IONIC AND MASS BALANCES IN A
DILUTE ACIDIFIED BROWN WATER LAKE

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Soldier Lake (1.98 km²) is an undeveloped, oligotrophic, brown water lake near the Halifax International Airport in central Nova Scotia, which has been acidified from leaching of pyritized metalliferous slates since the 1960s as a result of airport construction and development. Ionic and mass balances demonstrate the effects of strong mineral acids (principally H_2SO_4) and heavy metals from a small segment of the lake's catchment area.

Although based on only two weeks of detailed hydrologic and chemical sampling during the summer of 1983, the study demonstrates significant implications for loading and yield of major ions and heavy metals from widely different substrates within a single catchment.

Water chemistry and hydrology of sub-watershed components from 5-18 July, 1983 show substantial retention (30-80%) of potassium, hydrogen, aluminum, iron, and organic carbon in the lake, while sodium, magnesium, manganese, zinc, chloride and sulfate show little, if any, accumulation within the lake. Calcium shows moderate (19%) retention.

Accelerated weathering of bedrock and tills in the airport segment are reflected in elevated levels of calcium and magnesium in water samples from this portion of the catchment.

Reduction of acid loadings from the airport segment of the watershed (1.7% of the catchment area) could reduce acidic loadings of the lake by 50% and raise Soldier Lake pH by about 0.4 pH units, into the range of 4.8 to 5.0.

Soldier Lake (1.98 km²) est un lac non développé, oligotrophe dont les eaux sont brunes. Il est situé près de l'aéroport international d'Halifax, au centre de la Nouvelle-Ecosse. Depuis les années 60, le lessivage des schistes métallifères pyriteux causé par la construction et le développement de l'aéroport a provoqué l'acidification de ce lac. Les équilibres ionique et des masses démontrent les effets des acides forts (principalement H_2SO_4) et des métaux lourds prouvenant d'une petite partie du basin versant du lac Soldier.

Même si elle n'est basée que sur deux semaines d'échantillonnage hydrologique et chimique détaillé ayant eu lien pendant l'été 1983, cette étude démontre les implications importantes pour la charge et la production des ions principaux et des métaux lourds prouvenant de substrates largement différents à l'interieur d'un seul Basin.

La chimie de l'eau et l'hydrologie de segments du basin hydrologique, du 5 au 18 juillet 1983, montre une rétention substantielle (30-80 %) du potassium, de l'hydrogène de l'aluminum, du fer et du carbone organique dans le lac, alors que le sodium, le magnesium, le manganèse, le zinc, les chlorures et le sulfates montre une très faible accumulation dans le lac. La rétention du calcium est modérée (19 %).

L'atteration accélérié de la roche de fond et des argiles dans le secteur de l'aéroport est reflétée par les niveaux élévés de calcium et de magnesium dan les échantillons déau provenant de cette partie du basin versant.

Une réduction de la charge en acide provenant du secteur de l'aéroport du basin versant (1.7 % de la surface de captation des eaux) pourrait réduire la charge en acide du lac de 50 % et augmenter le pH dénviron 0.4 unité de pH, dan la zone des pH 4.8 - 5.0.

Introduction and Site Description

Soldier Lake is one of the headwater lakes of the Shubenacadie River system in

central Nova Scotia (44° 47' N, 63° 34' W) 5 km SW of the Halifax International Airport, a portion of which lies within the lake watershed (Fig. 1). The catchment (36.2 km²) is
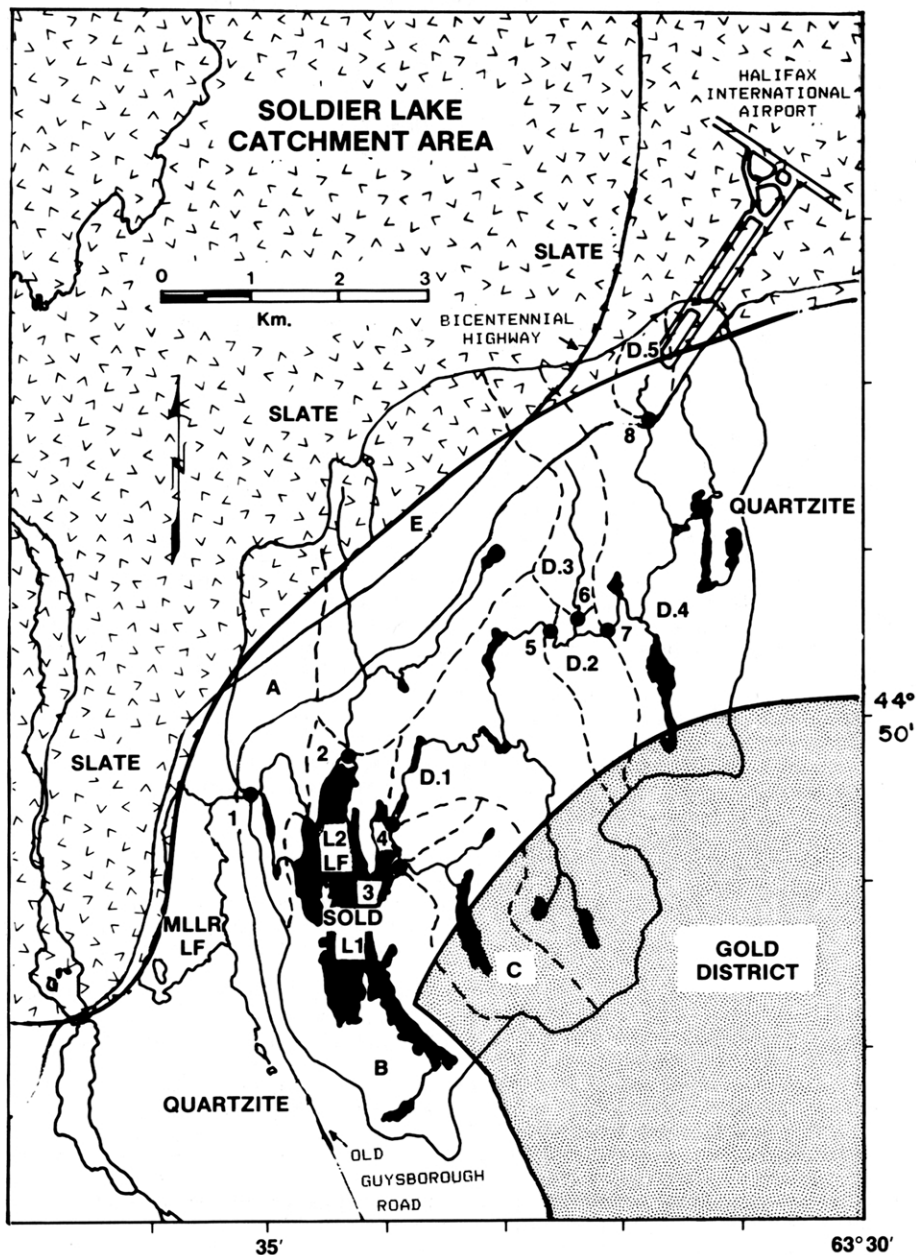

