

## MERCURY AS A GLOBAL POLLUTANT

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The Third International Conference on Mercury as a Global Pollutant was convened in Whistler, British Columbia, Canada, in July 1994. The 151 papers in this volume are the proceedings of that conference.

The apparent general increase of mercury in the global environment has highlighted the potential importance of anthropogenic mercury emissions. Environmental cycling of mercury leads to its bioaccumulation in the human food chain. The amount and toxicity of mercury in human foods is controlled by complex ecological and biogeochemical processes.

The Conference objectives were to integrate and synthesize current knowledge and to identify the information needs for the development of assessment frameworks. To these ends, the state of the science, integration of ecological and health studies, and the research - policy interface were explored in technical presentations on human health, ecological effects, emissions, biogeochemistry, analytical chemistry, and modeling.

The Whistler Conference was the third in a *de facto* series of recent international conferences on the problems of mercury in the environment. The growing interest in the topic is reflected in the numbers of attendees: 200 in Gavle, Sweden, in 1990, 300 in Monterey, California, USA in 1992, and 400 in Whistler in 1994.

The reader will see that knowledge of the behavior of mercury in the environment is rapidly building, and that assessment tools will soon be in hand. Further advances in our understanding will be reported at a fourth international mercury conference, being planned for 1996, in Hamburg, Germany.

Guest Editors:

John W. Huckabee  
Conference Cochairman

Brian Wheatley  
Conference Cochairman

Donald B. Porcella

# MERCURY ANOMALIES IN LAKE WATER AND IN COMMERCIALY HARVESTED FISH, KAMINAK LAKE AREA, DISTRICT OF KEEWATIN, CANADA

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**Abstract.** Mercury (Hg) was measured in approximately seven hundred samples of surface water collected from Kaminak Lake and nearby small and large lakes in a tundra environment located west of Hudson Bay. Mercury variations were expected to be related to sulphide mineralization, and patterns of Hg enrichment were to be used as pathfinders for locating potentially economic sulphide deposits. Water in the northern part of Kaminak Lake, which is underlain by sedimentary and volcanic bedrock with known potential for sulphide (base metal) mineralization, was consistently enriched in Hg, as were smaller lakes lying along the same bedrock trend. Mercury concentrations in lake trout from a commercial fishery on Kaminak Lake ranged from 0.57 ppm (parts per million = mg/kg or mg/l) to 2.0 ppm Hg (70 samples), exceeding the national consumption guidelines of 0.5 ppm. Subsequently, the Kaminak fishery was abandoned and relocated on nearby Kaminuriak Lake where similar fish species averaged less than 0.5 ppm Hg. High Hg concentrations in fish from this remote, unpopulated region, far from industrial sources of pollution, are related mostly or wholly to local geological phenomena.

## 1. Introduction

In 1970 and 1971 surface water was collected at over 700 sites and the water column was sampled at several sites in and near Kaminak Lake, located in open tundra about 100 km west of Hudson Bay. Kaminak Lake is a large, shallow, irregular lake with many bays. Its surface is about 53 m above modern sea level; Kaminak and all other lakes sampled were inundated by the sea as a result of glacioisostatic depression from 6000  $\pm$  500 years ago to as recently as 4000 years ago. Because of oxidation of organics, low productivity, and their young age, lakes generally have less than one metre of modern organic sediment, often overlying several metres of clastic marine sediment. Their waters are highly oxygenated with near neutral pH and very low conductivities (Klassen *et al.*, 1975; Shilts *et al.*, 1976).

## 2. General geology

The geology of the Kaminak basin is complex, consisting of belts of Archean, sulphide-bearing metavolcanic rocks (Kaminak Group) intruded by igneous rocks of similar age (Davidson, 1971). Set into this crystalline basement are the erosional remnants of a prominent belt of younger (Aphebian) metasedimentary and metavolcanic rocks of the Hurwitz Group. The latter group crops out under and beside the northern part of Kaminak Lake and beneath several of the smaller lakes sampled (Figure 1). The bedrock is overlain by a discontinuous mantle of glacial till and fine-grained marine sediment (Arsenault *et al.*, 1981). A prominent esker forms the northwest shore of Kaminak Lake (Shilts, 1973). The till is dominated compositionally by local material mixed with

significant amounts of debris glacially eroded from the red volcanic and sedimentary rocks of the late Precambrian Dubawnt Group, which outcrops over 100 km northwest of the study area. There is abundant evidence of temporary occupation of the shores of Kaminak Lake by nomadic Inuit who left significant deposits of caribou bones on the lake bottom, but there is no present population centre closer than 120 km, and the region is 1000's of km from any source of industrial airborne emissions.

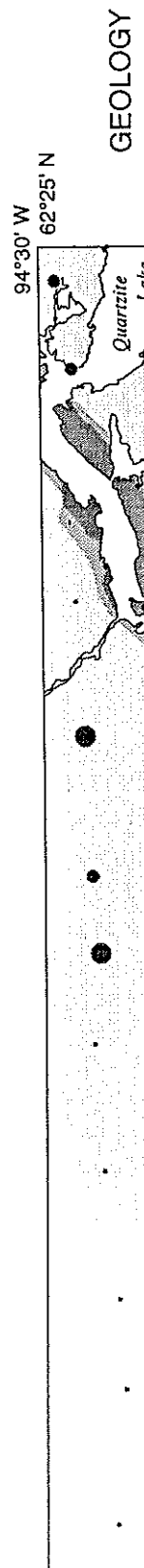
### 3. Sample collection, preparation and analytical methods

The water samples, collected in polypropylene bottles, were acidified upon collection with nitric acid ( $\text{HNO}_3$ ) to a final strength of 0.015 M  $\text{HNO}_3$ . Filtration was not carried out as the presence of particulate matter in these samples was considered insignificant. Mercury was determined by quartz tube/atomic absorption spectrophotometry (AAS) at 253.7 nm after vaporization to the elemental state by the reducing agent, stannous sulphate ( $\text{SnSO}_4$ ). 15 ml of 5%  $\text{SnSO}_4$  in 1 M sulphuric acid ( $\text{H}_2\text{SO}_4$ ) was added to a 100 ml aliquot of the sample and the resulting vapor swept into a heated ( $90^\circ\text{C}$ ) 1 m quartz cell in the light path of the AAS. The lower limit of measurement was 5 ppt (parts per trillion = ng/l); relative standard deviation at 20 ppt was typically 10%.

The results shown here are considered to be potentially low for two reasons. Firstly, the  $\text{HNO}_3$  added cannot be assumed to be fully effective in liberating organically bound or complexed Hg to form mercuric ions available for reduction by  $\text{SnSO}_4$ . Secondly, during the interval between collection and analysis Hg could have been lost to varying degrees through adsorption on container (polypropylene) walls and/or reduction to the elemental state by bacterial or chemical action. Nitric acid would have inhibited this loss, but not necessarily prevented it completely. Subsequent research at the Geological Survey of Canada (GSC) showed that addition of 1 ml of 5% potassium permanganate ( $\text{KMnO}_4$ ) and 2.5 ml of  $\text{H}_2\text{SO}_4$  to a 100 ml sample was effective in destroying active reducing bacteria and in oxidizing potential complexing material (Jonasson *et al.*, 1973).

### 4. Results and discussion

In 1971 a commercial fishery was established at a permanent base camp on the esker at the northwest corner of Kaminak Lake, with the objective of supplying lake trout (*Salvelinus namaycush*) and Lake Whitefish (*Coregonus clupeaformis*) to a processing plant in Rankin Inlet, for eventual sale in southern Canada. Most of the harvesting was carried out near the camp in the northwestern part of the lake, where underlying bedrock is the Hurwitz Group. Because Hg levels in fish were of general concern, Hg was monitored by analyses at the Freshwater Institute in Winnipeg (Sherbin, 1979). Lake trout were found to have Hg concentrations ranging from 0.57 to 2.0 ppm, exceeding the national guidelines of 0.5 ppm. In 1972 the fishery was abandoned and moved to nearby Kaminuriak Lake, where Hg concentrations were acceptable. Reconnaissance Hg data for waters sampled in 1970 indicated that surface waters over Hurwitz Group black slates and volcanic strata and, to a lesser extent, Kaminak Group volcanic strata had relatively high Hg concentrations (Figure 1) (Hornbrook and Jonasson, 1971). Further detailed sampling throughout Kaminak Lake in 1971 confirmed the enrichment of Hg in water in its northern



