

## Modelling Streamwater Chemistry with Snowmelt [and Discussion]

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## Modelling streamwater chemistry with snowmelt

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Simple hydrochemical reservoir models based on the mobile anion concept are described for the Birkenes and Storgama catchments in southern Norway with acidified streamwater. Key processes modelled include water routing, sulphate adsorption–desorption, ion-exchange reactions, weathering and a gibbsite equilibrium condition. The models reproduce much of the daily and seasonal variations in streamwater chemistry which have been observed over several years.

Model considerations have been used in an attempt to explain the acidification of streamwater in these two areas. It is hypothesized that soil acidification has occurred and that acid precipitation is at least partly responsible. The results are tentative largely because the models are derived from present-day streamwater chemistry.

### 1. INTRODUCTION

Southern Norway is one of several regions of the northern hemisphere severely affected by acid precipitation, acidification of freshwater and loss of fish populations (Likens *et al.* 1979; Overrein *et al.* 1980). The causal relationships leading to freshwater acidification in a given area, however, are complicated and not fully understood. A catchment is a very complex system, and a large number of processes may play roles in connection with acidification, for example, the CO<sub>2</sub>-pressure in soil, uptake and release of ions by vegetation, cation exchange, weathering and oxidation and reduction reactions.

Different processes may be important in affecting the water quality in various soil layers; for example, ion-exchange reactions may determine the cation composition in upper soil horizons rich in organic matter whereas in the deeper mineral layers weathering may be the dominating process. The pathways of the water through the catchment are therefore of great significance.

Hydrochemical models provide one way of quantifying and integrating important processes in a catchment, and several groups are developing such models (for example, Chen *et al.* 1982; Christophersen *et al.* 1982; Schnoor *et al.* 1982). In our modelling work, efforts have been directed mainly at identifying key processes in the catchments under study using primarily input–output measurements of water and major ions. Even though our models reproduce principal characteristics of the observed runoff concentrations, they are not necessarily physically and chemically accurate descriptions of the catchments. Our approach should be regarded as an iterative process. The ‘first generation’ model constitutes a set of hypotheses which can later be tested by new measurements or experiments, which in turn may be used to develop improved models.

The models (Christophersen & Wright 1981; Christophersen *et al.* 1982, 1983) are based on the ‘mobile anion’ concept with sulphate as the main vehicle for transport of cations through soils. For Scandinavian catchments the ammonium and potassium concentrations are usually small in runoff. Nitrate can also often be ignored but may be of importance in some areas

particularly during snowmelt. In the catchments we have considered  $\text{Na}^+$  and  $\text{Cl}^-$  are found in nearly equivalent amounts both in precipitation and runoff. As a first approximation we have therefore ignored these ions. The importance of sulphate for the transport of cations, including  $\text{H}^+$  and  $\text{Al}$ , in areas with low bicarbonate and organic anion concentrations is then evident.

## 2. SITE DESCRIPTIONS AND DATA BASE

In the Norwegian S.N.S.F.-project (Acid precipitation effects on forest and fish) water chemistry was studied in about 40 gauged catchments. The project ended in 1980, but four of these catchments are still monitored routinely through funding from the Norwegian State Pollution Control Authority (S.F.T.). We have so far constructed models for two of these four sites – Birkenes and Storgama – which have the longest data series of high quality. These two catchments are fairly typical for acidified regions of southern Norway.

Birkenes is a 0.4 km<sup>2</sup> catchment 200–300 m above sea level about 15 km north of Kristiansand on the south coast. The vegetation is mixed coniferous forest and about half the catchment soil depth is less than 20 cm. The bedrock is granitic. The catchment is in the zone of maximum deposition of acid precipitation with a total annual input of about 7 g  $\text{SO}_4^{2-}$  m<sup>-2</sup> (Christophersen & Wright 1981). The Birkenes brook was known as a particularly good spawning site for brown trout until about 1950 when the fish disappeared (Christophersen & Seip 1983). Measurements of streamwater chemistry have been carried out by the Norwegian Institute for Water Research (N.I.V.A.) since 1972. Apart from 1979 there exists a continuous record of observations made at least twice a week the first years, and later weekly (Christophersen *et al.* 1982). Amount and quality of precipitation as well as temperature have been measured daily by the Norwegian Institute for Air Research (N.I.L.U.). For recent years we have also daily air concentrations of  $\text{SO}_2$  and  $\text{SO}_4^{2-}$ .

Storgama is a 0.6 km<sup>2</sup> catchment with granitic bedrock about 30 km further from the coast than Birkenes and at 600–700 m elevation. It receives roughly half the deposition estimated for Birkenes. About 50 % of the area is characterized by sparsely soil-covered bedrock, and about 20 % is mainly bare rock. The rest is peatland and lakelets (Brække 1981). Individual pine, spruce and birch trees are found scattered throughout the catchment. Measurements similar to those made at Birkenes started at Storgama in 1974. The brook has probably never had fish because it is small and connects to higher order streams through a steep hillslope and a bog. Nearly all lakes in a surrounding 182 km<sup>2</sup> area lost their fish populations between 1940 and 1970 (S.N.S.F. 1977).

