

SNOQUAL, A Snow-Meltwater Quality Model

A Study of Model Variants

H.G. JONES

INRS-Eau, Université du Québec
CP 7500, 2700 Einstein
Ste-Foy, Québec G1V 4C7, Canada

J. STEIN

Faculté de foresterie et de géodésie
0870 Vachon, Université Laval
Laval, Québec G1K 7P4, Canada

W. SOCHANSKI

INRS-Eau, Université du Québec
Carrefour John Molson, 2800 rue Einstein
Ste-Foy, Québec G1X 4N8, Canada

ABSTRACT

SNOQUAL is a conceptual model that relates the quantity of meltwater released from the snowpack to the chemical composition of the discharge. Three versions of the model have been developed. These three variants (SNOQUAL1, SNOQUALR, and SNOQUALD) attempt to reflect the physical reality of the interaction of meltwater and the snowpack *in situ*. They take into account, respectively, the leaching process of ice crystals, the non-surficial ionic load which resides within the ice structure, and the presence of both rapid and slow leaching components (snow and canopy debris) in forested snowpacks. Laboratory and field experiments shows that on a local scale (open-, closed forest canopy) the leaching coefficients of the model variants are influenced by the quantity of organic debris (litter fallout) in the pack. The results also show that there is no significant differences in model performance between the three variants. The subsequent application of a model variant (SNOQUALR) to the simulation of the acidity (pH) of the first meltwaters that can be expected from snowpacks, deposited under conditions of either a reduction or an increase in the emissions of acidic pollutants (SO_2 , NO_x) on a regional scale is also given.

INTRODUCTION

In the southeastern region of the Canadian Shield the pH of the precipitation is often in the range of 3.8-4.5. In the "Réserve faunique des Laurentides", Quebec, Environment Canada has established an experimental program to develop a model of the effects of acid precipitation on the aquatic resources of a forested watershed. The program has centred on the development of a comprehensive model for the acidity of lake waters. A component of the lake water model is SNOQUAL - a model for the simulation of meltwater quality. SNOQUAL itself consists of two modules, SNOW-17 (Anderson, 1973) which simulates quantitatively the discharge of meltwater from the snowpack and a second module which simulates the release of chemical components from the snow by the meltwaters.

This paper outlines the meltwater leaching of ions from snow and other basic processes inherent to the chemical model. Laboratory studies to determine the probable range of

values for the leaching parameters of ionic species from the melting snowpack are described. The various versions of the model (SNOQUAL1, SNOQUALR, SNOQUALD) which have been used to simulate the chemical composition of meltwaters discharged from the snowpack on a local scale (boreal forest) are discussed. Application of a model variant (SNOQUALR) to estimating relative concentrations of acidity in meltwater discharge from snowpacks on a regional scale (Quebec Province) is presented.

STUDY SITE AND METHODOLOGY

The site: Lac Laflamme is a small catchment area (0.06 km²) in the boreal forest 80km north of Québec City. The mean annual temperature is 0.2°C (-15°C January; 15°C, July). The total snowfall (October-May) is approximately 400 mm (Snow Water Equivalent, SWE) and the pack usually attains a depth of 120-150 cm at the end of the accumulation period. The melt season generally begins towards the end of April and maximum meltwater discharge occurs during the first two weeks of May.

Field snow cover and meltwater study: four square shaped lysimeters (plastic covered fiberglass, 1 m by 1 m; sidewall height, 0.5 m) were installed for the 1988 melt season. Three were placed within a balsam fir stand under closed canopies. Snow cover sampling was carried out with an Adirondack-type corer; precipitation was sampled by means of a Sangamo wet-only collector. Meltwater samples representing the integrated sample of all meltwater discharges over 24 hours were taken at midday (noon to 14:00 hours) every day. All samples were conserved and analysed as reported by Jones, 1987.

Laboratory study: the snowmelt simulator consisted of four plastic (PVC) columns within which "clean" snow taken from open areas in the forest, and different combinations of clean snow and organic debris could be melted under carefully controlled conditions (Jones and Deblois, 1987). As in the case of the field lysimeters the meltwater samples were gathered every 24 hours and analysed in exactly the same manner.