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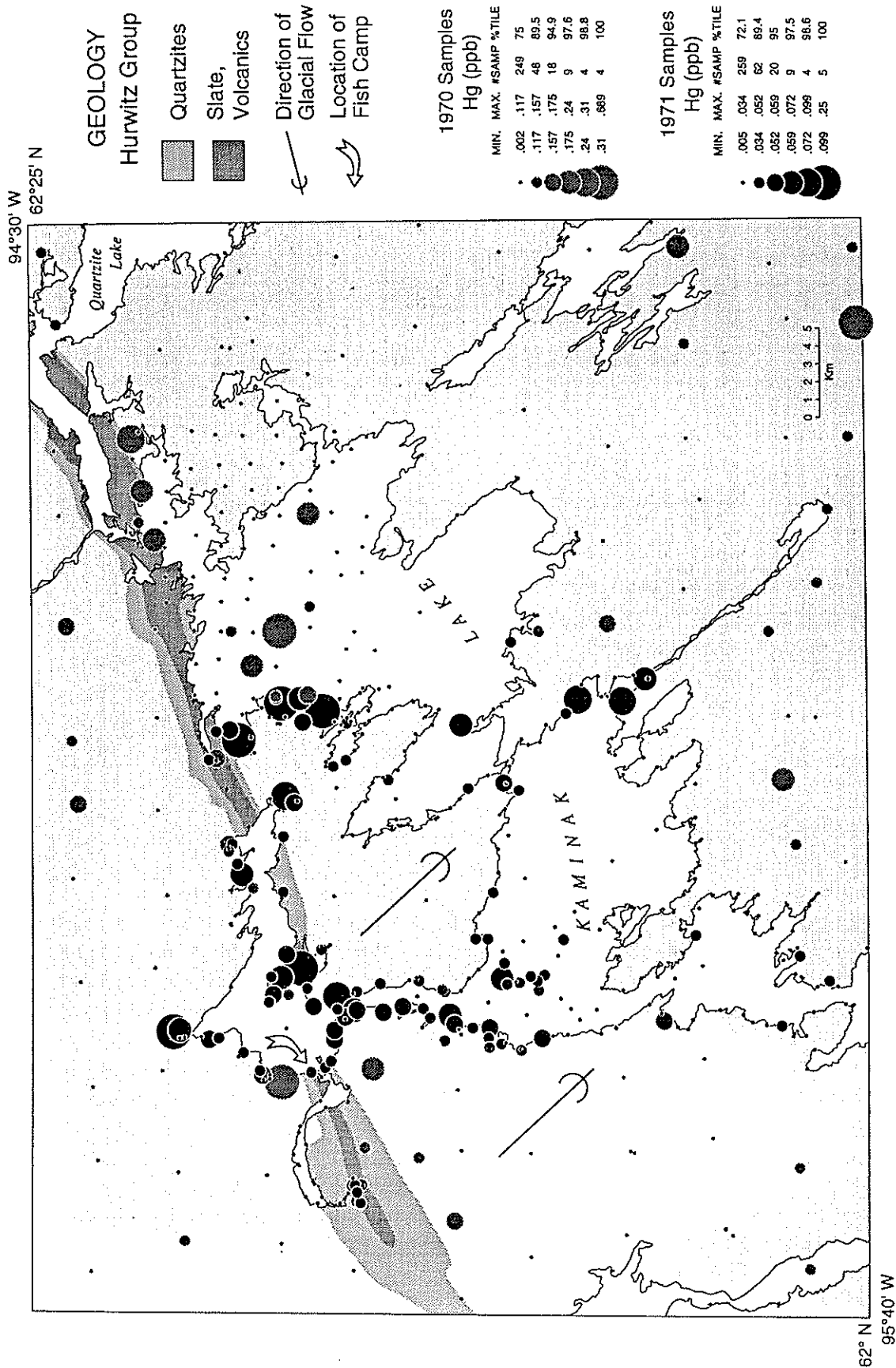


Figure 1: Concentrations of Hg (ppb) in water of Kaministiquia Lake and nearby lakes.

basins (Figure 1) where, coincidentally, most of the fish were harvested. These results were taken to indicate that widely dispersed sulphide minerals in the slate and/or volcanic members of the Hurwitz Group were releasing Hg as part of the ongoing weathering processes affecting these rocks or the glacial sediments derived from them. The fact that Hg was concentrated only in the northern waters of a large, shallow, freely circulating lake suggested that outgassing was a very local and ongoing process. Furthermore, it was and is hard to ignore the relationships between high Hg in the fish and the geographical coincidence of their harvest area with elevated Hg in the water. A similar relationship between Hg in fish and sulphide-bearing black slates of Aphebian age was postulated by Loukola-Ruskeeniemi (1990) in Finland.

### 5. Conclusions

- (1) The fact that fish from remote lakes near the study area have acceptably low Hg concentrations suggests that their enrichment in Hg in the Kaminak Lake area is related to local natural processes, which ultimately must create bioavailable Hg species.
- (2) The correspondence of high Hg concentrations in water only within those parts of Kaminak Lake underlain by Hurwitz slates and/or volcanic rocks suggests that ongoing local geological processes (eg. weathering) are largely responsible for the Hg enrichment in water.
- (3) The fact that there are large but coherent variations in Hg concentrations among the hundreds of remote lakes sampled and, indeed, among the hundreds of sites sampled on Kaminak Lake itself, suggests that long distance airborne pollution has a negligible overprint on local naturally generated Hg in this area. Any effects of any airborne sources of Hg are overwhelmed by Hg release from local sources.

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**COMPARISON OF MERCURY CONCENTRATIONS IN MODERN LAKE  
SEDIMENTS AND GLACIAL DRIFT IN THE CANADIAN SHIELD IN THE  
REGION OF OTTAWA/KINGSTON TO GEORGIAN BAY, ONTARIO,  
CANADA.**

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**Abstract.** An ongoing problem in evaluating the significance of mercury (Hg) in surficial materials is distinguishing sources of natural (spatial) variation of the geological/geochemical environment from sources (airborne, waterborne, etc.) of anthropogenic (temporal) variation. The Geological Survey of Canada (GSC) has carried out a series of sampling programs, including one in the southeastern part of the geologically complex Canadian Shield, in order to link the easily observable lithological variations of bedrock with the chemical composition of overlying glacial deposits and lake sediments. This research aims to provide a base against which observed variations in life systems can be judged as natural or anthropogenic. In the study area, high concentrations of Hg and other trace elements in lake sediment and glacial sediments can be related to glacial dispersal from mineralized bedrock and/or bedrock with high natural background concentrations of these elements.

## **1. Introduction**

Geochemists and geologists routinely gather and compile data that can provide important baseline information on the natural chemical status of the environment. It is only with an appreciation of natural compositional variations of the geological substrate, on which life systems are superimposed, that any attempt can be made to evaluate the extent to which humans have affected the chemistry of these systems.

Separation of natural geologically controlled (spatial) variations, sometimes referred to as the "status" of a landscape, from anthropogenic (temporal) variations is difficult. Lakes in geologically complex terrains, such as the Canadian Shield, have a wide natural range of metal concentrations that are clearly related to their geological setting (Hornbrook *et al.*, 1986; Kettles *et al.*, 1991). The challenge for geoscientists, then, is to devise strategies for distinguishing among natural and anthropogenic factors that influence the metal content of the surficial environment.

Geochemical surveys which map the natural variation of Hg and other metals in terrestrial and aquatic systems may be used to: 1) identify where naturally occurring metal enrichments may lead to environmental problems; and 2) predict where the worst effects due to any anthropogenic changes to the environment may occur.

Patterns of natural distribution of metals in lakes and soils aid in evaluating the extent to which these same metal species are deposited as airborne or waterborne pollutants. Likewise, it is important to understand the natural processes leading to elevated levels of metals near the sediment-water interface in lakes. Increasingly, these enrichments are cited as evidence of anthropogenic deposition (Norton *et al.*, 1990; Lindquist *et al.*, 1991; Swain *et al.*, 1992). Though deposition of metals from the atmosphere undoubtedly is widespread, natural areal and vertical variations make evaluation of the relative magnitude of the anthropogenic component problematic.

