

Precipitation Loading of Acid and Heavy Metals to a Small Acid Lake near Sudbury, Ontario

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The pH of Lumsden Lake was closely related to the measured amount of acid entering the lake from bulk precipitation. In 1972 it was estimated that an excess of 2135 kg of H₂SO₄ was added to the lake from the atmosphere. The predicted annual change in lake pH was from 5.2 to 4.8 and the actual measured change was from 5.2 to 4.7. In 1973 an estimated excess of 1271 kg of H₂SO₄ was added to the lake from the atmosphere. The predicted annual pH change was from 4.8 to 4.7 and there was no net change in the lake pH in 1973.

Lumsden Lake also had high concentrations of sulfate, manganese, zinc, and nickel in comparison with remote or "unpolluted" lakes. High concentrations of manganese and possibly some zinc in the lake appeared to result from increased mobilization from the lake sediments or watershed or both as the pH decreased. Atmospheric fallout also contributed substantial quantities of nickel and copper to the watershed, some of which appeared to be retained in the lake water. The high concentrations of lead in the precipitation were not retained in the lake.

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Le pH du lac Lumsden est étroitement lié à la quantité d'acide mesurée qui entre dans le lac avec la précipitation brute. On estime qu'en 1972 plus de 2 135 kg de H₂SO₄ ont été ajoutés au lac en provenance de l'atmosphère. Le changement annuel prédit dans le pH du lac était de 5.2 à 4.8, alors que le changement mesuré réel était de 5.2 à 4.7. En 1973 on estime à plus de 1 271 kg la quantité de H₂SO₄ ajoutée au lac en provenance de l'atmosphère. Le changement de pH prédit pour l'année était de 4.8 à 4.7, et il n'y eut pas de changement net de pH dans le lac en 1973.

Le lac Lumsden contient en outre de fortes concentrations de sulfate, manganèse, zinc et nickel comparativement aux lacs éloignés ou « non pollués ». Les hautes teneurs en manganèse et possiblement une certaine quantité de zinc dans le lac semblent résulter d'une mobilisation accrue depuis les sédiments du lac, le bassin hydrographique ou les deux, à mesure que le pH diminue. Les retombées atmosphériques fournissent également au bassin hydrographique des quantités substantielles de nickel et de cuivre, dont une partie semble être retenue dans l'eau de lac. Les hautes teneurs en plomb dans les précipitations ne sont pas retenues dans le lac.

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MANY lakes in the vicinity of Sudbury, Ont., have been found to be extremely acidic (Beamish and Harvey 1972) and earlier studies have concluded that precipitation was the most probable source of acid to these lakes. Because no measurements were available that directly related acid in the precipitation to changes in acid content of lakes, in 1972, a 2-yr study was undertaken to examine precipitation-induced changes in acid and heavy metal content in one of these acid lakes.

Lumsden Lake was chosen as the study site because it was one of the more acidic lakes, was small with a small drainage area, and was one of the more accessible (by foot) of the acidified lakes (see Beamish and Harvey 1972 for diagram of Lumsden and associated lakes). Extensive fisheries studies had also been conducted in Lumsden Lake and the disappearance of almost all species has been documented (Beamish and Harvey 1972; Beamish 1974).

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Materials and Methods

1973. Precipitation collectors for chemical analysis samples were set up on top of a small elevation of exposed bedrock. Precipitation was collected continually and also retrieved at least bimonthly. However, some samples were destroyed by animals. Clear polyethylene funnels supported by a 120-cm high wood frame drained into clear polyethylene bottles. Funnels with a small inside stem diameter were chosen to reduce the amount of evaporation. Collection bottles were protected from evaporation and spillage by a casing of gravel held in place by a wood frame. Distilled-water-rinsed clear polyethylene plastic bags replaced the funnels in the wooden frame for the collection of snow. Fallen snow was collected with an aluminum scoop, and a vertical section of snow was placed into acid-washed polyethylene containers and acid- and nonacid-washed clear polyethylene plastic bags. "Event" rains or snows were collected by placing the appropriate cleaned container in an open field after the event started and removing it before the end of the event.

A VanDorn water sampler was used to collect lake water in clean nonacid-washed polyethylene bottles for all determinations other than heavy metals. Acid-washed distilled-water-rinsed polyethylene bottles were used to store samples for heavy metal analysis. Inlet and outlet water samples were obtained by hand holding an empty bottle in the current such that one's hand was downstream of the bottle opening. The pH was determined and checked in a field laboratory within several hours of sampling using two pH meters. Concentrations of substances other than heavy metals were determined within the acceptable storage times according to the procedures currently in use at the Freshwater Institute (Stainton et al. 1974). Concentrations of heavy metals were determined by an ammonium pyrothidine dithiocarbonate-methyl isobutyl ketone procedure similar to the method described by Brooks et al. (1967) and VanLoon and Beamish (1977). The concentrations of these metals were determined using Perkin Elmer Model 303 and instrumentation laboratories Model 153 atomic absorption spectrophotometers. Standard reference samples of trace metals supplied by the Environmental Protection Agency, Cincinnati, Ohio, were also analyzed to evaluate the accuracy of the determinations. In an earlier study it was found that except for iron the concentrations of heavy metals in samples from these oligotrophic lakes were not affected by preserving the sample by freezing (Beamish 1974). Thus, samples that could not be analyzed for heavy metal concentrations within several days were frozen prior to analysis. As a consequence of freezing, the analyzed concentrations of iron may be low.

