 km<sup>2</sup>, 438-806 m a.s.l.) are located approximately 30 km east of the coast-line (Fig. 1). Climate and hydrology are highly influenced by the moist and mild westerlies and southwesterlies of the North Atlantic, and the average runoff is 3000-3500 mm yr<sup>-1</sup>.

The bedrock in Botnane and Breidvikdalen is basal gneisses of Caledonian structure, while Dyrtdalen is located on anorthosite and mangerite (Holtedal and Dons 1960). This difference contributes to more acid soils at the two former sites than at the latter one. Both in Botnane and in Breidvikdalen the indigenous populations of brown trout have been almost wiped out during the last decades, while the lake in Dyrtdalen is still over-populated by brown trout.

In Botnane and Breidvikdalen recent changes in agriculture, cattle manage-

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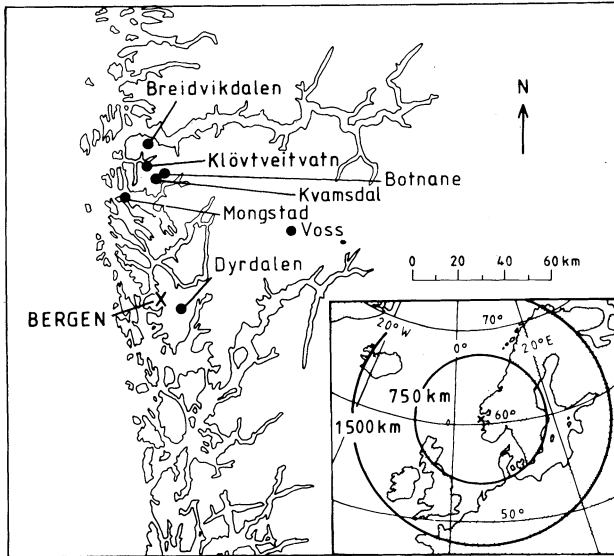


Fig. 1. Map of the western coast of Norway showing localities mentioned in the text. Insert: Distances from Bergen.

ment, and forestry have led to a forest regeneration during the last decades (e.g. Sundve 1977). Inspection of aerial photographs reveals that a rapid invasion of birch into former heath vegetation is going on, and in some areas a dense, but young canopy is being established (A. Skogen pers. comm.). These ecosystems are thus probably not exactly in steady state for the time being. Although neither the direction nor the magnitude of the corresponding changes in runoff acidity is obvious, the relevance of deviations from steady state in the context of soil acidity is generally accepted (Malmer 1976). In Dyrdalen extensive grazing has prevented any forest regeneration.

### Data Collection

The station at Botnane was in operation from July 1974 to August 1976, the station at Breidvikdalen from Nov. 1976 to June 1979, and the station at Dyrdalen from September 1977 to June 1979. Precipitation was collected in bulk collectors (made of polyethylen) on a weekly and partly on a daily basis. During the warm season evaporation from the collectors was prevented by leading the precipitation from a funnel into a storage bottle, while open collectors were used during winter. Runoff samples were taken from the outlet brooks once a week and more often for some periods. Precipitation and runoff samples were transferred to rinsed polyethylen bottles and sent to the laboratory for chemical analyses within a

couple of weeks at most. Interlaboratory comparisons, a close agreement between measured and calculated conductivity, and a close balance between anions and cations in precipitation samples all indicate that all ions of significance were measured and that the accuracy of the analyses is within a few percent (Skartveit et al. 1980).

Runoff amount was measured from Dyrdalen from December 1977, while no runoff measurements were made at the two other sites. The elevation range of the Breidvikdalen catchment is, however, so close to that of the nearby catchment of Klövtveitvatn (400-637 m a.s.l.) that runoff data from this latter site are used for the calculation of weighted mean values in Breidvikdalen. From Nov. 1976 to June 1979 the average runoff from the catchment of Klövtveitvatn was  $3,630 \text{ mmyr}^{-1}$ . By adding an estimated evaporation of  $300 \text{ mm yr}^{-1}$  (Forsman 1976) one obtains an average precipitation of  $3930 \text{ mm yr}^{-1}$ , while the corresponding measured precipitation at the two neighbouring stations (Fig. 1) Kvamsdal (75 m a.s.l.) and Breidvikdalen (295 m a.s.l.) were only 61% and 67% of this value, respectively. These rather significant differences are explained from limited collection efficiency of the unshielded precipitation gauges at Kvamsdal and Breidvikdalen, and from local differences in precipitation rate, due partly to differences in elevation. That both of the mentioned factors actually do contribute is indicated by the fact that the precipitation measured at a similarly exposed site (440 m a.s.l.) in Dyrdalen (Table 1) makes up 85% of measured runoff plus estimated evaporation ( $300 \text{ mm yr}^{-1}$ ), indicating a bulk collection efficiency of the precipitation gauges in the range 80-90% rather than in the range 60-70%. In addition, precipitation was measured and analysed on a daily basis at several sites in the neighbourhood of these catchments. Kvamsdal provides the most extensive (5 years) and complete data series (the only station where Na was analysed in precipitation).