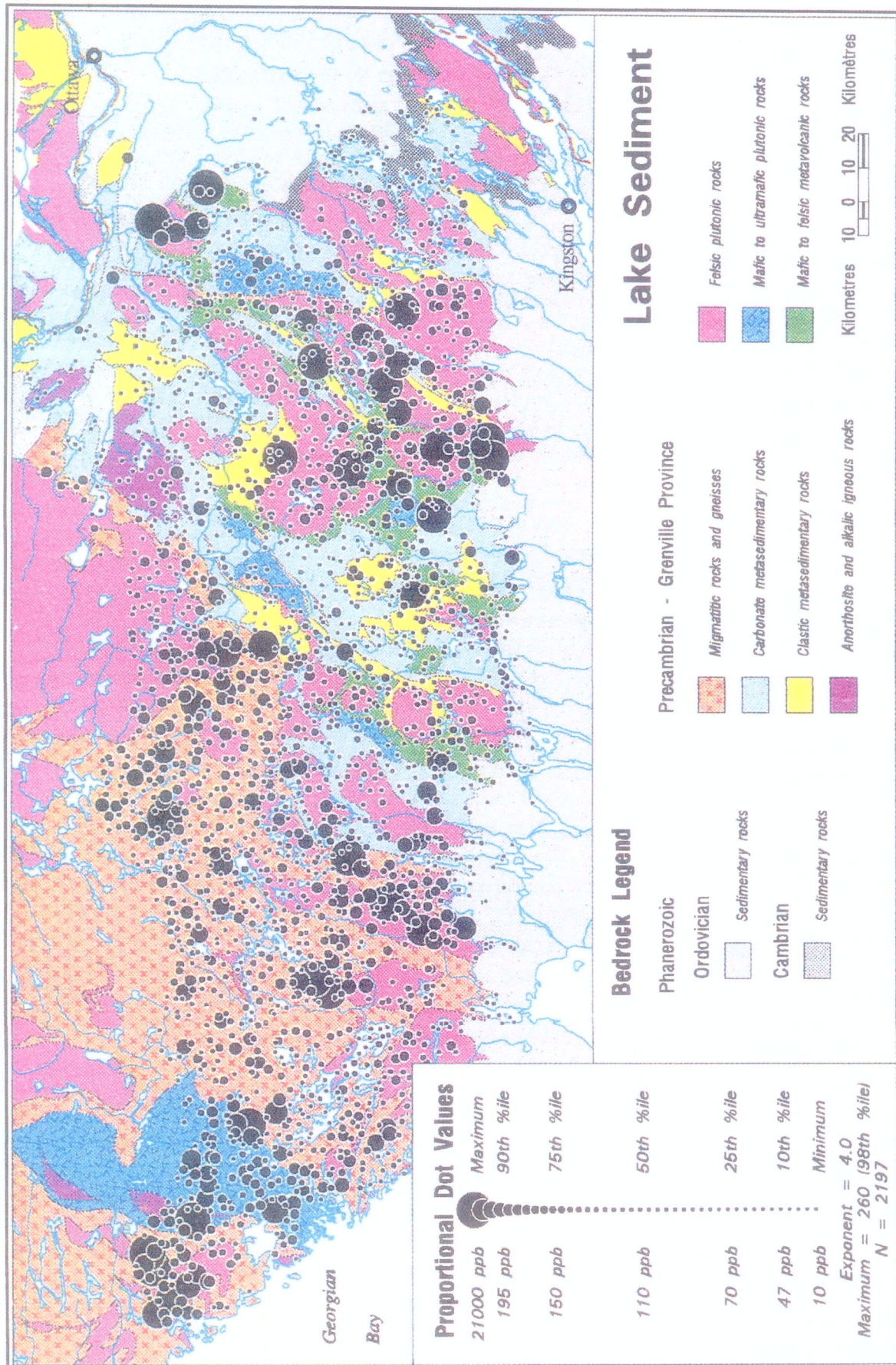


Figure 1. Natural, geologically controlled, levels of Hg (ppb) in the <180  $\mu$ m fraction of modern lake sediments in the Canadian Shield region of Ottawa/Kingston to Georgian Bay, Ontario, Canada.

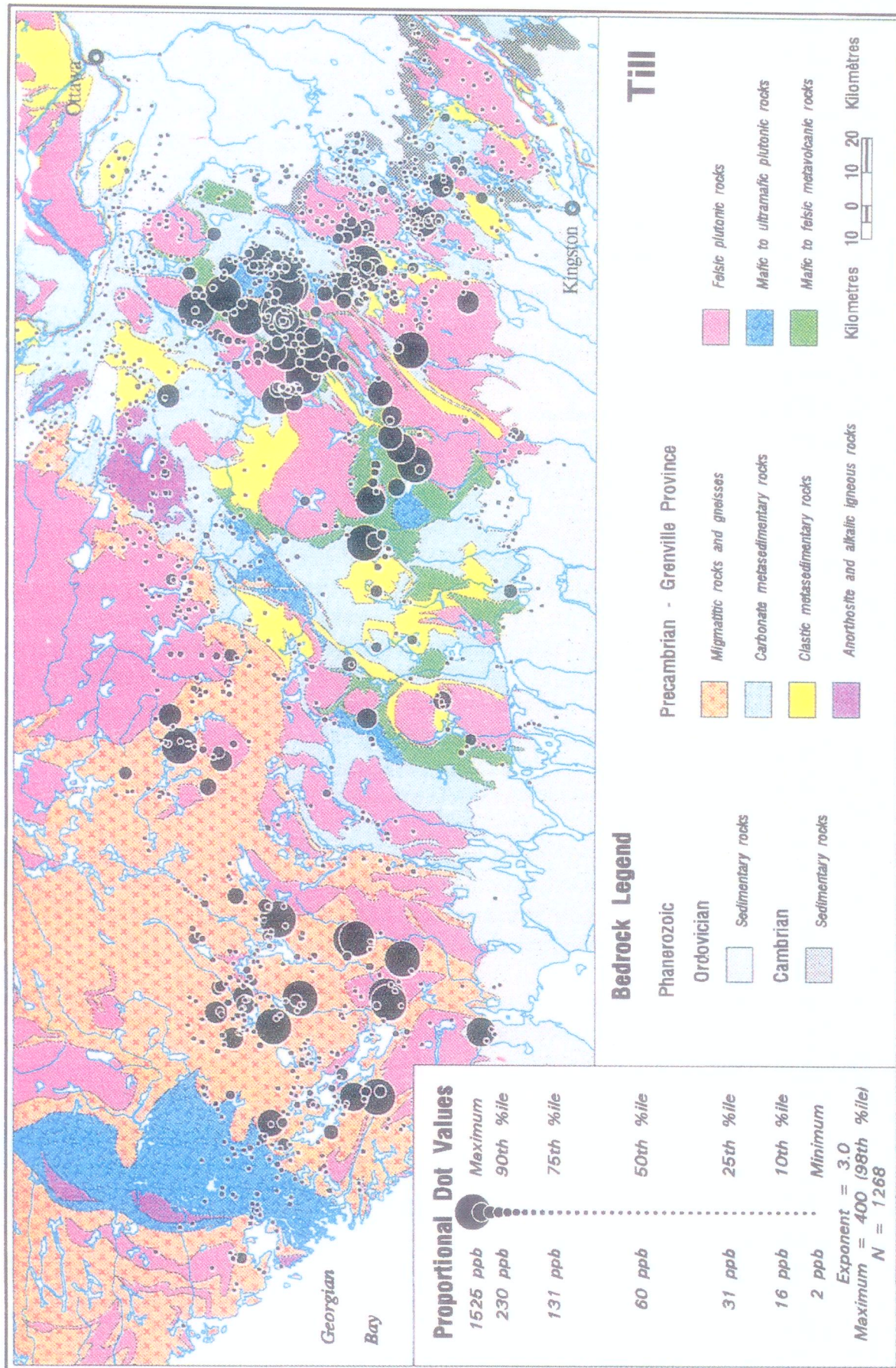


Figure 2: Natural, geologically controlled, levels of Hg (ppb) in the clay-sized (<2  $\mu\text{m}$ ) fraction of glacial sediments, primarily till, in the Canadian Shield region of Ottawa/Kingston to Georgian Bay, Ontario, Canada.

## 2. Sample collection, preparation and analytical methods

In southeastern Ontario, modern lake sediment samples were collected from approximately 2200 lakes (1 site per 13 km<sup>2</sup>) (G.S.C., 1977a,b; Hornbrook *et al.*, 1984a,b) (Figure 1). Sample collection, preparation and analyses followed National Geochemical Reconnaissance (NGR) protocols (for details see Friske and Hornbrook, 1991). Surficial (top 5-10 cm) sediment, which is physicochemically active and potentially anthropogenically impacted, was automatically excluded through sampler design so that the organic-rich sediment (gyttja) samples obtained were generally from >30 cm depth in the sediment column (Coker *et al.*, 1979) and thus the reported data represent natural (pre-industrial) levels of total Hg in lake sediments. The natural distribution of Hg and other trace elements, as determined by lake sediment geochemistry, has been used for several decades to successfully explore for and locate new mineral deposits (Coker *et al.*, 1979; Friske and Hornbrook, 1991).

Over the same area, glacial sediments (n = 1268), primarily till, were sampled at irregular intervals (1 site per 23 km<sup>2</sup>) from below the postglacial solum to avoid the effects of postglacial weathering and potential anthropogenic modification (Kettles and Shilts, 1994) (Figure 2).

After air drying, the <180 µm fraction of the lake sediment samples and the clay-sized (<2 µm) fraction separated by centrifugation from undried glacial sediments were analyzed for a wide range of elements. Mercury was determined by the cold vapour atomic absorption technique (Jonasson *et al.*, 1973). Quality control of all analytical data was monitored using reference standards and blind duplicates inserted at a frequency of 5% for lake sediments and 10% for glacial sediments. Precision and accuracy for total Hg measured in both media were in the ± 10% range.

The distribution and composition of various bedrock lithologies and mineralization influences regional element distributions within the secondary environment. The cover of glacial drift has a chemical composition that is related to local bedrock and to bedrock "up ice" from the sample site.

In the eastern and southern parts of the area sampled, flat lying, unmetamorphosed Ordovician limestones, dolomites, and shales crop out. In the west, crystalline igneous and metamorphic bedrock of the Grenville Structural Province of the Canadian Shield crop out (Baer *et al.*, 1977) (Figure 1). Sangster (1982) describes a wide variety of important mineral deposit types in the area.

The predominant ice flow direction during the last glaciation was towards the south-southwest and carbonate bedrock debris derived from Ordovician terrane has been transported in that direction over Precambrian bedrock. Along the Ottawa and St. Lawrence valleys and in low lying areas near Georgian Bay, glaciomarine and glaciolacustrine sediments form a fairly continuous surface cover.

## 3. Results

The dispersal and dispersion patterns of Hg in surficial media are a predominately, although sometimes glacially distorted, reflection of the composition of underlying bedrock. The large areas of natural Hg enrichment in drift (Figure 2) broadly outline the prominent belts of metavolcanic and metasedimentary rock (Shilts, 1984; Kettles and

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Shilts, 1989, 1994) as do areas of high Hg in modern lake sediments (Figure 1) (Hornbrook *et al.*, 1986). Though mercury-bearing minerals are known to occur in widely scattered quartz vein-hosted sulphide deposits within the metavolcanic and sedimentary rocks of the area (Sangster, 1982), individual deposits are small. Moreover, detailed studies of drift dispersal in the region (Sinclair, 1979; DiLabio *et al.*, 1982) show that detectable dispersal from sulphide occurrences is only on the order of 1 km. The observed elevated Hg concentrations in drift over such a large area (Figure 2) may indicate that there are many small, but overlapping Hg dispersal trains and/or Hg-rich mineral phases in the metasedimentary and metavolcanic host rocks, themselves.

