

## **Chemical Budgets and Chemical Quality of Snow and Runoff During Spring Snowmelt**

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In connection with water acidification and the subsequent disappearance of fish populations and also massive fish kills during spring floods, particular interest has been focused upon the fate and effects of ions released from the snowpack during melting.

Meltwater, enriched in ions, leaves the snowpack during melting episodes in winter. These (often small) amounts of water may via the ground-water reservoir have a long term influence upon the quality of winter runoff.

Data from catchments ranging from 0.04 to 232 km<sup>2</sup> indicate that, during spring snowmelt in Tovdal, South Norway, the equivalent sum of ions in runoff is mainly governed by the release from the snowpack of sulphate and chloride, which move more or less directly into the watercourses, carrying with them cations directly from the snowpack or from biological and geological material within the catchment.

The concentrations in bulk snow decrease during melting and, therefore, during early snowmelt, the concentrations of sulphate and chloride are 2-5 times higher in the runoff than in the snowpack, well in accordance with polyethylene lysimeter experiments. The composition of the cationic counterparts of these anions in the runoff varies with the runoff rate, with high runoff rate yielding the most acid water.

### **Introduction**

The Tovdal River is one of the main watercourses in southern Norway for which water acidification and the subsequent eradication of indigenous salmon and brown trout populations have been extensively documented, and massive fish kills

have been observed during spring floods (Leivestad et al. 1976). The cause is generally believed to be the acidification of precipitation, and particular interest has been focused upon the fate and effects of ions released from the snowpack during melting.

Johannessen and Henriksen (1978) report on lysimeter experiments carried out in the laboratory and in the field. They conclude that the ion enrichment of the meltwater leaving the snowpack is almost unaffected by the size and charge of ions and by the concentrations in the snow, while the type of the snow and the melting conditions cause some scatter between individual cases. From their data (Johannessen and Henriksen 1976), the enrichment factor,  $K$ , defined as the ratio of the mean concentration of an ion in the first  $N\%$  of the meltwater (before any ground contact) and in the remaining  $(100-N)\%$  of the snowpack, can be determined. From 64 observations (8 experiments with 8 ions) the following median values of  $K$  were found: 3.3, 3.3, and 3.9 for the first 2-6%, 6-12%, and 30% of the meltwater, respectively. Precise information about the magnitude of the meltwater fraction is thus not necessary when comparing the statistical distribution of independent sets of enrichment factors.

Aside from this ion enrichment within the snowpack, any difference in chemical quality between the snowpack and the runoff arises from interactions between the meltwater and biological and geological material (Rueslåtten and Jørgensen 1978). The relative importance of the meltwater chemistry can be determined by introducing radioactive tracers into the snowpack for measurements during melting and runoff (Dahl et al., in progress). An informative, but somewhat less precise method is the study of chemical budgets (Henriksen and Wright 1977). Finally, information concerning the order of magnitude of the bulk effects of biological and geological material may also be inferred from a comparison of the enrichment factors observed after ground contact (runoff) to those observed before ground contact (lysimeters).

## **The Catchment Area**

The investigated area (Fig. 1) comprises the upper parts of the Tovdal River catchment area.

Geologically, the area belongs to the south-western extension of the precambrian Baltic shield. The bedrock is granite and granitic gneisses with bands of amphibolite occurring in a few localities. However, the northernmost part of the catchment area around Straumsfjorden has quartzite sandstone and bands of basalt lava.

Birch forest goes up to about 800 m, while spruce and pine are found in the valley below Topsæ. The valley is sparsely populated, and the area above Dale is

