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by

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New Hampshire Water Resource Research Center
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The cover photo shows the main inlet to Cone Pond, New Hampshire. This stream drains one of six watersheds discussed in this report.

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ABSTRACT

Watershed history and geochemistry, and pond response to snowmelt were studied at six remote ponds in the White Mountains of New Hampshire. Changes in pond chemistry have resulted from watershed disturbances, particularly forest fires and beaver activities. These factors need to be considered in any evaluation of pond susceptibility to acidification. The relationships of pond chemistry to the hydrology and geochemistry of their watersheds were studied at Black and Cone Ponds. Deeper soils and more weatherable minerals in the watershed produced longer flow paths, higher pH, more basic cations, higher alkalinity, and lower SO_4^{2-} in the inlet stream of Black Pond. In contrast, the watershed at Cone Pond contained shallower soils with minerals more resistant to weathering, producing shorter flow paths, lower pH, fewer basic cations, no alkalinity, and higher SO_4^{2-} in the inlet stream. Acidic Cone Pond was intensively sampled in late winter to follow changes in water chemistry that resulted from "acid pulses" during snowmelt. During thaws the mass of H^+ in the pond increased but large changes were not permanent and were confined to surface waters. Under conditions of winter stratification the bottom 2 m became much less acidic because of anoxic SO_4^{2-} reduction. Characterization of acid buffering capacity of a pond should be based on detailed knowledge of watershed disturbances, hydrology, mineralogy, and pond chemistry.

INTRODUCTION

The studies presented in this report were stimulated by previous research which detailed the susceptibility of six ponds in the White Mountains of New Hampshire to acidification (Buso et al., 1984). Although these similar ponds and their watersheds are located within a 20-km radius and presumably receive the same acidic deposition, their water chemistries are quite different. For example, the ponds ranged in volume-weighted pH from 4.5 to 6.4, and there were differences in the degree of stratification, tendencies for anoxia, and concentrations of specific elements. Our objectives were to determine what watershed processes made these ponds different, and how such differences might affect their susceptibility to acidic deposition.

Three factors operating within watersheds that may affect pond acidification are examined in this report. These three projects are described and discussed separately. The first is an assessment of how past watershed disturbances affect pond chemistries today. Such disturbances are difficult to quantify, but watershed histories provide valuable clues about susceptibility to acidification. While all six ponds are remote and are located in the White Mountain National Forest, their protected status is relatively recent, and substantial disturbances have occurred.

The second factor was how differences in watershed hydrology, mineralogy, and geology affect stream and pond chemistry. We chose Black and Cone ponds, the two ponds with the most contrasting pH and alkalinity, for intensive geochemical studies. We sampled several sites along the major inlet streams to these ponds to relate stream chemistry to soils, bedrock, geology, mineralogy, and hydrologic characteristics.

The third factor was whether the influx of acidity that comes during the final spring snowmelt created a permanent increase in pond acidity. We intensively sampled acidic Cone Pond throughout late winter and early spring of 1984 to see how thaws affected pond chemistry.

THE IMPACTS OF WATERSHED DISTURBANCES
ON POND ACIDIFICATION

The chemistry of small ponds can be highly responsive to disturbances within the surrounding watershed. Disturbances may be subtle, such as acidic precipitation, or catastrophic, such as forest fires. The suggestion that watershed disturbances may have induced the acidification of lakes and streams in northern New England (Krug and Frink, 1983) has led to lively scientific debate (Johnson et al., 1984).

The objectives of this study were: 1) to compile comprehensive descriptions of the extent, intensity, and duration of both natural and anthropogenic disturbances to six ponds and their watersheds in the White Mountains of New Hampshire, 2) to estimate the importance of these changes in modifying current pond chemistries and their susceptibility to acidification and, 3) to separate the water quality changes induced by changes in land use from those caused by acidic precipitation.

The watersheds studied were those of Black, Black Mountain, Cone, East, Kiah, and Peaked Hill Ponds (Fig. 1). Earlier studies involving the chemical and physical characteristics of these ponds were reported in Buso et al. (1984). All the ponds are <5 ha in size, with watershed areas of <200 ha. Ratios of pond area to watershed area are small, ranging from 2:100 to 7:100. Because these ponds have large catchments relative to their surface areas, they are expected to respond quickly to watershed disturbances (Dingman and Johnson, 1971).

Methods

Disturbances were initially identified on aerial photographs taken for the USDA Soil Conservation Service in 1955, 1970, and 1982, and for the USDA Forest Service in 1942, 1943, 1958, 1959, 1960, 1966, and 1978. Locations of disturbance were then transferred to U.S. Geological Survey 7.5′ series topographic sheets, and areas were determined by dot-grid enumeration (Avery, 1966). The areas were confirmed by field mapping. Eight types of disturbances were recorded during reconnaissance of the watershed boundaries, stream networks, and surficial geology (Table 1).

UPPER PEMIGEWASSET RIVER WATERSHED
WHITE MOUNTAIN NATIONAL FOREST

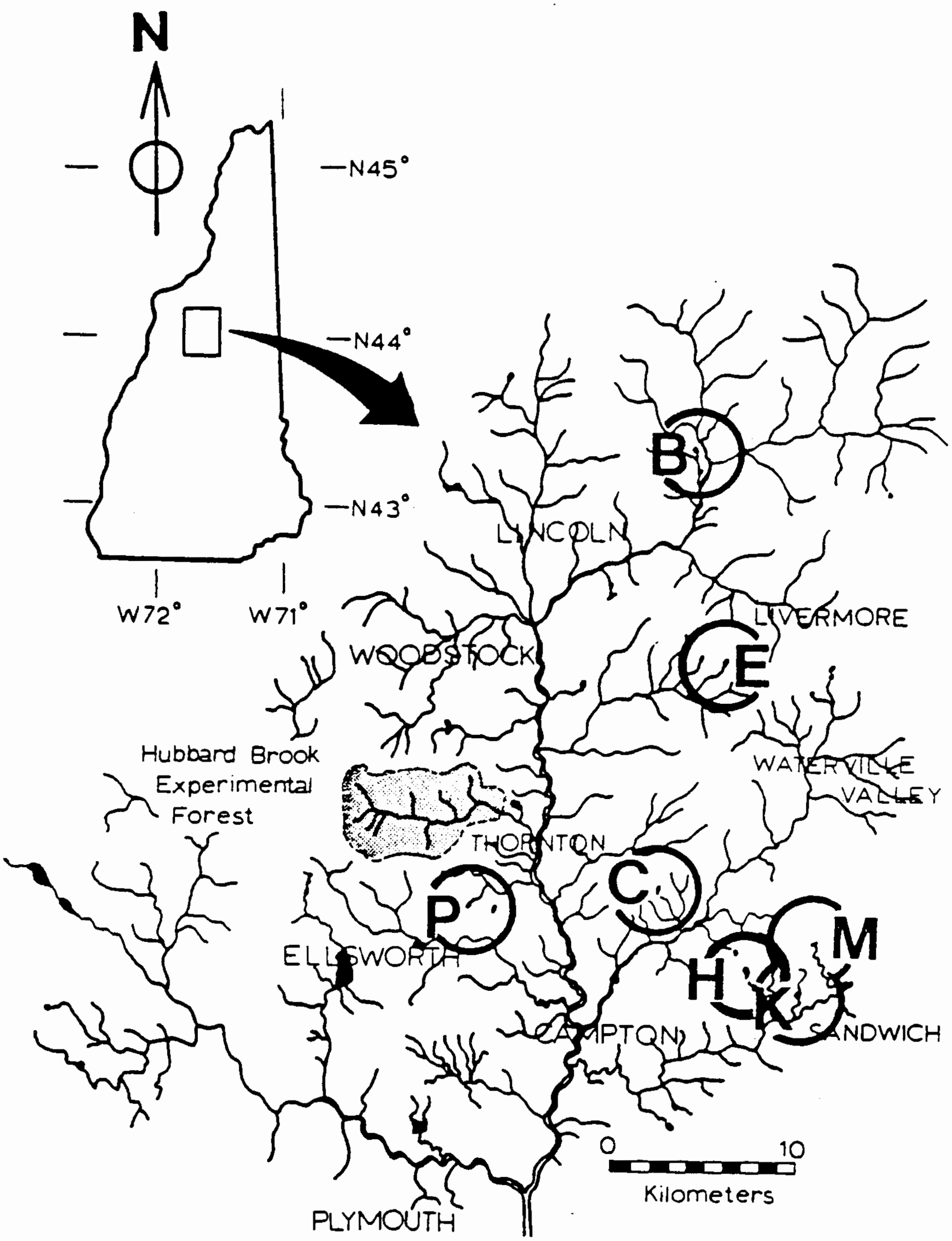


Figure 1. Locations of the study areas: Black (B), Black Mountain (M), Cone (C), East (E), Kiah (K), and Peaked Hill Ponds (P). The main inlet to Upper Hall Pond (H) is included for comparison.

Table 1. Categories and physical evidence of disturbance.

DISTURBANCE	EVIDENCE
Tree Throw	Fallen timber, soil mounds
Fire	Burned stumps, charcoal residue
Landslide	Freshly exposed mineral soil or boulders on steep slopes
Beavers	Dams, lodges, impoundments, fresh cuttings
Logging	Wood piles, cut stumps, roads, landings
Agriculture	Smooth (tilled) soils, rock walls, cellar holes
Dams	Archeological remains
Dredging	Submerged excavations, sediment piles at pond side

Increment cores were taken from trees growing on or near disturbed sites to date the disturbance using either year growth started or date of release. Particular attention was paid to coring open-grown trees or shade intolerant species. Cores were taken from close to the base of the tree, then mounted, sanded, and read through a binocular microscope. Of the 453 cores taken, 60% were from Black Mountain and Cone watersheds because recorded histories of these areas were more obscure.

Documentation of disturbances was obtained from a variety of federal, state, local, and private sources (Table 2). Actual physical evidence of agricultural disturbances was given greater credence than recorded information, because old property boundary lines could not be reliably located.

Table 2. Documentation sources

DISTURBANCE TYPE	LOCATION OF RECORDS
Tree throw, fire, landslide, logging	USDA Forest Service, White Mountain National Forest, Laconia, NH; USDA Forest Service, Pemigewasset and Saco Ranger District Offices; USDA Soil Conservation Service, Grafton County Office; New Hampshire Department of Resource and Economic Development, State Forester's Office.
Beavers	USDI Fish and Wildlife Service, White Mountain National Forest; New Hampshire Fish and Game Department; New Hampshire Water Supply and Pollution Control Commission.
Agriculture, man-made dams, dredging	Town records from Lincoln, Sandwich, Thornton, and Woodstock, NH; deeds registered in Carroll and Grafton Counties, NH; National Census, State Agricultural and Business Censuses from New Hampshire State Library; New Hampshire State Archives; New Hampshire Historical Society; Sandwich Historical Society.

Potential Impacts of Disturbances on Individual Ponds

Our study of disturbances encompasses only the 200-year post-European settlement period. The 8 categories of disturbances (Table 1) were subjectively classified as having: 1) potential impact today, 2) no impact today, 3) not present. Literature on the response of aquatic ecosystems to perturbation was used to justify the first 2 classes.

Potential effects of tree throw, fire, landslide, beavers, logging, agriculture, man-made dams, and dredging are listed in Table 3. The potential for current impacts of these disturbances are discussed for each pond in following sections.

Table 3. Potential impacts of watershed and pond disturbances.
↓ = reduces; ↑ = increases; Δ = changes.

DISTURBANCE TYPE Biogeochemical Effects	POTENTIAL IMPACTS Short-term	 Long-term	AMELIORATING FACTORS	REFERENCES
TREE THROW				
- ↓ forest canopy - ↑ light penetration - ↑ inlet temperature	- Δ mixing and stratification - ↑ algal growth	- Δ forest type - ↑ fuel for fire	- effects depend on extent, location - revegetation eliminates short-term effects	Bormann and Likens, 1979 Karr and Schlosser, 1977
FIRE				
- ↓ vegetation, soils, and nutrients - Δ soil structure and chemistry - ↑ runoff - ↑ inlet temperature	- ↑ productivity, pH, alkalinity, sedimentation - ↑ flushing rate - Δ mixing and stratification	- ↑ sediment depth - Δ sediment chemistry - Δ forest type	- effects depend on extent, intensity - revegetation eliminates short-term effects - morphometry, trophic status, hydrology influence recovery	Chittenden, 1904 McColl and Grigal, 1976 Teidemann et al, 1978 Wells et al, 1979 Wright, 1976
LANDSLIDE				
- ↓ vegetation, soils - ↑ exposed fresh rocks and mineral soil - ↑ inlet temperature	- ↑ sedimentation - ↑ turbidity - Δ productivity - Δ mixing and stratification	- ↑ sediment depth - Δ sediment chemistry - Δ forest type - Δ water pathways	- revegetation eliminates short-term effects - slope stability influences long-term effects	Bormann and Likens, 1979 Flaccus, 1958 Flaccus, 1959
BEAVERS				
- build dams on ponds and inlet streams - ↑ nutrients and humic compounds - ↓ runoff rate - ↑ evaporation - ↑ inlet temperature	- ↑ productivity - ↓ pH - ↑ pond depth - ↑ edge flooding - ↓ flushing rate - Δ mixing and stratification	- ↑ sediment depth - Δ sediment chemistry - Δ forest type - Δ water pathways	- short-term effects important only during habitation	Hodkinson, 1975 Knudsen, 1962 Malben and Foote, 1955 Rupp, 1955

DISTURBANCE TYPE	POTENTIAL IMPACTS		AMELIORATING FACTORS	REFERENCES
Biogeochemical Effects	Short-term	Long-term		
LOGGING				
- ↓ forest vegetation - ↑ nutrient losses - ↑ erosion - Δ soil chemistry - ↑ runoff - ↑ inlet temperature	- ↑ productivity, pH, alkalinity, sedimentation - ↑ flushing rate - Δ mixing and stratification	- ↑ sediment depth - Δ sediment chemistry - Δ forest type - ↑ fuel for fire	- effects depend on cutting intensity, extent, methods, site character - revegetation eliminates short-term effects	Anderson et al, 1976 Bormann et al, 1974 Martin et al, 1981 Patric, 1978
AGRICULTURE				
- ↓ forest vegetation - ↑ nutrient losses - ↑ erosion - Δ soil chemistry - ↑ runoff - ↑ inlet temperature	- ↑ productivity, pH, alkalinity, sedimentation - ↑ flushing rate - Δ mixing and stratification	- ↑ sediment depth - Δ sediment chemistry - Δ forest type	- effects depend on location of farm - revegetation eliminates short-term effects - morphometry, trophic status, hydrology influence recovery	Anderson et al, 1976 Brugam, 1978 Chittenden, 1904 Karr and Schlosser, 1977 Schindler, 1974 Uttormark et al, 1974
MAN-MADE DAMS				
- Δ natural water level fluctuations - ↑ edge flooding - ↑ nutrients and humic compounds - ↓ runoff rate	- Δ productivity - Δ flushing rate - Δ mixing and stratification	- Δ pond depth - Δ morphometry - Δ mixing and stratification	- effects depend on degree of water level manipulation, hydrology, and sedimentation	Baxter, 1977 Ryder, 1978 Wetzel, 1983
DREDGING				
- ↓ sediment - ↓ benthic organisms - ↑ pond depth - ↑ suspended sediments	- ↑ turbidity - Δ productivity - Δ mixing and stratification	- ↑ pond depth - Δ morphometry - ↑ exposed fresh sediments - ↓ sediment depth	- effects depend on chemistry of sediments	Loar et al, 1980 Morton, 1977 Pierce, 1970

Black Pond

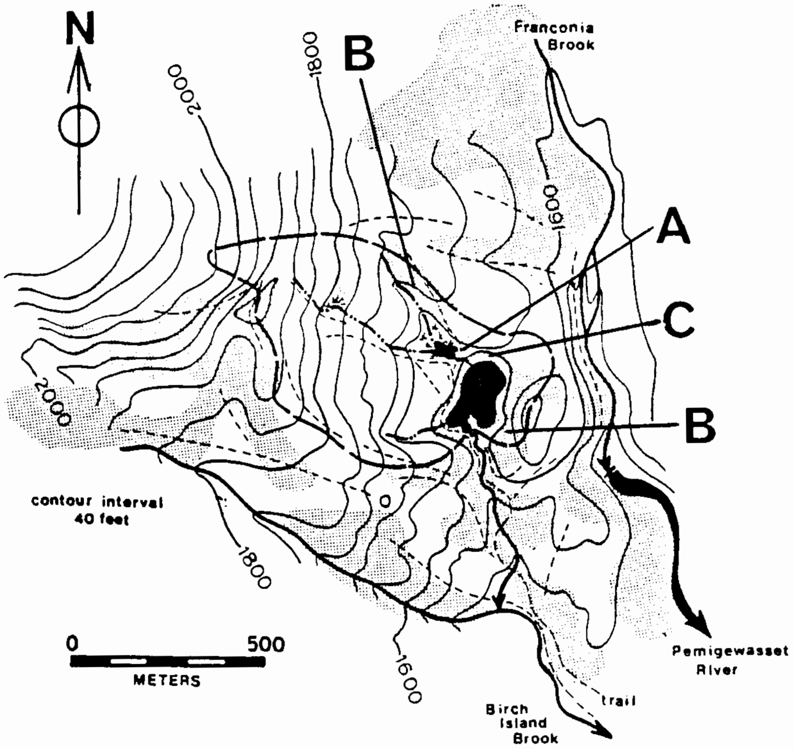
Black Pond is affected by the long-term effects of logging and by beaver activities (Fig. 2). Short term effects of harvesting are no longer present because of adequate revegetation (Table 3). A dramatic change in forest type affected pond chemistry by changing canopy shading, litter decomposition, and the soil chemistry of the watershed. For example, snow melts sooner (Federer et al., 1972), and inlet streams are warmer (Wetzel, 1983) under the present deciduous forest than under the coniferous shade that existed before 1900. Earlier snowmelt decreases opportunities for mixing of acidic runoff with pond water since the pond is more strongly stratified. Similarly, warmer streamwater will mix less deeply into a pond in the ice-free season (see third section of this report). These hydrologic changes may decrease the susceptibility of Black Pond to acidic deposition.

