EPISODIC ACIDIFICATION OF FRESHWATER SYSTEMS IN CANADA - PHYSICAL AND GEOCHEMICAL PROCESSES

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Abstract. The occurrence of episodic acidification in Canadian streams, lake waters and shallow groundwaters has been reviewed, and the contolling mechanisms identified. 'Episodes', which are periods of depressed alkalinity during hydrological events, have been studied mainly in southeastern Canada, and occur at all sites where there is sufficient time resolution of the observations, viz. Ontario, Quebec and Nova Scotia. An 'alkaline episode', where acidity decreases during an event, has been reported from one lake in the Canadian Artic. There is a bias towards the examination of episodes stimulated by snowmelt or rain-on-snow, since rainfall-stimulated episodes are poorly documented. Pre-event, rather than event, water dominates runoff during episodes. For this reason, biogeochemical reactions and the hydrological flowpaths in operation through the vadose and saturated zones are the principal controls on the chemical characteristics of episodes. Most episodes are dominated by base cation 'dilution' in circumneutral systems, and 'increase in strong acid anions' (particularly sulphate) in acidic systems. Episodes dominated by nitrification or organic acids or stimulated by sea salt input are rare or have not been decumented. Direct input of event water may dominate only during particular circumstances at snowmelt. Then, direct chemical inputs from lake ice and lake snow cover may be of importance in some systems.

1. Introduction

Chronic, or long term, acidification is known to have deleterious effects on aquatic ecosystems (Baker, 1990). In Canada, for example, the distribution of phytoplankton groups and species is dependant on the pH of lake water (Pinel-Alloul *et al.*, 1990; RMCC, 1990), as is the distribution of fish communities (Kelso *et al.*, 1990; RMCC, 1990). In addition, many aquatic ecosystems exhibit short term decline in pH, or acid neutralisation capacity (ANC), following snowmelt or rainstorms. This so-called 'episodic acidification' has potentially important implications for the assessment of the environmental impact of acidic deposition. Eshleman (1988) estimated that in six subregions of the eastern United States, the number of systems which

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are acidic (ANC < 0) increases by 40–640% when the impact of short term acidification, rather than simply the level of chronic acidification, was considered.

Here, we define episodic acidification or an 'episode' as the short term reduction in ANC which is observed in many streams, rivers and lakes during hydrological events (Wigington *et al.*, 1990). Episode acidification has been observed in many regions of North America and Europe (Wigington *et al.*, 1990; RMCC, 1990; Davies *et al.*, 1992). It is often associated with a reduction in pH and elevated concentrations of labile Al, and may be commonly associated with decreased concentrations of Ca. Such a combination of chemical changes may have adverse effects on the viability of fish populations and aquatic ecosystems (Baker *et al.*, 1990).

Reports of fish kill in Canada as a result of episodic acidification are limited, but this may be because of the difficulty in making field observations, rather than a true reflection of the frequency and extent of fish kill (Jeffries, 1990a). Reports of fish kill during episodes are documented in Ontario, at Plastic Lake (Harvey and Lee, 1982) and the Milford Bay trout hatchery (Harvey and Whelpdale, 1984), in Quebec, at Lac Laflamme (Papineau, 1987), and in Nova Scotia (Lacroix and Townsend, 1987).

Studies of episodic acidification in Canada are largely confined to the South-east, principally Ontario, Quebec and Nova Scotia (see Figure 1). The common characteristics of these sites are the relatively poor buffering capacity of the bedrock and overburden (which result in the terrain being sensitive to acidic deposition), and the 'significant quantity of acidic deposition of anthropogenic origin' (Jeffries, 1990a). The watersheds experience episodes stimulated by snowmelt, rain-on-snow and rainfall, although most attention has been given to the snowmelt season. There is also an unusal record of an 'alkaline' episode in a Canadian Arctic lake (Adams and Allen, 1987).

There are five main types of episodes, which are defined by the dominant reason for the loss of ANC (Wigington *et al.*, 1990). They are: an increase in organic acid concentrations; the sea salt effect; nitrification; a dilution of base cations; and an increase in strong acid anions derived from atmospheric depostion. Often, some of these factors operate concurrently, and are likely to be dependant on the acid-base status of the watershed (Molot *et al.*, 1989).

Episode chemistry is strongly influenced by the stimulus, the hydrological flowpaths in operation during the episode, biogeochemical reactions in the soil and regolith, and the antecedent conditions in the watershed (Wigington *et al.*, 1990). It is not surprising that a given watershed may experience episodes of different magnitude and duration throughout a period of study, and that the chemical composition of the episode will also vary. The rationale for the following survey is that only maximum changes in chemical species are recorded (from pre-episode levels to episode maxima), along with the typical duration of the episode. Clearly, there are numerous ways of characterising an episode. This simple scheme is adopted to given an indication of possible worse case scenarios, and is similar to that adopted for reviews of episodes in the Unites States (Wigington *et al.*, 1990) and Europe

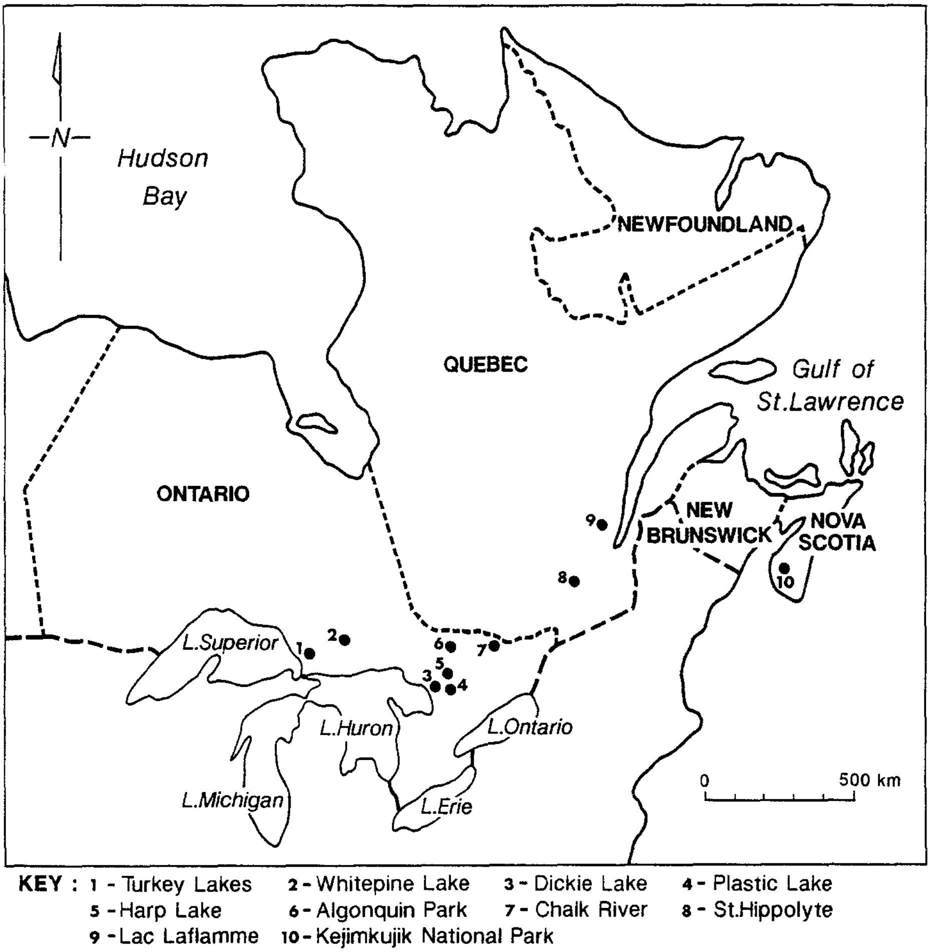

Fig. 1. The location of Canadian sites where episodic acidification has been reported.

