Ministry of Natural Resources
Hon. Alan W. Pope, Minister
John R. Sloan, Deputy Minister
Ontario

ONTARIO GEOLOGICAL SURVEY
MAP 80713
GEOCHEMICAL SERIES

Interdisciplinary Research for an Environmental Component (Acid Rain) in Regional Geochemical Surveys (Wawa Area)

Algoma District

NTS References: 42C/2, 3, 6, 7, 8, 9, 10, 15, 16

ODM-GSC Aeromagnetic Maps: 2192G, 2176G, 2177G, 2193G, 2207G, 2208G, 2194G, 2195G, 2209G

ODM Compilation Map: 2220

Introduction

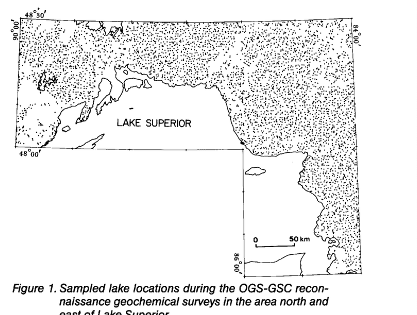


Figure 1. Sampled lake locations during the OGS-GSC reconnaissance geochemical surveys in the area north and east of Lake Superior.

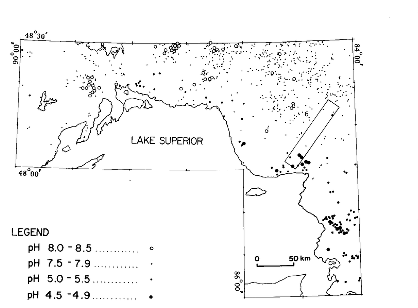


Figure 2. Locations of lakes sampled during the OGS-GSC reconnaissance geochemical surveys having relatively low, or high pH.

The Wawa interdisciplinary project

The interdisciplinary team approach to research

Serendipity from the project

The interdisciplinary team

The purpose of this broadsheet

Highlights of the research

General conclusion

THE 1980 PROJECT

The 1980 project: A Study of a Lake "pH Gradient"

A: Selection of field area.

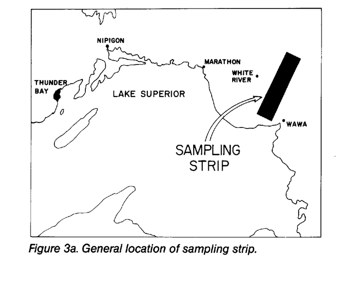


Figure 3a. General location of sampling strip.

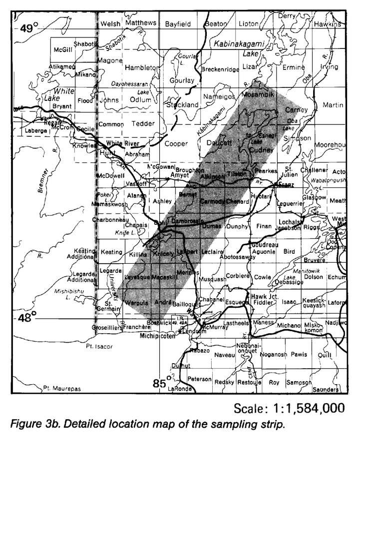


Figure 3b. Detailed location map of the sampling strip.

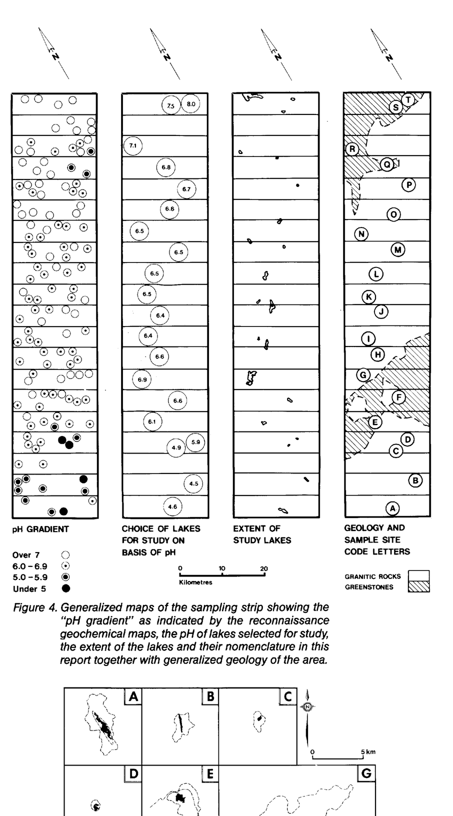


Figure 4. Generalized maps of the sampling strip showing the "pH gradient" as indicated by the reconnaissance geochemical maps, the pH of the selected lakes, the extent of the lakes and their nomenclature in this report together with generalized geology of the area.

General conclusion regarding the selection of lakes along a "pH Gradient"

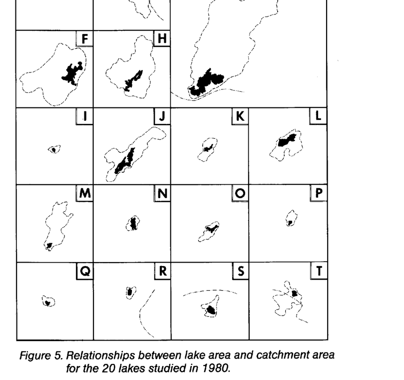
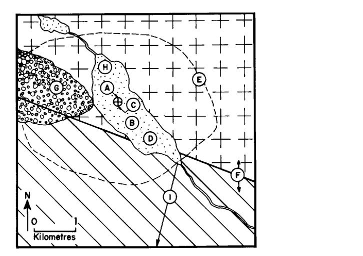


Figure 5. Relationships between lake area and catchment area for the 20 lakes studied in 1980.