Biogeochemical cycles may be altered by harvest and forest type conversion, but long-term impacts are not fully understood. In general, water from catchments supporting deciduous forests is higher in pH, lower in dissolved organic carbon (DOC), and less colored than from coniferous areas (Wetzel, 1983). At Black Pond, beaver activity may obscure such changes.

Beavers were considered extinct in New Hampshire in 1900, but populations have increased dramatically in recent years due to protection and habitat changes (Silver, 1957). Beavers have a major impact on Black Pond today. The conversion to deciduous forest at Black Pond created more forage and probably encouraged recolonization.

Beaver impoundments on the main inlet at Black Pond have a measurable effect on water quality. After beaver activity started in autumn of 1982, the mean DOC rose from 4.3 mg L^{-1} to 9.2 mg L^{-1}, and K^+ increased from a mean of 10 ueq L^{-1} to 24 ueq L^{-1} (Buso et al., 1984). pH of the inlet stream averaged 6.1 to 6.3 just above the impoundment, then dropped to 5.7 below. Since SO_4^{2-} decreased slightly, the drop in pH probably results from release of organic acids from drowned vegetation and soils.

It is unlikely that beaver activity can strongly acidify Black Pond because the inlet streams are relatively rich in basic cations (Table 4; also Bailey, 1984). However, the charge for organic anions in the pond water, calculated by the methods of Oliver et al. (1983), ranged from 25 to 70 ueq L^{-1}, or up to 92% of the SO_4^{2-} charge. Thus organic acid produced in part by beaver activities can be as important to Black Pond's total acidity as SO_4^{2-} derived from acidic deposition.



BLACK POND

Fig. 2. Black Pond

- POTENTIAL IMPACT TODAY -

LOGGING: Logging resulted in a radical change in forest type. Only mature conifers were cut in 1900 (Anon., 1955; USDA Forest Service files; Waldo, 1960). Spruce should have comprised 30 to 60% of the forest before cutting (Chittenden, 1904), but the forest today is about 90% even-aged deciduous trees. Cores from conifers (stippled portion) indicate extensive and simultaneous release, which suggests an intensive, widespread harvest.

BEAVERS: A colony has been active since 1951 (Newell, 1972), with one lodge on the pond and several dams on the outlet. Beavers became active on the main inlet (A) in Nov. 1982 (Buso et al., 1984), and have flooded about 0.5 ha since then.

- NO IMPACT TODAY -

TREE THROW: **About 0.5 ha of conifers (B) were blown down in a Dec. 1980 windstorm.**

FIRE: **Charred stumps and scattered charcoal were found along pond perimeter (C). Oldest trees growing on burned residue date to 1850.**

- NOT PRESENT -

No records or physical evidence of landslide, agriculture, man-made dams, or dredging were found.

Table 4. Average inlet water chemistry 1980-1982. All data are from Buso et al. (1984).

POND	n samples	pH	Alkalinity	$(Ca^{2+}+Mg^{2+})$	K^+	SO_4^{2-}	Total Al	DOC
			---------- ueq L^{-1}	------------			--mg L^{-1}--	
Black	13	6.00	36	129	10	92	.11	4.7
Black Mt.	12	4.95	3	64	7	123	.38	2.5
Cone	11	4.45	0	64	1	187	.79	4.5
East								
inlet	6	5.30	19	84	11	88	.33	1.0
spring	8	5.75	24	93	14	75	.19	0.3
Kiah	11	5.75	30	134	6	120	.07	7.2
Peaked Hill	5	5.70	23	138	9	123	.07	5.4

In summary, Black Pond is strongly stratified year-round, low in dissolved oxygen, humic colored, and there is evidence of SO_4^{2-} reduction and alkalinity production in the hypolimnion during prolonged periods of anoxia. Beavers sustain these limnochemical characteristics by raising concentrations of nutrients and organic compounds, which increase littoral productivity and hypolimnetic decomposition, and reduce light penetration to deeper waters (Hodkinson, 1975; Knudsen, 1962; Malben and Foote, 1955; Rupp, 1955). Both tree throw and fire have occurred in the Black Pond watershed, but neither has affected an extensive area or left evidence of intensive damage that would suggest an obvious impact on pond chemistry. Conversion to deciduous cover after extensive logging has probably changed the mixing of stream water inputs since 1900, and encouraged beaver recolonization. Beavers impact current chemistry of Black Pond by contributing to mild acidification from organic acids, and to acid neutralization through increased hypolimnetic decomposition.

Black Mountain Pond

Fire, landslide, and beavers have a potential impact on Black Mountain Pond today (Fig. 3). The short-term effects of landslide and fire disappeared with revegetation of the lower portion of the catchment (Table 3). However, fire at Black Mountain may have reduced the acid neutralizing capacity of the watershed.

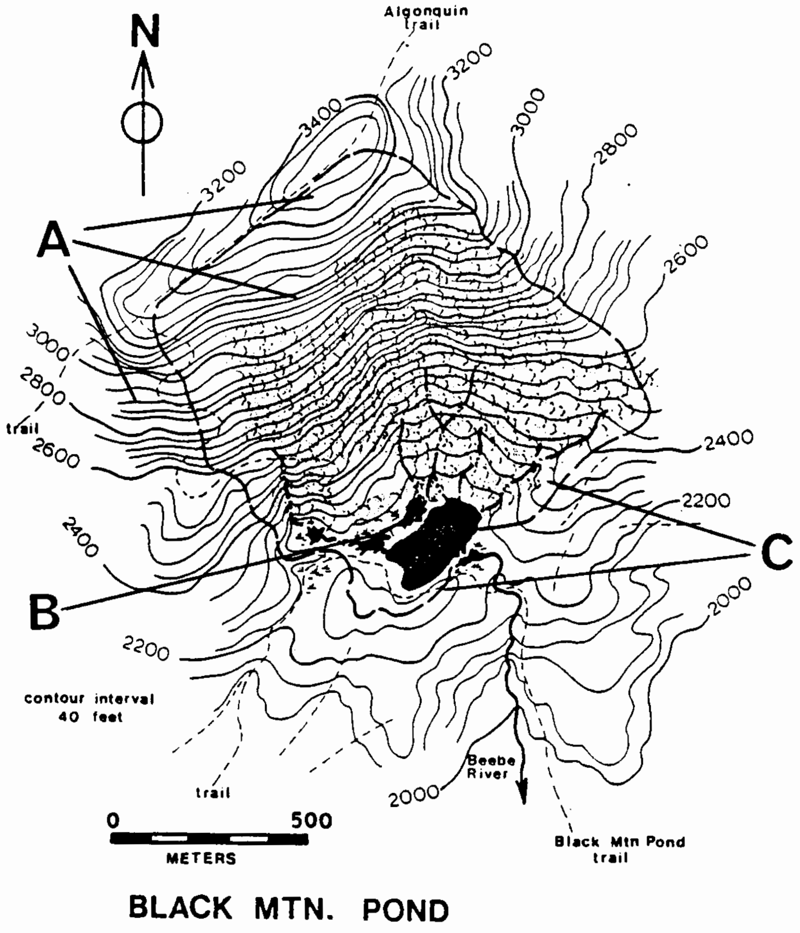


Fig. 3. Black Mountain Pond

- POTENTIAL IMPACT TODAY -

FIRE: Charcoal fragments are mixed with mineral soil throughout the catchment, and about 25% of the watershed is barren ledge (A). This indicates a widespread and intensive burn with subsequent erosion. The oldest trees growing on charcoal date to 1830.

LANDSLIDE: Unstable soils cover about 40% of the catchment. Evidence of this includes fresh boulder trains, lack of an organic soil horizon, and a predominance of 60 to 150 year-old, open-grown paper birch (stippled portion). These conditions may be a result of both fire and the steepness (mean slope 45%). Adjacent forests at this elevation have also been burned, but are mainly coniferous (USDA Forest Service files), which suggests that landslide or soil creep are continuing to influence forest cover today.

BEAVERS: Beavers spread from the pond in 1942 to impound all of the inlet streams by 1982 (USDA aerial photography). There are 4 beaver lodges, many small dams, and 3 actively maintained pools (total area 1 ha) upstream of the pond (B).

- NO IMPACT TODAY -

LOGGING: Logging was limited to < 5% of the watershed, based on dates of tree release and growth initiation, and on location of rotting cordwood piles. Harvest occurred along the south perimeter (C) between 1917 and 1924, and consisted of selective cutting of conifers for pulpwood (USDA Forest Service files).

- NOT PRESENT -

There was no evidence of significant tree throw. No records of agriculture, man-made dams or dredging were found.

Because of the fire, there are large areas of open ledge. The bedrock is relatively resistant to weathering, and soils, where present, are shallow. After intensive fires, significant Ca and Mg can be permanently leached away (Stark, 1977), and combusted soil particles can be physically altered to an inert condition (Wells et al., 1979). Inlet streams have low alkalinity, pH, and basic cations, with high SO_4^{2-} and Al (Table 4). This reflects the effects of shallow soils, unreactive bedrock, and acidic deposition.

With so little buffering in the watershed, the pond would be expected to have an acute susceptibility to acidification. However, some long-term effects of landslides in the watershed may be contributing to reduced susceptibility. First, analyses of stream chemistry suggest that accumulations of rubble and mineral debris from continuous debris slides may lengthen soil water pathways and add basic cations. Also, the open nature of the birch forest allows the snow pack to melt early in the spring. When snowmelt occurs early, the runoff will flush across a stratified pond without mixing (see third section of this report). This by-passing of acidic inputs during high flow periods could be especially important to the biota of Black Mountain Pond.

Another effect of landslide is that it has created an abundance of deciduous forage which supports a large beaver colony. The beavers directly impact pond chemistry by channelling all incoming streamflow through their impoundments. For example, the inlet averaged 2.5 mg L^{-1} DOC (Table 4), but increased to 8 mg L^{-1} DOC when beavers were constructing an inlet dam. Levels of DOC range from 1 to 3 mg L^{-1} in the pond, so that fluctuations in beaver activity could temporarily influence productivity. Because the inlet is relatively acidic and high in aluminum (Table 4), these inputs of DOC are critical to maintaining the low Al:DOC ratio (<2:5). At low pH (<5.5), aluminum toxicity is less likely if large amounts of DOC are present (Driscoll et al., 1980). The pH of the pond ranges from 5.2 to 6.0, and SO_4^{2-} concentrations are high (90 to 140 ueq L^{-1}), so that when calculated on a charge basis (Oliver et al., 1983), the contribution of DOC to total acidity is <20%.

The beaver impoundments serve 2 additional functions: 1) they trap sediment from the unstable watershed soils, and 2) they allow streamflow to warm before it reaches the pond. At Black Mountain Pond the warming of acidic inlet waters prevents flow from mixing deeper than the epilimnion in the ice-free season.

Logging involved too little of the watershed to have had an impact on Black Mountain Pond. Beaver activity, landslide, and fire have all modified current pond chemistry in a complex and interrelated way. Fire has increased the susceptibility of Black Mountain Pond to acidification, yet landslides and beavers appear to be reducing the vulnerability of the pond to the effects of acidic inputs.

Cone Pond

A fire around 1820, apparently fueled by dead material from tree throw, had a major impact on current chemistry of Cone Pond today (Fig. 4). Normally the effects of tree throw are brief (Table 3), but in this case it provided the dry fuel necessary for sustaining severe fires in this region (Bormann and Likens, 1979).

Short-term effects of the fire on the pond vanished with revegetation, but there have been long-term impacts (Table 3). Fire has reduced the acid buffering capacity of the Cone Pond watershed. There are large areas of exposed bedrock and remaining soils are shallow. The minerals of the bedrock, glacial deposits, and soils are relatively inert (see second section of this report), and because of large areas of bare rock, there is less tree canopy to neutralize precipitation (Vasudevan and Clesceri, 1982). As a result, the inlet stream chemistry is dominated by acidic deposition (Table 4). The inlet waters have no bicarbonate alkalinity, low pH, few basic cations, and SO_4^{2-} is high. Inlet Al is also high, and unlike most low-order watersheds (Johnson et al., 1981), increases in concentration as the stream flows downslope to the pond. Precipitated aluminum hydroxides, probably concentrated initially by the fire at higher soil pH (Smith, 1970), may be undergoing mobilization as soils become more acidic (van Breeman et al., 1984).

There are other long-term effects of the fire that currently affect Cone Pond. After the initial birch-aspen growth declined, conifers colonized the burned area (USDA Forest Service files). Because of its "scrubby quality" litle effort was made to log the forest (USDA Forest Service files). Today, the dense, year-round foliage along the inlet causes stream temperatures to be lower than pond temperatures, so that acidic inlet water can mix deeper into the pond in the ice-free season. Although the snow on the open ledges melts earlier, much of the shaded snow pack remains later in this watershed than in adjoining deciduous forests. As a result, Cone Pond may receive acidic snowmelt later in the spring, possibly during turnover.

The current acidity of Cone Pond (pH 4.6 - 4.8) appears to be the result of acidic deposition, exacerbated by the inert mineralogy and disturbance history of the watershed. Cone Pond may have been below pH 5 for the past several thousand years (Ford, 1984), possibly due to the lack of acid neutralizing minerals in the watershed. An increase in inlet alkalinity could have occurred following the fire (Table 3), but the regrowing forest would have eventually decreased alkalinity by assimilating basic cations and releasing organic acids (van Breeman et al., 1984). However, atmospheric inputs, not organic acids, are the major factors in the pond's acidity today. The average inlet stream DOC is 4.7 mg L^{-1} (Table 4). Because of the high SO_4^{2-} and low pH in the pond, a calculated five-fold increase in DOC (Oliver et al., 1983) would be needed for organic acids to equal the strong mineral acids added to the pond by the inlet.

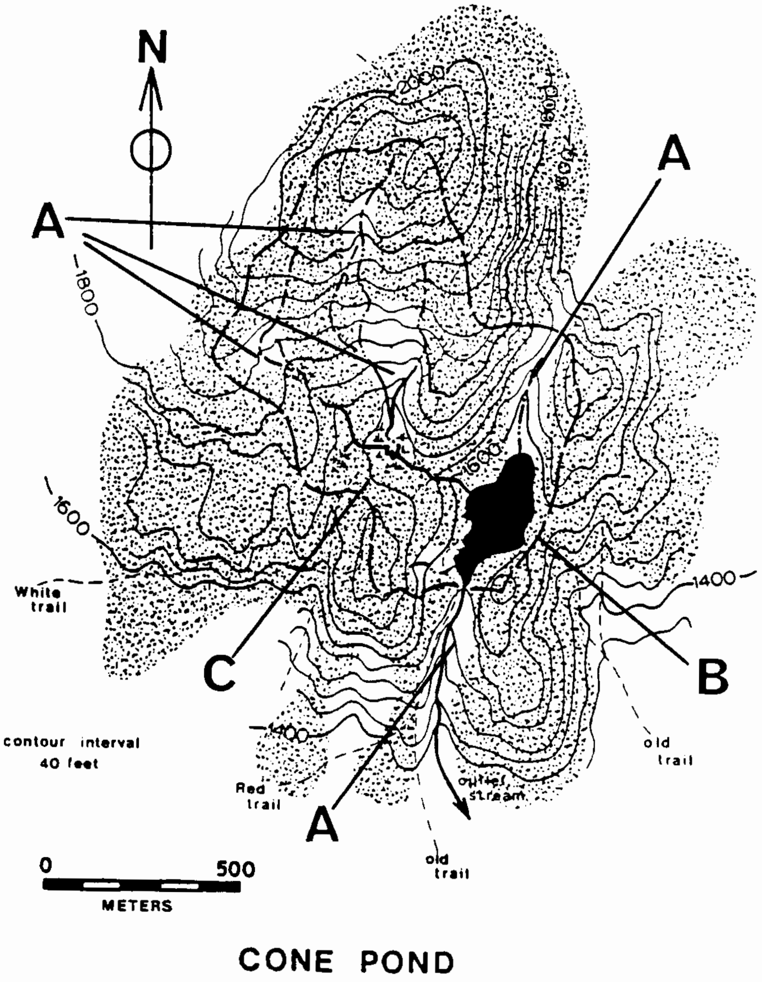


Fig. 4. Cone Pond

- POTENTIAL IMPACT TODAY -

TREE THROW: Cores from spruce and deciduous trees > 165 years old in unburned sections of the watershed show release or initiation about 1815. The correlation in growth ring patterns in scattered groups of trees (A) suggests that disturbance was extensive, but property records show that pre-1815 land clearing did not include the watershed (Town of Thornton records). The forest damage may have been caused by a hurricane that struck inland New England in 1815 (Ludlum, 1963).

FIRE: A widespread and severe fire followed the tree throw. The oldest trees growing on charcoal date to 1820. Charcoal was found over 90% of the basin (stippled portion), under organic soil horizons, mixed into the top layers of mineral soil, and lodged in rock crevices. Exposed bedrock ledge constitutes 15 to 20% of the watershed.

- NO IMPACT TODAY -

BEAVERS: Beavers dammed the outlet between 1958 and 1960 (USDA aerial photography), increasing the pond depth by 0.5 to 1.0 m and surface area by 10 to 20%. No active beaver colony exists today. The 2 lodges and the outlet dam are in disrepair, and the pond surface is back to 1958 levels.

