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GEOCHEMISTRY OF AQUATIC AND TERRESTRIAL SEDIMENTS, PRECAMBRIAN SHIELD OF SOUTHEASTERN ONTARIO

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ABSTRACT

Lake water and sediment samples from approximately 2200 lakes and glacial sediment (sub-solum) samples from about 1800 sites were collected throughout a 38000 km² rectangular area extending from Georgian Bay east to the Ottawa and St. Lawrence Rivers, Ontario, Canada. Lake water alkalinity and pH patterns are similar to the distribution of carbonate components in glacial drift. Carbonate-rich drift derived from the Paleozoic limestone terrain on the northeast flank of the Precambrian Frontenac Arch has been dispersed in a south-westward direction across a variety of non-calcareous metasedimentary and igneous rocks of the Canadian Shield, providing a buffering capacity to lakes situated in granitic terrain. The distribution patterns of mobile trace and minor elements are influenced by geochemical processes associated with subaerial weathering, ground and surface water transport, and the geochemical environment within the lakes themselves. Although composition of the drift is generally reflected by lake geochemistry, these post depositional processes can cause significant variations between patterns derived from the two sample types. Anions and cations such as SO₄²⁻, Cl⁻, Na⁺, and F⁻ exhibit concentration patterns thought to reflect both anthropogenic inputs and natural variations due to differences in the geology. All regional geochemical patterns may show evidence of local enhancement caused by high concentrations of chemically distinctive minerals in drift or nearby bedrock.

1. INTRODUCTION

Water and sediment samples from approximately 2,200 lakes and glacial sediment (sub-solum) samples from about 1800 sites (Figure 1) were collected from the Precambrian Frontenac Arch, and from an adjacent 100 km wide strip of the Canadian Shield, extending from Thousand Islands on the St. Lawrence River to Georgian Bay (Figure 2).

These samples were analyzed to determine concentrations of over 40 trace, minor and major chemical components including the content of clay-sized particles and carbonate minerals with potential buffering capacity. The objectives of the project were to map the regional distribution of environmentally critical components of the aquatic and terrestrial systems in order to: 1) determine to what extent patterns are related to the complex bedrock and glacial geology of the region; 2) establish regional trends that may be related to anthropogenic input as opposed to natural variations; 3) determine to what extent the composition of the aquatic elements is influenced by the composition of the terrestrial elements; 4) determine to what extent the aquatic chemistry is controlled by local atmospheric and hydrogeological factors; and 5) determine to what extent the chemical components of the sample media reflect known and probable mineralization in the bedrock and overlying glacial material.

2. METHODS

Glacial sediments, primarily till, were sampled from below the postglacial solum at easily accessible man-made exposures along public and private roads and from natural exposures along streams and rivers. In the Ottawa River valley and the St. Lawrence River valley, marine silty clay and proglacial lacustrine silty clay, which form an almost continuous surficial cover in lower areas, were sampled. The clay (<2 μ m) size fraction was removed from each of these samples by centrifugation. The silt-clay (<64 μ m) fraction was removed by sieving from a separate, dried sample split. Trace and minor element concentrations were determined on the clay fraction by Atomic Absorption using a hot HCl/HNO₃ leach (Cu, Pb, Zn, Co, Ni, Ag, Cr, Fe, Mn, Cd), colorimetric methods (As), and fluorimetric methods (U). Carbonate determinations were made on the <64 μ m fraction using a Leco Carbon Analyzer. The difference between C present in leached and unleached splits of the same sample was converted to CaCO₃ equivalent weight % using a formula modified from Foscolos and Barefoot (1970).

Open File 947 lists some of the geochemical data for till and other surficial sediments in this area. Compositional data similar to those described in Open File 947 are now routinely collected in regional surveys of drift composition, most of which are carried out primarily for mineral exploration purposes.

Lake sediment and water samples were collected utilizing helicopter support at an average density of one sample site per 13 km². Water samples were collected at least 25 cm below the water surface. Lake sediments were collected from profundal lake basins using a hollow pipe-like sampling apparatus and the upper 10 to 15 cm of the sediment core were discarded. The water samples were analyzed without any preparation but the field dried lake sediment samples were ball milled and sieved to minus 177 μ m. Appropriate quality control standards, field and analytical duplicates were incorporated into the analytical units.