(Davies *et al.*, 1992); this has the advantage of making these reviews directly comparable. At present, there is no commonly adopted scheme in the literature to define a suitable 'severity index' for episodes or to compare the frequency or class distribution of episodes between sites (Davies *et al.*, 1992). The stochastic modelling of the acidity of higher flow events, in terms of the probability of their magnitude, frequencey, duration and timing (Bobba *et al.*, 1990) seems to offer a way forward in better quantifying the latter categories. Episodic acidification of lakes is better represented in Canadian studies than those of other countries (cf Wigington *et al.*, 1990; Davies *et al.*, 1992). It appears that the chemistry of lacustrine episodes may be influenced by the composition of ice and snow cover on lakes (Adams and Allan, 1989). In Canada, approximately 10% of snowcover by area forms on lakes and rivers (Adams and Allen, 1989). Average annual lake ice thicknesses over eastern Canada range from ~75 cm at 50° N to ~200 cm at 65° N. The influence of lake ice and lake snowcover has been largely ignored most studies of lacustrine episodes. Hence an account of the potential of such influences is also included.

Research on episodic acidification in Canada is spread throughout a diverse literature, reflecting the interdisciplinary nature of the phenomenon. Here, we distil the existing literature with three main aims: to review the occurrence of episodes in Canada; to examine the hydrochemical characteristics of episodes; and to review the processes which govern the magnitude of the episodes.

2. Episodes Acidification in Ontario

The precence of higher quantities of carbonate minerals in the bedrock or overburden results in the surface waters of Ontario having generally greater ANC than Quebec and Nova Scotia (Jeffries, 1990a.) There are many studies of episodes in Ontario, and examples from the major sites are described below.

2.1. HARP, DICKIE AND PLASTIC LAKES

The location of the lakes is shown in Figure 1. Episodes triggered by rain on snow and snowmelt have been most frequently reported (Jeffries *et al.*, 1979; Servos and Mackie, 1986; Nalewajko and O'Mahoney, 1988; Hall *et al.*, 1988; Molot *et al.*, 1989). The lakes have several inflows which exhibit a range of pH and alkalinity (Dillon and Molot, 1989; Molot *et al.*, 1989). In these inlets, the greatest loss of alkalinity and decline in pH occurs in episodes in the more alkaline streams, while the more acidic streams exhibit the lowest episodic ANC and pH. Further, pH depressions are greater in small streams than in large rivers within the area (Jeffries *et al.*, 1979). In general, the severity of episodes, in terms of the lowest ANC and pH recorded, is greater in the inlets and lesser in the outlets (see Tables I and II), while surface lake waters show a variable response.

The spatial variation in the pH depression of lake waters during snowmelt is most marked in the littoral zone, where pH can be depressed from 5.7 to 5.0 for four weeks. The lowest recorded pH values (4.5–4.9) have been observed near the major inflows or regions of seepage (France and LaZerte, 1987; LaZerte and Dillon, 1984). Further from shore, shallow waters show greater pH depressions than deeper waters. Shallow waters may experience pH depressions from 5.6 to 5.0 for a week. In contrast, deeper waters show a gradual decline from pH 6.0 to 5.4 at ice-out (France and LaZerte, 1987).

Generally, dilution of base cations was responsible for the loss of alkalinity in circumneutral systems, whereas the impact of increase in sulphate or nitrate concentrations was more dominant in more acidic systems (Molot *et al.*, 1989).

2.2. MILFORD BAY TROUT HATCHERY

The Milford Bay Trout Hatchery (see Table I) consists of a series of ponds fed by springs and streams. Fish kills have been reported in the streams (Harvey and Whelpdale, 1986). During snowmelt, the pH of surface streams, which mainly consist

TABLE I

Summary of the alkalinity (μeq/L) and pH at pre-episode and peak-episode conditions in selected rivers, streams and lakes in Canada

Region/Site	Lake (L), Stream (S) or River (R)	Rain (R) or Snow (S)	Pre-episode pH	Peak-episode pH	Pre-episode alkalinity	Peak-episode alkalinity	Source
Ontario							
Dickie Lake	S	S	4.9	4.1	−100 to +50	−160 to 0	1,2
	L	S	5.7	4.8			1,2
Harp Lake	S	S	5.9	4.8	−10 to +100	−30 to +50	3
	L	S	6.1	5.4			3
Plastic Lake	S	S	4.8	4.3	−40 to +10	−30 to +50	1,3,4,5
	L	S	5.7	5.0			1,3,4,5
Turkey Lakes Watershed							
1st order stream	S	S	6.2	4.5			6
Lower order stream	S	S	6.4	5.4	+50 to +100	0	6,7
Batchwana Lake	L	S	6.2	5.0	+50	<20	8
Wishart Lake	L	S	6.3	4.9	+100	0	8
Little Turkey Lake	L	S	6.7	5.7	+160	+10	8
Turkey Lake	L	S	6.6	6.1	+220	+50	8
Milford Bay Trout Hatchery	S	S	6.0	4.6	+78	+0.5	9
	S	R	6.4	5.3	+292	+50	9
Whitepine Lake	L	S	5.7	5.4			10,11
Algonquin Park	S	S	~6.0	~5.0			12
Chub Lake	S	S	5.2	4.7			2
	L	S	5.7	4.7			2
Crossan Lake	L	S	6.0	5.2			2
Fawn Lake	L	S	5.8	4.7			2
Paint Lake	L	S	5.5	5.0			2
Lake St Nora	L	S	6.9	5.6			13
Quebec							
Lac Laflamme	S	S	6.1	5.0	+200		14
	L	S	6.4	4.6[a]	+220		14
Lac Pin Blanc	S	S	5.7	5.3			15
Hermine	S	S	6.0	5.4			15
Nova Scotia							
Kejimujik Park	R	S	7.0	3.8[b]			16
Mersey River	R	S	7.0	3.8			17

Note:

[a] A minimum value of 3.8 has been reported.

[b] A minimum value of 3.2 has been reported.