Table 1 shows the volume-weighted average concentrations of ions both in streamwater and precipitation. Both catchments have an average pH of 4.5 in streamwater, and sulphate (mainly of anthropogenic origin) is the major anion. The input–output sulphate budgets at both sites seem to be approximately in balance on a yearly basis (Christophersen & Wright 1981; Christophersen *et al.* 1983). It should be noted that the nitrate concentration is always very low at Birkenes, while at Storgama it may amount to 60  $\mu\text{eq l}^{-1}$  during snowmelt (see §4.3).

Chemical soil data (for example, base saturation) are most valuable in model development. It takes, however, a great effort to obtain representative data of this kind for natural catchments, and we have had only scattered observations at our disposal.

TABLE 1. VOLUME-WEIGHTED AVERAGE CONCENTRATIONS OF MAJOR IONS IN PRECIPITATION AND STREAMWATER AT BIRKENES AND STORGAMA

	Birkenes 1972–1978 (Christophersen & Wright 1981)		Storgama 1974–1978 (M. Johannessen, personal communication)	
	precipitation	stream	precipitation	stream
water/mm	1403	1078	1108‡	883‡
H <sup>+</sup> /μeq l <sup>-1</sup>	57	33	54	33
pH	4.24	4.48	4.27	4.48
Na	56	123	15	35
K	4	7	2	7
Ca	9	67	7	41
Mg	13	40	4	16
Al	—	71†	—	18†
NH <sub>4</sub>	38	< 5	27	—§
NO <sub>3</sub>	38	7	31	14
SO <sub>4</sub>	74	152	59	82
Cl	58	123	18	28

† Total Al as Al<sup>3+</sup>‡ From Christophersen *et al.* (1983).

§ Not measured

### 3. MODEL DESCRIPTION – BIRKENES

We will first describe the model as used for the Birkenes catchment; the modifications made for Storgama are discussed later. The number of parameters are kept low. Most of them have to be determined from streamwater observations. Part of the data (1973–1975) is used for this purpose (calibration period) while the rest serves as control. The Birkenes model was constructed in three stages corresponding to hydrology, sulphate chemistry and cation chemistry. A detailed discussion is given by Christophersen *et al.* (1982).

#### 3.1. Hydrological sub-model

This sub-model was developed by Lundquist (1977); we have made only a few minor modifications. It consists simply of two reservoirs (see figure 1). Basically the upper reservoir (A) supplies quickflow and can be thought of as water mainly in contact with or most recently in contact with the upper soil horizons. The lower reservoir (B) provides the base flow. This simple model simulates runoff volume on a daily basis given mean daily temperatures and precipitation amounts as input data.

#### 3.2. Chemical model

For reasons stated above, we have ignored nitrate, ammonium, potassium, sodium and chloride. The streamwater at Birkenes always has negligible concentrations of bicarbonate, and we have also disregarded organic anions. We are then left with sulphate as the only anion and the cations H<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, and Al<sup>3+</sup>. (Other Al species are only roughly accounted for; see below.)

The input of sulphur compounds to the catchment consists of both wet and dry deposition to the upper reservoir. The sulphate concentration in runoff from this reservoir is assumed proportional to the amount of water-soluble sulphate on the solid phase. Mineralization

(oxidation) of sulphur compounds to sulphate is included. In the lower reservoir, we consider adsorption and desorption of sulphate.

The cation model in the upper reservoir may be expressed by three equations:

$$[\text{H}^+] + 2[\text{M}^{2+}] + 3[\text{Al}^{3+}] = 2[\text{SO}_4^{2-}] \quad (1)$$

$$[\text{Al}^{3+}][\text{H}^+]^{-3} = *K_{\text{so}} \quad (*K_{\text{so}} = 10^{8.1}) \quad (2)$$

$$[\text{H}^+]/\sqrt{[\text{M}^{2+}]} = K_{\text{G}} \quad (K_{\text{G}} = 10^{-2.21}). \quad (3)$$

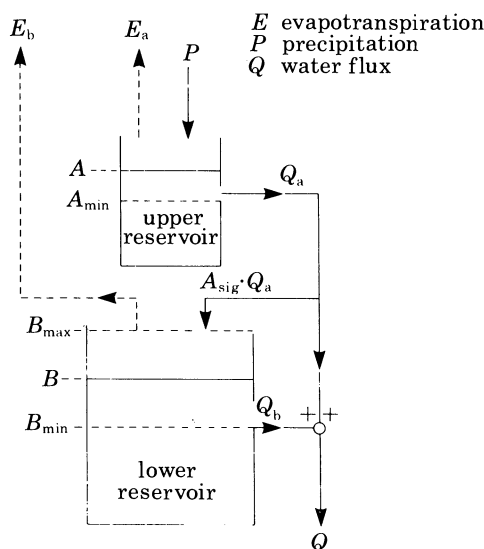


FIGURE 1. Hydrological sub-model, Birkenes.