LOGGING: Tree cores, records, and cordwood piles indicate that conifers were cut from < 10% of the watershed during 2 periods: 1890-1910 (B), and 1933 (C) (Grafton County Registrar of Deeds; USDA Forest Service files).

- NOT PRESENT -

No evidence was found of landslide, agriculture, man-made dams, or dredging.

Disturbance history may explain why a yellow perch population existed until removed in 1964 (New Hampshire Fish and Game Department files). An active beaver colony (Fig. 4) could have raised the DOC levels enough to chelate all toxic aluminum. Today, the beaver colony is gone, and the Al:DOC ratios can be as high as 2:1. At current pH's this ratio is probably too high for fish survival.

At Cone Pond, small areas of logging and a beaver colony in the past have had no obvious impact on current pond chemistry. The susceptibility of Cone Pond to acidification was enhanced by fire in the early 1800's, but the present acidity of the pond is not related to organic acids produced during forest aggradation. It is more likely the result of acidic deposition in conjuction with lack of acid buffering in the watershed.

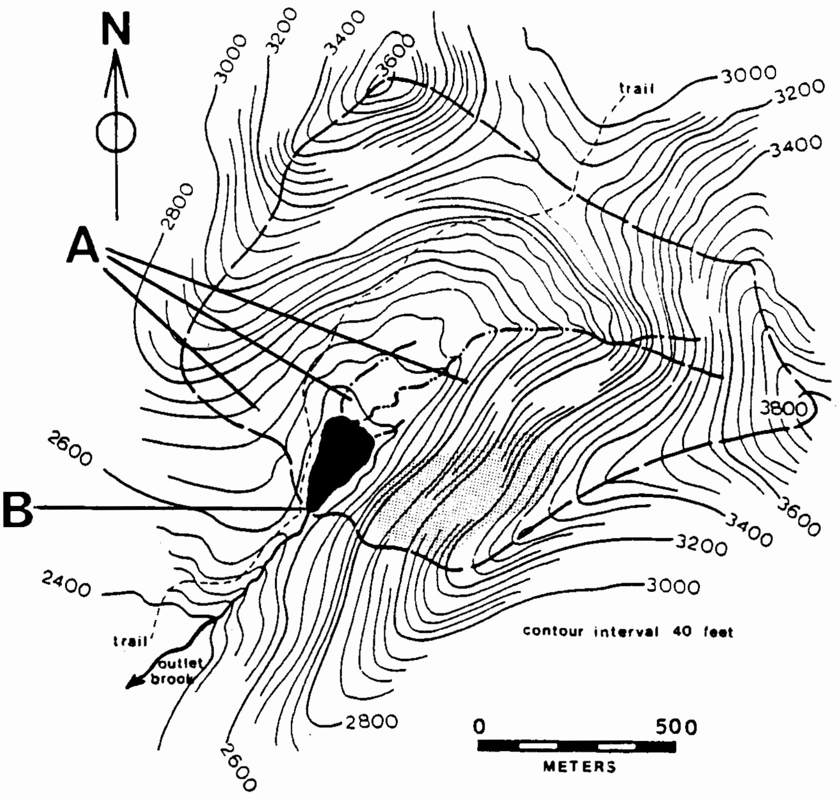
East Pond

Several disturbances have occurred in the East Pond watershed (Fig. 5). Small burned areas have revegetated and should not be important today (Table 3). Logging was substantial, but regrowth has eliminated any obvious short-term effects. The cutting created no long-term changes in forest type (Chittenden, 1904; USDA Forest Service files), but the current windthrow of balsam fir has promoted the growth of mountain maple, striped maple, yellow birch, and paper birch. These species may encourage beaver recolonization which represents a potentially important future impact on pond chemistry.

The short-term effects of extensive dredging and man-made dams (Table 3) at East Pond are no longer a factor in pond chemistry. The water is colorless, and sediments are covered with aquatic vegetation. The excavated material consisted primarily of hydrated silica, and "amorphous ooze" (McNair, 1941), which are non-toxic and relatively unreactive once allowed to settle from suspension (Loar et al., 1980; Morton, 1977; Schroeder, 1970). Dredging and dams altered the pond physically, but do not appear to have caused any permanent chemical changes.

At East Pond, the streams in the upper watershed are dominated by shallow subsurface flows (Table 4). With the exception of high run-off periods, this streamwater infiltrates gravel deposits around the pond, then enters the pond as springflow. In the process, Al and DOC decrease, alkalinity and pH increase, and seasonal variability in pond chemistry is dampened. Thus groundwater hydrology controls pond chemistry.

None of the past distrubances (logging, fire, beavers, dredging and man-made dams) at East Pond seem to have modified the current susceptibility of the pond to acidic deposition in any obvious way. These perturbations could have had short-term effects, but any inputs would have rapidly flushed out of the pond by continuous mixing and subsurface spring flows.



EAST POND

Fig. 5. East Pond

- POTENTIAL IMPACT TODAY -

No evidence was found of past disturbances that have an impact on East Pond today.

- NO IMPACT TODAY -

FIRE: Spruce and paper birch as old as 170 years comprise a 25-ha area east of the pond (stippled portion). Cores of trees, and charcoal fragments in the soil imply that a burn occurred there before 1810.

LOGGING: Conifers were harvested on about 75% of the watershed in 1911 (USDA Forest Service files). Numerous dugway roads and scattered trees with simultaneous release or initiation dates suggest a widespread and intensive cutting.

BEAVERS: Beavers were active from at least 1951 (Newell, 1972) to about 1966 (USDA aerial photography). In 1959, beavers dammed the outlet stream, increasing pond depth by > 1.0 m and surface area by about 30% (USDI Fish and Wildlife Service files). By the mid-1960's, beaver activity had ceased and pool level had receeded (USDA aerial photography).

TREE THROW: Dieback of balsam fir and subsequent windthrow (A) since the 1960's has increased to about 15% of the watershed (USDA aerial photography; USDA Forest Service files).

MAN-MADE DAMS: A concrete, rock, and log dam, with a wooden drain pipe, was built on the outlet about 1912 (B).

DREDGING: Between 1912 and 1915 the Livermore Tripoli Company dredged the pond for diatomaceous earth (NH State Archives; USDA Forest Service files). The pond was drained 2 to 3 m below present pool levels, reducing the surface area by 30 to 40%. After 1916, the outlet conduit clogged, and the pond rose to today's level by 1942 (USDA aerial photography).

- NOT PRESENT -

No evidence of landslide or agriculture was found.

Kiah Pond

Beaver recolonization at Kiah Pond (Fig. 6) and the expansion of their population upstream have had an impact on pond chemistry similar to that described for Black and Black Mountain Ponds. The levels of DOC, K^+, and organic acidity at Kiah seem to be controlled by beaver activities. For example, DOC rose from 1.3 mg L^{-1} above an upstream beaver pool to 6.8 mg L^{-1} below, and pH went from 6.2 above to 5.6 below. In abandoned impoundments at Kiah Pond incoming levels of K^+ decrease, while downstream of new dams, K^+ is released. Total area flooded above Kiah Pond is greater than the pond, and all inlet streams flow through these pools.

Pond chemistry resembles the inlet chemistry (Table 4), except during summer and winter stratification. Then alkalinity in the hypolimnion is much higher than in the epilimnion. The incoming nutrients and DOC provide a mechanism for this internal alkalinity generation by increasing productivity and SO_4^{2-} reduction. This buffering is an important part of Kiah Pond's ability to neutralize acidic deposition. Conversely the heavy DOC loading contributes to mild organic acidification. Based on the average seasonal pond pH (5.4 - 6.2), the calculated organic anion charge (Oliver et al., 1983) varies from 40 to 114 ueq L^{-1}, which is significant relative to the SO_4^{2-} charge (70 - 140 ueq L^{-1}).

At Kiah Pond, no current impacts are likely from fire, agriculture, or logging. Burned areas are too scattered and small to be important. The pond should have recovered quickly from any effects of agriculture and logging (Table 3). Forest type (mixed deciduous-coniferous) has not changed radically over the entire watershed (Chittenden, 1904; USDA Forest Service files). Recent selective cutting has had no obvious impact, except to provide additional beaver forage. Many characteristics of Kiah Pond, including humic coloring, high rates of oxygen consumption, and enriched trophic conditions, can be attributed in part to the impacts of beaver activities.

Peaked Hill Pond

Beavers and a man-made dam are the major influences on the current chemistry of Peaked Hill Pond (Fig. 7). The impacts of beavers are the same as the effects discussed in previous sections. For example, the inlet fork with a beaver swamp has a lower pH and up to twice as much DOC as the undisturbed inlet. Because Peaked Hill Pond is shallow (mean depth 1.7 m), stirred-up sediment and organics from beaver activities in late autumn can lead to oxygen deficits throughout the pond under ice cover. Simultaneously, these conditions allow the build-up of alkalinity derived from anoxic reduction processes. The dystrophic nature of Peaked Hill Pond is due in large part to the effects of beavers.

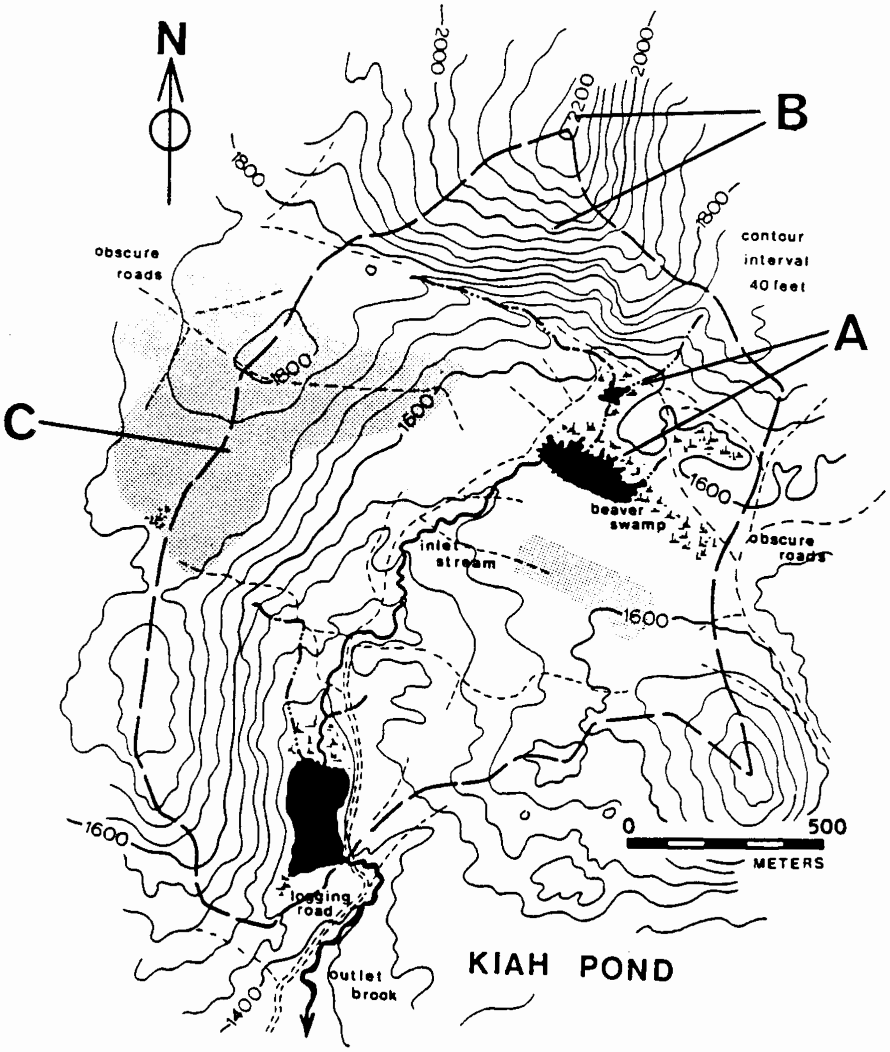


Fig. 6. Kiah Pond

- POTENTIAL IMPACTS TODAY -

BEAVERS: Beavers have maintained a dam on the pond since at least 1951 (Newell, 1972). There are 4 actively used lodges in the catchment. An increase in beaver activity along the main inlet stream started in the 1960's (USDA aerial photography). About 4 ha are now flooded upstream of the pond (A).

- NO IMPACTS TODAY -

FIRE: Small pockets of charcoal are located on remote ledges (B). Oldest trees growing on charcoal date to 1840.

AGRICULTURE: Several subsistence farms existed in the watershed between 1806 and the 1870's, along a road crossing the catchment 1 km upslope of the pond (Carroll County Registrar of Deeds; NH Agricultural Census; Sandwich Historical Society). An estimated 10 to 15% of the watershed was tilled (stippled portion). After farm abandonment, woodland grazing by cattle from adjacent farms kept fields open (C) until at least 1910 (Sandwich Historical Society), when conifers became established.

LOGGING: Cutting was extensive, but intermittant. A sawmill existed 1 km south in the 1820's (Sandwich Historical Society), but cores from trees > 200 years old indicate no disturbance on untilled areas before extensive harvest of conifers between 1916 and 1924 (USDA Forest Service files). Deciduous trees and old-field conifers were selectively cut from the 1940's to the early 1970's (USDA Forest Service files).

- NOT PRESENT -

No evidence of significant tree throw, landslide, man-made dams, or dredging were found.

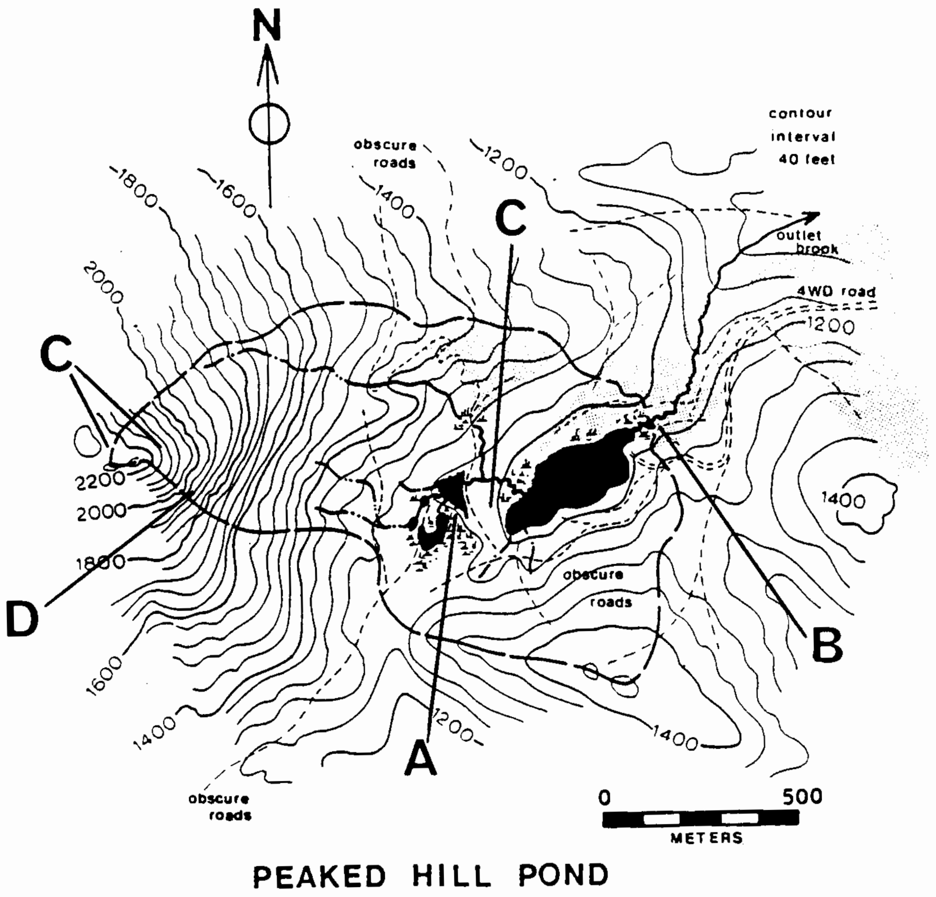


Fig. 7. Peaked Hill Pond

- POTENTIAL IMPACT TODAY -

BEAVERS: Beavers have maintained a dam on the pond since at least 1951 (Newell, 1972). There are 4 active lodges in the watershed. On the west tributary of the inlet (A), beaver activities have gradually increased since the 1950's; the total area flooded today is about 2 ha (USDA aerial photography).

MAN-MADE DAMS: A 2- to 3-m high, earth and cobble dam was built on the outlet (B) in the 1850's to provide power to a nearby sawmill (Grafton County Registrar of Deeds; Walling, 1860). The pond depth apparently was increased by 1 to 2 m, and surface area enlarged by 30 to 100% (Buso et al., 1984).

- NO IMPACT TODAY -

AGRICULTURE: Two subsistence farms existed near the pond between 1840 and the 1870's (Town of Thornton Records; Grafton County Registrar of Deeds; NH Agricultural Census). Tilled areas (stippled portions) are estimated to have been 10% of the catchment. After farm abandonment, cattle grazed along the pond shore until the 1940's (S. Ham and V. Levasseur, pers. comm.).

LOGGING: Cutting was extensive, but intermittant. White pine around the pond were removed in the 1850's (Grafton County Registrar of Deeds); upper slope conifers were cut between 1900 and 1920; old-field conifers and deciduous trees were selectively logged from the 1940's to the 1970's (USDA Forest Service files).

DREDGING: A 1-m deep trench was excavated in the pond in front of the dam about 1850.

TREE THROW: Minor amounts of windthrow occurred during the 1938 hurricane (USDA Forest Service files).