## Results and Discussion

### Precipitation Chemistry

Weighted annual mean concentrations of ions in the precipitation at the investigated catchments are given in Table 1.

$\text{Cl}^-$  is the predominant anion. Strong onshore surface winds produce high  $\text{Cl}^-$  concentrations, while the direction of the 850 mb trajectories plays a secondary role. Given the surface wind direction and the precipitation amount, the average  $\text{Cl}^-$  concentration in daily samples from Kvamsdal actually doubles by each  $2 \text{ m sec}^{-1}$  increase in wind speed measured 10 m above ground at Mongstad (Skartveit et al. 1980), nicely in agreement with observations made by Tsunogai et al. (1972) at Hachijojima in the Pacific Ocean. This corroborates the fact that  $\text{Cl}^-$  in these coastal areas mainly derives from sea-spray aerosols transported from neighbour-

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Table 1 – Weighted annual mean ionic concentration ( $\mu\text{eq l}^{-1}$ ) in precipitation and runoff at Botnane (BO), Breidvikdalen (BR), and Dyrdalen (DY) for 4 different years numbered as follow:

1 = July 1974 – June 1975; 2 = July 1975 – June 1976;  
4 = July 1977 – June 1978; 5 = July 1978 – June 1979.

	Precipitation					Runoff <sup>c</sup>				
	BO <sup>1</sup>	BO <sup>2</sup>	BR <sup>4</sup>	BR <sup>5</sup>	DY <sup>5</sup>	BO <sup>1</sup>	BO <sup>2</sup>	BR <sup>4</sup>	BR <sup>5</sup>	DY <sup>5</sup>
NO <sub>3</sub> <sup>-</sup>	12	10	18	10	12	6	5	5	5	5
SO <sub>4</sub> <sup>2-</sup>	36	41	49	45	46	42	44	47	44	45
Cl <sup>-</sup>	102	150	110	145	143	127	141	115	166	141
Anions	149	200	178	200	202	175	190	166	214	190
NH <sub>4</sub> <sup>+</sup>	11	10	15	11	15	2 <sup>a</sup>	2 <sup>a</sup>	2	2	1
H <sup>+</sup>	31	26	36	24	29	21	23	18	22	5
K <sup>+</sup>	3	4	2	4	3	4	5	3	5	11
Na <sup>+b</sup>	87	128	95	124	123	112	119	104	136	113
Mg <sup>2+</sup>	26	32	23	30	30	36	35	28	37	39
Ca <sup>2+</sup>	7	8	6	8	7	18	14	13	15	36
Al <sup>3+c</sup>	0	0	0	0	0	12	13	10	15	5
Cations	165	208	178	202	208	206	210	177	232	210
Water (mm)	3195	3609	2910	2763	3050	–	–	3712 <sup>d</sup>	4111 <sup>d</sup>	3305

a. Estimated.

b. Estimated in precipitation from Cl<sup>-</sup> by seawater proportion.

c. Arithmetic mean concentrations for BO<sup>1</sup> and BO<sup>2</sup>.

d. Kløvtveitvatn (runoff exceeds precipitation – see text).

e. Al counted as Al<sup>3+</sup> and assumed negligible in precipitation.

ing ocean and coast-line areas. Both graphical methods and multiple linear regression analysis indicate that the sea-spray contribution of SO<sub>4</sub><sup>2-</sup> can be estimated (equivalent basis) to within better than 5% as  $[\text{swSO}_4^{2-}] = 0.103 \cdot [\text{Cl}^-]$  ( $[\text{SO}_4^{2-}]/[\text{Cl}^-] = 0.103$  in sea-water). Trajectories based on 850 mb wind indicate that air masses from the highly industrialized European countries yield high concentrations of excSO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup>, while the local surface winds play only a secondary role ( $[\text{excSO}_4^{2-}] = [\text{SO}_4^{2-}] - [\text{swSO}_4^{2-}]$ ). These patterns result in high correlations between [NO<sub>3</sub><sup>-</sup>] and [excSO<sub>4</sub><sup>2-</sup>] ( $0.6 \leq r \leq 1.0$  on a daily basis) in this area, while both these ions are negatively correlated with [Cl<sup>-</sup>] ( $-0.4 \leq r < 0$ ).

Multiple linear regression analysis on 5 years of daily precipitation data from Kvamsdal reveals that, in a statistical sense, [NH<sub>4</sub><sup>+</sup>] and [H<sup>+</sup>] are coupled solely to [excSO<sub>4</sub><sup>2-</sup> + NO<sub>3</sub><sup>-</sup>], [Na<sup>+</sup>] and [Mg<sup>+</sup>] are coupled solely to [Cl<sup>-</sup> + swSO<sub>4</sub><sup>2-</sup>], while [Ca<sup>2+</sup>] and [K<sup>+</sup>] are coupled to both these anionic contributions. The computed partial »sea-spray« regression coefficients were (with the [cation]/[Cl<sup>-</sup> + swSO<sub>4</sub><sup>2-</sup>]