Fig. 1. Location and geology of the Soldier Lake catchment area. Sub-watersheds are identified by letter (A-E), stream sampling stations by number (1-8), and lake water samples by L1, L2, or LF (water samples by Nova Scotia Department of Lands and Forests). MLLR = Miller Lake, SOLD = Soldier Lake. Downstream Shubenacadie lakes shown but not identified.

underlain principally by quartzites of the Meguma formation, with outcroppings of the Halifax slate member in the northern (airport) portion and gold-bearing quartzites in the southern portion of the watershed. Soils are typically thin, composed principally of quartzitic till low in clay and clay minerals. In the northern portion of the catchment near the airport, slates are frequently overlain by up to 2m of a compact, silty clay till.
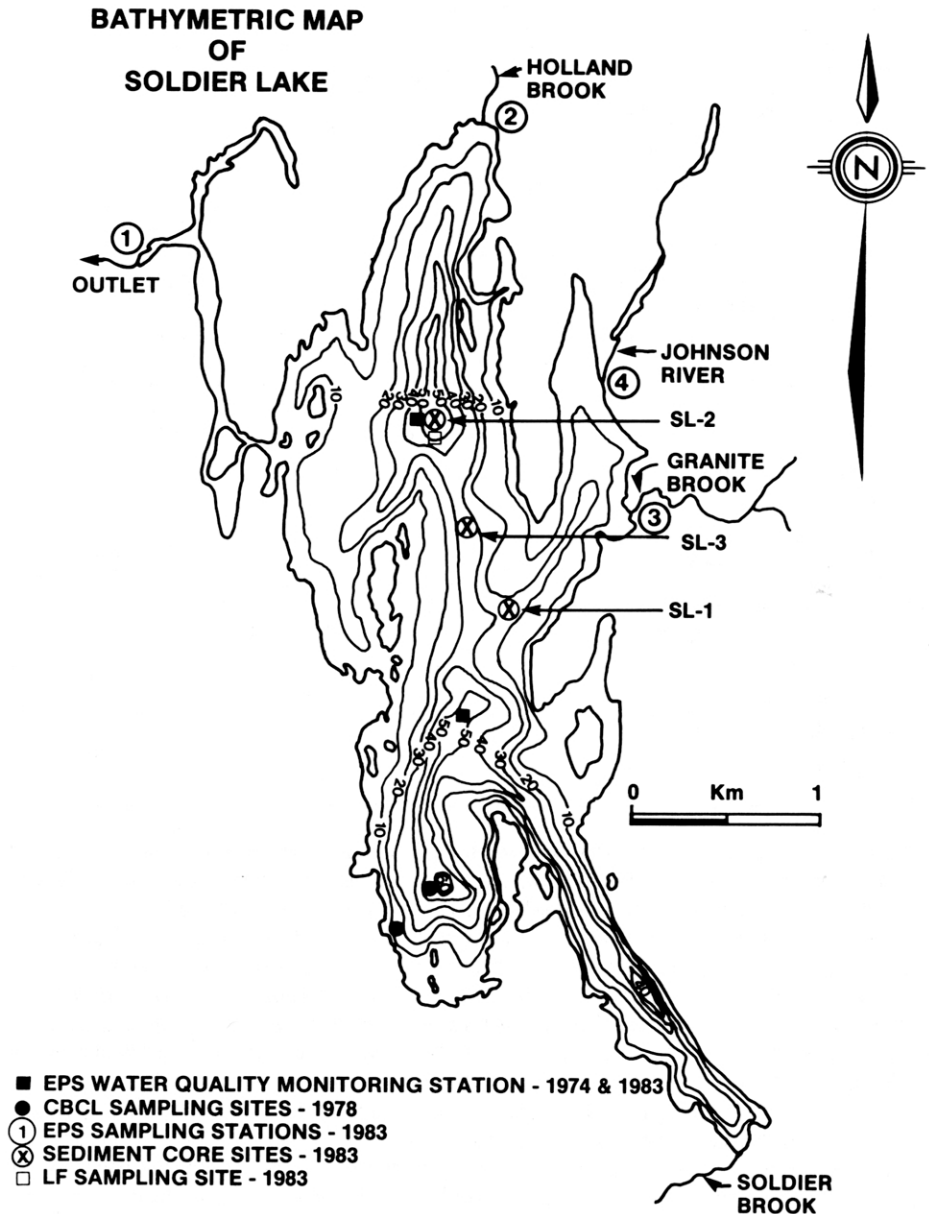
BATHYMETRIC MAP OF SOLDIER LAKE

Fig. 2.   Bathymetric map of Soldier Lake showing water and core sampling sites. Numbered open circles are EPS water sampling stations (this study).

The lake (Fig. 2) has a maximum depth of 19.5m and a volume -of 11.3×10^6 m^3. It is polymictic due to rapid flushing time and prevailing winds which parallel the long axis of the lake. Thermoclines mature between 6 and 8 m water depth. Mean annual precipitation (1961-1980) of 1400 mm gives a water retention time of approximately 4 months. Physical characteristics of the lake and sub-watersheds are summarized in Table I.