FIRE: Fires prior to 1900 occurred on the mountain and along the pond shore (C); total area < 1 ha.

LANDSLIDE: Boulder fields and unstable soil areas (D) amount to < 1 ha.

A dam constructed in the mid-nineteenth century also has an impact on current trophic conditions at Peaked Hill Pond. Because of the flat shoreline topography, water level manipulations would have led to considerable flooding of the pond perimeter. Substances dissolved from drowned soils and vegetation should have increased productivity in littoral areas (Baxter, 1977; Ryder, 1978; Wetzel, 1983). The pond today has a wide, well developed shoreline plant community.

Fire, landslide, tree throw, and dredging have no impact on current pond chemistry as none of these disturbances were extensive. Agriculture and logging involved much of the watershed, but reforestation has eliminated their short-term effects. Any long-term impacts due to subtle changes in forest type or to deposition of enriched sediments in the pond shallows are not obvious. Logging could have encouraged beaver recolonization.

The man-made dam left the pond slightly deeper, much larger, and more productive. Further enrichment due to beaver activities has resulted in an eutrophic pond with seasonal anoxia. In Peaked Hill Pond substantial alkalinity (>20 ueq L^{-1}) is only present under stratified, anoxic conditions. Thus the two disturbances that have contributed most to its productivity, a man-made dam and beavers, have increased the pond's ability to neutralize inputs from acidic deposition.

Conclusions

1. Disturbances capable of changing pond chemistry are a common occurrence in New Hampshire, even in relatively remote watersheds.

2. These disturbances can affect the response of ponds to acidic deposition. Severe forest fires and beaver activities within the watersheds are two important examples. Fire results in shorter water pathways by removing vegetation, reducing soil depth, and exposing bedrock. Thus, it reduces the long-term acid buffering capacity of burned watersheds. This is of special significance in New Hampshire where poorly buffered areas area already substantial and deposition is acidic. Beaver recolonization has had an important and continuing effect on the remote watersheds of New Hampshire since 1900. Ponds with active beaver colonies are more likely to have aluminum complexed organically, and may have increased acid buffering capacity because of enhanced productivity, even though some mild organic acidification is typical.

WATERSHED FACTORS AFFECTING STREAM AND POND CHEMISTRY

This phase of the study focuses on two ponds, Black and Cone, the extremes in terms of acidity of the six ponds studied by Buso et al. (1984). Cone Pond is widely publicized as one of the most acidic ponds in New England. To understand the chemistry of the inlets of these two ponds, we compared watershed geology, soils, stream hydrology, and stream chemistry along elevational gradients.

The objective of this portion of the study was to relate differences in aquatic chemistry to easily identifiable watershed characteristics, both between watersheds and along elevational gradients. This watershed approach can be used by pond managers to interpret chemical quality of individual ponds. Regional approaches to classifying susceptibility of ponds and lakes to acid deposition (Norton, 1980; Omernik and Powers, 1982) were unsatisfactory for the ponds reported in the Buso et al. (1984) study. If more were known about watershed influences on ponds, then models for classifying susceptibility to acidification could be made more sensitive.

Several recent studies are pertinent to our research. Johnson et al. (1981) studied stream chemistry along an elevational gradient at Falls Brook within Hubbard Brook Experimental Forest in New Hampshire. The study illustrated the relationships between meteoric, pedologic, and geologic origins of stream water solutes and the effect of residence time in the soil channel system on the proportions of each. At Falls Brook, acid components in upper stream reaches were replaced by chemical weathering products in lower reaches, particularly Ca^{2+} and Na^{+}, as path length of water in the soil-channel system increased. Elevational gradients at Black and Cone inlet streams were analyzed to see how these streams related to the Falls Brook model.

Newton and April (1982) showed that water flowing through the watershed of acid Woods Lake was "short circuited" by low permeability aeolian silt in lower soil horizons while water in neutral Panther Lake watershed flowed through deep till deposits. Mineralogy of these watersheds was similar; differences in pond chemistry were attributed to differences in flow paths. In our study we hypothesized that hydrologic flow paths might also be different between Black and Cone watersheds.

Johnson et al. (1981) discussed chemical weathering in terms of neutralizing acidic components. However, the opposite may be true in some watersheds as revealed by Parnell (1983) who documented production of sulfate by weathering of metasedimentary rocks containing small amounts of sulfides. According to Parnell's model, four equivalents of acidity are generated by dissolution of one mole of FeS_2. We initially suspected that weathering of sulfides might account for the high sulfate levels observed at Cone Pond by Buso et al. (1984).

Methods

Stream Sampling

Stream samples were collected at seven points along each inlet stream. In both watersheds, two branches of the inlet were sampled. Samples were collected in 500 ml, acid-washed, polyethylene bottles. During low flows, samples were obtained using a polyethylene syringe to minimize collection of sediment and organic detritus. Sampling was conducted from June 1983 through May 1984. Twelve sets were collected to represent various moisture, weather, and seasonal conditions. Detailed notes were made on stream responses to changing moisture conditions in the watersheds, and on flow levels at each station in order to characterize the hydrology of the streams. Stream gaging was not possible due to budgetary and physical constraints.

pH was determined potentiometrically at room temperature, within hours of collection. Samples were then refrigerated until further analysis. Calcium, Mg^{2+}, Na^+, and K^+ were determined using atomic absorption spectrophotometry. Sulfate and dissolved SiO_2 were determined by automated colorimetric analysis. Bicarbonate alkalinity was determined by potentiometric titration without a fixed end point. Dissolved organic carbon (DOC) was determined by persulfate digestion to CO_2 measured by gas chromatography. All determinations were made using standard methods as described and referenced by Buso et al. (1984).

Soil Sampling

Soils were mapped during this study by the USDA Soil Conservation Service. Using these maps, about 25 sample pits were located in each watershed. Soils were described and samples of Oe, Oa, E, upper B, and lower B horizons were collected. The method of the American Society of Agronomy (Black et al., 1965) was used to determine pH for each sample.

Weathering Contributions

The rocks present in each watershed were determined by field reconnaissance and soil excavations. In an effort to relate rocks present to the stream chemistry, a simple method was devised to show relative differences in chemical weathering. Samples of fresh rock were collected, crushed with a hammer, and sorted with wire sieves. 200 g of fragments that passed a 13 mm mesh but not a 6 mm mesh sieve were rinsed with distilled water to remove dust, then placed with 500 ml of distilled water in a capped, 1 L, acid-washed, polyethylene bottle.

At 2, 6, 13, 20, and 27 days a 2-ml aliquot was removed and analyzed for pH. After 27 days, the solutions were decanted into

500 ml, acid-washed, polyethylene bottles and refrigerated until later analysis.

Sixteen rock specimens from the study watersheds were chosen to represent the variety of rocks present. In addition, three rocks from the watershed of nearby Upper Hall Pond (Fig. 1) were included to test how known sulfidic rocks behave in the experiments. Several checks were used; (1) a control bottle containing only distilled water was maintained and analyzed, (2) the effect of rock fragment size and filtration of samples before analysis was checked, (3) the experiment was duplicated to check for reproducibility, and (4) analyses were duplicated after two months to check the stability of the solutions. These experiments provide a relative measure of the types of chemical weathering undergone by the various rock types. Ion availability in the watersheds is influenced by soil exchange properties, but is ultimately determined by chemical weathering of geologic materials.

Mineral Identification

Standard petrographic thin sections were commercially prepared for eight of the rocks involved in the weathering experiments. The modes of these rocks were estimated, and the rocks described. All other rocks were examined and described with the aid of a 10x hand lens. Mineralogic data were combined with the results of the weathering experiments to elucidate differences in stream and pond chemistry.

Site Description

Physical characteristics of the study areas are listed in Table 5. Each pond has one major inlet with 2-3 branches above a wetland area (Figs. 2 and 4). At Black, the inlet branches above a spruce flat which has been flooded by beavers. At Cone, the inlet branches above a late successional bog dominated by sphagnum and yellow birch. Both branches of the Black Pond inlet arise from springs. The inlet to Cone Pond flows through several rocky gorges, and over short waterfalls.

Black Pond watershed is completely mantled by glacial till. Much bedrock is exposed at Cone Pond watershed; the remainder of the watershed is mantled by glacial till, less than 2-3 m thick in most areas. The bedrock at Black Pond watershed has been mapped as Osceola Granite (Billings, 1956), while the bedrock at Cone consists of metasedimentary quartz schists and mica schists with scattered pegmatite intrusions. The soils of both watersheds are characterized by sandy spodosols.

Table 5. Study area description.

	Black Pond	Cone Pond
Area	1.7 ha	3.1 ha
Volume	92,000 m^3	101,000 m^3
Volume Weighted pH	5.3-6.4	4.5-4.8
Volume Weighted bicarbonate alkalinity	60-70 ueq L^{-1}	0 ueq L^{-1}
Location	N 44°06′, W 71°35′ Lincoln, NH	N 43°54′, W 71°36′ Thornton, NH
Watershed Area	31 ha	63 ha
Watershed Aspect	east-southeast	south-southeast
Watershed Mean Slope	23%	24%
Watershed Elevation	481-634 m	481-649 m
Watershed Cover Types		
northern hardwoods	90%	20%
conifer	10%	60%
bedrock outcrop	0%	20%
Watershed Land Use	cutover circa 1900 uninhabited light camping/hiking	burned circa 1820 uninhabited light camping/hiking

Results

Stream Chemistry

Figures 8 to 11 characterize the stream chemistry by showing average ion concentrations for each site plotted against elevation. Although averages are plotted on these figures, the same differences between sites were consistently noted on each sampling date. Stream length or watershed area are the parameters apparently responsible for differences in stream chemistry. Because of the similarity in topography and slopes in the study watersheds, elevational gradient can be used to represent these parameters. The chemistry of the upper portion of Falls Brook (Johnson et al, 1981) is also plotted for comparison. Falls Brook is part of the nearby Hubbard Brook watershed and has many similarities to our study watersheds.

For all parameters measured, the chemistry of Black Inlet is distinct from that of the Cone Inlet. Black Inlet is higher in

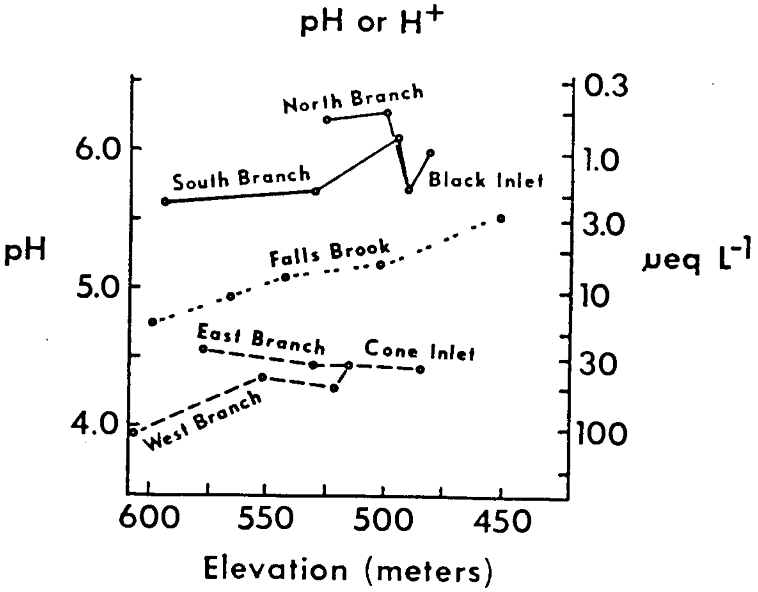


Figure 8. Streamwater pH.

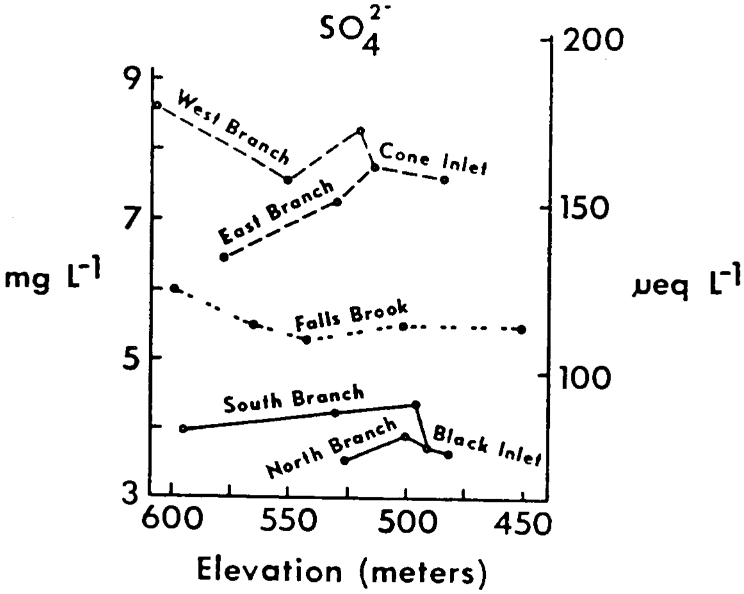


Figure 9. Streamwater SO_4^{2-}.

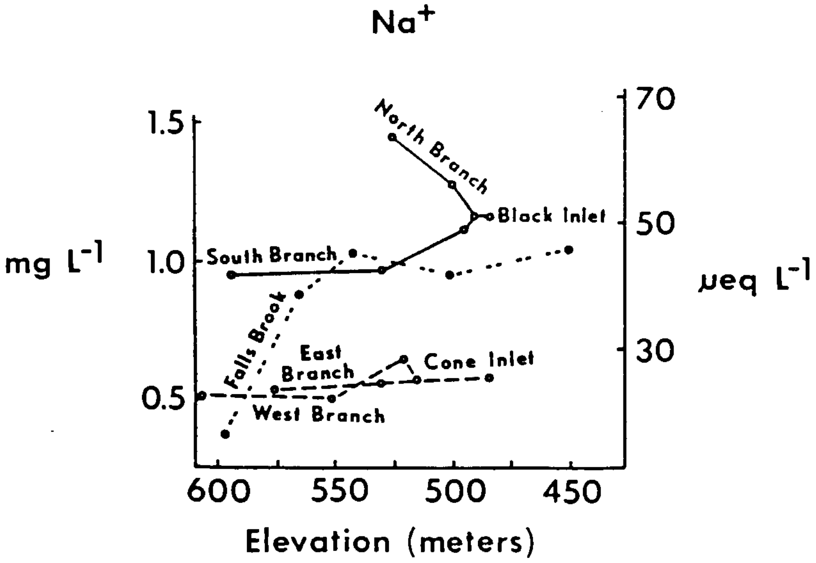


Figure 10. Streamwater Na^+.

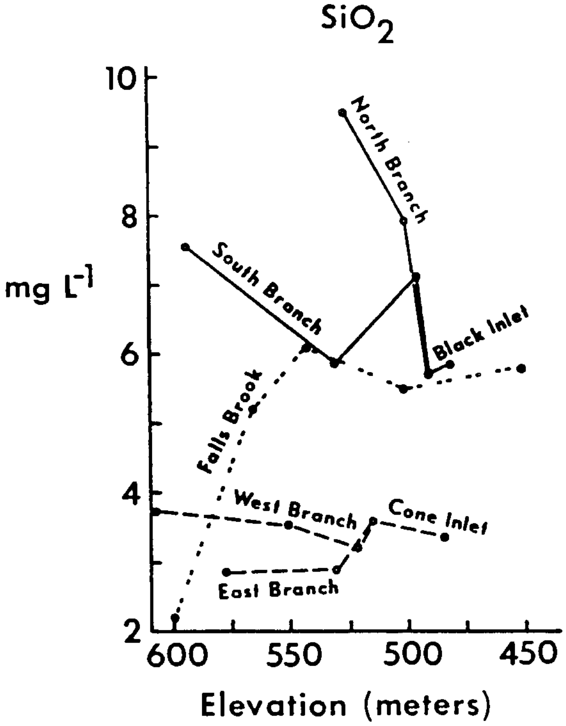


Figure 11. Streamwater SiO_2 .

basic cations and SiO_2. Cone Inlet is higher in H^+ and SO_4^{2-}. Black Inlet has appreciable alkalinity, while HCO_3^- alkalinity is nonexistent at the pH of Cone Inlet. Falls Brook lies intermediate to Black and Cone on all parameters except for Mg^{2+}, which is comparable to Black.

Although the chemistry of the study watersheds is quite different, temporal changes for most ions, as indicated by the standard deviations, are of about equal magnitude for both watersheds. Exceptions are SO_4^{2-} and H^+ which are relatively constant for Black Inlet, but fluctuate widely at Cone. All parameters show increases during drying periods, and decreases during wetting periods. Initial flows following extended dry periods show the highest concentrations.

Hydrology

At Black Pond watershed, the north branch spring maintained flow along the entire course of the north branch during the whole period of study. Flow along this branch is low and shows little response to changes in moisture conditions in the watershed. The south branch spring was also perennial during the study. However, streamflow immediately below the spring was rarely continuous. The south branch does show response to storms, and sections of it dried out during the summer and autumn.

The most significant point about the hydrology of Black Pond watershed is that the springs were perennial during the entire summer of 1983. During this period, which included several months with below average rainfall (USDA Forest Service, unpublished data), many area streams, some draining much larger watersheds, ceased flowing. The springs occur high in the Black Pond watershed indicating that groundwater storage, possibly from outside the topographic divide, is likely contributing to streamflow. The slope above the watershed divide continues up to the summit of Mount Flume at 1319 m. Subsurface flows may not be bound by the same features that define topographic watersheds in this area.

