

CHANGES IN STREAM CHEMISTRY DURING SNOWMELT RUNOFF  
IN TWO HEADWATER CATCHMENTS

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ABSTRACT

The influence of flow characteristics on changes in  $[H^+]$  and  $[SiO_2_{aq}]$  was investigated in two headwater streams (Harp-4, mean pH  $\approx$  6.2; Plastic-1, mean pH  $\approx$  4.4) on the Canadian Shield during snowmelt runoff. In both streams very similar  $[SiO_2]$  - discharge relationships were observed. These agreed well with a model conceptualizing the stream water as a mixture of soil/ groundwater and meltwater.  $[H^+]$ , however, was not as strongly correlated with discharge. Some of the residual variation could be explained by including the change in discharge and a hysteresis effect since  $[H^+]$  was lower on the rising limb than on the falling limb of the hydrograph. In Plastic-1,  $[H^+]$  was generally higher than in Harp-4 approaching meltwater levels during periods of high flow. There appears to be either insufficient contact time or different mechanisms of  $H^+$  neutralization operating during peak discharges in Plastic-1 compared to Harp-4. The lack of a consistent stoichiometric relationship between silica and hydrogen in both streams suggests that processes other than silicate weathering must influence the release of silica and/or the neutralization of hydrogen during snowmelt runoff.

Introduction

The spring runoff is of great importance to the hydrology and chemistry of small headwater streams on the Canadian Shield in Central Ontario. Previous investigations have shown that 50-75% of the annual runoff occurs in the months March-May in the Muskoka-Haliburton area (Scheider et al. 1984a) and that the highest rates of chemical exports occur at this time. Spring runoff also produces extreme concentrations of elements such as hydrogen and aluminum, which may reach environmentally critical levels (Sharpe et al. 1984). The rapid melt of an accumulated snowpack of very low pH can lead to pH depressions in streams in such areas where the overburden is incapable of neutralizing the meltwater (Jeffries et al. 1979). This increase in  $[H^+]$  is often associated with a decrease in those solutes with low concentration in meltwater such as the weathering product silica ( $SiO_2_{aq}$ ). Yet, there still remains a lack of information on how closely these changes are linked to the hydrologic response of a given basin.

Johnson et al. (1969) explained changes in stream chemistry solely by mixing of surface water (melt or rain water) with deeper soil water. A simple mixing model described the dilution of various weathering products ( $\text{Na}^+$ ,  $\text{Mg}^{2+}$  and  $\text{SiO}_2$ ) with increasing flow in small headwater streams in Hubbard Brook, N.H. very well. The increase in  $[\text{H}^+]$  was not in agreement with the decrease in the weathering products which was attributed to chemical reactions superimposed on the basic mixing process.

Several studies have attempted to represent the influence of flowpaths on stream chemistry by considering flow components derived from hydrograph separation. It was argued that baseflow (delayed flow) and surface flow (quickflow) have different concentration of total dissolved solids (TDS) whereby surface flow acts as a diluent (Pionke et al. 1972). They found that the ratio of surface to baseflow estimated the salinity of ephemeral streams more precisely than discharge alone. Walling (1974) incorporated discharge-dependent variations in surface flow [TDS] in order to improve the original concentration-discharge relationship in a small stream in the U.K.. Interflow (Hart et al. 1964) as well as antecedent flow as a surrogate of overland flow and/or increased interflow (Ledbetter and Gloyna 1964) have also been considered. However, none of these models has been applied yet to any other constituent but total dissolved solids (TDS).

The objective of this study is to investigate the relationships of the stream solutes silica ( $\text{SiO}_2$  ag) and hydrogen ( $\text{H}^+$ ) with hydrology in headwater catchments on the Canadian Shield during snowmelt runoff. Observed changes in stream chemistry are first related to discharge alone using the mixing model suggested by Johnson et al. (1969). In a second step the importance of other flow variables in influencing  $[\text{SiO}_2]$  and  $[\text{H}^+]$  will be determined applying multiple regression analysis. The analysis focuses on the solutes hydrogen and silica in order to investigate the role of hydrology as well as silicate weathering on the neutralization process during spring runoff.

