

Focus on: Catchment Pathways and Controls: A Geochemical Bridge to Applied Environmental Studies — Examples from Nova Scotia



By Peter J. Rogers

INTRODUCTION

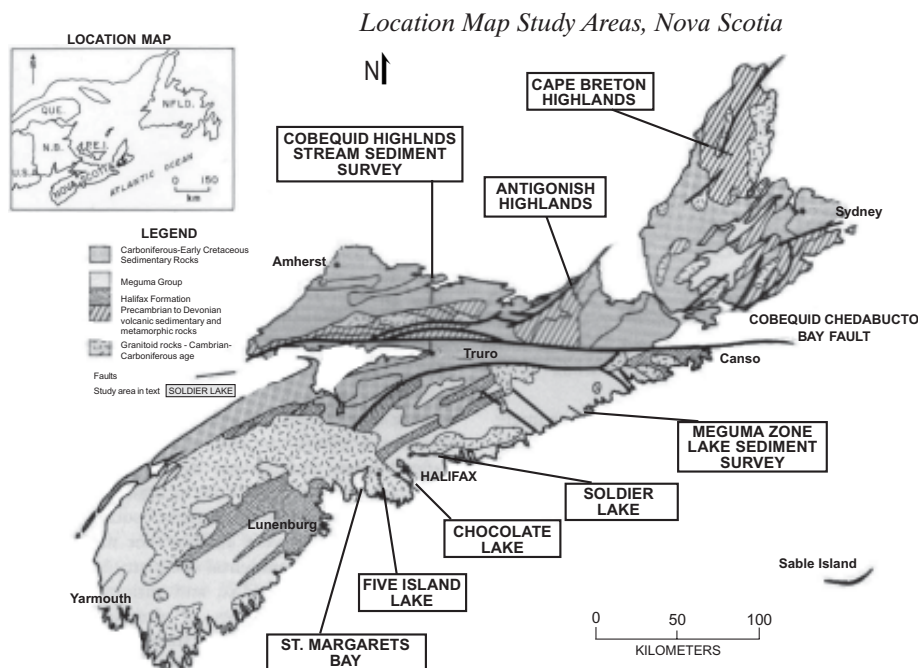
Modern man is now the most potent geologic force on this planet and it is gratifying to see that we - the Association of Applied Geochemists - are facing up to this reality by increased emphasis on environmental studies in the journal (GEEA Volume 1 part 1 2001, Volume 2 parts 2 and 3, 2002). The extent of man's activities is manifest in a number of ways, one of the most important of which is a chemical one. This provides a great opportunity for the Association to make a real difference, as we are a group of scientists with extensive knowledge of the movement, classification and determination of chemical pathways within the environment in which we all live.

Nova Scotia presents a good example of the separation between - and the potential synergy - of the disciplines of exploration and environmental geochemistry found in most jurisdictions in Canada, and I suspect the rest of the world. Nova Scotia has approximately 970,000 people inhabiting an area of about 53,000 km² a population density of around 18 that is quite high by Canadian standards. The economy is largely resource-based with fishing, forestry, agriculture, mining and manufacturing with a marked expansion noted since the mid 1950s resulting in ever increasing landscape pressure. Nova Scotia possesses extensive databases of chemical and biological information from lakes, streams, soils, bedrock, tills and plants in various regions of the province (Rogers and Lombard, 1991).

Most environmental studies in Nova Scotia have focussed on acidic precipitation, acid drainage and intracoastal pollution due to the impact of the oxides of nitrogen, sulphur and organic molecules on ecosystems. These studies indicate a significant man-made

(anthropogenic) component to the environment of Nova Scotia (Rogers and Ogden 1992).