In contrast to Black Pond, streamflow in the Cone Pond inlet system shows quick response to rainfall and snowmelt. All streams in the Cone Pond watershed stopped flowing in early June and did not flow again until a large storm on August 11-12. This flow peaked quickly and the streams were again dry until another rainstorm on October 24. Thereafter, streamflow was maintained through the rest of the study. Streamflow is highly variable and flashy. No springs were observed.

Soil Chemistry

Soil pH determinations showed similar patterns in both watersheds. The Oa horizon is the most acidic at about pH 3, followed by the Oe horizon with a mean pH of 3.5. pH increases with depth averaging 3.5 to 4.0 in the E, to 4.5 in the upper B, to nearly 5.0 in the lower B. Poorly drained soils have higher pH than well drained soils. This difference is especially pronounced at Black. No pattern is apparent on an elevation gradient.

The biggest difference in soil acidity between watersheds is observed in the Oa and E horizons. These horizons were, on the average, twice as high in H^+ at Black than at Cone. Both watersheds showed considerable variation, but variability was greater at Black Pond. In both watersheds, soils under conifers had a lower average pH than soils under hardwoods. This created a contradiction in that Cone had less acidic soils, yet had a much higher percentage of conifers.

Geology

The till in both watersheds is a loose, sandy till. At Black most of the recognizable rock fragments and abundant large surface boulders are Osceola Granite. Lafayette Granite Porphyry derived from the Franconia Ridge was found in minor amounts. Many other rock types, including porphyries, calc-silicate gneiss, camptonite, and slate were also present in trace amounts.

The bedrock at Cone Pond watershed is largely metasedimentary quartz schist and mica schist. These two rock types are interbedded in layers of varying thickness. These rocks have been mapped as Littleton Formation (Billings, 1956), but are presently undergoing reclassification. Small 2 m pods of pegmatite are scattered through the metamorphic rocks. Also, a narrow vertical dike of basalt cuts through the central portion of the watershed. Other rock types were rarely observed in the till.

Mineralogy

Compositions of typical rocks from each watershed are shown in Table 6. Quartz is a major constituent of the rocks from Cone, while feldspars are conspicuously absent. Micas are also abundant. Muscovite and chlorite, which are more resistant to weathering than biotite, are more abundant. The rocks from Black also contain a large amount of quartz. However, there are also large percentages of a variety of feldspars. Pyroxene, olivine, and a variety of amphiboles were also identified in rocks at Black. Sulfides are present in minor amounts in the metasedimentary rocks of Cone, and some of the porphyritic rocks from Black. Stability in the weathering environment, a measure of resistance to chemical weathering, is also listed in Table 6.

Table 6. Estimated modes of rock samples from watersheds, in percent. See Table 7 for sample identification. tr=trace. Stability in the weathering environment, and weathering products after Carroll, 1970.

MINERAL	~~CONE~~ BLACK POND				~~BLACK~~ CONE POND				STABILITY	WEATHERING PRODUCTS
SAMPLE NO.	2	3	4	5	7	8	10	13		
quartz	27	50	52		65	50	68	22	high	
plagioclase			2	40					mod. low	
perthite	66	9	20						mod. low	sources of Ca^{2+}, Na^{+}, K^{+}
orthoclase		34	tr						moderate	
biotite					15	tr	tr	9	moderate	
chlorite						20	10	13	moderate	sources of K^{+}
muscovite					15	20	18	53	mod. high	
pyroxene			2	14					low	
arfvedsonite	7								mod. low	
kaersutite				25					mod. low	sources of Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}
hornblende		6	15						mod. low	
olivine				6					low	
garnet		tr						tr	high	
apatite			tr						mod. low	source of Ca^{2+}
oxides	tr	1	7	10	5	8	3	1	high	
sulfides			2	5	tr	2	1	2	low	source of H^{+}, SO_4^{2-}
TOTAL	100	100	100	100	100	100	100	100		

Table 7. Weathering experiment solution chemistry. Concentrations are ueq L^{-1} except for SiO_2 which is mg L^{-1}. NA=not available due to lab error.

SAMPLE	ROCK TYPE	ABUNDANCE	H^+	Ca^{2+}	Mg^{2+}	Na^+	K^+	SO_4^{2-}	HCO_3^-	SiO_2
		BLACK POND WATERSHED								
1	granite	trace	2.2	0	0	8	6	24	<10	2.3
2	granite	major	1.2	100	12	19	70	8	80	9.4
3	granite porphyry	minor	1.0	80	3	21	28	17	NA	3.2
4	granite porphyry	trace	0.4	160	24	7	18	67	95	9.3
5	camptonite	trace	0.0	664	43	36	54	29	675	2.4
6	calc silicate gneiss	trace	0.2	190	10	15	16	29	135	7.4
		CONE POND WATERSHED								
7	quartz schist	major	2.8	0	2	2	14	28	<10	2.1
8	quartz schist	minor	3.5	0	2	4	14	27	<10	2.7
9	quartz schist	major	2.3	0	1	1	15	18	<10	0.8
10	quartz schist	major	10.0	5	5	1	16	69	0	1.5
11	mica schist	major	1.6	0	1	3	17	17	<10	1.5
12	mica schist	major	0.8	5	2	5	10	18	<10	3.0
13	mica schist	major	5.2	10	12	4	32	92	0	1.8
14	granite pegmatite	minor	1.7	0	0	3	5	23	<10	0.8
15	basalt	trace	0.5	20	16	10	32	12	80	3.6
16	quartz monzonite	trace	0.9	5	1	3	13	8	20	1.2
		UPPER HALL POND WATERSHED								
17	quartz schist	minor	13	206	92	3	55	458	0	3.1
18	pyrite mica schist	major	1050	110	574	3	18	24000	0	36
19	volcanic breccia	trace	0.1	857	44	15	18	12	780	1.7
		CONTROL								
20	control		1.1	0	0	0	0	0	0	0

Weathering Contributions

Boulders of granite in the Black Pond watershed were observed to be highly weathered to a whitish gravel composed of fragments about 1 cm across. This gravel was about 2-5 cm thick on the surface of boulders, and 10-30 cm thick in soil horizons. The metamorphic rocks at Cone Pond watershed appeared to be resistant to weathering. Exposed surfaces exhibit pits where biotite and chlorite have been weathered. Only one outcrop was found which exhibited rusty weathering crusts typical of sulfidic rocks.

Solutions in the artificial weathering experiments approached equilibrium by day two. Final solution chemistry for each sample is listed in Table 7. The solutions from Black contained high amounts of at least two basic cations. Of the six samples from Black, only one contained moderate SO_4^{2-}, and two samples had very high pH. Three samples were high in SiO_2. Alkalinity was much higher for Black samples compared to those from Cone.

None of the rocks tested from Cone yielded an appreciable amount of Ca^{2+}, Mg^{2+}, or Na^+. Only two showed moderate amounts of SO_4^{2-}. This was accompanied by higher H^+.

Samples of three rocks from the watershed of nearby Upper Hall Pond were tested to evaluate the behavior of known sulfidic rocks in the weathering experiments. Sulfate and H^+ were very high in 2 of these. High amounts of basic cations were also observed. Although these rocks are part of the same Littleton Formation as the Cone samples, they produced very different weathering products.

Discussion

Stream Chemistry

Stream chemistry in the Black Inlet does not show the expected elevational gradient shown by nearby Falls Brook on which the acid neutralization model of Johnson et al. (1981) was based. However, the chemistry of Black Inlet may still be explained by the same concepts which explain elevational gradients at Falls Brook: those of residence time and position along the stream channel. Since groundwater is introduced primarily in the uppermost sections of Black Inlet, this stream is in effect a "Falls Brook in reverse".

Groundwater would have a relatively long path length in the till, allowing longer reaction time between water and minerals. As pointed out by Johnson et al. (1981), long path implies more replacement of acidic cations by basic cations. Hydrologic evidence indicates that the streams are fed by a slow, steady supply of groundwater.

All springs at Black occur high in the watershed. Therefore, streamwater in the uppermost reaches has the highest proportions of groundwater. In the lower reaches, groundwater-rich streamwater is diluted with surface and shallow subsurface flow. Because of shorter flow paths within the system, these flows are characterized by higher H^+ and SO_4^{2-}, and lower basic cations and SiO_2.

Chemical gradients support this thesis as concentrations of Ca^{2+}, Na^+, K^+, HCO_3^-, and SiO_2, products of chemical weathering, all decrease in a downstream direction. Sulfate and DOC were observed to increase in a downstream direction.

At Cone Inlet, no consistent trends were noted on an elevational gradient. Again, the gradients observed at Falls Brook were not found. However, water with longer residence time in the soil and geologic materials is never introduced to Cone Inlet because of the shallow soils and expansive bedrock outcrops over the entire length of the stream. The last section of the inlet below the junction of the branches flows through a rocky gorge, and over waterfalls, which prohibit the introduction of subsurface flows. The result is that the entire length of the Cone Inlet resembles the uppermost portion of Falls Brook.

The hydrology of Cone Inlet is consistent with the above explanation. The streams are quick to respond to changing moisture conditions in the watershed indicating the dominance of shallow flows, and lack of deep, baseflows. The lack of feldspars and ferromagnesian minerals coupled with the dominance of quartz and muscovite results in minimal chemical weathering.

The same factors which contribute to the patterns noted in stream chemistry within the watersheds are responsible for differences noted between the two watersheds. Waters at Black are enriched in basic cations, SiO_2 and HCO_3^- compared to those at Cone. Overall, water at Black is subject to longer path lengths and residence time within the watershed than at Cone. Differences in soils, outcrop distribution, and runoff timing all support this conclusion. Also, the rocks at Black are more reactive in terms of basic cations and alkalinity than those at Cone. This results in a larger buffering reservoir at Black.

Pond Chemistry

For every constituent measured, the range in concentrations is similar between the pond and its inlet stream (Table 8). This demonstrates the important influence of the streams and the watersheds in determining the chemistry of the ponds. At Black Pond Inlet, chemistry changes abruptly at the beaver dam just above the mouth of the inlet. It remains to be seen how this relatively recent effect might eventually change the chemistry of the pond.

Table 8. Comparison of inlet stream and volume weighted pond chemistry. Pond chemistry is from Buso et al. (1984). Concentrations are ueq L^{-1}, except SiO_2 in mg L^{-1}. na=not available.

	Black Pond		Cone Pond	
	Inlet	Pond	Inlet	Pond
H^+	1.6 - 0.5	5.0 - 0.4	50.1 - 20.0	31.6 - 15.8
Ca^{2+}	75 - 130	100 - 175	25 - 50	25 - 80
Mg^{2+}	25 - 41	25 - 33	8 - 25	8 - 16
Na^+	44 - 61	48 - 70	17 - 39	17 - 30
K^+	10 - 51	10 - 13	0 - 3	0 - 5
HCO_3^-	39 - 85	61 - 120	0	0
SiO_2	2.7 - 9.1	na	1.3 - 8.1	na
SO_4^{2-}	64 - 85	71 - 110	139 - 218	121 - 164

Weathering Contributions

In the weathering experiment, rocks from Black Pond watershed produced an average of ten times the equivalent of basic cations as rocks from Cone. Sulfate production seems to be minor in the rocks of both watersheds. The rocks of Upper Hall Pond watershed weathered differently producing large amounts of basic cations and SO_4^{2-}.

Sulfate levels in the two watersheds are not completely explained by this study. Black Inlet has low SO_4^{2-} at 3-4 mg L^{-1} while Cone Inlet has remarkably high SO_4^{2-} at 7-15 mg L^{-1} compared to other small streams in the area (Johnson et al., 1981; Martin, 1979; Fisher et al., 1968). The inlet to Upper Hall Pond was sampled three times and found to have about average SO_4^{2-} for the area at 6-7 mg L^{-1}.

The rocks of Black Pond watershed are potentially minor sources of SO_4^{2-}. One rock type of minor abundance produced modest amounts of SO_4^{2-}, while others produced trace amounts. The major rocks of Cone Pond watershed as a group produced relatively small amounts of SO_4^{2-} in the weathering experiments. The rocks of Upper Hall Pond watershed are capable of producing large amounts of SO_4^{2-}.

These results indicate that the mineralogy of these watersheds is apparently not the controlling factor in determining SO_4^- levels in streamwater. Sulfidic materials exposed to cycling water may already be completely weathered of sulfides or coated by weathering crusts that inhibit further weathering. Other factors such as adsorption on soils, oxidation-reduction in wetlands, uptake by vegetation, and differential entrapment of dryfall may be influencing SO_4^{2-} cycling as well. Temporal patterns suggest that SO_4^{2-} accumulates in Cone Pond watershed during dry periods and is flushed out of the system in the first flows following heavy rains.

Implications for Acidification

Likens et al. (1977) show that SO_4^{2-} is the dominant anion in streamwater in the northeast. However, on a geologic time scale the H_2CO_3 system is considered to be dominant over the H_2SO_4 weathering system (Johnson et al., 1972). A change from H_2CO_3 to H_2SO_4 would have met little buffering from the mineral materials at Cone Pond watershed. Also path lengths and residence time of water are relatively short, so the opportunity for buffering reactions is limited. Based on these factors, acidification would have proceeded unhindered.

Increased H_2SO_4 inputs to Black Pond watershed would be buffered by reactions with the minerals in the rocks, till, and soil, as well as by the groundwater component of streamflow. How long this buffering would last in the event of increased H_2SO_4 levels is unknown. Buffering is present, but total dissolved solids are low compared to some other watersheds in the region (Johnson and Reynolds, 1977).

Our study indicates that identification of key minerals, each of which may be present in a large variety of rock types, is especially important in characterizing watershed buffer capacity. Carbonates obviously have high buffering capacity. Olivines, pyroxenes, and amphiboles are important sources of basic cations. On the other hand, minerals such as quartz and muscovite are relatively inert to chemical weathering. Weathering of sulfides yields strong acids. These may dissolve minerals that are relatively stable at higher pH.

The characterization of a watershed's buffering capacity or aquatic chemistry based on rock types as suggested by Norton (1980) may be misleading. In this study, we found a granitic watershed much better buffered than a metasedimentary watershed. This is just the opposite of what would have been predicted by the bedrock susceptibility scheme. It is more appropriate to characterize a watershed by the minerals present than by general rock types. The granite from Black Pond watershed contains the reactive mineral arfvedsonite. This granite has a very different influence on water chemistry than a granite with micas instead of amphiboles. Further, our experiments suggest that complex units, such as the Littleton Formation, can have widely different weathering characteristics.

The results of this study also point out that the regional approach to classifying the sensitivity of streams and lakes to acidification (Omernik and Powers, 1982) is often inappropriate for individual streams and ponds. Factors not easily obtainable from regional maps, such as stream hydrology, contributions from groundwater and springs, mineralogy, and soil depth and permeability, have strong influences on stream and pond chemistry. This results in each stream and pond having a unique character determined by the configuration and components of its own watershed.

SNOWMELT EFFECTS ON CHEMISTRY OF CONE POND

In the Northeastern United States, nitric and sulfuric acids derived from the atmosphere can accumulate in the winter snowpack until warmer temperatures cause melting. However, as snow melts it releases dissolved substances unevenly, so that most of the acids are found in the earliest meltwater fractions (Colbeck, 1981; Hornbeck et al., 1977; Johannessen and Henriksen, 1978; Leivestad and Muniz, 1976). Acid meltwater can mobilize aluminum as it percolates through soils (Cronan and Schofield, 1979). When the meltwater finally reaches streams and lakes, it can cause abrupt changes in chemistry known as "acid pulses". Pulses of meltwater high in acidity and aluminum have been described in Scandinavia (Henriksen and Wright, 1977), Ontario (Jeffries et al., 1979), and the Adirondack Mountains of New York (Schofield, 1977) and the White Mountains of New Hampshire (Buso et al., 1984).

Ice-covered lakes are strongly stratified and resistant to disturbance. At the surface of a lake the temperature next to the ice is near 0°C, while deeper waters are around 4°C, the temperature at which the density of water is highest. Inflowing streamwater will sink to the point where its density is equal to that of lakewater (Wetzel, 1983). Winter streamwater is usually barely above 0°C and will flow into a lake just beneath the ice. Hence the acid pulses that enter a lake during a midwinter thaw or the final snowmelt may have effects that are restricted to a narrow stratum just beneath the ice. The extent to which acid meltwater mixes with lakewater before leaving a lake via its outlet should depend upon the strength of the density gradient that results from temperature variation in the lake, and on the volume and velocity of the incoming stream. Since spring snowmelt contributes the largest single input of water to New England lakes (Likens et al., 1977), the extent of mixing between lake and streamwater during an acid pulse may be critical for evaluating the susceptibility of lakes to acid precipitation. It is of particular concern that high levels of acidity and aluminum can be toxic to fish and other aquatic organisms (Cronan and Schofield, 1979).

This report summarizes a study of the chemical changes that occurred in a small acidic pond during the winter of 1984. We tried to determine the following: 1) What is the spatial extent of an acid pulse? 2) How long does an acid pulse remain in a pond? 3) Is there mixing of streamwater and pondwater that causes permanent changes in pond chemistry during acid pulses?