## Hydrochemistry during Snowmelt

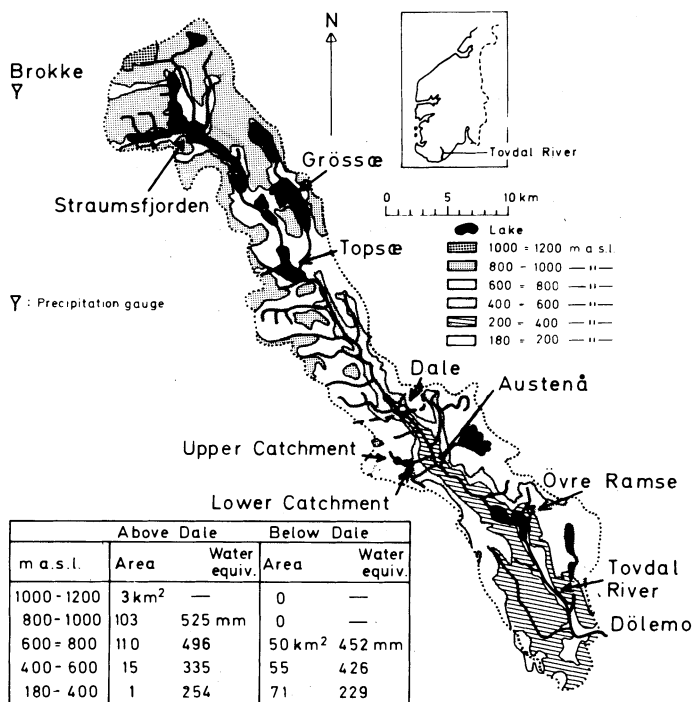


Fig. 1. Map of the upper parts of the Tovdal River catchment showing localities mentioned in the text. Area and mean water equivalent of the snowpack in late March within height intervals are inserted for the catchment above and below Dale, respectively.

uninhabited. Mountain grazing and collection of hay on the grass bogs has gradually declined since about 1890 and none of the summer farms have been used since 1950.

For the upper 1,759 km<sup>2</sup> of the Tovdal River basin, Dovland and Semb (1978) conclude from chemical budgets that precipitation is the main source of the sulphate run-off. Due to sulphur retention in soils and vegetation during the dry summer months and subsequent release, there appears to be a cyclic seasonal variation in the amount of sulphur stored in the catchment area. This particular sulphur storage is at a minimum before the beginning of the growing season, i.e. during snowmelt.

In the present paper, chemical budgets during the spring snowmelt are estimated for the catchment area above Dale (232 km<sup>2</sup>), based on a snow survey in late March 1977 together with precipitation and runoff measurements up to 4 June, when the snowmelt was finished.

Special studies were carried out in two small catchments during the spring snowmelt:

*Upper catchment:* (0.04 km<sup>2</sup>, 637-593 m a.s.l.) has a thin overburden of bottom moraine and peat, with many outcrops. The vegetation is heath, dominated by *Calluna vulgaris* and *Vaccinium uliginosum* with scattered trees of pine and birch.

*Lower catchment:* (0.07 km<sup>2</sup>, 365-308 m a.s.l.) has a rather thick overburden of bottom moraine and peat. The vegetation is dominated by *Calluna vulgaris* and *Vaccinium uliginosum*, forest of birch, spruce and pine, and some occurrence of large ferns.

## Methods and Data Quality

Snow samples comprising the entire snowpack were transferred to polyethylene bags for chemical analyses. The average theoretical conductivity calculated from H<sup>+</sup>, NH<sub>4</sub>, Na, Mg, Ca, K, Cl, SO<sub>4</sub>, and NO<sub>3</sub> amounts to 97% of the average measured conductivity ( $n=72$ , standard deviation = 5  $\mu\text{S}/\text{cm}$ ), while the correlation between theoretical and measured conductivity is 0.96 (discarding 1 observation raises the correlation to 0.98). Together with a fair balance between cations and anions this indicates that all ions of significance were measured, and that the accuracy of the analyses is within a few per cent. The effects of local variations and (presumably few) contaminations may be greater than this, but these effects were reduced by taking many samples.

Daily precipitation was measured at Øvre Ramse (227 m a.s.l., unshielded gauge) and Brokke (442 m a.s.l., Nipher shield) and was sampled daily at Øvre Ramse for chemical analyses. During the period from the start of snow accumulation (16 Nov. 1976) to 25 March 1977 the precipitation measured at Øvre Ramse and Brokke were respectively 399 mm and 280 mm, i.e. only 81% and 57% of 492 mm for the snowpack equivalent upstream Dale. The greater part of this excess found in the snowpack is probably due to the poor collection efficiency for snow of the precipitation gauges. Moreover, a simple "degree-day" method indicates that some winter melting has occurred even above 700 m a.s.l. For the areas 600-750 m a.s.l. and within 10 km from Øvre Ramse the mean concentration of acid components (H<sup>+</sup>, NH<sub>4</sub>, NO<sub>3</sub>, exc SO<sub>4</sub>) and sea salts in the snowpack make up only 60-70 per cent of the weighted mean concentration of winter precipitation. This indicates a "leakage" of ions from the snowpack. The same probably applies to the areas in the same height interval upstream Dale. Here, however, the absence of gradients in mean ion concentration from these levels and up to 930 m a.s.l. indicates that also these higher levels have been exposed to some winter melting. Water samples for chemical analyses were collected daily from the river at Dale and with varying frequency from the two small catchments (Fig. 1), where

also snow samples were collected weekly.