Position of lake in 'Staircase' (here second) .... H
Distance of lake from margin of Lake Superior I

Figure 6. Conceptual model of a catchment area studied including a list of parameters measured at each lake.

B: Lake surface water chemistry (I.T.)

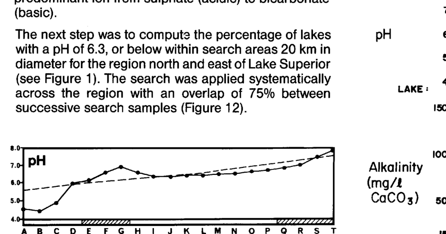


Figure 7. Section along the sampling strip showing the "pH gradient" in the 20 lakes selected for study.

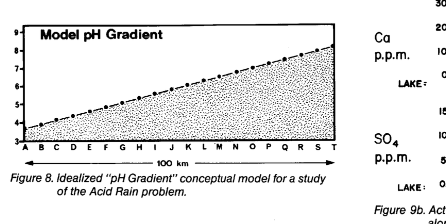


Figure 8. Idealized "pH Gradient" conceptual model for a study of the Acid Rain problem.

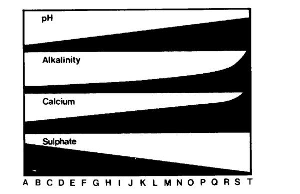


Figure 9a. Conceptual model for surface water chemical parameters along a "pH gradient".

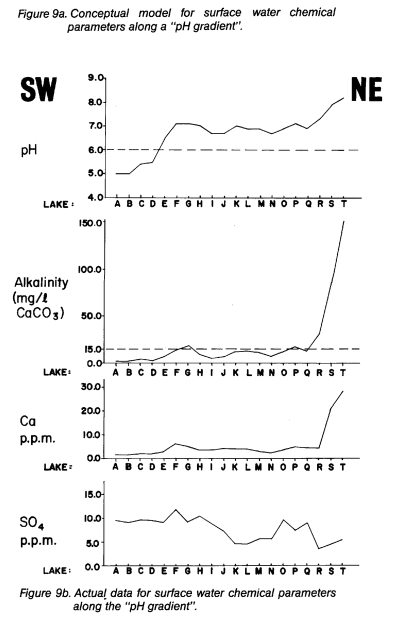


Figure 9b. Actual data for surface water chemical parameters along the "pH gradient".

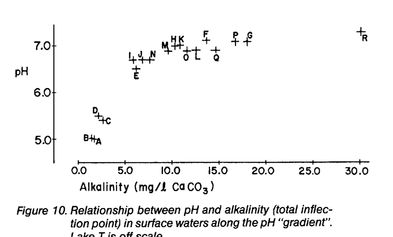


Figure 10. Relationship between pH and alkalinity (total inflection point) in surface waters along the "pH gradient". Lake T is off scale.

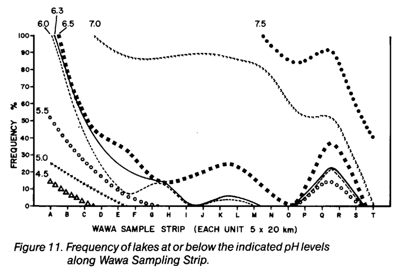


Figure 11. Frequency of lakes at or below the indicated pH levels along Wawa Sampling Strip.

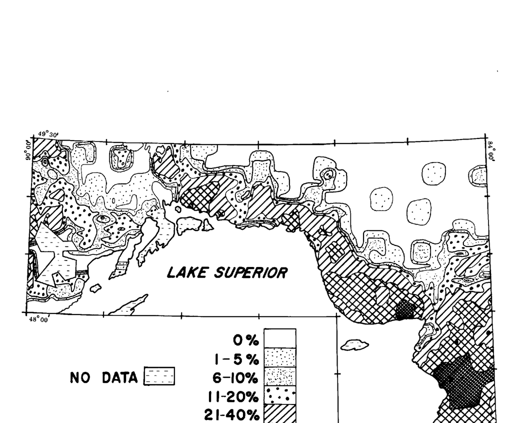


Figure 12. Frequency of lakes pH 6.5 or below.

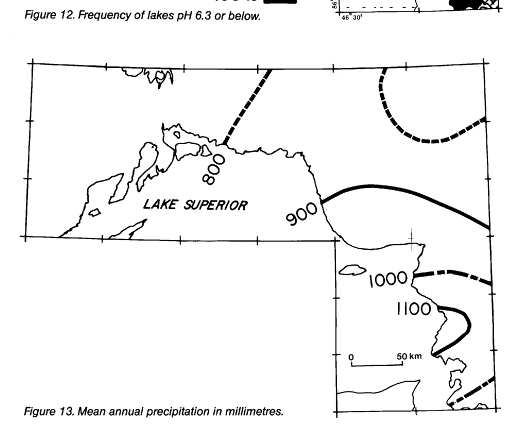


Figure 13. Mean annual precipitation in millimetres.

