

## Reconnaissance geochemistry and its environmental relevance

Scott Painter<sup>a</sup>, Eion M. Cameron<sup>b</sup>, Rod Allan<sup>a</sup>, Jeremy Rouse<sup>a</sup>

<sup>a</sup>*National Water Research Institute, Environment Canada, Canada Centre for Inland Waters,  
Burlington, Ontario, L7R 4A6, Canada*

<sup>b</sup>*Geological Survey of Canada, Ottawa, Ontario, K1A 0E8 and Department of Geology,  
University of Ottawa, Ottawa, Ontario, K1N 6N5, Canada*

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### Abstract

In Canada, geochemical reconnaissance using lake and stream sediments and waters has been a cooperative program between federal and provincial geological survey organizations since the 1970's. Similar methods of sampling, analysis and quality control were established to ensure comparable data across the country. As of 1992, 2.5 million km<sup>2</sup>, or approximately one quarter of Canada's landmass has been covered. The original purpose of this National Geochemical Reconnaissance (NGR) was to assist mineral exploration. However, with time, the relevance of the data to environmental issues has become increasingly apparent. The concentrations of metals in the natural environment vary widely and in some areas unaffected by human activity may reach levels that elsewhere have been considered to have an effect on the ecosystem. Environmental agencies need to incorporate the natural distribution of metals into assessments of ecosystem health and anthropogenic pollution. Sediment quality guidelines, standards or clean-up criteria, are required for the assessment and remediation of contaminated areas under a variety of programs in Canada. These standards need to take into account the natural background of metals in the affected areas. For instance, under the Canadian Environmental Protection Act, a sediment Cd concentration of 0.6 ppm is used to screen ocean dumping permits and yet 20% of the lake and stream sediment samples collected by the NGR exceed this level naturally.

We present Canada-wide maps illustrating the regional variability of As, Cd, Cu, Hg, Ni, Pb, Zn and U in sediments, together with more detailed maps for selected areas. Cumulative frequency distribution plots for these elements plus Cr have been constructed based on up to 250,000 samples. At the scale that the maps are presented, anomalies a few km<sup>2</sup> or tens of km<sup>2</sup> in extent, which may be associated with individual mineral deposits, are not visible. What may be observed are large, regional anomalies hundreds or thousands of km<sup>2</sup> in extent. In some cases these may mark important mineral districts, such as U around the Athabasca and Elliot Lake uranium districts and the suite of metals that are enriched in stream sediments from the Selwyn Basin, Yukon that contains a variety of Sedex, Mississippi Valley and intrusion-related mineral deposits.

## 1. Introduction

Regional-scale geochemical surveys have been carried out in Canada for many years, mostly using stream sediments as the sampling medium (Rose et al., 1979). Since the 1970's, lake sediments have been used to extend the coverage on to the Canadian Shield. The Geological Survey of Canada (GSC) and provincial geological survey agencies have been carrying out a regular program of regional geochemical mapping for the past twenty years. Some of the programs have been conducted under formal federal–provincial agreements and others have been conducted using similar procedures and techniques.

The geochemical data are released to the public by federal and provincial geological survey agencies at nominal cost in the form of digital data files and maps. Although the annual coverage exceeds the area of many of the world's nations, much of Canada remains to be sampled, because of its vast size. Under the direction of the senior author, Environment Canada has compiled a substantial part of the available data, which are presented as maps in this paper. This was done to draw to the attention of environmental agencies the availability and utility of these data. The absolute levels of elements in the environment and their geographic variability needs to be considered in preparing environmental assessments, guidelines and regulations. We also wish to illustrate to geological survey agencies the value of the data in addition to their primary purpose as an aid to mineral exploration.

## 2. Historical perspective

The first geochemical surveys in Canada, which included lake sediment sampling, were carried out by Hans Lundberg in Newfoundland during the period 1938 to 1940 (Lundberg, 1957). Starting in the 1950's, stream sediment and water sampling became a widely-applied method for mineral exploration in the Canadian Cordillera and Appalachians. Most of this work was by companies and the results are not available to the public. Stream sediment and water surveys by government were first carried out by the GSC in Nova Scotia in 1956 (Boyle et al., 1958). These pioneer surveys were generally over relatively small areas by samplers moving on foot or by motor vehicles. Canada, with a land mass of 10 million km<sup>2</sup>, would have been impossible to cover using such methods; it was the helicopter that made rapid coverage of broad areas feasible.

In the Cordillera and some parts of the Appalachians, sampling of streams was the obvious choice for the helicopter-supported reconnaissance surveys of broad areas that commenced in the 1970's. But streams are poorly developed in the Canadian Shield and here attention turned to the sampling of lakes. Despite Lundberg's use of lake sediments in the first geochemical surveys of Canada, very little experience had been gained in their use. The first large-scale geochemical survey, using nearshore lake sediments — the Bear–Slave Operation in the northern Shield in 1972 — proved that rapid coverage of large areas was possible. Sampling of lakes over 93,000 km<sup>2</sup> was completed in six weeks and the results released in 1973 (Allan et al., 1973). Further studies in the northern and southern Shield developed suitable survey methods for centre-lake sediments (Coker et al., 1979).

With technical and logistical methods in place, the essential political vehicle to fund the National Geochemical Reconnaissance (NGR) surveys came in 1975 with the start of the

federal–provincial Uranium Reconnaissance Program (URP) (Darnley et al., 1975). The economic justification for the URP, that demand for uranium fuel would grow at a rate of 15–20% per year, proved to be grossly high and the program was terminated in 1978. However, it permitted a demonstration of the value of the NGR surveys, which were continued under successor federal–provincial agreements, and provided a conceptual basis for the International Geochemical Mapping project (Darnley, 1990).

The importance of the NGR being carried out as a cooperative endeavour between the Geological Survey of Canada and the provincial geological survey organizations cannot be overemphasized. Similar sampling, analytical and quality control procedures were employed across Canada. Today data collected in Newfoundland during the earliest years of the NGR are consistent with data obtained in British Columbia in the 1990's, permitting the presentation of the geochemical maps shown in this paper. The exception to these federal–provincial agreements was the Province of Quebec, which carried out its own, independently-managed survey program.

At this time, more than 20 years on from the first large-scale survey, we present the results of the coverage of 2.5 million km<sup>2</sup> of Canada. While the primary objective of the surveys was to assist mineral exploration, their contribution to understanding the geochemical environment of Canada has become increasingly apparent.

### 3. Data integration

The methods employed in the NGR surveys have been described by Friske and Hornbrook (1991). The elements determined in the program and the analytical methods used in the years 1976 through 1990 are summarized in Table 1. Most of the surveys were carried out at a sampling site density of 1 per 13 km<sup>2</sup>. The geochemical maps shown in this paper include the Bear–Slave survey carried out in 1972, prior to the NGR program. This early survey, at a sample site density of 1 per 26 km<sup>2</sup>, is described separately below.

The first set of NGR lake sediment geochemical data compiled by Environment Canada were for Ontario. A question arose as to whether the NGR data, obtained using a 4 M HNO<sub>3</sub>–1 M HCl digestion, were comparable to data obtained using an aqua regia digestion by the Ontario Ministry of Environment and Energy, which the latter were using to establish environmental guidelines. A comparison by Lynch (1990) between total extraction methods (hydrofluoric–nitric–perchloric acids, neutron activation, or XRF), aqua regia, and the weak acid HNO<sub>3</sub>–HCl is summarized in Table 2. For the selected elements, there is little difference between data for the different analytical techniques. The Ontario lake sediment files contain data obtained by two different analytical techniques: Cr, Ni, As and Fe by neutron activation analysis and Cr by aqua regia extraction and Ni, As and Fe by HNO<sub>3</sub>–HCl. The acid extraction gives analyses which are approximately 70–80% of the neutron activation results. Davenport et al. (1993) also compared total with weak acid attacks and found good agreement.

Another consideration when integrating the data was that sediment samples came from both lakes and streams. Early in the study, we decided to use only one sample media within each province if both were available; the predominant type was chosen. Stream sediment data were used in British Columbia, Yukon, New Brunswick, and Nova Scotia and lake

Table 1  
Evolution in methods of analysis for NGR samples (from Friske and Hornbrook, 1991)

Year	Medium	Variables and analytical methods
1976	Lake sediment	Zn, Cu, Pb, Ni, Co, Ag, Mn, Fe (AAS1); As (COL1); Mo (AAS2); LOI (GRAVI), U (NADNC).
	Stream sediment	Zn, Cu, Pb, Ni, Co, Ag, Mn, Fe, (AAS1); Mo, (AAS2); U (NADNC); W (COL2).
1985	Lake sediment	Zn, Cu, Pb, Ni, Co, Ag, Mn, Fe, Cd (AAS1); Mo, V (AAS2); As, Sb (AAS3); Hg (AAS4); LOI (GRAVI), U (NADNC); F (ISE); Au (FANA).
	Stream sediment	As lake sediment plus W (COL2); Ba, Sn (AAS2).
1990	Lake sediment	Zn, Cu, Pb, Ni, Co, Ag, Mn, Fe, Cd (AAS1); V (AAS2); Hg (AAS4); LOI (GRAVI), U (NADNC); F (ISE); Na, Sc, Cr, Fe, Co, Ni, As, Br, Rb, Mo, Sb, Cs, Ba, La, Ce, Sm, Eu, Tb, Yb, Lu, Hf, Ta, W, Th, U, Au (INA).
	Stream sediment	As lake sediment plus Sn (AAS2).

AAS1, atomic absorption spectroscopy with air-acetylene flame; mAAS2, with nitrous oxide-acetylene flame; AAS3, with hydride evolution; AAS4, cold-vapour AAS; COL1, diethyldithiocarbonate colorimetry; COL2, with dithiol or zinc dithiol; FANA, fire assay concentration with neutron activation analysis of bead; GRAVI, gravimetric analysis at 500°C; NADNC, delayed neutron counting; INA, instrumental neutron activation. For AAS, lake sediment samples were extracted with hot 4 M HNO<sub>3</sub>-1 M HCl, stream sediments were extracted with hot, concentrated HNO<sub>3</sub>-HCl, except for Ba (HClO<sub>4</sub>-HF-HNO<sub>3</sub> digestion) and Sn (NH<sub>4</sub>I sublimation).

sediment data from areas on the Canadian Shield, i.e., Northwest Territories, Saskatchewan, Manitoba, Ontario, Quebec, Labrador, and Newfoundland. Therefore, comparisons could be assured within each province and between provinces with similar media without concerns for sample media differences. Could comparisons be made between lake sediment samples within the Shield and stream sediment samples in British Columbia and the Yukon? Davenport (1990), Garrett et al. (1990) and Garrett and Hornbrook (1976) have compared lake and stream geochemical data. Garrett et al. (1990) selected a number of sample pairs where the lake and stream sites were located in the same drainage system. The higher loss on ignition (LOI) for lake compared to stream sediments corresponds with higher contents of some metals in lake, compared to stream sediments (Table 3). LOI, as determined by ignition at 500 C, is a measure of the content of organic matter (Coker and Nichol, 1975). On average, lake sediments have a higher LOI than stream sediments from the same area. Thus, elements with an affinity for organic matter will have a higher average content of that element in lake sediments than in stream sediments. Note also that immobile elements, such as Pb, which are mainly transported in clastic form, may be more abundant in stream sediments than in centre-lake sediments.

Whereas centre-lake sediments represents material carried some distance, the clastic component of nearshore lake sediments (as used in the Bear-Slave survey) is of more local derivation. The nearshore sediments also tend to accumulate less organic material (LOI) than centre-lake sediments and would therefore be expected to show similar trends to stream sediments vs. centre-lake sediments. A comparison of U concentrations, an element that is quite mobile and which is fixed by organic matter shows that the centre-lake sediments have higher concentrations than the nearshore, less organic sediments (Fig. 1). However, both

Table 2

Comparison of total, aqua regia, and HNO<sub>3</sub>-HCl extractions on lake sediment samples. Values given in ppm (from Lynch, 1990)

Metal/sample	Total	Aqua regia	HNO <sub>3</sub> -HCl
Cd LKSD 1		1.2	1.2
2		0.8	0.6
3		0.6	0.4
4		1.9	1.9
Cu LKSD 1	44	44	44
2	37	36	36
3	35	34	34
4	31	30	31
Ni LKSD 1	16	11	12
2	26	23	23
3	47	44	46
4	31	32	31
Pb LKSD 1	82	84	83
2	44	40	34
3	29	26	21
4	91	93	91
Zn LKST 1	331	337	335
2	209	200	205
3	152	139	151
4	194	189	195

Table 3

Comparison of arithmetic mean contents, in ppm, for lake sediments and stream sediments from New Brunswick, British Columbia and northern Labrador

	LOI	Zn	Cu	Pb	Ni	As	Hg	Cd
<i>New Brunswick Open File 1638: 355 lakes, 1059 streams</i>								
Lakes, Mean	39.3%	88	10.8	21.5	8.7	6.8	0.13	0.91
Streams, Mean	10.1%	72	8.7	26.2	13.5	14.0	0.05	0.73
<i>British Columbia Open File 1360: 216 lakes, 950 streams</i>								
Lakes, Mean	27.9%	125	39.9	12.4	17.3	4.3	0.09	0.41
Streams, Mean	5.2%	83	33.8	7.8	12.3	6.2	0.04	0.17
<i>97 Northern Labrador Paired Lakes and Streams (Garrett et al., 1990)</i>								
Lakes, Mean	12.2%	96.5	82.3	2.6	60.7			
Streams, Mean	10.5%	57.7	43.7	8.8	45.2			

types of samples reveal the U-rich areas of the Bear Province east of Great Bear Lake and the general trend can be seen in both sample types.