In Nova Scotia most geochemical exploration activity has concentrated on stream or lake drainage systems by sampling sediments and (or) surface waters. Lake and stream catchment basins are important repositories of geochemical information concerning the composition and characteristics of their drainage areas. Modern drainage systems can be considered as mass storage devices (Ogden et al., 1988) which contain the 'geochemical genetic code' for each catchment. The extension of the catchment basin concept to exploration geochemistry (Bonham-Carter et al., 1987) forms a potent



bridge to environmental geochemistry. This paper relates the results of several applied geochemical studies of catchment basins, which illustrate the potential synergy and application of applied exploration geochemical methods to environmental issues in Nova Scotia and elsewhere.

METHODS

The exploration geochemical samples were collected from lakes and streams using field sieving (-1 mm) for streams and helicopter grab sampling for lakes (Rogers and Lombard, 1991). In the lake studies, sediment-water interface samples from short piston cores (coring drives were initiated 10-40 cm above sediment and penetrated 40-80 cm into sediment) were collected near defined inlets and outlets. Surface water samples were collected at lake inlets and outlets. Lake bathymetry was compiled using a boat-mounted sounder. All water and sediment samples were analyzed for major ions and heavy metals using the Environmental Chemistry Laboratory of Victoria General Hospital, Halifax, and various commercial laboratories including facilities of the Geological Survey of Canada (Rogers and Lombard, 1991). At each lake coring station a sub-sample was taken with a 1.0 cm³ volumetric piston

continued on page 13

Focus on: Catchment Pathways and Controls...

continued from page 8



sampler (Rogers and Ogden, 1992). The sub-samples were placed in snap-cap vials before processing for dry and ash weight determinations and microfossil analysis. Sediment long cores were recovered using a modified Livingstone piston sampler in 1.0 m contiguous segments. Core segments were sealed in the field and returned for storage at the laboratory. Sediment density and organic matter content were determined on the sub-samples of sediment cores. Cores were sealed in plastic stretch wrap after sampling and archived at 5°C. For lake sediment samples, organic matter was determined by loss on ignition (450°C > 6 hr) from oven-dried sub-samples ground to pass a 100 mesh screen (1.0 cm³ at 105°C for 24 hr). Chemical analysis was achieved using a combination of methods, including Atomic Absorption, Neutron Activation and Inductively Coupled Plasma (Rogers and Lombard, 1991; Rogers and Ogden, 1992). Preparation of samples for microfossil analysis followed standard procedures and involved wet sieving at 125 µm, deflocculation in 10% KOH, demineralisation in 48% HF, acetolysis (acetic anhydride: concentrated sulphuric acid 9:1) for pollen, and digestion with H₂O₂ (30%) and concentrated H₂SO₄ for diatoms.

Study Example 1:

Estimating, Modeling and Monitoring Land Use Impacts from Induced Hydrogen Ion or Proton Imbalance: Soldier Lake Geochemical Gradients Study.

RATIONALE

PostSecond World War cumulative acidification of lakes in Nova Scotia has been noted in numerous studies (Peterson et al., 1986; Gorham et al., 1986) including those at Soldier Lake (Figure 2). Soldier Lake is a large, deep (20m) and highly oligotrophic brown water lake of about 0.8 km² (198 ha) in surface area with a catchment basin of around 36.2 km² (Ogden and Rogers, 1988). The catchment geology includes both Halifax Slate and Quartzite of the Meguma Group, which intersects portions of the Halifax International Airport and the Bicentennial Highway (N.S. Route 102). Since the 1960's, construction activities at the airport and along the Bicentennial Highway exposed highly fractured, mineralised and numerous pyritic units of Halifax Slate. Oxidation and leaching of these sulphide minerals has created an acidic leachate with a pH of 2.9, which resulted in fish kills, closure of a federal fish hatchery and relocation of a municipal water supply at Enfield. The Johnson River sub-watershed (D, Fig.2) constitutes 49% of the system watershed and has an average inlet pH of 4.2. In comparison, the airport runway segment (Sta. 8, Fig. 2) covers 1.7% of the catchment area, yet is responsible for 63% of the total hydrogen ion loading to Soldier Lake (Ogden and Machell, 1985).