#### 4. Discussion and conclusions

Variation of Hg in deep, pre-industrial lake sediments and glacial sediments over the study area illustrates the strong and predictable influence of geology on patterns of chemical variation. These data are essential for evaluating the nature and extent of anthropogenic modifications of natural chemical systems. For example, knowing areas where Hg is naturally enhanced in lakes, glacial drift, and/or bedrock, offers some hope for identifying areas where this potentially toxic element may naturally lead to elevated levels of Hg in fish (e.g. Loukola-Ruskeeniemi, 1990; Rasmussen, 1993; Shilts and Coker, 1995) or where the landscape may be most likely to be most severely impacted by anthropogenic phenomena (i.e. acid rain, etc.) (e.g. Coker and Shilts, 1979; Shilts *et al.*, 1981). It also may lead to a realistic evaluation of the extent to which Hg, and other elements, are enriched in the surficial environment from airborne or waterborne pollutants.

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# TEMPORAL VARIATION OF MERCURY IN VEGETATION

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**Abstract.** Temporal changes in the Hg content of balsam fir needles (*Abies balsamea*) and white spruce needles (*Picea glauca*) were monitored at a control site over two growing seasons. Results indicated a significant increase in the Hg content of needles of both species over the course of a growing season and from one year to the next. The Hg content of new foliage more than doubled within each growing season, and was 5-10 ng g<sup>-1</sup> higher in the 1990 growing season than in the previous year. These results indicate that temporal variation is a potential source of error when mapping the spatial variation of Hg concentrations in vegetation. To minimize this source of error, field surveys should be completed as quickly as possible (i.e., within two or three weeks).

## 1. Introduction

Mapping the spatial variation of Hg concentrations in vegetation is a surveying technique used for determining the radius of influence of Hg released from industrial sources and in prospecting for mineral deposits (Siegel *et al.*, 1985; Shaw and Panigrahi, 1986; Kovalevsky, 1986). Consistency in sample collection is essential in order to properly interpret changes in Hg concentration between sites, as Hg concentrations within a plant vary significantly (>10%) with tissue age and type (Barakso and Tarnocai, 1970; Siegel *et al.*, 1985; Kovalevsky, 1986; Shaw and Panigrahi, 1986; Rasmussen *et al.*, 1991; Rasmussen, 1994). Observations of seasonal and annual changes in the trace element content of various plant tissues indicate that temporal variation is another potential source of error that must be considered when conducting a vegetation survey (Dunn, 1991).

The purpose of this study was to monitor temporal changes in the Hg content of vegetation by sampling the foliage of two trees at a control site over the course of a field study (1989-1990) in which the spatial variation of Hg was assessed in more than two dozen plant species over an area of approximately 150 km<sup>2</sup> (Rasmussen *et al.*, 1991; Rasmussen, 1994).

## 2. Materials and Methods

The study area is located in the southern Canadian Shield, west of the town of Huntsville, Ontario, Canada (long. 79°20' lat. 45°20'). Details of the study area and analytical method have been published previously (Rasmussen *et al.*, 1991; Rasmussen, 1994).

A balsam fir tree (*Abies balsamea*) and a white spruce tree (*Picea glauca*) located 2 m apart were sampled six times over a 23 week period from May to October 1990. Results of sampling the same two trees during the previous growing season (six times from June to August 1989) have been reported previously (Rasmussen *et al.*, 1991). Samples were

collected from boughs at waist height using unpowdered vinyl gloves and stainless steel clippers. Samples were triple-bagged in the field using Zip-Loc polyethylene bags, and stored frozen until time of preparation and analysis.

The samples were rinsed with distilled deionized water and oven-dried for 24 hr at 60°C. Analysis consisted of a 6-hr hot digestion using HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> in a 1:4 ratio, followed by dilution, SnCl<sub>2</sub> reduction and cold-vapor AAS detection. The analytical work was performed in a clean laboratory facility outfitted with gold air filters to adsorb airborne contaminant Hg. The detection limit, defined as three times the standard deviation of the blank, was 1.3 ng g<sup>-1</sup> calculated for a dry sample weight of 0.100 g. Accuracy and precision were monitored using NBS#1575 Pine Standard (certified value 0.15±.05 µg g<sup>-1</sup>) and NBS#1572 Citrus Standard (certified value 0.08±.02 µg g<sup>-1</sup>). Results were consistently within the certified range and reproducibility was within 5% RSD based on 13 duplicate analyses.

### 3. Results and Discussion

An increase in the Hg content of needles from both species occurred over the 23 week sampling period in 1990 as shown in Fig. 1. Needles produced in the 1990 growing season are labelled "1st year growth", and needles produced in the previous two years (1989 and 1988) are labelled "2nd year growth" and "3rd year growth" respectively (Fig. 1). Temporal variation was most pronounced in new growth: from July to October, the Hg content of 1st year needles approximately doubled in both species (Fig. 1). Temporal variation was significant compared to variation in the Hg content of needles collected from different parts of the same tree on the same day, which was 10% or less (Rasmussen *et al.*, 1991).

Wytenbach and Tobler (1988) observed similar increases in the Hg content of 1st and 2nd year needles of Norway spruce (*Picea abies* (L.) Karst) over the course of the growing season. Such evidence of temporal variation underscores the importance of restricting sampling to short time periods (Dunn, 1991). To minimize this source of error, Dunn (1991) recommended that vegetation surveys be completed within two to three weeks. The data reported in this study also indicate that it is best to conduct surveys in the late summer or early fall to take advantage of the higher Hg concentrations in samples relative to the analytical detection limit.

A comparison of 1st, 2nd and 3rd year needles (Fig. 1) indicates that the Hg content of the older tissue increases by about 5-10 ng g<sup>-1</sup> yr<sup>-1</sup>. Such variations with tissue age, caused by Hg accumulation within the plant, have been reported previously (Rasmussen *et al.*, 1991; Barghigiani *et al.*, 1987; Barakso and Tarnocai, 1970) and illustrate the importance of consistency when collecting living tissue. Based on the observation that older tissue contains higher Hg concentrations, Barakso and Tarnocai (1970) recommended the use of 2nd or 3rd year growth for surveying conifers.

A comparison of the 1989 data (Rasmussen *et al.*, 1991) and the 1990 data (Fig. 1) indicates significant annual variation. For example, the Hg content of 2nd year growth sampled in August 1990 (28 ng g<sup>-1</sup> in spruce, 26 ng g<sup>-1</sup> in balsam fir) was double that of

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2nd year growth sampled from the same trees in August 1989 (12 ng g<sup>-1</sup> in spruce, 15 ng g<sup>-1</sup> in balsam fir). A similar increase from 1989 to 1990 was observed in leaves of deciduous species growing in the same study area (Rasmussen, 1993). For example, in 1989 the Hg content of sugar maple foliage (*Acer saccharum* Marsh) ranged from 6 to 25 ng g<sup>-1</sup> (median 9 ng g<sup>-1</sup>), sampled at 95 sites over an area of 150 km<sup>2</sup> (Rasmussen *et al.*, 1991). In 1990, however, Hg content in foliage of the same species ranged from 17 to 41 ng g<sup>-1</sup> (median 24 ng g<sup>-1</sup>), sampled at 18 sites across the same watershed (Rasmussen, 1994). The increase from 1989 to 1990 could reflect annual variation in factors affecting growth rate, such as temperature and rainfall, or it could reflect annual variation in the amount of Hg available to the trees in the study area.

### Acknowledgements

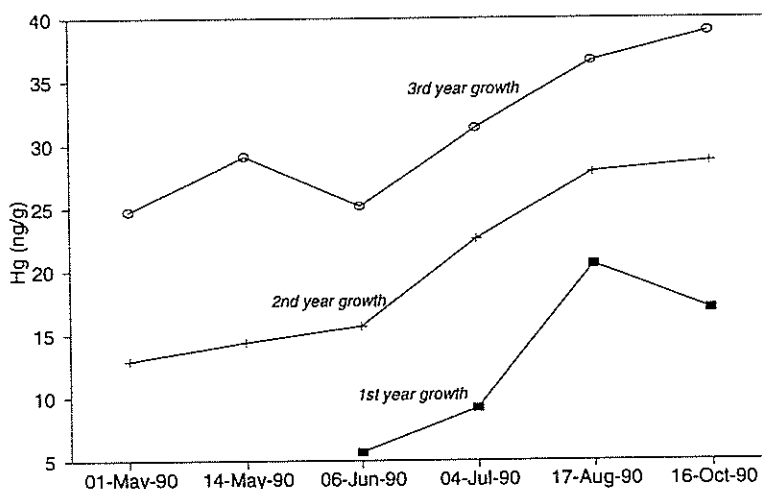
Field assistance by Andrew Devaney and use of the clean lab facilities at the Dorset Research Centre, Ontario Ministry of the Environment and Energy (MOEE) were greatly appreciated. This study formed part of the author's PhD thesis which was jointly funded by the MOEE, an NSERC Strategic Grant (P. Welbourn P.I.) and two Ontario Graduate Scholarships.

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### Changes in Hg content through time.

Needles collected from one BALSAM tree.



### Changes in Hg content through time.

Needles collected from one SPRUCE tree.