The lake sediment and water data for this area was published in the form of 1:250,000 scale geochemical value maps in Geological Survey of Canada (GSC) Open Files 899 and 900. Each of these files consists of 42 maps of geochemical variables: 28 for lake sediments (Zn, Cu, Pb, Ni, Co, Ag, Mn, As, Mo, Fe, Hg, LOI (500°C), U, CO₂, C (organic), S, Sr, Cr, SiO₂, Al₂O₃, Fe₂O₃, CaO, MgO, K₂O, P₂O₅, TiO₂, BaO and LOI (900°C)) and 14 for lake waters (U, F, pH (laboratory), Na, K, Ca, Mg, C (organic), Cl, NO₃, SO₄, alkalinity (equivalent CaCO₃), conductivity and dissolved O₂). These open files also include one sample site location map and a text of field measurements, analytical and statistical data. Similar surveys with 15 to 20 variables have been carried out across Canada totalling approximately 1,400,000 km², primarily in support of the mineral exploration industry and mineral commodity assessment studies, but the data include a number of environmentally significant parameters such as Hg, U, F, As, pH etc.

3. RESULTS AND DISCUSSION

Regional distribution of buffering components, such as carbonate minerals (Figure 3), in samples of glacial drift is closely mimicked by patterns of alkalinity, pH (Figures 4 and 5) and other carbonate-related parameters in both lake waters and lake sediments. The overall pattern of concentrations of components related to carbonate minerals reflects both the overprint of southwestward glacial dispersal of debris from the Paleozoic limestone terrain that flanks the Frontenac Arch along its northeastern side and the more limited dispersal of marble debris from outcrops on the Frontenac Arch. High alkalinities measured in lakes underlain by bedrock that generally provides few components capable of buffering the effects of acid rain, demonstrate how glacial processes can distort the mineralogical/chemical signature of local bedrock by transporting carbonate-rich debris over areas much larger than those of the source outcrops. It is important to recognize that aquatic and terrestrial systems in areas thought to be sensitive to acidic precipitation on the basis of bedrock geology alone, cannot necessarily be evaluated without considering the composition and distribution of the drift cover.

Comparison of concentration patterns for trace and minor elements between the clay-sized ($\sim 2\mu\text{m}$) fraction of drift and the $\sim 177\mu\text{m}$ fraction of lake sediments demonstrates that element mobility is related to a complex mix of influences of drift mineralogy/chemistry, geochemical processes associated with overland or groundwater transport, and local geochemical environment of lakes from which samples were collected. For example, U distribution in the clay size fraction of drift samples (Figure 6) bears only vague resemblance to its distribution in lake waters (Figure 7). Comparison of patterns of regional alkalinity, drift carbonate content, and concentration of U in lake waters suggests high solubility and hydromorphic transport of U in high bicarbonate waters. Elevated concentrations of U in lake waters mimic almost exactly regional patterns of 1) high alkalinity, 2) elevated pH in surface lake waters, and 3) high carbonate content in drift.

Uranium in lake bottom sediments (not shown here), on the other hand, more closely relates to regional distribution of U in drift. This indicates that U is not so mobile in non-carbonate regions and that it is being fixed in lake bottom sediments which are composed largely of organic material with minor contribution of silt and clays from surrounding glacial deposits. However, where bicarbonate waters are present, little U is fixed in lake sediment and it may be transported great distances from its source.

Arsenic, which is somewhat less affected by these processes, has concentration patterns that are broadly similar for both drift and lake bottom samples (Figures 8 and 9). The As map for drift clearly delineates strong anomalies over the meta-sedimentary and metavolcanic rocks that host the arsenical Au of the old Ontario gold mining belt. Lake sediment As reflects the eastern limb of the belt. The source of major lake sediment anomalies in the Tweed area is presently unknown, but may in part reflect contamination by arsenical byproducts of Au ore processing formerly carried out in the region.

Comparison of patterns of concentrations of trace and minor elements between terrestrial sediments and aquatic sediments and waters shows that the less mobile elements such as As (see Figures 8 and 9) tend to be concentrated in lakes in patterns corresponding to those for the terrestrial system. Conversely, the more mobile elements, Fe and Mn particularly (not shown), are concentrated in lakes in patterns that reflect local hydrochemical factors. A third group of anions and cations (such as SO_4^- (shown in Figure 10)) and Cl^- , Na^+ , and F^- (not shown), exhibit anomalous concentration patterns that may reflect anthropogenic inputs from acid precipitation or road salt, as well as natural variation due to differences in geology. For example, many of the areas characterized by higher sulphate concentrations are underlain by sulphide-rich bedrock.

