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MERCURY IN PERMAFROST REGIONS:
OCCURRENCE AND DISTRIBUTION IN THE
KAMINAK LAKE AREA, NORTHWEST TERRITORIES

(Report and 5 figures)

E. H. W. Hornbrook and I. R. Jonasson



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ABSTRACT

A major part of the Geological Survey of Canada's program concerning regional geochemical exploration has been the development and testing of regional hydrogeochemical methods. The program in the copper-rich Ennadai-Rankin Inlet belt of volcanic and sedimentary rocks near Kaminak Lake, southeastern Keewatin District, Northwest Territories, has discovered an unusual and unsuspected distribution of above background concentrations of mercury in natural waters.

Most of the mercury is considered to be bound by organic material, both soluble and suspended.

The distribution of mercury in natural waters throughout the 2,500-square-mile study area exhibits a definite relationship to the distribution underlying volcanic, sedimentary and granitic rocks; this feature is not shown by copper, zinc, and nickel. The ability of the present mercury method to define major structures and to discriminate between granitic plutons and adjacent volcanic and sedimentary rocks is of obvious benefit to mineral exploration for favourable host rocks and/or sulphide mineralization in this and similar areas that are covered by extensive glacial drift.

Natural contamination of the waters in this remote environment by mercury, which cannot be attributed to industrial, agricultural or mining sources, suggests the possibility that there may be other similar mercuriferous provinces in the Canadian Shield.

RÉSUMÉ

Le programme de recherche de la Commission géologique du Canada en ce qui concerne la prospection géochimique à l'échelle régionale a été consacré en majeure partie à l'élaboration et à l'application expérimentale des méthodes de géochimie des eaux naturelles. Pour la zone cuprifère d'Ennadai-Rankin Inlet, qui près du lac Kaminak, dans le sud-est du district de Keewatin (Territoires du Nord-Ouest) est constituée de roches volcaniques et sédimentaires, les recherches de ce programme ont amené la découverte d'une distribution inhabituelle et insoupçonnée des teneurs en mercure des eaux naturelles supérieures à la normale.

On estime que la majeure partie de ce mercure entre dans des composés organiques qui sont à l'état de solution et à l'état de suspension dans les eaux.

La distribution du mercure, dans les eaux naturelles de cette zone de 2,500 milles carrés, montre une relation certaine avec l'arrangement des roches volcaniques, sédimentaires et granitiques sous-jacentes; cette particularité ne se retrouve pas dans le cas du cuivre, du zinc et du nickel. La méthode actuelle de détection du mercure permet donc de définir les structures les plus importantes et de faire la distinction entre les plutons granitiques et les roches volcaniques et sédimentaires adjacentes; il est évident que ceci sera du plus grand intérêt pour la prospection minérale consacrée à la recherche des roches encaissantes favorables à la formation de gîtes et/ou des minéralisations sulfurées, qui dans cette région et dans les régions similaires sont recouvertes par une couche étendue de matériaux glaciaires.

La contamination naturelle des eaux par le mercure qui, dans cet environnement lointain ne peut-être attribuée à des sources industrielles, agricoles ou minières, nous fait entrevoir l'existence possible d'autres provinces également riches en mercure dans le Bouclier canadien.