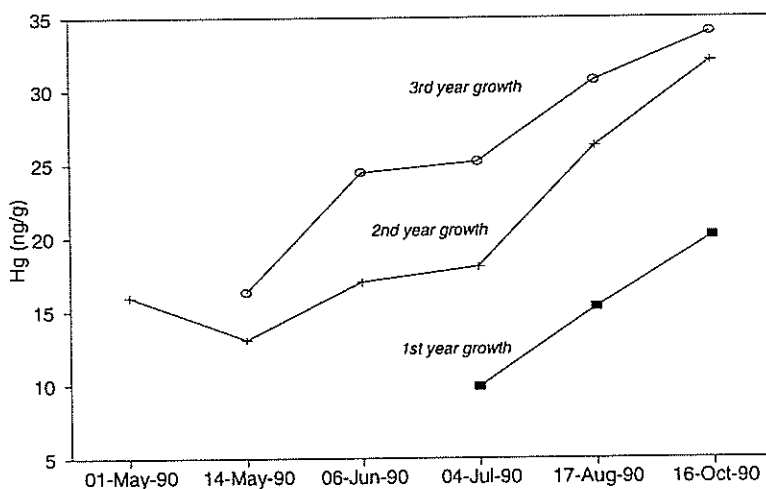


Fig. 1. Temporal variation in Hg concentration (dry wt.) of 1st, 2nd and 3rd year needles of a balsam fir tree (top) and a spruce tree (bottom) sampled in 1990. Variation between needles was 4.3%RSD for balsam (22 duplicate pairs) and 6.4% RSD for spruce (11 duplicate pairs). Variation between different boughs sampled on the same day was within 10% RSD.

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# MERCURY DISTRIBUTION IN HUMUS AND SURFICIAL SEDIMENTS, FLIN FLON, MANITOBA, CANADA

P.J. HENDERSON and I. McMARTIN

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Geological Survey of Canada Contribution No. 25594

**Abstract.** Regional humus and surficial sediments were collected in the vicinity of a base metal smelter in Flin Flon. Results of total mercury (Hg) analyses indicate that enrichment in humus is related to emissions from the smelter stack up to a distance of 40 km. In the immediate vicinity of the point source, total Hg values reach as much as 250 times the regional background (400 ppb). This enrichment is not reflected in the underlying surficial sediments. The Hg distribution pattern is similar for other known metal pollutants emitted from the smelter.

## 1. Introduction

Humus and surficial sediment samples were collected in the Flin Flon-Snow Lake area, northern Manitoba and Saskatchewan, as part of a regional surficial geological mapping and drift prospecting project undertaken by the Geological Survey of Canada. The Flin Flon area is of particular interest geologically and environmentally since it is the site of a base metal mining and smelting complex. The smelter in Flin Flon produces, on site, zinc, copper, and cadmium from ore extracted from local mines. Particulate emission tests in the smelter stack have indicated that various amounts of Zn, Pb, Fe, Cu, Cd and As are discharged into the environment.

Numerous studies have demonstrated that smelters act as point sources of airborne pollutants that are concentrated in soils and vegetation (Freedman and Hutchinson, 1980a,b; Hutchinson and Whitby, 1974, 1976; Lagerwerff *et al.*, 1972; Little and Martin, 1972). In the Flin Flon area, known pollutants emitted from the smelter have been found in increasing concentrations toward the smelter both in forest soils (Hogan and Wotton, 1984) and in peat (Zoltai, 1988). The emitted metals are deposited as dustfall and rainfall, mainly in the form of metal particulate, metal oxide and probably metal sulfates (Franzin *et al.*, 1979). Mercury, which is a volatile metal, is mostly emitted as very fine particles of its oxide.

Mercury has never been considered in regard to smelter emissions in the Flin Flon area. The purpose of this paper is to evaluate the distribution of total mercury in the humus and in the glacially derived sediments of the region.

## 2. Regional setting

The study area straddles the Paleozoic/Precambrian contact near the Manitoba-Saskatchewan border (Figure 1). The northern half is underlain by rocks of the Flin Flon-Snow Lake greenstone belts and their high grade metamorphic equivalent in the Canadian Shield; the southern half by flat-bedded Paleozoic dolostones of the Manitoba Plain. The bedrock is covered by discontinuous Quaternary and Holocene deposits, including till, glaciolacustrine sediments and peatlands. The dominant wind direction recorded in Flin Flon is towards the southeast and southwest, with strong components towards the north-northwest and south (Environ. Canada, 1990). The area is forested by a mixed coniferous deciduous boreal community comprised of jack pine, black spruce, white spruce, balsam fir, trembling aspen and balsam poplar (Hogan and Wotton, 1984).

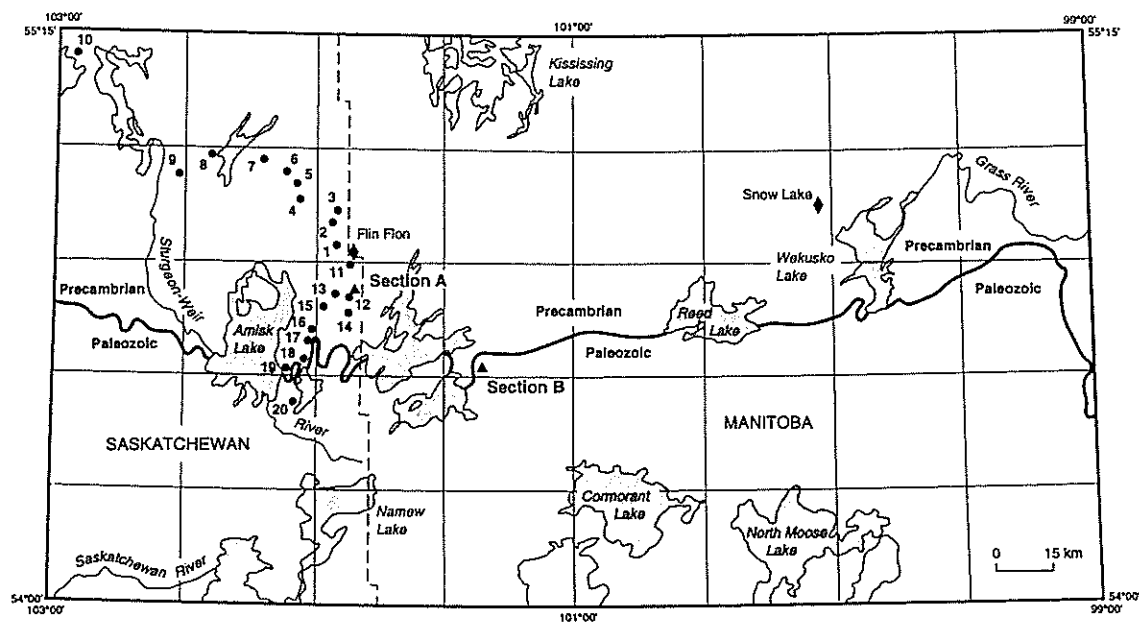


Fig.1. Study area showing location of transects and sections.

### 3. Methods

Humus and till samples were collected in the study area during the summers of 1992-93. The well decomposed, dark organic part of the uppermost soil horizon (A1) was preferentially sampled for humus. At some sites, however, both partially decomposed forest litter and mineral soil may constitute part of the humus sample since organic soil horizons are thin in areas of extensive logging or forest fires. For this study, approximately 50 to 100 g humus was collected from directly over or in an area immediately adjacent to a till sample. Till was collected from hand dug pits and exposed sections at a spacing of 1 to 5 km depending on access. Pits were dug to bedrock or 1 m maximum depth and, in nearly all cases, a 3 kg sample was collected below the upper B soil horizon in order to minimize local weathering effects.

Humus samples were air-dried and sieved to <35-mesh (0.425 mm); the clay-sized fraction (<0.002 mm) of till was separated by centrifuge and decantation. Geochemical analyses for a number of major and trace elements were conducted on these fractions using inductively coupled plasma atomic emission spectrometry, following an aqua regia digestion. Mercury was analyzed by cold vapour atomic absorption spectrometry, following aqua regia digestion. Loss on ignition (LOI) was used to assess the organic content. Analyses of duplicate samples and laboratory standards were used to monitor analytical accuracy and precision.

### 4. Results and discussion

On a regional basis, results show that Hg concentrations in the humus are consistently higher than those in the till. Statistical compilation gives a median value of 266 ppb in the humus and 50 in the clay size fraction of till. In humus, anomalous samples are as

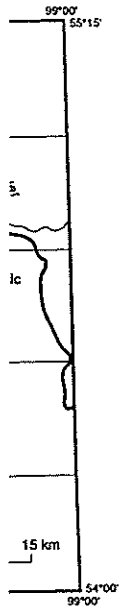
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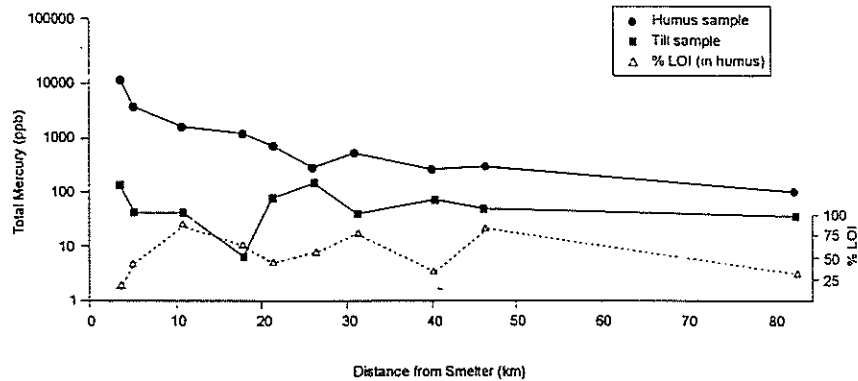
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much as 250x higher than background values (400 ppb); in till, only 7x higher (60 ppb). Anomalously high Hg concentrations in humus are found in the vicinity of the smelter, with values decreasing towards background levels at distances greater than 35 km. From our study, this general pattern is also reflected in the distribution of other emitted metals such as Zn, Pb, Cu, As, and Cd.