The concentrations are expressed in  $\text{mol l}^{-1}$ , and we do not distinguish between concentrations and activities. The first equation is simply an ionic balance condition valid within the accuracy of our assumptions.  $\text{M}^{2+}$  is the sum of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . (2) is the gibbsite equilibrium. Cation exchange is governed through a constant lime potential ( $L_{\text{P}}$ ) in (3) (see for example, Bache (1980)). We have  $L_{\text{P}} = -\lg K_{\text{G}}$  where  $K_{\text{G}}$  is constant as long as the amounts of adsorbed cations in the soil do not vary.

Only the total amount of Al has been measured. The total concentration comprises, in addition to  $\text{Al}^{3+}$ , simple inorganic complexes (hydroxy and fluoride compounds) and organic complexes, as well as colloidal forms. As a first approximation, we have estimated the  $\text{Al}^{3+}$  concentrations by subtracting  $360 \mu\text{g Al l}^{-1}$  ( $40 \mu\text{eq l}^{-1}$ ) from the observed, total values. The correction term mainly accounts for aluminium bound to fluoride and organic ligands. Recently various aluminium species have been determined in samples from Birkenes. The results indicate that the assumption made in the model is reasonable (Seip *et al.* 1983).

(1) and (2) also apply to the lower reservoir. A weathering process (7 d half-time,  $\text{pH} = 5.3$  as equilibrium value) reduces the  $\text{H}^+$  concentration in solution and increases the  $\text{M}^{2+}$  concentration correspondingly in this reservoir.

### 3.3. Results

Observations and simulation results for Birkenes are given for six years by Christophersen *et al.* (1982). The simulations are for the snowfree season only. Frequent winter melting periods make the winter season difficult to model for this catchment.

Important trends in the observations are reproduced by the model. High concentrations of  $H^+$  occur at high discharge, particularly if the sulphate concentration is high, as is found in the runoff during the first heavy rains after a dry summer. The sulphate concentrations do not show a similar increase after wet summers. The concentrations of aluminium correlate well with that of  $H^+$  (acid runoff with high Al-concentrations from the upper reservoir) while  $M^{2+}$  shows the opposite trend (higher concentrations in the baseflow from the lower reservoir).

## 4. MODEL MODIFICATIONS AND RESULTS FOR STORGAMA

The hydrological model for Storgama consists of four reservoirs. In addition to the two reservoirs in figure 1, a snowpack reservoir was introduced. Since the outlet is from a small pool, a reservoir in which the water from the three other reservoirs mixes completely was also included. Data from 1977 and 1978 were used for calibrating the Storgama model. The hydrological and sulphate submodels (including snowmelt) are described by Christophersen *et al.* (1983).

### 4.1. Snow accumulation and melting

At Storgama a considerable part of the precipitation falls and is stored as snow. Snow accumulation is difficult to compute from mean daily temperatures around 0 °C. We have introduced a 'sleet interval' where the precipitation changes linearly from snow to rain as the mean daily temperature increases from 0 °C to 1.6 °C. The daily amount of meltwater is computed by the commonly used degree-day method:  $M = C_0(\bar{T} - T_0)$ , where  $M$  is daily meltwater volume mm;  $C_0$  is degree-day factor  $\text{mm } (^\circ\text{C})^{-1}$ ;  $\bar{T}$  is mean daily temperature °C;  $T_0$  is threshold temperature °C.

Lundquist (1980) has shown that this simple model may perform as well as more complicated ones. The degree-day factor will, however, generally increase as melting proceeds owing for instance, to decreased albedo and increased radiation (Kuusisto 1980). We have followed a suggestion by Bergström (1975) whereby  $C_0$  increases linearly with the amount of snow already melted.

The fractionation effect observed during snowmelt (Johannessen & Henriksen 1978) is included in the model; that is, most of the ionic impurities in the snow are found in the first meltwater. The full curve in figure 2 shows measured  $\text{SO}_4^{2-}$  concentrations in successive fractions of collected meltwater relative to the initial average concentration before melting. The model uses the sum of two exponentials fitted to the observations.

### 4.2. Sulphate model

Where the A- and B-reservoirs are concerned, the sulphate sub-model for Storgama has a structure similar to that for Birkenes. In addition to mineralization the Storgama version also includes the reverse process, that is, reduction or adsorption of water-soluble sulphate in the A-reservoir during wet summer periods. Such processes (possibly in the bogs) must be

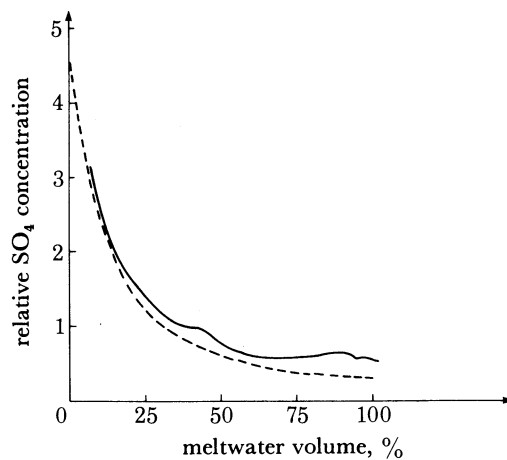


FIGURE 2. Observed (—) (Johannessen & Henriksen 1978) and fitted (----) relative  $\text{SO}_4$ -concentrations during snowmelt.

important at Storgama because the sulphate concentrations in streamwater are similar to those found in the rain during wet summers (compare figure 3 and table 1).