Methods

Location

The study area for the project was Cone Pond in West Thornton, New Hampshire (Figs. 1, 4 and 12). Background

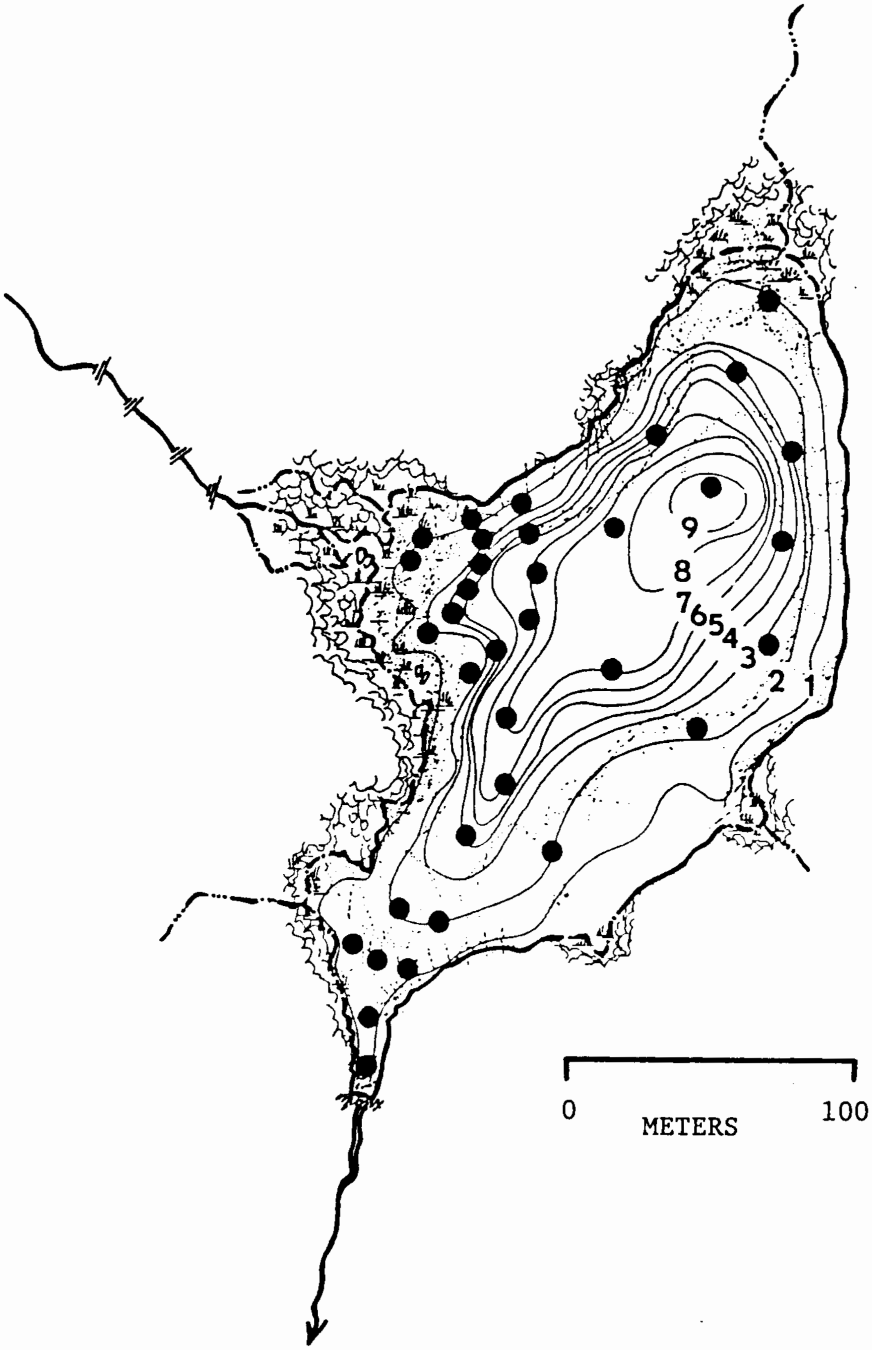


Figure 12. Morphometry of Cone Pond and location of sampling stations.

information on this lake was developed in an earlier study (Buso et al., 1984), including a description of lake chemistry based on three years of sampling. Cone Pond is an acidic (pH 4.5 - 4.8) clearwater lake 3 hectares in size surrounded by a predominantly coniferous watershed of 60 ha. About 15-20% of the watershed is exposed bedrock composed of quartz and mica schists (Bailey, 1984). The lake′s maximum depth is 9 m and its morphometry is such that the first meter below the surface occupies more than 25% of the total volume. This suggested that acid pulses from snowmelt were likely to change whole-lake chemistry since they could potentially affect a large percentage of the lake′s total volume while remaining in the 0-1 m stratum. The proximity of the lake to the Hubbard Brook Experimental Forest (10 km) made it possible to use meteorological and hydrological data that is routinely collected there by the U.S. Forest Service.

Sampling

Limnology in winter depends upon being able to collect water samples through the ice. Usually this is done by chopping a hole in the ice and collecting water samples or measuring temperature through the hole. However, the chopping of a hole induces physical mixing of the water just below the ice, where we were most interested in water chemistry. When there is standing water over the ice, as is often true during a thaw, it may pour into a freshly opened hole and further change the water chemistry. In addition we wanted to collect water samples and temperature profiles from a large number of stations around Cone Pond to find spatial differences in chemistry and temperature that could be used to trace water movements during thaws. For these reasons we designed an access pipe (Fig. 13) which could be left in place frozen into the ice, and which could be kept ice-free throughout the winter (Baird et al., 1985). A peristaltic or hand pump was used to collect samples through tygon tubing inserted into the pipes and a thermistor was used to measure temperature profiles. The array of 35 sampling stations is shown in Figure 12.

We collected water samples and recorded stream temperatures from the major inlet stream and the stream just below the pond outlet every week from February until May, more frequently during thaws. Samples for pond chemistry were collected at least biweekly at one-meter intervals at the station located over the pond′s deepest point. We collected additional water samples from ephemeral streams, ice and slush, and from other stations around the pond at various times throughout the season. In addition, on March 24, 1984 we collected 30-ml samples from three depths at each station and analyzed them for pH, to see the spatial extent of an acid pulse.

Laboratory Procedures

Water samples were analyzed for pH, alkalinity, sulfate,

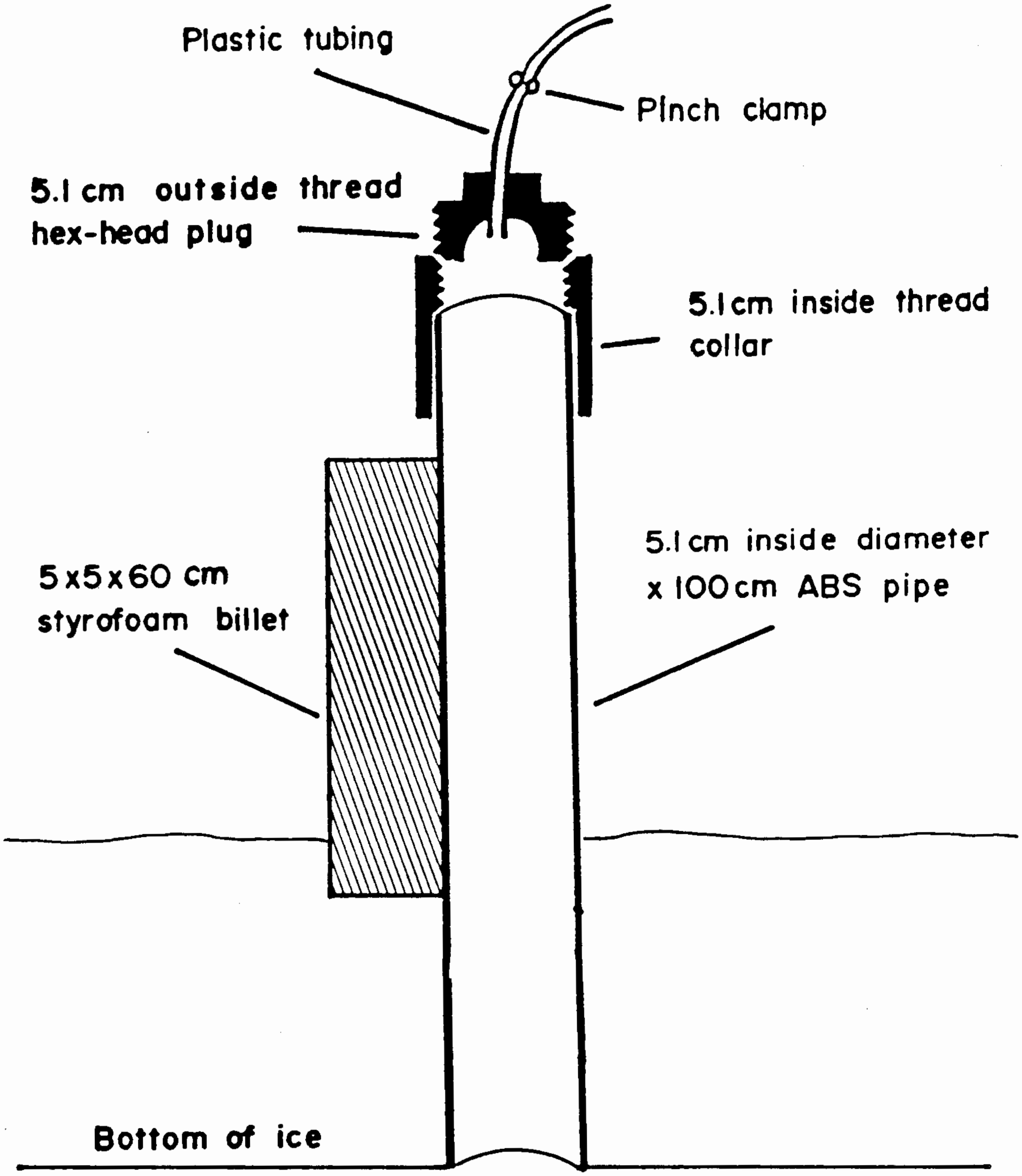


Figure 13. Design of access pipes used to collect water samples from below ice.

nitrate, aluminum, dissolved oxygen, and dissolved inorganic carbon. The methods used were the same as in previous Cone Pond studies (Buso et al., 1984) except for aluminum.

Aluminum was analyzed as total monomeric aluminum (Driscoll, 1984) using the hydroxyquinoline - methyl isobutyl ketone (MIBK) extraction technique of Barnes (1975). A 10:1 sample to MIBK ratio was used, and Al was measured by a Perkin-Elmer Model 603 atomic absorption spectrophotometer with a nitrous oxide-acetylene flame. Samples were extracted as soon as they were returned from the field, within 6 hours of collection. Reproducibility was ±5% between 0.01 and 1.00 mg L^{-1} Al.

Analysis

The data were used to prepare depth plots of water chemistry for each sample date. We estimated the volumes of 1 m strata using morphometric data and measurements of pool level, and combined these volumes with measured concentrations to calculate the mass of each element stored in the pond on each sample date. The hydrologic model BROOK (Federer and Lash, 1978) was used to simulate streamflows throughout the winter, using temperature and precipitation data from a weather station at Hubbard Brook with similar aspect and elevation to Cone Pond. BROOK allowed us to specify a number of environmental parameters specific to Cone Pond's watershed, such as amount of exposed bedrock, leaf area index, slope and aspect. The model was calibrated using weather data from 1980-82 in comparison with measured streamflow at Hubbard Brook's watershed 3, a gauged control watershed. We combined modelled streamflows and measured chemistries from the inlet stream and the outlet stream at Cone Pond to calculate daily addition and removal of H^+, SO_4^{2-} and Al. Budgets were prepared from sums of daily inputs and outputs between sample dates, in comparison with measured mass stored in the pond (Baird, 1984). Isopleth maps of pH on March 24 at three depths in Cone Pond were drawn with a computer contouring program, SURF2 (Sampson, 1978).

Results

Physical Factors

Daily streamflow for the Cone Pond watershed as modelled by BROOK for the period February - May 1984 is shown in Figure 14, with our sampling dates indicated. The hydrograph shows that before ice-out we sampled during four thaws and four days when thaws were not occuring. Averages of eight temperature profiles measured before ice out show the strong temperature stratification typical of lakes in winter (Fig. 15a). Water temperatures measured throughout the season above the pond inlet and below the outlet (Fig. 16a) show that the pond added heat to the stream throughout the study period.

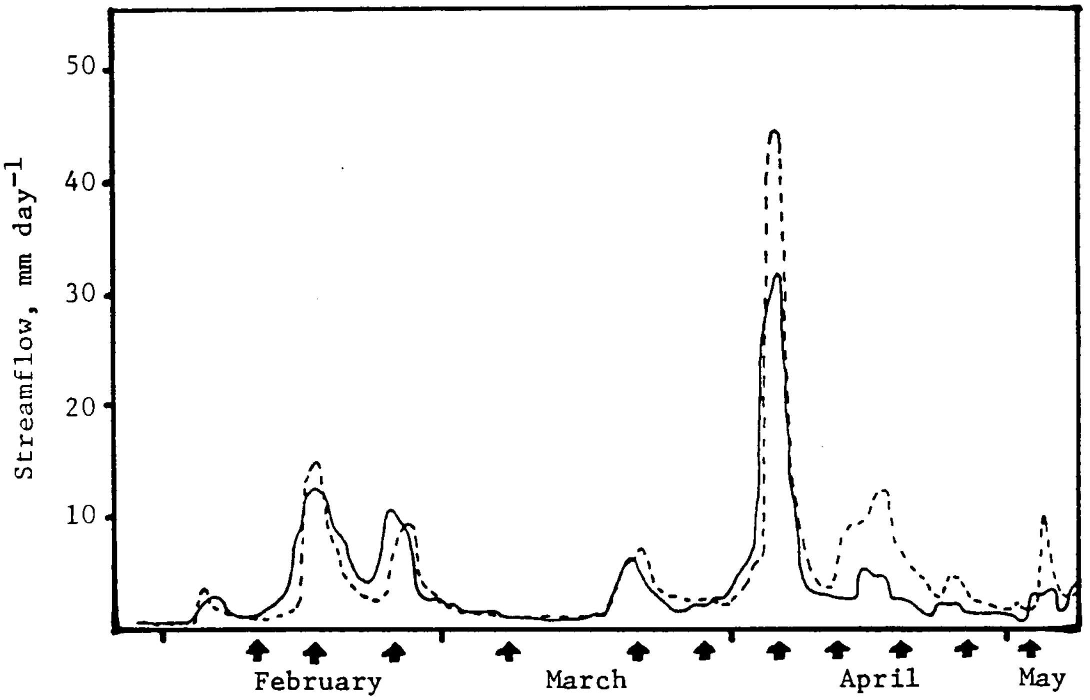


Figure 14. Simulated streamwater in mm day^{-1} for Cone Pond watershed. Dotted line shows measured streamflow at nearby Watershed 3, Hubbard Brook Experimental Forest. Arrows indicate dates pond chemistry was sampled.

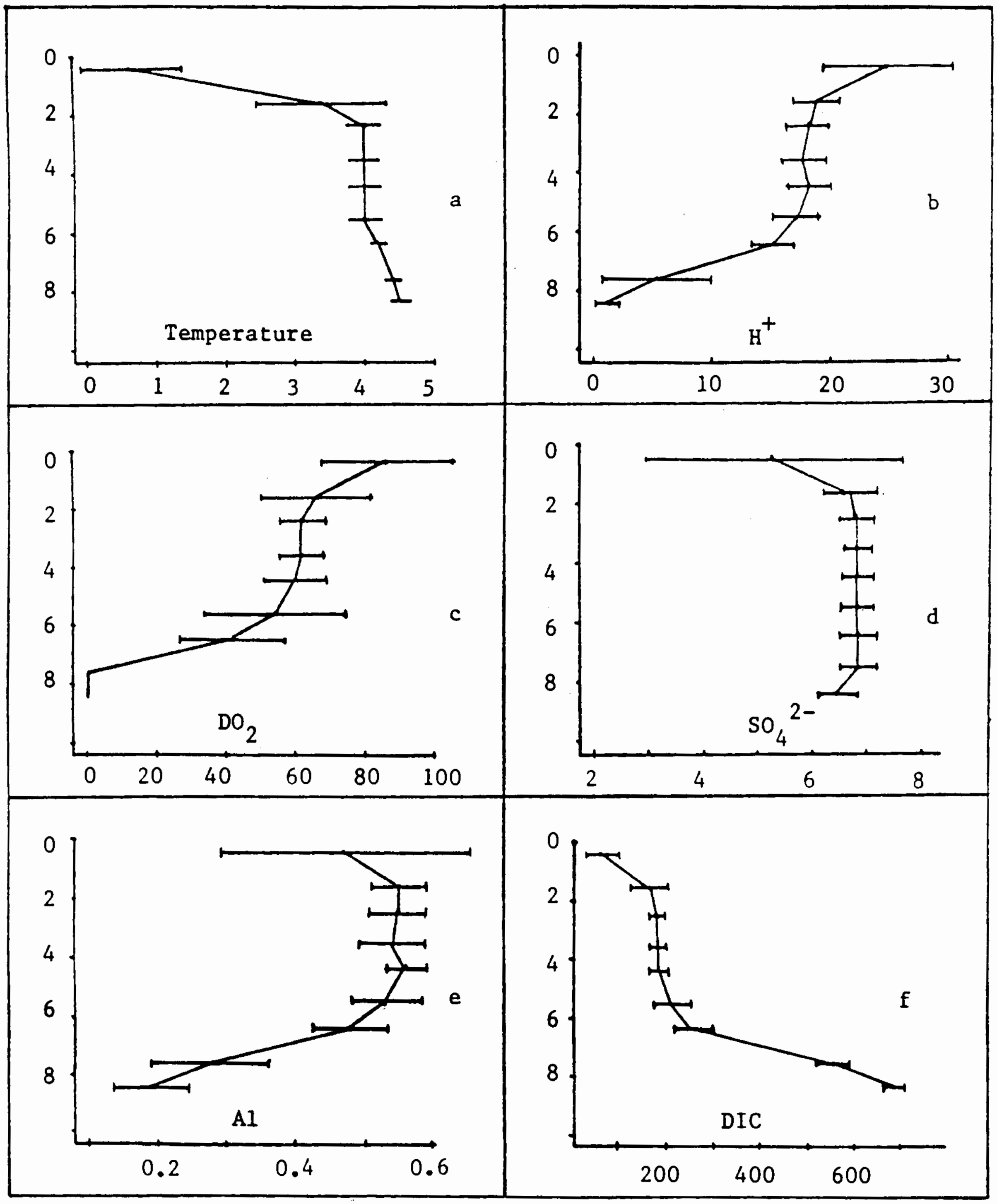


Figure 15. Averaged depth profiles in Cone Pond, based on eight sampling visits between February and April 1984. Bars show ±1 standard deviation of the mean. a) Temperature, °C. b) Hydrogen ion concentration, ueq L^{-1}. c) Dissolved oxygen, percent saturation. d) Sulfate, mg L^{-1}. e) Monomeric aluminum, mg L^{-1}. f) Dissolved inorganic carbon, umol L^{-1}.

