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Groundwater and Wetland Contributions to Stream Acidification: An Isotopic Analysis

CHRISTOPH WELS

Watershed Ecosystems Program, Trent University, Peterborough, Ontario, Canada

R. JACK CORNETT

Environmental Research Branch, Chalk River Nuclear Laboratories, Chalk River, Ontario, Canada

BRUCE D. LAZERTE

Dorset Research Centre, Water Resources Branch, Ontario Ministry of the Environment, Dorset, Canada

Stream water pH may be influenced by (1) the flow paths and (2) the residence time of water that contributes to streamflow, when these hydrologic factors interact with the biogeochemical processes that neutralize H^+ ions in the catchment. This paper presents measures of the volumes of groundwater contributing to streamflow, the groundwater residence times, and the sources of stream water acidity found during spring runoff in three basins on the Canadian Shield. Isotopic hydrograph separations were used to estimate the relative contributions of groundwater to spring runoff. The contributions of old (premelt) groundwater to spring runoff were greater (60%) in a well-buffered, third-order basin than in a more acidic first-order basin (49%). Using a simple mixing model, a larger groundwater reservoir (420 mm unit depth) and longer residence time (162 days) were estimated in the third-order basin. The lowest stream pH (4.8) was observed in a second-order basin with a wetland that collects drainage from about 79% of the basin. In this basin the principal source of H^+ ions was the conifer-sphagnum wetland. We conclude that the hypotheses that the pH of these streams was proportional to (1) a fraction of streamflow contributed by groundwater or (2) the residence time of water in a basin are rejected. More attention must be focused upon the source of acidity generated in wetlands, since these are ubiquitous in small basins.

INTRODUCTION

Acidification of surface water has been well documented in many regions of the northern hemisphere that receive acid depositions such as parts of Scandinavia [*Overrein et al.*, 1980], northeastern United States [*Cronan and Schofield*, 1979], and eastern Canada [*Dillon et al.*, 1978]. An identification of variables controlling the acidification of surface water is necessary for the prediction of (1) future trends of already acidified surface waters and (2) potential for an area or basin to become acidified in the future.

The wet and dry deposition of sulphuric and nitric acids are the dominant sources of the recent acidification of lakes and streams [e.g., *Cronan et al.*, 1978; *LaZerte and Dillon*, 1984]. However, the pH of most surface waters is higher than that of precipitation, indicating that watersheds buffer acid deposition, that is, neutralize hydrogen ions. The neutralization capacity varies among different regions [e.g., *Likens et al.*, 1979] and even between adjacent basins [e.g., *Sharpe et al.*, 1984; *David*, 1986]. Those observations lead to the question, Which watershed characteristics are controlling the neutralization capacity of a basin? On the basis of the existing knowledge of processes regulating soil water and stream water chemistry [*Galloway et al.*, 1983; *Reuss and Johnson*, 1985] and stream runoff generation [e.g., *Dunne*, 1978], two biogeochemical and two hydrological variables and their interactions may be identified. The two bio-

geochemical factors are (1) the chemical composition of the overburden [e.g., *Johnson*, 1984] and (2) the rate of acid neutralization and/or retention of strong acid anions in soils and wetlands [e.g., *Driscoll and Newton*, 1985]; the two hydrologic factors that interact with and influence these biogeochemical variables are (3) the flow path of precipitation water [*Chen et al.*, 1984] and (4) the residence time of groundwater [*Bottomley et al.*, 1986].

The biogeochemical variables 1 and 2 depend mainly on the geology of the basin, although processes controlling acid/base chemistry in wetlands may be more site specific. The hydrological variables 3 and 4 can modify the importance of biogeochemical processes [*Goldstein et al.*, 1984]. In two lake basins studied during the Integrated Lake Water Acidification Study (ILWAS), temporal and spatial variations in lake pH were related to surficial geology and flow paths. *Chen et al.* [1982] used the ILWAS model to show that lake water became acidic when hydrologic conditions forced precipitation to flow to the lake as surface flow or as lateral flow through the upper soil horizons. This analysis was based on the assumption that the relative contribution of groundwater to surface water flow is primarily controlled by the distribution and thickness of till and the permeability of these deposits. Further support for the ILWAS model was obtained from hydrometric analysis of the two basins [*Chen et al.*, 1984]. The application of the concept that different flow paths depend on soil depth and antecedent conditions was further extended to explain differences in neutralizing capacity of various stream watersheds in the Adirondacks, New York (ILWAS, e.g., *Peters and Driscoll*, [1987]). No
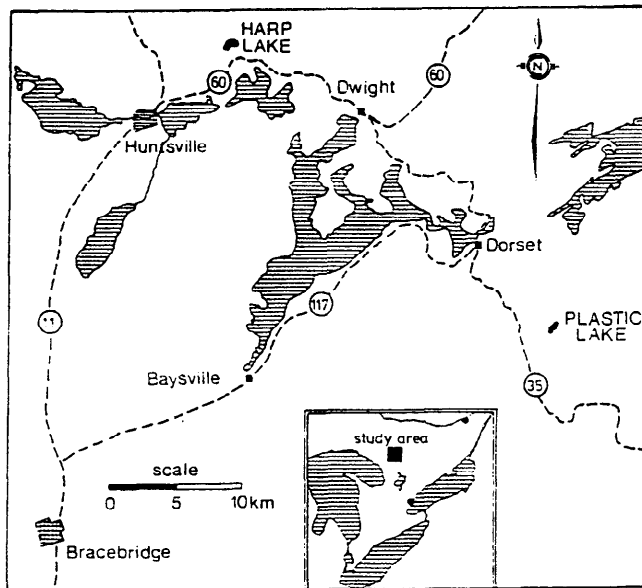
Fig. 1. The location of the Plastic Lake and Harp Lake watersheds in the Muskoka-Haliburton area, Ontario, Canada.

isotope studies were undertaken in the Adirondacks to test for the differences in groundwater contributions to streamflow hypothesized among various watersheds and in response to individual storm events.

Bottomley et al. [1984, 1986] used stable isotopes to study the influence of groundwater residence time on stream acidification during spring runoff in the Turkey Lakes Watershed, Ontario. They suggested that much of the first meltwater infiltrates the soils, limiting the extent of stream acidification during this period [*Bottomley et al.*, 1984]. However, this buffering mechanism may be ineffective where small groundwater reservoirs are rapidly flushed by infiltrating meltwater [*Bottomley et al.*, 1986]. This concept implies that the size of the groundwater reservoir and hence the residence time of groundwater will influence the sensitivity of a given basin to become acidified [*Johnson*, 1979].