4. CONCLUSION

In this necessarily brief and preliminary discussion, we have attempted to emphasize the dominant role played by bedrock and glacial geology in producing variations in geochemical and mineralogical patterns in environmentally significant surficial deposits of the Canadian Shield. We have demonstrated how both natural post or syndepositional processes and anthropogenic inputs may alter or otherwise influence the primary geological compositional signatures of the landscape. It is our opinion that the effects of the former processes must be evaluated more carefully than has heretofore been done with reference to the primary geological characteristics of any landscape for which an assessment of anthropogenic effects is being carried out.

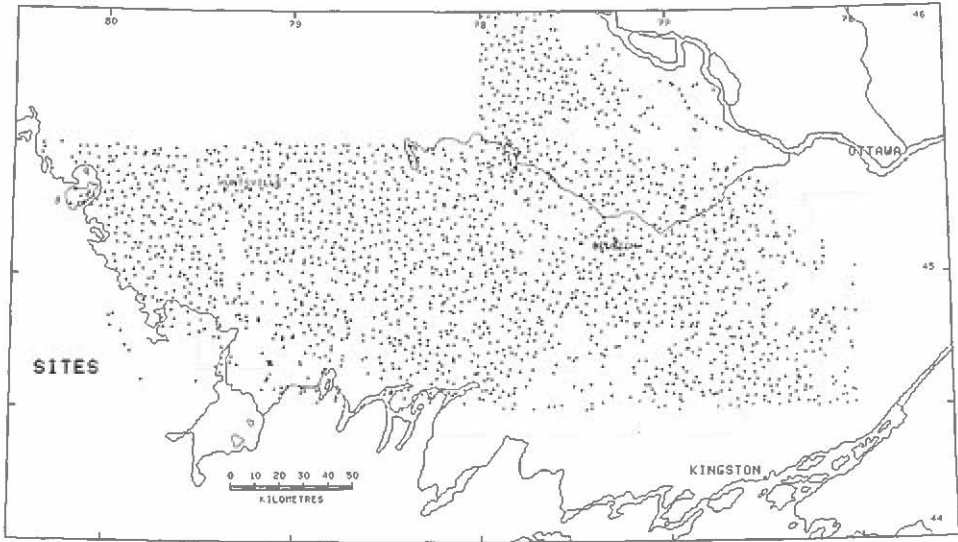


Figure 1 Map of lake bottom sediment and lake water sample sites. Over 1800 till samples were collected within the area outlined with a dotted line.