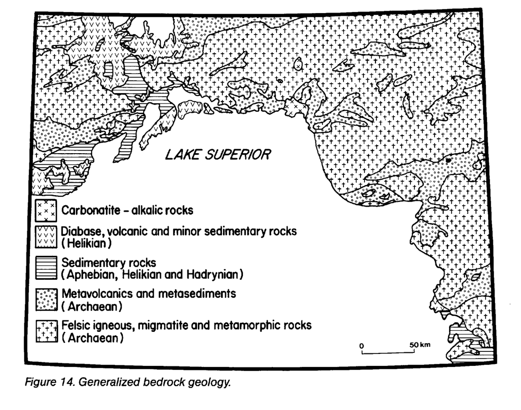


Figure 14. Generalized bedrock geology.

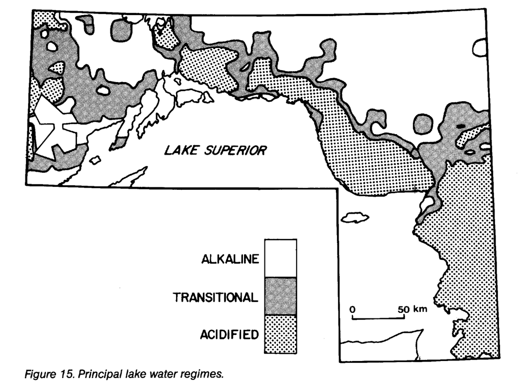


Figure 15. Principal lake water regimes.

C: Palynology (J.T.)

As a general rule fossil pollen found in sediments of small lakes reflects the vegetation in the surrounding area, commonly some tens of kilometres in diameter. In addition, some pollen is derived from aquatic vegetation within the lake, near shore vegetation (for example muskeg around the lake), and also distant sources.

The *Ambrosia* (ragweed) pollen found in the top 10-15 cm of lake sediment cores is presumed to be derived from distant sources by atmospheric transport, probably from sources south of Lake Superior. There is no obvious source of *Ambrosia* pollen in the immediate study area which is forested and has no agricultural land.

The same forest cover is indicated by all pollen diagrams with minor local variations and this is typical of the area to the north of Lake Superior. There are a few pollen grains of southern tree species present in some pollen assemblages, probably derived from the same source as the *Ambrosia* pollen.

Three examples of *Ambrosia* rise patterns are depicted in Figure 16 which includes data from sediment cores from lakes B, F and T. A comparison with the *Ambrosia* rise diagrams (Figure 16) and the Diatom inferred pH data diagram (Figure 21) focuses attention on the pH history of three lakes during post *Ambrosia* time.

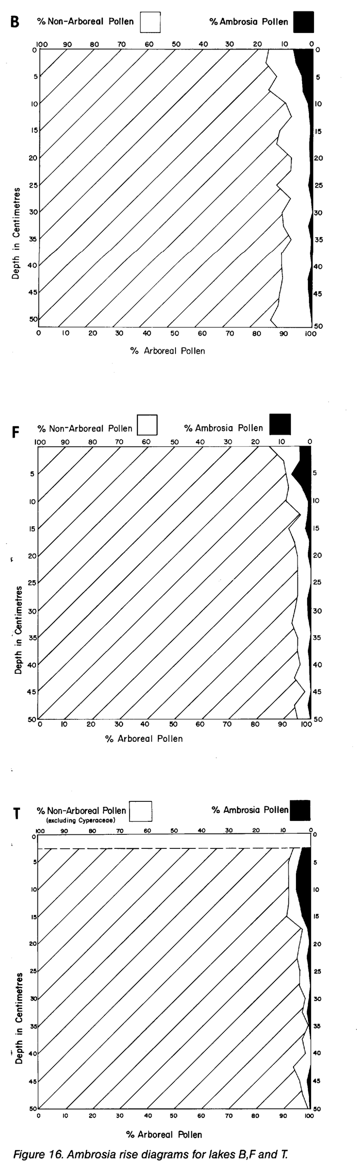


Figure 16. Ambrosia rise diagrams for lakes B,F and T.

D: Geochemistry of lake sediment cores (J.F.)

The conceptual model for the vertical distribution of an element in a lake sediment core is presented in Figure 17. Prior to the commencement of the field work it was envisaged that some elements would show an increase in abundance in post *Ambrosia* time, some a decrease owing to increased mobility due to Acid Rain and the majority remain at the same level. (Figure 17).

In order to facilitate comparisons between the abundance of elements within the same core and from core to core, the weight percent data as received from the chemistry laboratory (i.e. in % or ppm) was transformed to Clarke (K) units by dividing the analytical result (in parts per million) by the estimate for the abundance for the element in the Earth's Crust (also in parts per million). Data for Lake B, whose water was measured at a pH of 5.0 and Lake T whose water was measured at a pH of 8.2, are included here as examples of abundance geochemistry for typical lake sediment cores. (Table 2 and Table 3). Geochemical data sets for all the elements listed in Table 1 for sediment cores from all 20 lakes are included in the Open File Report (No 5342), together with details of the techniques used.

During the 1980 project the sample interval for all lake sediment cores was set at 2.5 cm making 20 samples within a 50 cm core (Tables 2 and 3). In most cores the top 4 samples were located in the post *Ambrosia* portion of the core. Let us consider briefly patterns for elements in cores from lake B (Table 2) and Lake T (Table 3).