Table I Soldier Lake Catchment - Physical Data

LOCATION (Outlet) - 44° 49′ 40″ N, 63° 35′ 10″ W
     NTS - (Uniacke) 11D/13 Edition 4 MCE, Ser. A, 791
     UTM - 20T-ME-538 637

AREA:
    Catchment A_c .... 3617 ha.

          Sub-watershed A + B .... 613 ha
          Granite Brook C .... 263 ha
          Johnson River D .... 1766 ha
          Holland Brook E .... 777 ha

          Total Watershed A_w - 3419 ha

    Lake .... A_1 .... 198 ha
          Islands .... A_i .... 12 ha
          Water .... A_o .... 186 ha

    Watershed: Lake A_w / A_1 .... 17.5

VOLUME:
    Lake .... V_1 .... 11.3×10^6 m^3
    Epilimnetic volume .... V_e .... 9.4×10^6 m^3

SHORELINE LENGTH .... S_1 .... 14.5×10^3 m
    Shoreline Development .... S_d 2.9

MAXIMUM DEPTH $\overline{Z}_{max}$ .... 19.5 m
    Mean Depth $\overline{Z} = V_1/A_1$ .... 6.1 m
    Secchi Disc (18 July, 1983) .... 4.6 m

FLUSHING RATE (1983) .... 3.1 yr^{-1}

Land clearance and excavation in the Halifax slate associated with construction of the Bicentennial Highway (Rte. 102) and Halifax International Airport in the 1960s are implicated in extensive fish kills and closure of a federal fish hatchery (Thompson 1978). Fish kills in the Johnson River portion of the Soldier Lake catchment have been associated with airport runway extension (Dept. of Lands and Forests, pers. comm.).

Pollen and diatom stratigraphy of short cores (to be published elsewhere) imply a progressive acidification of the Soldier Lake system since initial disturbance by logging operations in the early part of the 19th century. Incomplete historical records indicate that the area has never supported intensive agricultural activity.

At present, the principal disturbances in the watershed include: portions of the Halifax International Airport, a 4 km segment of a major highway (Rte. 102), about 8 km of gravelled roads, and a few small homesteads and cleared areas. Potential future sources of contamination include a new high-technology industrial Park (Aerotech) in the Holland Brook and Johnson River watersheds (D and E, Figure 1).

The pollen stratigraphic record implies removal of white pine (*Pinus strobus*) during the first half of the 19th century, and subsequent high-grading for spruce,

hemlock, and perhaps yellow birch. A gradual change to a more open heath woodland is implied by increasing percentages of balsam fir (*Abies balsamea*), jack pine (*Pinus banksiana*), and Ericaceae pollen.

Although no detailed biological investigations were conducted in the watershed, the consequences of water chemistry of leachate from exposed pyrites resemble those for nearby Springfield and Drain lakes described by Kerekes, et al. (1984a).

The area immediately adjacent to the lake has been a Provincial Wildlife Park since the early part of the century. The absence of roads to the lake shore has limited access and intensive recreational use of the lake waters.

Methods

As part of a water quality sampling program by the Environmental Protection Service of Environment Canada, 35 water samples were collected from various portions of the Soldier Lake catchment from 31 May to 23 August, 1983 (approximately biweekly), Samples were analyzed at the water quality laboratories of Environment Canada in Dartmouth, N.S. Major ions, heavy metals, pH, conductivity, colour, and total organic carbon (TOC) were determined by standard procedures and sulphate by the methylthymol blue (MTB) procedure (APHA 1976). Alkalinities were determined by the Gran method following recommended procedures (Anon. 1979).

Precipitation recorded at the Atmospheric Environment Service "A" station at the Halifax International Airport (<5 km to the north) for the sampling period (May-Sept. 1983) was compared with records from the AES "A" station at Shearwater Airport ca. 20 km to the south. No significant differences were found between the two stations.

Runoff data for the sampling period were obtained from the automatic gauging station on the East River at St. Margarets Bay (01EH003), maintained by the Water Survey Branch of Environment Canada. These data are shown in Fig. 3. During the test period of 5-18 July 1983, 38.2 mm of rain fell on the system, amounting to 382 m³ ha⁻¹ on the catchment. Runoff from the East River watershed (the headwaters of which adjoin the Soldier and Miller Lake catchments to the west) amounted to 33.1 m³ ha⁻¹. These data were used to calculate input/output hydrology and mass balances for the sub-watersheds of the Soldier Lake catchment.

It can be seen from Fig. 3 that runoff for the period 5-18 July, 1983 (shown in black) was quite uniform, and for samples collected on both 5 and 18 July, water chemistry results are also quite uniform. The coefficient of variation (CV) for paired samples during this period was <5%. Variability of multiple samples (n=10) from the airport station between 31 May 1985 and 23 August 1985 ranged from 2.6% for chloride to 29% for sodium. All CV values were less than 20% at the lake outlet for the entire summer sampling period.

Water samples and temperatures at 0,6, and 12 m from two stations in Soldier Lake and a central station in Miller Lake (Fig. 2) indicate only weak thermal stratification and uniform water chemistry throughout the lakes on 18 July 1983. The CV for all lake samples was <6%. Additional water samples taken at sub-watershed outlets (Fig. 1) on 18 July 1983 form the basis for determining the mass balances described in this paper. Ionic balances were calculated for all samples (Table II) using multiple ion sums after Kerekes et al. (1982, 1984a, 1984b), and clearly demonstrate the effects of metals, especially aluminum, in acidic waters and the importance of dissolved organic carbon (DOC) in ionic balances.