In preparing the maps, we attempted to minimize the differences between lake and stream sediment concentrations for some metals by using as wide a contour interval as possible,

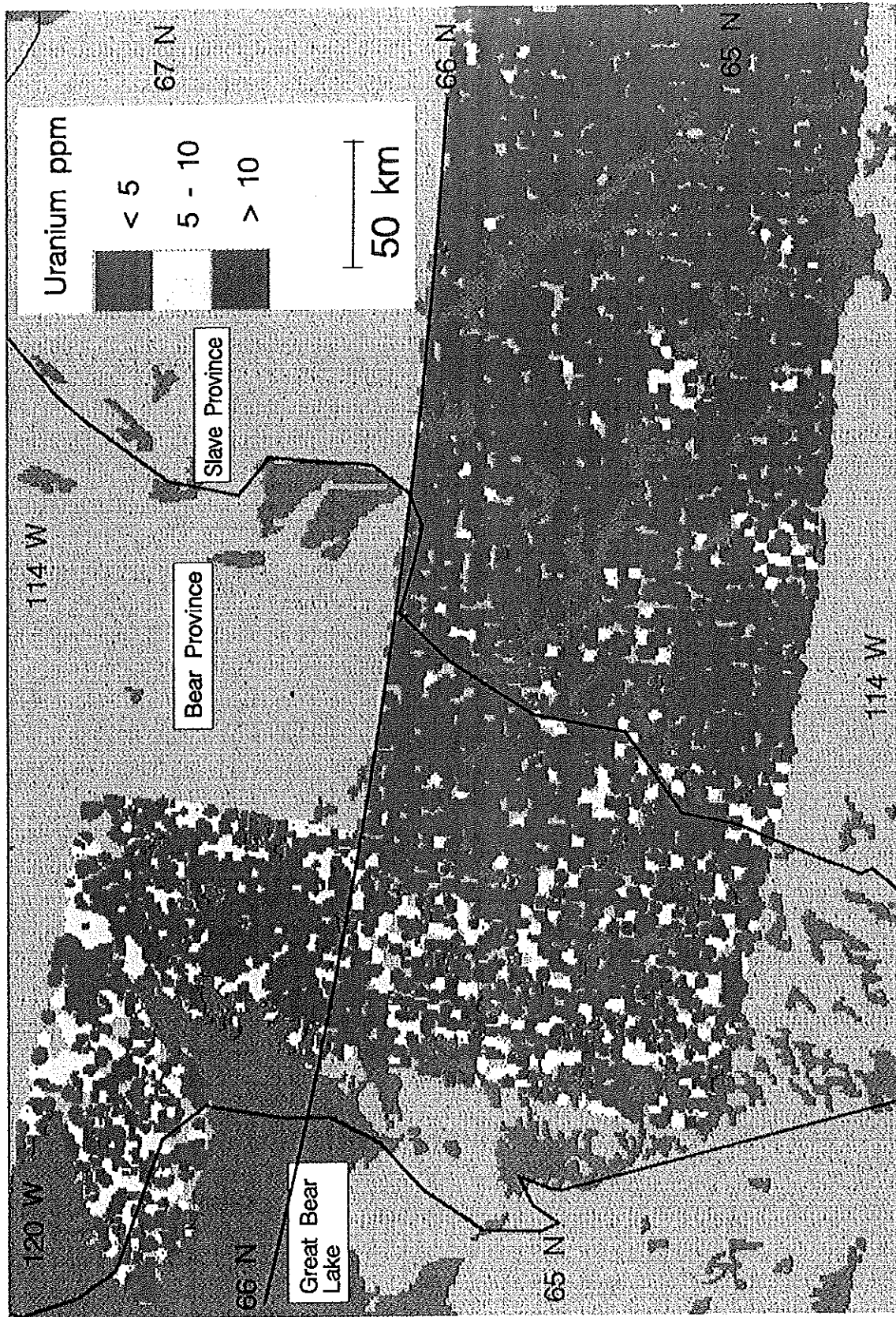


Fig. 1. Uranium in nearshore (south of 66°N) and centre-lake (north of 66°N) sediment samples near Great Bear and Slave Lakes.

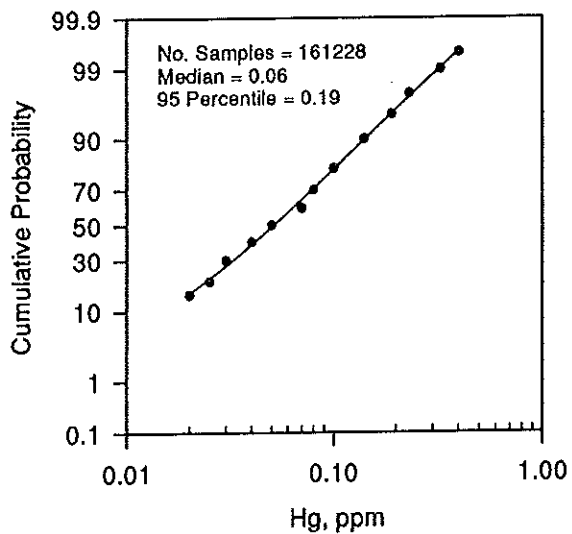
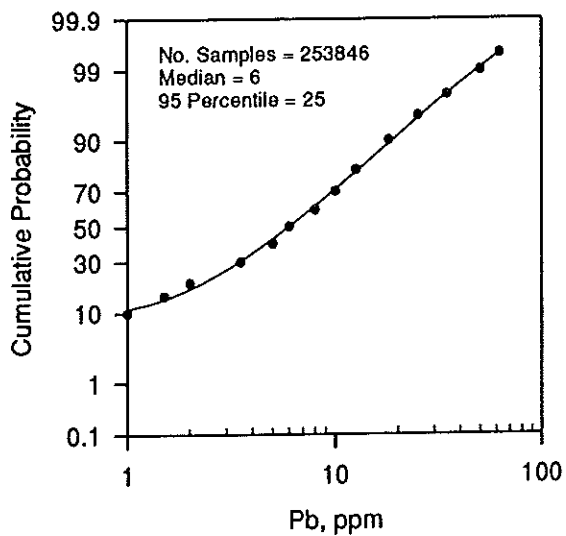
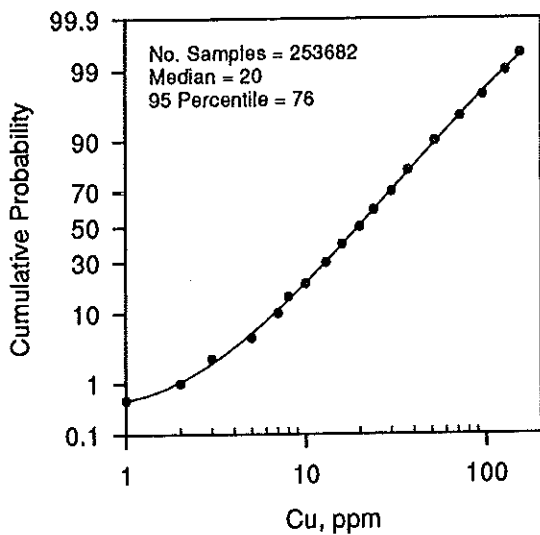
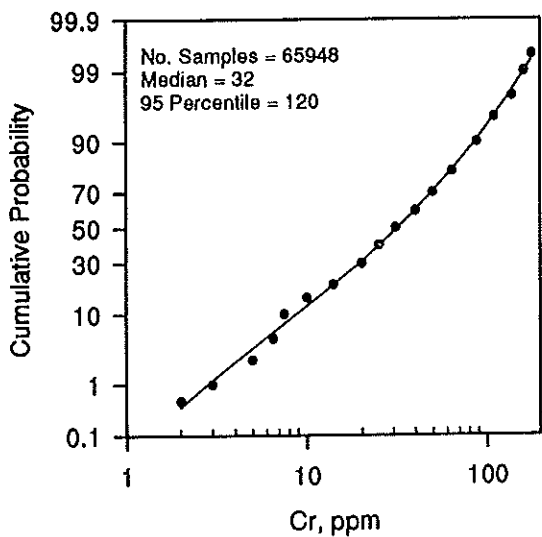
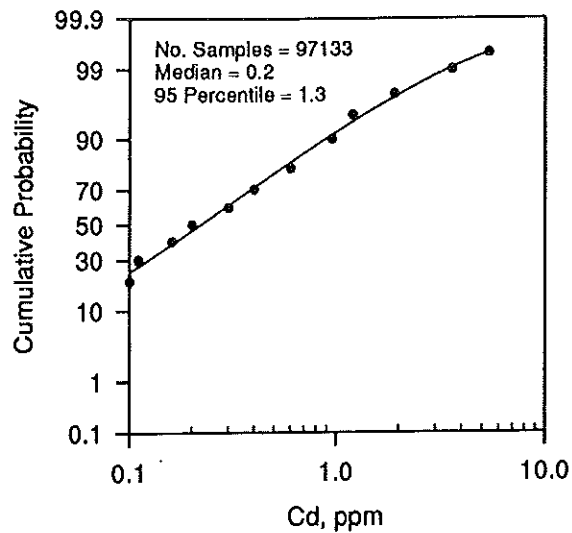
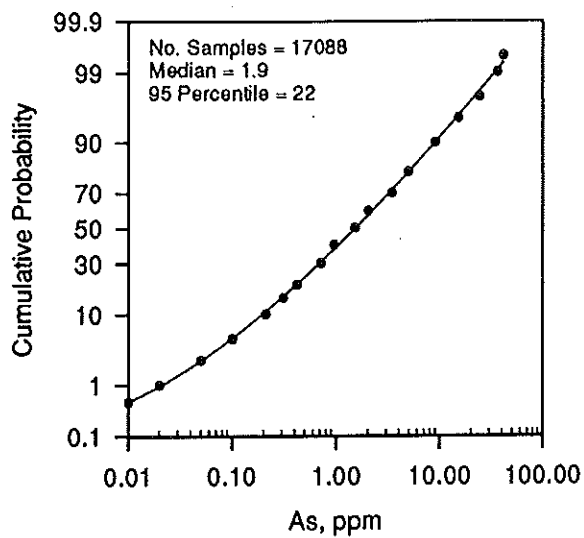
while still showing regional variability. As shown by the distribution plots (Fig. 2), the metal concentrations range over two to four orders of magnitude: ranges, which are much greater than differences between sample material. The distribution plots are a convenient way of summarizing the geochemical data. They do not, of course, represent a single population, but rather are a composite of multiple populations.

Geochemical data in the form of digital open file reports for British Columbia, Yukon, Northwest Territories, Saskatchewan, Manitoba, Ontario and New Brunswick were obtained from the Geological Survey of Canada. The data for Nova Scotia was obtained from the Nova Scotia Department of Natural Resources and for Newfoundland from the Newfoundland Department of Mines and Energy. The Ministère de l'Énergie et des Ressources du Gouvernement du Québec provided the data for that province. Data were imported into the IBM OS2 database manager DB2/2 as individual tables within provincial databases. Data for each element were taken from the tables along with the easting, northing and UTM zone and imported into SPANS-GIS for map creation. Point aggregation was used to create the Canada-wide maps because of the large number of data points. In point aggregation a minimum number of 3 sites per map cell was specified and the class was based on the average of the data within the cell. Use of point aggregation minimized the influence of outliers or errors in the dataset. For the larger-scale maps, the potential mapping routine within SPANS was used. In potential mapping, each site is given a radius of influence and interpolation between sites is performed where radii overlap. A radius of 8 km was used to minimize overlap, yet fill-in areas between sites. Various classification schemes were used to classify the data into 3, 4, 6, or 8 class maps. One classification scheme was based on Ontario's sediment quality guidelines and another was based on a frequency distribution analysis of the data (Fig. 2). The classification scheme used to derive the maps included in this manuscript were simply designed to bring out the regional differences across Canada (Figs. 4–11) and which may be related to the geology of the country (Fig. 3).

The maps do not include all of the available data for a number of reasons. Open files that were released only recently could not be included in this compilation. Only sufficient data from Quebec were purchased to illustrate the regional variability within that province. Lake sediment data are available for Nova Scotia and British Columbia and stream data are available for Newfoundland and Labrador but are not included for the reasons described above. When developing some of the maps, distinct differences between adjacent map sheets were apparent. In a few cases, incorrect column (element) definitions within the open files were found and corrected.

#### **4. Nature of regional-scale geochemical anomalies**

Large areas of Canada have metal contents substantially greater than the crustal abundance. The primary purpose of NGR surveys was to identify areas that might contain undiscovered mineral deposits. For the most part, such areas are shown by anomalies a few tens of km<sup>2</sup> or less in extent. But as the mapping proceeded, much larger features were revealed extending over hundreds or thousands of km<sup>2</sup>. It is these larger anomalies that are apparent on the geochemical maps presented here. Features such as the extensive anomaly for Cd in the eastern Yukon (Fig. 5) or As in the Foxe Fold Belt of Baffin Island (Fig. 4)