For a discussion of chemical budgets the catchment yield  $Q^x$  of an ion  $x$  at Dale during the period  $t_1 - t_2$  (spring snowmelt) can be expressed as

$$Q^x = Q_1^x + Q_2^x = (A_1^x + S_1^x) + (A_2^x + S_2^x) = (A_1^x + A_2^x) + (S_1^x + S_2^x) = A^x + S^x \quad (1)$$

Here subscript 1 represents water (excluding the snowpack) present within the catchment at time  $t_1$ , while 2 stands for water added to the watercourse as meltwater and precipitation during the time interval  $t_1 - t_2$ . These two waterbodies are expressed as sums of contributions from the atmosphere ( $A$ ) and from sources/sinks ( $S$ ) within the catchment.

In these areas neither the rocks nor the soils provide a significant primary source of chloride, and chloride is not accumulated in sizeable quantities within these ecosystems. Assuming then that  $S^{Cl}$  is negligible, that the ratio  $Q^x/Q^{Cl}$  is correctly measured, and that  $A^x/A^{Cl}$  equals the corresponding weighted ratio actually measured in the sum: (snowpack at time  $t_1$  + precipitation between times  $t_1$  and  $t_2$ ), the ratio  $Q^x/A^x$  can be written

$$\frac{Q^x}{A^x} = \frac{Q_m^x / A_m^x}{Q_m^{Cl} / A_m^{Cl}} = \frac{q^x / a^x}{q^{Cl} / a^{Cl}} = w \quad (2)$$

Here subscript  $m$  stands for measured values, while  $q$  and  $a$  are measured weighted mean concentrations. The ratio  $Q^x/A^x$  taken from (2) is, therefore, unaffected by measurement errors as long as these do not affect the concentration quotient  $w$ .

## Results and Discussion

### Chemical Budgets for the Discharge at Dale

Chemical budget data for the discharge at Dale during the spring snowmelt are given in Table 1.

The mean water equivalent of the snowpack in late March was 492 mm, while up to 4 June 134 mm of precipitation (Øvre Ramse) was added. The run-off up to 4 June was 522 mm, or 104 mm less than the water in snowpack + precipitation. The greater part of this difference is due to increased water storage in soil and lakes within the catchment and to evaporation losses that probably became significant during the 3 sunny weeks prior to 4 June.

On an equivalent basis, the snowpack + precipitation ( $A_m$ ) contains approximately equal amounts of sulphate (corrected for sea-spray) and hydrogen ions and

Table 1 - Chemical budget (mekv/m<sup>2</sup>) for the runoff at Dale during the spring snowmelt 1977 (1 April-4 June).  $A_s$  = snowpack ultimo March,  $A_p$  = precipitation at Øvre Ramse 1 April-4 June,  $A_m = A_s + A_p$ ,  $Q_m$  = runoff at Dale 1 April-4 June,  $w$  = runoff/atmospheric input corrected on the assumption that  $w = 1.00$  for chloride,  $S^x$  = contributions to the runoff from net sources within the catchment ( $= (1-1/w)Q_m^x$ ).  $w_{FyNi}$  =  $w$ -values (mean value  $\pm$  standard deviation) for 6 small catchments in the Fyresdal/Nissedal area (1 year, Gjessing *et al.* 1976).