Additional measured and calculated parameters, sodium: chloride ratio, calcium: magnesium ratio, theoretical pH and conductivity, calcite saturation index (CSI), as well as marine and excess sulfate are discussed elsewhere in this paper.
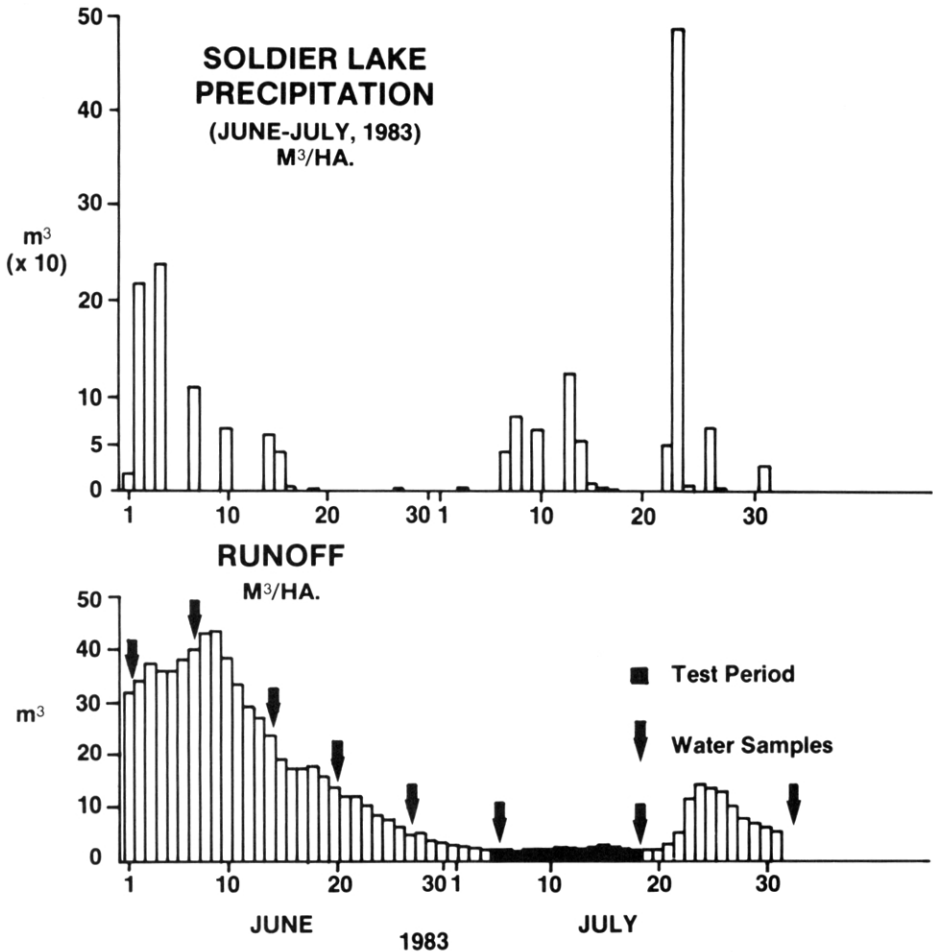
Fig. 3.   Precipitation and runoff from the Soldier Lake catchment, summer, 1983.
Water chemistry sampling dates shown by dark arrows. Ionic and mass
balance study period shown by black runoff values.

Results and Discussion

Raw water chemistry data were converted to microequivalents and are shown in
Table II. It can be seen that not only is there an excessive amount of H^+ in the airport
samples, but it is probable that accelerated weathering associated with clay tills and
bedrock has produced the elevated values of calcium and magnesium observed in
these samples.

Ionic balances for Soldier Lake and Miller Lake samples based on major ions (e.g.,
Cation 1/Anion 1, Table II) are quite acceptable (0.9 - 1.0). The airport samples,
however, imply a striking deficiency of cations, or an excess of anions (or both). The
following discussion explores the effects of H^+, DOC, and heavy metals on ion
balances.

H^+, DOC, Heavy Metals and Ionic Balances

Because of the obvious imbalances apparent for major ions in the airport samples

Table II Soldier Lake System Water Chemistry - Mean values in μeq/L except where specified

Sample Site		Airport Sta.	Johnson River	Granite Brook	Holland Brook	Soldier Lake	Soldier Outlet	Miller Lake
Number of samples		10	1	1	1	9	10	3
Sodium		135	209	83	383	213	220	345
Potassium		53.8	23.1	7.7	17.9	10.8	11.3	6.8
Calcium	(Cation 1)	1475	87.5	25.0	228	80.0	96.5	88.5
Magnesium		1402	68.9	19.7	70.5	49.2	55.7	51.6
H+		1023	66.1	19.5	0.7	25.1	24.0	6.5
Aluminum		1824	63.3	10.0	2.8	25.2	28.9	ND
Iron		687	113	10.2	23.6	6.4	9.7	ND
Manganese	(Cation 2)*	683	25.1	1.1	1.1	14.2	13.7	ND
Zinc		11.1	.9	.5	.5	.5	ND	ND
Other Metals**		16.3	.6	.2	.2	.1	ND	ND
Cations 1		4089	454.6	154.9	700.1	378.1	407.5	498.4
Cations 1 + 2		7310	657.5	176.9	728.3	424.5	459.8	498.4
Chloride		107.2	278.9	112.7	439.4	233.8	234.9	358
Sulfate***		8090	275.9	58.8	121.9	172.3	172.6	158
Nitrate	(Anion 1)	—	ND	ND	1.0	2.0	.5	.5
Phosphate		—	1.0	2.0	1.0	1.4	1.9	ND
Bicarbonate		—	0	0	164	0	0	—
Organic anion	(Anion 2)	13.9	84.5	28.7	15.6	17.3	24.3	8.6
Anions 1		8197	555.8	173.5	727.3	409.5	409.9	516.5
Anions 1 + 2		8211	640.3	202.2	742.9	426.8	434.2	525.0
Cation 1/Anion 1		.499	.818	.893	.963	.923	.994	.965
Cation 1 + 2/Anion 1 + 2		.890	1.027	.875	.980	.995	1.059	.949
Non-marine SO4 (C1)		8076	332	76	92	165	179	130
Non-marine SO4 (Mg)		7341	335	79	98	164	174	139
Marine SO4 (Cl)		11	28	12	46	28	24	37
Marine SO4 (Mg)		745	35	9	39	26	29	28
Conductivity (μS/cm)		997	90	25	95	56.2	61	71.6
Theor. Cond. (μS/cm)		1067	100	33	86	63.2	64	72.3
Alkalinity (Gran)		—	-76	-20	(164)	-17	-14	—
Calcite Sat. Index		-4.04	-3.65	-4.07	-1.05	-3.35	-3.27	-2.36
Na:Cl (Seawater = .86)		1.348	.763	.732	.869	.913	.958	.964
Ca:Mg (Seawater = .20)		1.097	1.366	1.518	3.103	1.657	1.773	2.269
Colour (T.C.U.)		10.5	225	55	15	11.5	22	5
DOC (calc. mg/L)		2.83	16.8	5.7	3.1	2.89	3.59	2.5
TOC (meas. mg/L)		—	23	10	6	4.41	5.5	—
pH (meas.)		2.99	4.18	4.71	6.18	4.60	4.62	5.19
pH (theor.)		2.31	4.31	4.35	4.82	4.34	4.73	5.73