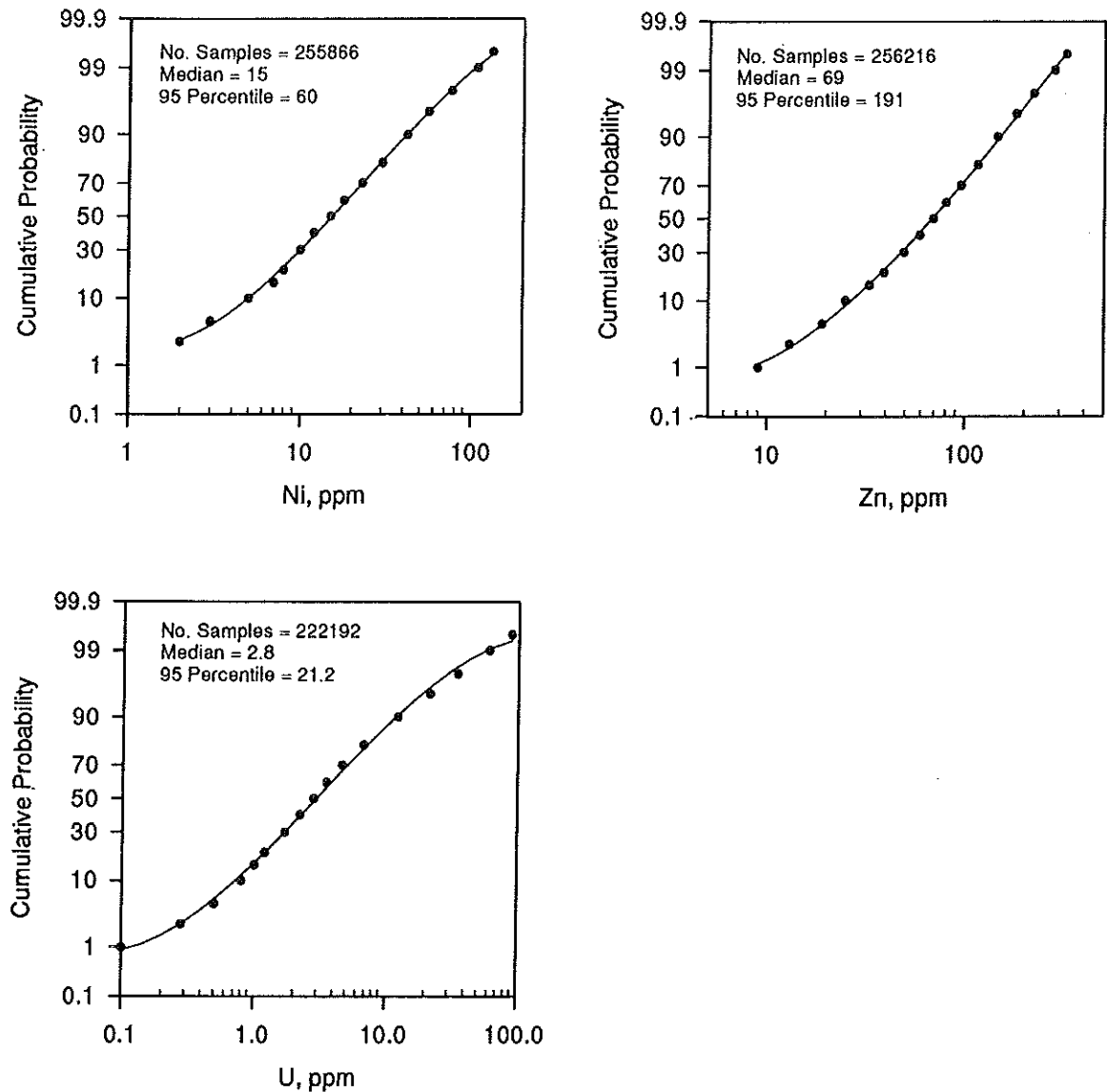


Fig. 2. Cumulative frequency distributions for As, Cd, Cr, Cu, Pb, Hg, Ni, Zn and U in the combined data files for lake and stream sediment samples collected under the National Geochemical Reconnaissance and the Quebec survey programs.

denote areas where these elements are substantially enriched over a wide area of the surface environment and bedrock. It is not possible to discuss all of these major anomalies. Instead, in the following sections we discuss a number of examples, with the purpose of identifying general principles that control their distribution.

#### 4.1. Mineralized sedimentary basins

Like other parts of the Cordillera, the geology of the Yukon is comprised of an ancient inboard craton flanked to the west by younger terranes of varied origin. Over much of its length the dextral transcurrent Tintina fault is the outer boundary of the craton (Fig. 12). The western part of the craton was tectonically active over a long period during which an

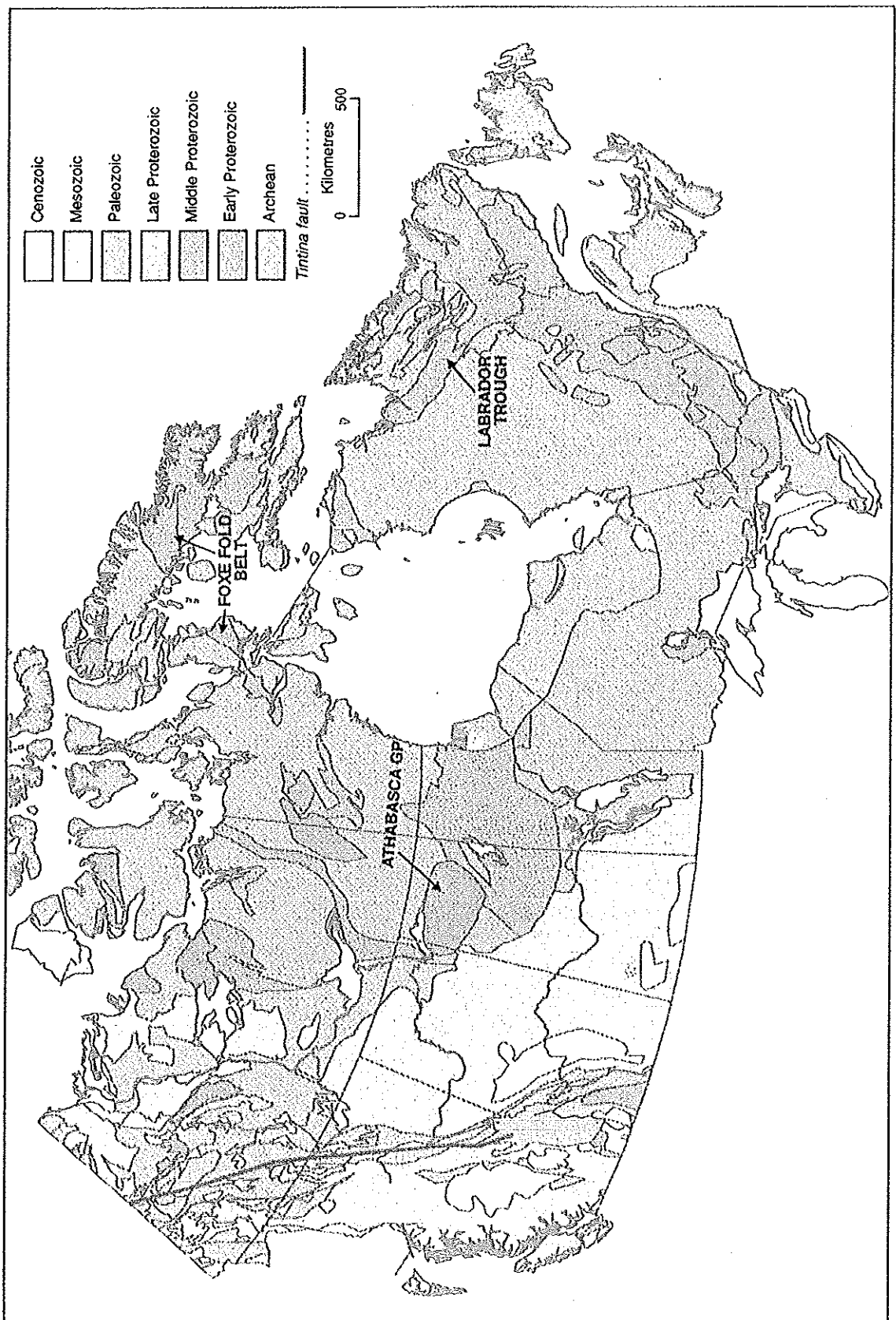


Fig. 3. Geological map of Canada. Modified from Geological Survey of Canada (1994).

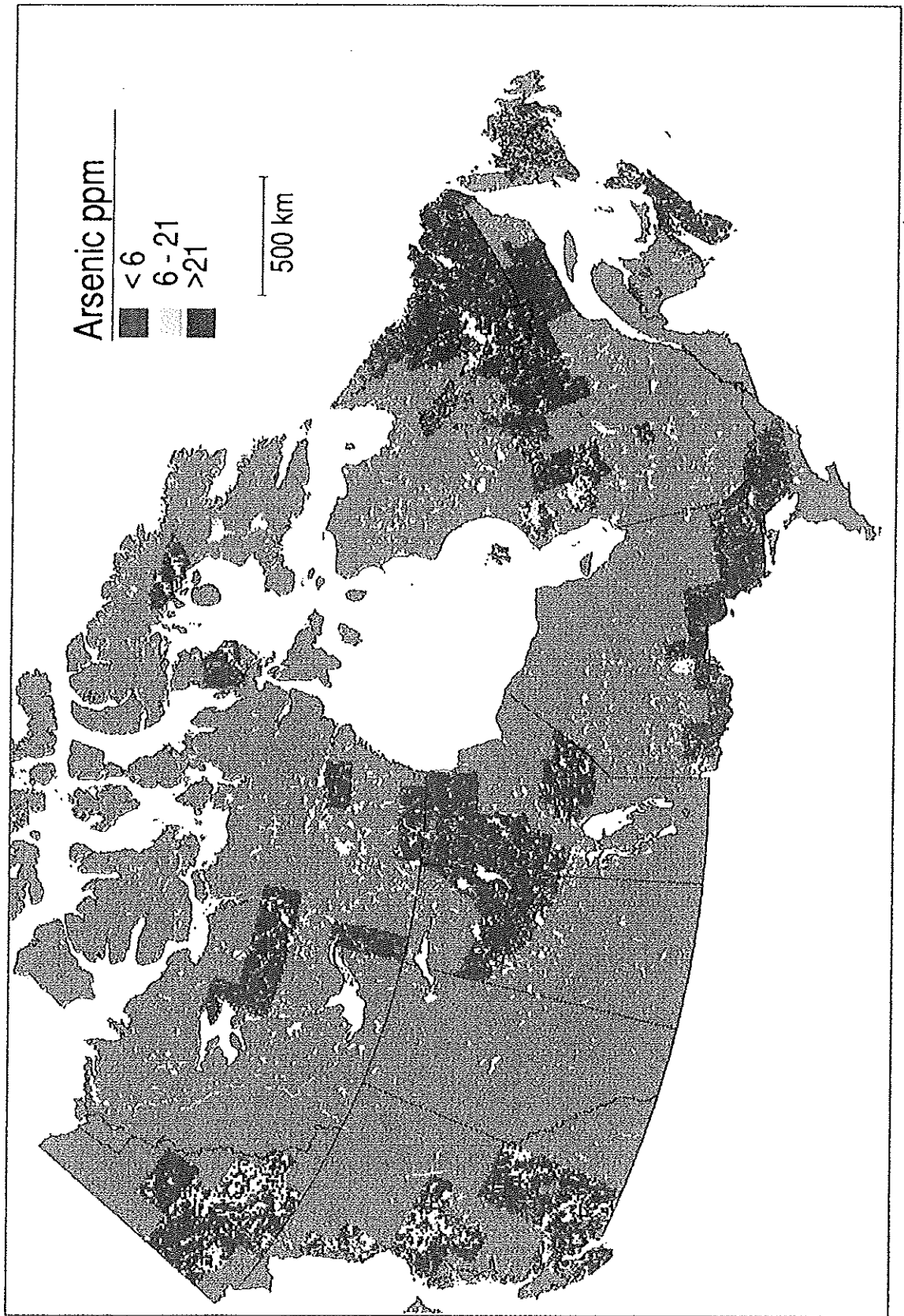


Fig. 4. Arsenic in lake and stream sediment samples.

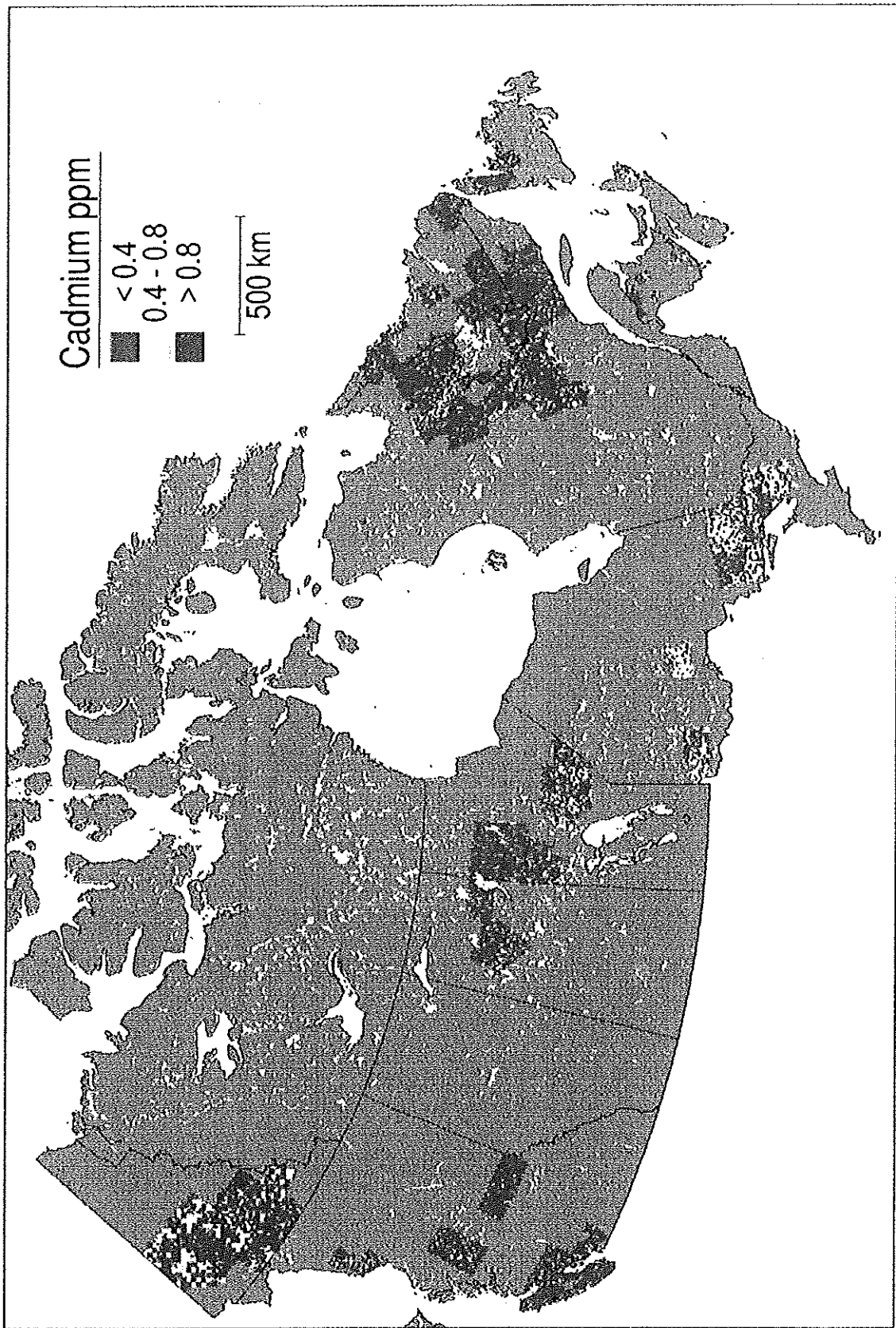


Fig. 5. Cadmium in lake and stream sediment samples.