The primary objective of this study was to investigate the influence of hydrology on stream acidification in headwater regions on the Canadian Shield. The study was conducted during spring runoff in three headwater streams which differ greatly in their capacity to neutralize acidic deposition. A priori, it was presumed that differences in soil chemistry could not account for differences in stream water chemistry of the three streams because of similar surficial geology (glacial till) and pedology (podzol) [*Jeffries and Snyder*, 1983; *Girard et al.*, 1985]. Three hypotheses were tested: (1) the stream water pH and acid neutralization capacity (ANC) of the watersheds were positively correlated with relative contributions of groundwater to streamflow; (2) mean stream pH during spring runoff was positively correlated with groundwater volumes and residence times; and (3) wetlands acidified streamflow by exporting strong acids.

STUDY SITE

The study was performed in the Plastic Lake and Harp Lake watersheds located in the Muskoka-Haliburton area near the southern fringe of the Canadian Shield (Figure 1). The discharge and stream chemistry of the Harp Lake and

LEGEND

— watershed boundary
- - - subwatershed boundary
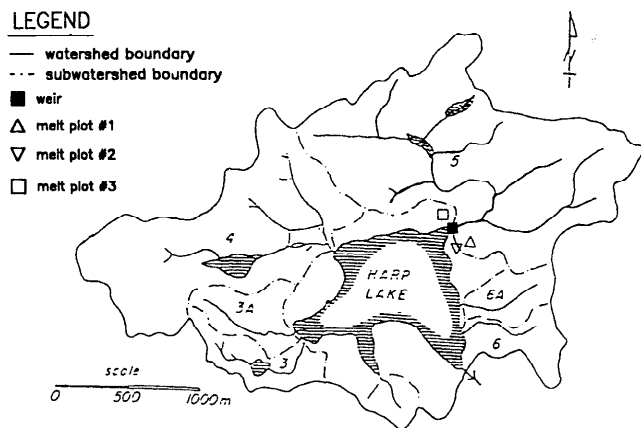■ weir
△ melt plot #1
▽ melt plot #2
□ melt plot #3

Fig. 2. The Harp-5 watershed showing the location of field instrumentation and the drainage pattern.

Plastic Lake watersheds have been monitored since 1976 and 1980, respectively, as part of the Acid Precipitation in Ontario Study (APIOS) [*Dillon et al.*, 1978; *Scheider et al.*, 1979]. The study area was selected since it receives relatively high rates of acid deposition (bulk deposition pH ≈ 4.2; *Dillon et al.* [1982]), whereas the buffering capacity of the soils and underlying bedrock is very limited [*Dillon et al.*, 1982]. The Plastic Lake and Harp Lake watersheds are less than 30 km apart (Figure 1) and experience very similar climatic conditions. The mean annual January and July air temperatures are −11.0° and 17.7°C, respectively. The mean annual precipitation depth is ≈1000 mm/yr (1941–1980), with approximately 26% (260 mm/yr) falling as snow [*Shibatani*, 1988]. Spring runoff is the dominant hydrological event in this region. The long-term annual runoff is 400–600 mm/yr, with 50–75% occurring during March–April in response to snowmelt [*Scheider et al.*, 1983].

The streams of the subbasins Harp-5 (Figure 2) and Plastic-1 (Figure 3) as well as Plastic-108, a tributary to the swamp in Plastic-1 (Figure 3), were selected for this study. They are very responsive headwater streams with peak discharges up to 30 mm/d during spring runoff and very little or no flow during the late summer period. The physiography of the three subbasins studied as well as their geology and land use are compared in Table 1 and Table 2, respectively. Harp-5 is a third-order basin with a well-developed drainage network (Figure 2, Table 1). Bedrock consists of hornblende-biotite gneiss which is often exposed on ridges and steep slopes. The discontinuous basal till is usually less than 1 m in depth. However, much thicker surficial deposits (5–10 m) are present in the central lowland portions of the basin. Well-developed podzolic soils dominate the well-drained areas, whereas organic soils occur in the poorly drained central lowlands. Plastic-1 has extremely low neutralizing capacity (Table 2). Seventy-nine percent of the watershed drains into a large conifer-sphagnum swamp in the center of Plastic-1 via ephemeral streams (e.g., Plastic 108) or subsurface flow (Figure 3). Tracing experiments indicated an average residence time for tributary water from Plastic-108 within the swamp of approximately 2 days during spring runoff [*Wels and Devito*, 1988]. Plastic-108 is the only tributary in the Plastic-1 watershed that flows through a well-defined valley (Figure 3). This first-order basin has no permanent wetlands and a large percent of exposed bedrock
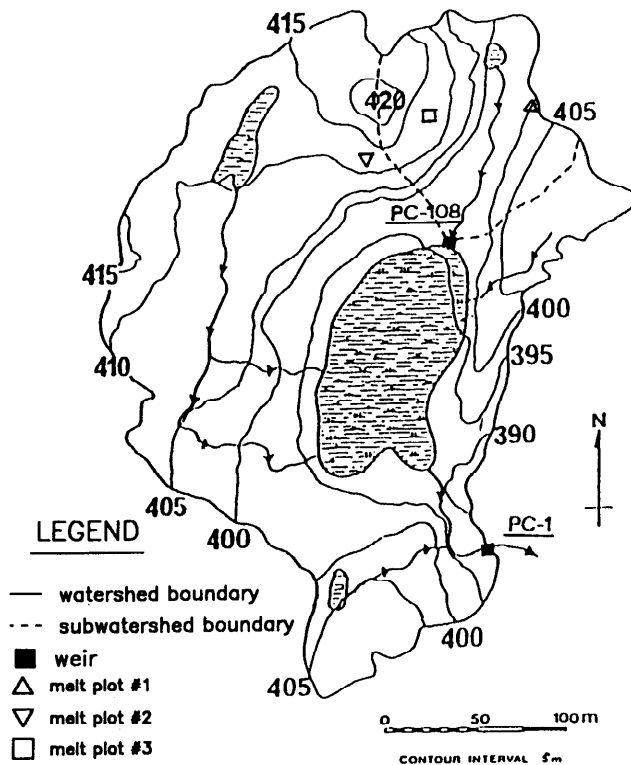
Fig. 3. The Plastic-1 subbasin showing major drainage pattern and wetlands. The first-order stream Plastic-108 drains the northeastern portion of the Plastic-1 subbasin [after *Shibatani*, 1988].

(Table 2). The entire Plastic-1 subcatchment is covered with thin (<1 m) surficial deposits of Pleistocene glacial till overlaying Precambrian metamorphic silicate bedrock (Table 2). The soils in the well-drained upland areas are weakly developed podzols, while the soils in poorly drained depressions (e.g., conifer-sphagnum swamp) are organic [*Lozano et al.*, 1987].