ratios in surface sea-water in parenthesis).  $\text{Na}^+$  : 0.741 (0.778);  $\text{Mg}^{2+}$  : 0.185 (0.177);  $\text{Ca}^{2+}$  : 0.039 (0.034);  $\text{K}^+$  : 0.019 (0.0165). It thus seems plausible that also the sea-spray contribution of metal cations can be estimated to within a few percent from the  $\text{Cl}^-$ -content. The actual deviations between regression coefficients and sea-water mixing ratios result in fact partly from the limited accuracy of the chemical analyses at high concentrations. For example for  $\text{Cl}^-$ -concentrations less than  $7 \text{ mg l}^{-1}$  (88% of the observations) the regression equation between  $[\text{Na}^+]$  and  $[\text{Cl}^-]$  deviates less than 1% from the sea-water mixing ratio, and the individual deviations are similar to the random analytical errors as inferred from interlaboratory comparisons. It is therefore reckoned quite safe to estimate  $[\text{Na}^+]$  in precipitation from the measured  $\text{Cl}^-$ -content and the sea-water mixing ratio in cases when  $\text{Na}^+$  is not analysed.

At the coastal stations in Table 1 [ $\text{excSO}_4^{2-} + \text{NO}_3^-$ ] accounts on average for 23% of the anions, while  $[\text{NH}_4^+ + \text{H}^+]$  and [ $\text{excCa}^{2+} + \text{excK}^+$ ] account for 22% and 1.6% of the cations, respectively. These percentages generally rise as all ionic concentrations decrease with increasing distance from the coast. Thus, the weighted annual mean concentration of acidifying compounds at Voss (Fig. 1 – average precipitation about  $1100 \text{ mm yr}^{-1}$ ) was 60-65% of that at the coastal stations, while the corresponding percentage for seaspray ions was only 38-40% (Skartveit et al. 1980). Since onshore winds prevail during precipitation events this difference demonstrates that sea-spray debris, existing mainly as comparatively large particles in the very lowest atmospheric layers, is more rapidly diluted by scavenging and vertical mixing than are long range transported sulphur and nitrogen compounds, which are generally distributed in the form of smaller particles and gases through deeper layers of the atmosphere. The mean ratios [ $\text{excSO}_4^{2-}$ ] : [ $\text{NO}_3^-$ ] : [ $\text{H}^+$ ] : [ $\text{NH}_4^+$ ] are 2.4 : 1.0 : 2.3 : 1.0, which are well in agreement with what is generally found in precipitation in southern Norway (Dovland et al. 1976).

Precipitation is highly variable, and a substantial part of the total annual wet deposition of ions occurs on a few days, often referred to as episodes (OECD 1977). For each one of 5 years (200-240 precipitation days per year) daily values of precipitation amounts and wet deposition of ions at Kvamsdal were listed in order of descending magnitude. Cumulative totals of deposition, given in percent of the respective annual total, were then prepared. The average cumulative totals of precipitation amount and wet deposition of  $\text{Cl}^-$  and  $\text{excSO}_4^{2-}$  are plotted in Fig. 2. It is seen that as much as 30% of the annual deposition of  $\text{Cl}^-$  occurs, on the average, on 5-6 episode days, while it takes, on an average, about 10 episode days to deposit 30% of the annual  $\text{excSO}_4^{2-}$ -deposition. Only about 19% of the annual precipitation amount falls, as an average, on the 10 days with highest precipitation amount. The coefficients of variance (standard deviation/mean value) of the 5 annual values were 0.43 for wet deposition of  $\text{Cl}^-$ , 0.21 for wet deposition of  $\text{excSO}_4^{2-}$ , and 0.29 for precipitation amount. Sea-spray thus contributes both the greatest and the most variable part of the wet deposition of ions in this area, and the variation in deposition

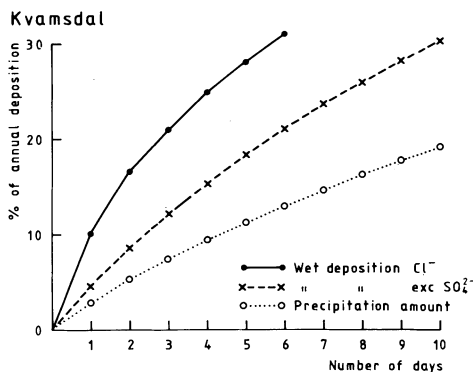


Fig. 2. Average (June 1974-July 1979) cumulative distributions of daily values of precipitation amount, wet excSO<sub>4</sub><sup>2-</sup> deposition, and wet Cl<sup>-</sup> deposition during one year at Kvamsdal. The distributions were prepared after ranking each one-year series of daily values in order of descending magnitude.

is therefore dominated by the variation in sea-spray deposition.