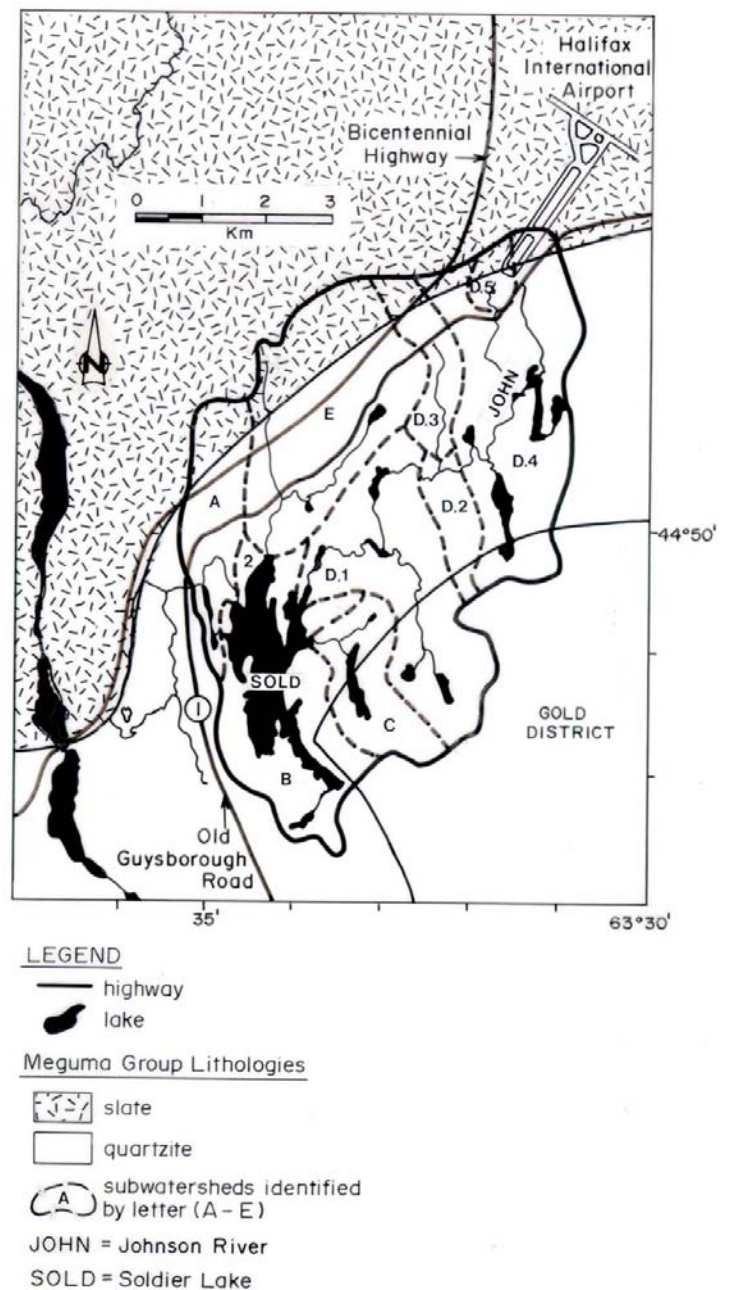


Figure 2. Location, geology, and catchments of the watershed of Soldier Lake, Sub-Watersheds are labelled A to E.

continued on page 14

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Focus on: Catchment Pathways and Controls...