Christophersen *et al.* (1984) give simulation results for a continuous six year period; the results for one of the control years (1980) are shown in figure 3. The large concentration change during snowmelt caused mainly by the fractionation effect is underestimated, but the general trend is well reproduced. In spite of the introduction of a reduction or adsorption process which is active during wet summer periods, the model tends to overestimate sulphate concentrations during the summer and early autumn. With the current model, wet summers seem to pose more of a problem than drier ones.

There are typical successive periods of sulphur accumulation and depletion even though the long-term budget seems to be in balance. At Storgama the snowmelt washout is particularly effective; the loss always exceeds the amount of sulphate in the snowpack.

#### 4.3. Cation model

The typical day-to-day correlation between acidity and discharge at Birkenes is not found at Storgama. Trial simulations with the Birkenes model indicated that as a first approximation equations (1)–(3) might be used for Storgama irrespective of the discharge. This implies that cation exchange is the dominant process compared to weathering. In the barren Storgama area this might not be unreasonable.

To test this hypothesis, (1) was changed to

$$[\text{H}^+] + 2[\text{M}^{2+}] + 3[\text{Al}^{3+}] = 2[\text{SO}_4^{2-}]_o + [\text{NO}_3^-]_o \quad (1a)$$

where the subscript *o* indicates observed values. In this way, errors in the sulphate model do not disturb the partitioning of cations, and nitrate (important during the snowmelt) is included (compare, figure 3).

Solving (1a)–(3), the results are depicted in figure 3 for 1980. Aluminium species other than  $\text{Al}^{3+}$  are roughly accounted for by adding a constant  $90 \mu\text{g Al l}^{-1}$  ( $10 \mu\text{eq l}^{-1}$  as  $\text{Al}^{3+}$ ) to the computed  $\text{Al}^{3+}$  value (compare, Seip *et al.* 1983). There are some discrepancies between observed and computed cation concentrations, but important trends are accounted for. We find