Lumsden Lake was estimated to have a volume of $240 \times 10^4 \text{ m}^3$, a surface area of 21 ha, a maximum depth of 22 m, and a mean depth of 7 m. Drainage area was estimated from topographical maps and by visual observation to be 98 ha. The lake surface and surfaces that drained directly into the lake were considered to represent the drainage area. Areas draining into the inlet were not added to the drainage area.

Outflow volume was determined initially using a current meter; however, after May 1972 the amount

of water passing through a "V" notch was monitored with a continuous water-level recorder and converted to volume.

The total annual amount of precipitation was estimated using the values measured by the Department of Transport records of meteorological observations in Canada at Sudbury Airport. Although this site was approximately 60 km N.E. of the lake, it provided a better estimate of total precipitation because in situ gauges were periodically overturned by animals.

The outlet volume in 1972 was $269 \times 10^4 \text{ m}^3$ and $297 \times 10^4 \text{ m}^3$ in 1973. Total annual precipitation in 1972 was $95 \times 10^4 \text{ m}^3$ and $81 \times 10^4 \text{ m}^3$ in 1973. The larger outlet volume in 1973, despite the reduced amount of precipitation, resulted from breakage of a beaver dam blocking a lake several lakes upstream of Lumsden Lake. The flushing period of the lake was estimated to be 11 mo in 1972 and 10 mo in 1973. Inlet volume was calculated as the outlet volume minus precipitation volume plus one third of precipitation volume to account for evapotranspiration (Hutchinson 1957, p. 524-525). The inlet volumes were calculated monthly and summed to be $241 \times 10^4 \text{ m}^3$ in 1972 and $249 \times 10^4 \text{ m}^3$ in 1973.

The total hydrogen ion content of the lake was calculated using an average annual pH calculated from the monthly or bi-monthly samples (Table 1). Monthly pH values were used to calculate total input of hydrogen ion to the lake from the inlet and precipitation and that being lost via the outlet. If a monthly pH value was missing, the pH of the preceding monthly sample was used. Hydrogen ion concentrations were assumed to be equivalent to hydrogen ion activity and the result of sulfuric acid additions. Hence, weights or concentrations of sulfuric acid are used when considering the effects of precipitation on lake pH. To change the pH of the lake, acid must be added to the lake either from precipitation or from inlet in concentrations higher or lower than already present. In theory, a base or buffer would perform the same function. However, additions of buffer were not important, as the precipitation and inlet waters were strongly acidic.

The net weight of acid added annually to the lake in excess of the January concentration was computed using the following formula: excess acid = (mean inlet concentration - January lake concentration) inlet volume + (mean precipitation concentration - January lake concentration) precipitation volume - (mean outlet concentration - January lake concentration) outlet volume.

The expected change in the pH of Lumsden Lake to acid loadings was estimated using a titration curve produced prior to the study by adding 0.01 N HCl to a 200-ml sample of Lumsden Lake water (Fig. 1). The amount of acid required to acidify the volume of water in the lake plus the volume added to the lake each year was determined using this titration curve. We compared the response of Lumsden Lake to additions of acid with other lakes from the Experimental Lakes Area (ELA) and a less acidic lake (George Lake) in the vicinity of Lumsden Lake (Fig. 1). In the pH range 5.2-4.8 the George Lake curve had the steepest slope, thus requiring the least acid

TABLE 1. pH (H⁺) concentrations from Lumsden Lake and precipitation. A dash indicates no data available.

	Inlet	Lake	Outlet	Precipitation		Surface snow
				Station	Event	
<i>1972</i>						
Mean ± (2 SE)	5.0 (.22)	4.8 (.14)	4.8 (.14)	4.3 (.1)	4.3 (.46)	4.5 (.12)
Range	4.7-5.5	4.7-5.3	4.7-5.2	4.1-4.4	3.7-4.8	4.0-4.7
No. samples	7	8	7	8	4	12
Total annual wt H ⁺ (kg)	30.8	48.5	38.5	54.8	—	—
<i>1973</i>						
Mean ± (2 SE)	4.8 (.06)	4.8 (.04)	4.8 (.08)	4.5 (.3) ^a	4.4 (.22)	4.3 (.10) ^b
Range	4.7-5.0	4.8-4.9	4.7-5.0	4.2-5.3	4.0-5.5	4.0-4.4
No. samples	8	8	8	9	13	7
Total annual wt H ⁺ (kg)	41.7	38.4	41.6	32.6	—	—

^aSignificantly higher than 1972 ($P \leq 0.05$).