METHODS

Streamflow was gauged at the respective basin outflows using an H-flume with low flow structure in Harp-5 (Figure 2) and a 90° V notch weir in Plastic-1 and in Plastic-108 (Figure

3). The weirs were heated to maintain ice-free conditions throughout the winter and spring months. Stage (water level) was recorded continuously at these sites with a Leupold-Stevens Model 71 float-operated recorder. Hourly discharge values were calculated from the stage-discharge (Ontario Ministry of Environment, unpublished data, 1986) relationship. Stream water samples were collected with ISCO automatic water samplers which were placed in the heated weirs to prevent the suction lines and samples from freezing. The sampling interval was 3 hours during periods of high flow and 6 hours or more during base flow and following peak flow.

Meltwater was sampled at three sites in Plastic-1 (Figure 3). Two snowmelt lysimeters (#1 and #2) were installed on the west- and east-facing slope of Plastic-108 (Figure 3). They consisted of a clear polyethylene sheet held by a wooden frame (1 m^2) laid out before the first snow. The combined runoff of meltwater and rainwater from the snowpack was collected into a 20-L carboy and sampled at least once a day. The volume of the water that had accumulated in the carboy was recorded to estimate the runoff from the melt plots. The third site (#3) was located in the center of a large bedrock outcrop and was much more exposed than the two forested sites #1 and #2 (Figure 3). Here, a plastic eaves trough intercepted the meltwater at the base of the snowpack. In Harp-5, meltwater was also collected directly from the snowpack using eaves troughes (Figure 2). At sampling site #1 and #2, meltwater was intercepted from well-shaded snowpacks on a northwest-facing, steep slope. At site #3, an exposed, south-facing snowpack was sampled which melted much earlier than those at #1 and #2. At all three sites, composite meltwater samples were usually taken every 2 days as long as a snowpack remained. Deuterium and pH were also measured in composite snow samples prior to melt, in precipitation, and in soil/groundwater [*Wels*, 1989].

The pH of all samples was determined within a few hours after collection. The analyses were done at the Dorset Research Station using a Corning pH meter, model 150, and a Fisher reference electrode which was submersed in the unstirred sample. The pH meter was calibrated using standard solutions of pH 6.8 and 4.3. The samples that were collected automatically were measured only after the sampling sequence was completed (2–3 days) and gave considerably higher pH values than those taken manually, unless the samples were very acidic. Therefore only pH values of manually collected samples and all acidic stream water

TABLE 1. Physiography of the Study Basin

Basin	Location	Topography	A_c, km^2	$\bar{o}h^*$ m	Basin Slope†	Stream Slope
Plastic-1	45°11'N,78°50'W	concave slopes; centrally located swamp	0.233	36	7	9‡
Plastic-108	45°11'N,78°50'W	convex slopes; stream in narrow fault zone; little wetland	0.033	23	13	6§
Harp-5	45°23'N,79°08'W	concave side slopes; flat central lowland with swamps and beaver ponds	1.95	90	6	···

*$\bar{o}h$ is the maximum altitude difference.
†Mean slope of the basin $= \bar{o}h/\sqrt{A_c}$, where A_c is basin area in square kilometers and $\bar{o}h$ is the maximum altitude difference in kilometers.
‡Mean slope of the stream from main swamp to Plastic-1 outflow weir.
§Mean slope of the Plastic-108 stream channel [from *Shibatani*, 1988].

TABLE 2. Geology and Land Use of the Study Basins

	Bedrock	Surficial Geology	Soils and Vegetation	Wooded, %	Wetland, %	Percent Exposed Bedrock	Volume-Weighted Stream pH	ANC, ueq/L*
Plastic-1	Ortho-gneiss; igneous granites and metasedimentary†	discontinuous sandy basal till (<2 m) and exposed bedrock†	weakly developed podzolic soils (<1 m); coniferous forest‡	80§	10	10	4.3	21.5
Plastic-108	Ortho-gneiss; igneous granites and metasedimentary	discontinuous sandy basal till (<2 m) and exposed bedrock	weakly developed podzolic soils (<1 m); coniferous forest	79‖	≤1	20	4.8	1.5
Harp-5	Hornblende-biotite gneiss¶	shallow sandy basal till (<2 m); exposed bedrock; thicker deposits (5–10 m) in the central lowland¶	humo-ferric podzolic soils; mixed hardwood forest**	73††	9	18††	5.3	−20.2

ANC, acid neutralization capacity.
*1982–1986 (Ontario Ministry of Environment, unpublished data, 1986).
†*Girard et al.* [1985].
‡*Lozano et al.* [1987].
§Estimates from *Girard et al.* [1985]; *Lozano et al.* [1987] estimated 10% exposed bedrock of total area in Plastic-1.
‖Estimated based on saturated area mapping by *Shibatani* [1988].
¶*Bottomley et al.* [1984].
**Soil data from adjacent Harp-4 subbasin [*Lozano et al., 1987*].
††Estimates from *Scheider et al.* [1983] using air photographs; field observations suggest smaller fraction of exposed bedrock (<10%).

samples of Plastic-1 (pH <4.8) were used. In Harp-5 and Plastic-108, routine measurements by the Ontario Ministry of Environment (OME) were used to complement the data base. The precision of the pH analysis, expressed as mean standard deviation (σ) of the duplicate analyses, was approximately 0.03 pH units [*Wels*, 1989].

Deuterium was measured by mass spectrometry at the Chalk River Nuclear Laboratories using the technique of direct injection and reduction of the water sample in the mass spectrometer inlet system [*International Atomic Energy Agency*, 1984]. This method measures absolute deuterium concentrations, since a simultaneous measurement of the sample and a reference is not possible. Therefore deuterium concentrations can be expressed in parts per million, which can be converted to δ D (per mil) SMOW by the relationship

$$\delta \text{ D (per mil) SMOW} = [(\text{D}_{ppm}/157.6) - 1] * 1000$$

where 157.6 ppm is the deuterium content in SMOW, as determined by Atomic Energy of Canada Limited, Chalk River [*Brown et al.*, 1971]. The mean σ for the deuterium analysis was 0.13 ppm D [*Wels*, 1989]. No significant change in the deuterium concentration was observed as a result of automatic sampling or sample storage for at least 6 months [*Wels*, 1989].