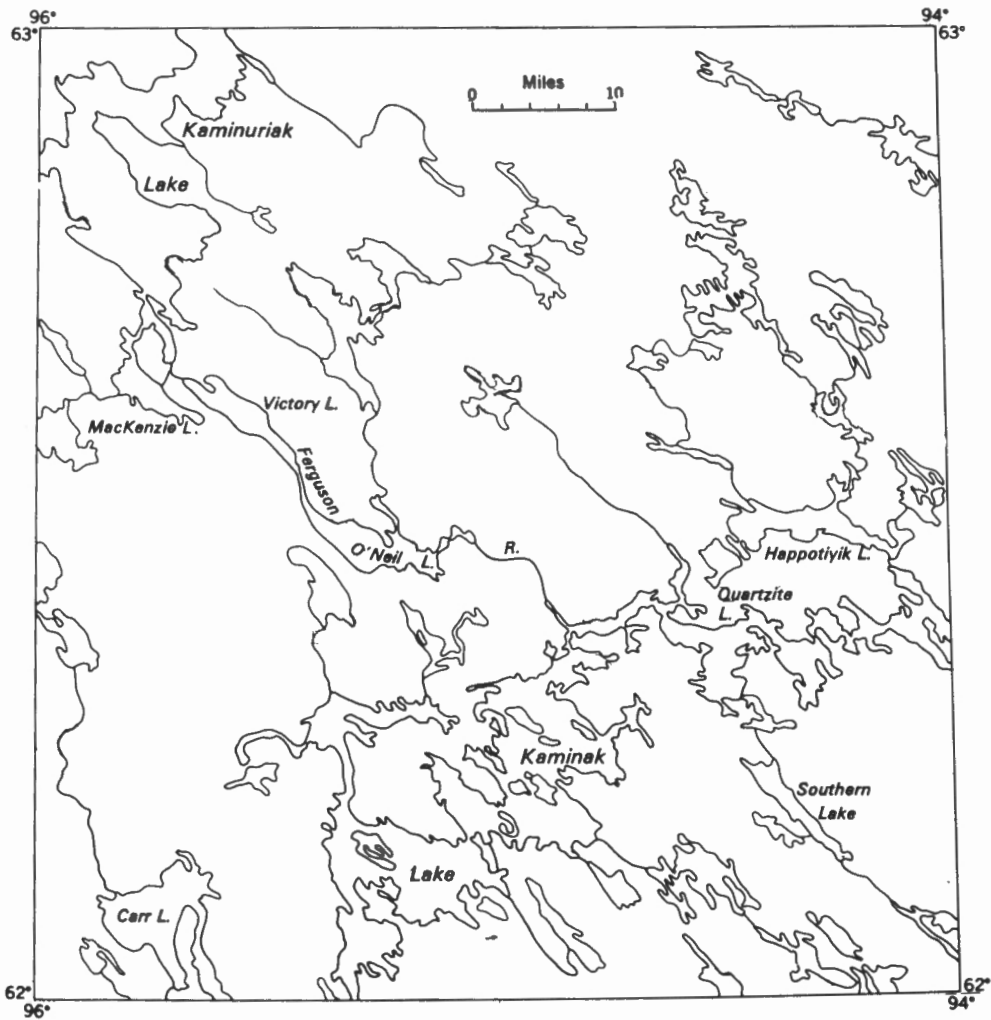


Figure 1. Location map: Kaminak Lake area, Northwest Territories.

MERCURY IN PERMAFROST REGIONS: OCCURRENCE AND DISTRIBUTION IN THE KAMINAK LAKE AREA, NORTHWEST TERRITORIES

INTRODUCTION

In 1969 the Geological Survey of Canada initiated a continuing program to develop regional geochemical exploration methods for application in the continuous and discontinuous permafrost regions of Canada. A major part of the program has been the development and testing of regional hydro-geochemical methods.

The program in the Kaminak Lake area of the Keewatin District, Northwest Territories (Fig. 1), a part of the copper-rich Ennadai-Rankin Inlet belt of volcanic and sedimentary rocks, has discovered an unusual and unsuspected distribution of above background mercury concentrations in natural waters. The distribution of mercury throughout the 2,500-square-mile study area exhibits an excellent relationship with the distribution of underlying volcanic, sedimentary and granitic rocks, a feature not shown by Cu, Zn and Ni in waters. The contamination of these natural waters in this remote environment by mercury cannot be attributed to industrial, agricultural or mining sources.

Thus, the occurrence and distribution of mercury is interesting from the viewpoint of its potential use in mineral exploration for appropriate host rocks and/or sulphides and from the viewpoint of its natural contamination of a remote environment. It is significant that commercial fishing is carried out in Kaminak Lake.

GEOLOGY

The bedrock geology, geochemistry and the overlying glacial deposits have been recently studied by many authors including: Wright (1967), Davidson (1970), Ridler (1971), Shilts (1971), Hornbrook (1971), and by Hornbrook (*in* Boyle *et al.*, 1971).