^bSignificantly lower than 1972 ($P \leq 0.05$).

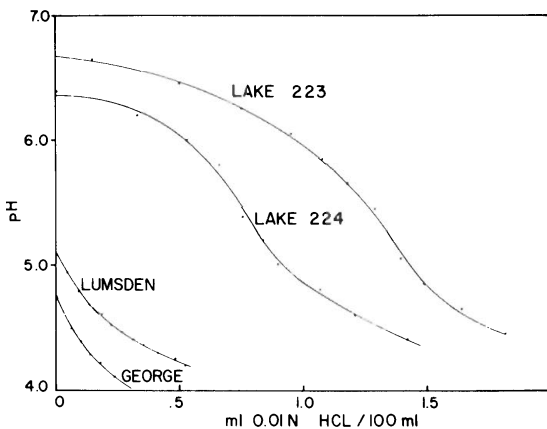


FIG. 1. Lake titration curves for two ELA and two Sudbury area Lakes.

to acidify an equivalent volume of water. The Lumsden Lake curve had the second steepest slope in this range followed by the ELA lakes, Lake 222 and Lake 224. The Lumsden Lake titration curve (Fig. 1) was used to predict the effect of acid additions to Lumsden Lake; however, other curves have been retained in this report as an example of differences among lakes. All lakes had low concentrations of major ions (Table 2).

One attempt was made to estimate the importance of accumulations of acid and heavy metals on surfaces between precipitation events. This study was conducted at a location 2 km N.W. of Lumsden Lake and while the chemical concentrations measured at this site could not be directly related to the chemistry of samples collected at Lumsden Lake, we considered that conclusions concerning the importance of accumulations of substances between precipitation

TABLE 2. Major ion concentrations (milligrams per litre) for two ELA and two Sudbury area lakes.

	Lake 224	Lake 223	Lumsden	George
Na	.7	.9	.4	.8
K	.3	.3	.3	.5
Ca	1.4	2.3	2.2	3.2
Mg	.5	.6	.6	1.0
Surface area (ha)	13.0	24.3	21	182

events were applicable to the Lumsden Lake study. After a 10-day dry period, rain was collected early in an event at the same time run-off was being sampled. Runoff was sampled by holding a nonacid-washed container under a rock shelf so that water trickled into the container without the bottle touching the rock surface.

To assess the importance of concentrations found in the Lumsden Lake study, samples from lakes and precipitation from areas remote from industrialization were collected, analyzed, and compared with the Lumsden data. Surface snow samples were collected from a remote area in northern Manitoba. Lake water was analyzed (Beamish et al. 1976) from lakes situated in the Experimental Lakes Area (ELA) in northwestern Ontario, near the Ontario-Manitoba border. The ELA lakes (Table 3) have been considered to be "unpolluted". While this may not be true, the samples probably are only very slightly altered by human wastes. The 109 lakes sampled are remote from large industrialized areas, but Barica and Armstrong (1971) have shown that, occasionally, significant amounts of substances are deposited in the area from the atmosphere.

TABLE 3. Reference concentrations for precipitation and lake water. ND = not detected.

Constituent	"Unpolluted" snow (March 1972)	ELA lakes (109) (September 1973)	Lumsden Lake avg (1972 + 1973)
pH	6.3	6.5	4.8
SO ₄ (mg/ℓ)	.2	4	10.7
Cl (mg/ℓ)	.4	.8	.9
Na (mg/ℓ)	.1	.9	.5
K (mg/ℓ)	ND	.3	.3
Mg (mg/ℓ)	ND	.6	.6
Ca (mg/ℓ)	.1	2	2.2
Cond (μmhos/cm)	< 10	19	32
TDS (mg/ℓ)	—	—	18.3
TSS (mg/ℓ)	< 3	2	1.0
Fe (μg/ℓ)	< 2	81	35
Cu (μg/ℓ)	< 1	2	4
Zn (μg/ℓ)	< 1	< 1	33
Pb (μg/ℓ)	< 1	< 1	2
Ni (μg/ℓ)	< 2	< 3	8
Cd (μg/ℓ)	—	< .1	.4
Mn (μg/ℓ)	< 1	3	257
Alk (CaCO ₃)(mg/ℓ)		10	< .5

Results

In 1972 the mean annual concentration of acid entering from the inlet converted from total weights (Table 2) to concentrations was 6.12×10^{-4} kg H₂SO₄/m³ and the outlet concentration was a slightly higher 6.88 kg H₂SO₄/m³. Since the lake concentration was 3.07×10^{-4} kg H₂SO₄/m³ at the start of the study, the additional acid in the outlet water must have been added directly into the lake from precipitation or indirectly from runoff from the surrounding watershed. (Dry or aerosol fallout and wet fallout were collected by the bulk precipitation samplers and the term precipitation as used in this report refers to both types of fallout. Event precipitation samples contain only wet fallout). Precipitation contributed a mean concentration of 27.81 kg H₂SO₄/m³ to the lake during 1972. It was calculated that 2050 kg H₂SO₄ was added to the lake and volume of water passing into the lake during 1972, in excess of the January lake concentration. A weighted titration curve (Fig. 2) was calculated for the annual volume of water in the lake and the total volume of water passing into the lake. Using the curve calculated for 1972, it was estimated that the pH change would be from 5.2 to 4.8. The actual measured change was from 5.2 to 4.7.