#### Data Base

The Harp Lake and Plastic Lake watersheds are located on the Precambrian Shield in the Muskoka-Haliburton area, Central Ontario. They have been monitored since 1976 as part of the Acid Precipitation in Ontario Study APIOS (Dillon et al. 1978 ; Jeffries et al. 1979 ; Scheider et al. 1979a ; Dillon et al. 1982). The streams of two small subcatchments, Harp-4 and Plastic-1, were selected for this study since they differ greatly in their capacity to neutralize acidic deposition. A summary of catchment characteristics is given in Table 1. They are small headwater catchments feeding first and second order streams with peak discharges < 30 mm/d during spring runoff and very little or no flow during the late summer period. Wetlands (beaver ponds and/or swamps) further influence the stream hydrology and stream chemistry.

Runoff from the two basins were gauged at V-notch weirs and continuously recorded using Stevens water level recorders. The daily mean discharge was expressed as specific discharge  $q$  (in mm/d) for comparison among watersheds of different size. Water samples were taken by the Ontario Ministry of Environment (O.M.E.) and analyzed for pH on the day of

sampling using a pH meter. Dissolved silica ( $\text{SiO}_2$  ag) was analyzed within a few weeks using colourimetry. Analytical methods are described in more detail by Locke and Scott (1986). Stream hydrological and chemical data used in this analysis covered an observation period from 1977-1984 for Harp-4 and from 1980-1984 for Plastic-1. The study was restricted to spring runoff data because; (1) highest flows and highest exports of the year are generally observed during this period; (2) Plastic-1 is an ephemeral stream which tends to dry up in some summers; and (3) during the growing season high biological/chemical activity in wetlands (swamps /beaver ponds) combined with very low flows are known to alter chemistry as redox conditions change (LaZerte unpubl. data). Therefore, only observations from January 1 until the 'end of melt runoff' of each year were considered in this study. The 'end of melt runoff' was defined as the day of peakflow prior to the final recession of the last melt-dominated storm event and thus prior to any considerable increase in water temperature. Snowcover records (Environment Canada 1977-84) from Dorset, Ontario (for Plastic-1) and Dwight, Ontario (for Harp-4) were used to identify the end of melt runoff.

Table 1. Description of the study watersheds. Chemical values are obtained from spring data base (1977-1984 Harp-4, 1980-1984 Plastic-1),  $[\text{SiO}_2]$  in mg/l Si,  $[\text{H}^+]$  in  $\mu\text{g/l}$ .

	Plastic-1	Harp-4
size & location <sup>1</sup>	23.34 ha 45°11' N 78°50' W	119.1 ha 45°23' N 79°08' W
general morphology <sup>2,3</sup>	moderate slopes (<5%) containing centr. located swamp covering $\approx$ 9% of the total drainage area	variable slopes (4-5%) containing beaver pond covering $\approx$ 5% of total drainage area
bedrock geology <sup>2,3</sup>	Ortho-gneiss; mainly igneous granites & meta- sedimentary formations near fault zones	Amphibolite & schist; $\approx$ 15% is underlain by biotite gneiss
surficial geology <sup>2,3</sup>	shallow discontinuous sandy basal till (<2m) & exposed bedrock	unsorted till (1-5m), exposed bedrock & clean well-sorted sand
soils & vegetation <sup>4</sup>	weakly developed podzolic soils (<1m) supporting a coniferous forest	humo-ferric podzolic soils (1-3m) supporting a mixed hardwood forest
stream <sup>5,6</sup>		
$[\text{SiO}_2]$	2.33 (1.55-5.10)	3.00 (1.95-6.10)
$[\text{H}^+]$	45.0 (6.00-63.0)	0.17 (0.13-3.80)

<sup>1</sup> Reid et al. (1987)

<sup>2</sup> Jeffries and Snyder (1983)

<sup>3</sup> Girard et al. (1985)

<sup>4</sup> Lozano et al. (1987)

<sup>5</sup> P.J. Dillon (unpubl. data)

<sup>6</sup> flow weighted average, values in brackets indicate minimum and maximum observed concentration

Table after Jeffries et al. (1979)

## Data Analysis

First,  $[\text{SiO}_2]$  and  $[\text{H}^+]$  were related to discharge alone applying the mixing model suggested by Johnson et al. (1969). The model assumes that stream water is a mixture of two distinct water types, "original" solution (soil/groundwater with volume of  $V_o$ ) and "added" solution (precipitation volume,  $V_a$ ) with their respective constant concentrations  $C_o$  and  $C_a$ . The removal of soil water (and its contained chemical load) from a watershed occurs by replacement and/or mixing with precipitation. The concentration of a given solute in the stream can be expressed as (after Johnson et al. 1969) :

$$C = \frac{C_o - C_a}{(1 + \beta * q)} + C_a \quad (1)$$

where  $C$  is the solute concentration in the stream,  $C_o$  and  $C_a$  are the solute concentrations in the original (soil/groundwater) and added (melt/rain water) solution respectively and  $q$  is the mean daily discharge in mm/d.  $\beta$  is an optimization parameter describing the ratio of residence time of water to a minimum volume of water stored in the system during baseflow. Non-linear regression analysis using the Marquardt iterative method (SAS 1985) was performed to determine the best estimate of the parameters  $\beta$ ,  $C_o$ , and  $C_a$  for each solute in the two catchments.