ISOTOPIC HYDROGRAPH SEPARATION

Stream runoff was separated into old water (soil/groundwater and swamp water stored in the catchment prior to melt) and new water (meltwater/rainwater) using the stable isotope deuterium (^{2}HHO or HDO) as a nonreactive tracer [*Dinçer et al.*, 1979]. Using a single reservoir mixing model with volume V, the change in HDO concentrations in the groundwater (C_{GW}) with respect to time (t) is [*Rodhe*, 1987]

$$\frac{dC_{GW}}{dt} = \frac{Q_S * X_{GW}}{V_{GW}} * (C_N - C_{GW}) \qquad (1)$$

where Q is discharge, C is the concentration of HDO, X is the fraction of flow from one source, and the subscripts S, GW, and N refer to the stream, groundwater, and new (melt) water components, respectively. The relative contribution of groundwater X_{GW} or old water X_o expressed as fraction of total streamflow is given by

$$X_O = \frac{C_S - C_N}{C_{GW} - C_N} \qquad (2)$$

This model assumes that only two flow components exist and that the new water that infiltrated the soils mixes, instantaneously, in a groundwater reservoir of constant, finite volume. This model formulation differs from other isotope separations [e.g., *Sklash and Farvolden*, 1979; *Hooper and Shoemaker*, 1986] because a finite, rather than an infinite, groundwater volume is used in the analysis [*Rodhe*, 1987]. The value of V_{GW} is chosen by trial and error so that C_{GW} changes from the measured preevent to the postevent D value of stream water [*Rodhe*, 1987]. In the present study, (1) was used in finite difference form to calculate the temporal variation of C_{GW} during the spring runoff. Then the fraction of groundwater (X_{GW}) contributing to streamflow can be calculated from (2).

GROUNDWATER CONTRIBUTIONS TO SPRING RUNOFF

Here the hypothesis is tested that relative contributions of groundwater to spring runoff are positively correlated with stream pH in the three study watersheds. In order to perform isotopic hydrograph separation and to calculate groundwater contributions to streamflow, several criteria for the input variables to equation (2) have to be evaluated [*Sklash and*
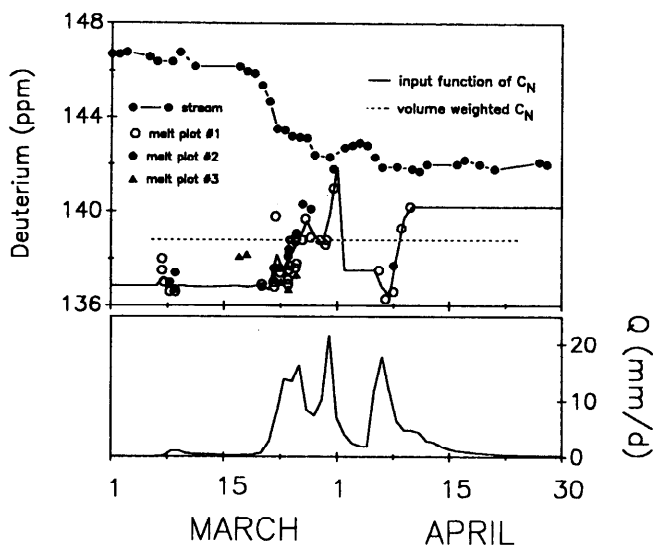
Fig. 4. Temporal trends in D of streamflow and runoff from three melt plots in Plastic-108. Mean daily discharge is shown for comparison. The dashed line indicates the volume-weighted mean for C_N; the solid line shows the splined input function for C_N. The D in rainwater was $\approx$144.2 ppm on March 26 and $\approx$142.3 ppm on March 30.
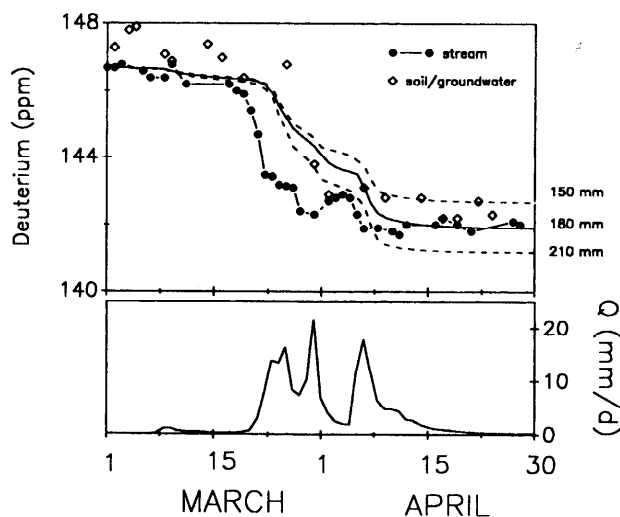

Fig. 5. Temporal trends in groundwater D in Plastic-108 simulated by *Rodhe*'s [1987] mixing model. C_{GW} used for hydrograph separation was simulated for the entire spring runoff using a model reservoir, V_{GW}, of 180 mm. Dashed curves show confidence limits in C_{GW} based on uncertainty in the fitted volume of V_{GW} (see text). The temporal trends in D of stream water (circles) and soil/groundwater (diamonds) are shown for comparison.

Farvolden, 1979], and C_{GW} has to be simulated [*Rhode*, 1987]. Both aspects are discussed in the following two sections, based on data from Plastic-108 which are representative for all three subbasins. A comparison of old water and groundwater contributions to spring runoff and their influence on stream pH are discussed in the final two sections.

Criteria for Input Variables

Four criteria have to be evaluated for isotopic hydrograph separation [*Sklash and Farvolden*, 1979; *Kennedy et al.*, 1986]: (1) the isotopic content of new water is significantly different from that of old soil/groundwater, (2) new meltwater/rainwater is characterized by a single isotopic content C_N, or variations in the isotopic content are accounted for, (3) contributions of soil water to streamflow are insignificant, or the isotopic content of soil water is equal to that of groundwater, and (4) surface storage contributions are negligible.

The 1987 spring runoff was extremely favorable for isotopic hydrograph separation. Because of the large initial difference of C_n and premelt base flow ($\approx$10 ppm D) and the small inputs of "heavy" rain, the D in stream water, C_S, remained well above C_N except on March 31 (Figure 4). Therefore a hydrograph separation of the entire spring runoff was possible.

Melt plots were used to estimate the isotopic input, since they account for the temporal variability and, in particular, the influence of rain inputs [*Sklash*, 1986; *Hooper and Shoemaker*, 1986]. The average input of C_N to the basin is given by the volume-weighted mean D of the total runoff from the two gauged melt plots (#1 and #2), which was 138.8 ppm (Figure 4). However, the use of this constant D of new water for hydrograph separation does not account for the temporal changes in C_N. The average value overestimated C_N during the onset of each melt event while underestimating C_N later on (Figure 4). To obtain a "basin mean"

input function for C_N that accounts for the temporal and spatial variation, D measures obtained from all three melt plots were splined in daily increments (method of *Londry* [1987]; Figure 4). Estimates of mean X_{GW} for spring runoff, based on the two techniques, were in agreement. We chose to use daily values of C_N as the input variable to equation (1), since it may provide more realistic estimates of the temporal changes in X_O than the volume-weighted mean C_N. Meltwater inflow to the stream was assumed to be instantaneous, that is, less than a day, the time step used for hydrograph separation.