In 1973 the mean annual concentration of acid added to the lake from the inlet was 8.04×10^{-4} kg H₂SO₄/m³. The January lake concentration was 7.68×10^{-4} kg H₂SO₄/m³ and the mean annual outlet concentration was 6.73×10^{-4} kg

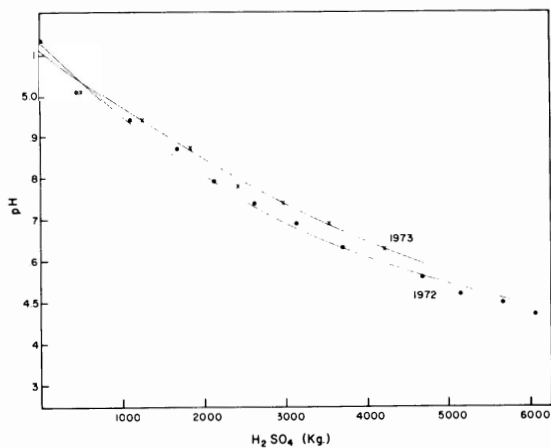


FIG. 2. Computed weight of sulfuric acid that must be added to total volume of water in and passing into Lumsden Lake to produce a change in pH.

H₂SO₄/m³. Precipitation in 1973 contained an average of 19.41×10^{-4} kg H₂SO₄ and contained significantly ($P \leq 0.05$) less acid than in 1972. The calculated excess acid added to the lake in 1973 amounted to 1314 kg H₂SO₄. Using the titration curve for 1973 that has been adjusted for the volume of water in and passing into the lake, it was estimated that the pH would change from approximately 4.8 to 4.7. The January 1973 and the December 1973 lake pH values were both 4.8; thus, there was no net change in pH in 1973. These pH values were identical to the 1973 mean

TABLE 4. Ionic balance of precipitation and lake water. NA = not applicable.

	Precipitation (mEq/ℓ) stations		Lake (mEq/ℓ) stations	
	1972	1973	1972	1973
Cation				
Ca	.025	.034	.117	.098
Mg	.007	.003	.053	.053
Na	.012	.013	.019	.020
K	.003	.003	.007	.007
NH ₄	—	—	NA	NA
H ⁺	.051	.032	.020	.016
Mn	NA	NA	.009	.009
Total	.098	.085	.225	.203
Anion				
SO ₄	.115	.094	.223	.223
Cl	.020	.020	.031	.020
HCO ₃	NA	NA	<.01	<.01
Total	.135	.114	.254	.243

annual concentrations found for the inlet, lake and outlet (Table 1).

Precipitation during 1973 was less acidic than in 1972 and reduced in volume. The mean pH of 4.5 at the precipitation stations in 1973 was significantly higher than the 1972 mean of 4.3 (Table 1). In contrast, the surface snow samples collected in 1973 were significantly more acidic than the 1972 samples ($P \leq 0.05$). Such differences emphasize that the pH of precipitation can be extremely variable. The mean pH of precipitation events and surface snows were similar to the mean monthly pH obtained from the precipitation collectors. Event samples were not available in sufficient quantity throughout the year to allow quantitative comparisons between precipitation station readings to be made. The conductivity values of event precipitation and precipitation station samples were similar, but there was some variation in total dissolved and suspended solids, indicating that the precipitation collectors probably were not contaminated except perhaps by organics such as pollen. The mean annual concentrations of cations and anions from the precipitation collectors did not balance (Table 4). A reasonable balance of anions and cations was achieved for the mean annual concentrations from lake water (Table 4); thus, the poor balance from the precipitation collectors probably was not a result of analytical errors. It is known that ammonium concentrations are high in polluted precipitation (Likens et al. 1976) ranging from 0.01 to 0.03 mEq/ℓ. Ammonium was not mea-

sured in this study and it is probable that much of the difference between anions and cations would be accounted for by this cation.

Large changes in vertical pH profiles were not observed in this study (Fig. 3) or in other studies in the same area (Beamish 1974) possibly because, in part, major loadings of acid were greatly reduced during the periods of reduced rainfall in the summer months when the lake was stratified.

HEAVY METALS

There was no significant change from 1972 to 1973 (t -test, $P \leq 0.05$) in the mean annual concentrations of heavy metals from any of the locations listed in Table 5. When concentrations of zinc, nickel, and manganese that were measured from Lumsden Lake and three other lakes during the study were compared with pH, the functions for zinc and nickel were weakly linear [$r = 0.34$ (Zn) and $r = 0.47$ (Ni)] but significant, indicating waters of lower pH contained higher concentrations of these metals. When only the Lumsden Lake samples were compared, zinc was the only heavy metal that could be shown to be significantly related to changes in pH ($P = 0.05$, $r = 0.61$). No relationship between differences in pH and manganese concentrations could be demonstrated for samples collected during this 2-yr period.