The second step of the analysis involved a multiple regression analysis. In addition to flow magnitude ( $q$ ) already used in the mixing model, four other independent variables were regressed on silica and hydrogen concentration characterising various other aspects of flow such as antecedent flow, absolute and relative change in flow as well as rise/fall of the hydrograph (Table 2).

Table 2. Independent flow variables used for multiple regression on stream solute concentration.

Variable	unit	transformation
$X_1$ flow magnitude <sup>1</sup>	mm/d	log
$X_2$ antecedent flow <sup>2</sup>	mm/7d	log
$X_3$ absolute change in flow <sup>3</sup>	mm/d	none
$X_4$ relative change in flow <sup>4</sup>	unitless	none
$X_5$ rise/fall of hydrograph <sup>5</sup>	unitless	none

- 1 mean daily specific discharge at day of sampling ( $q$ )
- 2 cumulative  $q$  of seven days prior to sampling
- 3 absolute difference between  $q$  at day of sampling and  $q$  at day prior to sampling
- 4 ratio of  $q$  at day of sampling to  $q$  at day prior to sampling; inverse ratio on descending limb of hydrograph
- 5 dummy variable dividing the population into observations on ascending and descending limb of hydrograph

The wetness of the basin expressed through antecedent flow ( $X_2$ ) is believed to influence the infiltration rates of precipitation and consequently the amount of surface runoff (Ledbetter and Gloyna 1964). A large increase in flow ( $X_3$ ) may indicate a larger contribution of stormflow with a chemical composition closer to precipitation than to groundwater, analogous to the concept of quickflow and delayed flow (e.g. Pionke et al. 1972). The relative change in flow ( $X_4$ ) may also indicate changes in flowpaths independent of the flow magnitude. Although the total volumes involved may be small, a change in stream chemical concentration, a relative measure itself, can be expected. A dummy variable ( $X_5$ ) was introduced to account for a possible hysteresis effect (e.g. Walling 1974).

All independent variables were tested for collinearity. The variables flow magnitude ( $X_1$ ) and antecedent flow ( $X_2$ ) were highly correlated ( $R^2 > 0.7$ ). Antecedent flow ( $X_2$ ) was therefore excluded from the analysis. However, it should be noted that this correlation is largely influenced by the dominant number of observations taken at baseflow, when both flow variables are very low. During periods of high flow when solute concentrations are changing most rapidly both flow variables are only slightly correlated with one another. If the analysis were to focus on changes in stream solute concentration during periods of high flow alone, i.e. storm solute behaviour, antecedent flow ( $X_2$ ) should be considered besides flow magnitude ( $X_1$ ). All remaining flow variables were introduced into an initial multiple regression. The partial regression coefficient of each independent variable, was tested on its significance ( $p < 0.001$ ) using Student's t-test. Only those significant independent variables were employed into the final regression model.