- —Both the wet weight and the dry weight of the cores tend to increase down core but such variations are slight compared with the errors involved.
- —The Loss on Ignition in samples of both cores decreases slightly down core as might be expected.
- —Aluminium is slightly lower in post compared with pre *Ambrosia* material in core B whereas there is an increased level of this element in the post *Ambrosia* of core T.
- —Calcium increases slightly down core in core B and is extremely high in Lake T as expected.
- —Phosphorus increases slightly down core B and remains relatively constant in core T but is high in the surface sample from this core.
- —Arsenic is enhanced in the top 6 cm of core B with a sharp positive gradient of concentration. A similar gradient occurs in core T except that the pre *Ambrosia* material has a higher content than in core B.
- —Chromium is slightly higher in core B compared with core T but both cores show a uniform level close to the error of the methods.
- —Copper is slightly enhanced in the top 5 cm of core B and this pattern is somewhat more pronounced in core T.
- —Mercury increases slightly upwards in both cores although the overall level is higher in core B. Both cores have a sharp increase in mercury, in post *Ambrosia* time.
- —Nickel is relatively uniform in both cores and at the same general level of concentration.
- —Lead, like arsenic, sharply increases in late pre *Ambrosia* time and in post *Ambrosia* time. This is considered to be an anthropogenic effect.
- —Uranium is relatively uniform in both cores except in the top sample which has over 2 K in the core T sample compared with around 1 K lower down and 0.87 K in core B compared 1.5 K lower down.
- —Vanadium is relatively uniform in content in both cores.
- —Zinc is like Arsenic and Lead in having a positive concentration gradient in samples laid down in post *Ambrosia* time.

Element	0.01K(ppm)	0.1K(ppm)	K(ppm)
Al	836	8360	83600
Fe	633	6220	62200
Mn	10.6	106	1060
K	184	1840	18400
Na	227	2270	22700
Mg	276.4	2764	27640
Ca	466	4660	46600
P	11.2	112	1120
Ti	63.2	632	6320
Zr	1.62	16.2	162
As	.018	.18	1.8
Co	.29	2.9	29
Cr	1.22	12.2	122
Cu	.68	6.8	68
Hg	.86	8.6*	86*
Ni	.99	9.9	99
Pb	.13	1.3	13
Sr	3.84	38.4	384
Th	.081	.81	8.1
U	.023	.23	2.3
V	1.36	13.6	136
Zn	.76	7.6	76

*ppb

Table 1. Clark Values for elements included in the follow-up project from Ronov and Yaroskevsky (1972)

Table 2. Sample weight data, loss on ignition and element abundance data for each of 20 subsamples for Core B1

Table 3. Sample weight data, loss on ignition and element abundance data for each of 20 subsamples for Core T 1.

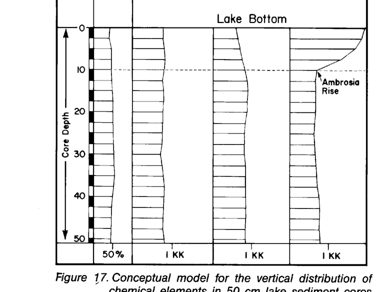


Figure 17. Conceptual model for the vertical distribution of chemical elements in 50 cm lake sediment cores sampled at 2.5 cm intervals.

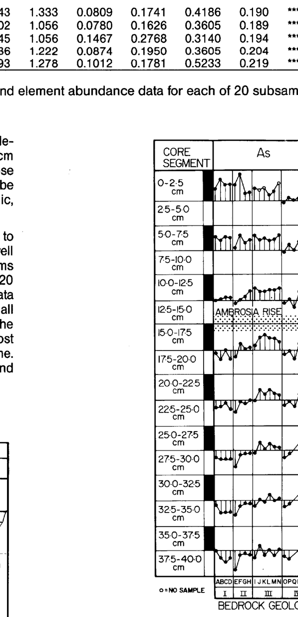


Figure 18. Fingerprint diagrams for Arsenic and Lead in lake sediment cores from the Wawa sampling strip.

E: Diatom inferred pH (M.D.)

Diatom indicators of lake pH

Nygaard Omega vs Plankton Omega

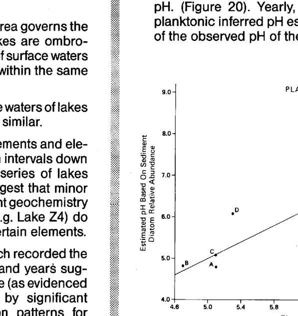


Figure 19. The relationship between lake surface pH and diatom inferred pH based on surface sediment diatoms: Plankton Omega.

Variance associated with the estimation of pH from Diatom counts

When six hundred frustules were counted for each of two replicate slides, the average pH ranged between ±0.4 pH units of the mean. Although the precision of this estimate can be improved slightly by increasing the number of frustules to 2,000 per slide, and the number of slides to five (pH = mean ± 0.2 of a pH unit), we feel that the added precision does not warrant the enormous increase in expended effort. In addition, accuracy may not improve significantly with increased replication. For this reason, we recommend counting 600 frustules on each of two to three replicate slides.

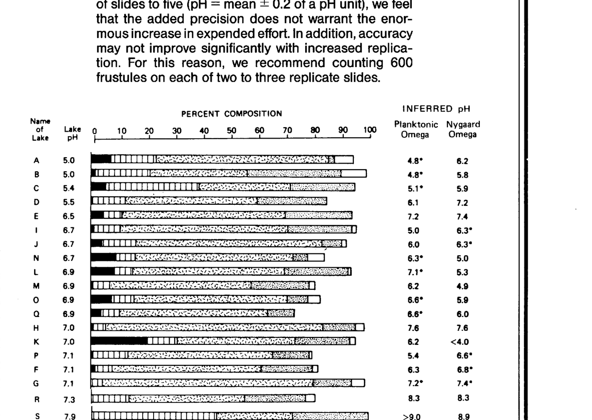


Figure 20. Percent change in composition of lakes A to T with corresponding inferred pH values.