* Mean valence of + 3 assumed
** Arsenic + Copper + Cobalt
*** MTB-SO4 - A-
— No Data
ND Not Detected

shown in Table II, the contribution of polyvalent metal ions was investigated. It should be noted that MTB sulfate results tend to overestimate sulfate in organic waters due to colour interference (Underwood et al. 1982, Kerekes et al. 1984b). Sulfate results for Soldier Lake for June, 1983 by other workers using a colour corrected method are lower than the present results by 1.18 mg L^{-1} (25 μeq L^{-1}). This difference reflects the inclusion of organic anions in the MTB sulfate determination as noted by Kerekes et al. (1984b). For Soldier Outlet samples organic anions are estimated as 24.3 μeq L^{-1}, and are equal to the observed difference in 1983 lake sulfate values. Therefore, sulfate values in Tables II and III have been corrected by the amount of the estimated organic anion. As shown in Table II, the sum of major cations for the airport station has a mean value of 4.0 meq L^{-1}, with total anions of 8.2, giving a cation: anion ratio of 0.50. Because several of the metal ions analyzed are polyvalent, a mean valence of 2, 2.5, and 3 was tested. As shown in Table II, the sum of metal cations (valence +3) is 3.2 meq L^{-1} for the airport station, yielding a total cation contribution of 7.3 meq L^{-1}, which gives a more acceptable cation: anion balance of 0.89.

The lake outlet samples, on the other hand, give a total major cation value of 0.41 meq L^{-1}, yielding a cation: anion balance of 0.99. Metal ions amount to only 0.05 meq L^{-1} which changes the cation: anion ratio to 1.06.

Although TOC values are shown in Table II, and are consistent with our derived DOC values, we have chosen to estimate organic anion [A⁻] from calculated DOC as outlined below.

Underwood et al. (1983) have observed a relationship between colour and dissolved organic carbon (DOC) as follows:

$$DOC = \frac{Colour\,(Pt/Co) + 32.59}{15.29}$$

Using formulae developed by Oliver et al. (1984) relating organic anions to pH and DOC, a value for organic anion can be estimated. Table II shows that DOC values for the airport station of 2.83 mg L^{-1} gives 13.9 μeq L^{-1} as organic anion. Similarly, for the Soldier Lake outlet samples, a DOC value of 3.59 mg L^{-1} provides an estimate of organic anion of 24.3 μeq L^{-1}. Organic anions have very little influence on the airport station ionic balances, amounting to <.2% (Cations 1+2/Anion 1).

In the more dilute Soldier Lake outlet samples, however, DOC amounts to nearly 6% of the anion sum. The cation: anion value of major ions alone (i.e., cations 1/Anions 1) is 0.99, a very acceptable ion balance. Inclusion of the organic anion (-metals) depresses the ratio to 0.94. Addition of the metal cations brings the ion balance to 1.06. It can be seen (Table II) that in the outlet waters, the organic anions account for nearly 50% of the metal ion equivalents (24.3:52.3).

Measured vs Theoretical pH and Conductivity, Marine vs Excess Sulfate

Table II also demonstrates that theoretical pH = (-Log [(Σ anions - (Σ cations - H⁺])) and theoretical conductivity (Σ eq. cond. of each ion (25° C) x conc. (meq L^{-1})) show an acceptable level of agreement in most cases. Differences in theoretical and measured pH average <5% of total cations in all samples except those from Granite Lake Brook (14%) and the airport (53%).

Marine and excess (non-marine) sulfate were determined from magnesium: sulfate and chloride: sulfate ratios in seawater as described in Underwood et al. (in press) and Ogden (1980, 1982). Overestimation of marine sulfate for the airport station by magnesium: sulfate ratio reflects the other terrestrial sources of magnesium, presumably from weathering of tills and bedrock. Elevated concentrations of magnesium and calcium are characteristic of the very acidic drainage leaving the airport at a number of locations (unpublished data, EPS). With the exception of the airport station, excess sulfate data, corrected by magnesium: sulfate ratio in sea water, the

mean value of marine sulfate contribution (25.7 ± 9 μeq L^{-1}) reflects the >25 km distance of the Soldier Lake catchment from the Atlantic coast (Ogden 1982).

The Granite Brook sample (Sta. 3, sub-watershed C, Fig. 1) is considered to represent "background" water chemistry because of remoteness and lack of roads or development within the watershed. Non-marine, or excess sulfate from this watershed is 76-79 μeq L^{-1} (Table II), or about 7X greater than marine sulfate and is presumably produced by natural weathering, proximity to the Halifax International Airport and urban emissions from Halifax-Dartmouth, as well as distant emissions. Underwood et al. (in press) review the water chemistry of 234 rural Nova Scotian lakes and found the average ratio of non-marine: marine SO_4 to be about 3.

Extraordinarily high excess sulfate values from the airport station reflect oxidation of metalliferous pyrite in Halifax slate exposed by airport development which substantially influences downstream and lake water marine and excess sulfate ratios.