(a) North-northwest Transect (Sites 1 - 10)



(b) South-southwest Transect (Sites 11 - 20)

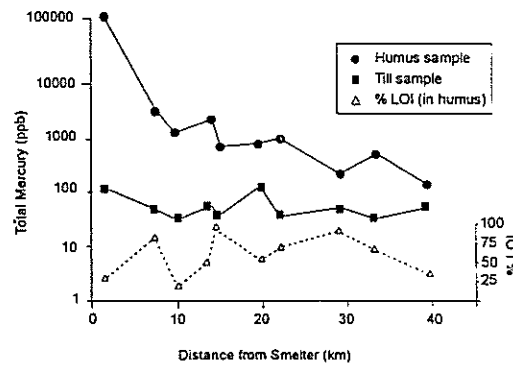


Fig.2. Total Hg concentrations in humus and till along transects. Total Hg is plotted on a log scale. Organic content in humus (% LOI) is shown with a dashed line.

The regional distribution in total Hg concentration is illustrated in two transects: one extending approximately 80 km north-northwest, the other extending 40 km south-southwest from the smelter stack (Figure 2). In both cases, total Hg concentrations in humus exceed those in till for all sites. Values in humus decrease markedly with distance from the smelter while Hg concentration in till remains fairly constant. Although the organic content of the humus, as indicated by %LOI, varies in the samples taken along the transects, the Hg concentrations appear unrelated to these variations. This suggests that the distribution of Hg in humus near Flin Flon is related to contamination associated with the smelting activities. In the immediate area of the smelter, the low organic content of the humus suggests that Hg concentrations may be linked more to fallout of particulate matter than incorporation into organic complexes.

Two till sections within the area were also sampled in detail in order to examine vertical variations in trace element concentrations through humus and the underlying till. Section A (Table I) consists of homogeneous, massive, sandy diamicton, located on

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Precambrian terrane 8.75 km south of the smelter. Section B is located 40 km southeast of Flin Flon and forms a vertical exposure on the Paleozoic bedrock. It consists of calcareous massive sandy-silty diamicton. Results show an enrichment in humus for both sections although concentrations are much higher in section A, exceeding those in till by more than a factor of 10. In section B, the value in humus is more consistent with the regional background. Although Hg has a tendency for adsorption by organic matter and secondary hydrous oxides within humus, the magnitude of the enrichment in Section A must reflect deposition of smelter emissions. Enhanced Hg concentrations in the upper portion of the mineral soil in both sections suggest migration of Hg from the surface layer to a depth of 40 cm approximately.

TABLE I

Vertical distribution of total Hg in two soil profiles			
Section A		Section B	
Depth (cm)	Hg (ppb)	Depth (cm)	Hg (ppb)
Humus	2800	Humus	260
5	270	15	70
15	190	30	90
25	130	80	50
35	100	130	50
45	60	180	40
55	50	230	50
65	70	280	50
75	50	320	50
85	50	380	50
95	70	430	50
		480	40
		530	50

## 5. Conclusion

In the vicinity of Flin Flon, the enrichment of mercury in humus is clearly related to emissions from the smelter. This enrichment is not reflected in the underlying glacially derived sediments, as seen both in the transects and in the soil profiles. Hg concentrations appear unrelated to variations in organic content of the humus, as indicated by %LOI.

## Acknowledgments

This study is part of the Geological Survey of Canada NATMAP Shield Margin Project and was funded in part by the Canada-Saskatchewan Partnership Agreement on Mineral Development (1990-1995). Thanks to Erik Nielsen, Christine Kaszycki, Martin Roy.

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# THE IMPORTANCE OF GEOLOGICAL CONTROLS ON THE NATURAL DISTRIBUTION OF MERCURY IN LAKE AND STREAM SEDIMENTS ACROSS CANADA

P.W.B Friske and W.B. Coker

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**Abstract.** The Geological Survey of Canada (GSC) has surveyed a significant portion of Canada using systematic stream and lake surveys under the National Geochemical Reconnaissance (NGR) program. Total mercury (Hg) data, available for most of the sites, reveal significant natural variation. Much of the observed variation in Hg concentration can be directly related to the composition of the bedrock, regolith and glacial deposits in the surrounding watershed. Some of the highest Hg values within the sediments of Ontario lakes occur southwest of Thunder Bay in an area underlain by shales known to be naturally enriched in Hg and other trace metals.

## 1. Introduction

Since 1973, a significant part of Canada has been covered by systematic stream and lake surveys under the National Geochemical Reconnaissance (NGR) program designed to establish and maintain a nationally consistent geochemical database. To date (1994), more than 200 surveys have been completed to NGR standards, representing over 180,000 sites, covering 2.2 million km<sup>2</sup> throughout Canada (Figure 1). A detailed description of NGR survey methodology is given by Friske and Hornbrook (1991). Data for up to 35 elements are available for many of the sediment samples. The purpose of this paper is to draw attention to the voluminous amount of NGR data available on the natural distribution of Hg and other elements and to illustrate the relevance of these data to environmental issues.

## 2. Sample collection, preparation and analytical methods

All sample collection, preparation and analyses follow the stringent NGR protocols (Friske and Hornbrook, 1991). The organic-rich lake sediments (gyttja) were generally collected from >30 cm depth in the sediment column to exclude the surficial sediment which is physiochemically active and potentially anthropogenically impacted. Stream sediments were collected from the active part of first and second order streams. Both media were air dried, and a <63 µm fraction prepared. Mercury was determined by the Hatch and Ott (1968) cold vapour atomic absorption technique, with some modifications (Jonasson *et al.*, 1973). Quality control of all analytical data was maintained by monitoring control reference standards and blind duplicates, inserted at a frequency of 5%.

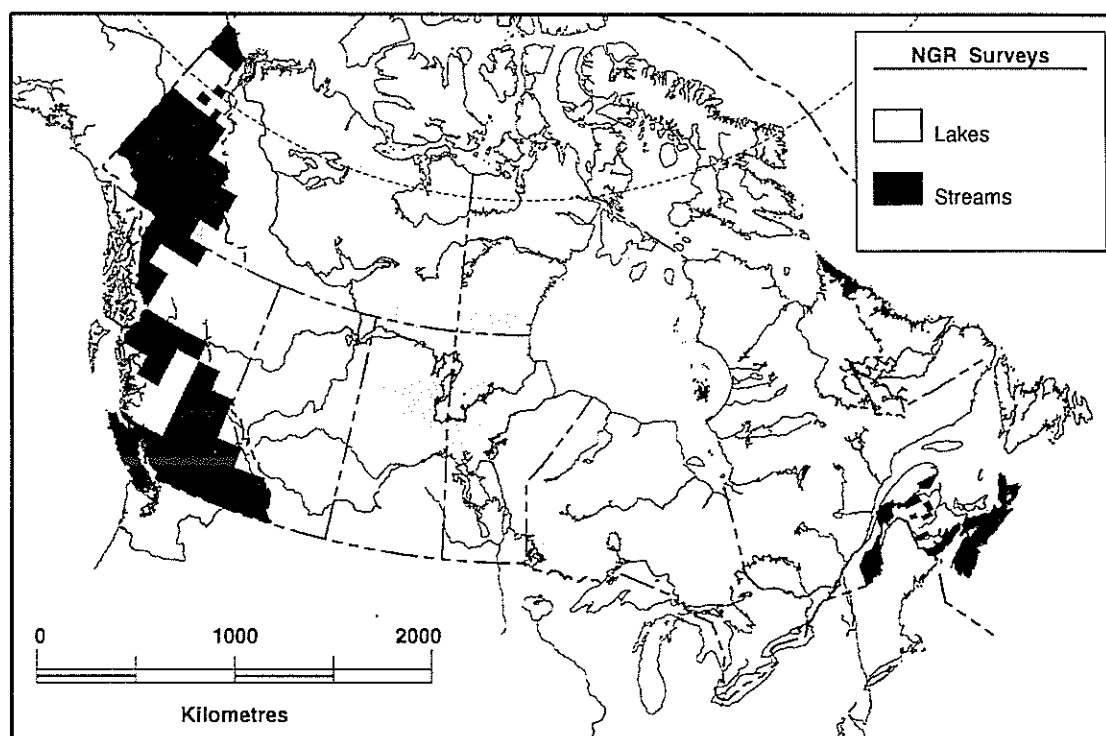


Fig. 1. National Geochemical Reconnaissance (NGR) stream and lake survey coverage (1973 to 1994) in Canada

### 3. Results and discussion

Mercury, like other elements, is preferentially concentrated in certain rock types through igneous, metamorphic and sedimentary processes. In Cannon's (1978), tabulation of the concentration of 21 elements in 10 natural materials, average Hg concentrations vary from 40 to 50 ppb in limestones and sandstones up to 500 ppb in black shales.