Diatom inferred pH for three Wawa study lakes

Three lakes were chosen for diatom analysis on the basis of their location in the 100 km long transect. Lake B was a clearwater, poorly buffered lake at low pH near the start of the transect. Lake F was a humic lake of neutral pH in the central area of the transect and lake T was located furthest from Lake Superior in a carbonate-rich clay overburden area.

Cesium-137 data indicated that the top 2 cm of sediment in each of the replicated cores taken from these three lakes represents an age of roughly 10 to 15 years. Thus, it is evident that during the last 10-15 years, only lake B was acidifying. The diatom inferred pH has a precision of approximately ½ a pH unit. Therefore, it is not surprising that the diatom inferred pH of Lake B at 0 cm (4.6) is not identical to the pH we observed in the field in 1980 (5.0). In 1978 the observed field pH of the lake was 4.5. The precision of the field pH technique was fairly high (0.1 of a pH unit). However, seasonal variation in pH may exceed 0.5 of a pH unit. The surface sediment diatom inferred pH is based on a composite sample of the average pH of the lake over the last five years. For this reason it reflects long term trends while ignoring or averaging out short term seasonal fluctuation.

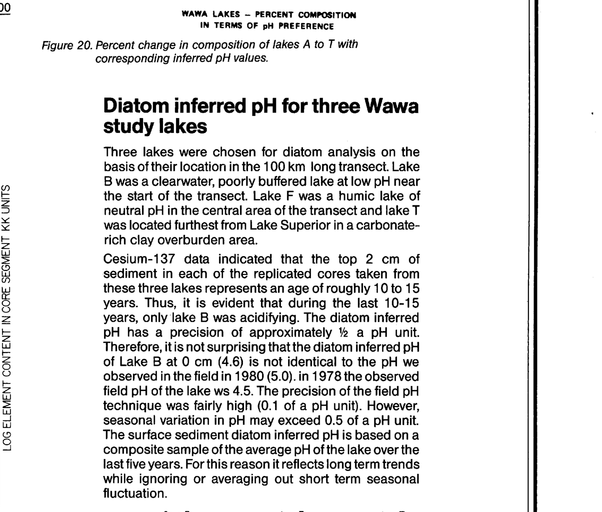


Figure 21. Sediment depth diatom inferred pH for Lakes B, F and T, Wawa Sampling Strip.

Lake B reached its lowest level (pH 4.0 at a depth of 8 cm) roughly 40 years ago (according to Cesium-137 projections). Possibly a forest fire or logging operation caused this decrease in pH at that time. Further work is planned to permit us to pin down the changes in pH as inferred by diatom analysis and the actual changes that have been recorded in the lake's watershed.

The diatom inferred pH of Lake F based on its surface sediments was 6.9 (Figure 21). The observed pH was 7.1. Over the last 10-15 years, Lake F appears to be becoming less acid. In 1978 the Ontario Geological Survey measured a pH of 6.6 in Lake F indicating that its pH has shifted over half a unit in pH in just two years. The diatom inferred pH pattern supports this observation of rapid de-acidification. The reasons for this shift and those preceeding it (Figure 21) are not known.

The lowest diatom inferrered pH of this humic lake was 5.4 and the highest diatom inferred pH was 7.8. Increase in the amount of humic matter generated in and around the lake will act to alter its buffering capacity, according to recent studies. Further study is clearly needed to better understand the reason for the large shifts in pH over the last 200 years in Lake F.

Lake T ranged in diatom inferred pH from a low of 7.0 to a high of 8.8. During the last 10-15 years it appears to be becoming more alkaline. In 1978 its observed summer pH was 8.0 while in 1980 its summer pH was reported as 8.2. The diatom inferred pH at the surface was 8.8 while at 2 cm it was 7.8 confirming the above trend of increasing pH. The fact that even well buffered lakes such as "T" may change 1-2 pH units over a 200 year history was unexpected. Classically, these lakes have been thought to be fairly pH stable due to their huge buffering capacity.

Conclusions: 1980

1. The pH pattern in surface lake waters is verifiable from year to year even though the absolute pH values vary from year to year.
2. Regional geochemical element abundance patterns in sediment collected deeper than 25 cm below the lake bottom are uniform and repeatable.
3. Alkalinity of surface lake waters relates to geological conditions within the catchment area. It is low in granitic areas, medium in areas underlain by metasediments and metavolcanics and high in areas of carbonate-rich volcanics. Hence, geology usually determines the alkalinity and pH of lake waters.
4. Palynological investigations of center lake sediment cores confirmed that the *Ambrosia* rise can be detected in lakes in the Wawa area.
5. Arsenic, Lead, Mercury, Zinc and, possibly Copper levels increase in lake sediment cores in post *Ambrosia* time probably due to anthropogenic effects although some other mechanism may be involved for some elements.
6. The "Diatom inferred pH" method as tried on 3 cores shows promise of being an important component of "Acid Rain" research.
7. There is some evidence that small lake basins at the top of the lake series in a given catchment area are more susceptible to Acid Rain than lakes further down in the catchment.
8. Among the softwater lakes (i.e. those with low total dissolved solids) there are two types, one brown in colour due to humic substances, it is less easily acidified than the other, which is clear.

THE 1981 PROJECT

The 1981 project: The Study of "Lake Staircases"

The interpretation of the data and information obtained during the 1980 activity focused attention on small lakes located at the highest point in catchment areas as being those likely to be most susceptible to the effects of Acid Rain. This was because they tended to have both low pH and low alkalinity.