| $x$                | $A_s^x$ | $A_p^x$          | $A_m^x$ (In)     |                  | $Q_m^x$<br>Out | $Q_m^x/A_m^x$<br>Out/In | $w$<br>Out/In<br>corr. | $S^x$<br>Source/<br>Sink | $w_{FyNi}$<br>$\pm$ Std. dev. |
|--------------------|---------|------------------|------------------|------------------|----------------|-------------------------|------------------------|--------------------------|-------------------------------|
|                    |         |                  | Total            | Sea <sup>e</sup> |                |                         |                        |                          |                               |
| SO <sub>4</sub>    | 13.1    | 9.1              | 22.2             | 1.4              | 31.2           | 1.40                    | 1.03                   | 0.9                      | .93 $\pm$ .05                 |
| NO <sub>3</sub>    | 11.2    | 4.7              | 15.9             | 0.0              | 6.3            | 0.40                    | 0.29                   | -15.4                    | .12 $\pm$ .08                 |
| Cl                 | 10.4    | 3.2 <sup>c</sup> | 13.6             | 13.6             | 18.5           | 1.36                    | 1.00                   | 0.0                      | -                             |
| Anions             | 34.7    | 17.0             | 51.7             | 15.0             | 56.0           | 1.08                    | 0.80                   | -14.5                    | -                             |
| NH <sub>4</sub>    | 9.5     | 5.7              | 15.2             | 0.0              | 0.0            | 0.0 <sup>a</sup>        | 0.0                    | -20.7                    | -                             |
| H <sub>+</sub>     | 13.8    | 6.1              | 19.9             | 0.0              | 8.6            | 0.43                    | 0.32                   | -18.3                    | .42 $\pm$ .09                 |
| K                  | 2.2     | 1.3 <sup>b</sup> | 3.5              | 0.2              | 4.4            | 1.26                    | 0.92                   | - 0.4                    | 1.2 $\pm$ .2                  |
| Na                 | 8.9     | 2.8 <sup>c</sup> | 11.7             | 11.7             | 21.6           | 1.85                    | 1.36                   | 5.7                      | .90 $\pm$ .08                 |
| Mg                 | 2.2     | 0.6              | 2.8              | 2.6              | 10.6           | 3.8                     | 2.8                    | 6.8                      | 2.0 $\pm$ .6                  |
| Ca                 | 2.7     | 1.6              | 4.3              | 0.5              | 16.4           | 3.8                     | 2.8                    | 10.5                     | 2.8 $\pm$ .7                  |
| Al <sup>3+</sup>   | -       | -                | 0.7 <sup>d</sup> | 0.0              | 6.6            | 9.9                     | 6.9                    | 5.6                      | 12 $\pm$ .4                   |
| Cations            | 39.3    | 18.1             | 58.1             | 15.0             | 68.2           | 1.17                    | 0.86                   | -10.3                    | -                             |
| Cations/<br>Anions | 1.13    | 1.06             | 1.12             | 1.00             | 1.22           | -                       | -                      | -                        | -                             |
| Water (mm)         | 492     | 134              | 626              |                  | 522            | 0.83                    |                        |                          |                               |

a. NH<sub>4</sub> assumed negligible in runoff

b. K/Ca-ratio assumed identical in  $A_s$  and  $A_p$

c. Na and Cl estimated from Mg by seawater proportions

d. Al<sup>3+</sup>-concentration assumed equal to 10  $\mu$ g Al/l

e. Contributions from sea-spray estimated from Cl (seawater proportions)

of nitrate and ammonium ions, as is generally found in precipitation in southern Norway (Dovland et al. 1976). These four ions account for 65.5% of the measured ions.

Significant amounts of Cl, Na, and Mg are found in close to sea-water proportions, and the estimate of total sea-spray contribution amounts to 27.5% of the measured ions. The remaining 7% consist mainly of K and Ca.

The measured cationic excess is 6% for the precipitation ( $A_p$ ), 13% for the snowpack ( $A_s$ ), and 22% for the runoff ( $Q_m$ ). At these low pH-levels this cannot be explained from neglecting the bicarbonate ion in the sum of anions, but possibly from neglecting organic anions of humic origin and from an increasing fraction of the measured metal elements being present in the form of electrically-neutral complexes, colloids, or particles. In particular aluminium is hardly present as a free trivalent ion at these pH-levels.

The chloride data show that 1.4 times more Cl was discharged from the catchment than was measured in the snowpack + spring precipitation. This arises mainly from a decreased chloride storage within the catchment, since dilute meltwater from the final snowmelt phase partly replaced the more chloride-rich water that was present in late March. In fact the chloride concentration in the streamwater at Dale in early June was about one half of that in late March. Scaling the various output/input ratios by the corresponding ratio of chloride (Eq. (2)) shows that a) input approximately equals output for Cl (by assumption),  $SO_4$ , K, and Na; b) there is a net retention of  $H^+$ ,  $NO_3$ , and  $NH_4$ ; and c) there is a net loss of Ca, Mg, and Al. The net uptake of  $H^+$  and  $NH_4$  ( $39.0 \text{ mekv/m}^2$ ) approximately balances the net loss of metal cations ( $28.2 \text{ mekv/m}^2$ ). The retention of  $H^+$  and  $NH_4$  thus apparently produces losses of metal cations, possibly through cation exchange reactions in biological and geological material (Wiklander 1975).