Source of data:

1. Dillon and Molot, 1989
2. Jeffries *et al.*, 1979
3. Servos and Mackie, 1986
4. France and LaZerte, 1987
5. LaZerte and Dillon, 1986
6. Bottomley *et al.*, 1986
7. Jeffries and Semkin, 1983
8. Kwain and Kelso, 1988
9. Harvey and Whelpdale, 1986
10. Gunn and Keller, 1984
11. Gunn and Keller, 1986
12. Hall and Idle, 1987
13. Nalewajko and O'Mahony, 1988
14. Papineau, 1987
15. Hendershot *et al.*, 1984
16. Freedman and Clair, 1987
17. Howell, 1989

TABLE II

Pre-episode and peak-episode chemistry in streams and lakes from selected studies in Canada

Location	Rain (R) Snow (S)	Pre-episode and peak-episode values[a,b]												
		pH		SO_4^{2-}		NO_3^-		C_B[d]		Ca^{2+}		Al[e]		Source
Ontario														
Dickie Lake														
Inflow	S	4.6	4.1	120	160	0	15	240	220					1
Outflow	S	5.7	4.9	150	160	2	12	240	190					1
Harp Lake														
Inflow	S	5.9	4.8	240	280	20	120	360	410					1
Outflow	S	6.3	5.0	170	180	10	22	300	270			50	100	1
Plastic Lake														
Inflow	S	4.8	4.3	140	180	10	22	190	180			300	400	1
Outflow	S	5.7	5.0	160	110	5	15	175	120			40	100	1
Milford Bay Trout Hatchery (stream)	S	6.0	4.6									50	250	2
Turkey Lake Watershed (stream)	S	6.2	4.5	140	160	20	25	230	200			50	200	3,4
Batchwana Lake, South	S	6.2	5.0			10	35					80	120	3,4
Little Turkey Lake	S	6.7	5.7									30	70	3,4
Whitepine Lake	S	5.7	4.6	200	270	2	4			130	150			5
Nova Scotia														
Mersey River	S	7.0	3.8	50	70					65	40			6
Quebec														
Lac Laflamme														
Inflow	S	6.6	4.6	50	90	20	40			190	40			7
Outflow	S	6.5	4.0	80	100	14	30			150	50	100	250	7
Lac Pin Blanc (stream)	S	5.7	5.3									14	27	4,8
Hermine (stream)	S	6.0	5.4									80	170	4,8

[a] First value for each parameter is pre-episode; second is peak episode. Values are not necessarily synchronous for various chemical parameters.

[b] DOC = mg L^{-1}; pH = pH units; Al = μg L^{-1}; the remainder of the parameters are μeq L^{-1}.

[c] Snow may include rain on snow.

[d] Sum of base cations.

[e] Total dissolved Al.

Source of data: 1. Dillon and Molot, 1989; 2. Harvey and Whelpdale, 1986; 3. Jeffries and Semkin, 1983; 4. Jeffries and Hendershot, 1989; 5. Gunn and Keller, 1984, 1986; 6. Freedman and Clair, 1987; 7. Papineau, 1987; 8. Hendershot *et al.*, 1984.

of event water, can decrease from 6.0 to 4.6 for a duration of at least 3 days (see Tables I and II). The Al concentration increased from 150 to 260 μg L^{-1}.

2.3. TURKEY LAKES WATERSHED

The Turkey Lakes Watershed (TLW), shown on Figure 1, has been the focus of multidisplinary research into the biogeochemistry of headwaters lakes and streams, and has given rise to important information on the processes which are responsible for promoting episodes.

Streamwater Chemistry During Episodes

Snowmelt or rain on snow stimulates hydrological events during the spring (Jeffries *et al.*, 1988). Greatest pH depressions may follow a succession of freeze-thaw events. Episodes are most pronounced in first-order headwaters streams (see Tables I and II) because the contribution, and the alkalinity, of the groundwater component may be lowest (Bottomley *et al.*, 1986; Jeffries and Semkin, 1983; Lam *et al.*, 1986, 1988). During snowmelt stimulated episodes, NO_3^- concentrations may be slightly elevated, whereas SO_4^{2-} concentrations may either decline or rise only slightly (Jeffries and Semkin, 1983). However, dilution of base cations is likely to be the dominant cause of the loss of alkalinity.

Rain storm discharge leads to a variable pH response, depending on the antecedent conditions in the watershed (Wigington *et al.*, 1990). For example, in 1983, during 3 weeks of drought, the pH of a particular stream was 6.0. The end of the drought was signalled by a 2 hr, 32 mm raifall (pH 4.4) which resulted in a variation of streamwater pH from 5.8 to 6.3 (Bottomley *et al.*, 1984). About 90% of the water was pre-event.

During rain storm events, the pH and alkalinity of groundwaters may be depressed by infiltrating solution (Bottomley *et al.*, 1986; Craig and Johnson, 1988a,b). Groundwaters at depths of $<$ 1 m experience acidification for between 1–10 days, when alkalinity can fall from 30 to 0 μeq L^{-1} and pH can fall from 5.1 to 4.6. These effects are believed to be kinetic, where the H^+ loading rate is greater than that of alkalinity regeneration by chemical weathering.

Lake Water Chemistry During Episodes

Lakes in the TLW are typically ice-covered during snowmelt (Jeffries and Semkin, 1983). In general, lake water is more alkaline at the lake bottom than at the surface. Furthermore, event water tends to remain near the lake surface during an episode. Hence, pH depressions and loss of alkalinity are usually most marked in surface waters.

For example, as shown in Figure 2, alkalinity of bottom water at Batchawana Lake varies from 80 to 100 μeq L^{-1} during the year (Jeffries and Semkin, 1983). During snowmelt (Jeffries and Semkin, 1983), rain events, or rain-on-snow events (Kwain and Kelso, 1988), the alkalinity of surface water (1–2 m) can change from 50 to $<$20 μeq L^{-1} while decreasing very little in bottom water. The pH shows