Figure 2 is a geological sketch map of the area deduced by minor extrapolation under glacial deposits of the boundaries between mafic and felsic volcanic rocks, sedimentary rocks and granitic plutons mapped by Davidson (1970). He has summarized the geology as follows: "A deformed assemblage of stratiform rocks, the Kaminak Group (Archean) predominantly volcanic in origin but locally with minor greywacke and iron-formation, is intruded by a variety of plutonic rocks ranging in composition from gabbro to granite. Northerly trending diabase dykes cut all these rocks, but are themselves older than the sedimentary and volcanic rocks of the Hurwitz Group (Aphebian) that occupy a fault-bounded trough extending from Happtiyik Lake to Carr Lake." Figure 2 shows that the geological structure of the area is marked in the west by the elliptical configuration of the Kaminak Lake complex of sedimentary and mafic and felsic volcanic rocks approximately peripheral to the intrusive plutonic core. The Hurwitz belt forms a prominent southwest-northeast linear feature of the area.

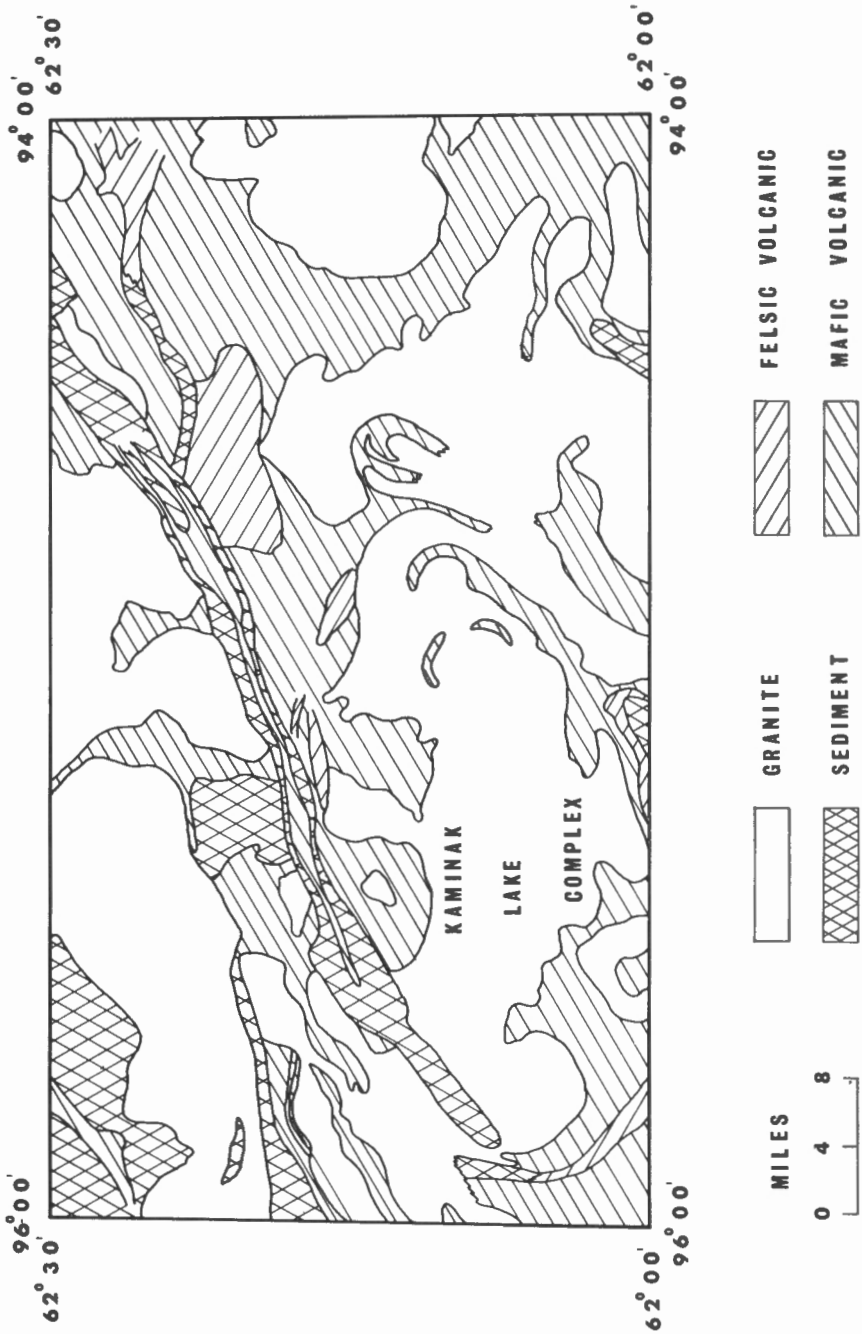


Figure 2. Geological sketch map: Kaminak Lake area, Northwest Territories. (after Ridler, 1971)