The correlations between precipitation amount and concentrations of ions are negative. Given the winds, the concentrations of excSO<sub>4</sub><sup>2-</sup> and Cl<sup>-</sup> in daily samples from Kvamsdal are both, on an average, halved by a four to tenfold increase in precipitation amount, reasonably consistent with previously reported relationships between precipitation amount and SO<sub>4</sub><sup>2-</sup>-concentration (Scott 1978). This mainly reflects that higher precipitation amounts in general are associated with deeper cloud layers where the air rises to higher levels, resulting in an increase in precipitated water per unit mass of air. Since wet removal is a very effective process the corresponding increase in contaminants scavenged from the same mass of air is effectively limited by the rapid depletion of remaining contaminants.

The precipitation regime is characterized by heavy rainfall during September-November. The weighted concentration of sea-spray in precipitation is high during the 8 rather windy months September-April, and smaller during May-August (Fig. 3). The concentration of acidifying compounds has a spring maximum when the precipitation rate is at minimum. The [NO<sub>3</sub>]/[excSO<sub>4</sub><sup>2-</sup>] ratio varies more or less regularly between a late winter maximum 0.5-0.6 (February-March) and an early summer minimum 0.3 (May-June), while the [NH<sub>4</sub><sup>+</sup>]/[NO<sub>3</sub>] ratio varies from 0.4-0.6 in December-February and up to 1.2 in May-July. A similar pattern was observed during 1963-1974 at the Hubbard Brook Experimental Forest (44°N, 72°W) where the [NO<sub>3</sub>]/[excSO<sub>4</sub><sup>2-</sup>] ratio varied in an approximately sinusoidal manner between 0.78 in February and 0.26 in July, and the [NH<sub>4</sub><sup>+</sup>]/[NO<sub>3</sub>] ratio varied between 0.3-0.4 in November-March and 0.6-0.7 in July-August (Likens et al. 1977). These seasonal variations are partly explained from varying emissions, e.g. enhanced biological NH<sub>3</sub>-releases during summer (Lenhard and Gravenhorst 1980) and increased anthropogenic emissions of NO<sub>x</sub> and sulphur compounds during winter (Semb 1978). Moreover, the mentioned ions descend by somewhat different chemical pathways through the atmosphere, and the various pathways are differently affected by the pronounced seasonal variations in the atmospheric environment.

### Chemical Budgets

In these areas neither the rocks nor the soils provide a significant primary source of  $\text{Cl}^-$ , and  $\text{Cl}^-$  is not accumulated in sizeable quantities within these ecosystems. Over sufficiently long periods, the ratio  $Q^{\text{Cl}}/A^{\text{Cl}}$  between runoff and atmospheric depositions therefore equals unity, and the corresponding ratio for an arbitrary ion  $x$  can be written

$$\frac{Q^x}{A^x} = \frac{Q^x/A^x}{Q^{\text{Cl}}/A^{\text{Cl}}} = \frac{q^x/p^x}{q^{\text{Cl}}/p^{\text{Cl}}} \frac{1+d^{\text{Cl}}}{1+d^x} \approx \frac{q^x/p^x}{q^{\text{Cl}}/p^{\text{Cl}}} = w \quad (1)$$

where  $q$  and  $p$  are measured mean concentrations in runoff and precipitation, and  $d$  is the ratio between dry deposition (strictly, that part of the dry deposition which is not already included in the wet deposition data) and wet deposition. Ions like  $\text{Na}^+$  and  $\text{Mg}^{2+}$ , which originate mainly from sea-spray in the same way as does  $\text{Cl}^-$ , have a dry/wet ratio very close to that of  $\text{Cl}^-$ , so that the ratio  $(1+d^{\text{Cl}})/(1+d^x)$  equals unity. Ions that originate from other sources and which are also linked to gas phase reactions, may well have a dry/wet ratio significantly different from that of  $\text{Cl}^-$ . The ratio  $(1+d^{\text{Cl}})/(1+d^x)$  may nevertheless be close to unity, provided the dry/wet ratios are both small. According to OECD (1977) the dry deposition of excess sulphur in this area may be estimated to  $1.0 \text{ gSO}_4^{2-}\text{m}^{-2}\text{yr}^{-1}$ , which, compared to the wet deposition data in Tab. 1, yields a dry/wet ratio for  $\text{excSO}_4^{2-}$  of between 0.20 and 0.25. For our purposes this ratio is rather on the big side since part of the dry deposition is already included in our wet deposition data (bulk collectors) and since the precipitation amounts are biased towards the lower side due to limited collection efficiency of the precipitation gauges.