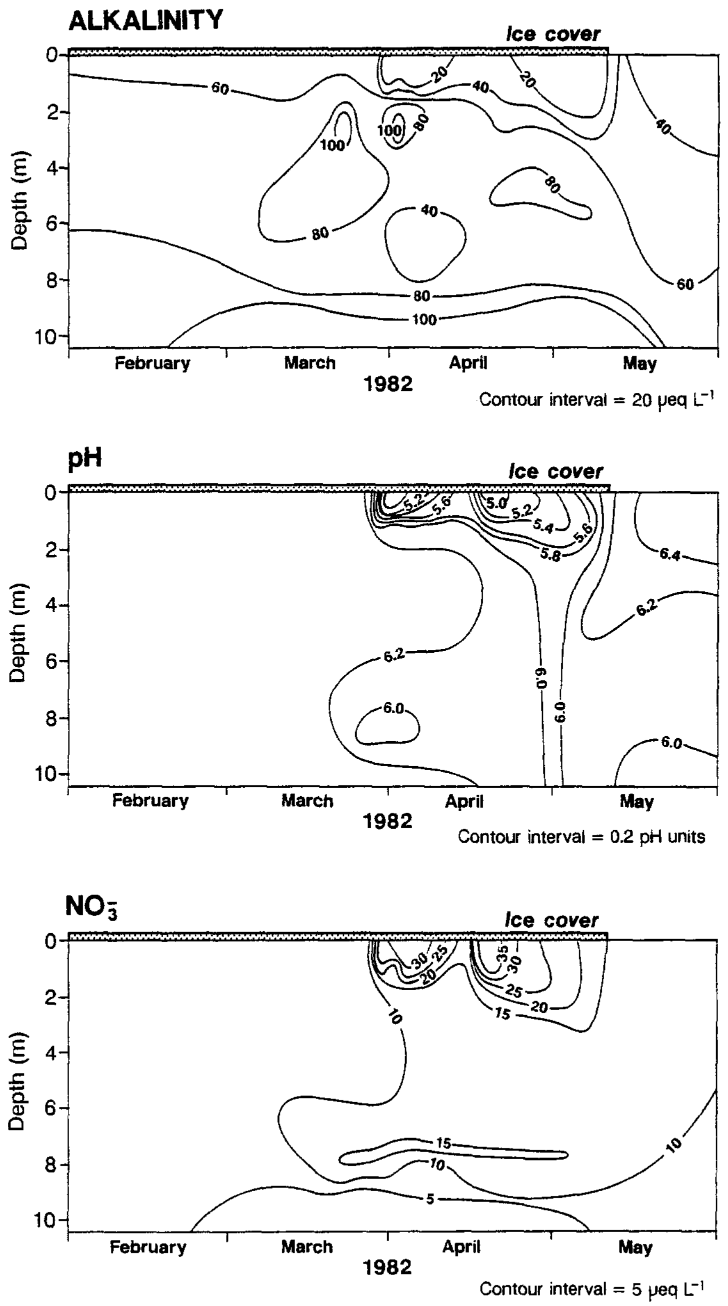

Fig. 2. The variation in pH, alkalinity and nitrate concentration prior to and during snowmelt at Batchawana Lake South in 1982 (from Jeffries and Semkin, 1983). It can be seen that the greatest change in alkalinity, nitrate and pH occurs in the surface layer (~1m deep), prior to the disappearance of the ice cover. Thereafter, the turnover gives rise to a more homogeneous distribution of these species throughout the lake.

a marked depression in surface water, from 6.2 to 5.0 (Jeffries and Semkin, 1983; Kwain and Kelso, 1988), while remaining relatively constant (6.2–6.0) at the bottom. The pH of surface water can be depressed for 4 to 10 days. Similar patterns of change are exhibited by Wishart and Turkey Lakes (see Table I).

The above example of episodic acidification is not unique to TLW in a regional context. In a 1981 survey of 30 lakes in the Algoma region of north-central Ontario, in which the TLQ is located, all lakes experienced loss of alkalinity during the spring thaw (Kelso *et al.*, 1986).

2.4. WHITEPINE LAKE

Whitepine Lake (see Figure 1) has been the subject of investigations into the temporal and spatial variation in episodic acidification.

Nearshore water experiences several pH depressions (minimum change, pH 5.7 to 5.2; maximum change, pH 5.5 to 4.5) during April through mid-May (when the ice cover was completely ablated) and could have been stimulated by acidic rain (pH 4.8–3.6) or snowmelt (Gunn and Keller, 1986). The minimum recorded pH of the lake water was 4.1. Individual episodes may last between 3 to 7 days, although the period with pH <5 can last for as much as 26 days. Acidic runoff from the watershed forms a surface layer on the lake, 15–20 cm thick, immediately beneath the ice. There is little mixing with underlying waters, whose pH remains largely unchanged (Gunn and Keller, 1985, 1986). Figure 3 shows the variation in the pH of lake water (at ~1 m depth) prior to, and during, snowmelt, for 1982, 1983 and 1984.

There is little spatial variability in the pH and conductivity of the shoreline waters before snowmelt and following ice breakup prior to the spring overturn. During snowmelt, however, the range of pH may increase approximately twofold as the mean pH decreases. Sites near drainage channels have more extended periods of pH depression, of up to 26 days (Gunn and Keller, 1985, 1986).

Also shown in Figure 3 is the depression of the pH of interestital waters in the lake sediment during the thaw, which is assumed to be the consequence of the lateral flow of acidic groundwater into the lake sediment. In general, the interstitial waters have higher pH than those of the ambient lakewater. However, pH depressions from 5.5 to 5.0 have been recorded.

2.5. OTHER ONTARIO STUDIES

Other examples of pH depression during snowmelt in lakes within Ontario are given in Table I, and further information may be found in Jeffries *et al.* (1979) and Gunn and Keller (1986).

3. Episodic Acidification in Quebec

The most extensive studies of episodes in Quebec have been conducted at Lac Laflamme, located 80 km north of Quebec City in the Laurentian Mountains. Other

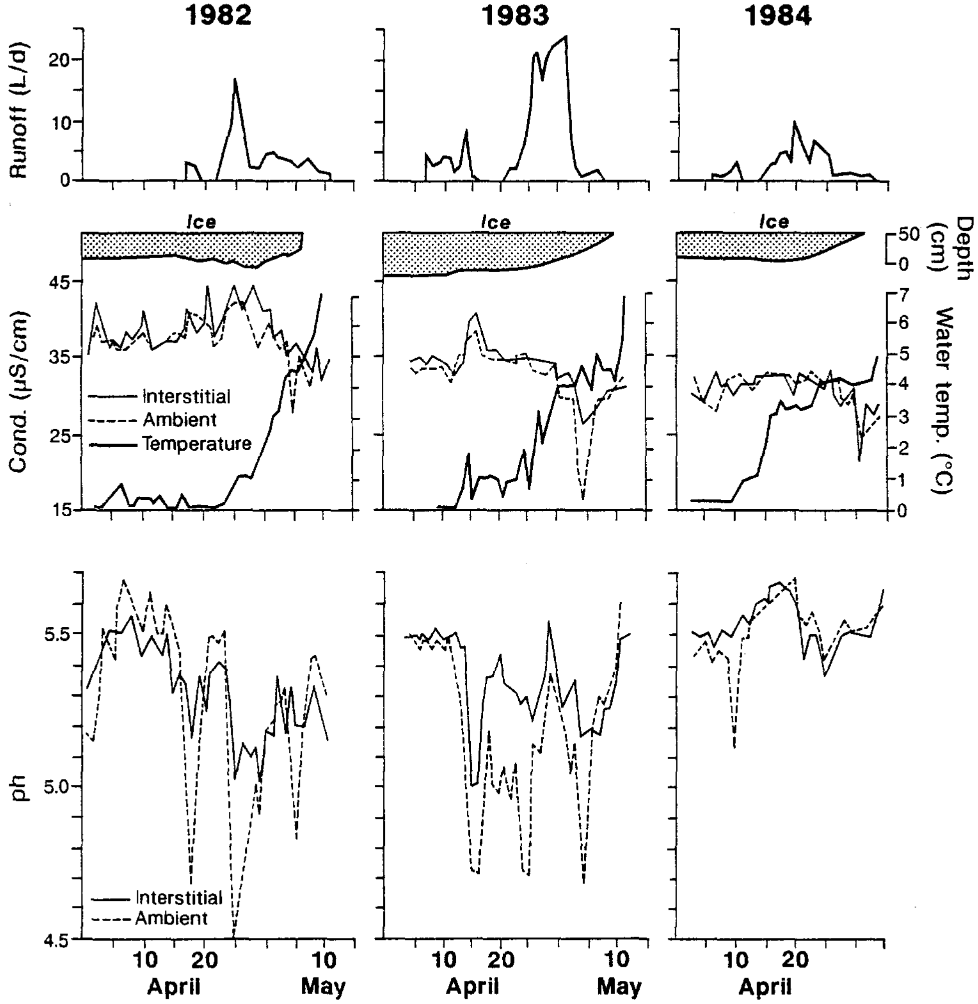

Fig. 3. The variation in the runoff, ice cover and the pH of interstitial waters in lake sediment and ambient lake water (at ~1 m depth) in Whitepine Lake prior to and during snowmelt for the 1982–84 melt seasons (from Gunn and Keller, 1986). Depression of pH in both the ambient and the interstitial waters occurs during runoff. Conductivity (a crude measure of total dissolved solids) and temperature variations are included to aid interpretation of the pH data.

studies have been undertaken at St. Hippolyte (see Figure 1). Research has focused on the biogeochemical controls on surface water pH and Al content, and the flowpaths which operate during hydrological events within boreal forest catchments.