Since soil water and groundwater are difficult to distinguish, the alternative condition of criterium 3, that of isotopic equality of both types of waters, was tested. The isotopic content of stream base flow was assumed to be representative of that of groundwater [*Bottomley et al.*, 1986; *Hooper and Shoemaker*, 1986]. This way, only groundwater actually contributing to streamflow was considered, and possible spatial variations in groundwater D were averaged out [*Rhode*, 1987]. Soil water samples collected in the deep mineral horizon were isotopically enriched about 0.4 ppm compared to stream base flow prior to melt (Figure 5). This systematic difference introduced a positive bias in X_O of less than $\approx$5% at peak flows. This bias is estimated by recalculating values of X_O using the 0.4 ppm higher value of C_O in (2). The uncertainties in X_O and in X_{GW} can be calculated by taking the derivative of (2) and estimating the variance of the mean deuterium concentration in each reservoir. The uncertainties in X_O and in X_{GW} are also inversely proportional to C_O-C_N [*Rodhe*, 1987]. The deuterium concentrations of old water or groundwater and meltwater differed by 5–10 ppm during this study. Using the technique of *Rodhe* [1987], we estimate uncertainties of 10–15% and 10–40% in the daily estimates of X_O and X_{GW}, respectively.

In Harp-5 and particularly in Plastic-1 the old water component also included surface water (i.e., swamp water) stored in the basin prior to spring runoff. Surface water

sampled in wetlands prior to spring runoff had an isotopic content indistinguishable from old soil/groundwater, which conforms to the assumption of a uniform tracer concentration C_O. Isotopic enrichment of surface water due to evapotranspiration was insignificant because of the low air temperatures and short residence times during spring runoff.

Simulation of C_{GW}

Soil water as well as stream water data indicated that the isotopic composition of groundwater was not constant over time but gradually approached that of new meltwater (Figures 4 and 5). Apparently, the original old water reservoir was recharged with infiltrating meltwater, decreasing the D concentration in the groundwater reservoir. This temporal change in the isotopic content of groundwater was simulated using (1). A model reservoir volume $V_{GW} = 180$ mm gave the desired change in C_{GW} from premelt to postmelt base flow in Plastic-108 (Figure 5). The uncertainty in the fitted volume of the average V_{GW} was ± 30 mm (or $\pm 15\%$) assuming a random error in the D of premelt or postmelt base flow of ± 1 ppm (dashed curves in Figure 5). The simulated C_{GW} lagged behind the response of stream water D, that is, decreased slower and less rapidly than stream water D (Figure 5). This indicates the contribution of meltwater to a stream that is isotopically lighter than groundwater. During periods of flow recession, the stream water D increased toward the C_{GW}, suggesting that the relative contribution of groundwater to streamflow increased again. An increase in C_{GW} was not observed, since the infiltrating meltwater remained isotopically lighter than the groundwater throughout the runoff period. An independent field test of the simulated trends of groundwater D are the D measurements in the deep mineral horizons. The simulated C_{GW} were consistently lower than soil water D from the BC horizons (3 sites) as a result of the differences in D of premelt soil water and stream base flow discussed earlier (Figure 5). The overall temporal trends agreed, and most soil water D from the deep mineral horizons was within the range of simulated C_{GW} values (dashed curves in Figure 5).

Comparison of Old Water and Groundwater Contributions

In Plastic-108 the contributions of groundwater to streamflow were consistently higher than those of old water during the entire period of spring runoff (Figure 6). For the total spring runoff the difference in estimates of X_{GW} and X_O was 50 mm or 25% of the total spring runoff (Table 3). Similar trends were observed in the other study streams Plastic-1 and Harp-5 (see below). The estimated groundwater inputs may have been even greater, since the assumptions of (1) constant volume and (2) complete mixing, used in simulating C_{GW}, both underestimate groundwater contributions to streamflow [Wels, 1989]. The use of a single, constant C_O for spring runoff hydrograph separation generally underestimates groundwater contributions to streamflow in basins with small groundwater reservoirs.

Hooper and Shoemaker [1986] found similar differences in old water and groundwater fractions in a headwater stream in the Hubbard Brook Experimental Forest, New Hampshire. They used linear interpolation between premelt and postmelt base flow to determine the change in C_{GW} during
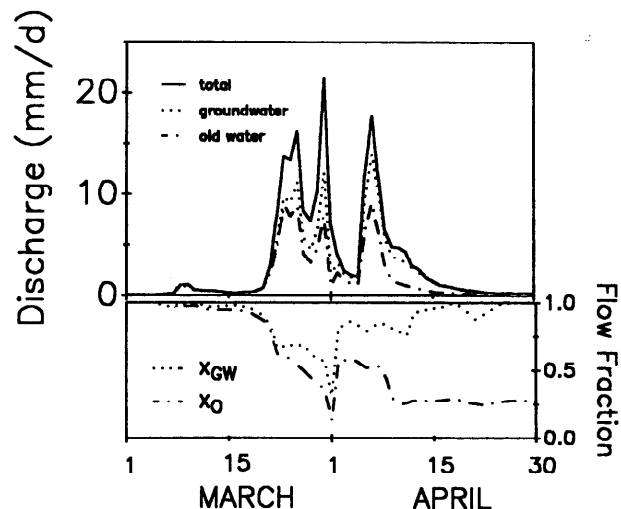
Fig. 6. Isotopic hydrograph separation of the 1987 spring runoff 1987 for Plastic-108. The contributions of old water and groundwater to streamflow are shown in the upper panel. The fractions of old water and groundwater (lower panel) were calculated using a constant C_O and a time variable C_{GW}, respectively.

the event. However, isotopic hydrograph separation could only be performed on the first, small runoff event. For this event, differences in X_O and X_{GW} ranged from 4% during the early part to 14% during the later stages, with an event total difference of $\approx 10\%$ [*Hooper and Shoemaker*, 1986]. The underestimation of X_{GW} by using a constant C_O would have been even greater during the remainder of spring runoff, as C_{GW} deviated further from the constant C_O. In contrast, *Rodhe* [1987] found smaller differences (3–6%) in estimates of X_O and X_{GW} for several small basins in Sweden. However, the meltwater inputs were much smaller than those observed in the present study. Thus a smaller dilution of the relatively large groundwater volumes in those basins (250–500 mm, *Rhode*, [1987]) is plausible.