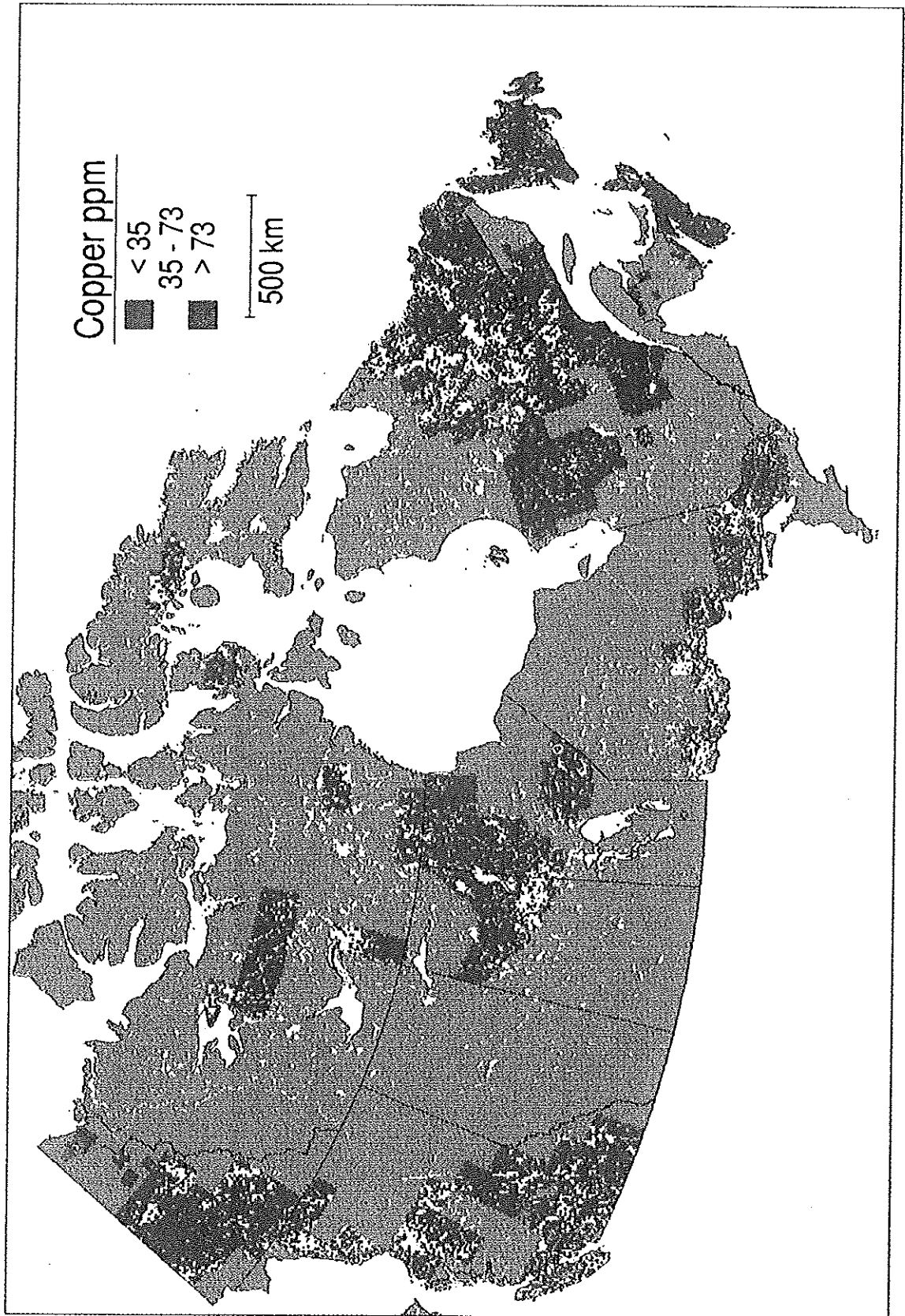


Fig. 6. Copper in lake and stream sediment samples.



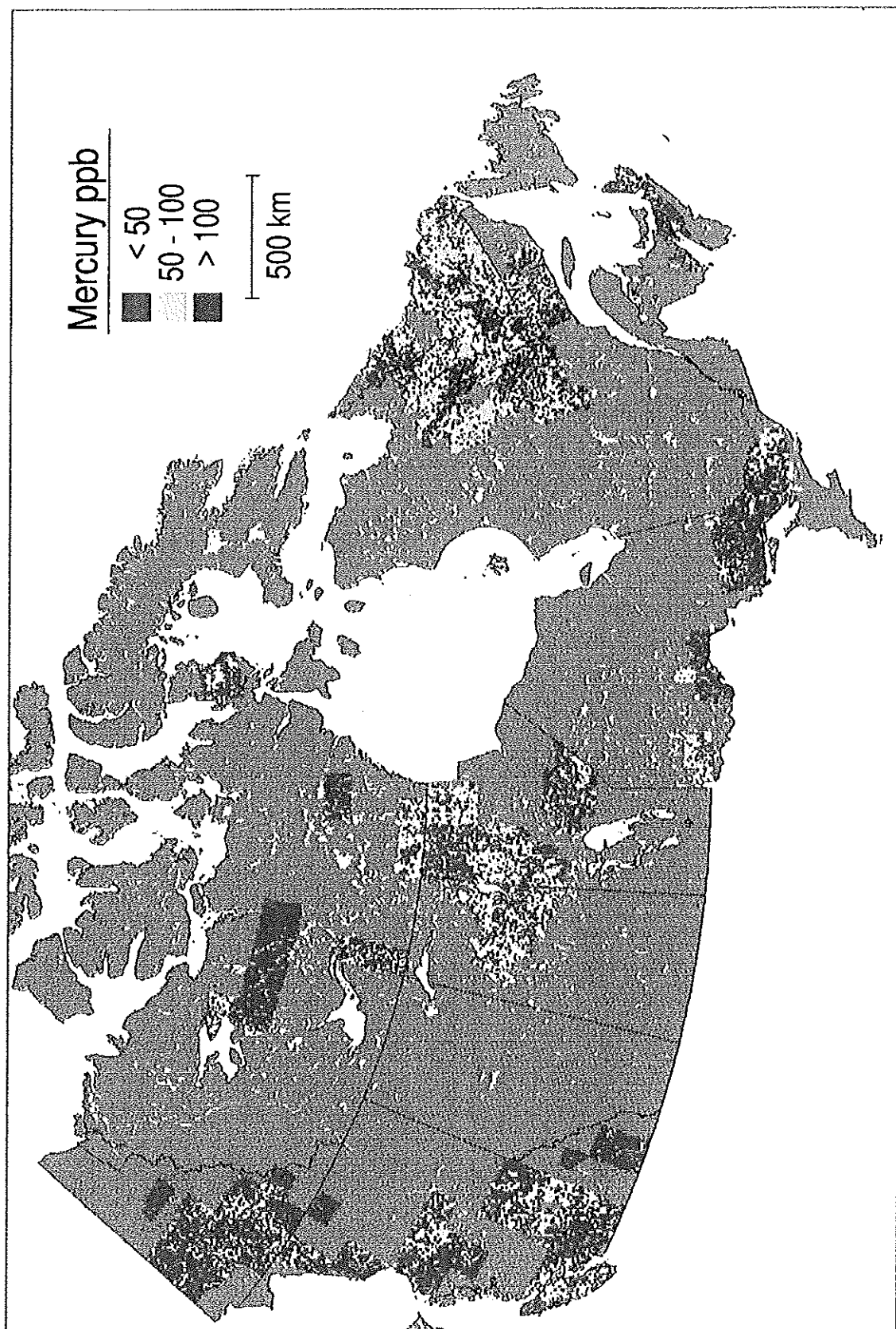


Fig. 7. Mercury in lake and stream sediment samples.

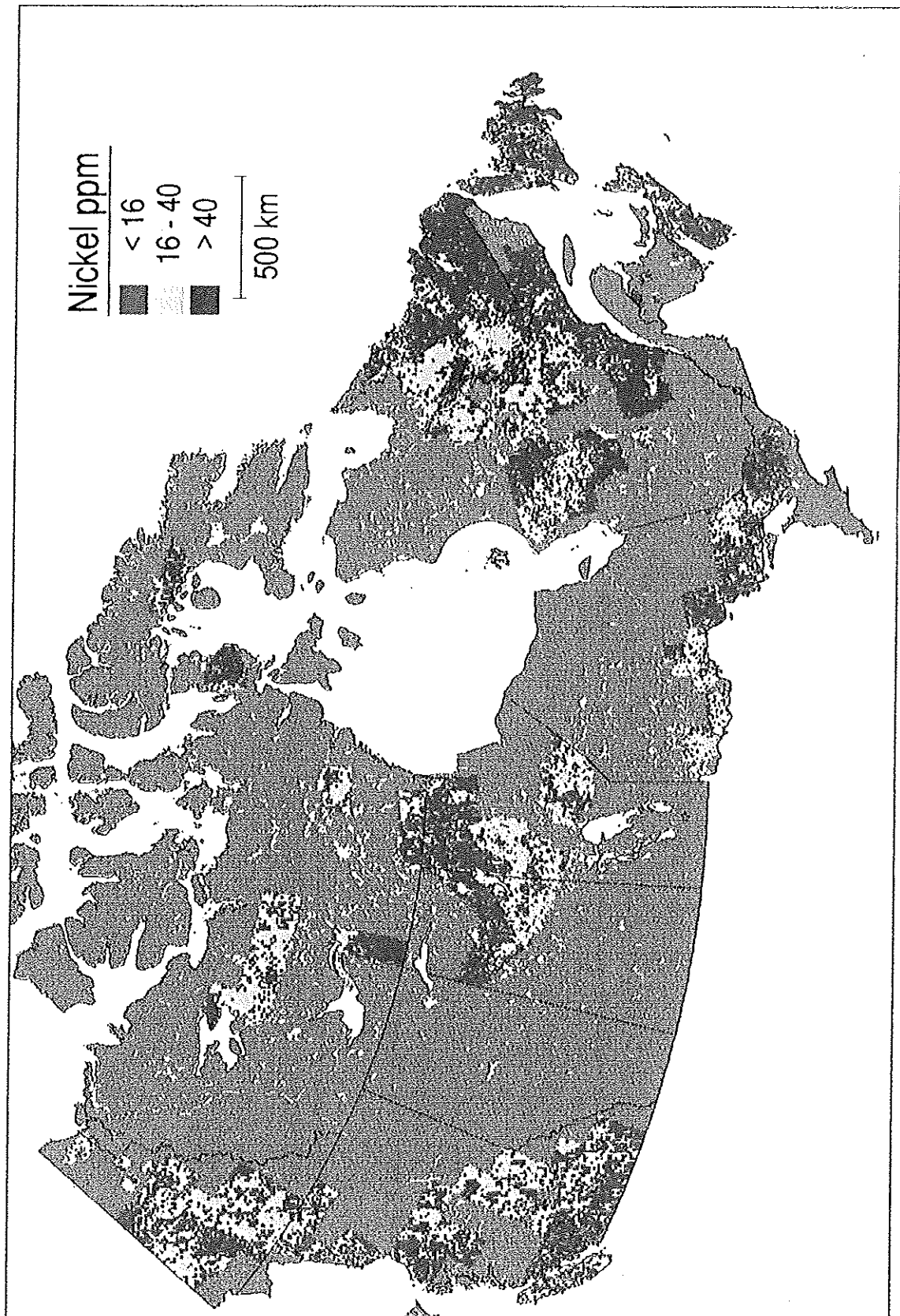


Fig. 8. Nickel in lake and stream sediment samples.

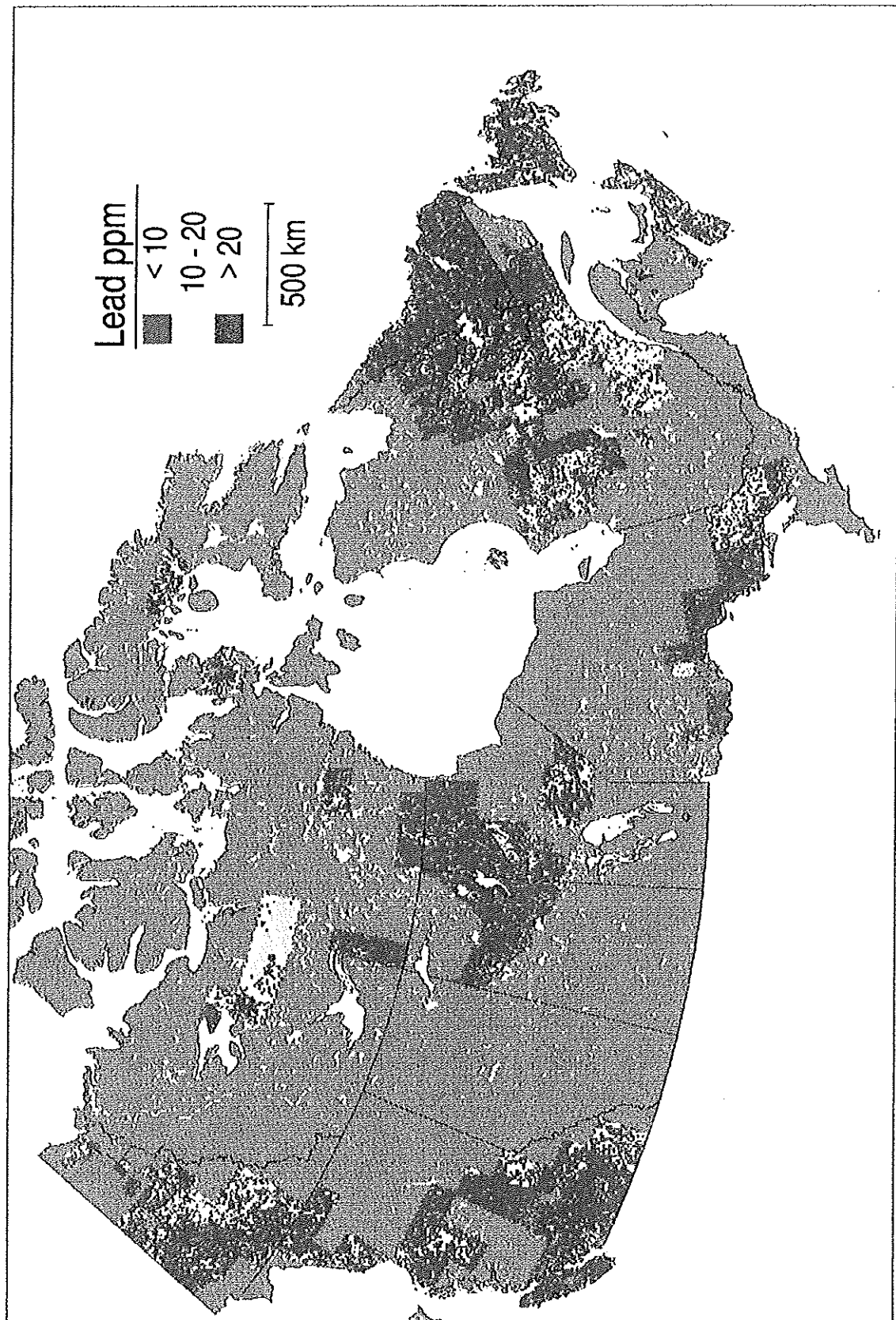


Fig. 9. Lead in lake and stream sediment samples.