3.1. LAC LAFLAMME

Streamwater pH in the small inlet exhibited a range of pH from 4.6 to 6.6 (Jones *et al.*, 1984). During the snowmelt period, Al can increase from 50 to 250 μg L^{-1} and DOC concentrations can double, which reflects a greater proportion of routing through the organic layer (Papineau, 1987). The alkalinity of shallow groundwater

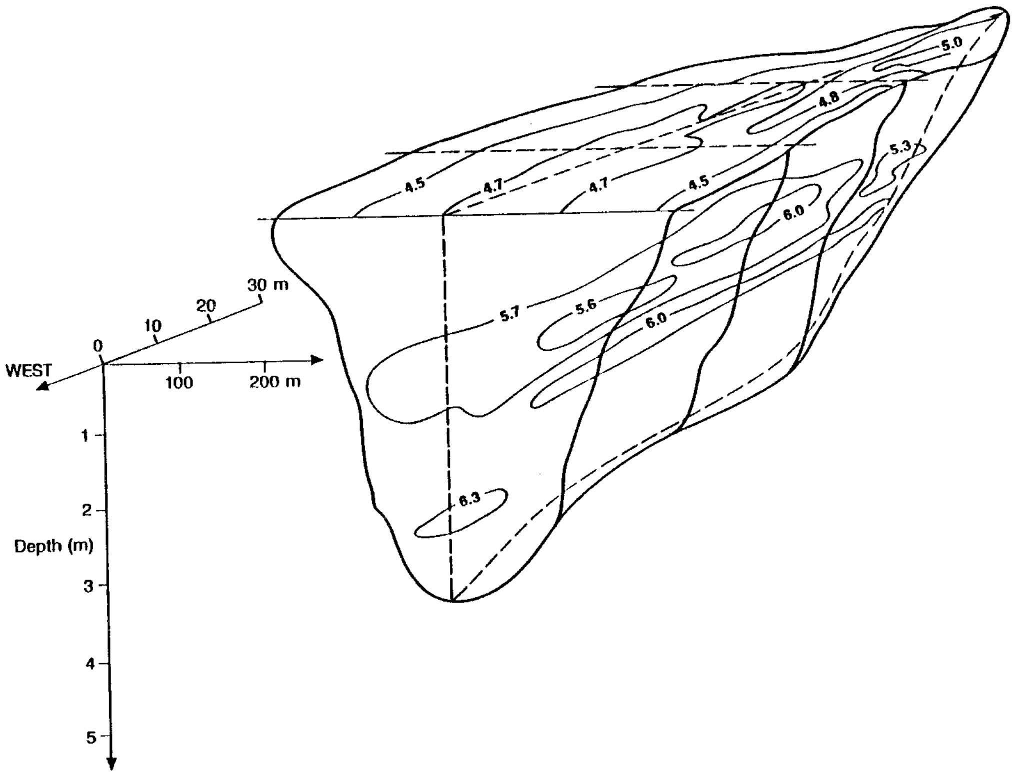

Fig. 4. The spatial variation of pH in Lac Laflamme on May 1, 1983 (from Jones, 1987). The pH is lowest in the surface waters around the lake perimeter.

may fall from ~50 μeq L^{-1} to 0 during such periods (Papineau, 1987). Jones and Bedard (1987) demonstrated the influence of biogeochemical reactions in the soil on the flux of sulphate and nitrate through the system. The sulphate concentration of streamwaters are more dependant on concentrations in the lower soil (B1, B2 horizons). During snowmelt, the soil acted as a source of sulphate to streamwaters. By contrast, nitrate concentrations in streamwaters are dependant on reactions in the upper soil organic layers, where, depending on antecedent conditions, these layers may act as a source or sink of nitrate. Hence the kinetics of leaching and biological transformations of N-containing compounds determine whether or not the organic layers act as a source or sink.

An important observation on the infuence of flow routing during episodes has been reported by Roberge and Plamondon, (1987). Overland flow accounts for little of the downslope flow at Lac Laflamme, which is dominated by groundwater flow in the till aquifer. When the saturated level reaches the top of the mineral soil, pipe throughflow in the organic layer is generated, the intensity of which strongly depends on the groundwater level. Pipe throughflow is likely to be an important process during snowmelt and can contribute to the extent of acidification. The pH of ground waters in 0.5–1.0 units higher than that of throughflow in the organic horizon.

Acidic meltwaters derived from pipe throughflow in the organic layer float atop the lake and beneath the ice cover, causing pH depressions from 6.2 to 4.4. The duration of pH depresssion is up to 34 days (see Tables I and II). These variations may be largely confined to the surface waters (~1 m), as illustrated by Figure 4. In 1981, however, pH values as low as 3.8 were recorded, although the reasons for this are inclear (Jones, personal communication). Dilution of base cations and an increase in nitrate concentration contribute to the loss of alkalinity of lake waters during episodes (Papineau, 1987).