MODEL PROCESSES

The models are chemical subroutines of the global model for the simulation of snow meltwater quantity and quality (SNOQUAL, Stein et al, 1986). They are based both on the physical phenomena that are known to occur when snow meltwaters move down through the pack and on observations of meltwater composition from meltwater studies in the field (Jones, 1987) and the laboratory (Jones and Deblois, 1987). The models are of three types all of which are based on the physical concept of the leaching of solubles from the pack matrix by a diminishing reserve of ice meltwaters. In all of the models the leaching or removal of solubles from the pack is defined by a first order equation in which the parameter for the rate of leaching is a leaching coefficient 'k' (Foster, 1978).

The first model, SNOQUAL1, is a bulk model; the value of the leaching coefficient represents the net leaching effect of the removal of solubles from both the surface of snow crystals and other material (mostly fallout of organic matter from the canopy) in the pack.

The second model (SNOQUALR) is a discrete partition model. In this model the material to be removed from the snowpack is partitioned into two components. The first component resides on the surfaces of snow and other materials. A residual component of the composition of the snow resides within the ice lattice structure of the grains. As the melting snow removes more and more of the concentrated surface solutions from the snow grains (plus surface leaching of organic matter), the composition of the meltwaters discharged from the pack approaches that of the residual concentrations in the ice lattices of the snow grains. This residual component is expressed by means of a constant, R, the fractionation coefficient.

The third model (SNOQUALD) is similar to (SNOQUALR) in that the model segregates the material to be leached from the pack into components. In this model, however, a distinction is not only made between surface leachables and residual concentrations in the ice structure but also between snow and other pack components (e.g. organic matter). A constant, s, the segregation coefficient, is used to distinguish between the contribution of the snow to the meltwater composition and that of the other matter. The model thus contains two leaching coefficients, k_s and k_m , representing respectively the leaching of snow and the leaching of the other components, particularly the organic matter.

MODEL STRUCTURES

In all these models (SNOQUAL1, SNOQUALR, SNOQUALD) the common model parameters are the concentration of ions in the snow, C ($\mu\text{eq l}^{-1}$), the height of the pack, H (snow water equivalent, SWE, mm), and k (net leaching coefficient, mm^{-1}) or k_s and k_m in the case of SNOQUALD. Model inputs are C_0 , the bulk ionic concentration of the snow prior to melt, H_0 , the height of the pack at the beginning of the melt, and H_i , the height of the pack at the end of a specified melt period. The leaching coefficient(s), k, can either be an input or an output, the latter being the result of curve-fitting of the numbers generated by the models to the real data of snow and/or meltwater compositions in the field. C_i , the concentration of an ionic species in the snow at the condition $H = H_i$ is the primary output which transposed into the meltwater concentration, C_m , is used as the basis for the curve fitting exercises to determine other model parameters (Jones et al, 1986).

The expressions 1, 2, and 3 represent SNOQUAL1; SNOQUALR, and SNOQUALD respectively.

$$C_i = C_o e^{-k(H_o - H_i)} \quad (1)$$

$$C_i = C_o(1-R) e^{-k(H_o - H_i)} + RC_o \quad (2)$$

$$C_i = C_o(1-R)s e^{-k_s(H_o - H_i)} - C_o(1-R)(1-s)e^{-k_m(H_o - H_i)} + RC_o \quad (3)$$

In SNOQUALR the term, R, the fractionation coefficient, is either an input to the model, the value being determined from laboratory studies, or an output, the value being determined by default during the calibration procedure. In SNOQUALD, R is an input determined from observations in the field or the laboratory (the value of R is usually calculated as the mean value of measured concentration in the last 10-20% of the residual meltwaters). In this model, the second constant, the segregation coefficient, s, which quantifies that part of the total bulk concentration of the pack associated with the snow grains is an input to the model (see "model calibration").