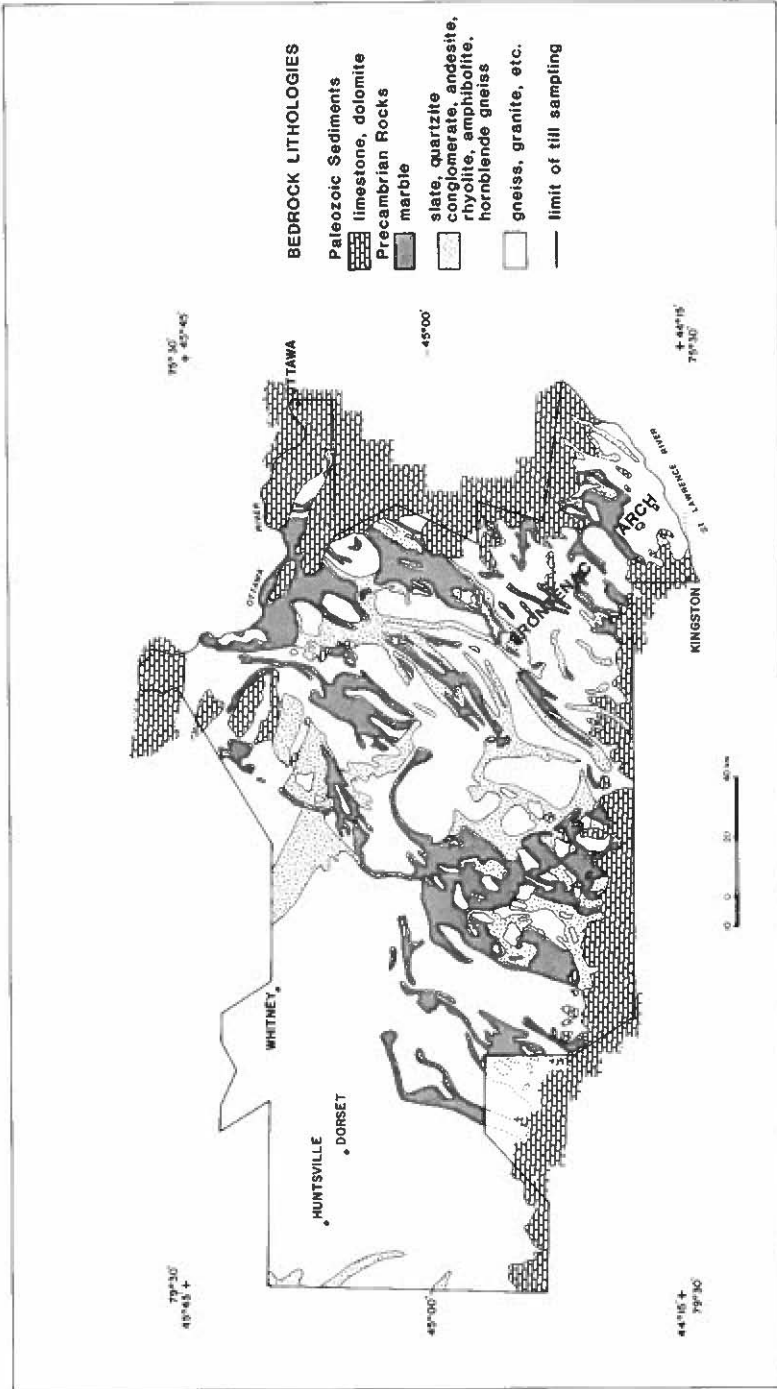


Figure 2 Map of bedrock geology of the Frontenac Arch area, Ontario, Canada.

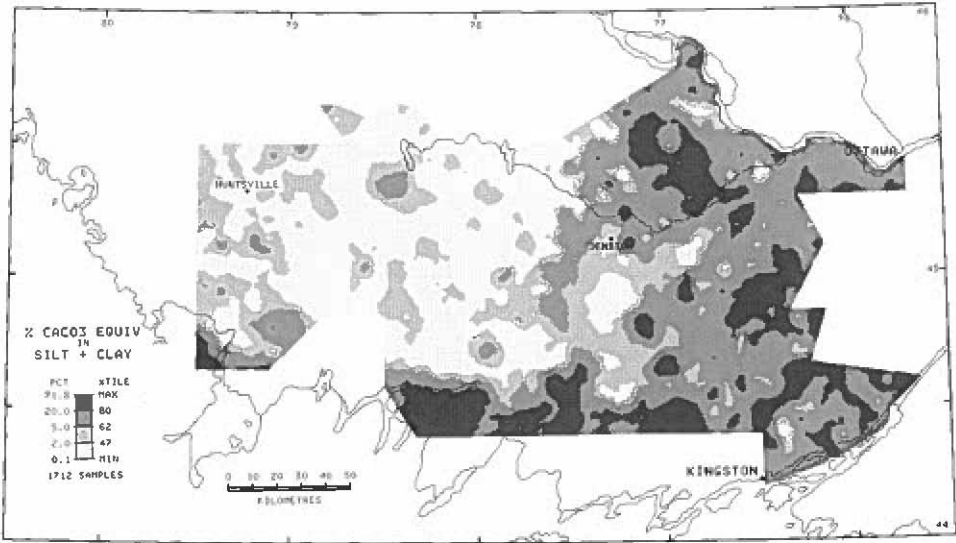


Figure 3 Map of carbonate concentrations (%CaCO₃ equivalent in $\leq 63 \mu\text{m}$ fraction) in till and other glacial sediments.