Calcite Saturation Index

Conroy et al. (1974) present a formula relating pH, calcium and alkalinity which yields a logarithmic value implying sensitivity to acidification. CSI values were determined from the equation;

$$CSI = \log \left(\frac{[Ca] \times [HCO_3]}{[H]} \right) + \log \left(\frac{K_2}{K_s} \right)$$

where K_2 is the acid dissociation constant of bicarbonate, K_s is the solubility product of calcium carbonate, pH = -log $[H^+]$ is assumed, and $[HCO_3]$ = [Alk] + [H], which permits calculation of CSI values corresponding to negative alkalinities and assumes that bicarbonate is the dominant base (Wiltshire and Machell, 1981). Alkalinity values for Miller Lake were obtained from unreported outlet data and values for the airport station were estimated from pH.

Values <-3.0 imply a loss of alkalinity and probable failure of fish survival or reproduction. Values >-2.0 imply a reserve of alkalinity and buffering capacity in the soil-water system with decreasing sensitivity to acidification and reduced threat to fish stocks (Malmer 1976).

On this scale, it can be seen in Table II that Holland Brook (CSI = -1.05) is the only station in the entire system that may be considered suitable, or safe, for fish stocks. Parenthetically, it is interesting to note that this is the only station where trout (*Salvelinus fontinalis*) have been observed to spawn successfully in recent years (Dept. Lands and Forests, pers. comm.).

The airport samples are uniformly less than -4.0, and a review of the water chemistry at that station (Table II) implies an extremely hostile environment. The effects of airport drainage persist throughout the lake as the mean Soldier Lake outlet CSI values of -3.27 (n=10) imply substantial risk, especially to salmonids.

Interestingly, the epilimnetic CSI value of -2.36 for Miller Lake may indicate photosynthetic bicarbonate alkalinity returning to Miller Lake, an inference supported by the occurrence of positive Gran alkalinities only during the summer months (unpubl. EPS data) which is also consistent with observations by Schindler (in press) on sources of alkalinity in acid-stressed lakes.

Mass Balance of Major Ions

Table III and IV summarize the hydrology and materials balance for the Soldier Lake catchment for the period 5-18 July 1983. Table III contains the raw data for each of the sub-watersheds sampled in this study.

Individual ions are shown as concentrations (mg L^{-1}), loadings (kg to system) and yield (g ha^{-1}) for the period 5-18 July 1983. The portions of the watershed bordering the lake without defined inflows (Fig. 1, A & B) amount to ca. 17% of the catchment.

Table III Soldier Lake Hydrology and Materials Budget 5-18 July, 1983

Subwatershed (see Fig. 1)		Runway (D.5)	Johnson River (D)	Granite Brook (C)	Holland Brook (E)	D + C + E	A + B (est.)
Sample Station		Sta. 8	Sta. 4	Sta. 3	Sta. 2	—	—
Area (% of total)		61 ha (1.7%)	1766 ha (48.8%)	263 ha (7.3%)	777 ha (21.5%)	2806 ha (77.6%)	613 ha (16.9%)
Water Output (1000 m³)		2.02	58.5	8.7	25.7	92.9	20.3
SODIUM							
conc.	mg/l	4.4	4.8	1.9	8.6	—	—
load	Kg	8.9	281	17	226	524	40
yield	g/ha	146	159	64.6	291	186.7	65.3
POTASSIUM							
conc.	mg/l	2.5	.9	.3	.7	—	—
load	Kg	5.1	52.7	3	18	73.7	7.1
yield	g/ha	83.6	29.8	11.4	23.2	26.2	11.6
CALCIUM							
conc.	mg/l	35	1.8	.5	4.6	—	—
load	Kg	70.7	105.3	4	118.2	227.5	9.5
yield	g/ha	1159	59.6	15.2	152.1	81.1	15.5
MAGNESIUM							
conc.	mg/l	25.3	.8	.24	.9	—	—
load	Kg	51.1	46.8	2	23.1	71.9	4.8
yield	g/ha	838	26.5	7.6	29.7	25.6	7.8
H+							
conc.	mg/l	1.413	.066	.0195	.001	—	—
load	Kg	2.85	3.9	.17	.026	4.1	.4
yield	g/ha	46.7	2.2	.6	.033	1.5	.7
ALUMINUM							
conc.	mg/l	18.1	.57	.09	<.025	—	—
load	Kg	36.6	33	.8	<.6	33.8	1.9
yield	g/ha	600	18.7	3	<.8	12	3.1

IRON							
conc.	mg/l	11.9	2.12	.19	.44	—	—
load	Kg	24	124	1.7	11.3	137	4
yield	g/ha	393	70	6.5	14.5	48.8	6.5
MANGANESE							
conc.	mg/l	—	.46	.02	.02	—	—
load	Kg	—	26.9	.2	.5	27.6	.5
yield	g/ha	—	15	.8	.6	9.8	.8
ZINC							
conc.	mg/l	.31	.02	.01	<.01	—	—
load	Kg	.63	1.2	.1	<.3	1.3	.2
yield	g/ha	10.3	.7	.4	—	—	.3
SULFATE**							
conc.	mg/l	452	13.2	2.8	5.9	—	—
load	Kg	933	722	24.4	152	948	56.8
yield	g/ha	15299	437	92.6	195	338	92.7
CHLORIDE							
conc.	mg/l	4	9.7	4	15.6	—	—
load	Kg	8.1	567	34.8	401	1003	82
yield	g/ha	133	321	132	516	357	134
ORG. CARBON							
conc.	mg/l	2.79	16.9	5.73	3.11	—	—
load	Kg	5.6	983	50	80	1113	116
yield	g/ha	92	557	190	103	397	190

* Based on runoff est. 33.1 m^3 ha^{-1} (see text).
** MTB-SO_4 - A

Table IV Summary Hydrology and Materials Balance, Soldier Lake, N.S., 5-18 July, 1983