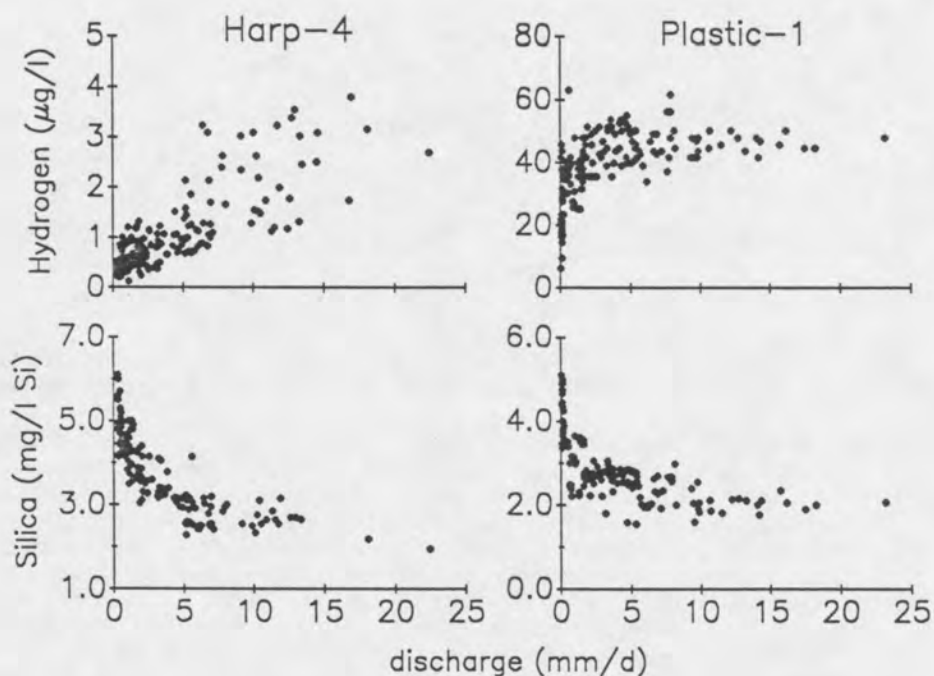


Fig. 1. Concentration-discharge relationships for silica and hydrogen during spring runoff in Plastic-1 (1980-1984) and Harp-4 (1977-1984).

## Results

The concentration-discharge relationships for silica were very similar in both streams, i.e. an exponential dilution with increasing discharge (Fig. 1). Although  $[H^+]$  was positively correlated with discharge in both catchments, the observed range of  $[H^+]$  in Harp-4 was much smaller ( $0.1-4 \mu\text{g/l } H^+$ ) compared to Plastic-1 ( $10-60 \mu\text{g/l } H^+$ ). Furthermore, most of the scatter of  $[H^+]$  in Harp-4 was observed at high flows whereas in Plastic-1 the observed  $[H^+]$  was relatively constant ( $\approx 50 \mu\text{g/l } H^+$ ) for discharge values  $> 2.5 \text{ mm/d}$  (Fig. 1).

The non-linear relationship of  $[\text{SiO}_2]$  with discharge resembles an exponential decay function consistent with mixing of two bodies of water with different concentrations of a solute (Hall 1970). The mixing model after Johnson et al. (1969) described the silica in Harp-4 and Plastic-1 very well (Fig. 2). Both models intercepted at  $\approx 2.1 \text{ mg/l Si}$ , an approximate minimum value maintained even at highest flows (see below). Yet, the Harp model had a greater regression coefficient, i.e. a steeper slope, indicating a stronger response of silica to changes in flow in Harp-4 than in Plastic-1 (Fig. 2).

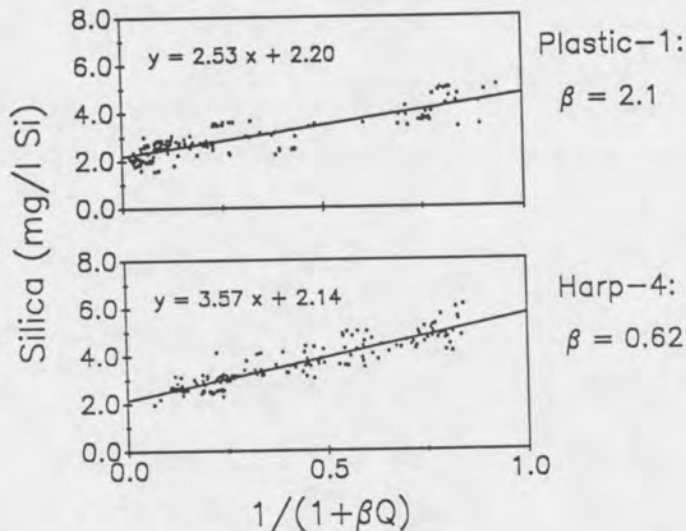


Fig. 2. Johnson mixing model applied to silica in Harp-4 and Plastic-1. The best estimate for  $\beta$  and the regression equation are shown as well.

The goodness of fit (as  $R^2$ ) of the mixing models for the various solutes in the two streams are summarized in Table 3. The  $R^2$  values for a regression of solute concentration on a non-transformed discharge is given for comparison. The mixing model explained the silica behaviour in both basins much better than the non-transformed discharge suggesting that the dilution pattern of silica could be explained by the mixing of surface and groundwater (Table 3). The Johnson model, however, was less successful in describing the concentration pattern of  $[H^+]$ , i.e. the increase in  $[H^+]$  with increase in flow, explaining less than 68% of the variation in both streams (Table 3). The 95% confidence intervals for the optimised  $\beta$  values in the hydrogen models were furthermore considerably larger than for the silica models (see footnote in Table 3). The weak performance of the mixing model applied to hydrogen suggests

that, as expected, other processes than mixing alone must influence the concentration pattern of this solute in the studied streams.