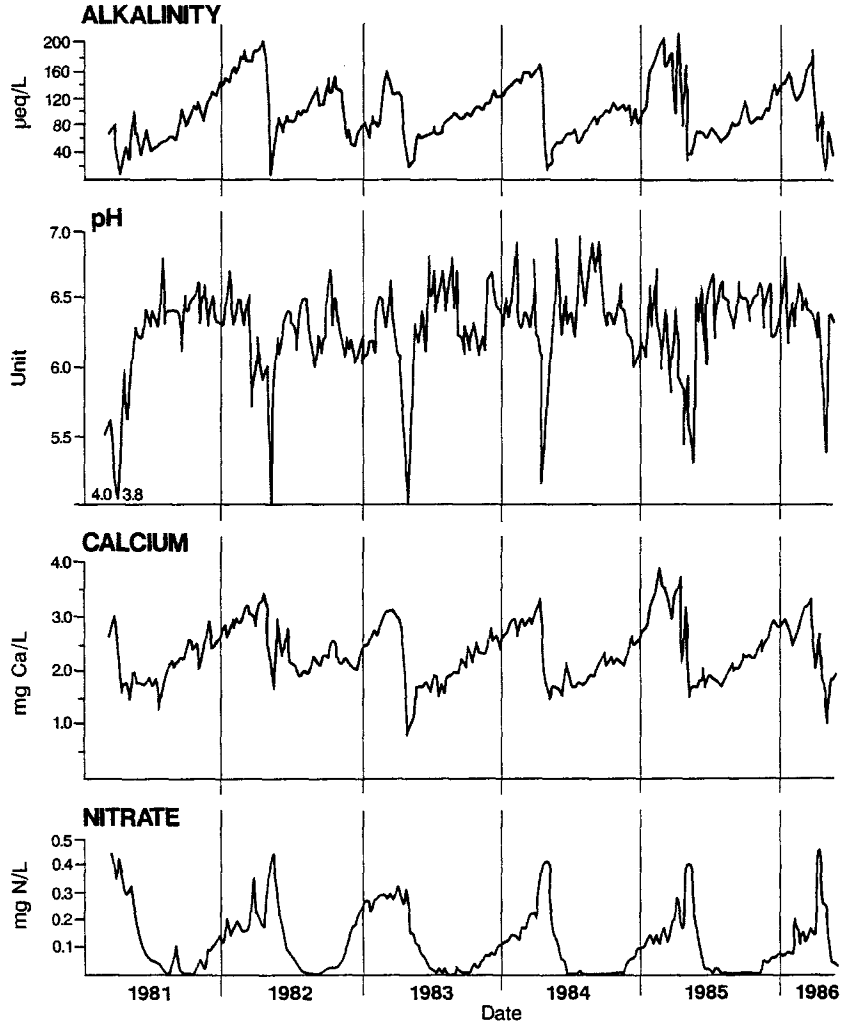

Fig. 5. The variation in pH and alkalinity at the Lac Laflamme outlet from 1981 through Spring 1986 (from Papineau, 1987). The pronounced depression of pH and alkalinity occurs during the thaw.

Lake outflow shows more temporal variation in composition than water at the lake centre, although patterns of change are similar. Figure 5 shows the temporal variability in pH and alkalinity for 1981 through spring 1986, and illustrates the dramatic decline in alkalinity and pH during snowmelt. Also illustrated is the dilution of calcium and the increase in nitrate during this same period.

3.2. St. HIPPOLYTE WATERSHEDS

Hermine

Snowmelt stimulated episodes gave rise to a depression of pH of 0.6 units, from ~6.0 to ~5.4, concurrent with an increase in acid extractable and total monomeric Al concentrations, up to peak values of ~190 and ~80 μeq L^{-1} respectively. Background concentrations were ~80 and ~30 μeq L^{-1} (Jeffries and Hendershot, 1989).

Lac Pin Blanc

Recorded pH depressions in the stream which were stimulated by snowmelt or rain-on-snow were typically from pH 5.7 to 5.3. The duration of recorded episodes was ~3 weeks. Total reactive aluminum concentrations (the sum of organic, monomeric, complexed and polymeric Al) increased from 125 to 180 μg L^{-1} during the first recorded snowmelt event (Hendershot *et al.*, 1984). After the first event, total reactive Al concentrations declined to 90 μg L^{-1} as the Al-poor event water passed into the stream (Jeffries and Hendershot, 1989).

4. Episodic Acidification in Nova Scotia

Studies of episodic acidification in Nova Scotia have been conducted in or near to Kejimujik National Park (Freedman and Clair, 1987; Kerekes and Freedman, 1989; Howell, 1989), as shown in Figure 1. Waters in this region are typically oligotrophic and are tea-coloured due to leachate from peaty, poorly drained soils (Kerekes and Freedman, 1989). Discharge is low during the summer months, because of evapotranspiration, and the composition of groundwater has a great influence on the composition of river waters. Rainfall and frequent snowmelt events leads to higher discharge during the winter months (Freedman and Clair, 1987). Fishkill has been reported following autumnal rainstorms (Lacroix and Townsend, 1987). Interest has focused on the relative extent to which organic and anthropogenically derived strong acids contribute to acidification in the region.

4.1. MERSEY RIVER

The Mersey River has a drainage area of 295 km^2 (Howell, 1989). The river waters exhibit an inverse association between discharge and pH, although peak acidity does not necessarily coincide with peak discharge. The duration of pH depression is longer than in other Canadian catchments (~50 days). DOC is srongly correlated with pH. However, organic anions are not the major contributors to free acidity during episodes, which is more likely controlled by sulphate (Freedman and Clair, 1987; Kerekes *et al.*, 1986a, b; Howell, 1989).

High concentrations of DOC, Na^+, Mg^{2+}, Ca^{2+}, Cl^-, and Al coincide with high flow during the late fall only, and are attributed to the leaching of solutes from terrestrial ecosystems, where they accumulate over the summer (Freedman and Clair. 1987). The Al is primarily associated with organic complexes and is non labile (Clair and Freedman, 1986). During the winter, a relatively high water table or frozen soil allows relatively little contact between water and rock, and there is little opportunity for weathering reactions to neutralise inputs of mineral acidity and for adsorption of organic acids in the mineral soil (Howell, 1989; Lam *et al.*, 1989).

The depression of pH is typically from 6.2 to 4.5. Figure 6 demonstrates a high sampling intensity over several years, and it can be seen that peak depressions may be as large as from 7.0 to 3.8. Values as low as 3.2 have been recorded. Minimum pH are typically recorded around the New Year, and coincide with flow routing through the upper soil horizons. Episodes result from a combination of increase in strong acid anions (principally sulphate) and base cation dilution (Howell, 1989).

Sulphate in the Mersey is largely derived from anthropogenic sources and sea salt. Isotopic evidence shows that there are few internal sources of sulphur in the basin (Clair *et al.*, 1989). Approximately 75% of the sulphur input is by wet deposition, with the remainder from dry deposition (Howell, 1989). There is evidence for storage of sulphur by the watershed during May through November, while there is net export of sulphur during the remainder of the year (Howell, 1989). Since sulphate is the major anion associated with free acidity during episodes, the internal cycling of sulphur within the watershed is clearly of importance to the magnitude of episodes. As at Moose Pit Brook (see below), uptake of sulphur into organic compounds or adsorption of sulphate by organic compounds may be important mechanisms in the internal sulphur cycling by watersheds.

4.2. MOOSE PIT BROOK

Moose Pit Brook exhibits maxima in DOC and base cations during late summer and early fall rainstorms. As in the Mersey River, sulphate concentrations peak during December through February, and are low during the summer months. Hence, sulphate and DOC concentrations are inversely associated throughout the season (Howell, 1989). Suphate is associated with free acidity during episodes in the winter and spring, when increase in strong acid anions and dilution of base cations are of similar magnitude (~40 μeq L^{-1}).