Manganese concentrations were extremely high (compared to ELA lakes) in the inlet, lake, and outlet (Tables 3, 5). These concentrations were significantly higher ($P \leq 0.01$) than the manganese from the precipitation station samples indicating that precipitation could not be considered to be an important supplier of manganese to the lake.

Concentrations of copper were high in precipitation and especially in snow (Tables 3, 5). Concentrations greater than 20 $\mu\text{g}/\ell$ were not uncommon in snow samples. In 1972 and 1973 concentrations of copper in the inlet, lake, and

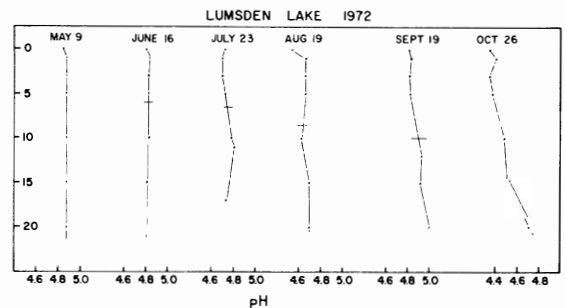


FIG. 3. Vertical pH, Lumsden Lake, 1972.

TABLE 5. Mean (± 2 SE) heavy metal concentrations (micrograms per litre).

	Inlet	Lake	Outlet	Precipitation		Surface snow
				Station	Event	
<i>1972</i>						
Zn	27.6 (3.8)	36.4 (14.6)	38.4 (12.6)	22 (12)	25 (30)	10.2 (6.4)
Cu	6 (2.6)	5 (5.6)	2 (0.4)	9 (8.6)	5	24 (16.2)
Ni	9 (1.2)	8 (1.2)	7 (2.4)	9 (5.8)	4 (1)	3 (1.6)
Fe	95 (88)	34 (20)	42 (22)	38 (22)	16 (12)	17 (12)
Mn	246 (54)	251 (22)	260 (28)	21 (14)	10	24 (14)
No. sample ^a	4-8	4-8	4-8	3-5	2	2-9
<i>1973</i>						
Zn	28.2 (3.8)	26.5 (5.6)	25.8 (6.2)	30.8 (32.8)	70.9 (41.2)	19 (20.6)
Cu	2 (1.4)	3 (2.8)	4 (5)	13 (11.8)	5 (2.6)	31 (16)
Ni	8 (0.4)	8 (0.4)	8 (0.6)	4 (2.6)	3 (1.4)	8 (3.4)
Fe	63 (18)	35 (8)	58 (42)	34 (36)	18 (6)	51 (22)
Mn	281 (50)	264 (20)	261 (28)	38 (16)	83 (11.6)	—
No. samples ^a	5-7	6-7	5-8	4-9	3-13	5-8
<i>1972-73</i>						
Pb	2	2	2	21	20	11
Cd	0.4	0.4	0.4	0.6	0.5	0.7
No. samples	7-10	9-10	8-10	10-13	11-14	13-14

^aThe number of samples analyzed for each heavy metal is reported in Beamish and VanLoon 1977.

outlet waters were highest in the early winter, probably as a result of high concentrations in snow. Precipitation was an important source of copper to the lake and watershed. The uptake of copper in soils, vegetation, or lake sediments possibly maintained a lower concentration in the lake than in the precipitation.

Concentrations of iron were extremely variable, possibly as a result of the difficulty in preserving and maintaining samples for analysis. Inlet concentrations were consistently higher than samples from other areas and iron deposits were observed on rocks in the inlet. Thus, precipitation and natural sources may contribute to the lake concentrations of iron. The concentration of iron in the lake was lower than the ELA lakes (Tables 3, 5) and thus does not appear to have been greatly altered by the fallout of acid and heavy metals.

Determinations of lead and cadmium were not made as routinely as the other heavy metals. The combined 1972 and 1973 concentrations of lead (Table 5) indicated that the inlet, lake, and outlet concentrations were low but slightly higher than the ELA lakes. Concentrations in the precipitation were much higher than lake concentrations or arctic snow (Table 3). Because the event precipitation samples were similar to the precipitation station determinations, apparently the elevated precipitation concentrations were real. Low con-

centrations in the lake indicated that lead was being removed either in the watershed or lake sediments or both.

Cadmium concentrations were also higher than in the ELA lakes (Tables 3, 5). Mean precipitation concentrations were slightly higher than lake concentrations and precipitation was apparently a contributor of cadmium to the lake. Some extremely high concentrations were measured in precipitation (1.8 and 2.7 $\mu\text{g}/\ell$) that were approaching lethal concentrations of 5 $\mu\text{g}/\ell$ for aquatic crustaceans (Biesinger and Christensen 1972).