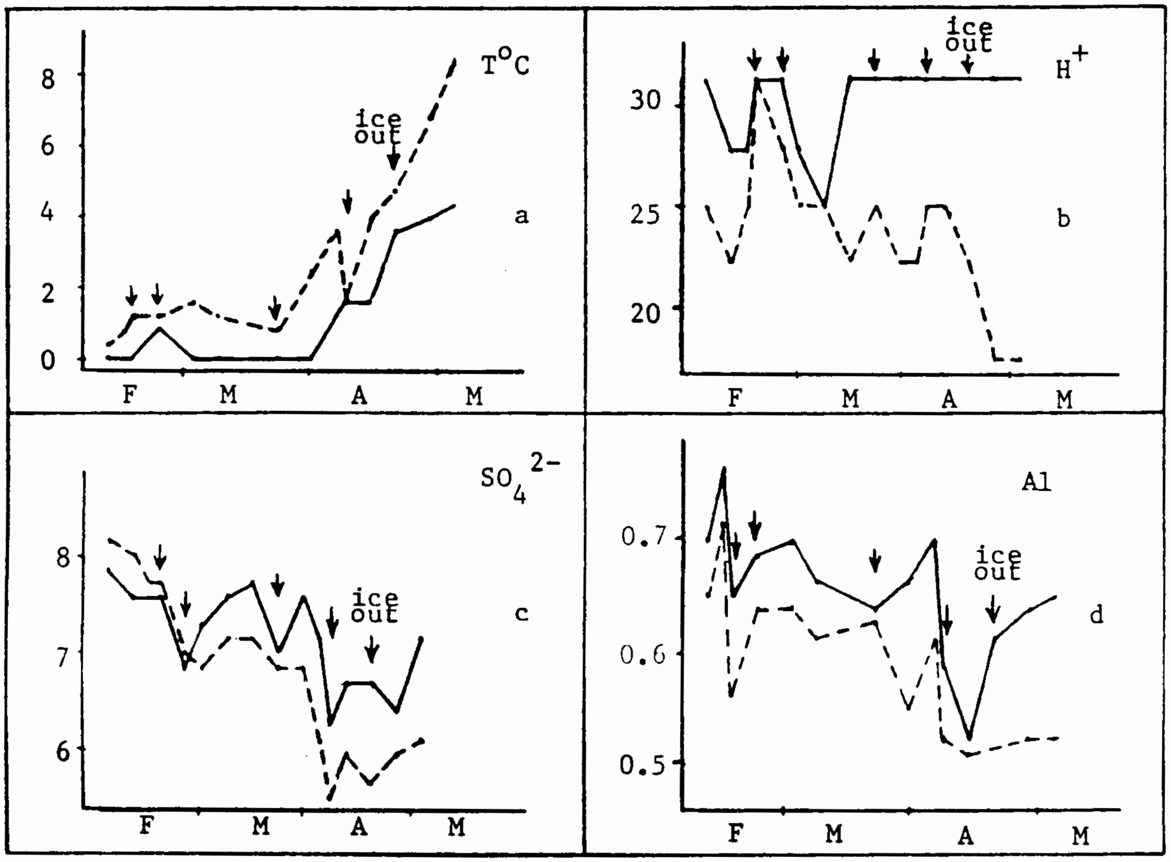


Figure 16. Temperature and chemistry at inlet stream (solid line) and outlet stream (dashed line), Cone Pond, February - May 1984. a) Temperature, °C. b) Hydrogen ion concentration, ueq L^{-1}. c) Sulfate, mg L^{-1}. d) Monomeric aluminum, mg L^{-1}. Arrows indicate thaws.

Hydrogen Ion Concentration

Buso et al. (1984) reported an acid pulse in Cone Pond on April 1, 1982, during which the pH dropped to 4.3 at 1 m. We never observed a pulse this severe in the spring of 1984, but thaws did lower the pH of surface waters. Mass of hydrogen stored in the pond was highest when a thaw was occurring (Fig. 17), with the greatest fluctuations noted in the top third of the pond's volume. However, these mass influxes to the top of the pond did not persist, and mass stored always decreased in the week following a thaw. There was an increased H^+ in the lower strata associated with the earliest thaw, but this was not a permanent addition. No trend over the season is evident for any of the three strata.

Figure 18 shows results of the pH analysis done for 105 samples collected from Cone Pond on March 24. On this day the inlet stream had a pH of 4.50 while the stream below the outlet had pH 4.55. A lobe of water with pH less than 4.55 is seen adjacent to the inlet at the 0.5 m depth, but this lobe is absent at 1.0 m.

The distribution of acidity in Cone Pond was not solely influenced by changes at the surface brought on by thaws. Figures 15b and 15c show averaged profiles of H^+ and of dissolved oxygen throughout winter statification. The pond was anaerobic in the bottom 2 meters until after spring turnover, and this anaerobic layer held buffering capacity sufficient to raise the pH to 6.0 at the bottom, compared with about 4.7 for most of the water column. Measured HCO_3^- alkalinity at the bottom reached a high of 190 ueq L^{-1} in April before ice-out, compared to 0 for the aerobic part of the water column.

H^+ concentration for the inlet and outlet streams is shown in Figure 16b. Early in the season the streams were similar in H^+ concentration; later the inlet stream maintained a higher level of acidity, while the outlet stream fluctuated at a lower level. This suggests that late in the season the pond was neutralizing the stream outflow slightly. Such neutralization could result from dilution by melting ice or from chemical and biological reactions within the pond.

Sulfate

In contrast to H^+, thaws did not always elevate the mass of SO_4^{2-} stored in the pond (Fig. 19). The lower two strata show small decreases in SO_4^{2-} stored over the season, while the top shows no trend. Ice-out brought an increase of SO_4^{2-} to the top stratum. The difference between inlet and outlet concentrations of SO_4^{2-} increases as the season progresses (Fig. 16c), much the same as for H^+ concentration. There is also a crossover in late February, with the pond evidently switching from producing SO_4^{2-} to consuming it. Before the crossover, differences between inlet and outlet are no larger than 8%.

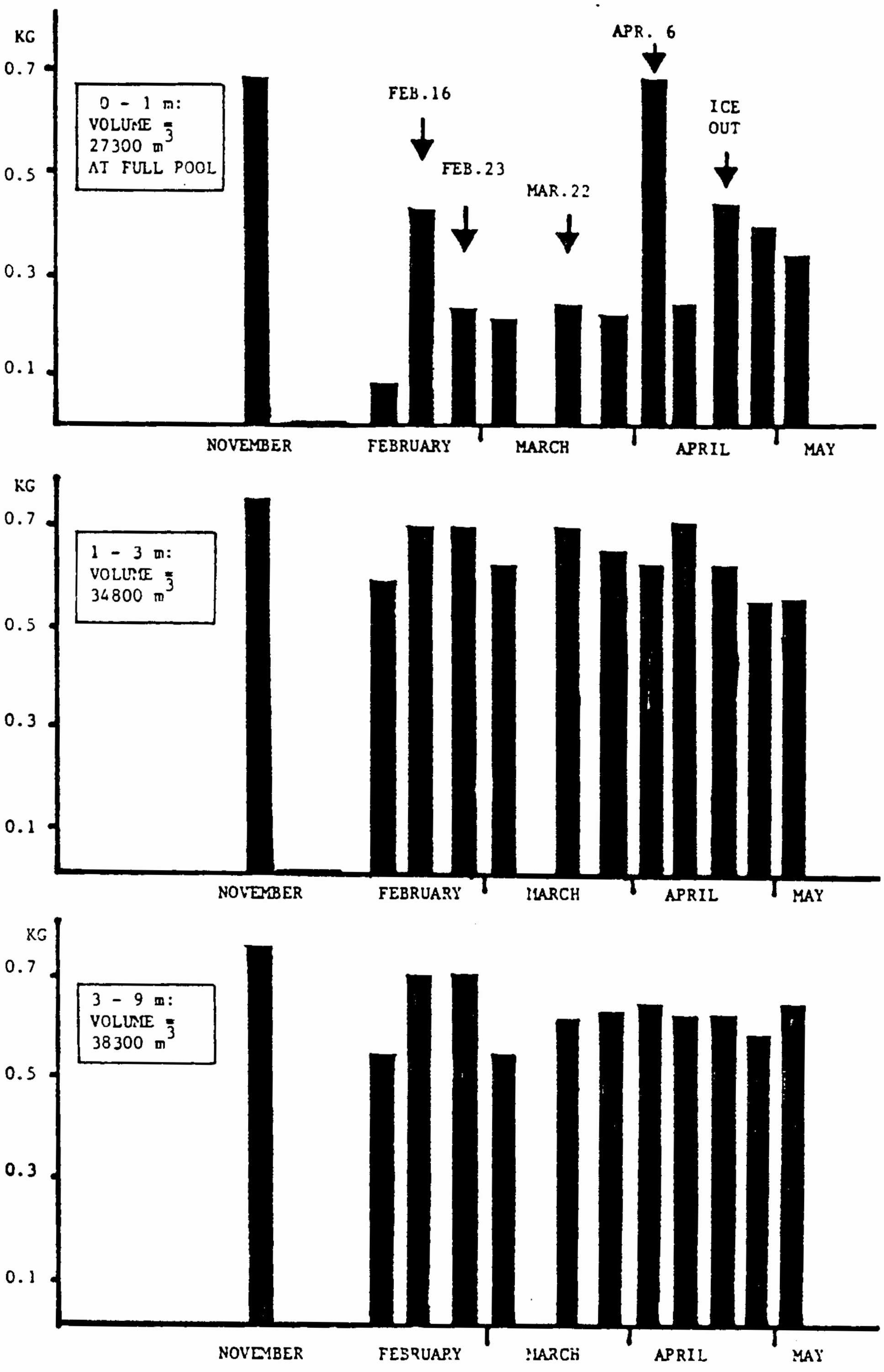


Figure 17. Mass (kg) of H^+ stored in Cone Pond, winter 1983-84. Arrows indicate thaws. The top stratum volume varied over the season as pool level changed.

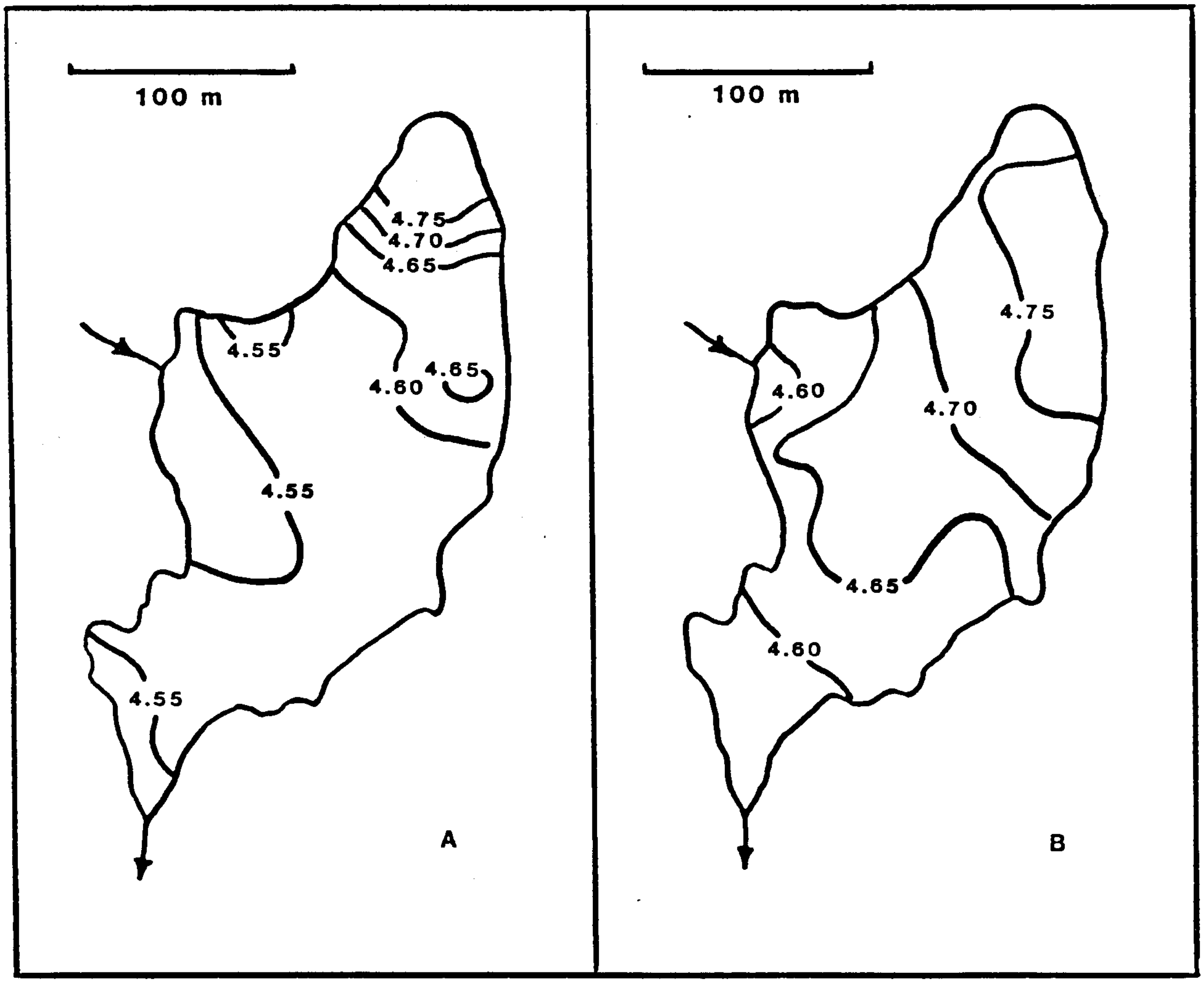


Figure 18. Isopleths of pH in Cone Pond at two depths on March 24, 1984. a) Depth 0.5 m, about 0.2 m below bottom of ice. b) Depth 1.0 m. Ice thickness was 0.35 m.

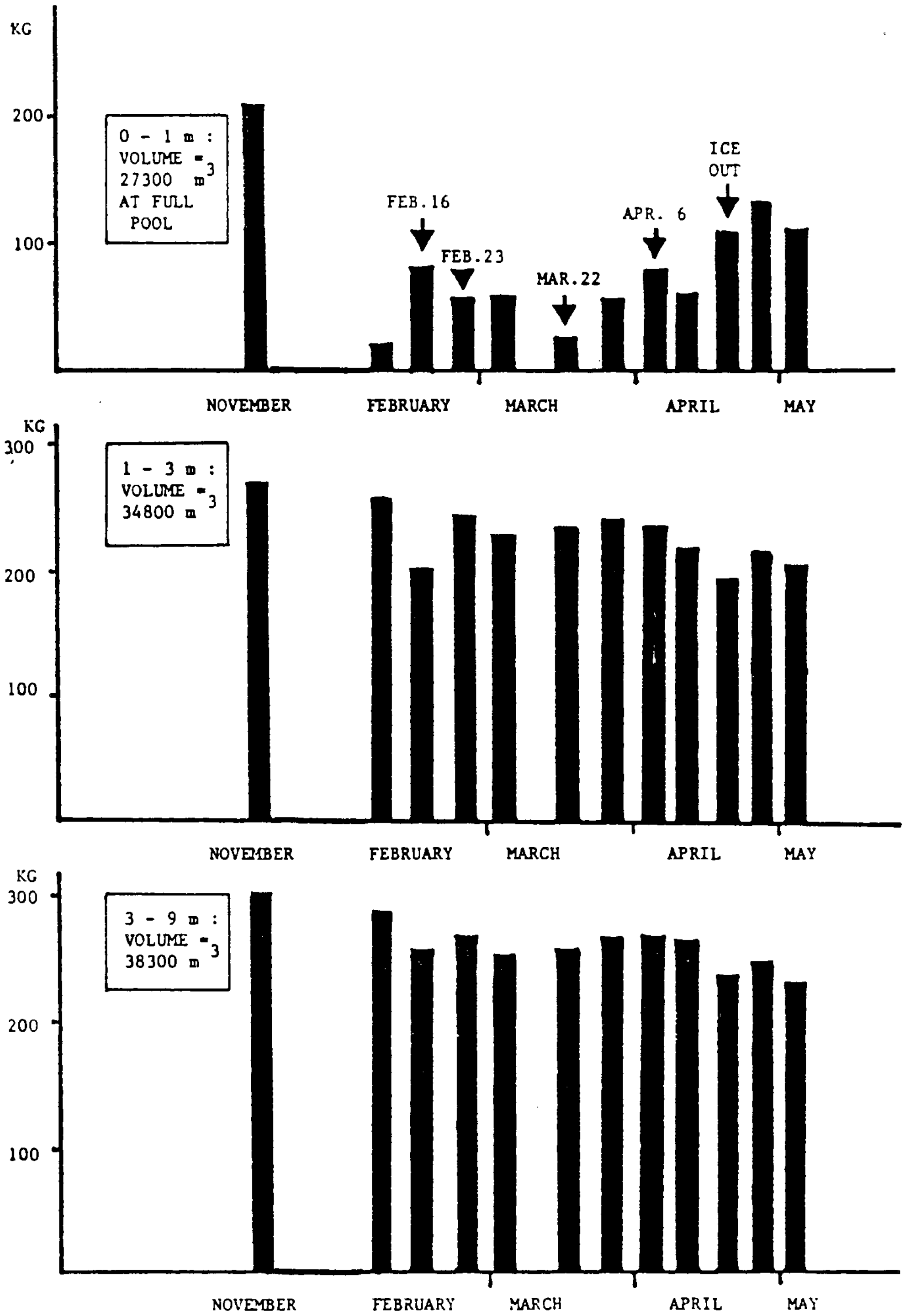


Figure 19. Mass (kg) of SO_4^{2-} stored in Cone Pond, winter 1983-84. Arows indicate thaws. The top stratum volume varied over the season as pool level changed.