In 1981 the same team planned to update the 1980 methods and apply them to a set of 20 lakes located in fours in each of five catchment areas. The catchment areas were chosen so as to have relatively uniform geological substrate.

An idealized conceptual model of a catchment area suitable for study was drawn (Figure 22) and a list of parameters expected to change in each area selected was also included in the pre-planning process (Figure 24).

The location of the catchment areas selected for study is indicated on Figure 23 where it is seen that the two areas (X and Z) with the lowest pH were close to the Montreal River. The original intention was to take a long core from each catchment area but for practical reasons this was not possible. A core from Doc Greg lake (relatively acid), was collected but it proved unsuitable for detailed study. Consequently the core from Furnival Lake (Lake U3) was chosen for detailed study using both palynology and geochemistry (see Figure 26). The data and information for the five staircases is not suitable for discussion in detail here. Instead a diagram is included which shows the vertical distribution of each of 14 elements in the four cores taken from the Z series of lakes.

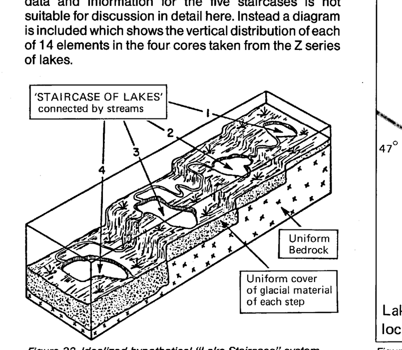


Figure 22. Idealized hypothetical "Lake Staircase" system.

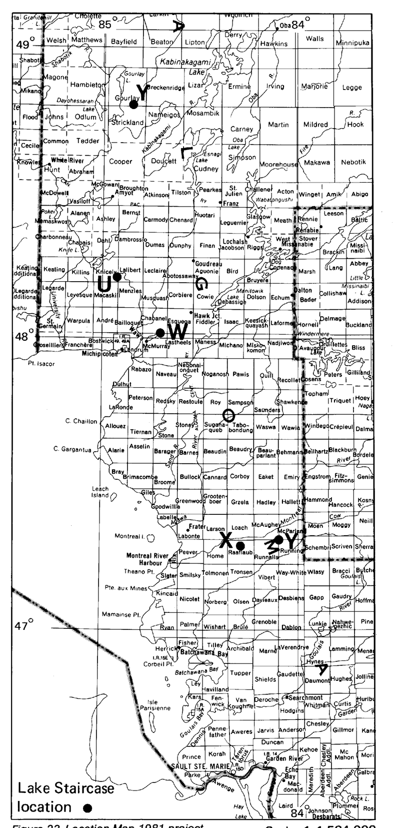


Figure 23. Location Map 1981 project. Scale 1:1 584 000

Parameter
Lakewater pH
Lakewater Alkalinity
Lake Area
Lake Depth
Plant Cover Types Around Shoreline
Relief Around Shoreline
Surficial Cover
Bedrock
Pollution

Figure 24. Listing of the parameters in a hypothetical "Lake Staircase" for the 1981 Follow-up Level study in the Wawa area.

Geological Substrate	Lake	pH	Alkalinity mg/$CaCO_3$
X (gneiss)	3	4.95	1.15
	4	5.18	1.15
Y (calcareous drift)	1	8.07	84.50
	2	7.90	113.50
	3	7.62	63.50
	4	7.97	108.50
Z (gneiss)	1	5.17	1.25
	2	5.59	1.90
	3	5.28	1.30
	4	5.64	2.00

Table 4. Surface water chemical data for staircase lakes.

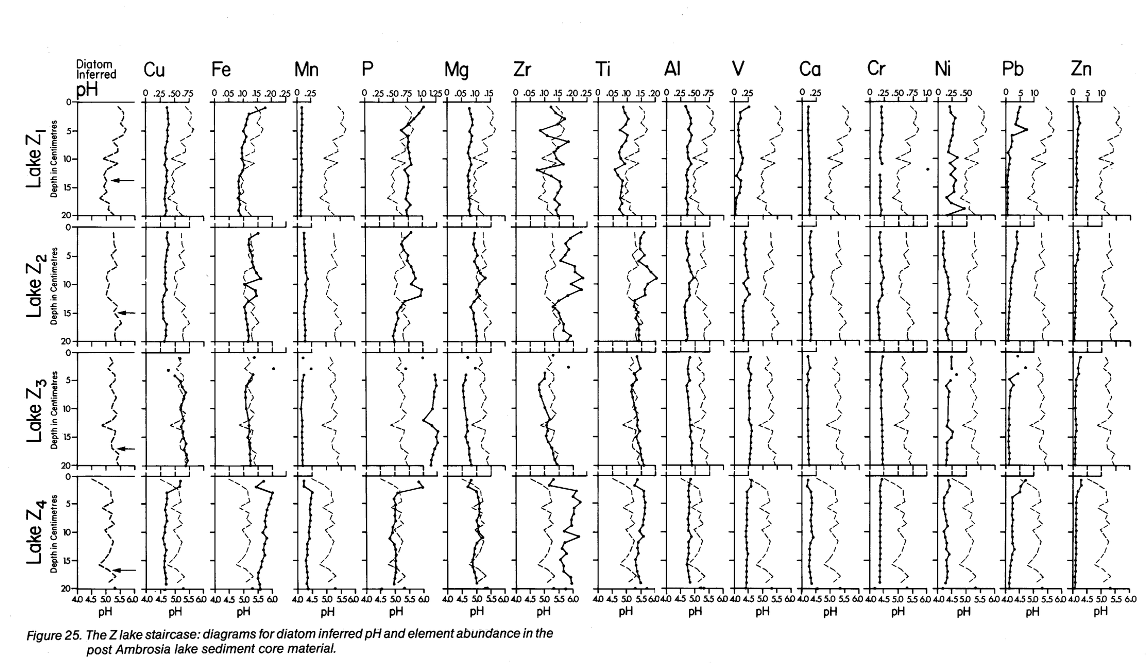


Figure 25. The Z lake staircase: diagrams for diatom inferred pH and element abundance in the post Ambrosia lake sediment core material.