The principal features of the chemical budget for the catchment yield at Dale during snowmelt are also characteristic for the annual budget for 6 small catchments in the Fyresdal/Nissedal area some 20 km northeast of Tovdal (Gjessing et al. 1976).

### **The Ion Enrichment in the Runoff from the Two Small Catchments**

The two small catchments can be regarded as large natural lysimeters. Here the meltwater is allowed to interact freely with the undisturbed ground before the sampling, in contrast to the sampling from polyethylene lysimeters (Johannessen and Henriksen 1978). Moreover, any moment is regarded as the initial melting phase of the snowpack present at that moment. The observed time series of enrichment factors thus comprise cases with varying melting conditions, as did the experiments with polyethylene lysimeters.

In Table 2 are given the observed concentrations in the snowpack and in the

Table 2 - Observed concentrations in river water and in the snowpack (in brackets) in »Upper Catchment« and »Lower Catchment«, respectively.

| Date             | H <sub>+</sub><br>µekv/l | NO <sub>3</sub><br>µgN/l | SO <sub>4</sub><br>mg/l | Cl<br>mg/l | Na<br>mg/l | K<br>mg/l | Mg<br>mg/l | Ca<br>mg/l | NH <sub>4</sub><br>µgN/l | Al<br>µg/l |
|------------------|--------------------------|--------------------------|-------------------------|------------|------------|-----------|------------|------------|--------------------------|------------|
| Upper Catchment: |                          |                          |                         |            |            |           |            |            |                          |            |
| 4 April          | 20(42)                   | 210(430)                 | 4.8(1.8)                | 1.9(.80)   |            | .38(.08)  | .40(.05)   | .87(.07)   | (385)                    | -          |
| 10 April         | - (45)                   | - (490)                  | - (1.9)                 | - (1.1)    | - (.63)    | - (.10)   | - (.07)    | - (.10)    | (420)                    | -          |
| 16 April         | 19(34)                   | 220(380)                 | 4.5(1.6)                | 2.0(.85)   | -          | .33(.08)  | .41(.06)   | .85(.09)   | (340)                    | -          |
| 21 April         | 26(45)                   | 290(415)                 | 4.5(1.9)                | 2.0(.90)   | 1.62(.36)  | .38(.02)  | .40(.05)   | .79(.08)   | (388)                    | 390        |
| 26 April         | 38(40)                   | 250(363)                 | 4.4(1.8)                | 2.0(.65)   | 1.62(.45)  | .36(.01)  | .37(.04)   | .71(.05)   | (373)                    | 398        |
| 2 May            | 56(39)                   | 500(330)                 | 5.0(1.2)                | 2.2(.80)   | 1.70(.45)  | .60(.03)  | .47(.05)   | .98(.05)   | (332)                    | 480        |
| 6 May            | 63(27)                   | 230(210)                 | 3.2(0.9)                | 1.3(.65)   | 1.00(.36)  | .44(.01)  | .27(.02)   | .43(.05)   | (290)                    | 230        |
| 12 May           | 65(15)                   | 150(210)                 | 2.5(0.2)                | 1.1(.95)   | 0.75(.51)  | .32(.01)  | .18(.01)   | .28(.04)   | (205)                    | 190        |
| Lower Catchment: |                          |                          |                         |            |            |           |            |            |                          |            |
| 4 April          | 10(28)                   | 40(280)                  | 3.6(0.9)                | 2.2(.60)   | 1.45(.33)  | .40(.07)  | .32(.03)   | .79(.06)   | (300)                    | 100        |
| 10 April         | 7(10)                    | 50(170)                  | 3.6(0.3)                | 1.8(.30)   | 1.48(.18)  | .41(.13)  | .31(.02)   | .78(.05)   | (310)                    | 120        |
| 16 April         | - (27)                   | - (310)                  | - (1.2)                 | - (.65)    | - (.36)    | - (.05)   | - (.03)    | - (.07)    | (320)                    | -          |
| 21 April         | 8(44)                    | 50(413)                  | 3.1(2.0)                | 1.8(.85)   | 1.41(.49)  | .42(.05)  | .30(.05)   | .78(.08)   | (402)                    | 120        |
| 26 April         | 10(22)                   | 45(234)                  | 3.5(0.7)                | 1.6(.55)   | 1.40(.31)  | .34(.01)  | .28(.02)   | .81(.07)   | (285)                    | 120        |
| 2 May            | - (14)                   | - (155)                  | - (0.4)                 | - (.45)    | - (.30)    | - (.05)   | - (0.2)    | - (.18)    | (208)                    | -          |
| 6 May            | 18(14)                   | 30(140)                  | 2.7(1.3)                | 1.4(1.8)   | 1.00(.98)  | .39(.02)  | .25(.02)   | .55(.04)   | (260)                    | -          |
| 12 May           | 20(-)                    | 10(-)                    | 3.0(-)                  | 1.3(-)     | 1.02(-)    | .38(-)    | .24(-)     | .29(-)     | -                        | 120        |