Neglecting both dry deposition and changes in chloride storage, the annual evaporation  $E$  is given from precipitation amount ( $P$ ) and  $\text{Cl}^-$ -concentrations by

$$E = P \left( 1 - \frac{P^{\text{Cl}}}{q^{\text{Cl}}} \right) \quad (2)$$

On the assumption that the bulk collection efficiency of the precipitation gauges is 0.85, as indicated by the data from Dyrdaalen, (2) yields an average evaporation of  $200 \text{ mm yr}^{-1}$  (standard deviation  $390 \text{ mm yr}^{-1}$ ) for the 5 budget years in Table 1. During the same period duplicate collection and analysis of precipitation at Kvamsdal showed 5% higher weighted mean  $\text{Cl}^-$ -concentration and 10% higher  $\text{excSO}_4$ -concentration in weekly samples than in daily samples, presumably due mainly to dry deposition into the weekly samples during dry spells. By correcting for this (reducing  $p^{\text{Cl}}$  in (2) by 5%) one obtains an average evaporation of  $350 \text{ mm yr}^{-1}$  (standard deviation  $370 \text{ mm yr}^{-1}$ ). The unrealistically high standard deviations stress the limited accuracy, but the low mean evaporation estimate ( $200 \text{ mm yr}^{-1}$  is probably on the small side of the actual evaporation rate) does confirm that the part of the chloride dry deposition that is not already included in our weekly precipitation samples, is small compared to the measured wet deposition. It thus



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Table 2 – Chloride-scaled output:input ratios (w) computed from Tab. 1 by eq (1), together with the net contributions to the ionic composition of runoff from sources/sinks within the catchments – expressed as  $\mu\text{eq}$  per 1 runoff water by the formula  $(1-1/w)^x$ .

	w = output:input					Sources (+)/Sinks (-) ( $\mu\text{eq}$ per 1 runoff water)				
	BO <sup>1</sup>	BO <sup>2</sup>	BR <sup>4</sup>	BR <sup>5</sup>	DY <sup>5</sup>	BO <sup>1</sup>	BO <sup>2</sup>	BR <sup>4</sup>	BR <sup>5</sup>	DY <sup>5</sup>
NO <sub>3</sub> <sup>-</sup>	.42	.58	.24	.41	.38	- 9	- 4	-14	- 7	- 7
SO <sub>4</sub> <sup>2-</sup>	.94	1.14	.92	.85	.98	- 3	5	- 4	- 8	- 1
Cl <sup>-</sup>	1.0	1.0	1.0	1.0	1.0	0	0	0	0	0
Anions	.94	1.01	.90	.94	.96	-11	2	-18	-14	- 8
NH <sub>4</sub> <sup>+</sup>	.12	.18	.11	.13	.10	-12	- 8	-14	-11	-13
H <sup>+</sup>	.55	.93	.49	.81	.17	-17	- 2	-19	- 5	-23
K <sup>+</sup>	1.17	1.37	1.10	.97	3.31	.6	1.3	.3	-0.1	8
Na <sup>+</sup>	1.03	.98	1.05	.95	.93	3	- 2	5	- 7	- 9
Mg <sup>2+</sup>	1.10	1.17	1.16	1.06	1.31	3	5	4	2	9
Ca <sup>2+</sup>	2.11	1.86	1.90	1.77	5.00	10	6	6	7	29
Al <sup>3+</sup>	$\infty$	$\infty$	$\infty$	$\infty$	$\infty$	12	13	10	15	5
Cations	1.00	1.07	.96	1.00	1.03	0	14	- 8	1	6

seems warranted that, due to frequent and heavy precipitation, the dry/wet ratios in this area are small enough to make the approximation  $(1+d^{\text{Cl}})/(1+d^x) = 1.0$  sufficiently realistic for our purposes.

The precipitation climate is fairly similar at Botnane, Breidvikdalen, and Dyr-dalen (Table 1). Nevertheless, due to differences primarily in geology there is a marked contrast between the sites with regard to cationic composition in runoff. This spatial contrast is in fact substantially more pronounced than are the changes in concentrations from year-to-year, actually well in accordance with what is generally found by more extensive surveys of Norwegian lakes (Mohn et al. 1980). The water in Dyr-dalen is more Ca<sup>2+</sup>- and K<sup>+</sup>- rich and poorer in H<sup>+</sup> and Al<sup>3+</sup> than at the two other sites. It should be noted that there is no such marked intersite difference in anionic composition.

The chemical budget data (Table 2) demonstrate that all three catchments derive highly significant amounts of N from the hydrological cycle, and that the net retention of NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> amounts to 10 kg N ha<sup>-1</sup>yr<sup>-1</sup> as an average. This is one order of magnitude greater than estimates of the rate of biological N-fixation in coniferous forests (Hovland 1978), but roughly the same rate as that by which N is incorporated in the biomass and thereby stored in an undisturbed forested ecosystem at Hubbard Brook, 44<sup>0</sup>N (Likens et al. 1977).

On an annual basis, SO<sub>4</sub><sup>2-</sup> appears, like Cl<sup>-</sup>, to be discharged at roughly the same rate as it is deposited from the atmosphere. The same holds true with even

greater precision for  $\text{Na}^+$ , while there is a net export of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ , and  $\text{Al}^{3+}$  together with a net retention of  $\text{H}^+$ . These results agree well with what is generally found for input-output budgets of major ions at catchments in Norway on a variety of geologic substrates and over a wide range of precipitation qualities (Wright and Johannessen 1980).

### Seasonal and Episodic Variations

As an example, weighted monthly mean concentrations in precipitation and runoff in Breidvikdalen are plotted for the period November 1976 – June 1979 in Fig. 3.