Table 3. Variation in stream chemistry explained by discharge and the mixing model after Johnson et al. (1969) ( $R^2$  values in %).

Site	Model <sup>1</sup>	SiO <sub>2</sub> (n=146)	H <sup>+</sup> (n=182)
Harp-4	C vs. q	52.7	66.9
	C vs. 1/(1+βq)	80.7	67.8
Plastic-1	C vs. q	38.5	24.2
	C vs. 1/(1+βq)	72.0	59.0

<sup>1</sup> optimization parameter in Johnson model estimated to  $\beta = 2.1$  ( $\pm 1.1$ ) in Plastic-1 and  $\beta = 0.62$  ( $\pm 0.26$ ) in Harp-4 using silica. For the hydrogen mixing models the estimate of  $\beta$  was similar in Plastic-1 ( $\beta = 2.6 \pm 1.6$ ); however,  $\beta$  was much smaller in Harp-4 ( $\beta = 0.02 \pm 0.02$ ).

Results of the multiple regression analysis are summarized in Table 4. The independent variables selected for the silica and hydrogen models and their goodness of fit (expressed as  $R^2$ ) are very similar in both catchments. In the case of silica, only flow magnitude was identified as an important flow variable. No other introduced flow variable could improve the regression model significantly. (Antecedent flow ( $X_2$ ) described the silica behaviour in Plastic-1 even better than flow magnitude; however it was not employed for multiple regression analysis due to problems in collinearity (see above). Similarly, Hooper (1986) used average discharge over some period rather than instantaneous discharge when establishing concentration-discharge relationships of stream solutes in Hubbard Brook, N.H., in order to account for seasonal trends superimposed on changes during melt events. However, in his study, this "memory" effect was the least pronounced for silica.)

Table 4. Summary of multiple regression analysis of selected flow variables on stream concentration of silica and hydrogen ion.

site	solute <sup>1</sup>	selected independent variables <sup>2</sup>	$R^2$ (in %)
Harp-4	SiO <sub>2</sub> (144)	$X_1$	81.4
	H <sup>+</sup> (178)	$X_1, X_3, X_5$	60.3
Plastic-1	SiO <sub>2</sub> (147)	$X_1$	83.3
	H <sup>+</sup> (178)	$X_1, X_3, X_5$	66.9

<sup>1</sup> degrees of freedom in brackets  
<sup>2</sup> in order of significance

For hydrogen, flow magnitude ( $X_1$ ) remained the dominant independent variable. However, the absolute change in flow ( $X_3$ ) and the rise/fall of hydrograph ( $X_5$ ) could explain some of the variation not accounted for by  $X_1$  (Table 4). The hysteresis variable showed a similar negative relationship with  $[H^+]$  in Harp-4 and Plastic-1, indicating that  $[H^+]$  were generally lower on the rising limb than on the falling limb of the hydrograph. Absolute change in flow ( $X_3$ ) was positively related to  $[H^+]$  in Harp-4, but showed a negative relationship with  $[H^+]$  in Plastic-1. The hydrogen models described the observed concentrations in the stream less successful than the silica models, although several independent variables were used for the hydrogen models as opposed to only one independent variable ( $X_1$ ) for the silica models (Table 4).

## Discussion

A general decrease in stream silica concentration during periods of high flow has been well documented for various streams (Johnson et al. 1969 ; Lewis and Grant 1979 ; Hunt and Foster 1985 ; Kennedy et al. 1986 ; Hooper 1986). In both studied headwater streams silica exhibited a strong dilution with increase in discharge (Fig. 1). The success of the mixing models in describing this behaviour (Fig.2; Table 3) supports the hypothesis that  $[SiO_2]$  in the stream is dominantly a result of the mixing of two components with differing silica concentrations  $C_0$  and  $C_a$ .