There are many examples in the literature illustrating the effects of changing bedrock chemistry on the composition of related lake sediments (c.f., Hornbrook and Garrett, 1976; Jonasson, 1976; Cameron and Ballantyne, 1977; Maurice, 1977; Coker and Shilts, 1979; Friske, 1985; Johnson *et al.*, 1986; Kerr and Davenport, 1990; Fortescue and Vida 1990; Garrett *et al.*, 1990). Table I summarizes the distribution of approximately 100,000 analyses for Hg in stream and lake sediments. Assuming that the 5th and 95th percentiles are reasonable estimates of the range of background variation, the contrast between the lower and upper limits of background is almost 9 times for lake sediments (N=69,884; 5th=20 ppb, 95th=175 ppb); and 23 times for stream sediments (N=26,124; 5th=10 ppb, 95th=230 ppb). Table I shows how geological factors affect the distribution of Hg in drainage basins in Ontario. Using a lower value of 5 ppb (5th percentile for marble) and an upper value of 305 ppb (95th percentile for shale), 'normal' background values

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within the survey area range from 5 to 305 ppb depending on the local bedrock geology (a range of 61 times the lower background value). This illustrates the importance of determining 'local background' values for an area. For example, a sample with a concentration of 200 ppb Hg coming from a lake underlain by marble is highly enriched (anomalous), whereas the same concentration from a lake over shales is well within the range of normal background variation.

TABLE I

Hg (ppb) summary statistics for lake and stream sediment data from the NGR database and for lake sediments for specific rock types within Ontario.

	Total Dataset		Ontario Lake Sediments			
	Lakes	Streams	Total	Rock Type		
				Shale	Marble	Diabase
Number of Values	69,884	26,124	13,813	38	38	277
Mean	74	72	119.4	169.2	54.7	190.4
Std Deviation	99	114	198.3	70.5	36.4	366
<b>5th Percentile</b>	<b>20</b>	<b>10</b>	<b>35</b>	<b>90</b>	<b>5*</b>	<b>45</b>
10th Percentile	30	15	47	90	19	60
25th Percentile	40	25	70	110	28	97
<b>50th Percentile</b>	<b>60</b>	<b>40</b>	<b>110</b>	<b>165</b>	<b>45</b>	<b>140</b>
75th Percentile	90	80	150	192.5	80	199
90th Percentile	140	151	195	291	110	251
<b>95th Percentile</b>	<b>175</b>	<b>230</b>	<b>222</b>	<b>305</b>	<b>132</b>	<b>295</b>

\* Detection limit for Hg is 10.0 ppb. Values less than 10.0 set to 5.0 for calculations.

Figure 2 is a 'smoothed' contour plot of Hg data for sediments from Ontario lakes. The area of elevated Hg southwest of Thunder Bay coincides with shales known to be enriched in Hg (Coker and Shilts, 1979; Friske, 1985). The discontinuous band of elevated Hg, extending east from Sault Ste. Marie and then northeast to New Liskeard, is associated with sporadic exposures of diabase sills and dykes that are relatively enriched in Hg. Some of the lowest Hg levels encountered in Ontario lake sediments occur west of Ottawa in areas underlain by marble. It is particularly noteworthy that some of the highest Hg concentrations occur in relatively isolated areas, while some of the lowest values are encountered in southeastern Ontario, the more highly populated and industrialised region.

#### 4. Summary

Anthropogenic inputs of Hg and other trace elements into the environment are superimposed on a highly variable natural geochemical background. Variations in the natural abundance levels in bedrock vary widely, and can range over several orders of

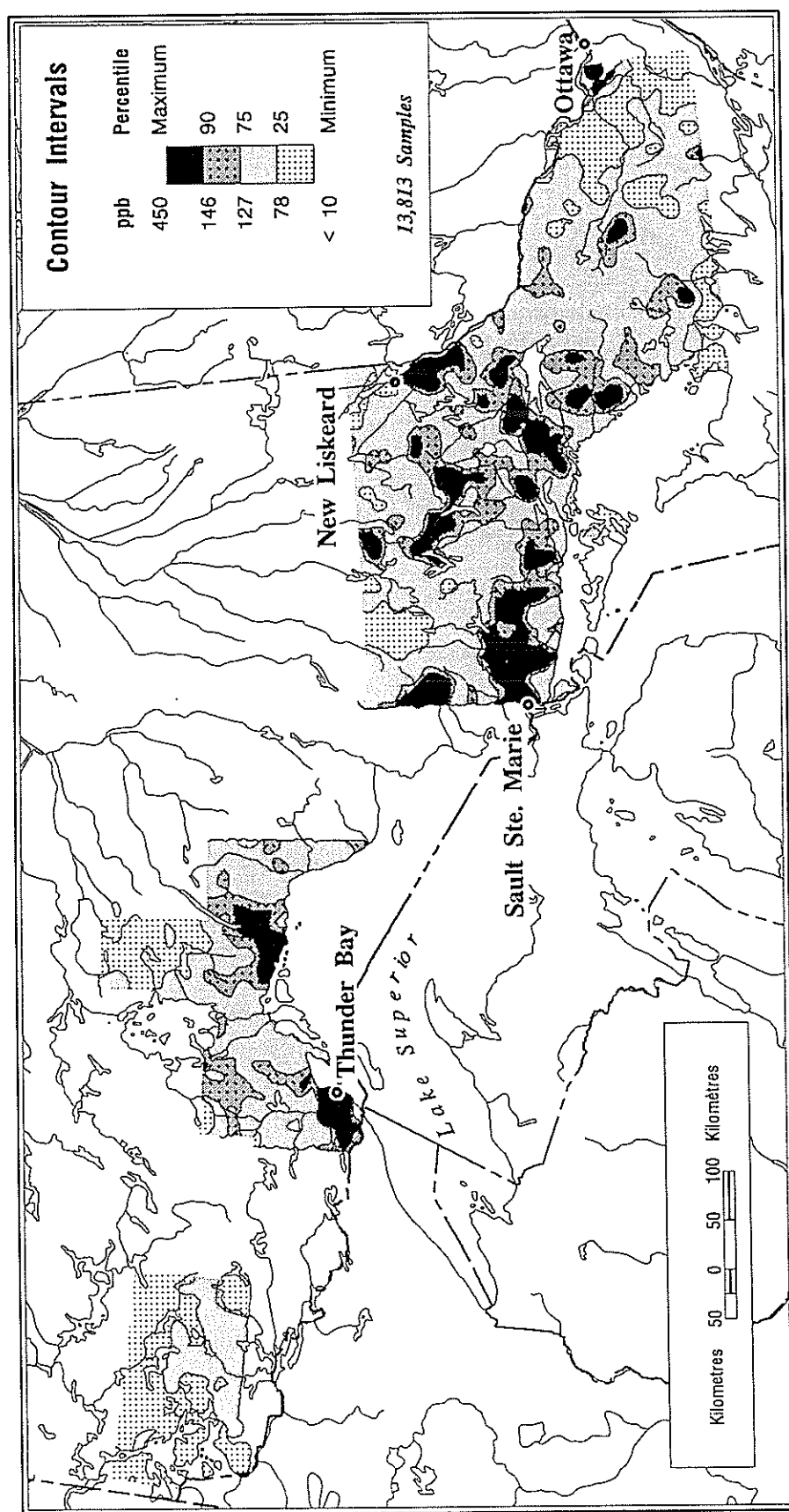


Fig. 2. Regional distribution of Hg in Ontario lake sediments.

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magnitude. These natural geochemical variations are reflected in the chemical composition of the waters, soils, drainage and glacial sediments associated with each bedrock type.

Distinguishing Hg and other trace element contributions from natural sources from those related to anthropogenic inputs is a major challenge, particularly for agencies charged with developing sediment quality guidelines. Any assessment of possibly 'contaminated' areas needs to be evaluated in the context of the local natural background. The NGR database provides a voluminous amount of data pertinent to establishing this background for many elements in the surficial environment.

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# GLACIAL DISPERSAL OF MERCURY FROM BEDROCK MINERALIZATION ALONG PINCHI FAULT, NORTH CENTRAL BRITISH COLUMBIA

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**Abstract.** Mineralized occurrences of Hg in bedrock are abundant along Pinchi Fault, in north central British Columbia, two of which have been mined in the early to mid 20th century. Distribution patterns of mercury concentrations measured in the clay sized fraction ( $<2\ \mu\text{m}$ ) of till reveal anomalous levels on and down-ice from the fault. Mercury in the till is interpreted to be of detrital origin. In other words, during glaciation, glacier ice eroded bedrock and older sediments enriched in mercury and transported them in a down-ice direction, finally depositing the sediment load at a distance from the source. Consequently, the area with anomalous mercury concentrations in the till is several orders of magnitude larger than the area of mercury mineralization in bedrock.

## 1. Introduction

As ice flows over a substrate, it erodes bedrock and older unconsolidated sediments and transports debris from those sources in a down-ice direction. Subsequently, debris is deposited from the ice, as till, at a certain distance from the original source. If bedrock with a distinctive character (lithology, color, geochemical signature, etc.) is eroded by ice, it will result in a perceivable train of debris in the till, i.e. a dispersal train (DiLabio, 1990; Shilts, 1973). Concentrations of fragments from that rock type will be high in the till near the source and will eventually get diluted by debris from other sources, further down-ice.

The purpose of this paper is to present a case where mercury concentrations in the till are anomalously high on and down-ice from a fault (Pinchi Fault) in central British Columbia. Patterns of mercury concentrations in the till are attributed to glacial erosion, transport and deposition of debris derived from cinnabar (HgS) mineralization located along the fault.