MODEL CALIBRATION

The structures of the above models are based on simple physical concepts of meltwater leaching. In the laboratory the calibration of the leaching models is facilitated by the controlled experimental conditions. Meltwater leaching, in the field, is, however, complicated by meteorological and in-pack physical and chemical conditions which make it difficult to calibrate the models. The calibration is thus restricted to melt periods in which there are no major perturbations of the meltwater production.

The main factor which has to be taken into account in the calibration of the models in the field is the combined influence of fallout of organic debris, dry deposition, wet deposition, and in-pack biological activity on pack chemistry. The result of these processes is such that the total amount of chemical load removed from the pack is not equal to the load that resided in the pack just prior to the melt (i.e. C_o). The total amount of water discharged may also be different from that indicated by the reduction in the SWE of the pack during periods of light rain or condensation. At the present time we do not have enough information on these phenomena which would facilitate the calibration of the models at each successive time step (24 hrs). To partially compensate, however, for this lack in model calibration, the calibration procedure first calculates the contribution of all these spurious inputs to the pack for any one calibration period (non-perturbed melt sequence) by an ionic mass balance calculation on the snow-meltwater system. The calculated values are then integrated into the model, as if all the chemical load associated with these inputs had been originally present in the pack at the start of the melt sequence. Consequently, instead of using the original values of C_o and H_o measured directly in the field to calibrate the models, apparent values of C_o and H_o at the beginning of the melt are calculated from the field data. For any one period these apparent values of C_o and H_o are calculated from C_m and H_m , the

concentration and the height of meltwater discharge respectively, and the residual concentration, C_r , and height, H_r , of the pack measured at the end of the period (expressions 4, and 5).

$$C_o \text{ (apparent)} = (\Sigma C_m * H_m + C_r * H_r) / (\Sigma H_m + H_r) \quad (4)$$

$$H_o \text{ (apparent)} = \Sigma H_m + H_r \quad (5)$$

These apparent values of C_o , H_o are used for the models SNOQUAL1 and SNOQUALR.

In the case of SNOQUALD the real measured value of the bulk concentration of any ion in the snowpack just prior to the melt and the calculated apparent value for the bulk concentration from expression 4 are used to determine the value of 's', the segregation constant (expression 3). s is assigned the value of $C_o(\text{real})/C_o(\text{apparent})$. The contribution of snow to the overall pack composition is thus designated to be the original value of C_o as measured directly in the field prior to melt (i.e. $C_o[\text{real}] = C_o[\text{apparent}] * s$). The remainder ($C_o[\text{apparent}] - C_o[\text{real}] = C_o[\text{apparent}](1-s)$) is designated as the contribution of all the other spurious inputs (canopy fallout, dry deposition, wet deposition, and in-pack biological activity) to the final chemical composition of the pack responsible for meltwater concentration during the specified calibration period.

Once $C_o(\text{apparent})$ and $H_o(\text{apparent})$ have been calculated, a mean value of k is determined for SNOQUAL1 (expression 1) from the meltwater data of the four field lysimeters by curve fitting (method of least squares). The same procedure is used to determine k and R for SNOQUALR (expression 2). In the case of SNOQUALD the value of R from SNOQUALR is taken as an input, the value of s is also an input, and mean values for k_s and k_m are also found by curve fitting the field data.

DISCUSSION

Model calibration: laboratory, field

The calibration of the different variants of the model (SNOQUAL1, SNOQUALR, and SNOQUALD) using the real concentrations of SO_4 in meltwaters from controlled melts in the laboratory is shown in figures 1 and 2. Melt experiments for both clean snow taken from large open areas in the forest and clean snow to which organic matter (lichens, twigs, bark, needles, and leaves) taken from the forest canopy was added, were carried out. The influence of the organic matter on the leaching process may be clearly seen by comparing the elution concentrations reproduced in figures 1 and 2. The organic matter increases the SO_4 load of the meltwaters over that of meltwaters from clean snow by desorption of the ion from the organic surfaces. The decrease of meltwater

concentrations is thus less acute in the case of snow containing organic matter than that of snow meltwaters alone. This production of ions by the organic matter during the melt by desorption and/or microbiological processes causes an apparent decrease in the leaching coefficient (see below).