Hooper (1986) argued that the physical interpretation of the Johnson model had to be modified since the factor  $\beta$ , which Johnson et al. defined as the ratio of the residence time to minimum storage capacity of the watershed, i.e. a hydrologic constant, varied for several studied ions in the Hubbard Brook watershed, N.H.. He pointed out that  $\beta$  may depend on the chemical properties of the solute, e.g. yielding higher "effective" residence times (greater  $\beta$ ) for ions which undergo ion exchange and are biologically active. Hooper concluded that the model should be viewed as an empirical model, not one that describes physical or chemical mechanisms.

Nevertheless, the mixing model may be useful for comparison of hydrological and geochemical basin characteristics when comparing the model performance for a solute that has a similar behaviour in the watersheds. Silica was chosen for comparison of Harp-4 and Plastic-1 since it was believed to be relatively conservative in the sense that it would quickly reach solution equilibrium and thereafter not interact with soil and biota. According to the derivation of the model of Johnson et al. (1969), the constant ( $C_a$ ) of the regression model expresses the concentration level which pedologic processes are able to sustain during periods of rapid replacement of soil water by rain or melt water (non-equilibrium soil concentration). In both studied streams this regression parameter was  $\approx 2.1$  mg/l (Fig. 2) suggesting that the rates of silica release from the soils under non-equilibrium conditions might be very similar in both catchments. Johnson et al. (1969) found similar  $C_a$  values for silica in small mountainous headwater streams at Hubbard Brook, N.H. (1.4-1.8 mg/l).



The fact that such  $C_a$  values were still several orders of magnitude higher than the concentration found in the precipitation strongly argues for a compensating, fast chemical reaction within the soil or the streambed. The phenomenon that silica can be picked up by infiltrating event water rapidly has been documented both in studies using stream response (Kennedy et al. 1986) as well as soil leaching experiments (Bricker et al. 1968; Kennedy 1971). Wels et al. (in press b) were able to simulate the silica response of a small upland stream in the Plastic-1 watershed during spring runoff assuming that  $[SiO_2]$  of meltwater is a function of discharge and approaches a minimum value of 1.8 mg/l at peak flow.

The equilibrium concentration in stored soil/groundwater ( $C_o$ ) achieved during periods of baseflow when sufficient time is provided for geochemical processes to reach equilibrium is defined as the sum of the regression coefficient of the model plus the non-equilibrium stream concentration  $C_a$  (Johnson et al. 1969). The higher equilibrium constant obtained for Harp-4 ( $C_o = 5.7$  mg/l) than for Plastic-1 ( $C_o = 4.7$  mg/l) indicates that an equilibrium  $[SiO_2]$  in the soil provided by slow weathering processes might be higher in this basin. The much deeper soils in Harp-4 may support higher silicate weathering rates in this catchment due to longer residence times and/or more contact of meltwater with well developed mineral horizons.

Similarly, differences in the optimization parameter  $\beta$  for Plastic-1 and Harp-4, determined from the silica mixing models, may be explained on the basis of basin characteristics. Plastic-1 was expected to have a much smaller capacity to store soil/groundwater because (1) of the very shallow overburden (<1 m) compared to the several meters deep surficial deposits in Harp-4 (Table 1); and (2) it's smaller basin size. The hydrological response of the Plastic-1 catchment to a melt event should therefore be much more rapid resulting in shorter residence times for water moving through the system (larger  $\beta$ ).

The multiple regression analysis for silica confirmed the dominant position of discharge among all flow variables in explaining  $[SiO_2]$  during spring runoff (Table 4). For TDS, which also is also subject to dilution during storm events, an introduction of antecedent discharge (Ledbetter and Gloyna 1964), absolute change in flow (Pionke et al. 1972) or flow components (Walling 1974) did not improve the predictive power of the regression models greatly beyond the level obtained using discharge alone. The simple C-log(Q) regression model further appears to be superior over the Johnson mixing model considering that no additional optimization parameter was required to achieve the same goodness of fit (compare Table 3 and Table 4).

The increase in  $[H^+]$  with increasing discharge has also been found in other watersheds which receive acidic deposition (Johnson et al. 1969 ; Bottomley et al. 1984 ; Damsleth 1986 ; Sharpe et al. 1984 ; Lynch et al. 1986, Hooper 1986). A concentration of this solute in streamwater has to be expected during periods of high flow when more acidic meltwater reaches the stream. However, despite identical input values of  $\approx 50 \mu g l^{-1}$  in precipitation, the concentration-discharge relationships in Harp-4 and Plastic-1 differed greatly in shape and intensity (Fig. 1).