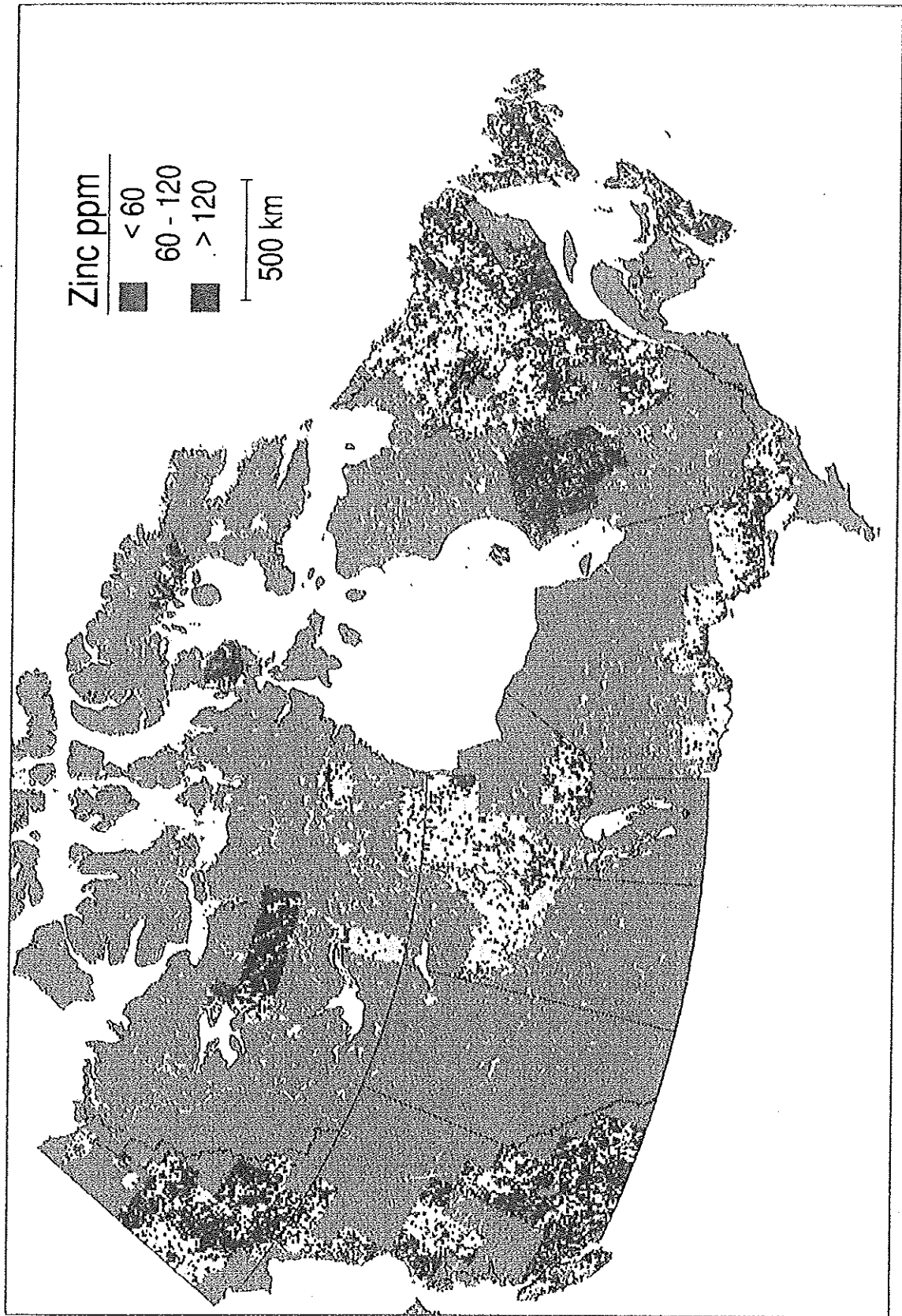


Fig. 10. Zinc in lake and stream sediment samples.

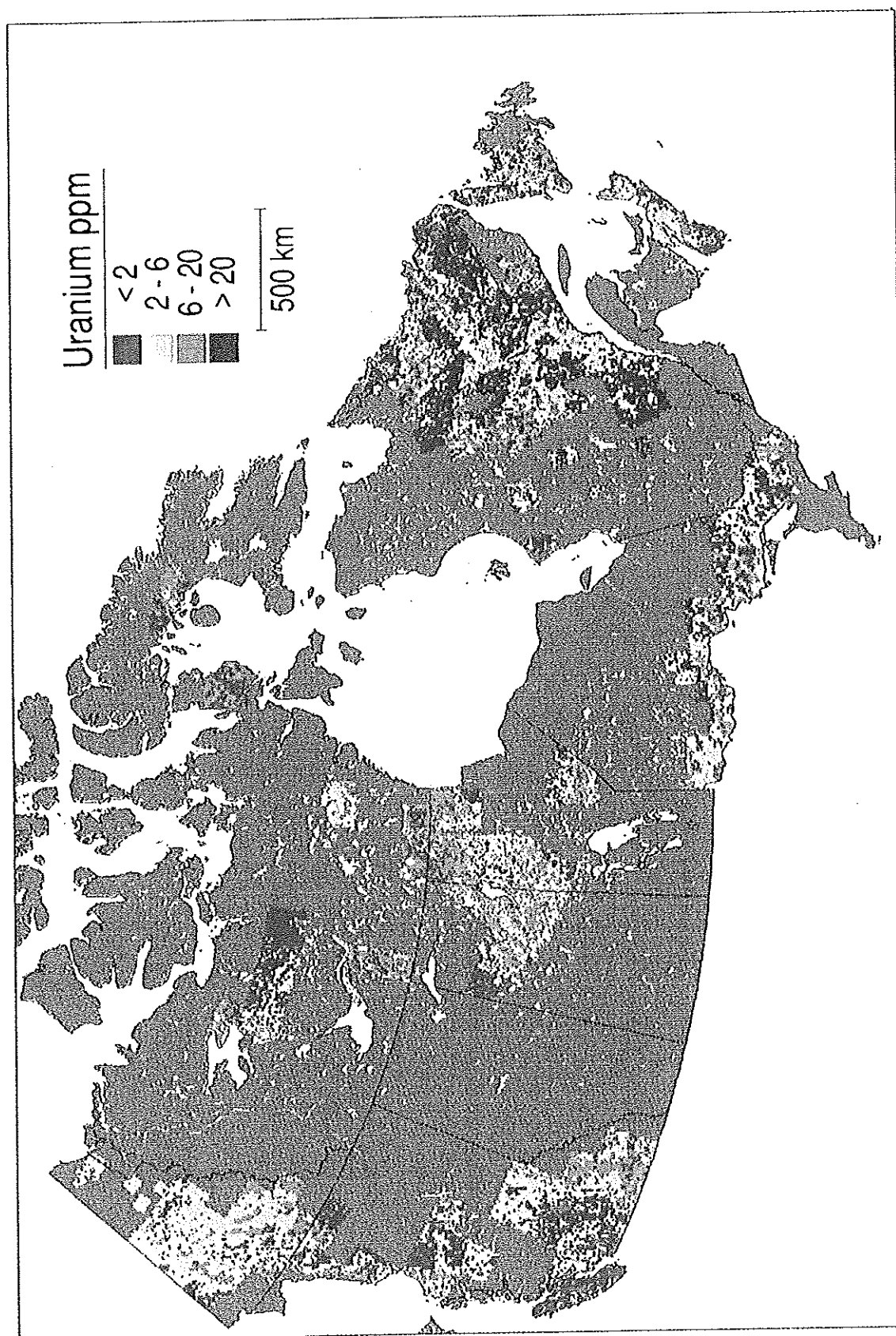


Fig. 11. Uranium in lake and stream sediment samples.

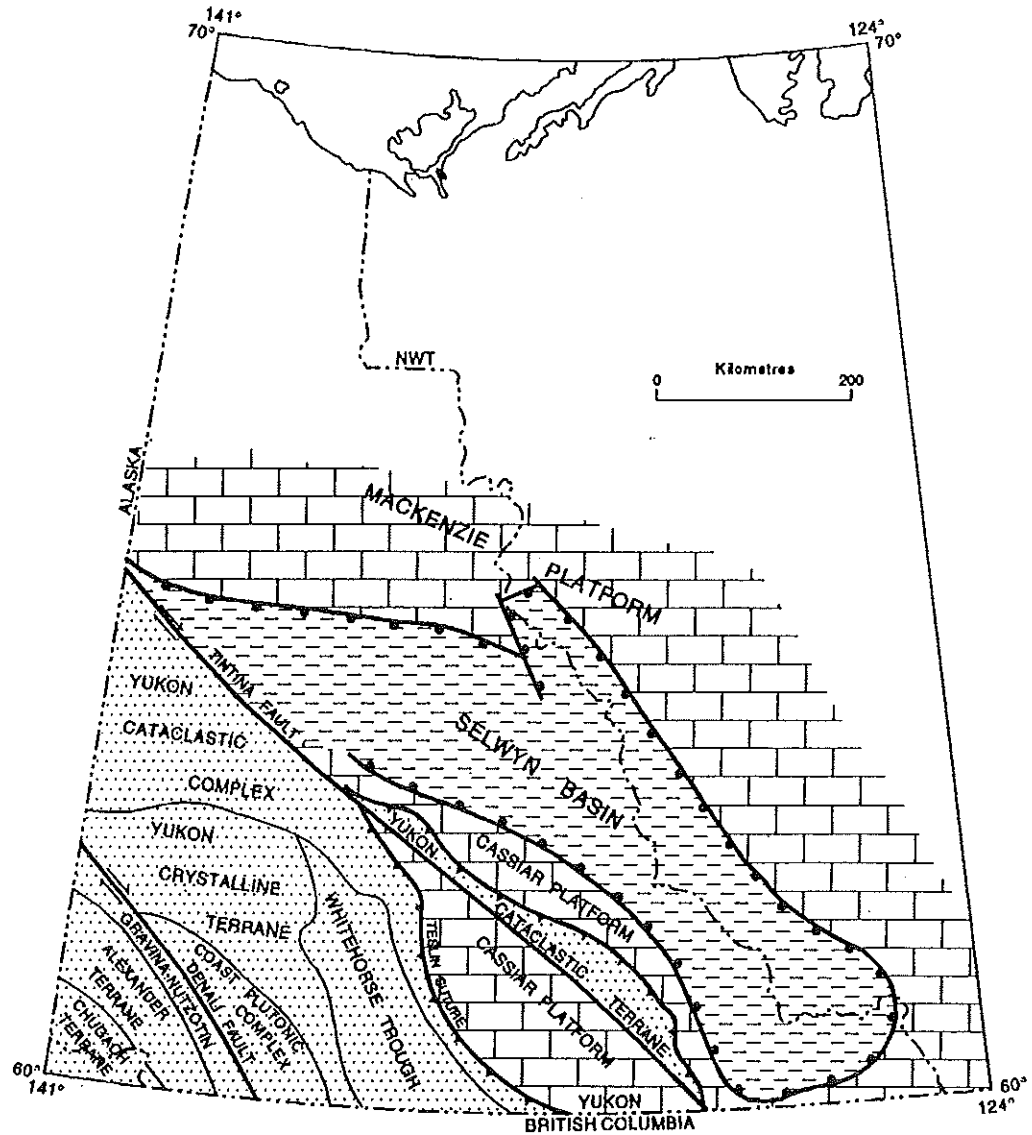


Fig. 12. Tectonic elements of the Yukon (from Goodfellow and Aronoff, 1988).

easterly-tapering wedge of mainly sedimentary rocks of mid-Proterozoic to Jurassic age was deposited on crystalline basement. It is in this tectonically active sector of the craton that many of the strongest and most extensive geochemical anomalies are located, most notably in the Selwyn Basin.