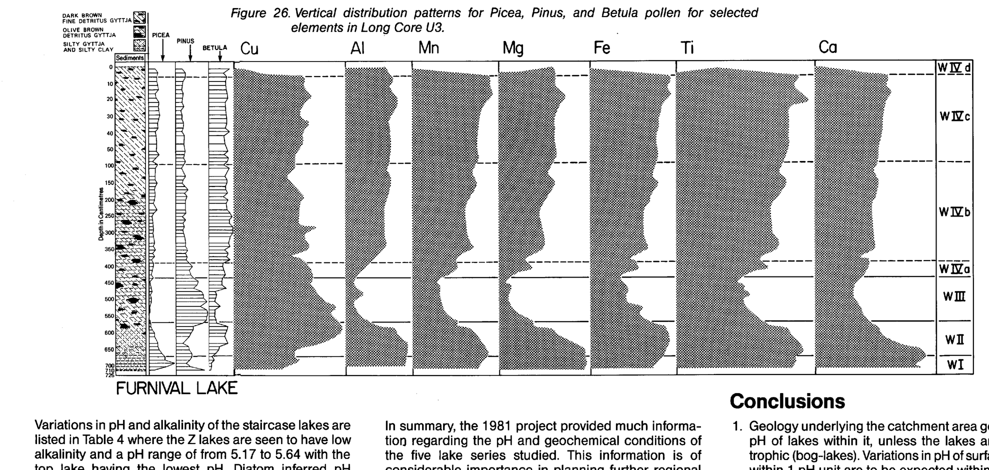


Figure 26. Vertical distribution patterns for Picea, Pinus, and Betula pollen for selected elements in Long Core U3.

Conclusions

4. A study of a deep sediment core which recorded the history of the lake for several thousand years suggests that changes in plant cover type (as evidenced by palynology) are accompanied by significant changes in the vertical distribution patterns for elements. This may provide an opportunity for the study of acid/alkaline cycles in lake basins in pre *Ambrosia* time by diatom inferred pH.

THE 1982 PROJECT

The 1982 project: Verification and Standardization

As a result of the interpretation of the 1980 and 1981 data it became clear that effort was needed to verify and standardize the performance of the different analytical techniques in order to obtain the most reliable data. Another aspect of this activity was to examine a relatively small number of new lakes in order to further clarify the data collection process particularly under marginal conditions—for example in an old tailings pond. The lakes sampled during the 1982 project are indicated in Figure 27.

Perhaps the most important verification study of the whole project is shown in Figure 28 where the surface water pH data from the 1978 reconnaissance geochemical map are plotted with the 1980 data from the same lakes which are located along the "pH gradient".

Verification of a different kind is included in Figure 29 where element abundance data together with diatom inferred pH data (where available) for eight lakes with different pH of their waters. This diagram demonstrates that the methodology for multi-element chemical analysis of small (i.e. 0.5 cm) subsamples of lake sediment core materials is appropriate for describing details of the multi-element patterns. The figure also illustrates the diatom inferred pH history for the lakes and the sample to sample variation expected in this method.

An example of the advantage of multi-element geochemical data (transformed to Clarkes) is shown in Core B (Figure 29) where all elements show effects of compaction of the core. If only calcium had been determined, one might think the concentration gradient might be due to the effects of Acid Rain.

Lake	pH		Alkalinity MEQ/L		SO_4 ppm		Ca ppm	
	1980/1	1982	1980/1	1982	1980/1	1982	1980/1	1982
Lake B (1980)	5.02	5.19	.032	0.50	9.0	*	1.5	1.8
Lake X_1 (1981)	5.02	5.57	.024	.043	–	10	1.4	2.2
Lake W_1 (1981)	6.70	6.88	.265	.332	57	38	21.0	21.6
Lake W_4 1981)	7.34	7.69	.305	.469	53	42	21.4	24.2

Table 5. Verification of lake water chemical data in two different years.

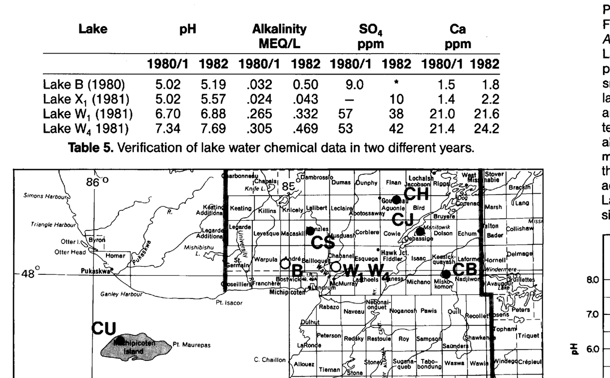


Figure 27. Location Map 1982 project. Scale: 1:1 584 000 or 1 inch to 25 miles

Progress with the Acid Rain project is summed up in Figure 30 where diatom inferred pH diagrams for post *Ambrosia* time are given for cores from four acid lakes. Lake W4 illustrates clearly the major shift to acidity in pH in a lake located in the fume kill area of the Wawa smelter. This event is fully documented. The diagram for lake CF shows a similar shift in pH in post *Ambrosia* time and also a return to more normal conditions. This is tentatively interpreted as being due to a forest fire although to date the detailed fire history of the catchment area CF is not known. The other two lakes are in the Sudbury area. Lake KN4 is a humic lake which has acidified naturally during post, and pre *Ambrosia* time. Lake KH4 is an example of a lake which has gone acid since 1963 probably due to Acid Rain.