continued from page 13



RESULTS

In 1987, nine water samples were taken as short cores from just above the sediment-water interface below the main upstream inlets in the northern part of the lake system (Figure 3). Stations 1, 4 and 5 below the Johnson River inlet show an acidic pH from 4.2 to 4.5 with a corresponding drop in Fe and Al and with higher Zn in the sedimentary column which indicate a mobility barrier related to differing pH of the lake bottom (Figure 4). Although aluminium shows a slight increase in deposition from pH 4.2 to pH 6.2, there is nearly a three-fold increase in iron deposition at the higher pH values. Virtually all of the aluminium and at least 88% of the iron comes from the Johnson River watershed (inlet pH 4.2) according to mass balance studies reported in Ogden and Machell (1985) for a two-week period in July, 1983 which also showed that 33% of the aluminium and 85% of the iron entering the lake was retained in the lake. In contrast the Holland Brook inlet shows a more basic profile, with pH from 4.9 to 6.2 and increased Fe and Al and lower Zn compared to the Johnson River inlet (Table 1). The increased hydrogen ion concentration and acidic pH values of around 4.5 are attributed to a build-up of excess protons from the acidified drainage due to oxidation of pyritic slate exposed during the construction of the airport runway.

Repeat sampling in 1990 detected no gradients and an increased pH of outlet water by 0.5 pH units. This

a)

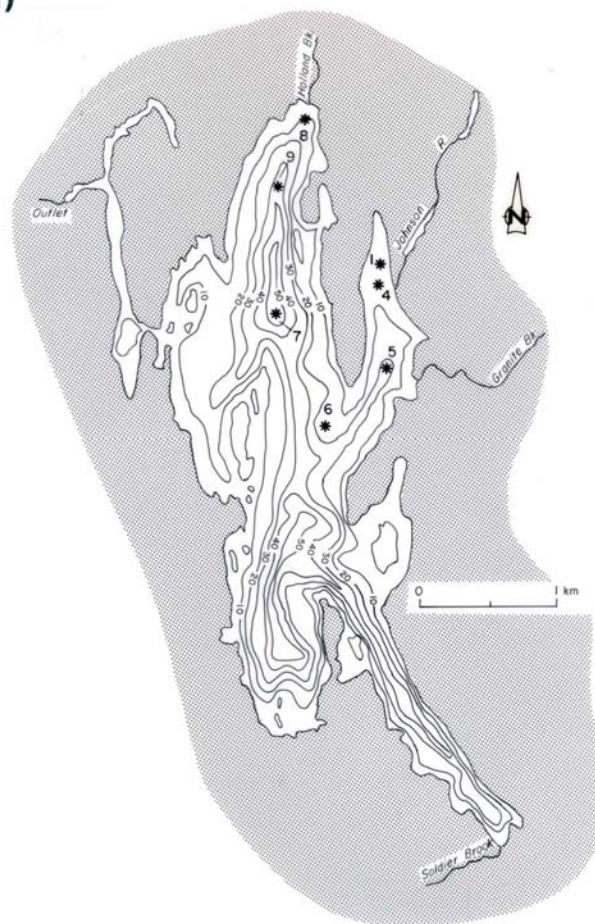


Figure 3. Sample locations and bathymetry of Soldier Lake.

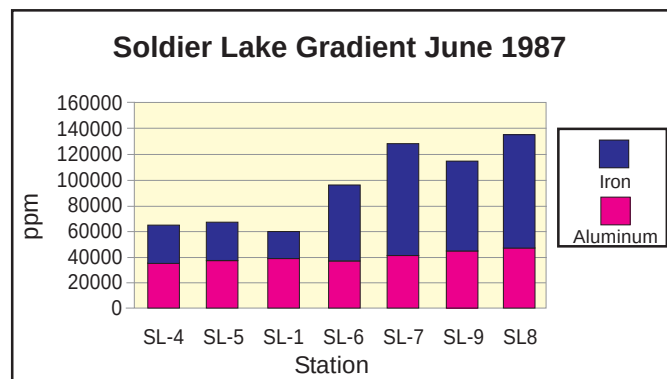


Figure 4. Plot of Al and Fe at sampling stations with pH gradient.

amelioration is due to sheet-creting (cement, fly ash and polypropylene fibre) of the exposed bedrock at the airport which has prevented further proton imbalance.

Although the difference in water column length may explain the differences in sediment density and loss on ignition for these two samples, overall the major factor appears to be the hydrogen ion gradient imposed by Johnson River and consequent geochemical precipitation.