The efficiency of each variant of the model to conform either to laboratory or to field measurements of meltwater quality by the calibration procedure may be judged by comparing the Standard Error of Estimation (SEE, Table 1; equation 6).

$$SEE = \sqrt{\frac{\sum (C_i - C_m)^2}{N - 2}} \quad (6)$$

where: C_i = simulated concentrations
 C_m = measured concentrations
 N = number of samples

The laboratory experiments showed that the calibration of SNOQUALR gave lower values of SEE than SNOQUAL1 or SNOQUALD. The same result was observed in the case of the field trials; table 1 records the SEE Values for both SO_4 and NO_3 for each of the four field lysimeters. The difference, however, between the performances of SNOQUAL1, SNOQUALR and SNOQUALD are small (< 1%, SNOQUAL1 vs SNOQUALR; 12%, SNOQUALR vs SNOQUALD) and not statistically significant considering the number of melt periods studied. In general, SNOQUALR generates meltwater concentrations which are the closest to those measured in the field. The very similar closeness-of-fit for all the model variants suggests that the leaching processes (k or $k_s + k_m$, equation 1-3) are dominant and that physical inhomogenities of pollutant distributions in snow crystals or snow-particulates have but a minor influence on model simulation.

Figures 3 and 4 show the real concentrations of SO_4 in snow meltwaters for the two melt periods during the spring melt in 1988 at Lake Laflamme and the concentrations generated by SNOQUALR. The figures are of the concentrations in meltwaters discharged by a lysimeter under the forest canopy and of a lysimeter in the clear cut area. The lysimeter in the clear cut was in a relatively shallow snowbank; it finally discharged 360 mm of snowmelt and rain compared to the 480 mm discharged by the lysimeter in the forest. The lysimeter in the open area also discharged low amounts of meltwater during the first days of the melt compared to the lysimeter in the forest. This explains the apparent anomaly, of similar patterns of forest and open lysimeter concentrations occuring at different points on the meltwater cumulative discharge axes of figures 3 and 4.

CALIBRATION, SNOQUAL LABORATORY MELTS, NO ORGANICS

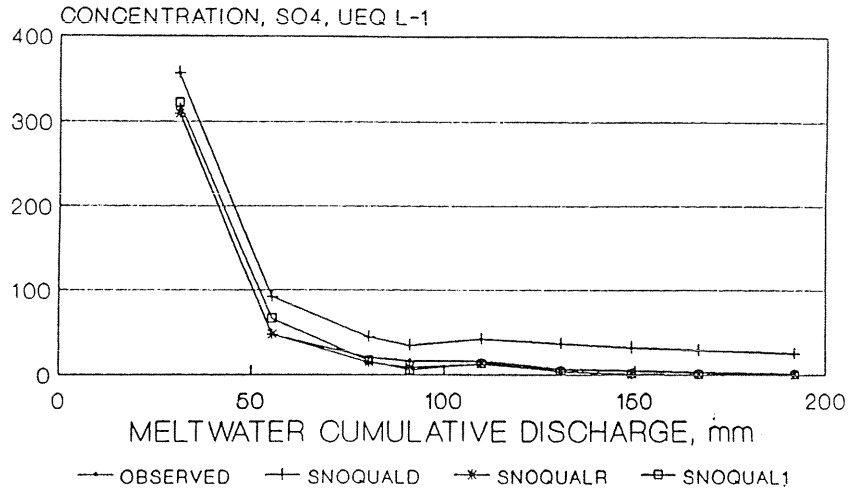


FIGURE 1: Calibration of SNOQUAL variants with data on meltwater SO_4 concentration values from laboratory melts: clean snow.