## 2. Setting

Pinchi Fault is a major NW-SE oriented structural lineament which extends over 450 km through central British Columbia (Armstrong, 1949; Paterson, 1977). The fault separates Cache Creek Terrane to the west from Triassic Takla Arc Terrane to the east (Fig. 1). Mercury occurrences, with cinnabar as the principal mineral, are abundant along the fault (Fig. 2) (Armstrong, 1948; 1949). Two mercury mines (Pinchi Lake and Bralorne Takla) were active in the early to mid 20th century.

Previous work indicated that chemical analysis of plant materials reflects mercury mineralization along Pinchi Fault (Fig. 2) (Siegel et al., 1985; Warren et al., 1983a; 1983b).

During the last glaciation, ice advanced onto lower areas of interior British Columbia with ice flow directions depicted on Figure 1.

### 3. Results and conclusion

As part of the Canada-British Columbia Agreement on Mineral Development (1991-1995), a geochemical sampling program was implemented by the Geological Survey Canada in the central part of the province in an area which includes a long section of

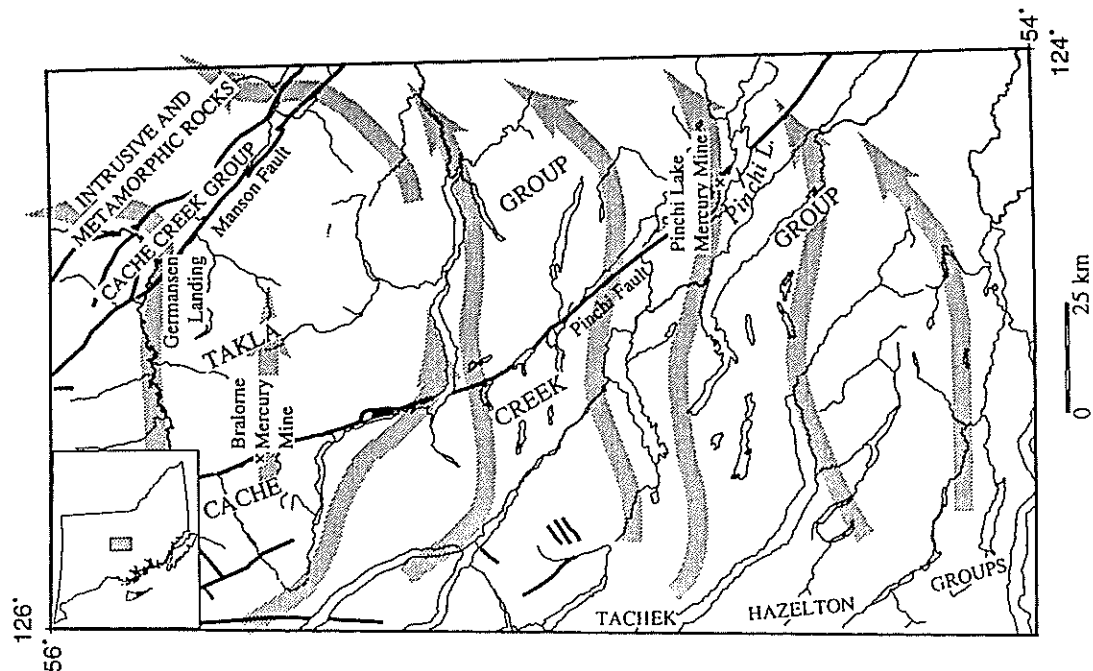


Figure 1. Generalized bedrock geology and ice flow patterns of the study area. All faults are shown as thicker black lines.

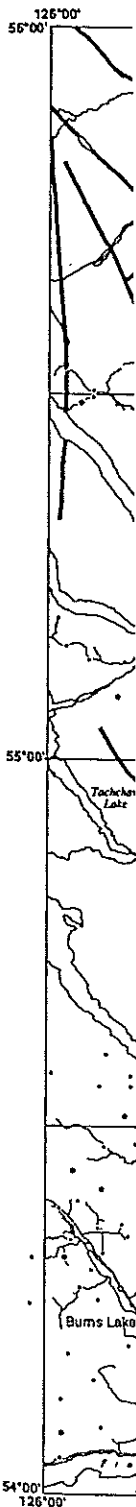


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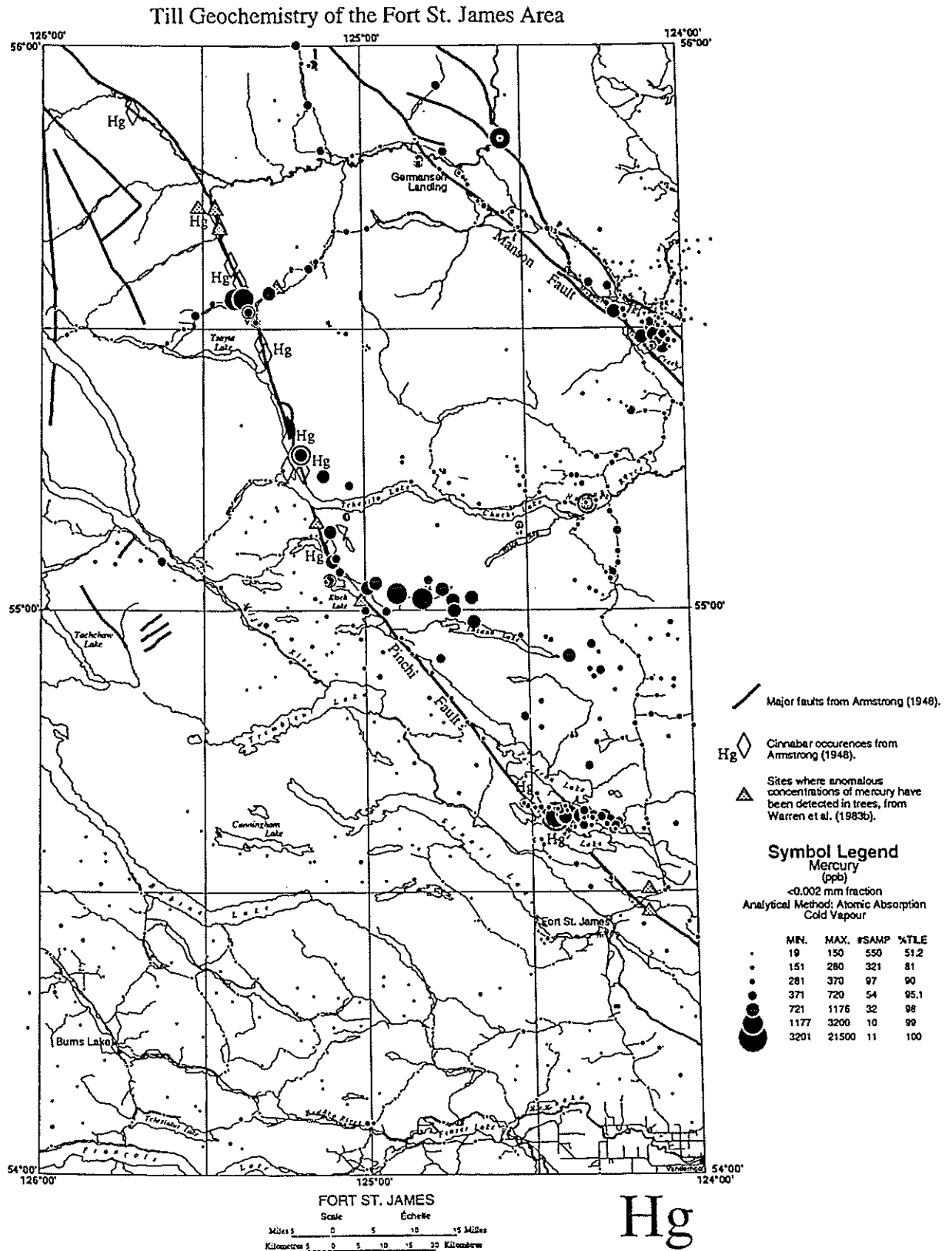
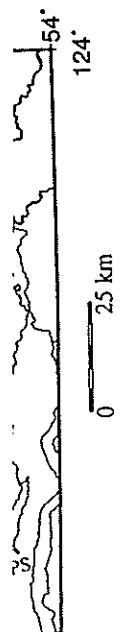


Figure 2. Geochemical map for mercury concentrations measured in the clay size ( $<2 \mu\text{m}$ ) fraction of till. Dot sizes are proportional to the mercury concentration present in the till.

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Pinchi Fault (Plouffe and Ballantyne, 1993). The clay sized fraction of till samples collected from the C soil horizon or the transition zone between the B and C horizons (depth greater than 1 m) from sections found along roads and river banks was analyzed for mercury by cold-vapor atomic absorption. Results indicate that natural mercury concentrations in till on and down-ice (east) from the fault zone are 4 to 100 times higher than concentrations in till on the up-ice side (west). Such mercury distribution in the till is attributed to the effect of glacial erosion, transport and deposition. In other words, during glaciation, glacier ice eroded bedrock and older sediments enriched in mercury, transported them in a down-ice direction, finally depositing the sediment load at a distance from the source. Detailed sampling completed north of Pinchi Lake (Fig. 2) showed that the measurable length of the glacial transport of mercury-bearing debris is in the range of 12 to 18 km. This implies that the area of till that is anomalous in mercury is several times larger than the surficial expression of bedrock mercury mineralization.

Total mercury detected in the till is thought to be primarily derived from a natural source and not from airborne pollution since: (1) till, a pre-industrial sediment, was sampled at a depth of one meter, (2) enrichment patterns are on and down-ice from Pinchi Fault, and (3) other studies conducted in areas polluted by airborne contaminants revealed minimal or no downward leaching of metals (Henderson and McMartin, 1994).

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