In part, Zn anomalies (Fig. 10) reflect Mississippi Valley-type Zn–Pb deposits within the carbonate platform. However, the most extensive Zn anomalies in and around the Selwyn Basin are related to stratiform sedimentary exhalative (Sedex) Zn–Pb mineralization in strata of Cambrian to Mississippian age. Sedex deposits are located in submarine grabens, within which carbonaceous and calcareous shales were deposited. Hot metalliferous fluids rose along the faults that define the grabens. As the fluids reached the basin floor, metals were precipitated by sulphide contained in anoxic bottom waters (Goodfellow and Jonasson, 1986). One of the reasons for the extensive nature of the anomalies is that some metal

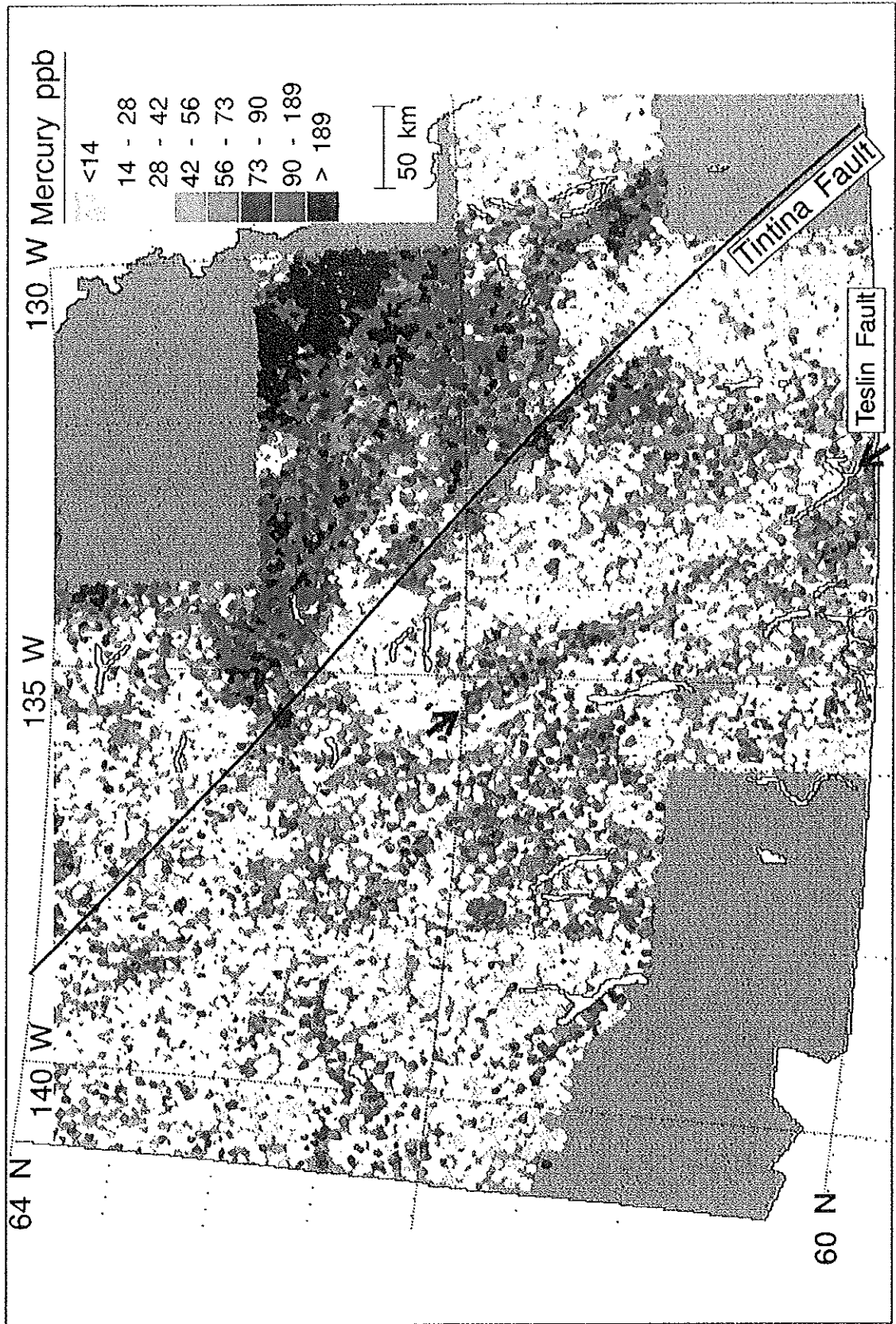


Fig. 13. Mercury in stream sediment samples from the Yukon.

dispersed widely in sea water around the hot spring source, precipitating in the shaly sediments.

A variety of other elements, including Ba, Cd, Cu, Ag, As and Hg, are present in the Sedex mineralization. Goodfellow and Jonasson (1986) report 1300 to 4200 ppm Cd in sphalerite from a Sedex deposit in Howards Pass. This accounts for extensive Cd anomalies (Fig. 5) that are coincident with anomalies for Zn. Sphalerite, which also contains substantial Hg, is readily weathered and elements that it contains disperse in the drainage waters and sediments. This is a second factor for the widespread nature of anomalies for Zn, Cd and Hg (Fig. 13) in and near the Selwyn Basin. In contrast, galena tends to form insoluble lead sulphates when exposed to the atmosphere. This restricts the dispersion of Pb in the drainage system, so that anomalies are weaker and less extensive than those for Zn and Cd. In terms of its ease of weathering, pyrite is intermediate between sphalerite and galena. Metals present in pyrite related to Sedex deposits, such as Ni, Co, and As (Goodfellow and Jonasson, 1986), have dispersed moderately widely in the drainage system: behaviour which is reflected in the geochemical patterns for these elements.

A second group of anomalies relate to granitic plutons of Cretaceous age, some of which have formed tungsten–skarn deposits. The anomalies arise, in part, from elements introduced by fluids from the granite magma and, in part, from the modification of the sedimentary rocks in the vicinity of the granite. Where the intrusions cut the shales of the Selwyn Basin, large thermal aureoles were created. At high temperature in the low redox environment of carbonaceous shale, pyrrhotite replaced pyrite as the stable iron sulphide phase. Pyrrhotite is more susceptible to near-surface oxidation than pyrite. Additionally, graphite is formed as a result of the thermal effect of the intrusions. At the weathering surface graphite forms an electrochemical cell with sulphide minerals, which greatly accelerates the oxidation of the sulphides (Cameron, 1979a). Where carbonate is not available as a buffer, stream waters in the vicinity of the thermal aureoles are acidic and stream sediments may contain strongly anomalous levels of As, Sb, Cu and Ag (Goodfellow and Aronoff, 1988).

Southwest of the Tintina fault, rocks are of diverse origin, including accreted oceanic and arc terranes and metamorphosed rocks of pericratonic terranes. Whereas the mainly sedimentary regions at the edge of the craton give broad anomalies for mobile metals, these highly diverse metamorphic, igneous, or mixed igneous and sedimentary terranes have anomalies that are more restricted in areal extent and which often occur around igneous intrusions. These mineral deposits and the associated anomalies include Cu and Au skarns; porphyry Cu and Mo; Cu and Zn volcanogenic massive sulphides, and Cu and Ni in ophiolites. There are also mesothermal Au veins and the Klondike Au placer district. Although the local anomalies can be quite intense, they show as small, patchy anomalies on the regional-scale maps, such as those on the maps of Hg and As for the southwest Yukon and British Columbia. Thin, elongate trends of some Hg patterns (Fig. 13) may relate to migration of this element up terrane-boundary faults, such as the Teslin fault.

The Foxe Fold Belt extends from Melville Peninsula in the west through central Baffin Island to the west coast of Greenland. The belt is composed of Lower Proterozoic supra-crustal rocks that were folded, metamorphosed and intruded by Hudsonian granites. Metamorphic grade varies from greenschist to amphibolite. An unusually high percentage of the lake sediment samples collected over the belt are strongly anomalous for a number of elements. On Baffin Island the belt contains a broad and intense As anomaly.



There are similarities both in the tectonics and in the geochemical patterns of this area to those discussed above for the Yukon. Along the northern margin of the belt, carbonate rocks, quartzite and graphitic schist lie on Archean basement, analogous to the edge of the craton in the Yukon. The main portion of the belt is metagreywacke and schist. Along the southern margin there is amphibolite and ultramafic rocks, marking a possible suture zone.

Along the northern margin of the belt on Baffin Island there are strong anomalies for Zn, Ni, Co, Cu, F and Mn, the Zn values reaching 3200 ppm. The most intense portion of this anomaly is in lakes with strongly acidic waters (pH to 3.8) developed over sulphidic, graphitic schist. During the deposition of these rocks hot metalliferous fluids rising along faults mixed with anoxic basin waters (Cameron, 1986), similar to the Sedex deposits of the Yukon. Although there has been very little mineral exploration in this remote region, sphalerite and galena occur quite commonly in the carbonate rocks.

Follow-up studies in the portion of the belt on Melville Peninsula (Cameron, 1979b) showed that high Zn and Ni values are associated with paragneiss, which is frequently sulphidic and graphitic, and with metaquartzite. The sulphidic nature of the paragneiss is most obvious from the air as large, red-weathering gossanous zones. Zinc and Ni are highly mobile and disperse into the lake waters, to be precipitated in the lake sediments. At one locality, where an NGR lake sediment sample contained 3400 ppm Zn and 530 ppm Ni, lake waters contain as much as 1200 ppb Zn and 320 ppb Ni. Lead is strongly anomalous in some soils, but since it is immobile, it tends not to enter the lakes. As discussed for the Yukon, the mineralogical form of the metal is of the greatest importance in its dispersion. In the paragneiss Zn occurs as sphalerite and Ni occurs as inclusions of pentlandite in pyrrhotite. Pyrrhotite, which formed as a result of the metamorphism of carbonaceous shale, is highly susceptible to surface oxidation and Ni is released as the pentlandite is also dissolved. The intense oxidation leads to strongly acidic surface waters. In contrast to pyrrhotite, pyrite is less affected by weathering; crystals of pyrite stand out prominently on weathered rock surfaces and yellow streaks of fine, detrital pyrite may be seen along watercourses. Copper is present in the paragneiss as chalcopyrite, which is also readily oxidized during weathering, contributing to the high levels of this element in the Cu map of Canada (Fig. 6).

The central portion of the fold belt on Baffin Island contains one of the most strongly arsenical regions in Canada, and possibly in the world. Large areas average over 90 ppm As (Cameron, 1986) and the highest value for lake sediment samples in this area is greater than the 999 ppm upper determination limit. Finland contains fold belts of broadly similar geology and age to the Foxe Fold belt. The geochemical map for As in Finland, represented by 1039 till samples, contains no values above about 50 ppm As (Koljonen, 1992). The cause for the high As content of the bedrock underlying the Foxe Fold belt anomalies is unknown, since no follow-up surveys to investigate the NGR data have been undertaken in this area.

A comprehensive series of coloured regional geochemical maps have been published for the island of Newfoundland by P.H. Davenport and colleagues at the Newfoundland Department of Mines, based on centre-lake sediment samples at a site density of one per 7 km<sup>2</sup>. Newfoundland is a complex of terranes analogous to those of the Cordillera, separated by major faults. The map for As (Davenport et al., 1993) shows strong anomalies in the centre of the island over the Dunnage Zone, comprising Lower Palaeozoic submarine volcanic

rocks and ophiolites, with some of the highest values over the Exploits Subzone with thick sedimentary sequences interbedded with and overlying volcanic rocks. The Exploits contains widespread anomalies for Au, which may reflect Au widely dispersed through the sedimentary rocks, rather than Au present in veins (Davenport and Nolan, 1991). In contrast, the most important gold deposit on the island at Hope Brook in the southwest, a vein-type deposit, is marked by a relatively weak regional anomaly for Au. This contrast parallels that found in the Yukon, where Sedex deposits are associated with extensive, strong anomalies, while districts containing vein deposits are not so well marked on regional-scale geochemical maps.

One further example of the environmental importance of metal widely dispersed within sedimentary rocks concerns Hg in lower Proterozoic shales of the Canadian Shield. Cameron and Jonasson (1972) found that these rocks were unusually rich in Hg, averaging 513 ppb Hg for 396 samples from 54 localities. This compares to averages of 129 ppb Hg for Archean shales from the Shield and 42 ppb Hg for Palaeozoic shales from the eastern seaboard of Canada. Lake sediments collected over sedimentary rocks of lower Proterozoic age reflect these high Hg contents of the bedrock, which shows as anomalies around such locales as Thunder Bay and Cobalt, Ontario (Fig. 14) and in the Labrador Trough (Fig. 7). At Cobalt, silver-bearing veins may also have contributed to the enhanced Hg contents. The assimilation of Hg into fish in some of the anomalous areas has been an important environmental issue.

In summary, mineralization formed from metalliferous fluids that debouch into the waters of sedimentary basins can form intense and extensive geochemical anomalies. Primary dispersion is on a horizontal plane. In effect, hot fluids have extracted metal from several kilometres of crust and have concentrated them in a relatively narrow layer. After uplift and erosion the metal-rich strata often lie sub-parallel to the erosional surface, ensuring a wide area of exposure. Contrast this with quartz-carbonate gold veins and other types of vein deposit where the plane of dispersion is normal to the erosional surface. Although such veins may extend vertically over several kilometres they are narrow and give rise to weak and restricted geochemical anomalies.

Sedex deposits also illustrate how elements, such as Zn and Cd, that are chemically mobile and are present in a mineral, sphalerite, that is readily weathered can disperse widely in the surface environment. The host rock is important too. Metamorphism of sulphidic, carbonaceous shale forms graphitic, pyrrhotite-bearing rock that is chemically reactive at the weathering surface. Examples are Penryn paragneiss of the Foxe Fold Belt and thermal aureoles around intrusions into the Road River shale of the Selwyn Basin. In the absence of carbonate as a buffer, the rapid oxidation of sulphide minerals creates an acidic environment which adds to the mobility of metals.