† Na in the snowpack estimated from the Cl-content



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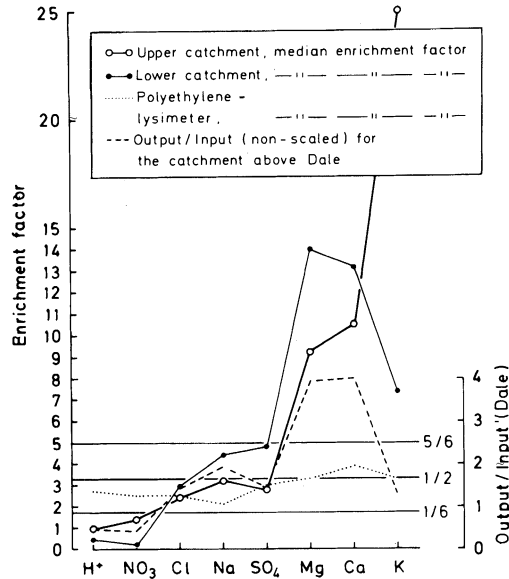


Fig. 2. Non-scaled output/input ratios for the discharge at Dale, median enrichment factors in runoff from the upper and the lower catchment, and the statistical distribution of the enrichment factor in the first 2-6% of the meltwater from polyethylene lysimeters (median (1/2) and the upper (5/6) and lower (1/6) limit of the central 2/3 of 64 observations (see text), and the median for each ion).

meltwater sampled from runoff. Median enrichment factors,  $K$ , are calculated from Table 2 and compared to the statistical distribution of the enrichment factors for the first 2-6% of the meltwater from polyethylene lysimeters (Fig. 2). Since the enrichment factor for the meltwater does not differ between ions before ground contact (Johannessen and Henriksen 1978), it can be shown that the ratio  $K^x/K^{Cl}$  for ion  $x$  and chloride is analogous to the chloride-scaled output/input ratio for the ion  $x$  (Eq. (2)). Therefore, the various non-scaled output/input ratios for the catchment yield at Dale (Tab. 1) are included in Fig. 2 for comparison, and it is seen that the various ratios differ between ions in nearly the same manner for the three catchment areas. The only marked deviation from this pattern is that *potassium* is considerably more enriched in the runoff from the two small catchments than in the catchment yield at Dale. This contrast may be due to differences in area, geology, and vegetation between the catchments. However, the possibility of getting sediment and plant debris into the samples is probably greater when sampling the small trickles draining the small catchments than when sampling the main river at Dale, and such debris might contribute potassium to the samples.

Both *magnesium* and *calcium* are considerably more enriched than chloride in the runoff from both the catchments, and also clearly more enriched than in the polyethylene lysimeters. This indication of net sources for magnesium and calcium within the two catchments is also in agreement with the results arrived at by the costly chemical budget approach for the catchment above Dale (Tab. 1).

Analogously Fig. 2 indicates net sinks for  $H^+$  and *nitrate* within the two catchments, as did the chemical budget approach in the case of the catchment above Dale.

The good agreement between the enrichment factors for *chloride* as observed in our two catchments and as measured by polyethylene lysimeters support the assumption that there is no important sources or sinks for chloride within these catchments. The observed enrichment factor for chloride – and for the other ions – fluctuates markedly more in the lower catchment than in the upper catchment. This is probably due to considerable snow quality gradients at a small scale in the lower area, due to earlier melting episodes. These gradients rendered representative snow sampling difficult. In both the catchments, the observed enrichment factors for *sodium* and *sulphate* agree reasonably well with the polyethylene lysimeters measurements. This also conforms with the conclusion drawn from chemical budgets that net sources/sinks within the catchments are small compared to the atmospheric input of these ions.