Aluminum

Before ice-out, surface Al concentrations were low; they rose at the middle of the water column, then decreased at the bottom (Fig. 15e). The decrease at the surface may be caused by dilution, while the decrease at the bottom may be due to the lower solubility of Al at higher pH. The final snowpack melt brought more Al to all three strata, especially the top; but by the following week, there was a decrease in all three strata (Fig. 20). Another gain in Al for all strata was seen after ice-out. Figure 16d shows that inlet and outlet stream concentrations of Al were similar until ice-out, when inlet Al concentration began climbing and outlet concentration stayed constant. This loading increase changed Al mass in the pond after ice-out (Fig. 14).

Nitrate

Nitrate in water samples from Cone Pond was nearly always undetectable. Of a total of more than 200 samples analyzed for NO_3^-, only 11 contained measurable levels. These samples were of three types: water samples collected from just beneath the ice late in spring or during thaws (0.16 to 0.63 mg L^{-1}), slush (0.25 to 0.89 mg L^{-1}), and ice (0.53 mg L^{-1}). The outlet stream had measurable NO_3^- (0.49 mg L^{-1}) on one date, March 22, but the inlet stream never had measurable NO_3^-.

Discussion

Mass Changes During Thaws

Thaws increased the mass of H^+ in the surface stratum (Fig. 17). During thaws there was usually a decrease in pH at the surface, and usually a large increase in the volume of water in the top stratum. During the thaws on February 16 and April 6 the pool level rose by 0.4 m, a volume addition of more than 10,000 m^3, or about a tenth of Cone Pond's volume. Clearly such a volume change would increase the mass of measured ions, but such increases were not always noted for Al and SO_4^{2-}. Figure 16 shows that H^+ in the inlet stream was highest during thaws. However, for SO_4^{2-} and Al the maximum concentrations were measured on days when thaws were not occurring. The acid pulses at the inlet were high in H^+, but not as high in SO_4^{2-} and Al as was expected. Since Al is more soluble at low pH, we expected that increases in inlet stream Al would accompany increased H^+, but this was only seen after ice-out (Fig. 16d). Pond chemistry fluctuations reflect this difference in loading.

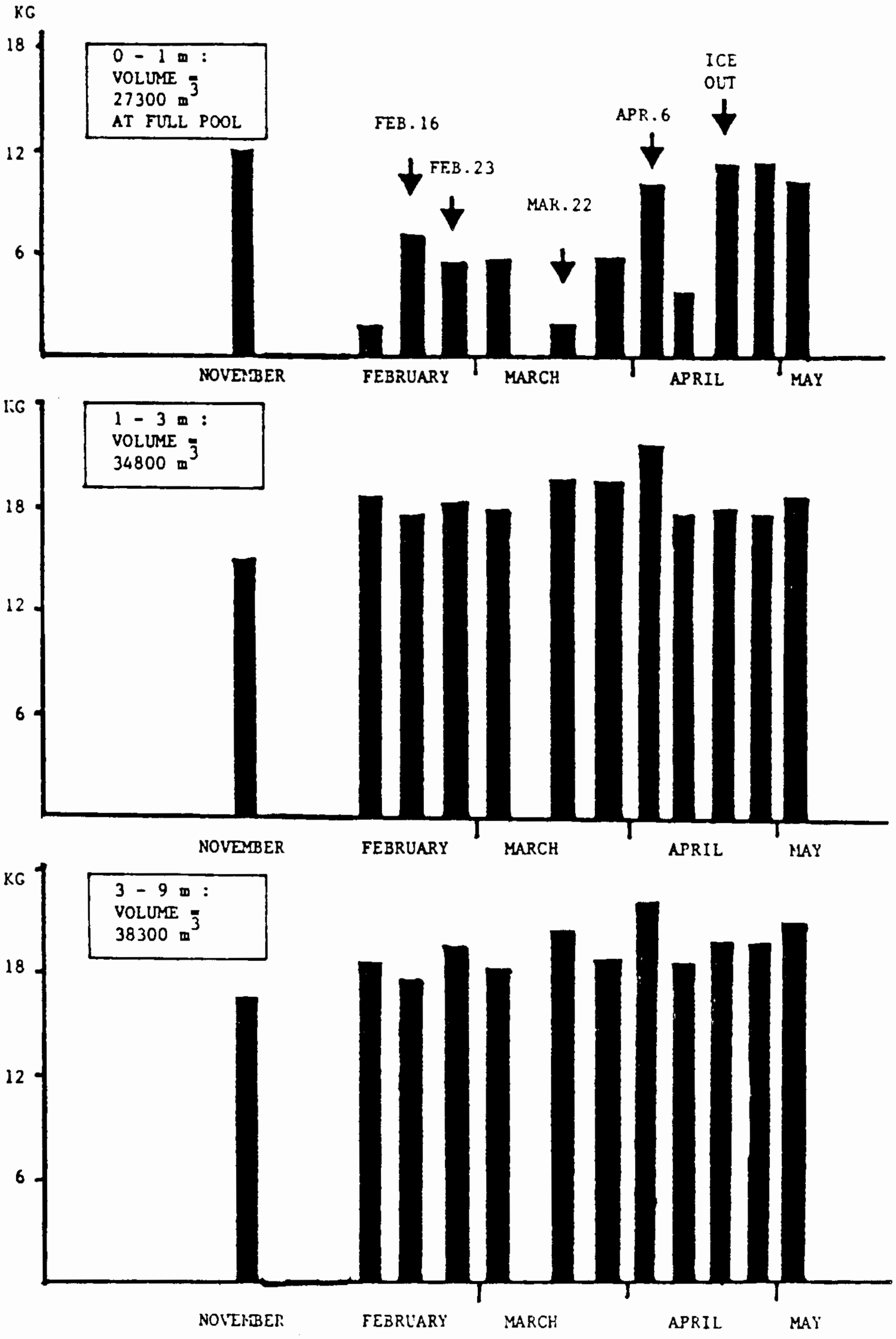


Figure 20. Mass (kg) of monomeric aluminum stored in Cone Pond, winter 1983-84. Arrows indicate thaws. The top stratum volume varied over the season as pool level changed.

Mechanisms for Transport to Deeper Waters

We hypothesized that we would not see mass changes in deep waters during the winter because of the stability of the thermally stratified lake and the tendency of cold, less dense streamwater to "float" over warmer, more dense lakewater. However, analysis of the results showed that mass in deeper strata was not related to thaw events. Exceptions were seen in the thaw on April 6, when there was more Al mass in the 3-9 m stratum, and on April 12 when there was a drop in Al throughout the pond.

There are two possible sources for the Al which appeared in elevated concentrations in the hypolimnion on April 6. During this final snowmelt, Al would be expected to mobilize in large quantities from watershed soils (Cronan and Schofield, 1979). Yet inlet stream concentrations of Al were lower on April 6 than on April 4 before the thaw had begun (Fig. 16), and in general, Al concentrations in the inlet stream correlate negatively with streamflow. This suggests there was an internal Al source, perhaps from mobilization of sediment Al in the pond on this date because of higher acidity in the littoral zone. Temperature profiles suggest that there was instability below the thermocline late in the season. Density currents might be especially important on warm days in winter because of these instabilities. In a thaw, comparatively warm waters entering through weakened ice at the pond margins could set up strong density currents, and mobilized Al from sediments in the shallows could move with the density currents towards the deepest part of the lake.

The accumulation of Al has important consequences. For example, Cone Pond's Al concentration is much higher than the level at which Al is toxic to fish (0.2 mg L^{-1}, Schofield 1977). Acidic deposition may have changed water chemistry in the pond from control of pH by dissolved organic acids, to control of pH by mineral acids. Since dissolved organic carbon has the ability to chelate dissolved metals and incorporate them into stable organic compounds (Reuter and Perdue, 1977), the change over to a mineral-acid dominated system could have been responsible for the release of toxic aluminum.

Implications of Anoxia in Cone Pond

It has been suggested that when enriched lakes receiving acid precipitation become anoxic, SO_4^{2-} reduction is favored over other bacterial processes because there is abundant SO_4^{2-} in such lakes (Kelly et al., 1982; Kilham, 1982). SO_4^{2-} reduction is accomplished by certain anaerobic bacteria and produces bicarbonate ion, whereas other more commonly found bacterial processes do not. Our results suggest that SO_4^{2-} reduction was occurring in the anoxic bottom of Cone Pond in winter 1983-84. Between 8 November 1983 and 10 February 1984, dissolved inorganic carbon increased at the bottom of Cone Pond, from 10 umol L^{-1} to 790 umol L^{-1} while dissolved oxygen dropped from 92% of saturation to 0. Alkalinity increased from 0 to 10 ueq L^{-1} at 8.5 m while pH rose from 4.7 to 5.9. There was a decrease in SO_4^{2-} concentration, from 8.0 to 7.0 mg L^{-1}. Throughout the rest of the winter, pH and DIC remained high at the bottom and we regularly noted the smell of hydrogen sulfide, a product of SO_4^{2-} reduction, in samples from the bottom.

The alkalinity produced by SO_4^{2-} reduction in lakes during anoxic periods is permanent only if the sulfide produced is precipitated as FeS (Kelly et al., 1982), which requires high iron concentrations. Iron from anoxic Cone Pond bottom waters ranged from 1 to 6 mg L^{-1} in winter 1983-84, making precipitation of FeS possble. Thus SO_4^{2-} reduction might have produced a small amount of permanent alkalinity.

If SO_4^{2-} reduction were to occur in Cone Pond regularly over a period of several years with incomplete mixing during spring and fall turnovers, it is possible that the alkalinity produced could eventually drive pH to a less toxic level. Since Al is less soluble at higher pH, a decrease in Al concentration would presumably accompany the increased pH. This has important implications for biota. Attempts by the New Hampshire Fish and Game Department to stock brook trout in Cone Pond have failed, probably because the combination of the low pH and high Al concentration is toxic (Cronan and Schofield, 1979). A comparison of H^+ mass present during a November 1983 sampling visit with mass found after ice-out shows there was more H^+ in Cone Pond in November than May 1984 (2.2 kg in November, 1.5 kg in May). The alkalinity produced over winter 1983-84 by SO_4^{2-} reduction may have lowered acidity, but this winter was the first time that anoxia has been clearly documented in Cone Pond, and it is not known whether it occurs regularly.

Since NO_3^- is found in precipitation at Hubbard Brook (Likens et al., 1977) and there is little biological acitivity in the watershed to remove NO_3^- in winter, we expected to see NO_3^- in the inlet stream and just below the ice during thaws, in a pattern similar to H^+. However, the NO_3^- that was measured at 0.5 m on several thaw dates was evidently not coming from the inlet, since it was never found there. Ice tends to accumulate NO_3^- over the winter (Barcia and Armstrong, 1971) and we did find NO_3^- in the central layer of the ice (Baird, 1984). The highest NO_3^- concentration (0.89 mg L^{-1}) was in a sample of slush collected near the outlet on March 15. The NO_3^- that we found in the pond therefore apparently originated from the melting ice rather than the inlet stream. Streamwater during the spring at Hubbard Brook is usually at its peak concentration of NO_3^- for the year. Likens et al. (1977) report a weighted average NO_3^- concentration for the period March - May of 2.57 mg L^{-1}, based on ten years of data. Cone Pond's watershed is less than 10 km from Hubbard Brook and has somewhat similar physical characteristics, and so absence of NO_3^- in the pond and its inlet stream deserves further study, especially since NO_3^- is so important in aquatic habitats.

Cone Pond and Acid Deposition

Acid pulses can profoundly affect streams, but their effects were limited to pond surface waters in this study. The deeper waters of ponds could provide shelter for stream organisms that cannot tolerate acid pulse conditions. This study took place over a single season, and its results depend somewhat on a unique combination of meteorological events and conditions. Yet what happened at Cone Pond can be generalized to other water bodies in New England because of two physical realities. First, a strong temperature stratification can be expected under ice cover, and will prevent mixing between cold streamwater and warmer lakewater. Second, most atmospherically derived solutes in the snowpack will enter streams, lakes, and ponds during the final snowmelt in early spring, when ice cover and stratification are still present. The time period between snowmelt and ice-out will vary from year to year, but snowmelt will always precede ice-out because the water equivalent of lake ice is much higher than that of the snowpack.

Winter stratification provides a recovery period for ponds under ice cover. Not only is a pond sealed off from stream inputs by the thermocline, but SO_4^{2-} reduction is possible if the hypolimnion becomes anoxic. This can add to buffering capacity, as in the present study. Thus even though more than 50% of the annual export of H^+ and SO_4^{2-} from Hubbard Brook watersheds occurs in the period March-May, there was no evidence in the present study that this loading permanently changed pond chemistry. In contrast, autumn rains during fall turnover will provide stream inputs that mix with pondwater, and may be more important in permanently changing water chemistry, as was seen in Norway (Henriksen and Wright, 1977).

The study of acidic environments such as Cone Pond can warn us of what might be expected if a watershed loses its ability to buffer acid deposition. For example, the precipitation falling at Hubbard Brook has an average H^+ concentration of 78.4 ueq L^{-1} during the period March-May (Likens et al., 1977). Streamwater H^+ concentration for the same period at Hubbard Brook's undisturbed watersheds over 10 years averages 12.9 ueq L^{-1}, suggesting that much of the H^+ entering in precipitation is retained or removed by the watershed. In contrast, Cone Pond's inlet stream had an average H^+ concentration of 30.7 ueq L^{-1}, more than twice as high as Hubbard Brook's, in March-May of the present study. Thus Cone Pond's watershed evidently has much less buffering capacity than is seen at Hubbard Brook.

Summary

Acid pulses during snowmelt were found to cause fluctuations in H^+ mass in waters just beneath ice cover in Cone Pond. Intensive sampling during a March 1984 thaw showed that horizontal variation in pH beneath the ice was strongly influenced by proximity to perennial and ephemeral inlet streams. The vertical extent of acid pulses was usually less than 1 meter.

Below this there was little variation in chemistry over the winter. These observations suggest that in ice-covered lakes during snowmelt the pH will be lowest at the surface and near streams with low pH. The effects and severity of acid pulses will be overestimated if only surface samples are collected during thaws.

In Cone Pond the large changes in chemistry seen during thaws usually subsided in the week following an event. In contrast to H^+, concentrations of SO_4^{2-} and Al were unrelated to thaws. Anoxic bottom waters produced alkalinity, probably because of SO_4^{2-} reduction, which may have markedly reduced the H^+ mass stored in the pond. NO_3^- was not found in the inlet stream and was only detectable in ice, slush, and in waters in contact with ice. Our observations suggest that winter stratification under ice cover may provide a recovery period for ponds that recieve acidic streamwater inputs, and that a surprising amount of alkalinity can be produced in anoxic waters. Cone Pond shows the unexpected importance that SO_4^{2-} reduction may have in oligotrophic freshwater ponds.

RECOMMENDATIONS AND APPLICATIONS

The susceptibility of New Hampshire's ponds to acidification is affected by disturbances, minerology, and hydrology of watersheds; and the hydrology and trophic characteristics of ponds themselves. Only a sampling scheme designed to evaluate biogeochemical variability will properly measure the sensitivity of an aquatic resource to acidic deposition. Such a scheme should include investigations of:

Fire

Severely burned watersheds are not uncommon in New Hampshire. Burned catchments with unreactive surficial geology could be the most poorly buffered areas in the state. These areas should be identified.

Beavers

Beavers are common and their presence should not be ignored. Important fluctuations in water chemistry can occur within and downsteam of active beaver impoundments.

Watershed Mineralogy

The minerology of geologic formations in New Hampshire is very complex. Some granites can neutralize acids, while some metasedimentary rocks are inert or even acidic. We suggest a "beaker test" as a simple, inexpensive means of estimating the potential contribution of a rock type to watershed geochemistry.

Watershed Hydrology

To study watershed neutralization processes, we recommend sampling streams along elevational or catchment-area gradients. In addition, hydrologic observations are needed to understand water analyses. The character of stream flow under varying conditions can be an indication of comparative water path lengths in small watersheds.

Pond Hydrology

Ponds are not continually mixed reservoirs. The timing and completeness of turnover, and the degree of stratification should be studied in each pond because the mixing of acidic inlet stream water is dependent on many factors.

Nutrient Cycles

The biochemical cycling of the anions that accompany acidic deposition should be considered as an additional acid buffering source in New Hampshire's ponds. The reduction of SO_4^{2-} can produce alkalinity. This process may be important even in oligotrophic aquatic systems. We suggest that more attention be given to ponds with a tendency toward hypolimnetic anoxia.

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