CALIBRATION, SNOQUAL LABORATORY MELTS, ORGANICS

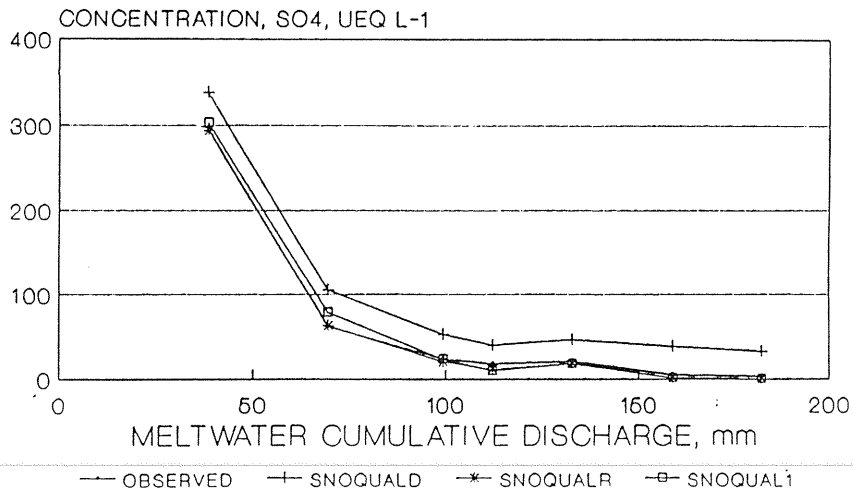


FIGURE 2: Calibration of SNOQUAL variants with data on meltwater SO_4 concentration values from laboratory melts: snow plus organic matter.

CALIBRATION, SNOQUALR FIELD MELTS, CANOPY

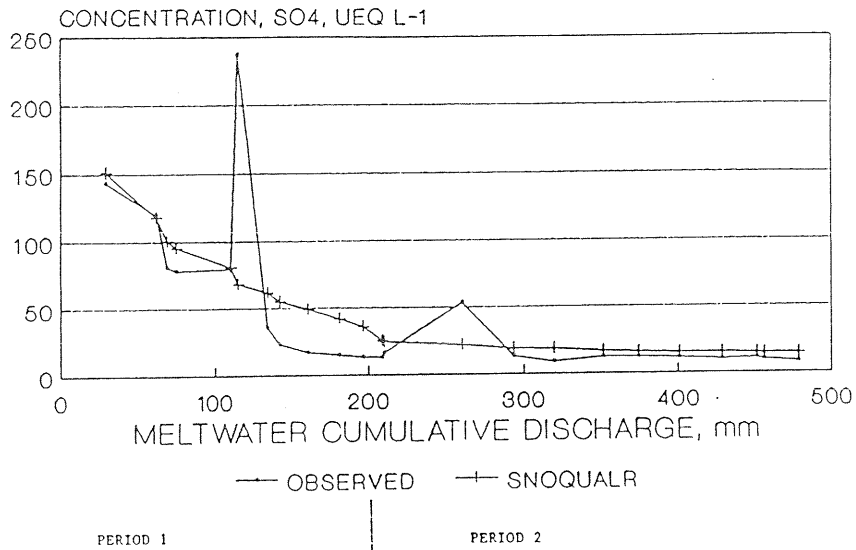


FIGURE 3: Calibration of SNOQUALR with data on meltwater concentrations values from field lysimeter discharges: lysimeter in forest; SO_4 .