In all three study catchments the relative contributions of old water to the individual melt periods were very similar, whereas groundwater fractions were considerably greater during the second melt period (Figure 6; Table 3). The fraction of groundwater can be expected to diverge more from that of old water during consecutive melt periods, since the old water in the groundwater reservoir is progressively displaced by infiltrating meltwater. A seasonal increase in groundwater contributions to streamflow was also observed by *Turner et al.* [1987]. They reported an increase in groundwater fractions in five consecutive rainfall events from 69 to 95% over a period of 2 months in an Australian headwater stream. Turner et al. suggested that consecutive rainfall events mixed and diluted in a shallow groundwater reservoir which progressively increased in volume during the runoff season.

Stream pH and Groundwater Contributions

It was hypothesized that the relative contribution of groundwater to streamflow was positively correlated to the acid-neutralizing capacity of the three study watersheds. To test this hypothesis, total X_{GW} and X_O for spring runoff 1987 was compared to the mean, flow-weighted stream pH (Table 2).

TABLE 3. Contributions of Old Water and Groundwater to Streamflow in Plastic-108

Period	Total Runoff, mm	Old Water		Groundwater		$(X_{GW} - X_o)^*$, %
		Millimeters	Percent	Millimeters	Percent	
M1†	118	57	48.7	77	65.5	16.8
M2‡	69	30	43.5	57	82.4	38.9
total§	203	99	48.7	149	73.6	24.9

*Difference of groundwater fraction and old water fraction.
†First melt period (March 22–April 4).
‡Second melt period (April 5–April 14).
§Total spring runoff (March 1–April 30).

The pH measurements in the three study streams were consistently different throughout spring runoff (Table 4). Harp-5 had the highest pH in the base flow and peak flow, while Plastic-1 exhibited the lowest pH. Stream pH in Plastic-108 remained intermediate between those of Harp-5 and Plastic-1 throughout the spring runoff period (Table 4). The pH depressions in all three streams ranged from 0.2 to 0.4 pH units (Table 4). Such depressions in stream pH during spring runoff are common for headwater streams in the Muskoka-Haliburton area [Jeffries et al., 1979]. The ranking of the three study watersheds from high to low catchment ANC, Harp-5 > Plastic-108 > Plastic-1, is best illustrated by comparing the total hydrogen export from the watershed (Table 4). Since the rates of acid deposition during spring runoff were very similar between the Harp Lake and Plastic Lake watersheds, the amount of H^+ neutralization differed greatly between the three basins.

Chen et al. [1984] argued that differences in lake pH of two adjacent basins in the Adirondack Mountains, New York, resulted from differences in relative flow contributions from acidic near-surface and more alkaline deep mineral soil horizons. This hypothesis was supported by a comparison of soil water and stream water chemistry in two adjacent stream watersheds in the same region [David, 1986]. However, in both studies the relative contributions from different soil horizons were not measured directly. In this study the differences in watershed ANC and in mean stream pH cannot be explained by relative contributions of groundwater to streamflow (Table 5). X_{GW} values were almost identical in all three watersheds despite the differences in stream pH response. However, the contribution of premelt groundwater (old water) to streamflow was larger in the well-buffered Harp-5 basin (60%) compared to both Plastic-1 watersheds (49%) (Table 5). This suggests that the residence time of contributing groundwater might be a more important

control on stream water pH than the relative contributions of groundwater to streamflow. These findings are inconsistent with the ILWAS hypothesis that stream and lake acidity depends on flow path [Chen et al., 1984].

GROUNDWATER VOLUMES AND RESIDENCE TIMES

Bottomley et al. [1986] suggested that the volume of the groundwater reservoir and the residence time of groundwater may play an important role in stream acidification. Here the hypothesis is tested that groundwater volumes and residence times are positively correlated with mean stream pH in the three study watersheds. In the first two sections the estimates of groundwater volumes and residence times of groundwater are presented. All volumes are reported as unit depths in millimeters to compare groundwater volumes in watersheds of different size. In the final section the influence of groundwater on the acid-neutralizing capacity of a basin is discussed.

Unit Depths of Groundwater

Two estimates of unit depth of groundwater were obtained from the isotope analysis discussed in the previous section: (1) total discharge of old water and (2) groundwater reservoir volume of Rodhe's mixing model.

The total unit depth of old water discharged during spring runoff (V_O) has to be considered a lower limit of soil and groundwater stored in the basin prior to spring runoff. Estimates of V_O are certainly smaller than the actual reservoir volumes, since not all old water was replaced by new water during spring runoff (Figure 6). The model reservoir volume (V_{GW}) was obtained from fitting Rodhe's mixing model (equation (1)) to observed changes in deuterium during spring runoff (Figure 5). The estimates of V_{GW} varied depending on which time periods were considered for the simulation of C_{GW}. The model reservoir volume for the first melt period ($V_{GW} = 145$ mm) was considerably smaller than for the second melt period ($V_{GW} = 280$ mm) [Wels, 1989].

TABLE 4. Stream pH Response During the 1987 Spring Runoff in Three Study Watersheds

	Harp-5	Plastic-108	Plastic-1
Stream pH			
maximum*	5.59	5.17	4.76
minimum†	5.25	4.74	4.27
mean‡	5.35	4.85	4.34
pH depression§	0.24	0.32	0.42
H^+ export, eq/ha	9.5	28.7	80.9

*Maximum stream pH measured during premelt base flow.
†Minimum stream pH measured on March 30 (peak flow).
‡Estimated flow-weighted mean for total spring runoff period.
§Maximum pH–mean pH.

TABLE 5. Contributions of Old Water and Groundwater in Three APIOS Headwater Streams

	Harp-5	Plastic-108	Plastic-1
Total spring runoff,* mm	213	203	177
Percent old water	60.2	48.7	49.2
Percent groundwater	72.7	73.6	65.3

The uncertainty in X_O and X_{GW} was estimated to be 7 and 14%, respectively [Wels, 1989]. APIOS, Acid precipitation in Ontario Study.
*March 1–April 30, 1987.

TABLE 6. Estimates of Unit Depths of Groundwater in the Study Watersheds

	Harp-5	Plastic-108	Plastic-1
Watershed			
Area, ha	195	3.3	23.4
V_{GW},* mm	420 ± 60	180 ± 30	200 ± 30
V_O,† mm	129 ± 9	99 ± 13	88 ± 13

The uncertainties in the estimates of V_O and V_{GW} are given also (see text).
*Obtained from Rodhe's mixing model.
†Total discharge of old (premelt) soil/groundwater.

TABLE 7. Estimates of Groundwater Residence Times and (Premelt) Groundwater Chemistry in the Study Watersheds

	Harp-5	Plastic-108	Plastic-1
Residence time for spring runoff, days	162	72	102
Premelt base flow			
pH	5.59	5.17	4.76
D, ppm	145.3	146.7	146.7
Tritium, TU	57 ± 6	54 ± 4	64 ± 6

Rodhe [1987] found similar temporal increases in V_{GW} in small basins in Sweden. In this analysis the estimate of V_{GW} for the entire spring runoff, that is, 180 mm, was assumed an average groundwater reservoir. The estimates of V_{GW} for the first and second melt period were considered lower and upper limits of this average V_{GW}.