Surface pollen samples from Johnson Brook (Sta. 4), Mid-lake (Sta. 7), and Holland Brook (Sta. 9) are shown in Figure 5 and imply relatively uniform deposition of allochthonous air-borne materials (multiple Spearman correlation coefficients $r_s = >.85$ ($N=23$) and epilimnetic mixing across the lake basin.

continued on page 15

Focus on: Catchment Pathways and Controls...

continued from page 14

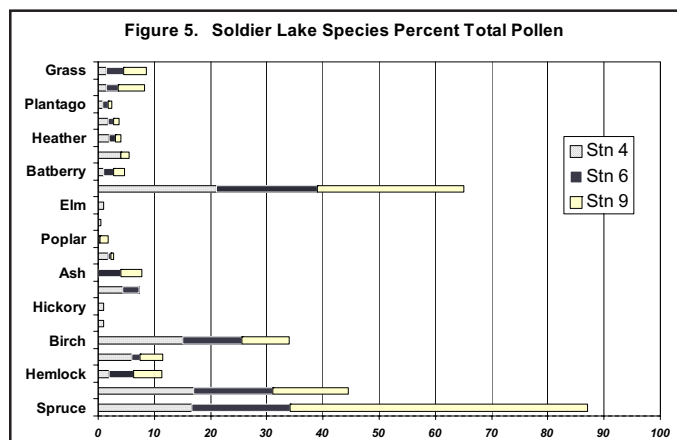


Table 1

SITE pH	SL-0.4 4.2	SL-0.5 4.3	SL-0.1 4.5	SL-0.6 4.5	SL-0.7 4.9	SL-0.9 5.8	SL-0.8 6.2
Aluminum	36760	38900	40420	36390	42340	48110	47560
Barium	185	190	245	160	180	245	240
Calcium	2070	2470	1690	1760	1190	1690	1410
Chromium	41	51	51	33	42	46	40
Copper	110	110	50	57	82	64	72
Iron	29900	29600	21000	59020	86780	66290	86490
Magnesium	1910	2060	2400	1720	2400	3070	3050
Manganese	360	410	450	350	710	880	1850
Nickel	93	100	57	40	39	49	39
Lead	67	70	55	67	82	73	80
Vanadium	74	71	73	70	110	98	110
Zinc	900	190	550	210	140	120	76
ORGANIC (mg/g)	159	220	205	301	380	353	416

Metals near or below detection limits:

Boron	<3.5	<3.5	<3.5	<3.5	<3.5	<3.5	<3.5
Beryllium	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Cadmium	<2.0	<2.0	2.7	<2.0	<2.0	<2.0	<2.0
Cobalt	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0

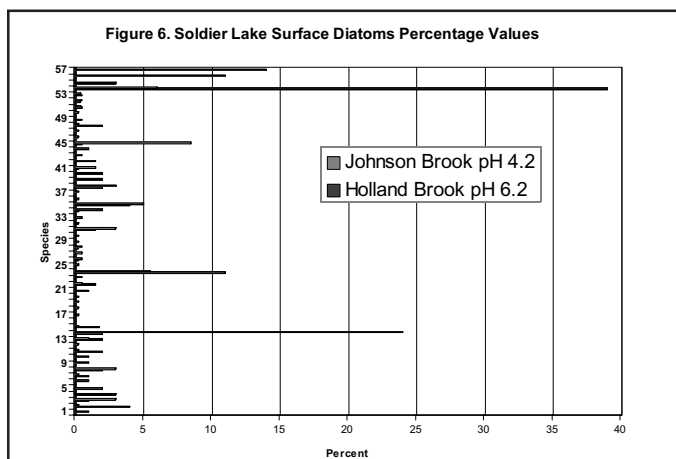


Diatom samples, on the other hand, are almost wholly autochthonous, and reveal the presence of very distinct domains within the lake system. The acidic Johnson Brook Inlet (pH 4.2) samples and more alkaline Holland Brook (pH 6.2) samples are compared in Figure 6. Spearman rank correlation coefficients for these samples give $r_s = .46$ ($N=81$), and ranges from 0.32 to 0.74 for other pairs in the sample series. In the comparison shown here, 9 species are restricted to the more acidic environment, and 10 are found only in the more alkaline Holland Brook Bay samples. Dramatic differences in percent abundance of diatoms common to both environments are indicated in Figure 6 (see page 16).