OTHER SUBSTANCES

Mean concentrations of sulfates were higher in the lake, inlet, and outlet than in the ELA lakes and mean concentrations remained unchanged throughout this study (Tables 3, 6). Precipitation station concentrations averaged about one half of the lake concentrations and were similar to average event precipitation samples. Average surface snow concentrations of sulfate in 1972 and 1973 were almost identical but were lower than concentrations from the precipitation station. Precipitation could be an important supplier of sulfate to the lake; however, sulfate was also apparently supplied from sources other than precipitation.

TABLE 6. Mean (± 2 SE) concentrations of other substances sampled.

	Inlet	Lake	Outlet	Precipitation		Surface snow
				Station	Event	
<i>1972</i>						
SO ₄	10.8 (1)	10.7 (.4)	10.9 (.6)	5.5 (1.2)	8.8 (5.4)	3.5 (.8)
Cl (mg/ℓ)	0.9 (.2)	1.1 (.4)	1.0 (.2)	0.7 (.2)	0.6 (.2)	0.7 (.2)
K (mg/ℓ)	.26 (.06)	.26 (.04)	.26 (.04)	.13 (.06)	.13 (.04)	.12 (.02)
Na (mg/ℓ)	.51 (.08)	.44 (.08)	.45 (.06)	.27 (.18)	.28 (.24)	.21 (.04)
Ca (mg/ℓ)	2.43 (.2)	2.35 (.2)	2.39 (.2)	.5 (.42)	.55 (.26)	.53 (.46)
Mg (mg/ℓ)	.66 (.12)	.64 (.12)	.62 (.08)	.09 (.06)	.18 (.12)	.10 (.02)
Cond						
($\mu\text{mhos}/\text{cm}^3$)	31.6 (2.2)	32.5 (.4)	33.5 (1)	39 (16.4)	36.5 (23.4)	20.8 (5.4)
TDS (mg/ℓ)	19.9 (6.2)	18.3 (5)	21.1 (6.8)	23.8 (16.4)	7.3 (5.6)	6.2 (3.2)
TSS (mg/ℓ)	1.3 (1)	0.7 (.4)	1.1 (.6)	4.0 (4.6)	22.4 (25)	12.6 (11)
No. samples ^a	7-9	8-10	8-10	5-10	5-6	5-14
Total CO ₂						
($\mu\text{mol}/\ell$)	22.8 (10.6)	24.2 (9.2)	23.3 (9.4)	—	—	—
No. samples	5	5	5			
<i>1973</i>						
SO ₄ (mg/ℓ)	10.6 (.8)	10.7 (.6)	10.5 (.6)	4.5 (1)	5.6 (2.2)	34 (1.4)
Cl (mg/ℓ)	0.7 (.2)	0.7 (.2)	0.8 (.4)	0.7 (.2)	0.6 (.2)	1.7 (1.4)
K (mg/ℓ)	.26 (.04)	.27 (.04)	.25 (.02)	.11 (.02)	.13 (.08)	.09 (.02)
Na (mg/ℓ)	.45 (.02)	.47 (1)	.42 (.02)	.30 (.2)	.2 (.16)	.59 (.64)
Ca (mg/ℓ)	2.00 (.34)	1.97 (.28)	1.93 (.34)	.25 (.08)	.68 (.66)	.20 (.2)
Mg (mg/ℓ)	.56 (.08)	.65 (.12)	.57 (.06)	.04 (.02)	.08	.08 (.02)
Cond						
($\mu\text{mhos}/\text{cm}^3$)	32.9 (2.2)	31.5 (1.8)	32.4 (2)	29.3 (14.8)	43 (6.4)	33.2 (6.4)
TDS (mg/ℓ)	21.8 (6.6)	18.3 (5.2)	25.0 (2.4)	19.7 (14.2)	5.5 (1)	10.2 (9.2)
TSS (mg/ℓ)	1.6 (.8)	1.2 (.8)	1.0 (.2)	13.4 (6.8)	5.3 (3)	4.6 (2)
No. samples ^a	6-8	6-8	6-10	3-9	2-10	4-5
Total CO ₂						
($\mu\text{mol}/\ell$)	39.3 (27)	44.9 (89.8)	48.5 (21.8)	—	—	—
No. samples	4	7	4			

^aThe number of samples analyzed for each substance is reported in Beamish and VanLoon 1977.

Chloride concentrations were similar to ELA lakes and were similar in the inlet, lake, outlet, and precipitation samples (Tables 3, 6). Mean chloride concentrations were slightly lower in 1973 than in 1972. Chloride concentrations in the precipitation were only slightly higher than the northern Canadian snow sample (Table 3).

Mean potassium concentrations were similar to the ELA mean (Tables 3, 6). There was little variation in the mean concentrations of all samples between 1972 and 1973. Precipitation concentrations of potassium and sodium were about one half of the lake concentrations and were higher than the concentrations from the northern snow samples (Table 3). Mean sodium concentrations in the inlet, lake, and outlet were approximately one half of the ELA mean (Tables 3, 6).