The unit depths of groundwater, V_{GW}, were similar in Plastic-1 and Plastic-108 but significantly smaller than V_{GW} for the larger Harp-5 watershed (Table 6). Those estimates are in agreement with differences in the depth of the overburden which could store groundwater (Table 2). The entire Plastic-1 subcatchment is covered with only a thin (<1 m) discontinuous layer of glacial till overlying bedrock. A similar surficial geology is found in the headwater regions of the Harp-5 watershed. However, much thicker surficial deposits (5–10 m) are present in the central lowland (Table 2). To store the estimated unit depth of groundwater in a sandy soil (porosity 0.53 [*Lozano et al.*, 1987]) the average depth of saturated soil would be ≈0.3 m in Plastic-1/108 and ≈0.8 m in the Harp-5 watershed.

The unit depth of old water V_O was also larger in Harp-5 than in the two Plastic watersheds (Table 6). This is consistent with the differences in V_{GW} among the three watersheds. The inputs of new water should be more "diluted" in a larger (old) groundwater reservoir. V_O was smaller than V_{GW} in all three watersheds, since (1) the old groundwater reservoir was recharged by infiltrating meltwater, and (2) not all old groundwater had been replaced by new water. However, the differences between V_{GW} and V_O were much larger in Harp-5 than in the Plastic watersheds. This indicated a slower turnover of old water in the larger groundwater reservoir of Harp-5 compared to the smaller reservoirs in the Plastic watersheds. The residence times of groundwater in the three study watersheds are discussed in the following section.

Residence Times of Groundwater

Groundwater residence times depend on the size of the groundwater reservoir (V_{GW}) and the groundwater flow (Q_{GW}). The mean residence time of groundwater during spring runoff 1987 was calculated by dividing the estimated volumes of the groundwater reservoir V_{GW} by the total groundwater flow for this period obtained from isotopic hydrograph separation. The longest mean residence time of groundwater, τ, of approximately half a year was computed for Harp-5; the watershed with the largest groundwater reservoir (Table 7). The mean residence time of groundwater in the small headwater basin Plastic-108 was 72 days, that is,

less than half the τ in Harp-5 (Table 7). The mean residence time of groundwater in Plastic-1 (102 days) was intermediate between those of Harp-5 and Plastic-108. The differences in τ between Plastic-1 and Plastic-108 are larger than one might expect from estimates of the unit depth of groundwater (Table 6). However, the total unit depths of groundwater discharged during spring runoff 1987 were considerably greater in Plastic-108 (Table 5).

The uncertainty in estimates of V_{GW} (Table 6) may affect the absolute numbers of τ more than the relative differences of τ between the three watersheds. Therefore independent estimates for the groundwater residence times were sought in the literature. Unfortunately, those were only available for the Harp-5 watershed. *Bobba et al.* [1986] estimated the half-life times for an "upper" and a "lower" soil water reservoir and for the "groundwater" reservoir by fitting a three-reservoir hydrological model to the runoff records in Harp-5. Their residence time of groundwater (125 days) agreed well with the estimated τ in this study (162 days). The half-life residence times of the upper and lower soil reservoirs were only 32 and 1.3 days, respectively. The comparison suggests that the estimated residence time of groundwater is of the right order of magnitude.

The faster flushing rates in the Plastic watersheds relative to the Harp-5 watershed were consistent with differences in premelt groundwater D concentrations (Table 7). The higher deuterium in the stream base flow of Plastic-108 and Plastic-1 indicated more displacement of isotopically light groundwater, remaining from the previous spring runoff, by isotopically heavy rain during the last summer and fall. In Harp-5 the seasonal fluctuations were not as pronounced.

Since D in precipitation exhibits seasonal fluctuations, the isotopic hydrograph separation based on D identifies "old" water, that is, water that has been stored in the ground for one season. The residence times suggested that in all three study watersheds most of the groundwater is replaced within one year (Table 7). This hypothesis was tested independently by using the environmental isotope tritium. Tritium was introduced into the environment in the late 1950s and early 1960s during tests of nuclear weapons. Since then it has been used to identify older groundwater of different age [e.g., *Maloszewski et al.*, 1983]. Tritium concentrations in old groundwater (base flow) of all three basins were indistinguishable (Table 7). The tritium values were close to recent precipitation values (63–79 tritium units). This supports the hypothesis that groundwater in those basins has similar seasonal residence times. Very old groundwater (>15 years) was not an important contributor to streamflow in any of these small basins on the Canadian Shield.
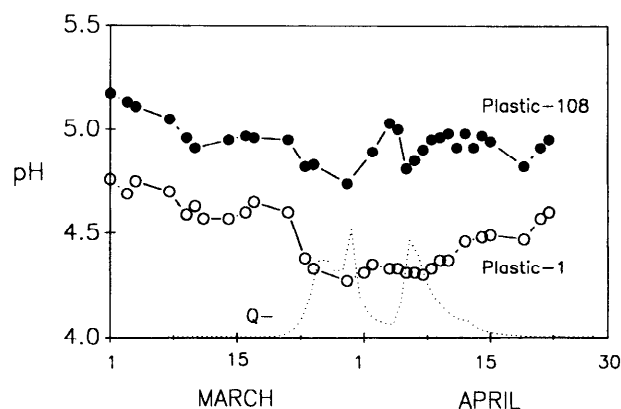
Fig. 7. Temporal trends in stream pH in Plastic-1 and Plastic-108 during the 1987 spring runoff. Mean daily discharge in Plastic-1 is shown for comparison.
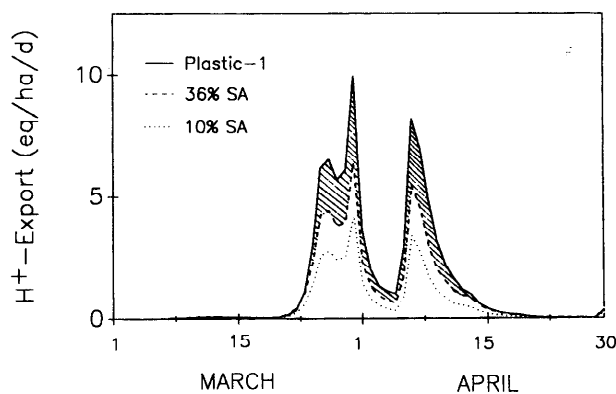

Fig. 8. Total hydrogen export from the Plastic-1 watershed during spring runoff 1987. Possible contribution of acidic DPS (pH 4.2) on the swamp only (dotted curve) and maximum saturated areas (dashed curve) are shown also. Shaded area estimates the release of hydrogen from within the swamp based on those mass balance calculations (see text).