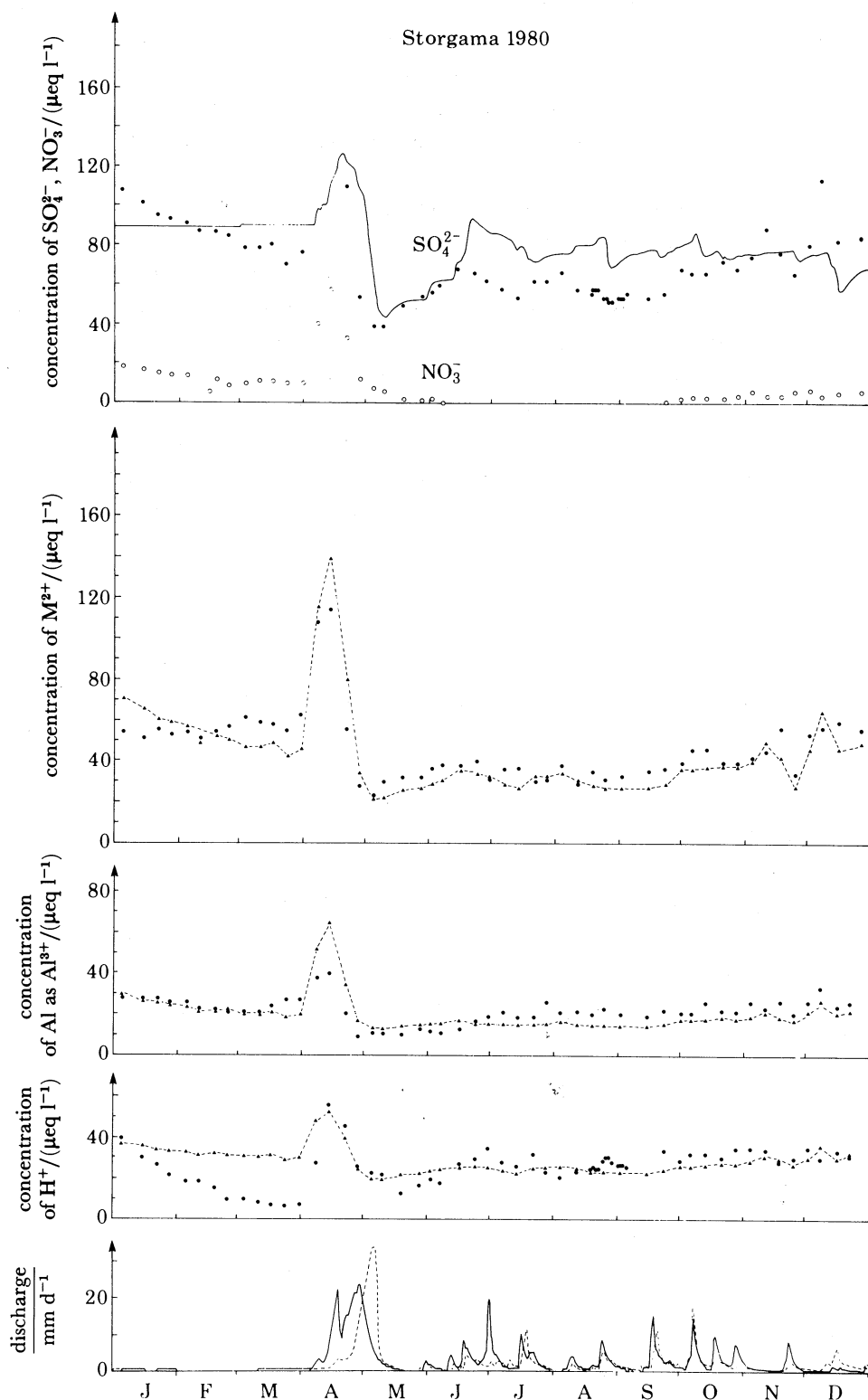


FIGURE 3. Storgama 1980. Observed (single dots) and simulated (line or connected dots) ionic concentration together with observed (—) and simulated (---) hydrogram. (Data from S.F.T. 1981).



it noteworthy that the parameters determined for the upper reservoir Birkenes model also seem to fit for Storgama. A more systematic feature that this model does not reproduce is the decrease in  $[H^+]$  and increase in  $[M^{2+}]$  which occur every winter during low flow. Here weathering may nevertheless be a key process in neutralizing the water because of particularly long residence times. A second generation model for Storgama could include weathering under such circumstances.

Within the framework of our model, (1a)–(3) imply sufficient soil–water interactions for the lime potential condition and gibbsite equilibrium to be valid even during snowmelt. Previous studies using radioactive calcium ( $^{45}Ca^{2+}$ ) in two mini-catchments (264 m<sup>2</sup> and 1300 m<sup>2</sup>) in the Storgama area show that soil–meltwater contact can be considerable. Only about 15% of the tracer added to the snowpack was found in runoff (Dahl *et al.* 1979).

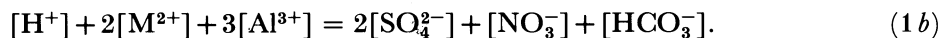
The Storgama model seems to give a rough picture of important processes, but it may be improved in several ways in addition to the introduction of weathering during winter low flow. Recent analyses of various Al-fractions in water samples from Storgama indicate undersaturation with respect to gibbsite (Seip *et al.* 1983); the assumption of equilibrium should therefore probably be modified. Further, an anion model including both sulphate and nitrate ought to be constructed.

##### 5. RELATIONSHIP BETWEEN DEPOSITION AND FRESHWATER ACIDIFICATION

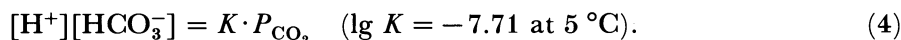
A most important question today is how a reduction in European emissions of sulphur and nitrogen compounds will affect freshwater chemistry, particularly in Scandinavia. The simulation models were originally constructed to describe present day-to-day and seasonal variations in streamwater chemistry. We have, however, tentatively investigated their potential for prognosis. A regional and more empirical approach has been discussed by Henriksen (1983) and Wright & Henriksen (1983).

In this section we will only consider the cation reactions in the upper reservoir in figure 1. As described previously, a model based on this reservoir gives a reasonable description of the cation chemistry at Storgama. For Birkenes the same model is appropriate at high flow, since the runoff then contains predominantly water from the upper reservoir.

The starting point is at (1a)–(3). To use the model at lower deposition levels, bicarbonate should be included. (1a) is therefore replaced by:



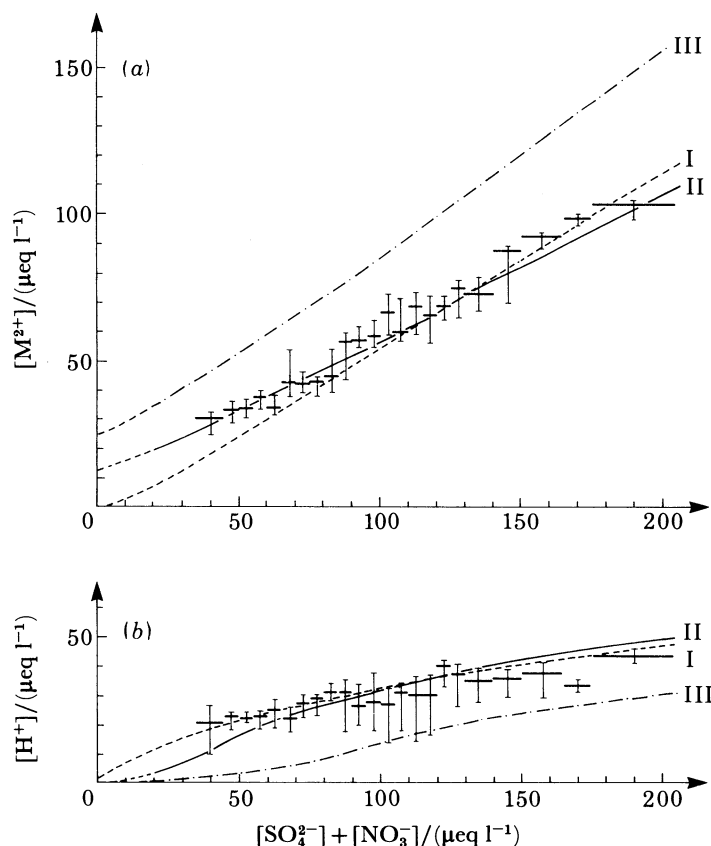
In addition we have the equation:



$P_{CO_2}$  is the partial  $CO_2$  pressure which in the atmosphere is about  $3.2 \times 10^{-4}$  atm† ( $P_{CO_2}^a$ ). In soils  $P_{CO_2}$  depends on the biological activity and will vary with season; it may be more than 100  $P_{CO_2}^a$  under anaerobic conditions (Bolt & Bruggenwert 1976). As the water leaves the soil, a new equilibrium is not reached instantaneously. Natural streamwaters are often supersaturated (for example, 2–10 times, Norton & Henriksen (1983)) with respect to the atmospheric  $CO_2$  pressure.

Figure 4 shows medians of  $[H^+]$  and  $[M^{2+}]$  at Storgama together with the 25% and 75%

† 1 atm = 101325 Pa.



Medians of observed  $[H^+]$  and  $[M^{2+}]$  with 75% and 25% quartiles as functions of  $[SO_4^{2-}] + [NO_3^-]$ . All available data ( $n = 424$ ) from 1974 to 1982 are included together with three theoretical curves (see text). (Data from Johannessen & Joranger (1976); M. Johannessen, personal communication; S.F.T. (1981–1983).)

quartiles plotted against the sum of sulphate and nitrate. No interval contains less than 10 observations. Three sets of theoretical curves are also given:

$$\begin{array}{ll}
 (1a)-(3), & *K_{so} = 10^{8.1}, \quad K_G = 10^{-2.21} & \text{I} \\
 (1b)-(4), & *K_{so} = 10^{8.1}, \quad K_G = 10^{-2.15} & \text{II} \\
 & P_{CO_2}^{soil} = 100 P_{CO_2}^a, \quad P_{CO_2}^{water} = 2 P_{CO_2}^a & \\
 (1b)-(4), & *K_{so} = 10^{8.1}, \quad K_G = 10^{-2.37} & \text{III} \\
 & P_{CO_2}^{soil} = 100 P_{CO_2}^a, \quad P_{CO_2}^{water} = 2 P_{CO_2}^a. & 
 \end{array}$$

In cases II and III (1b)–(4) are first solved with the indicated  $P_{CO_2}^{soil}$ . The curves in figure 4 are obtained after adjusting  $[H^+]$  and  $[HCO_3^-]$  to  $P_{CO_2}^{water}$ . The gibbsite equilibrium (2) was retained during the adjustment, but the ratio in (3) was not.

Though the observations display considerable scatter, curves I show that the A-reservoir chemistry of the Birkenes model explains general trends for the complete data record from 1974–1982 for Storgama. Curves II were included as an example to show that similar results may be obtained with a high  $P_{CO_2}^{soil}$  value and a slightly increased soil acidity (larger  $K_G$ , smaller  $L_P$ ). Certainly, other combinations of parameter values may give a similar fit. For given  $K_G$  and  $[SO_4^{2-}] + [NO_3^-]$  an increased  $P_{CO_2}^{soil}$  results in increased  $[M^{2+}]$  (and  $[HCO_3^-]$ ) and decreased  $[H^+]$  and  $[Al^{3+}]$ .

If past or future levels of sulphate and nitrate can be estimated, curves like those in figure 4 (compare, table 2) should be useful for predicting cation concentrations. By using the same curve for various deposition levels it is implied however, that the lime potential does not change in the period considered. But a reduction in the lime potential could have occurred since preindustrial times. Consider the preindustrial concentrations of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  ( $[\text{SO}_4^{2-}]_{\text{pi}}$  and  $[\text{NO}_3^-]_{\text{pi}}$ ). Available evidence suggests  $[\text{SO}_4^{2-}]_{\text{pi}} + [\text{NO}_3^-]_{\text{pi}} \approx [\text{SO}_4^{2-}]_{\text{pi}} \approx 20 \mu\text{eq l}^{-1}$ . This value is approximately the same as found at the unpolluted Todalen catchment in western Norway (Overrein *et al.* 1980; S.F.T. 1980, 1982). If the small marine contribution at Storgama is neglected, it also agrees with Henriksen's (1979) non-marine background estimate for southern Norway.