4.3. OTHER WATERSHEDS

An outline of water chemistry in other watersheds of the Kejimujik National Park may be found in Kerekes and Freedman (1989). From these data, it appears that base cation dilution and increase in strong acid anions cause episodes in winter

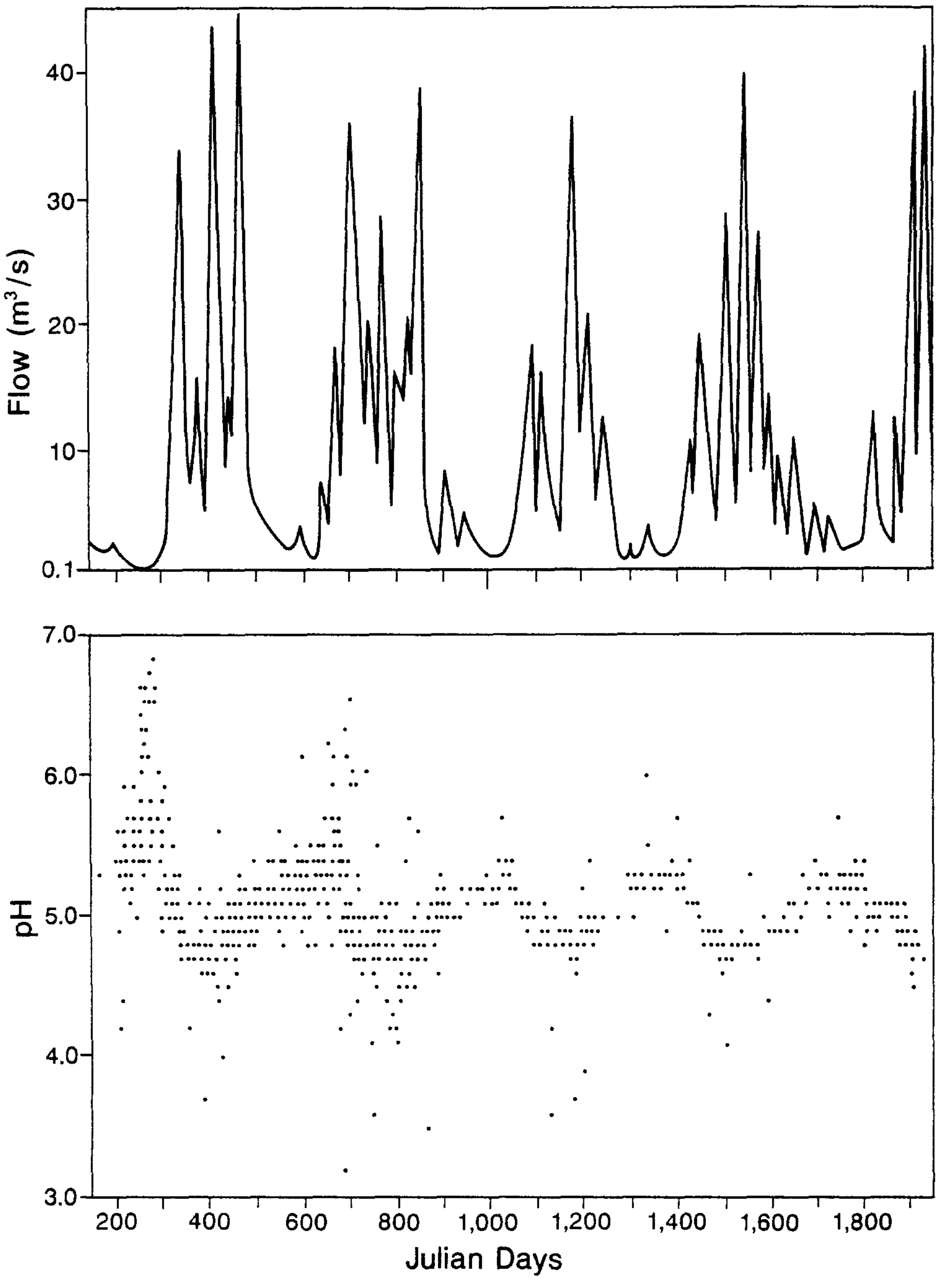

Fig. 6. The relationship between pH and discharge for the Mersey River, from June 1, 1980 to April 30, 1985 (from Freedman and Clair, 1987).

and spring. The features in the seasonal chemistry of these other watersheds are similar to those of the Mersey River. Further data on episode chemistry can be found in Lacroix and Townsend (1987).

5. The Influence of the Composition of Lake Snowcover and Ice on Episode Chemistry

Lakes in the Canadian Arctic are usually underlain by permafrost, and hence receive little groundwater input. Episodes in these lakes are influences by the physical and chemical charateristics of the snow and ice cover (Welch and Legault, 1986). Lake ice has a layered character, and up to three layers may be present, black ice, white ice and snowcover (Adams and Alan, 1987). Basal black ice is formed during the initial freezing of the lake surface, and is dilute, because of ion exclusion. A solute-rich water layer may accumulate beneath the black ice. The first formed black ice is often covered by snow and slush. Differential loading may lead to the formation of cracks in the black ice and solute enriched water may then rise through the cracks and mix with the snowcover to give rise to the second or white ice layer. Unlike the case of black ice, there is little loss of solute during white ice formation, yet the first-formed white ice is depleted in solute relative to the remaining slush (Adams and Allan, 1987).

The relative thickness of the layers varies by region. Generally, there is thick black ice and relatively little snowcover in the Canadian High Arctic and the Prairies, slushing via cracks in black ice and white ice formation dominate the lake snow and ice cover in the subarctic regions of northern Quebec and Labrador, and slushing due to terrestrial runoff, rainfall or snowmelt dominates white ice formation in more temperate southern Ontario and Quebec (Adams and Allan, 1987). In general, episodes triggered by the melting of black ice are likely to be dilution dominated, whereas acidic episodes may be generated by the melting of white ice, snowcover or the drainage of slush waters into the lake, that will show greater influence of increase in strong acid anions.

An example of an unsusual episode has been reported from Colour Lake (Adams and Allan, 1987), which is located on Axel Heilberg Island (79°N). The lake is at least 25 m deep, amd is unusual because it is both hard (125 mg L^{-1} CaCO3; conductivity, 800 μS cm^{-1}) and acidic (pH 3.6). The hardness derives from the dissolution of evaporitic gypsum, and the acidity is derived from the oxidation of pyrite in sorrounding shales. There is little opportunity for weathering reactions to consume the acidity of the lake water, and the formation of relatively pure ice during the winter further concentrates solute within the lake and decreases lake pH (Schindler *et al.*, 1974). 'Episodes' in Colour Lake are 'dilution' events, but the pH increases because the event water is depleted in solute and acidity with respect to the lake water. Where cracking occurs, and water drains into lake from the overlying snow and ice cover, conductivity values may decrease from ~720 to 120 μS cm^{-1} for between 1–3 days. Waters down to 5.5 m may be affected.

After the drainage event ceases, the influence of the dilute water is normally restricted to the upper 1 m of the lake. Inspection of data in Adams and Allan (1987) suggests that pH might increase from ~3.6 to ~5.0 or 6.0 during an 'episode'.

The lake ice cover may prevent terrestrial runoff from entering the lake. Instead, marginal moats may form on top of the ice. The moats may be envisaged as channels incised into the lake ice, running around the lake perimeter (Adams and Allan, 1987). In Colour Lake, the transit time for terrestrial runoff around the marginal moat is of the order of 6 hours, after which the waters enter the outflow. The composition of the terrestrial runoff varies widely, from pH 3.9–6.3. During the Spring thaw, the outflow pH may increase from 4.6 to 6.0, and may remain elevated for 12 days. When the marginal ice has melted and retreated from the shore, terrestrial runoff may enter the lake directly. Then, the less dense, less acidic and dilute runoff may displace lake water along the margins for some 7 m from shore. Elsewhere, a layer some 0.5–1 m deep forms along the surface. Conductivity decreases at this time from ~700 to ~50 μS cm^{-1}. Hence, both the physical and chemical properties of lake snow and ice cover may influence the type of episode observed in such systems.