The seasonal variations in  $\text{SO}_4^{2-}$ - and  $\text{Cl}^-$ -concentrations in runoff are apparently governed largely by the precipitation chemistry, with the exception of May and June when the  $\text{SO}_4^{2-}$ -concentration drops in runoff in spite of a rising concentration in precipitation. Part of this phenomenon is obviously related to the fact that most of the ionic impurities in the snowpack are found in the first meltwater (Skartveit and Gjessing 1979), leaving the lakewater during May and June heavily influenced by the very dilute meltwater from the final snowmelt phase. Moreover, several studies have demonstrated significant sulphate accumulation in catchments, particularly during periods of plant growth and moderate precipitation. Subsequent sulphate release most often restores the long-term input-output balance (Seip 1980).

The  $\text{NO}_3^-$ - and  $\text{K}^+$ -concentrations are apparently highly dependent on the time of year and appear to be more or less unaffected by precipitation chemistry. Due to biologic activity, the  $\text{K}^+$ -concentration is low and the  $\text{NO}_3^-$ -concentration is almost negligible during summer. These concentrations then rise and reach their highest values during February, March, and April. These high values are thus already reached when the runoff is at its minimum in February prior to the initiation of the spring snowmelt. Much of this  $\text{K}^+$  and  $\text{NO}_3^-$  probably comes from plant remnants, which are shown to be particularly susceptible to  $\text{K}^+$ - and  $\text{NO}_3^-$ -losses when exposed to water after freezing (Uhlen 1978).  $\text{NH}_4^+$  is obviously unaffected by precipitation chemistry and is almost vanishing in runoff throughout the year.

The high  $\text{H}^+$ -concentrations, typical of periods with high runoff (rain in September–November, and early snowmelt in March–April - prior to the »dilution phase« in May), are accompanied by high concentrations of aluminium, indicating a chemically effective contact between the runoff water and the ground even during floods. Particularly during the sea-salt enriched autumnal rain-storms, the runoff from this catchment with acid soils is apparently acidified by cation exchange between  $\text{H}^+$  in the soil and metal cations (from sea-spray) in the precipitation (Wiklander 1975). Thus,  $[\text{H}^+]$  exceeded  $[\text{excSO}_4^{2-} + \text{NO}_3^-]$  in September while  $\text{Na}^+$  was apparently retained in the catchment ( $[\text{excNa}^+] < 0$ ). The lowest pH actually observed thus occurred in September 1978 in connection with great

## Precipitation, Hydrology, and Acidity

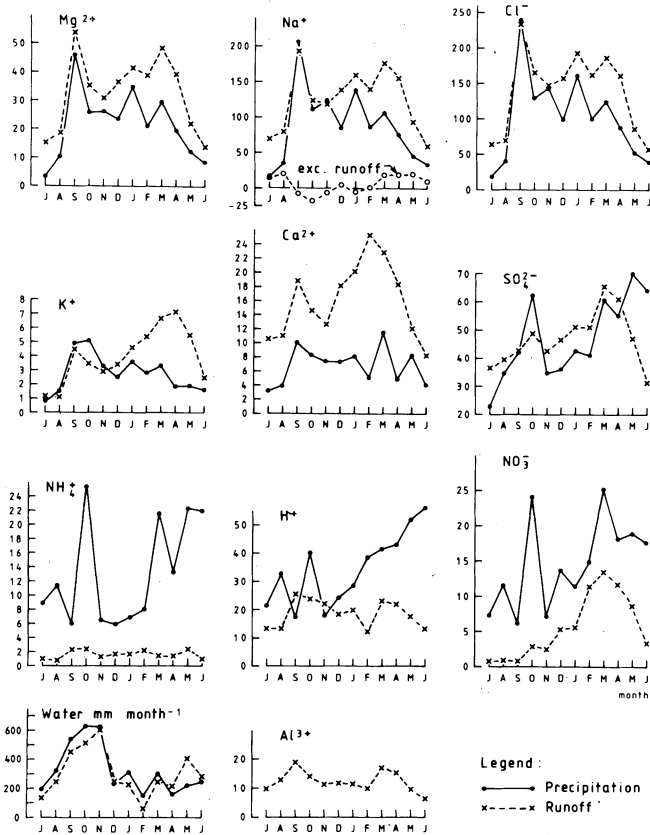


Fig. 3. Monthly weighted mean concentrations of ions ( $\mu\text{eq l}^{-1}$ ) in precipitation and runoff at Breidvikdalen (Nov. 1976–June 1979) together with runoff measured at Kløvtveitvatn and 1.63 times the precipitation amount measured at Kvamsdal (both in  $\text{mm month}^{-1}$ ).

amounts of heavily sea-spray loaded precipitation with low acidity. At the end of this episode the runoff was high, pH had dropped to 4.3, and the anionic sum was  $583 \mu\text{eq l}^{-1}$ , whereof  $\text{NO}_3^-$  was below detection limit ( $0.7 \mu\text{eq l}^{-1}$ ), and the  $[\text{SO}_4^{2-}]/[\text{Cl}^-]$  ratio was 0.110 (sea-water: 0.103). While the anionic composition thus nicely reflected the quality of the preceding diluted sea-water rain, the runoff acidity was apparently governed largely by cation exchange processes in the acid top soil. The retained  $\text{Na}^+$  was possibly washed out later, since (1) applied to the period Nov. 1976 – June 1979 yields an output/input ratio equal to 1.00. This balance may, however, partly be a fortuitous result of  $\text{Na}^+$ -sinks due to cation exchange reactions in (possibly accumulating) acid humus, and  $\text{Na}^+$ -sources due to weathering processes.