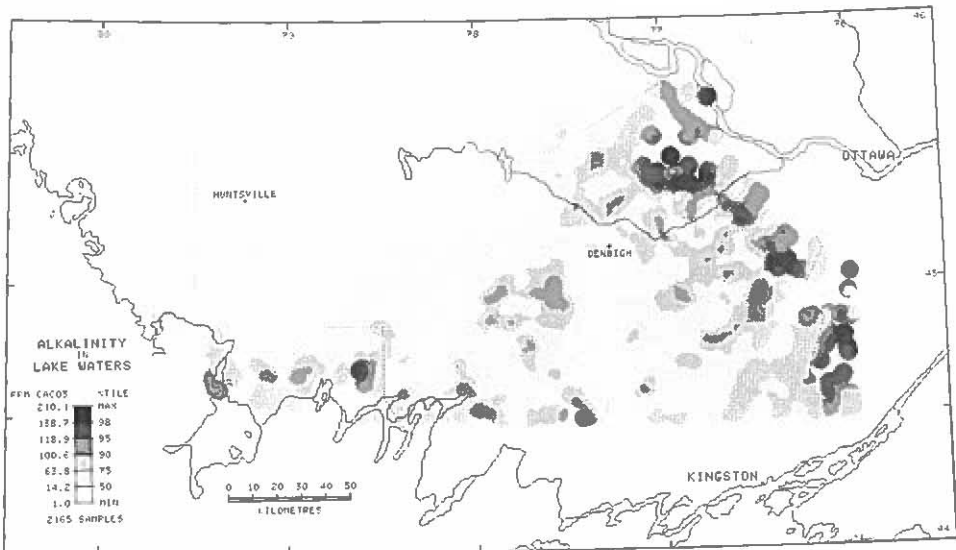


Figure 4 Map of alkalinity (as ppm CaCO₃) in lake waters.

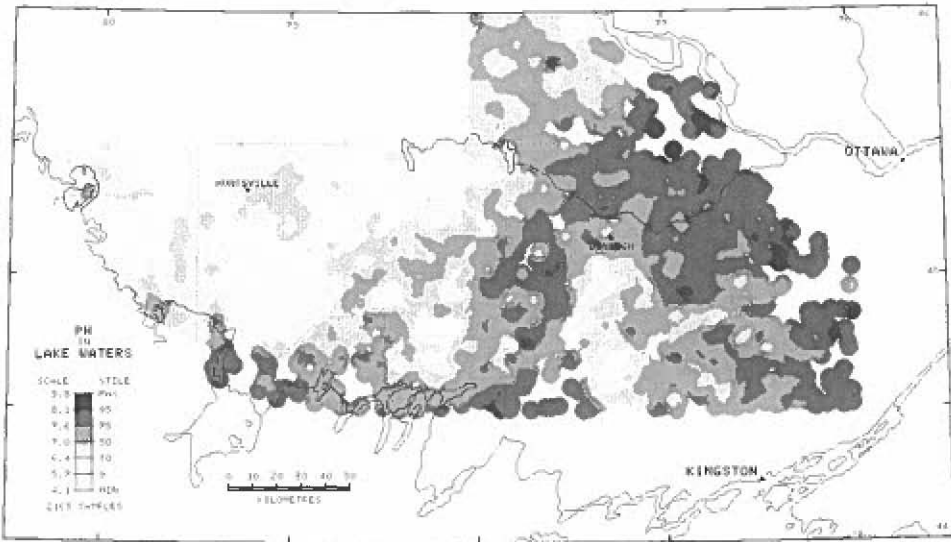


Figure 5 Map of pH levels in lake waters.

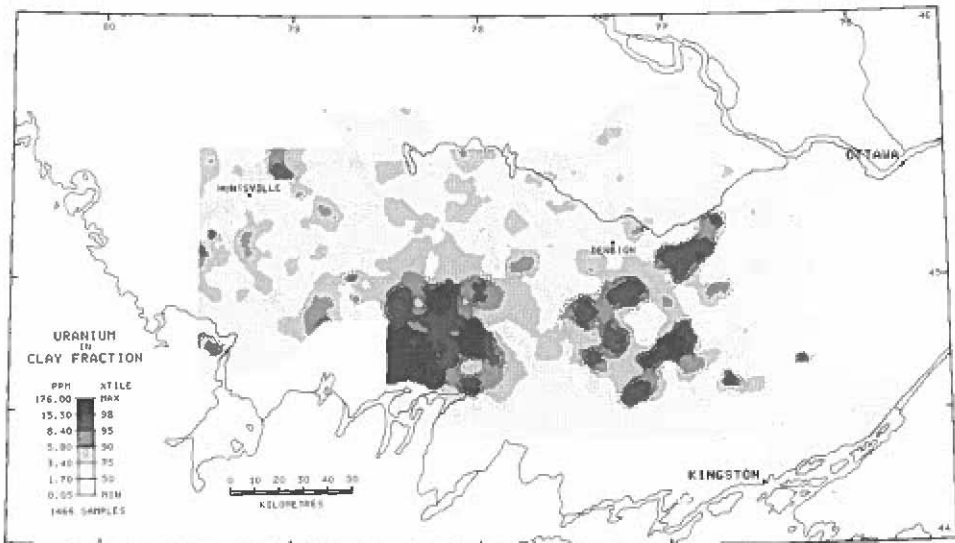


Figure 6 Map of U concentrations in till and other glacial sediments (< 2 μm fraction).