Groundwater Residence Time and Stream pH

The differences in groundwater volumes and groundwater residence times correlated with the different base flow pH and neutralization capacity in Plastic-108 and Harp-5 (Table 7). The longer residence time of groundwater in Harp-5 would allow for increased slow weathering reactions and acid neutralization. The higher base cation concentrations in Harp-5 compared to Plastic-108 support this hypothesis (OME, unpublished data, 1988). Peters and Driscoll [1987] related flow duration curves of several watersheds in the Adirondacks region to average concentrations of the weathering products, silica, base cations, and acid neutralization capacity. They concluded that the residence time of water in contact with the neutralizing minerals in the till and groundwater contributions to surface flow were primary factors controlling stream acidification. However, no clear differentiation was made between the influence of flow paths and residence time, that is, relative contributions versus age of groundwater [e.g., Chen et al., 1984; David, 1986]. This study has shown that differences in the residence time of groundwater between basins are not necessarily related to differences in the relative contributions of groundwater. The different stream pH in Harp-5 and Plastic-108 might be explained by longer residence times of groundwater but not by differences in the relative contributions of groundwater.

INFLUENCE OF WETLANDS

The lower stream pH in the second-order basin Plastic-1 compared to its first-order subbasin Plastic-108 (Table 4) cannot be explained by smaller contributions of groundwater (Table 5) or by shorter residence times of groundwater (Table 7). Plastic-108 drains into Plastic-1 via a centrally located conifer-sphagnum swamp (Figure 3). The stream pH changes significantly during the short passage through the swamp (Figure 7). The difference in stream pH remained fairly constant and appeared to be independent of changes in flow (Figure 7). Clearly, the conifer-sphagnum swamp must contribute to the high H^+ export from the Plastic-1 watershed (Table 4). Assuming that the hydrogen export from the headwater stream Plastic-108 was representative for the entire terrestrial part of Plastic-1, 65% (52.2 eq/ha) of the total H^+ export from Plastic-1 must have originated from the swamp.

There are two possible sources of H^+ ions measured in runoff below the swamp: (1) direct inputs from meltwater on the swamp, and (2) internal H^+ release within the swamp. Contributions of direct precipitation onto saturated areas (DPS) from the wetland area itself (10%) were not large enough to match the total H^+ export (Figure 8). The direct inputs of H^+ in meltwater and rainwater to the conifer swamp via DPS were estimated to be less than 14.1 eq/ha during spring runoff 1987 (assuming a pH of 4.2). This leaves 47% (38.1 eq/ha) of the total H^+ export from Plastic-1 unexplained. However, the swamp itself comprises only a minimum extent of saturated area in the Plastic-1 watershed. Shibatani [1988] has mapped the increase in saturated areas along the perimeter of the swamp and the development of several transient wetlands in upland areas of Plastic-1. His field survey in the 1985 spring runoff yielded an event mean of 36% of saturated areas (including the swamp). It could be argued that DPS on those saturated areas which develop during spring runoff contributed acidity to streamflow. Even those large contributions of DPS from the entire watershed could not explain the total H^+ export from Plastic-1 (Figure 8). For the entire 1987 spring runoff at least 30% (20 eq/ha) of the total H^+ export from Plastic-1 remained unexplained (shaded area in Figure 8). These mass balance calculations suggest that biogeochemical reactions in the swamp must release additional acidity. Much of the water that passed through the swamp must have taken up H^+ even during periods of high flow (Figure 8). These findings agree with those of Christophersen et al. [1985], who postulated that acid organic soils in effluent areas may acidify spring runoff dominated by old water in Birkenes, Norway. LaZerte and Dillon [1984] found that sulphate (SO_4^{2-}) dominated the proton-contributing anions during spring runoff in Plastic-1. They concluded that organic acids were not the main source of the H^+ supplied by the swamp. Similar observations were made during spring runoff in a small watershed in Sweden where half of the watershed was bog land [Jacks et al., 1987]. They observed a decrease in organic acids despite the increase in stream acidity and suggested that pH depressions in the stream were caused by sulphuric acid from the snowpack. The exact mechanisms of the H^+ release from the Plastic-1 swamp are not fully understood yet and are

currently being studied [*Dillon et al.*, 1987; B. D. LaZerte personal communication, 1989].

This study has shown that the Plastic-1 conifer-sphagnum swamp contributed to stream acidity by exporting strong acids. However, these findings may not be applicable to other types of wetlands with different characteristics. For example, several wetlands are located in the well-buffered Harp-5 watershed (Table 2). One can only speculate why those wetlands do not acidify streamflow in Harp-5 the same way as in Plastic-1. Most wetlands in Harp-5 are open ponds or covered with light stands of black spruce compared to the shallow, densely vegetated conifer-sphagnum swamp in Plastic-1. Furthermore, some wetlands in Harp-5 are not linked directly to the main stream channel so that they may influence only a small fraction of the total spring runoff. Several small wetlands dispersed over a watershed may not have as large an effect on stream water quality as one larger, centrally located wetland such as in Plastic-1. More research on the controlling mechanisms is needed in order to generalize about the influence of wetlands on stream acidification.

SUMMARY

We have measured the concentration of HDO in stream and subsurface water, stream pH, and stream discharge in three catchments located in an acid-sensitive area on the Laurentian shield. Isotopic hydrograph separations were used to estimate the quantity of groundwater and meltwater to spring runoff and to calculate the volume of the groundwater storage reservoir and the groundwater residence times. Then we estimated the significance of different sources of H^+ ions to the stream. On the basis of these measurements we conclude the following:

1. The contribution of old (premelt) groundwater to spring runoff ranged from 49 to 60% and was not correlated with the mean pH measured during this period.

2. Groundwater storage reservoirs held 180–420 mm (unit depth) of water with residence times of 72–162 days during the spring melt. The largest reservoir and longest residence time was measured in the basin with the highest stream pH.

3. The lowest stream pH (4.8) was measured below a wetland that collects drainage from >75% of the basin. In this basin, H^+ ions were released from the conifer-sphagnum wetland. More attention must be focused on the acidity generated in wetlands, since wetlands are ubiquitous in small basins in many acid-sensitive areas.

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R. J. Cornett, Environmental Research Branch, Chalk River Nuclear Laboratories, Chalk River, Ontario K0J 1J0 Canada.

B. D. LaZerte, Dorset Research Centre, Water Resources Branch, Ontario Ministry of the Environment, P. O. Box 39, Dorset, Ontario P0A 1E0 Canada.

C. Wels, Watershed Ecosystems Program, Trent University, Peterborough, Ontario K9J 7B8 Canada.