The relatively poor performance of the hydrogen mixing models (Table 3) in describing this behaviour is not surprising considering the highly reactive nature of the hydrogen ion. The higher standard error of all regression parameters for the hydrogen model in Harp-4 and its orders of magnitude smaller  $\beta$  value compared to the silica model (Table 3) suggest that the mixing model may be particularly inappropriate in the case of hydrogen in Harp-4, most likely due to neutralization of  $[H^+]$  in the soil and stream.

The shallower and more acidic soils in Plastic-1 may provide less alkalinity to neutralize the incoming  $[H^+]$  resulting in a  $[H^+]$ -discharge relationship resembling more that of a less reactive solute such as silica. The similar  $\beta$ 's obtained for silica and hydrogen in Plastic-1 would support this hypothesis (Table 3). If one visualizes stream water as a mixture of soil/groundwater and meltwater then the stream  $[H^+]$  close to meltwater values for discharge  $> 5$  mm/d would suggest that the soil/groundwater reservoir in Plastic-1 is completely exhausted during periods of high flow. However, isotope studies within the same basin suggest that pre-melt soil/groundwater remains an important flow component throughout spring runoff (Wels et al. in press b). Instead, a centrally located swamp in Plastic-1 was found to release additional  $[H^+]$  during spring runoff thus further complicating the simple mixing concept of the Johnson model (Wels et al. in press b).

The dominance of discharge in the multiple regression model for hydrogen may reflect the influence of flow rates on neutralization processes occurring within the soils of the two basins. In contrast to the silica models, absolute change in flow (X3) and rise/fall of hydrograph (X5) could explain some of the considerable remaining variation which may be attributed to the non-conservative nature of hydrogen. For example, the inclusion of the hysteresis variable in the hydrogen model agrees well with the observation that hydrogen values recover to lower baseflow levels much slower than the discharge itself (e.g. Bottomley et al. 1984; Lynch et al. 1986). The consistent inclusion of X3 and X5 in the hydrogen models of both streams places some confidence on their importance. However, their use for prediction is limited since both variables never explained more than 10% of the variation in  $[H^+]$ . A variable which better reflects chemical interactions is needed to improve substantially the hydrogen models. A more flexible 'hysteresis variable' which considers the volume of the previous storm or the time elapsed since peak flow may be one possible improvement.

The most striking difference between Harp-4 and Plastic-1 is their potential to buffer the acidic precipitation (rain and snow) inputs. Considering the relatively similar silica behaviour during spring runoff in those two catchments (particularly the similar  $C_a$  values), it seems very unlikely that the large differences in the buffering capacity result from different direct contributions of meltwater (via saturated overland flow) to the two streams. Biogeochemical processes leading to the neutralization of infiltrating meltwater must be considerably different or occur at different rates in those two catchments. The longer residence times of infiltrating meltwater in Harp-4 due its larger catchment size and the deeper surficial deposits (i.e. smaller  $\beta$  in the silica model) could lead to higher rates of silicate weathering. If silicate mineral weathering was the dominant component to buffer acid precipitation input (Johnson 1984), Harp-4 should also yield higher stream  $[SiO_2]$  compared to Plastic-1 assuming that; (1) weathering of

silicate minerals such as feldspars (e.g. plagioclase) and clay minerals (e.g. kaolinite) is the only source of silica in the stream; and (2) silica is neither taken up nor precipitates in the soil or streambed. The relationship of  $[\text{SiO}_2]$  with  $[\text{H}^+]$ , however, do not show such a clear trend. Although there is a general increase in  $[\text{SiO}_2]$  with decreasing  $[\text{H}^+]$ , particularly in Plastic-1, the stoichiometric ratios of the two elements were very different in the two catchments (Fig. 3). Under the above assumptions the silica release in Harp-4 would consume more than ten times the amount of  $[\text{H}^+]$  than it would in Plastic-1 (Fig. 3).

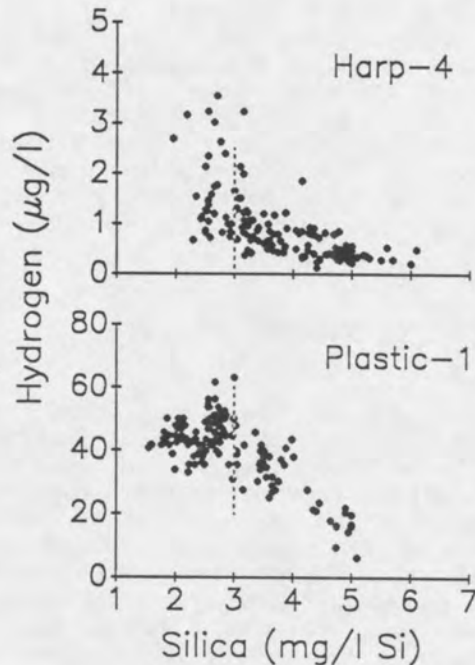


Fig. 3. Hydrogen versus silica during spring runoff in Harp-4 (1977-1984) and Plastic-1 (1980-1984).