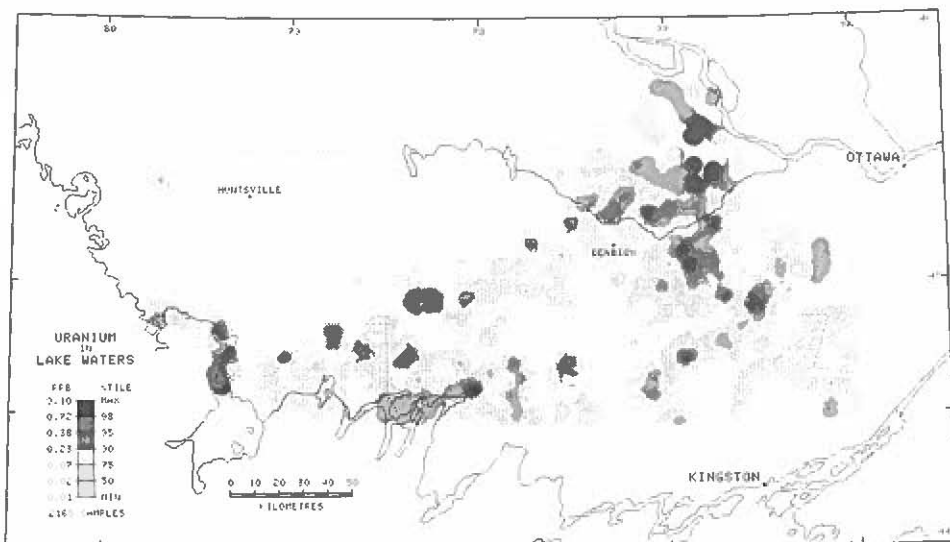


Figure 7 Map of U concentrations in lake waters.

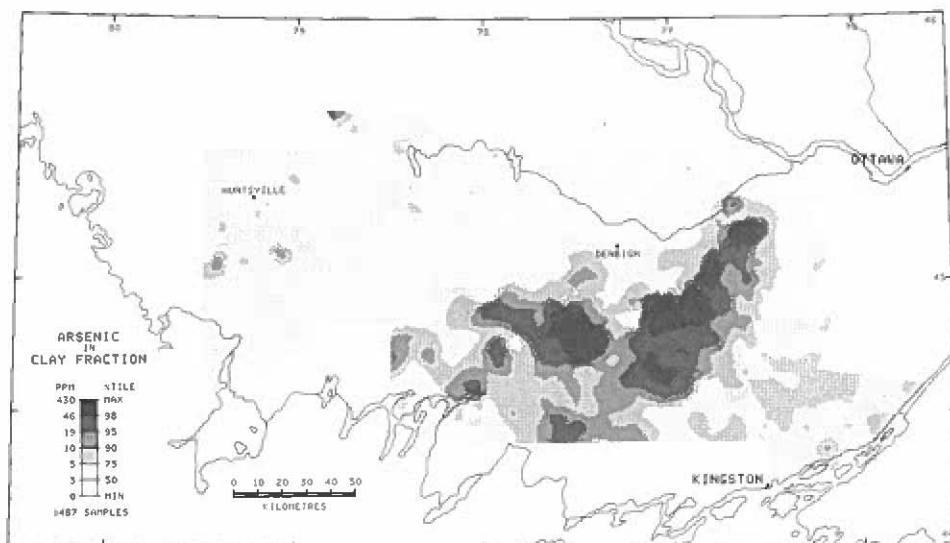


Figure 8 Map of As concentrations in till and other glacial sediments (< 2 μm fraction).