Ordination analysis using root-root transformations to minimize differences between zero cells and large cell moments were performed using the Czekanowski quantitative index measure of association (Legendre and Legendre, 1983). Standard Q analysis revealed a linear association of stations corresponding to the pH gradient. Reverse, or R-analysis provided 8 groups among 81 species

continued on page 16

Focus on: Catchment Pathways and Controls... *continued from page 15*



of diatoms implying a close degree of association between diatom assemblages and pH domains.

Study Example 2: Estimating and Modelling Land Use Impacts from Large Scale Geochemical Reconnaissance Surveys.

RATIONALE

One of the principal aims of exploration geochemistry is the estimation of geochemical background to define threshold levels and indicate anomalies. Recognition of 'natural' background levels in surface materials of various elements is needed to define baseline element levels and principal controls and to monitor changes in the ecosystem. Widely different element levels can be found in stream and lake systems. It is possible to define various natural and imposed geochemical controls present in stream and lake drainage systems. Principal geochemical factors governing background levels include catchment lithology, chemical mobility, and dispersion and dilution of metals during transport; pH is one of the most active geochemical factors and also the one most readily affected by imposed external loading such as from acidified rainfall. To estimate the pH effect on heavy metal mobilities, background levels and vector properties of these metals in natural systems must be elucidated (Ogden et al., 1988).

Results

The results of numerous studies of reconnaissance geochemical data for background monitoring have been presented elsewhere (Rogers and Lombard, 1991) and will not be considered further. In Central Nova Scotia one such study was performed by the Geological Survey of Canada in conjunction with the Nova Scotia Department of Natural Resources (Daneshfar et al., 2001). The survey collected surface water samples at a density of 1 per 10 km² from first and second order streams; samples were filtered at 45 micron; cation samples were acidified with 0.4% HNO₃ within 12 hours of collection to stabilise them before shipment; the anion samples were untreated.

The survey denoted the role of bedrock factors in the geochemical patterns elucidated by GIS data reduction techniques (Daneshfar et al., 2001). However, one of the more interesting results concerns the identification of a significant presence of N₂ ions in surface water near to lowland areas primarily used for agriculture (Figure 7). This study illustrates the tremendous application that this type of data reduction and surveying methods have for the extension to fields such as precision agriculture amongst others.

Example 3:

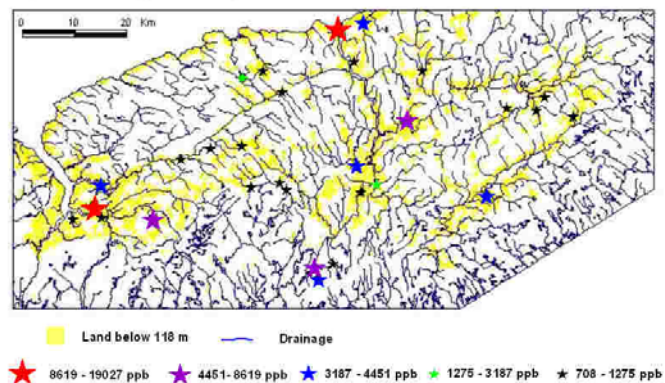


Figure 7. Profile of N distribution, Soldier Lake

Estimating and Modeling Geochemical Baselines Using Lake Sediments

RATIONALE

Grab samples of lake bottom sediment are commonly used for mineral exploration or resource appraisal type geochemical mapping (Hornbrook, 1989) as lake drainage systems cover large parts of the Canadian landmass and present a very convenient means of surveying large areas quickly and cheaply. However, these random grab samples lack the more precise stratigraphic detail needed for environmental studies including baseline mapping, pollution and climate change (Rogers and Ogden, 1992). Small or long cores of lake sediment are very precise mapping tools as they obtain data related to the spatial and temporal aspects of landscape evolution and have been likened to a mass storage device for catchment historical geochemical data (Ogden et al., 1988).