Mean concentrations of calcium were significantly lower ($P \leq 0.05$) in the lake and inlet in 1973 than in 1972 (Table 6). Outlet concentra-

tions were also lower in 1973 but the differences were not significant. In 1972 the mean concentrations of calcium from all three types of precipitation samples were similar and the mean concentration from the precipitation station was significantly higher ($P \leq 0.05$) than the 1973 mean. The mean precipitation concentrations were about 5 times the concentrations measured in the northern snow sample (Table 3). However, precipitation did not appear to be an important supplier of calcium to the lake as lake concentrations were about 5 times higher than precipitation means. Mean lake concentrations were similar to the mean ELA concentration.

Magnesium concentrations were similar to ELA concentrations (Table 6). Precipitation concentrations were well below mean lake concentrations and did not appear to be major contributors to the lake concentration of magnesium. There was no change in the lake concentration from 1972 to 1973.

TABLE 7. Comparison of chemical composition of an event rain and of runoff during the event. (November 11, 1973).

Constituent	Rain	Run-off ^a	Run-off ^b	Run-off ^c	Run-off ^d
pH	4.2	3.8	3.8	4.0	4.4
SO ₄ (mg/ℓ)	4.0	12	14.4	10.6	9.2
Cl (mg/ℓ)	.8	.4	1	.6	.6
Na (mg/ℓ)	.2	.2	.2	.3	.2
K (mg/ℓ)	.1	.2	.2	.1	.7
Mg (mg/ℓ)	ND	.1	.1	.2	.2
Ca (mg/ℓ)	.1	.5	.5	.4	1.0
Cond (μmohs/cm)	37	97	106	74	48
Fe (μg/ℓ)	18	69	128	57	37
Cu (μg/ℓ)	6	14	6	18	4
Zn (μg/ℓ)	120	110	135	100	185
Pb (μg/ℓ)	42	18	9	29	5
Ni (μg/ℓ)	3	121	19	21	18
Cd (μg/ℓ)	.8	.7	.8	1.1	1.0
Mn (μg/ℓ)	20	20	50	20	100

^aBedrock cliff face exposed to the S.E.

^bExposed bedrock cliff face.

^cBedrock cliff face exposed to the N.W.

^dSoil covered.

Conductivity, total dissolved solids (TDS), and total suspended solids (TSS) mean concentrations were similar in the inlet, lake, and outlet in 1972 and 1973 (Table 6). TDS were slightly higher in the inlet and outlet probably as a result of increased turbulence in the shallow water. TDS concentrations from mean precipitation stations were higher than the event samples. Since there was no indication of contamination of the precipitation by other substances, the increase in TDS probably resulted from additions of organic material such as pollen.

Major ion concentrations from event precipitation samples and precipitation stations were similar indicating that contamination or excessive evaporation had not seriously altered the precipitation station samples.

Carbon dioxide concentrations were low as would be expected in such acid water (Table 6). Mean total CO₂ concentration in ELA lakes was about 150 μmol/ℓ at a pH of 6–7 (D. W. Schindler unpublished data). Mean CO₂ concentrations were significantly higher in 1973 in the lake and outlet than in 1972 ($P \leq 0.05$).

Nitrate (NO₃) was measured as 550 μg/ℓ in one event rain sample and 570 and 550 μg/ℓ in two snow samples.

RUNOFF ANALYSIS

Runoff from soilless, almost vertical rock faces (20–30 m high) was more acidic than rain (Table 7). Runoff from soil-covered bedrock was

slightly less acidic than the rain. Sulfate ion concentrations were much higher in the runoff samples than from the event rain sample. Sulfate concentrations in the runoff samples were highest from the samples of lowest pH suggesting that sulfuric acid or sulfuric acid-producing substances had accumulated on the rock surfaces during the period of no rainfall. Other major ion concentrations (Na, K, Ca, Mg, and Cl) were unchanged or changed very slightly from the runoff of rock surfaces. The runoff from soil had higher concentrations of potassium and calcium than rain samples. The conductivity of runoff from rock surfaces was double to triple the event precipitation concentration, while there was little change in the conductivity of the soil runoff. Runoff concentrations of manganese, cadmium, and zinc from rock surfaces were similar to event rain concentrations; however, concentrations of manganese and zinc were increased in the runoff from soil. Nickel was 6–7 times more concentrated in all the runoff samples than in the precipitation event. Copper was unchanged in two runoff samples but double to triple the event concentration in two of the rock runoff samples. Iron varied between 2 and 5 times more concentrated in all the runoff samples.

Concentrations of lead in runoff were lower than in the precipitation event. The greatest reduction in lead concentration occurred in the soil runoff. This uptake of lead corroborates the previous observation that lead concentrations in Lumsden Lake were much lower than the pre-

precipitation concentrations, possibly because of accumulation of lead in the watershed or lake sediments.