Furthermore, the  $[\text{SiO}_2]$  -  $[\text{H}^+]$  relationships were not consistent over the entire discharge range. For  $[\text{SiO}_2] > 3.0$  mg/l, i.e. during periods of low flow,  $[\text{H}^+]$  remained fairly constant in Harp-4, whereas in Plastic-1, the  $[\text{H}^+]$  show a negative relationship with  $[\text{SiO}_2]$  (Fig. 3). For  $[\text{SiO}_2] < 3$  mg/l, i.e. during periods of high flow, no relationship between  $[\text{SiO}_2]$  and  $[\text{H}^+]$  could be observed in either basin, with  $[\text{H}^+]$  in Plastic-1 ranging from 35-65  $\mu\text{g/l}$  as compared to only 0.5-3.5  $\mu\text{g/l}$  in Harp-4 (Fig. 3).

These inconsistent trends suggest that biogeochemical processes other than silicate weathering influence the  $[\text{H}^+]$  and  $[\text{SiO}_2]$  in the studied streams. These processes may not only differ between the two catchments but also depend on the flow conditions in a basin. The release of  $[\text{H}^+]$  from a conifer swamp within the Plastic-1 catchment is one processes that does not occur in the Harp-4 catchment and this process is probably independent of silica uptake within the swamp.

Alternatively, the silica in the stream may also not be directly related to rates of silicate weathering and/or hydrogen consumption. First, silica may stem from other sources than silicate minerals which do not involve hydrogen consumption, such as dissolution of amorphous silica or quartz from the soil or streambed. Bennett and Siegel (1987) pointed out that dissolved organic carbon may greatly enhance the solubility of quartz. This complexation may contribute silica to the stream without buffering acidic meltwater, particularly in the organic-acid rich top layers of the soils and in the conifer swamp in Plastic-1. In contrast, silica could also precipitate as amorphous silica due to changing redox conditions in the soil solution or stream.

Second, the release of silica from a feldspar may be independent of the exchange of cations and thus hydrogen neutralization. Kennedy (1971) and Kennedy et al. (1986) pointed out that silica was not correlated to major base cations during periods of high flow in the Mattole River, CA. Nesbitt and Muir (1988) observed a preferential removal of silica compared with Al from the near-surface of a freshly weathered plagioclase of the Plastic-1 catchment. All three studies suggest that the silica release from silicate minerals is controlled by a diffusion mechanism independent of the actual hydrogen consuming dissolution.

#### Summary

The influence of hydrology on the  $[\text{SiO}_2]$  and  $[\text{H}^+]$  during spring runoff was investigated in two Canadian Shield watersheds which differ greatly in their capacity to buffer acid deposition. In both catchments, the  $[\text{SiO}_2]$  was dominantly influenced by stream discharge. The Johnson model that assumes the mixing of two distinct water reservoirs, a soil/groundwater component and a meltwater component with distinct  $[\text{SiO}_2]$ , described adequately the silica behaviour in Harp-4 and Plastic-1. This suggests that the principal hydrological mechanisms may be very similar in those two catchments. The same model failed to explain the hydrogen behaviour particularly in Harp-4 since chemical processes are superimposed on the mixing process. The regression of various flow variables on stream  $[\text{H}^+]$  illustrated the overall importance of hydrology. However, discharge was not the only important flow variable. The rate of change and fall/rise of flow further improved the hydrogen model indicating that kinetic chemical processes have to be considered as well. Differences in the buffering capacity of the two catchments are believed to result from differences in the neutralization processes occurring within the soil, swamp and stream rather than from different direct inputs of acidic meltwater to the stream. The lack of a consistent stoichiometric relationship between silica and hydrogen in both streams suggests that processes other than silicate weathering alone must influence the release of silica and/or the neutralization of hydrogen during snowmelt runoff. Stream silica is thus not a useful indicator for the contribution of silicate weathering to the neutralization process of  $[\text{H}^+]$  in the studied basins.

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