While for precipitation there is a marked difference between cations statistically

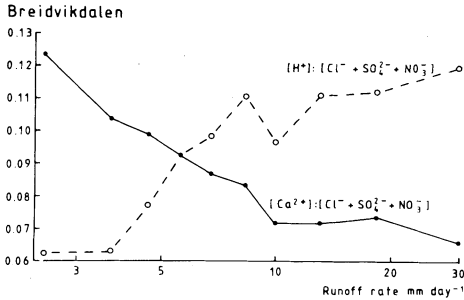


Fig. 4. Group mean values ( $n=12$ ) of  $[H^+]$ : [anions] and  $[Ca^{2+}]$ : [anions] in runoff at Breidvikdalen as a function of runoff rate at Kløvtveitvaten.

coupled to sea-spray anions and cations coupled to other anions, no corresponding difference is observed in runoff water (Skartveit et al. 1980), confirming the fact that cation exchange processes strongly govern the cationic composition of the runoff. Given the sum of anions,  $[H^+]$  (and also  $[Al^{3+}]$ ) increases and  $[Ca^{2+}]$  decreases with increasing runoff rate (Fig. 4), while the other metal cations appear unaffected by the runoff rate. This apparently confirms the fact that during floods, when surface runoff is predominant, the organic humus-rich top soil tends to yield acid runoff water because this soil acts as an ion-exchange system mainly in the hydronium state (Rosenqvist 1978). At low runoff rates, when interflow and groundwater seepage prevail, a considerable fraction of the runoff water penetrates deeper mineral soils. There, neutralization and weathering processes yield water that is particularly enriched in  $Ca^{2+}$  since Ca-rich minerals are the least stable in an acidic chemical regime (Likens et al. 1977, p. 93).

### Interannual Variations

Two consecutive annual mean values with fairly comparable precipitation amounts are available both from Botnane (July 1974 – June 1976) and from Breidvikdalen (July 1977 – June 1979), while the year July 1976 – June 1977 is not covered completely at any of these two sites. From the first to the second year at Botnane the annual mean  $H^+$ -concentration decreased by  $5 \mu\text{eq l}^{-1}$  in the precipitation and increased by  $2 \mu\text{eq l}^{-1}$  in the runoff (Table 1). This pattern was nicely repeated at Breidvikdalen where from the first to the second year the  $H^+$ -concentration decreased by  $12 \mu\text{eq l}^{-1}$  in the precipitation and increased by  $4 \mu\text{eq l}^{-1}$  in the runoff. This negative correlation between precipitation acidity and runoff acidity may appear puzzling at first sight. However, the  $H^+$ -concentration in runoff proves to be remarkably constant when expressed as a percentage of the sum of anions  $[SO_4^{2-} + Cl^- + NO_3^-]$ , i.e. 12.1% and 11.9% for the two years at Botnane, and 11.0% and 10.4% for the two years at Breidvikdalen. The corresponding percentages in precipitation were, on the contrary, quite variable, i.e. 21% and 13% at Botnane, and 20% and 12% at Breidvikdalen. In a similar way,  $Na^+$ - the predominant cation in sea-spray – made up for a rather variable fraction of the anions in the precipitation, i.e. 58% and 64% for the two years at Botnane and

53% and 62% for the two years at Breidvikdalen. Again, the corresponding percentages were remarkably stable in the runoff: 64.2% and 62.5% at Botnane and 62.3% and 63.4% at Breidvikdalen. The data are limited, and the differences are small. However, it appears that the cationic composition of the precipitation has, at most, a minor influence upon the cationic composition of the runoff – as far as the time scale is restricted to year-to-year or shorter variations. Regarding the anions the situation looks different. Both for  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$ , the increased concentration in precipitation is nicely accompanied by increased concentration in runoff. The  $\text{NO}_3^-$ -concentration in runoff is, on the other hand, low and apparently unaffected by the rather variable concentration in precipitation.

The interannual variation in the concentration of  $\text{H}^+$  (and other cations) in runoff is thus strongly governed by variations in anion concentration caused mainly by varying concentration of mobile anions ( $\text{SO}_4^{2-}$  and  $\text{Cl}^-$ ) in the precipitation. In western Norway the sea-spray dominates the variation of mobile anions in precipitation, and the concentration of sea-spray is also negatively correlated with acidity. The concentration of mobile anions in precipitation is thus negatively correlated with precipitation acidity and at the same time positively correlated with runoff acidity. This explains the observed negative correlation between precipitation acidity and runoff acidity. In areas with similar geology and where the variation of mobile anions in the precipitation is dominated by  $\text{SO}_4^{2-}$ , which is statistically coupled to acid cations, a positive correlation between precipitation acidity and runoff acidity should be expected and is in fact also observed (Wright and Johannessen 1980).