Focus on: Catchment Pathways and Controls... continued from page 16

Results

Data from Ontario and Nova Scotia lake cores demonstrate that spatial landscape correlations and temporal markers from lake system to lake system are established by these methods. Temporal correlations across vast areas are obtainable by pollen analysis of these controlled cores. For example, a ragweed (*Ambrosia* spp.) pollen layer in Ontario and a *Plantago* spp. pollen layer in Nova Scotia have both been used extensively to date the chemical stratigraphy of lake sediment cores collected from these areas (Figure 8). This layer is a well known time marker when wooden ships brought this foreign species into Canadian waters during the 17th century and later, its phased arrival denoting the progressive surveying of Canada. Any anthropogenic inputs are therefore easily charted by their appearance above this layer.

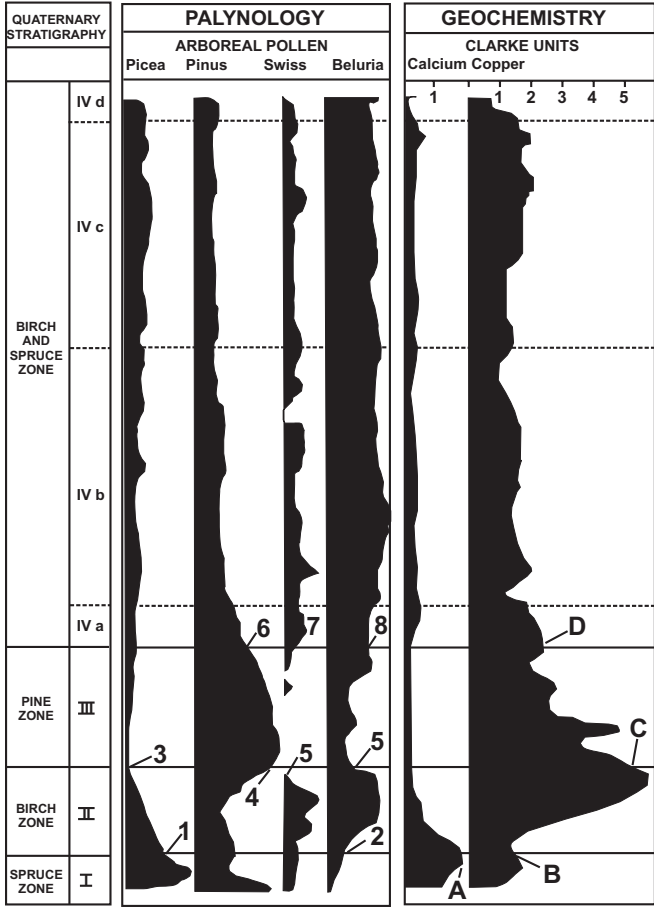


Figure 8. Comparison profile of Ontario lakes, after Fortescue, 1986.

Lake sediment core case histories describe at least four types of Canadian acid lakes. While some lakes are naturally acidic, others have been affected by proton build-up due to acid rain, pollution and/or environmental degradation. The geochemistry of post-Ambrosia environmental disturbances has been noted from lakes near smelters in Ontario (Fortescue 1986) and from the post-*Plantago* layer at Chocolate Lake, Nova Scotia. Dramatic increases in baseline

metal values (e.g. by Pb due to automobiles, Cu due to modern plumbing, V due to home heating oil, etc.) are observed in most lake sediment cores (Rogers and Ogden, 1992). Cores from some Nova Scotia lakes include a geochemically distinct ‘backhoe’ horizon caused by accelerated bedrock weathering due to excavation and construction activities in catchment areas about 40 years ago (Ogden et al., 1988). Certain elements can also be used as time and spatial or ballistic markers. For example Ni, Cu, U, Br, As, Sb and Co have been found useful in Ontario and Al and Zn at Soldier Lake in Nova Scotia (Fortescue, 1986; Ogden and Rogers, 1988).