### **The Evolution of Concentrations in Snow and Runoff**

The parallel evolution in the concentration of sulphate in the snow and in the runoff from the upper small catchment is shown in Fig. 3. In addition, the sulphate concentration in the Tovdal River at Dale, the discharge for the Tovdal River at Austenå, and the amount and sulphate concentration of precipitation at Øvre Ramse are plotted. The concentrations in run-off of  $H^+$ , Ca, and K counted as percentages of the sum of the metal cations Na + Mg + Ca + K (on an equivalent basis) are also given.

The discharge in the Tovdal River from late March until about 20 April is low and we see no noteworthy change in the snowpack's sulphate concentration. This must be due to insignificant melting, and light precipitation of practically the same sulphate concentration as the snowpack.

After about 20 April, the discharge in the Tovdal River begins to increase slowly, and then increases strongly during the first few days of May to reach a peak 12-13 May. Simultaneously, the sulphate concentration in the snow cover decreases evenly until the sampling was terminated due to lack of snow.

If the snow's water equivalent is  $m$  and its content of an ion  $x$  is  $m_x$ , then the meltwater ( $mw$ ) leaving the snowpack has an instantaneous concentration (neglecting evaporation and precipitation):

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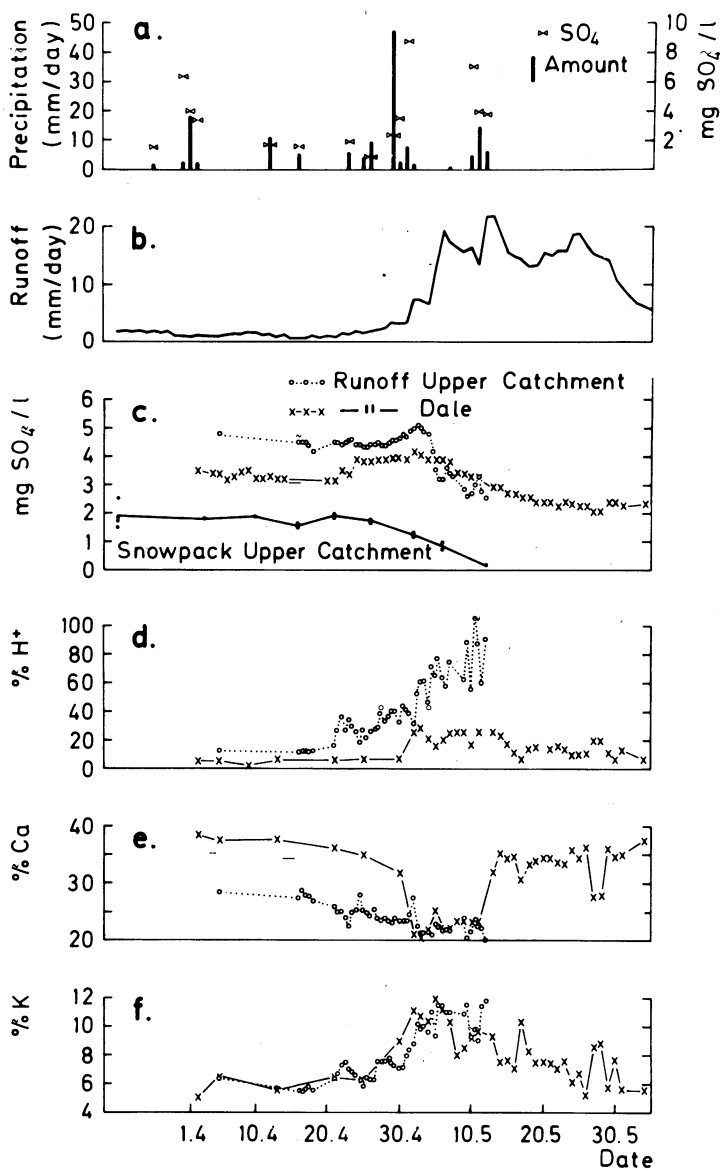


Fig. 3. Precipitation amounts and sulphate concentration at Øvre Ramse (a.), runoff amount at Austenå (b.), and sulphate concentration in runoff and snowpack (c.). The concentrations of H<sup>+</sup>, Ca, and K in the runoff are given in % of the sum (on an equivalent basis): Na + Mg + Ca + K (d.-f.).