CALIBRATION, SNOQUALR FIELD MELTS, OPEN

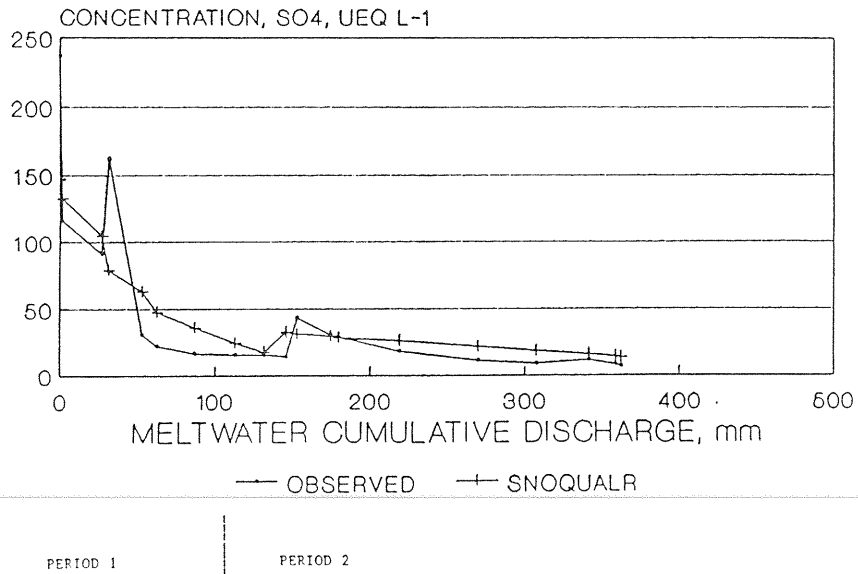


FIGURE 4: Calibration of SNOQUALR with data on meltwater concentrations values from field lysimeter discharges: lysimeter in clear cut; SO_4 .

TABLE 1

Standard Error of Estimation (SEE, $\mu\text{eq L}^{-1}$) for calibration of SNOQUAL1, SNOQUALR, and SNOQUALD, Lac Laflamme, 1988.

Standard error of estimation (SEE)				
	FIRST MELT PERIOD		WHOLE MELT PERIOD	
	SO ₄	NO ₃	SO ₄	NO ₃
SNOQUAL1	61.10 ¹	41.00	40.94	27.45
	63.50 ¹	67.64	45.61	46.97
	261.57 ¹	174.10	169.80	111.53
	42.56 ²	56.73	27.55	34.96
	112.62 ³	97.32	71.37	61.16
MEAN	108.27	87.36	71.05	56.41
SNOQUALR	61.10	41.00	40.80	27.40
	63.5	67.60	45.58	46.90
	261.53	174.10	168.70	111.53
	42.51	56.10	27.07	34.96
	112.59	97.30	71.33	61.12
MEAN	108.24	87.34	70.69	56.38
SNOQUALD	67.52	41.74	48.57	43.17
	64.20	66.34	49.31	46.65
	256.47	170.85	166.70	109.57
	43.69	57.63	28.87	35.39
	112.30	95.87	73.04	60.33
MEAN	108.83	86.48	79.30	59.02

¹) lysimeters in forest; ²) lysimeter in clear cut area
³) combined lysimeter discharges.

The melt periods (1 and 2) are separated by a five-day cold event in which the production of meltwater was very low. A rain event occurred during the first period, the meltwater discharge during this event was very concentrated. As only a small amount of melt had been discharged at that time the calibration period was not terminated at this point. The effect of the rain, however, is evident in the fact that the model does not generate a satisfactory fit to the meltwater concentrations after this event. Observed concentrations are much lower than those generated by SNOQUALR showing that an appreciable amount of the ionic load had been removed by the rain. As noted above the calibration procedure does not presently take into account any leaching of the pack by rain. The procedure, however, could be modified by attempting to estimate the amount of material leached from snow by rain; data on rain-on-snow events such as those published by Jones et al (1989) could be used for this purpose.

The influence of organic matter on the performance of each variant of the model is reflected by the values of the leaching coefficient. Table 2 shows the values for the leaching coefficients determined by model calibration of SNOQUAL1 and SNOQUALR using data from both field and laboratory studies. In the case of the controlled laboratory melts the value of k is lower in the case of the snow containing organic matter than that of clean snow; the difference in value being statistically significant; in the field the same observation may be made i.e. the values of k for the three lysimeters

placed in the forest are lower than for that of the fourth lysimeter which, being situated in a clear cut area, had relatively little canopy fallout. The differences between the laboratory and field results also show the influences of all the other spurious inputs to the pack that occur in the field (local dust deposition, dry deposition and deposition from light rain or condensation on the pack). Values of k in the field are approximately three times smaller than laboratory studies for clean snow and five times smaller for snow plus organic matter. In the case of SNOQUALD the preliminary results from the same calibration are complex. They suggest that at certain times ions are released in greater quantities from organic matter than from the snow crystals. Fluctuation in leaching rate during one melt period is not a criterion of the models; calibration of SNOQUALD with two leaching coefficients may thus lead to anomalies in the values of k_s and k_m which cannot be reconciled with the physical processes of the original model.