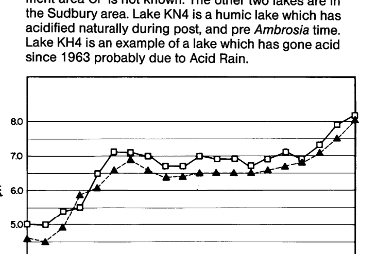


Figure 28. Verification of the 1978 reconnaissance geochemical survey data for surface water samples from lakes along the 1980 "pH gradient".

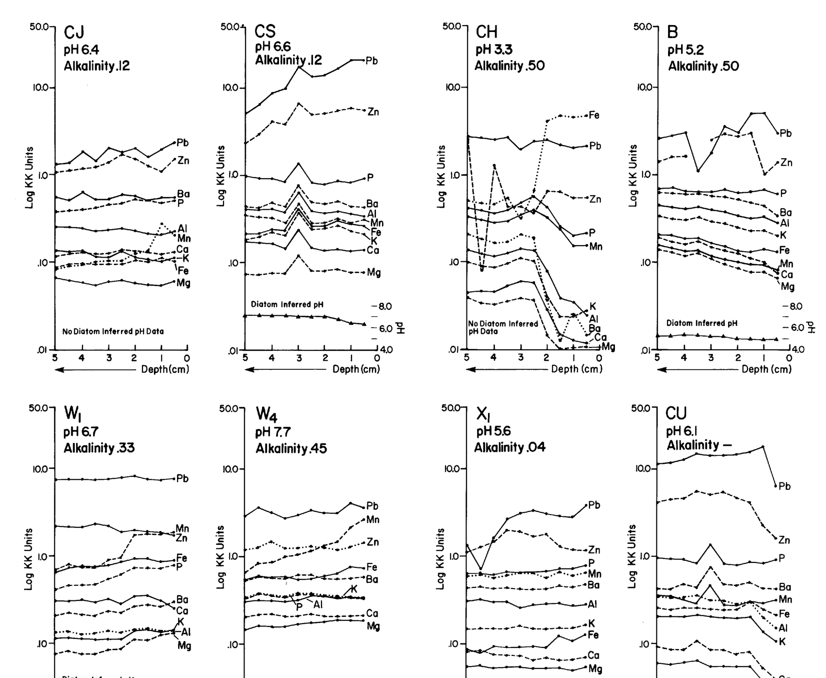


Figure 29. Concentration levels of elements in eight lake sediment cores from the Wawa Area, 1982.

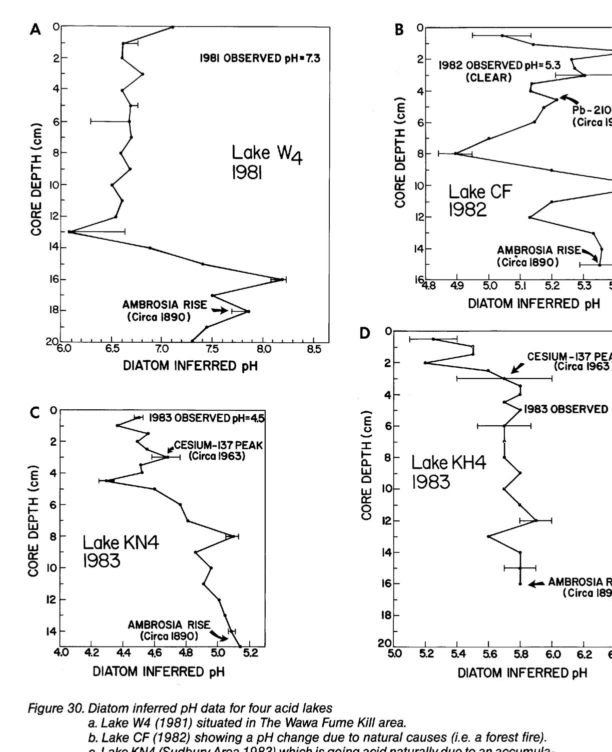


Figure 30. Diatom inferred pH data for four acid lakes.

Conclusions

1. In general, the methodology developed during the project for surface water chemistry, sediment geochemistry, palynology and diatom inferred pH measurements is suitable for inclusion in regional lake sediment surveys and is capable of distinguishing between acid lakes which are natural and those which have been affected by man's activities.
2. The surface water chemistry and the multi-element geochemistry of the lake sediment core samples is relatively simple to carry out and could be incorporated in future regional geochemical surveys. The study of palynology and diatom inferred pH are more complicated and not practical as components of regional geochemical surveys.
3. Further studies are required to develop techniques for the identification and description of lakes affected by Acid Rain which are as effective as palynology and diatom inferred pH but are less time consuming and costly.
4. The Wawa project data base provides a unique opportunity to continue this research to a successful conclusion. Using an approach similar to that used so far.

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CREDITS

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