#### 4.2. *Lithophile elements*

A second group of processes that results in widespread geochemical anomalies is the transfer of large ion lithophile elements (LILE) from the lower to the upper crust during magmatism and high-grade metamorphism. LILE are stable in the open crystal lattices of micas, amphiboles and other hydrous minerals that are formed in the upper crust. When subjected to high-grade metamorphism deep in the crust these minerals are converted to

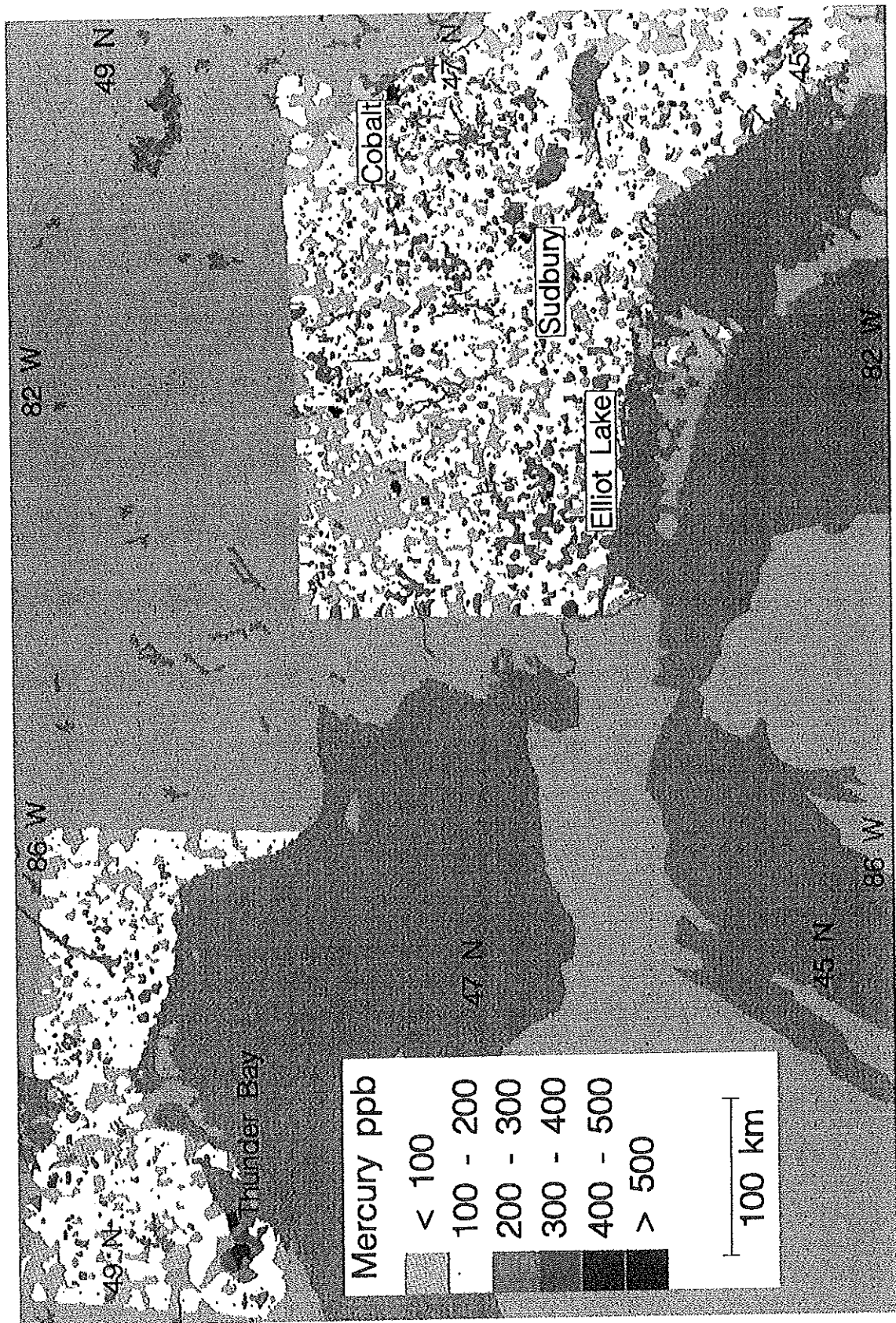


Fig. 14. Mercury in lake sediment samples from northern Ontario.



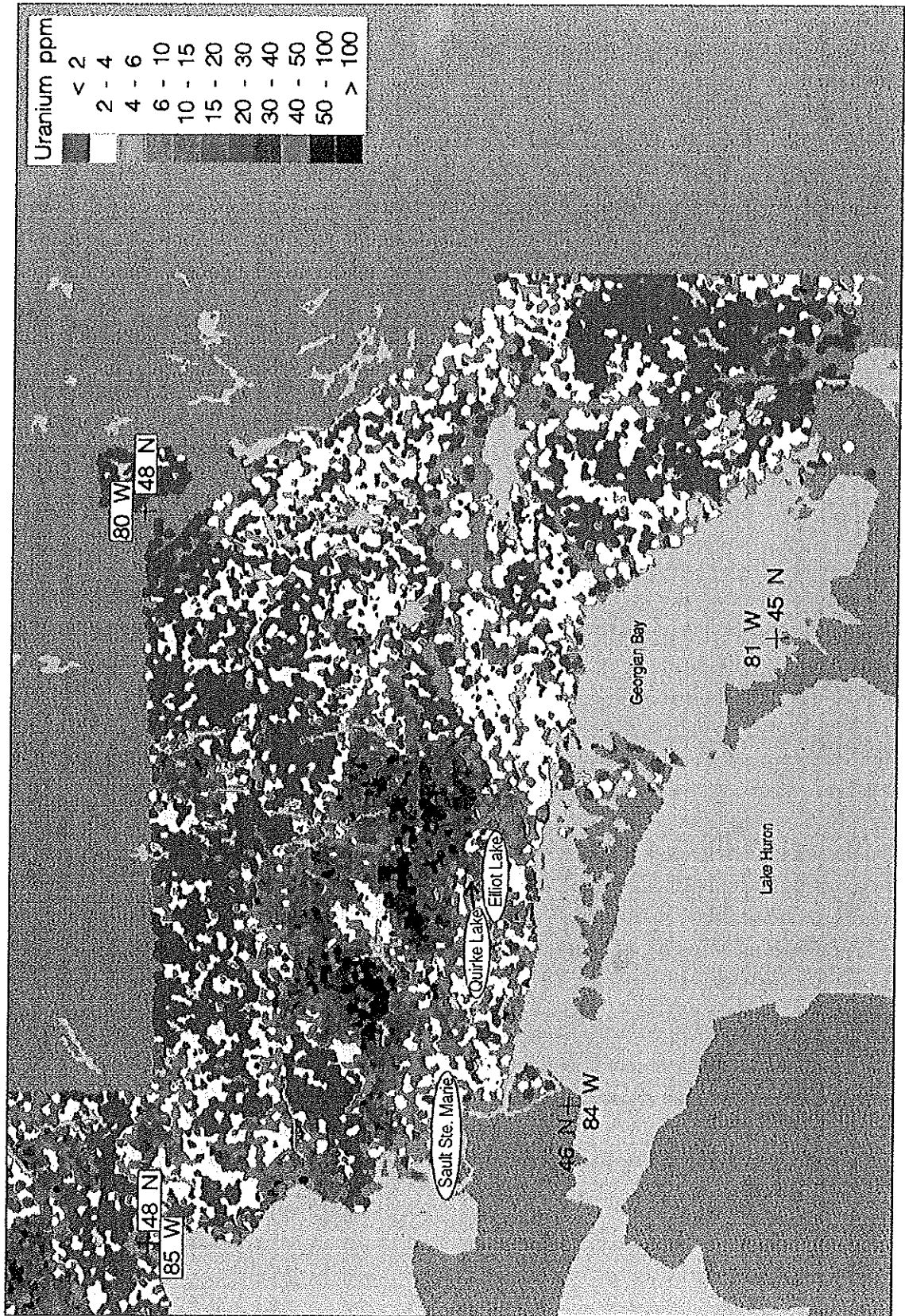


Fig. 15. Uranium in lake sediment samples from northern Ontario.

anhydrous minerals, such as pyroxene. The LILE contained within hydrous minerals are expelled along with H<sub>2</sub>O since they no longer easily fit the tight crystal structure of pyroxene. The expelled H<sub>2</sub>O causes melting to granitic compositions into which LILE enter. The low-density melts rise and transfer LILE to higher levels of the crust where they either remain within the crystallizing granites or are contained within pegmatites that vein the country rock.

The U map of Canada (Fig. 11) contains several examples of the broad, regional nature of U anomalies. One of these lies in granite terrane north of Elliot Lake, Ontario (Fig. 15), which is also rich in Hg (Fig. 14). Uranium-bearing minerals from these rocks were carried south in rivers and streams to be concentrated in placer uranium deposits of earliest Proterozoic age near Elliot Lake. There is a similar region of U-rich basement north and northeast of the Athabasca Group in northern Saskatchewan (Fig. 11). The region also shows as a high on airborne radiometric surveys (Charbonneau, 1982). Some of the most prominent anomalies occur within three 1:250,000 map sheets surveyed within the Northwest Territories immediately north of the Manitoba border. Within the three sheets the highest values are found in samples from the outcrop area of Hudsonian granite, with the average U content of lake sediment samples of 50 ppm. High values are found also over a variety of other geological units, including quartz monzonites of lower Proterozoic and Archean age, sedimentary units of lower Proterozoic age, and Archean paragneiss, suggesting a general enhancement in U within the crust of this region. The richest U deposits in the world occur near the basal unconformity of the Athabasca Group on crystalline basement. The group is comprised mainly of sandstone and conglomerate. The most widely accepted model for genesis of the deposits is for the dissolution of U from clastic minerals in the Athabasca Group by heated groundwater, followed by precipitation of the U at redox traps situated near pelitic zones in the basement (Hoeve and Sibbald, 1978; Ramaekers, 1983). Paleocurrent directions for the Athabasca Group indicate that these sediments were derived, in part at least, from the areas of the basement that are rich in U. Thus U-rich detritus carried into the Athabasca Group from areas of high U basement was the likely source of these metals in the ore deposits.

Lake sediment samples for Newfoundland have been analyzed for Cs, an element with a large ionic radius, which is very strongly lithophile. A prominent regional anomaly for this element (Davenport et al., 1994) is associated with a band of granitic and other intrusive rocks that sweeps along the south coast of the island and through the Gander Zone. Other elements that show a regional pattern similar to Cs are Pb (Davenport et al., 1993), Ce, Rb, Th, U and W. Lithophile elements in lake sediments have been used in exploration for mineral deposits, such as Sn, that are associated with granites (Rogers and Garrett, 1987).

The converse of LILE enrichment is LILE depletion. This may be observed in lower amounts of LILE, such as U and Zn, and rather higher contents of compatible elements, such as Ni, in some areas of granulite of lower crustal origin, as in northern Quebec and Labrador.

## **5. Role of regional geochemical data in environmental programs**

Sediment in a lake or stream is a sink for elements derived from the surrounding watershed. Metals, such as As, Cd, Cr, Cu, Pb, Hg, Ni and Zn, occur naturally within the bedrock,

glacial sediments and soils of the watershed and are transported to accumulate in the lake and stream sediments. The challenge for environmental agencies is to differentiate between naturally occurring concentrations of metals and anthropogenic pollution. Sediment quality guidelines, standards or clean-up criteria, are required for the assessment and remediation of contaminated areas under such programs as: the Remedial Action Plans (RAPs) for the Great Lakes Areas of Concern (AOCs), the Atlantic Coastal Action Plan (ACAP) for harbours in Atlantic Canada, the Fraser River Action Plan (FRAP) in British Columbia, the Federal Contaminated Sites Program of Environment Canada, and the Ocean Dumping Regulations of the Canadian Environmental Protection Act. Lead and Hg are toxic substances under this act and As, Cd, Cr and Ni are being reviewed.

The Ontario Ministry of Environment and Energy has developed sediment quality guidelines. The guidelines describe the need to incorporate into the assessment the regional background concentration and indicate that chemical guidelines are only screening tools to be confirmed by biological testing. The chemical guidelines, however, can be taken out of context, and their derivation, assumptions and correct application are often forgotten. There are three aspects to consider when performing a sediment assessment using the Ontario guidelines: (1) background concentrations of metals in sediment need to be known; (2) chemical criteria are only expedient screening tools; and (3) biological criteria ultimately dictate whether or not a problem exists.

The Ontario Ministry of Environment and Energy (OMOEE) published sediment quality guidelines established concentrations at the Lowest Effect Level (LEL) and Severe Effect Level (SEL) for various metals and organic contaminants (OMOEE, 1992). These guidelines were based on a combination of: (1) background concentrations in the Great Lakes; (2) a benthic invertebrate screening level (the contaminant concentration that eliminates 5% (LEL) and 95% (SEL) of the benthic invertebrate species); and (3) an equilibrium partitioning approach. Sediment with a single contaminant at or above the LEL is assumed to have an adverse effect on some benthic invertebrate species and would be labeled marginally to significantly polluted. Sediment with a single contaminant at or above the SEL would be considered highly contaminated and would likely affect benthic invertebrate communities.

In Ontario the discovery of a single metal in sediment above the guideline triggers a biological assessment using a variety of bioassays. Table 4 lists the Ontario sediment quality guidelines for metals and background metal concentrations from the Great Lakes as reported by Mudroch et al. (1988).

Metals such as Cd, Cr, Cu and Ni occur naturally in the Great Lakes at concentrations close to or greater than the LEL, and, in some cases, the SEL. Often, agencies such as the regional OMOEE offices in northern Ontario must deal with the reality that most lake sediments in their area naturally exceed the LEL for one or more metals. This makes the province-wide guidelines of little value as a screening tool for their area. Regionally-derived chemical guidelines or a contamination factor above background as described by Håkanson (1992) could be more usable screening tools.

A fundamental problem in relating sediment chemistry to biological impact is a lack of understanding regarding biological availability of metals contained within sediment. Sediments may be characterized by using a total analysis method (neutron activation, hydrofluoric–nitric–perchloric or XRF) or by partial extraction using a weaker acid or other

Table 4

Range in background sediment metal concentration in ppm from the depositional basins of the Great Lakes (Mudroch et al., 1988) and the lowest and severe effects levels established by the Ontario Ministry of Environment and Energy (OMOEE, 1992)

	As	Cd	Cr	Cu	Pb	Hg	Ni	Zn
Lowest effect level	6	0.6	26	16	31	0.2	16	120
Severe effect level	33	10.0	110	110	250	2.0	75	820
<i>Background levels</i>								
Ontario	—	0.9–3.7	63–86	35–56	18–32	0.03–0.09	42–48	83–163
Erie	0.2–1.0	0.1–1.7	9–25	20–48	21–49	0.01–0.19	10–76	8–128
Huron	—	0.2–1.8	30–47	31–48	14–36	0.04–0.08	30–51	60–88
Michigan	5–8	0.5–0.7	50	15	8–10	—	20	40–50
Superior	—	0.4–0.7	26–73	30–84	20–68	0.04–0.68	24–70	53–137
Thunder Bay, Watershed		0.9	92	151	11	0.23	44	182
Thunder Bay, AOC	8	0.8	58	49	22	0.23	31	112

solvent. Sediment-metal bioavailability is complex and influenced by redox gradients, pH, temperature, adsorption, sedimentation, complexation, precipitation, grain size, organic content, bacterial metabolic processes, pore-water volatile solids, acid-volatile sulfides and will vary for different invertebrate species (Burton, 1992; Power and Chapman, 1992). Mobile metals, such as Cd and Zn, are transferred from the watershed into the sediment mainly in dissolved form and will have immediate biological availability; other metals, such as Cr in chromite, may be mainly transferred in clastic form. Environment Canada scientists have used the geochemical data to explore the relationship between sediment chemistry and biological response. Similar research is underway in several provincial agencies as well as environmental agencies in other countries. As our understanding of this complex issue improves, the geochemical reconnaissance data will provide valuable information on locations to test hypotheses.