Discussion

The decrease in lake pH in 1972 from 5.2 to 4.7 from January to December represents a real uptake of hydrogen ion and this increase in acid content was calculated to be closely associated with additions of acid from atmospheric fallout. Three other nearby lakes showed this increase in acidity in 1972 (Fig. 4), confirming that considerable fallout of acid occurred in this area in 1972. In 1973 there was no net change in pH in the lake over the 12-mo period. Precipitation loadings of acid were significantly ($P \leq 0.05$) lower than in 1972 and the predicted change in 1973 was from 4.8 to 4.7. As in 1972 the predicted change was very close to the observed change. All of the three lakes that were monitored as part of another study (Fig. 4) decreased in acid content during 1973, confirming that a reduction in acid loading did not occur only in the vicinity of Lumsden Lake.

Clearly the acid loading calculations are approximations of the actual concentrations being added. All acid that fell out onto the lake surface and surrounding drainage area and all acid that entered from the inlet, in excess of the lake concentration, was considered to be capable of directly reducing the pH of the lake. Changes in the acidity of precipitation falling on soils prior to entering the lake or changes within the lake were not considered. The relative importance of some of these problems was reduced by the choice of the study area. The surface area of the lake accounted for 21% of the drainage area (including the lake) and much of the area surrounding

the lake consisted of exposed quartzite slopes. Some lakes in the area first showed signs of becoming acidified in the early 1960s (Beamish and Harvey 1972); thus, acid fallout probably had occurred in the area for some time allowing for a build up of acids in the soils. The lake was already acidic at the time of the study and probably many of the organisms normally found in this lake had been removed or reduced in abundance by earlier periods of low pH. Thus, many of the factors that might normally modify the acidity of precipitation may be of reduced importance in this study. Because the sampling program necessitated using the calendar year to calculate budgets, much of the December precipitation, which was mostly snow, contributed to the next year's budget. Errors caused by this method of calculation were minimized because acid loads during December did not fluctuate greatly. Finally, the calculations of the acid budget were based on bulk precipitation samples which presumably collected dry and wet fallout. Dry fallout was demonstrated to occur, and the use of bulk collectors to calculate acid fallout probably describes a "maximum" budget for the lake. While the importance of some of these factors in the acidification process can be disputed, the good correlation between the actual measured change in pH of the lake and the predicted change for 1972 and 1973 must be regarded as more than fortuitous and clearly demonstrates a close dependence and immediate response of the pH of this lake to atmospheric loading of acid.

Atmospheric fallout also contributed to the loading of heavy metals to the lake. Increased zinc concentrations were closely associated with pH and were similar to concentrations found in acid lakes in Europe and the United States (Beamish and VanLoon unpublished data; Hörnström et al. 1973; Schofield 1976). The similarity of response of lakes from different areas and the association of zinc concentration with pH suggest that increased mobilization of zinc in acid waters as well as atmospheric fallout may be important factors controlling zinc concentrations in acid lakes. The one runoff sample also indicated that increased mobilization may occur in soil runoff.

No significant linear relationship between pH and manganese was found for samples collected during the study from Lumsden Lake and three other lakes combined. Manganese concentrations were significantly higher ($P \leq 0.05$) in Lumsden and other nearby lakes, than in the precipitation. Manganese concentrations were also consistently high in the acidic lakes in Europe and the United

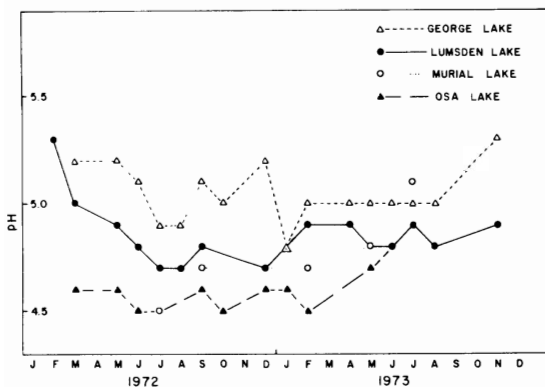


FIG. 4. pH of Lumsden and three nearby lakes during the study period.

States. Despite the absence of a relationship between pH and manganese in this study, the high concentrations of manganese in acid lakes appears to result from increased mobilization from sediments or drainage area or both. The fivefold increase in manganese concentration between runoff samples from soils and event rain or rock runoff supports the conclusion that increased mobilization of manganese in waters of low pH is an important factor controlling manganese concentrations in acid lakes.

Concentrations of sodium, potassium, magnesium, or chloride were similar to concentrations found in the ELA lakes and these major ions did not appear to have been altered by the acidification process, to the same extent that sulfate, hydrogen, and perhaps calcium ions have been altered. As would be expected alkalinity was greatly reduced in Lumsden Lake in comparison with less acidic lakes.

Copper and nickel concentrations were higher in Lumsden Lake than in samples collected from acidified Swedish lakes (Beamish and VanLoon 1977). It is known that the smelters close to Lumsden Lake emit large quantities of nickel and copper as well as sulfur dioxide (Beamish 1974). The occurrence of elevated concentrations of these metals only in the waters in Lumsden and other nearby lakes (Beamish et al. 1975a; Beamish et al. 1975b) is strong evidence that much of the material that falls out into these lakes originates locally.

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