All post-glacial lakes in central and eastern Canada show an increased organic content with time from ca. 10,500 to 9,000 radiocarbon years before present (RYBP). This increase is a consequence of decreased soil erosion and increasing vegetation as post-glacial warming permitted a re-establishment of closed boreal forests. In Nova Scotia, lake sediment cores record a distinct climatic change to a warm, dry maximum at ca. 3500-5500 RYBP, the xenothermal interval. Reduced precipitation and runoff during this time lowered flushing rates and increased organic sedimentation. The possible effects of future global warming can be inferred from such data on previous periods of global warming recorded in long cores.

Studies at Chocolate Lake (Figure 9) have indicated significant anthropogenic input of elements during the past few hundred years when compared to the advent of modern man in lake catchments in Nova Scotia and Ontario. A

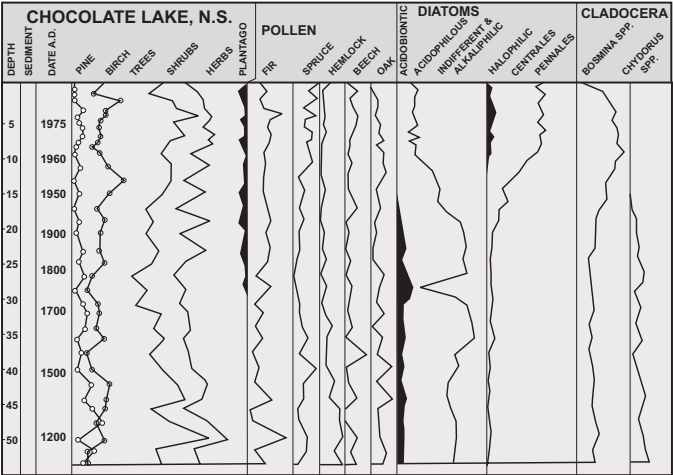


Figure 9. Stratigraphic profile of micro organisms Chocolate Lake.

continued on Page 18

Focus on: Catchment Pathways and Controls...

continued from page 17



number of significant chemical changes are noted (Figure 9). Increasing bedrock exposure, weathering and additions from human activities have resulted from changing land use within the lake catchment. Increased heavy metal deposition of Al, As, Fe and Mn has resulted from accelerated excavation and construction activities since about 1950. Anthropogenic input of Cr, Pb, V and Zn are noted and use of road salt for increased halophilous diatoms indicate ice control. Deforestation is indicated by changes in the record of tree pollen and diatoms since ca. 1750. Increasing lake water eutrophication from leaching of domestic waste is reflected by increases in the presence of alkaliphilous diatoms, which show pH changes from approximately 4.5 prior to 1900 to near neutral (pH 7) in the 1970s (Ogden et al., 1988).

In the St. Margaret's Bay area, development and construction activities have been primarily limited to the Five Island Lake catchment area, and are mostly residential and seasonal cottage developments. A number of new residential developments are currently under way in this watershed and may be expected to change both runoff and water quality as development pressures continue to affect many of the present hydrogeochemical parameters. With increasing acidification, we infer the development of geochemical deposition domains in these lakes in future, similar to those described for Soldier Lake.

CONCLUDING REMARKS

The adoption of several exploration geochemical techniques including sampling, data analysis and data models offers great promise for the synergy of the two disciplines. This is especially relevant when desktop mapping technologies are used to map and model the spatial variables of the exploration and environmental datasets.

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