TABLE 2

k values, mm^{-1} , for laboratory and field experiments.

k values				
		Laboratory*		Field (1988)
		Snow	Snow + organics	
S N O Q U A L D	SO ₄	.04835	.03379	.00636 ¹
		.05281	.03535	.00723 ¹
		.05050	.03420	.00756 ¹ .01708 ²
	Mean St.Dev.	.051 ±.002	.034 ±.001	.009 ±.004
	NO ₃	.03831	.02000	.00525
		.04676	.03075	.00734
		.04212	.02542	.00738 .01503
	Mean St.Dev.	.042 ±.004	.025 ±.005	.008 ±.004
S N O Q U A L R	SO ₄	.06067	.04094	.00636
		.06976	.04426	.00723
		.06491	.04173	.00756 .01708
	Mean St.Dev.	.065 ±.005	.042 ±.002	.009 ±.004
	NO ₃	.06038	.02388	.00525
		.06482	.03895	.00734
		.06171	.03144	.00738 .01503
	Mean St.Dev.	.062 ±.002	.031 ±.008	.008 ±.004

* 3 experiments
¹) Lysimeters in forest; ²) Lysimeter in clear cut area.

The overall results of the calibration showed that under the experimental conditions (2 melt periods; 4 field lysimeters), there was no significant differences between the simulation of meltwater quality by the three model variants. The studies indicate that the k values are much lower in the field than the laboratory. In addition the values for k for snow in similar physical environments are relatively constant (i.e. the three lysimeters under the forest canopy). These preliminary results lead us to suggest that we can assign values of k a priori to melts; this is an important step in the use of the model in a predictive manner.

Model Validation: problems of initialisation of C_0

In previous studies we were able to validate the first original model of SNOQUAL (Jones et al, 1986; Stein et al, 1986) as the C_0 value used in this model was the real value for the concentrations of ions in the snowpack prior to the melt. Model validation in the case of SNOQUAL1 and SNOQUALR will require methods of estimating C_0 according to the new definition of C_0 (eq. 4). It is possible that this can be achieved by incorporating short-term forecasting of meteorological and air quality parameters into the procedure for model use. This would allow the estimation of meltwater rates, dry deposition and rainfall quantity and quality as inputs to the model during an immediate forthcoming melt period. In the case of forest systems this procedure would have to be complemented by estimation of organic matter fallout onto the pack; it may be predicted from calculated rates of canopy fallout based on a statistical analysis of winter litter fall (Taylor and Jones, 1990).

Model utility: regional meltwater chemistry and changing air quality

In spite of the problems in model validation, the model (SNOQUALR was chosen for application studies) can still be used to evaluate the relative concentrations of meltwaters that one would expect from snowpacks with different heights and bulk concentrations of ionic species (H_0 , C_0) in similar regional environments. This is useful in attempting to predict the large scale effects of the reduction of total emissions of acidic pollutants on the acidic pulses that are discharged from snow covers during the spring melt.