Despite the uncertainty relating sediment chemistry to biological impact, incorporating knowledge of background concentrations of metals is essential to environmental assessment. Chemical analyses are less expensive and quicker than a biological assessment and can be used as a screening tool to cover a much larger area than would be possible with bioassays or benthic invertebrate community analysis. Determination of local background concentrations is critical to the assessment of whether an area is anthropogenically polluted. Håkanson (1992) describes the concept of contamination factor that compares the sediment contaminant concentration at the sediment surface to the concentration deep within the sediment core. However, diagenetic processes that cause natural cycling of some metals into the upper layers of sediment (Farmer, 1991), and which are poorly known, render this approach uncertain. Ginn and Pastorak (1992) compare contaminated areas to reference areas. Both approaches are often used.

Anthropogenic pollution can only be determined by a comparison to background and since the background concentration varies across Canada, no one guideline concentration

will suffice. For example, under the Canadian Environmental Protection Act, a sediment Cd concentration of 0.6 ppm is used to screen ocean dumping permits and yet over 18,804 of 97,133 (20%) lake or stream samples exceed this concentration (Fig. 2). Ocean Dumping permits are also screened based on sediment Hg concentrations above 0.75 ppm. Only 277 of 161,228 (0.17%) lake or stream sediments exceed this concentration. Regional staff of Environment Canada have often commented on the Cd guideline being too low and obviously with good reason whereas the Hg guideline appears to be reasonable. For areas of Canada with no available background data, the 95th percentile concentrations presented in Fig. 2 could serve as a preliminary screening guideline only until geochemical data are available.

### *5.1. Environmental assessment and remediation of mining activities*

The coring devices used to collect the centre-lake sediments (Friske and Hornbrook, 1991) are designed to void at least the top 25 cm that could have been affected by recent contamination, including atmospheric deposition. Thus the detailed maps for Hg, U and Ni in Ontario (Figs. 14–16) show the natural concentrations of these elements in the lake sediments. Fig. 16 shows one of the most spectacular features in the geochemical map of Canada, perhaps the world, situated over the Sudbury Structure. Forming an outer ellipsoidal ring, 40 km long, is the Sudbury Igneous Complex, which contains Fe–Ni–Cu sulphide ores. In lake sediments lying over and marginal to the structure are intense geochemical anomalies for Ni, Cu, Co, As and Au, with less extensive anomalies for Ag and Sb. The anomalies have been displaced to the south, along the direction of ice movement.

The U map shows higher concentrations in an area of mainly granitic rocks north of the Elliot Lake uranium mining area. In such cases, these natural values should be taken into account when considering the impact of the mining activities as well as the eventual remediation of the areas. For example, it is unrealistic to require remediation to take the environment to lower metal concentrations than existed naturally before the mines came into operation.

### *5.2. The Great Lakes areas of concern*

The Ontario Ministry of Environment and Energy's sediment quality screening guidelines are too low for northern Ontario so regional staff have used the NGR geochemical data to assist in sediment assessment issues for the Areas of Concern (AOC) in Lake Superior (Table 4). In Thunder Bay, for example, even though the average Cu, Cr and Ni concentrations exceed the provincial LEL, the values are not dissimilar to the surrounding watershed. Lead concentrations exceed what would be considered natural within the watershed so anthropogenic pollution may be present. However, the Pb concentrations are less than the provincial LEL. Arsenic, Cd, Hg and Zn concentrations are similar to the watershed sediments and the provincial LEL.

### *5.3. The Arctic*

Contaminants in Arctic ecosystems are the subject of a five year study by Environment Canada, Health and Welfare Canada, Indian and Northern Affairs and the Yukon and



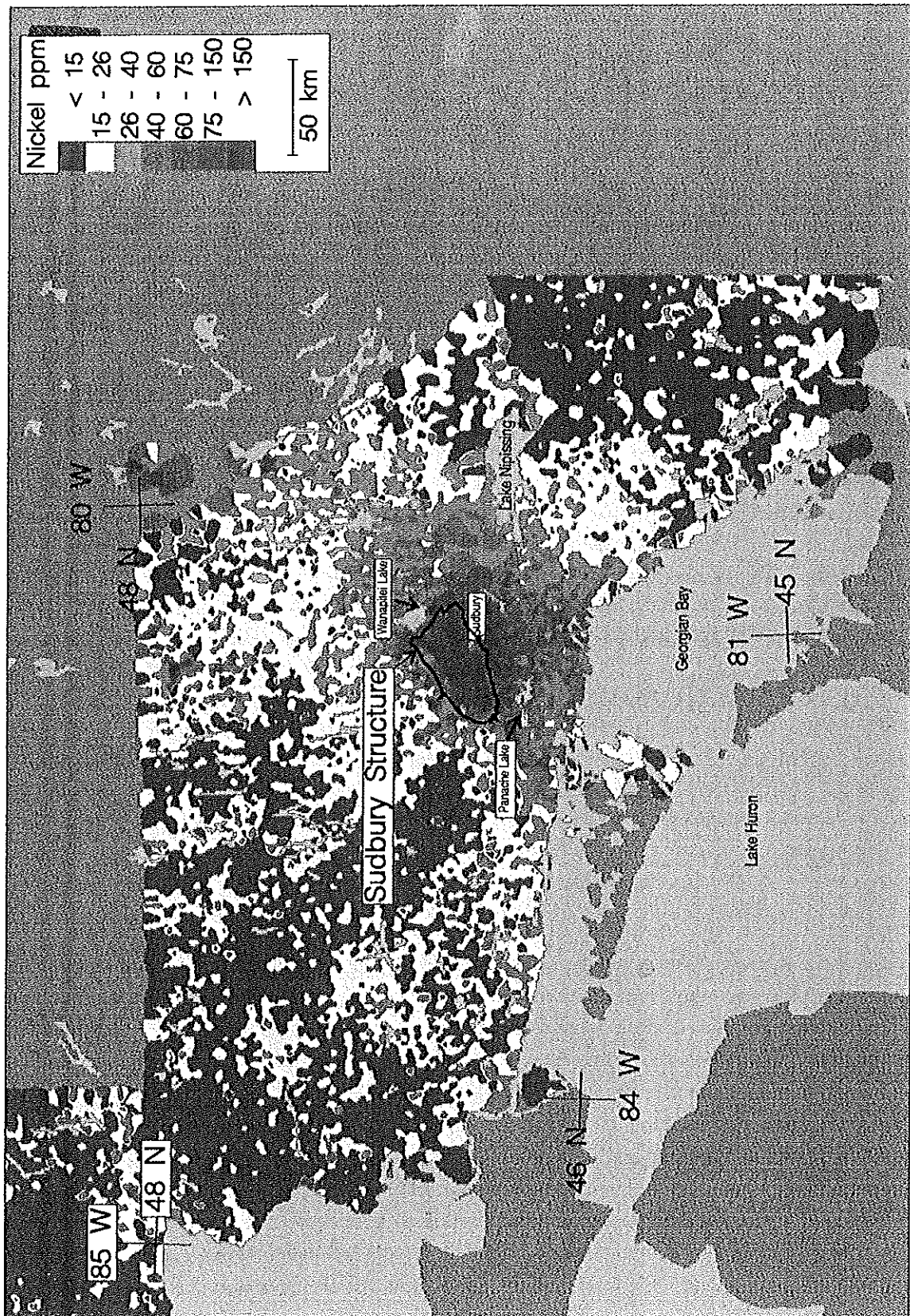


Fig. 16. Nickel in lake sediment samples from northern Ontario.

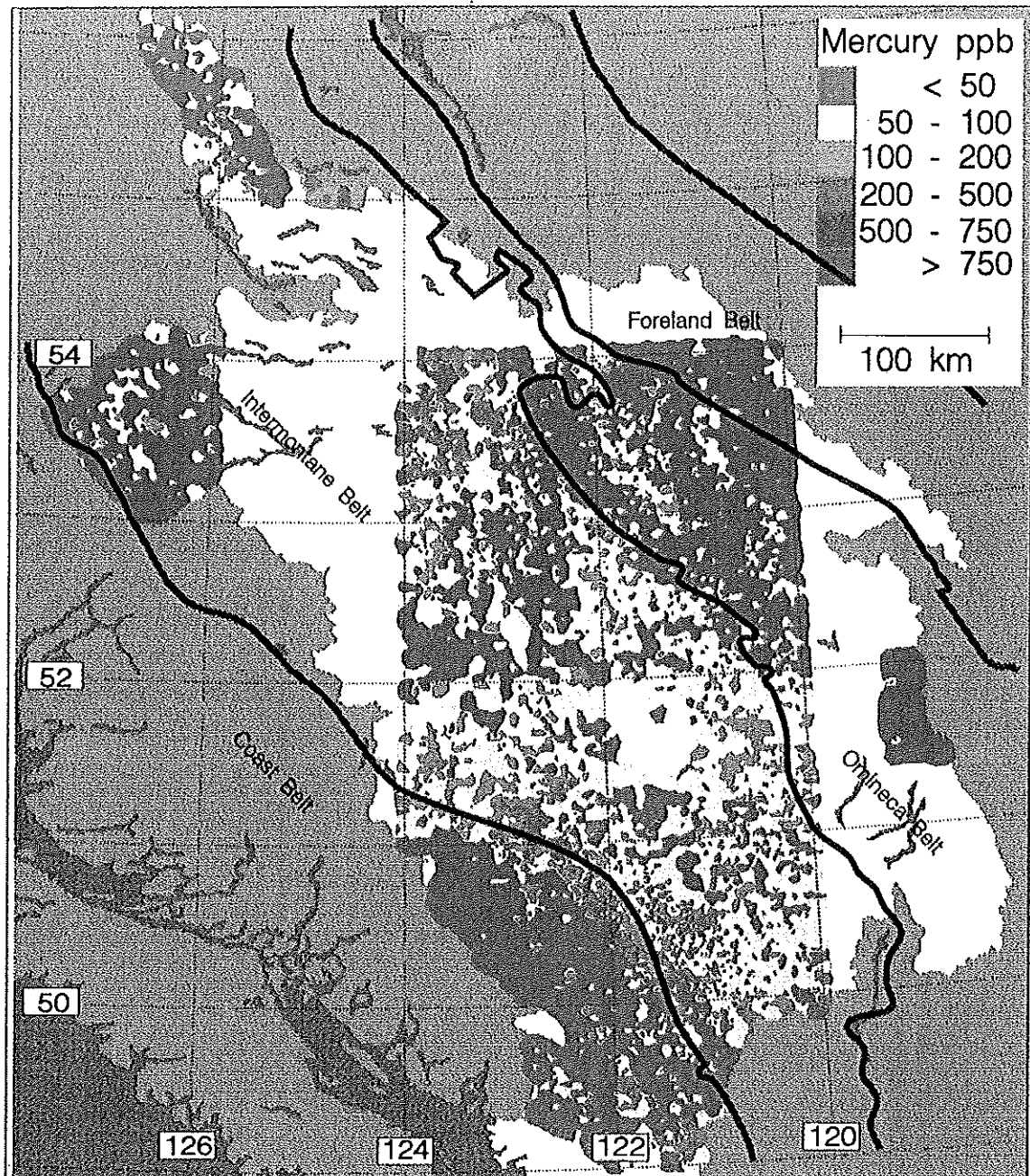


Fig. 17. Mercury in stream sediment samples from the Fraser River watershed.

Northwest Territories governments. High levels of Cd in caribou from Quebec and elsewhere have prompted health advisory warnings by provincial authorities. Baseline studies are underway to measure contaminants, especially Cd, in herds from the Yukon and Northwest Territories. Significant regional variability exists in stream sediment Cd levels throughout the territory (Fig. 5). The data would be valuable in determining site selections for lichen Cd analysis and differentiating between geochemical background concentrations and long range transport of atmospheric pollutants.

#### 5.4. Atlantic coastal action plan areas

The Atlantic Coastal Zone Information Steering Committee consists of provincial and federal representatives whose mandate includes providing a Canadian focus for the proposed

East Coast of North America Strategic Assessment Project. The objectives of this joint Canada/US project are to enhance the ability to assess the nature, condition and sensitivity of coastal and marine resources. Environment Canada is developing Action Plans for several Atlantic coastal areas. Many streams have concentrations in excess of the 0.6 ppm Ocean Dumping Guideline. Most of the Atlantic Coastal Action Plan areas have geochemical data available from either lakes, streams or both. The data will be valuable in the East Coast assessment project as well as ACAP.

### *5.5. Fraser River Action Plan*

The pollution of the Fraser River from pulp mill effluents and other industrial and urban wastewater discharges led to the recently announced Fraser River Action Plan (FRAP). The environmental impact of present and abandoned mines is an issue both for the Fraser River watershed and for British Columbia as a whole. Mercury was often used in the gold extraction process. Fig. 17 shows the distribution of Hg within the Fraser River Basin, together with the boundaries of the geological belts that cross the basin. Note the strong geological control on the Hg concentration. Areas of high concentration are largely within the Intermontane Belt, which is a diverse assemblage of accreted terranes and cover rocks comprising volcanic, sedimentary and plutonic rocks that range from upper Paleozoic to Cenozoic in age. Only detailed studies within districts can assess the degree and extent of mining-related pollution. However, viewing Fig. 17, it is apparent that the major control on Hg distribution is geological.

## **6. Conclusions**

NGR surveys, which now cover more than 2.5 million km<sup>2</sup>, or approximately one quarter of Canada's landmass, show that the background concentrations of metals in the environment vary widely over several orders of magnitude and, in some areas unaffected by human activity may reach levels that elsewhere have been considered to have an effect on the ecosystem. Environmental agencies can incorporate these data into assessments of ecosystem health or anthropogenic pollution and regional variability is a reality which sediment quality guidelines need to incorporate. For example, the sediment Cd concentration of 0.6 ppm presently used in Canada to screen ocean dumping permits is exceeded by 20% of the NGR lake and stream sediment samples. The Canada-wide maps show anomalies that are hundreds or thousands of km<sup>2</sup> in extent and related to geological features. In some cases, these relate to important mineral districts, while in others, such as the As-rich Foxe Fold Belt on Baffin Island, there are no known mineral deposits. The identification of undisturbed, metal-rich regions provides reference areas to test the effects of the metals on the flora and fauna.

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