W. W. Shilts (pers. comm.) describes the glacial deposits as follows:

The Kaminak Lake area lies southeast of the Keewatin Ice Divide (Lee, 1959). Drumlins and striations indicate that the last glacial movement was towards the southeast, away from the divide. Lee (1959, p. 11) presented evidence for an earlier movement, S10°E, that occurred in the Kaminak area and west of the divide and was, therefore, independent of the divide. Near Kaminak Lake, sections expose up to 5 m of till, and at the exposures examined, grey sandy till (<3% clay) occurs as 0.3-1m-thick thrust plates intercalated with thrust plates of red clay (5%-15%) till. The two tills may have been deposited during the two flow phases noted, but it is not known which till is associated with which flow phase. Dispersion of Cu, Zn, Ni, Pb, and Ag in till near Carr Lake is both south and southeast from known sources with the southward-trending fan being the most prominent.

ORE MINERALOGY

According to Davidson (1970) gossans and rusty zones are common throughout the area and are usually developed from pyrite-pyrrhotite disseminations in greenstones or from pyrite disseminated in sheared felsic volcanic rocks. Pyrite is also frequently found in small quartz veins locally associated with pyrite and pyrrhotite and is present in thin quartz veinlets that occur locally in the mafic lava flows of the Hurwitz Group. Galena, sphalerite and chalcopyrite occur on the Dee group of claims, west of Carr Lake, and sphalerite is known to occur west and northeast of Kaminak Lake and south of the east end of O'Neil Lake. Similar scattered occurrences of sulphides occur in the eastern part of the area.

Ridler's studies (1971) have shown that sulphide, carbonate and oxide facies iron-formations are well developed regionally in a pattern consistent with a "shelf to basin to shelf" land configuration. He further states that the abundant occurrences of chalcopyrite as disseminations, laminae and discordant veins in the interflow sediments of the mafic platform (Kaminak Group) under the rhyolitic accumulation suggest that the carbonate sulphide facies which overlies the rhyolitic accumulation should contain base-metal-rich portions as do analogously younger stratigraphic zones in the Superior Province. Ridler also suggests that chemical and clastic sedimentary rocks, felsic volcanic rocks and hypabyssal intrusive rocks, favourable for occurrences of precious metal mineralization, are abundant. Thus, the area has considerable potential for sulphide and precious metal mineralization in structurally favourable sites. It is essential, therefore, to develop methods for detecting sulphide or precious metal deposits and/or their favourable host rocks through the extensive overlying glacial deposits of the area.

GEOCHEMISTRY

As described by Hornbrook (in Boyle et al, 1971) Cu, Zn and Ni have a similar distribution in the study area (Fig. 3). Many of the small-station anomalies can be correlated with isolated mineral occurrences or gossans in exposed bedrock, but the larger multi-station anomalies are probably developed on anomalous till originating from a mineralized bedrock source. Thus, the major distribution patterns of Cu, Zn and Ni are a reflection of their