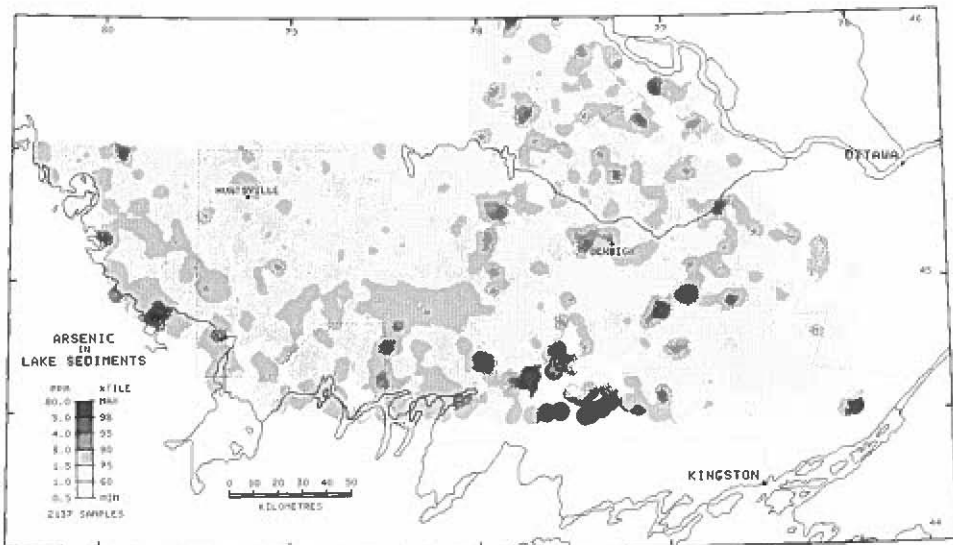


Figure 9 Map of As concentrations in centre lake bottom sediments (< 177 μm fraction).

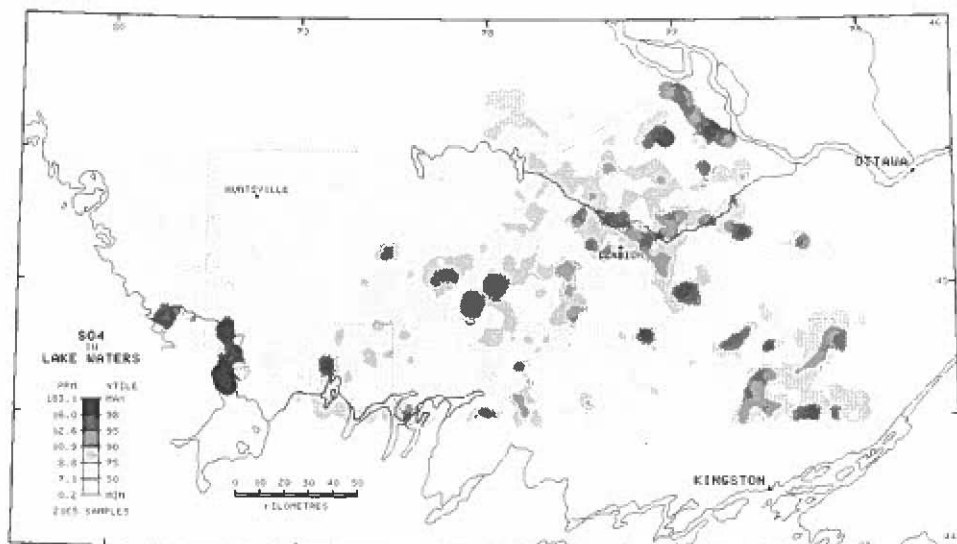


Figure 10 Map of SO_4 concentrations in lake waters.

REFERENCES

- Foscolos, A.E. and Barefoot, R.R.: 1970, A rapid determination of total organic and inorganic carbon in shales and carbonates; Geological Survey of Canada, Paper 70-11.
- Hornbrook, E.H.W., Lund, N.G. and Lynch, J.J.: 1984, Regional lake sediment and water geochemical reconnaissance data, Ontario 1982, parts of NTS 31C(S/2) and 31F (Ontario only); Geol. Surv. Can., Open File 899.
- Hornbrook, E.H.W., Lund, N.G. and Lynch, J.J.: 1984, Regional lake sediment and water geochemical reconnaissance data, Ontario, 1982, parts of NTS 31D, 31E, and 41H; Geol. Surv. Can., Open File 900.
- Kettles, I.M. and Shilts, W.W.: 1983, Reconnaissance geochemical data for till and other surficial sediments, Frontenac Arch and surrounding area, Ontario; Geol. Surv. Can., Open File 947.