6. Discussion

Studies in southeastern Canada reveal that many headwater lakes, low order streams and rivers exhibit episodic acidification. Most attention has been focused on the spring snowmelt season when the lowest annual pH may be recorded (Jeffries, 1990a, b). However, rainfall stimulated episodes are also likely to occur in many locales (see data in Papineau, 1987, and Dillon and Molot, 1989).

In low order streams, episodes stimulated by snowmelt may give rise to maximum pH depressions of between 0.4 to 2.6 units, and maximum depression of alkalinity of 100 to 200 μeq L^{-1} (see Tables I and II). Minimum recorded pH values are 3.8 at Lac Laflamme (Papineau, 1987) and 3.2 at Keyimkujik (Freedman and Clair, 1987), although the more typical range of minimum recorded pH is 5.3 to 4.1 (see Tables I and II). Higher order streams typically exhibit episodes which have higher pH and alkalinity then contemporaneous episodes in lower order streams (Bottomley *et al.*, 1986).

Lakes exhibit episodes which vary in magnitude throughout the systems (see Figures 2, 3 and 4). Episodes are most pronounced in surface waters, typically to a depth of 1 to 2 m (Jeffries and Semkin, 1983; Jones *et al.*, 1984; Gun and Keller. 1984), and close to freshwater inlets (Gunn and Keller, 1984). It is of some concern that interstitial waters in near-shore sediments may also become acidified during snowmelt, since such sediments may be the spawning ground of various species of fish (Gunn and Keller, 1984).

The mechanisms of episodic acidification in southeastern Canada are generally similar across the study catchments. Base cation dilution episodes dominate in circumneutral systems, and increase in strong acid anions dominates in acidic systems (Molot *et al.*, 1989). Episodes dominated by an increase in organic acids have not been reported in Canadian studies (LaZerte and Dillon, 1984), but an increase in organic acids may augment other factors, principally an increase in sulphate (Molot *et al.*, 1989; Dillon and Molot, 1989). Similarly, sea salt stimulated episodes have not been reported, but may occur in coastal catchments with organic soils in Nova Scotia, where studies that focus on episode chemistry are limited. Nitrification related and nitrate dominated episodes are not well documented. In general, elevated nitrate concentrations occur only during the early stages of snowmelt (LaZerte and Dillon, 1984; Papineau, 1987; Dillon and Molot, 1989), and it is unclear whether the source of nitrate is snowmelt or nitrification (Jeffries, 1990 b). Studies in the boreal forest of Quebec show that organic layers in the upper soil may act as both a net source or a net sink of nitrate during snowmelt (Jones and Bedard, 1987).

The major mechanism of episodic acidification in acidic systems is an increase in strong acid anions (Molot *et al.*, 1989), principally sulphate. Biogeochemical reactions may accumulate and release sulphur from reservoirs within the soil (Jones and Bedard, 1987). Since soils in southeastern Canada are not themselves the ultimate source of the sulphur, it can be assumed that most is ultimately derived from the atmospheric deposition of anthropogenic emissions (Jeffries, 1990a; Clair *et al.*, 1989). Even though base cation dilution is the dominant mechanism of episodic loss of alkalinity in circumneutral systems, there is sill an influence of atmospherically derived sulphur, which results in alkalinity and pH reaching lower levels during episodes than would occur if the sulphur were not present (Wigington *et al.*, 1990). Similar conclusions were reached by Galloway *et al.* (1987), in a study of the episodic acidification of lake water in the Adirondacks, that have similar terrain, deposition characteristics and climate to SE Canada.

Most studies demonstrate that event water comes into contact with the soil or regolith, and studies at TLW demonstrate that pre-event water, rather than event water, is the dominant component of discharge during episodes (Bottomley *et al.*, 1984. 1986). Hence, the flowpaths which operate during episodes are important controls on the chemistry of episodes (Jeffries and Hendershot, 1989). Direct input of event water may dominate during snowmelt under three scenarios. Firstly, ice may inhibit infiltration when an impermeable ice layer seals the base of the snowpack or the soil (Prince and Hendrie, 1983), and when ice channels within the snowpack (English *et al.*, 1986; 1987) may deliver water directly into the water course (LaZerte and Dillon, 1984). Secondly, overland flow occurs when the rate of snowmelt, which may be enhanced by rain-on-snow, delivered to soil is greater than the rate of infiltration (Stottlemyer and Toczydlowski, 1990). Rain-on-snow may also enhance the chemical composition of snowmelt (Semkins and Jeffries, 1986, 1988). Finally, input of snowmelt from snowcover on ice-covered lakes may make a significant contribution to the hydrogen ion budget during snowmelt (Adams and Allan, 1987). The influence of lake ice and snowcover is largely undocumented in studies of lacustrine episodes, but is clearly of importance to the chemistry of episodes in Arctic lakes (Adams and Allan, 1987).

Chemical reactions within the soil and regolith are likely to modify the composition of infiltrating water (Jeffries, 1990b). Weathering reactions, which operate on relatively long timescales, increase both the pH and alkalinity of waters and operate in the deeper mineral soil and aquifer (Craig and Johnson, 1988a, b; Papineau, 1987). By contrast, reactions in the upper soil may promote low pH and alkalinity, but these reactions are only understood in a rather qualitative way. Organic matter in particular may buffer throughflow to $\mathrm{pH} < 5$ (Roberge and Plandamon, 1987), and following dry periods, washout of oxidised sulphur compounds by rainstorms may result in event water or return flow becoming more acidic (Seip *et al.*, 1985). Nitrification reactions acidify throughflow in northeastern American catchments (Galloway *et al.*, 1987), but the importance of these reactions has not been unequivocally demonstrated in Canadian episodes to date, other than at Lac Laflamme (Jones and Bedard, 1987).

7. Conclusions

Episodic acidification accurs in streams, shallow groundwaters, lakes and the interstitial waters of lacustrine sediments in southeastern Canada, the location of most of the Canadian studies published in the mainstream scientific literature. Studies have concentrated on snowmelt stimulated episodes, where the dominant strong acid anion is sulphate. Base cation dilution is the dominant mechanism of episodic loss of alkalinity in circumneutral systems, but it is important to remember that the minimum recorded levels of alkalinity and pH are still influenced by atmospheric deposition of sulphur. In acidic systems, the increase in strong acid anions, principally sulphate which is ultimately derived from atmospheric deposition of fossil fuel sulphur, is the dominant mechanism of episodic loss of alkalinity. This increase in sulphate may be augmented by an increase in organic acids and nitrate. The influence of nitrate is largely confined to the early stages of snowmelt, and it is not usually clear whether the nitrate is derived from nitrification or direct inputs. Canadian studies clearly demonstrate the importance of shallow, hydrological flowpaths in governing the composition of episode water.

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