TABLE 2. COMPUTED CONCENTRATIONS FOR  $\text{M}^{2+}$ ,  $\text{H}^+$ , AND  $\text{HCO}_3^-$  FOR THREE LEVELS OF  $\text{SO}_4^{2-} + \text{NO}_3^-$  AND THREE DIFFERENT SITUATIONS (SEE TEXT)

$\text{SO}_4^{2-} + \text{NO}_3^-$ $\mu\text{eq l}^{-1}$	$\text{M}^{2+}$ $\mu\text{eq l}^{-1}$			$\text{H}^+$ $\mu\text{eq l}^{-1}$			$\Delta\text{pH}$			$\text{HCO}_3^-$ $\mu\text{eq l}^{-1}$		
	I	II	III	I	II	III	I	II	III	I	II	III
100	55	57	86	32	31	13	—	—	—	—	0.2	0.9
50	24	33	52	21	15	2	0.2	0.3	0.8	—	0.7	5
20	7	20	35	12	3	0.7	0.4	1.0	1.3	—	4	16

$\Delta\text{pH}$  refers to the change in pH compared with the first row.

Table 2 shows  $[\text{M}^{2+}]$ ,  $[\text{H}^+]$  and  $[\text{HCO}_3^-]$  for the present, the preindustrial and an intermediate level of  $[\text{SO}_4^{2-}] + [\text{NO}_3^-]$ . Both situations I and II give a low  $[\text{M}^{2+}]_{\text{pi}}$  and a negligible  $[\text{HCO}_3^-]_{\text{pi}}$ . These values seem unrealistically low compared to, for example, Todalen where on the average  $[\text{M}^{2+}] \approx 35 \mu\text{eq l}^{-1}$  and  $[\text{HCO}_3^-] \approx 15 \mu\text{eq l}^{-1}$ . One could also follow Henriksen (1983) and define

$$F = \frac{\Delta[\text{M}^{2+}]}{\Delta([\text{SO}_4^{2-}] + [\text{NO}_3^-])},$$

where  $\Delta$  is typical or average change in concentration since preindustrial times, where we have included nitrate which Henriksen generally considers negligible in southern Norway. Henriksen suggests  $F = 0.2$  as a reasonable value and his procedure gives us  $[\text{M}^{2+}]_{\text{pi}} = 42 \mu\text{eq l}^{-1}$  and  $[\text{HCO}_3^-]_{\text{pi}} = 19 \mu\text{eq l}^{-1}$  for Storgama.

Situation III (figure 4 and table 2), corresponding to a higher lime potential (higher base saturation) might be more representative of past conditions. If correct, this could imply soil acidification at Storgama particularly because  $P_{\text{CO}_2}^{\text{soil}} = 100 P_{\text{CO}_2}^{\text{a}}$  used in situations II and III may well be an overestimate for the area. Combining model studies and information on fish records, Christophersen & Seip (1983) found similar indications of soil acidification at Birkenes considering only the period since 1950.

Acidification of soils is a natural long-term process occurring, for example, during podzolization. A growing acid humus layer may have similar effects on freshwater quality. These processes can be accelerated by changes in land use and vegetation (Rosenqvist 1978), and acid precipitation could also play a role in soil acidification by increased leaching of base cations. Without mobile anions from strong acids, however, a catchment is not likely to produce progressively more acid streamwater resulting in fish kills, but a decrease in alkalinity could

certainly occur. In Norway, loss of fish populations is only a problem in areas receiving anthropogenic sulphur and nitrogen compounds.

No major vegetational or other changes seem to have occurred within the Birkenes (Christophersen & Seip 1983) and Storgama catchments during recent decades, though a pollen-analysis study by Høeg (1980) of three bogs near Storgama indicated that grazing has decreased during the last 100 years. It seems therefore possible that acid precipitation does play a role in soil acidification in these areas, but other contributions cannot be excluded. It should be remembered that most of the water follows the largest pores through the soil (Beven & Germann 1982). To affect the water chemistry it is therefore sufficient if a relatively small soil volume close to the macropores becomes acidified.

Based on the above discussion, we propose that a reduced deposition of sulphur and nitrogen compounds will affect streamwater chemistry in two ways (compare Seip 1980). First, a reduction in mobile anion concentrations will lead to lower levels of cations (figure 4). In addition a slow increase in base saturation could occur, thus altering the ratio between the cations. Very little is known about the rate of latter process. It is important, however, that areas still supporting fish in southern and western Norway may presently undergo soil acidification. A reduced deposition may be necessary to prevent adverse effects on freshwater chemistry in these areas.