		SOLDIER IN 3419 ha (94.5%) 188.8*	SOLDIER OUT (Sta. 1) 3617 ha (100%) 119.7	Input - Output Lake load in Kg	% Retention in Lake
SODIUM					
conc.	mg/l		4.6		
load	Kg	564	551	13	2.3
yield	g/ha		152		
POTASSIUM					
conc.	mg/l		.4		
load	Kg	81	47.9	33	40.7
yield	g/ha		13.2		
CALCIUM					
conc.	mg/l		1.6		
load	Kg	237	191.5	46	19.4
yield	g/ha		52.9		
MAGNESIUM					
conc.	mg/l		0.7		
load	Kg	76.7	85.0	8.3	10.8
yield	g/ha		23.5		
H+					
conc.	mg/l		.025		
load	Kg	4.5	3.0	1.5	33.3
yield	g/ha		.8		
ALUMINUM					
conc.	mg/l		.2		
load	Kg	35.7	24	11.7	32.8
yield	g/ha		6.6		
IRON					
conc.	mg/l		.18		
load	Kg	141	21	120	85.1
yield	g/ha		5.8		
MANGANESE					
conc.	mg/l		.26		
load	Kg	28	31	-3	(10.7)
yield	g/ha		8.6		
ZINC					
conc.	mg/l		<.01		
load	Kg	<1.5	<1.2	<.3	—
yield	g/ha		—		
SULFATE**					
conc.	mg/l		8.8		
load	Kg	1005	1053	-48	(4.8)
yield	g/ha		291		
CHLORIDE					
conc.	mg/l		8.1		
load	Kg	1085	970	115	10.6
yield	g/ha		270		
ORG. CARBON					
conc.	mg/l		3.77		
load	Kg	1229	451	778	63.3
yield	g/ha		125		

* NOTE: SOLDIER IN includes watershed Runoff (113.2 DAM³) plus precipitation on lake (75.6 DAM³).
Difference (69.1 DAM³) is attributed to evaporation from the lake surface (3.5 cm) for the sample period.
** MTB - SO₄ - A-

Loading and yield values were calculated from measured Granite Brook samples. We have termed this portion the "residual watershed." These values are discussed for each of the ions in the following section of this paper.

Table IV summarizes the sub-watershed contributions to Soldier Lake (SOLDIER IN). The terrestrial (watershed) portion of the catchment is 3419 ha (94.5%) and system total precipitation input is 188.8 dam^3. SOLDIER OUT summarizes the system outlet hydrology (119.7 dam^3 which includes lake evaporation of 3.5 cm, confirmed by readings from a standard evaporation pan maintained by the Halifax Urban Watershed Program for the period 5-18 July 1983; HUWP, D. Thirimurthi, pers. comm.). Data are shown as mean concentration, loading, and yield, based on outlet water chemistry.

Table IV also reviews the fate of major ions in the Soldier Lake system for the two-week study period, and indicates that the lake is a major sink for potassium, hydrogen, aluminum, iron, and organic carbon (30-80%). Lesser amounts of calcium (19%) are retained within the lake. Sodium (2%), magnesium (11%), and chloride (11%), are retained poorly, if at all. The implication that the lake is a source for manganese (-3 kg) or sulphate (-48 kg) is not acceptable, as both the number of samples and the brief sampling period (two weeks) are insufficient to provide confidence in such small differences (5-11%).

The following considers each of the individual ion concentrations, loads, and yields throughout the system:

Sodium

The yield of sodium from the Granite Brook sub-watershed (C) of approximately 65 g ha^{-1} presumably represents normal or background values from atmospheric input of marine aerosols and rock weathering (considered to be a minor source in Meguma bedrock). Elevated concentrations and yields from the Runway area (Sta. 8, Fig. 1), Johnson Brook (Sta. 4, Fig. 1), and Holland Brook (Sta. 2, Fig. 1) reflect seasonal leaching of road salt applied to the Bicentennial Highway and the Goffs/Guysborough (gravel) road which crosses the northern part of the watershed.

Potassium

An external source for potassium is possibly associated with the inferred calcitic and dolomitic sources in sub-watersheds E and D referred to previously. In any event, the load to Soldier Lake (74 kg) from 78% of the total watershed is sharply diminished in the lake (48 kg at the outlet) implying that the lake is a sink for potassium, a property earlier noted by Hart and Ogden, (1977) for the Fink Cove system.

Calcium

Loading and yield calculations for this element imply about 19% removal of calcium in the lake. If the background concentration of calcium is about 0.5 mg L^{-1} (Granite Brook, sub-watershed C), system loading to the outlet should be about 52 kg. Because the drainage from sub-watersheds D and E is a source of calcium, the total system input is ca. 237 kg. The outlet value, 191.5 kg indicates retention (presumably in lake sediments) of about 19% of the calcium entering the lake during the study period.

Magnesium

Background (Granite Brook) yield values (7.6 g ha^{-1}) imply a normal loading of ca. 28 kg at the lake outlet. The fact that the sum of measured inputs to the lake (77 kg) is similar to the output value (85 kg) implies that little, if any, magnesium is retained in the system.

H+

System loading values (>4.5 kg in, vs. 3.0 kg out) indicate consumption of at least 33% of the H+ entering the system. Interestingly, system yield at the outlet (.8 g ha^{-1}) is only 25% greater than from the undisturbed area represented by Granite Brook (.6 g ha^{-1}).

A mass balance model, based on water chemistry input and output values using data from a "background" watershed source (Granite Brook) implies that restoration of the Runway segment of the Johnson River system to output loading values from the Granite Brook system would reduce the H$^+$ loading from the Johnson River by at least 50% and of the entire Soldier Lake system by 25%. A reduction in [H$^+$] of this magnitude could raise Soldier Lake pH values by 0.4 pH units, into the range of pH 4.8 to 5.0.

Sulfate

Despite a prodigious yield of sulfate from the airport runway segment of nearly 15 kg ha^{-1}, the outlet loading is only about triple the inferred background value based on Granite Brook (92.6 g ha^{-1} x 3617 ha = 335 kg). It can be seen that about 72% of the sulfate delivered to Soldier Lake is from sub-watershed D, and that a substantial amount of sulfate is retained in the Johnson Brook segment of the watershed. Total sulfate inputs and output values imply little change in sulfate loading within Soldier Lake during the study period.

Chloride

Since the residual watershed (613 ha) would presumably add no more than about 81 kg (based on Granite Brook yield), the difference in system loading (1085 kg) and Outlet (980 kg) is not considered significant.