Table 3 shows the pH values generated by SNOQUALR for the first meltwaters discharged from the snowcover in spring in four regions of the Province of Québec, Canada. The simulation conditions were 1) the present conditions of SO_2 emissions and 2) three hypothetical conditions for future emissions i.e. a 30% reduction, a 50% reduction and a 30% increase in SO_2 loadings. The simulations maintain a constant loading for NO_x emissions. The procedure assumes that all atmospheric SO_2 fluctuations are reflected by the SO_4 concentrations deposited by snowfall onto the pack. The constant loading of NO_x is represented by a constant value for the concentration of NO_3 in the pack at any one

site. Values for the bulk initial concentration of SO_4 and NO_3 were taken from data on the Lac Laflamme snowpack prior to melt in 1988. Snowpack concentrations in the snow at other sites representing southeastern Québec, northwestern Québec and eastern Québec were extrapolated from the Lac Laflamme data using the recorded winter-time concentrations of SO_4 and NO_3 at Hemmingford, Parent and Cap Seize, Québec, respectively (Jacques and Boulet, 1986). Snow water equivalent data for these sites was taken from snow survey records compiled by the Québec Government for March, 1988 (Environment Québec, 1988). The leaching coefficients (k) and the fractionation coefficients (R) are assumed to be constant for each ionic species over the whole study area. pH is finally calculated from the simulated SO_4 and NO_3 meltwater concentrations according to the relationship established between $[\text{H}^+]$ and $[\text{NO}_3 + \text{SO}_4]$ by Jones (1988).

TABLE 3

Simulated pH value by SNOQUALR for pH values of the first meltwaters (20 mm) discharged from snow cover in 4 regions of Québec under present conditions of SO_2 emissions and hypothetical conditions of reduction and increase.

Région	Height (water equivalent of pack, mm)	pH values for first meltwaters (20 mm) ⁵			
		Present emissions	50% reduction	30% reduction	30% increase
Lac Laflamme ¹	350	3.95	4.07	4.03	3.90
	350	4.00	4.12	4.05	3.93
	250	4.06	4.17	4.13	4.01
Southwestern Québec ²	150	4.01	4.17	4.06	3.94
	100	4.11	4.26	4.15	4.04
Southeastern Québec ³	350	4.16	4.31	4.24	4.10
	300	4.21	4.36	4.29	4.15
	250	4.27	4.41	4.35	4.20
Northwestern Québec ⁴	200	4.13	4.24	4.19	4.07

- ¹ Mountainous region, $[\text{SO}_4]$, $22.5 \mu\text{eq L}^{-1}$; $[\text{NO}_3]$, $28 \mu\text{eq L}^{-1}$; March-April 1988
² Plain; St-Lawrence Lowland, $[\text{SO}_4]$, $45 \mu\text{eq L}^{-1}$; $[\text{NO}_3]$, $32.7 \mu\text{eq L}^{-1}$; Extrapolated
³ Mountainous region, $[\text{SO}_4]$, $17 \mu\text{eq L}^{-1}$; $[\text{NO}_3]$, $14 \mu\text{eq L}^{-1}$; Extrapolated
⁴ Low plateau, $[\text{SO}_4]$, $22.5 \mu\text{eq L}^{-1}$; $[\text{NO}_3]$, $29.3 \mu\text{eq L}^{-1}$; Extrapolated
⁵ Leaching coefficients: 0.009 mm^{-1} , SO_4 ; 0.008 mm^{-1} , NO_3
 Fractionation coefficients: 0.02 , SO_4 ; 0.02 , NO_3

From table 3 it can be seen that the reductions or the increase in SO_2 emissions do not have a large effect on the pH of the meltwaters at any one site (0.1 - 0.15 units of pH). This is due, in part, to the fact that NO_3 is the dominant acid anion in the pack in winter and it controls to a large extent the pH of the meltwaters. A reduction of 50% for both SO_2 and NO_x emissions would lead to a meltwater discharge of pH 4.25 at Lac Laflamme. It should be noted that even if the emissions of SO_2 (SO_4) and NO_x (NO_3) were reduced by 90% the first meltwaters at Lac Laflamme would still show a pH value of 4.94. This aspect of the simulation shows how dominant the leaching process is in determining the acidity of melt waters. Acidic meltwaters have in fact been reported for the melting of snow cover with relatively low concentrations of SO_4 and NO_3 (e.g. alpine meltwaters, Delmas 1989). At very low values of SO_4 and NO_3 the pH of the first meltwaters at the Lac Laflamme would be in the range of 5.6 - 6.0.

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