### **Long-term Variations**

Reported eradication of brown trout populations during the last decade indicates that a long-term acidification of the runoff has occurred at Breidvikdalen and Botnane. Although a close short-term relationship between sea-spray input and runoff acidity seems obvious from the preceding discussion, such a long-term change cannot be explained by increased sea-spray input. More likely the increased atmospheric deposits of pollutant sulphur have increased the  $\text{excSO}_4^{2-}$ -concentration in runoff. This increase cannot exceed today's  $\text{excSO}_4^{2-}$ -concentration, which, on an average, accounts for 15-20% of the anions in the runoff. Provided no change in cation selectivity has occurred over time, all cations may thus have risen by up to 15-20% on an average. In the case of  $\text{H}^+$  such an increase corresponds to a pH drop of less than 0.1 pH-unit. However, a change in the cation selectivity may have resulted from decreased base saturation in the soils – caused by, for example, long-term deposits of acid precipitation ( $50\text{-}100 \text{ meqH}^+ \text{ m}^{-2} \text{ yr}^{-1}$  at present), and possibly also due to unquantified factors like changes in land use and humus build-up. In addition, the possibility of a direct effect of the cationic composition (the  $[\text{H}^+]/[\text{Na}^+]$  ratio in particular) in precipitation upon runoff acidity cannot be ruled out. It is well-known that  $\text{Na}^+$  is comparatively

easily displaced in humus and is, therefore, compared to other cations, more poorly represented in humus samples than in precipitation (Låg 1968). Due to this high mobility and low storage capacity for  $\text{Na}^+$  in soils, it may well be the case that a given long-term rise in the atmospheric depositon of acid sulphates (causing increased sulphate runoff) is accompanied by little or no long-term  $\text{Na}^+$ -rise in the runoff, provided that only small amounts of  $\text{Na}^+$  originate from weathering. To preserve electroneutrality, the long-term percentage rise of other cations like  $\text{H}^+$  must then considerably exceed the long-term percentage rise of anions in the runoff.

## Conclusions

The western coast of Norway is an area well-suited for studies of certain relationships between precipitation chemistry, hydrology, and runoff acidity.

Precipitation is frequent and the amounts are high. The wet deposition of ions therefore outweighs the dry deposition and varies strongly, dependent mainly on meteorological conditions, season and distance from the coast. Sea-spray aerosols, transported mainly from neighbouring ocean- and coast-line areas, contribute both the greatest and the most variable part of the wet deposition of ions. The remaining ions, which are negatively correlated to the sea-spray ions, are almost exclusively acidifying compounds ( $\text{H}^+$ ,  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ), transported mainly from the industrialized European countries.

Pristine catchments in this area derive highly significant amounts of N from the hydrological cycle since  $\text{NH}_4^+$ -runoff is negligible and  $\text{NO}_3^-$ -runoff is significant only during periods of vegetation dormancy. On an annual basis the rather mobile anions  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  are discharged at roughly the same rate as they are deposited from the atmosphere. This flux of  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  is apparently the most direct link between the ionic composition of precipitation and runoff in this area. The composition of the cationic counterpart of this anionic flux shows little short-term dependency on the cationic composition of precipitation, but varies above all with geological and hydrological conditions. The high aluminium- and  $\text{H}^+$ -concentrations typical of periods with high runoff arise largely from cation exchange reactions in acid top soils, while neutralization and weathering processes in deeper mineral soils yield less acid and more  $\text{Ca}^{2+}$ -rich water at low runoff rates.

A long-term acidification, indicated by declining fish populations, does probably arise from a  $\text{SO}_4^{2-}$ -increase in runoff, caused by increased atmospheric deposition. Increased soil acidity, caused by acid precipitation and possibly also by changed vegetation, may also have contributed to this long-term freshwater acidification.

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## List of principal symbols

$A^x$	atmospheric deposition of ion $x$	(mass·area <sup>-1</sup> ·time <sup>-1</sup> )
$E$	evaporation (water)	(mass·area <sup>-1</sup> ·time <sup>-1</sup> )
$P$	precipitation (water)	(mass·area <sup>-1</sup> ·time <sup>-1</sup> )
$Q^x$	runoff of ion $x$	(mass·area <sup>-1</sup> ·time <sup>-1</sup> )
$d^x$	dry deposition: wet deposition for ion $x$	(dimensionless)
$p^x$	concentration of ion $x$ in precipitation	(mass·volume <sup>-1</sup> )
$q^x$	concentration of ion $x$ in runoff	(mass·volume <sup>-1</sup> )
$w$	hydrological output: atmospheric input	(dimensionless)
[Na <sup>+</sup> ], [Cl <sup>-</sup> + SO <sub>4</sub> <sup>2-</sup> ], etc. concentration of ions in $\mu\text{eq l}^{-1}$		

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