Aluminum

With a possible total system loading of about 36 kg of aluminum, an outlet value of 24 kg indicates retention of ca. 33% within the system. It is also clear that the Johnson Brook segment (48% of the catchment area) provides >90% of the aluminum delivered to the lake.

Iron

Total system loading for iron is about 141 kg, based on estimates from the residual watershed using Granite Brook yield (6.5 kg from 613 ha). Since the outlet apparently releases only 21 kg, more than 80% of the iron is presumably precipitated within the lake.

Manganese

The residual watershed contributes about 0.5 kg of manganese to the system for a total input of approximately 28 kg. Outlet values of 31 kg imply no retention of manganese within the Soldier Lake system and lead to the testable hypothesis that changes in iron and manganese ratios in sediments may reflect varying H$^+$ loadings from disturbance within the watershed.

Zinc, Cobalt, Copper, and Arsenic

Analytic values for these substances are in general below detection limits at the outlet, and in most of the lake input samples. An anomalous value of 0.13 mg L^{-1} of arsenic at the outlet is not accepted because it implies a system loading of 15.6 kg, for which the only apparent source, the runway segment (D.5) is clearly inadequate (0.24 kg).

Conclusions

Water chemistry results in summer 1983 show that the Johnson River sub-watershed of Soldier Lake is primarily responsible for acid and heavy metals loading of Soldier Lake. The Johnson River watershed (ca. 50% of the Soldier Lake catchment) contributed approximately 85% of the H^+, 92% of the aluminum, and 88% of the iron entering Soldier Lake during a two-week period in July 1983. Also, 63% of the H^+ loading came from 1.7% of the catchment area (Airport Station).

Of a total of 141 kg of analytically detected iron entering Soldier Lake, only 21 kg were accounted for at the outlet, implying substantial retention within the lake, presumably by coprecipitation with organic anions of which 63% (778 kg) were retained.

This study clearly demonstrates that Johnson River is the principal source of acid and heavy metals to the Soldier Lake system, and that control measures implemented in a small segment of the watershed (Airport Station = 1.7% of catchment area) could substantially reduce acid loadings to the entire system.

These results also imply that future development of the Aerotech Park will require careful management to prevent further deterioration of an already severely stressed aquatic ecosystem.

Acknowledgements

Literature Cited

American Public Health Association. 1976. *Standard Methods for the Examination of Water and Waste Water.* 14th ed. American Public Health Assoc., Washington, D.C.

Anonymous. 1979. Determination of the susceptibility to acidification of poorly buffered surface waters. Ontario Ministry of the Environment, Rexdale, Ontario. 21 p.

Conroy, N., Jeffries, D.S. and **Kramer, J.R.** 1974. Acid shield lakes in the Sudbury, Ontario region. Pp. 45-60. *in* Zojic, J.E., Kosanic, N., (eds), *Proc. 9th Symp. Water Poll. Res. Canada.*

Hart, W.C. and **Ogden, J.G. III.** 1977. Precipitation and nutrient export from a small coastal ecosystem in Nova Scotia. Pp. 153-165. *in* Correll, D. (ed), *Watershed Research in Eastern North America.* Vol. I. Smithsonian Inst., Washington, D.C.

Kerekes, J.J., Howell, G., Beauchamp, S. and **Pollock, T.** 1982. Characterization of three lake basins sensitive to acid precipitation in central Nova Scotia (June, 1979 to May, 1980). *Int. Revue ges. Hydrobiol.* 67:679-694.

Kerekes, J.J., Freedman, B., Howell, G. and **Clifford, P.** 1984a. Comparison of the characteristics of an acidic eutrophic and an acidic oligotrophic lake near Halifax, N.S. *Water Poll. Res. J. Canada* 19:1-9.

Kerekes, J.J., Howell, G. and **Pollock, T.** 1984b. Problems associated with sulphate determination in colored humic waters in Kejimkujik National Park, Nova Scotia (Canada). *Verh. internat. verein. Limnol.* 22:1811-1817.

Malmer, N. 1976. Acid precipitation. Chemical changes in the soil. *Ambio.* 5:231-234.

Ogden, J.G. III. 1980. Comparative composition of continental and Nova Scotia precipitation. Pp. 126-127 *in* Drablos, D. and Tollan, A. (eds), *Proc. Int. Conf. Ecol. Impact Acid Precipitation.* SNSF Project, Norway.

Ogden, J.G., III. 1982. Seasonal mass balance of major ions in three small watersheds in a maritime environment. *Water, Air, and Soil Pollution* 17:119-130.

Oliver, B.E., Thurman, E.M. and **Malcolm, R.L.** 1984. The contribution of humic substances in the acidity of colored natural waters. *Geochim. et Cosmochim. Acta* 47:2031.

Schindler, D.W. 1986. The effects of acid precipitation on *in situ* sources of alkalinity in lakes. *Water, Air, and Soil Pollution* (in press).

Thompson, B.D. 1978. An investigation of Meguma bedrock leaching in the Shubenacadie-Stewiacke river basin. Tech. report #18, Shubenacadie River Basin Board, 48 p.

Underwood, J.K., McCurdy, R.F. and **Borgal, D.** 1983. Effects of colour interference on ion balances in Atlantic Canada lakewaters using methylthymol blue SO_4 results: some preliminary observations. Pp. 1811-1817 *in* Kerekes, J.J. (ed), Workshop Proceedings, Kejimkujik Calibrated Catchments Program on the Aquatic and Terrestrial Effects of the Long-Range Transport of Air Pollutants. Env. Protection Service, Dartmouth, N.S.

Underwood, J.K., Ogden, J.G. and **Smith, D.L.** 1986. A review of contemporary chemistry of Nova Scotian lakes. *Water, Air, and Soil Pollution* (in press).

Wiltshire, J.F., and **Machell, J.R.** 1981. A study of acidification in sixteen lakes in mainland Nova Scotia and southern New Brunswick; a preliminary report. EPS-5-AR-81-4, Environmental Protection Service, Atlantic Region, Halifax, Nova Scotia.