$$C_{mw} = \frac{dm_x}{dm} \equiv \frac{d}{dm} (C_S m) \equiv C_S + m \frac{dC_S}{dm} \quad (3)$$

Here  $C_S$  is the average concentration of  $x$  in the snowpack. Thus,

$$\Delta C_{mw} = C_{mw} - C_S = m \frac{C_S}{\dot{m}} \quad (4)$$

where  $\dot{\phantom{x}}$  signifies the time derivative. The following consequences of this differential equation are worth noticing in connection with Fig. 3:

1) In winter the ratio  $m/\dot{m}$  is very large such that  $\Delta C_{mw}$  can be significant even though  $\dot{C}_S$  approaches 0. Thus, the high concentrations of sulphate in the runoff before the spring snowmelt can be explained from the contribution of ions from the snowpack, even though changes in concentration in the snowpack are small. This meltwater influence during winter occurs partly via the groundwater, since the groundwater reservoir is replenished through winter melting.

2) The typical maximum in  $\Delta C_{\text{runoff}}$  during the initial phase of the spring snowmelt (Fig. 3) may be explained as a contribution of ions from the snowpack if  $|\dot{C}_S|$  increases faster than  $|m/\dot{m}|$  during this phase. The following rapid decline in the run-off water's sulphate concentration should then be associated with a period where  $|m/\dot{m}|$  increases faster than  $|\dot{C}_S|$ . It is readily seen from Fig. 3 that the rapid decline in runoff sulphate concentration following the peak in early May does coincide with a period of increased melting rate (increased runoff) and apparently constant  $|\dot{C}_S|$ .

3) The ratio  $\dot{C}_S/\dot{m}$  is finite during the spring snowmelt and, therefore, both  $\Delta C_{mw}$  and  $C_{mw}$  tend to 0 toward the end of the snowmelt, since  $m$  and  $C_S$  tend to 0. In the upper catchment  $\Delta C_{\text{runoff}}$  declines markedly, but does not tend to 0. This probably arises from sulphate contributions from other sources than the snowpack, e.g. precipitation and groundwater seepage, the relative importance of which increases as the melting rate tends to 0 in its last phase.

The concentrations of chloride show a similar pattern to that shown for sulphate in Fig. 3. Our data, thus, fit the assumption that the major part (80-100%) of the runoff water's anions during early snowmelt in this area, are attributable to inputs (chloride and sulphate) from the atmosphere. This indicates that the chemical quality of the precipitation is a highly decisive factor for the chemical quality of the runoff water in this area.

The composition of the cationic counterparts of these anions apparently varies with the runoff rate, in that the relative contributions of  $H^+$  and potassium increase and the relative contributions of calcium and aluminium decrease when the runoff rate increases (Fig. 3 and Tab. 2). These cationic changes are probably linked to changes in the contact of water with soils and residence times in various geological zones within the catchment.

## **Conclusions**

The snow survey in the upper parts of the Tovdal River catchment area, South Norway, in late March 1977 demonstrated the inadequacy of observed winter precipitation data as a measure of the amount and quality of snow in the area before the spring snowmelt.

In the sum of snowpack and spring (April, May) precipitation, sulphate (in excess of sea-spray contribution), nitrate, ammonium, and hydrogen ions account for 65.5% of all ions (on an equivalent basis), while 27.5% of the ions originate from sea-spray. The last 7% consist mainly of K and Ca.

Data from catchments ranging from 0.04 to 232 km<sup>2</sup> indicate that, during early snowmelt, the most direct link between the quality of snow and runoff in Tovdal is the release from the snowpack of sulphate and chloride. These anions move more or less directly into the watercourses, carrying with them cations directly from the snowpack or from material within the catchment. The equivalent sum of ions in runoff is mainly governed by this flux of chloride and sulphate, while the composition of their cationic counterparts varies with the runoff rate. In areas where the base saturation of the soils is low this will lead to low pH in the watercourses during the spring flood.

The concentrations in bulk snow decrease during melting and, therefore, the concentrations of sulphate and chloride are 2-5 times higher in the runoff than in the snowpack, well in accordance with laboratory and field lysimeter experiments.

Net sinks within the catchments are observed for H<sup>+</sup> and ammonium, and net sources are observed for magnesium, calcium, and aluminium. Chemical budgets suggest that acid precipitation provides a major part of the protons to drive chemical weathering.

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