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#### Discussion

I. TH. ROSENQVIST (*Oslo University, Box 1047, Blindern, Norway*). Has Dr Christophersen tried to introduce univalent cations other than H<sup>+</sup> into his model? From laboratory experiments and from field data it is easily demonstrated that Cl<sup>-</sup> is just as important as SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> as anion and Na<sup>+</sup> in precipitation acts in the same direction as does Ca<sup>2+</sup> and Mg<sup>2+</sup>. Although the treatment of the mathematical model will be more complex it will certainly be nearer to the real conditions if Na, K and Cl are introduced. Finally a back transport from Dr Christophersen's lower box to the higher one will improve the verisimilitude to nature.

N. CHRISTOPHERSEN. We have so far not tried to include other univalent cations other than H<sup>+</sup>. But this is not difficult in principle and has been done by Grip (1982).

We regard our existing models as the result of a *first* iteration and this is a main reason for not including Na<sup>+</sup> and Cl<sup>-</sup>. Thus as a *first* approximation these ions, predominantly derived from seasalt, are assumed to follow each other through the catchment. Chloride is generally known to be mobile in soils and Na<sup>+</sup> is a relatively mobile cation. In the Storgama area there is actually experimental evidence (Christophersen *et al.* 1982) that ion exchange involving Na<sup>+</sup> is not important for streamwater acidity.

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- B. A. THRUSH, F.R.S. (*University of Cambridge, Department of Physical Chemistry, Cambridge, U.K.*). Most of the atmospheric chlorine derived from coal burning and incineration of chlorine-containing materials such as PVC is rapidly removed from the atmosphere near its source because hydrogen chloride is very soluble in water. Most the chlorine in rain in southern Norway must have come from the sea.

N. A. SORENSEN (*Institute of Organic Chemistry, Norway Institute of Technology, Trondheim, Norway.*). In the lectures of Dr Goldstein and Dr Christophersen we were presented with typical examples of 'acid surge' episodes. This is a very important phenomenon. Of the lakes in Scandinavia which have become fishless during this century, only a minority belong to the Lake Woods type described by Dr Goldstein with a constant pH below 5.0. The majority of these fishless lakes and rivers belong to the type where pH is in a safe range – let us say 5.5–6.5 – most of the year, but where sharp drops in pH do occur. They are very limited in time, but very drastic in the change of pH, from close to 7.0 down to about 4.5 is a change that will kill the most valuable salmonids.

A very bad habit we have inherited from Swedish scientists is to connect these 'acid surges' to the 'fractionation effect' in early snowmelt. The concept was introduced by Professor Frank Odén in his opening lecture at the Ohio conference in 1975. Odén presented a diagram for pH and fulvic acids for the river Ljnsnan and explained the pH minima and coexisting organic matter maxima by the processes caused by the snowmelt. In the four years presented by Odén none had a large autumn flood. A year and a half before Odén gave that famous lecture, the river Ljnsnan had an autumn flood as large as the ordinary spring floods. The depression in pH during this autumn flood was just as large as in the regular spring flood; the changes in the concentrations of the other main ions of course also corresponded. The autumn flood of 1973 demonstrated that the acid surges pointed out by Odén have nothing to do with the fractionation occurring during snowmelt.

For this reason I am sorry to meet this fractionation effect again in Dr Christophersen's lecture. He knows that the supervision project which has followed the S.N.S.F. project was clever enough to demonstrate an extremely sharp autumn acid surge while they were suspicious enough to take daily samples. If I remember the figures correctly the minimum day had pH = 4.02 and the two neighbouring days pH = 4.8–4.9; the average was usually about 6.3.

It is of utmost importance if we are to avoid fishkills that we get measuring procedures that catch these episodes early enough and that we get a scientific explanation for these remarkably sharp peaks. One thing ought to be clear: they have nothing to do with the fractionation effect during snowmelt. As these pH minima are of such remarkably short duration, two or three days to one week, remedial action ought to be cheap.

P. F. CHESTER (*C.E.G.B. Central Electricity Research Laboratories, Kelvin Avenue, Leatherhead, Surrey KT22 7SE, U.K.*). The models just presented describe the short term variations in surface water composition. Could Dr Christophersen tell us what parameter(s) would have to change in his model to account for long term changes in surface water chemistry. How can simple models of long term surface water acidification (such as that of Henriksen) be reconciled with these models?

N. CHRISTOPHERSEN. The main problem in modelling long-term trends in freshwater chemistry is the estimation of changes in soil properties (for example, base saturation). The change in  $K_G$  (equation 3) must be determined. As mentioned, soil changes close to macropores may be particularly important. It is also, of course, necessary to include bicarbonate if the model is going to be used for low deposition levels. Bicarbonate was neglected in the original model, but has now been included in one version. For more details see §5 where Henriksen's approach is also mentioned. To obtain  $F$  ratios (see §5) in agreement with Henriksen's estimate, soil acidification must be assumed in our model.