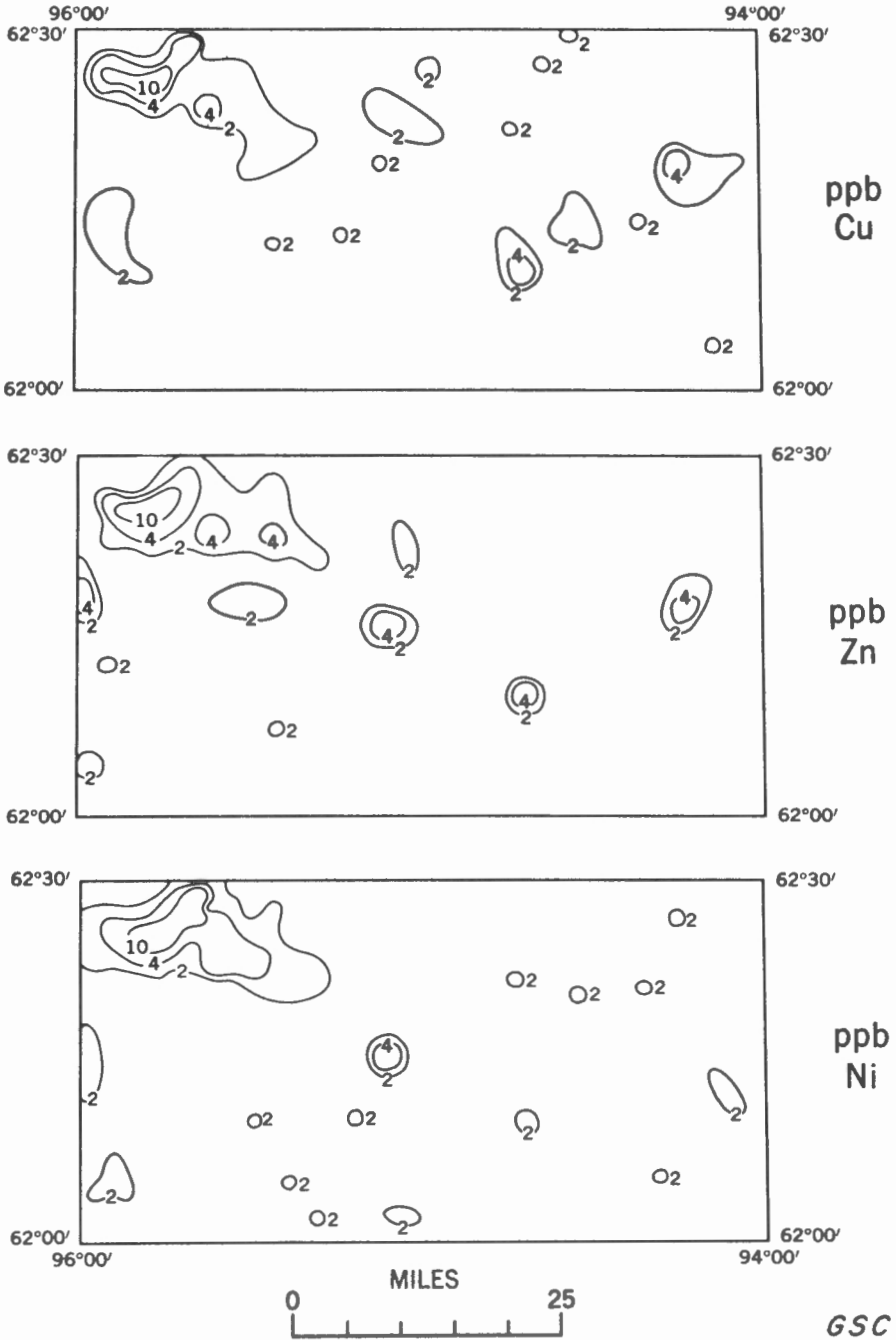


Figure 3. Regional hydrogeochemical anomaly maps, Kaminak Lake area, Northwest Territories. Sample density — one sample per 10 square miles.

content in the transported glacial deposits of the area and not underlying bedrock. This lack of a relationship to bedrock is evident for the down-ice portion of the 150-square-mile Cu, Zn, or Ni anomaly in the northwest corner because it overlies the huge granite pluton west of Savage Lake. The effectiveness of Cu, Zn and Ni hydrogeochemical exploration in this study was limited, because it could not reflect underlying bedrock lithology and structure and was restricted by the complexities of relating anomalies to probable up-ice direction bedrock sources.

As described previously, there are many showings of both precious metals and base metals in an area considered to be structurally favourable for economic deposits. In view of this predicted high mineral potential it was expected that the wide distribution of mineral occurrences would be reflected in the host rocks and subsequently in the lake waters as elevated trace metal contents. Therefore, it was not anticipated that the regional background levels found for Cu, Zn and Ni in the waters would be so low, in fact less than 1 ppb. Analytical methods were not available to provide meaningful data at these low metal concentrations. By increasing the analytical sensitivity to improve precision at low background levels, the effectiveness of the method should be enhanced.

The distribution of mercury in lake waters is shown in Figure 4. There is an obvious relationship between Hg distribution and the linear configuration of the Hurwitz Group rocks, and the elliptical configuration of the Kaminak Group in the Kaminak Lake complex. Regional background Hg concentrations of about 0.035 ppb generally correspond to areas underlain by granitic rocks and are similar to background concentrations of 0.01 to 0.05 ppb found by Dall'Aglio (1971) in some natural waters of the Tuscany region, Italy. His anomalous concentrations in the vicinity of cinnabar deposits were approximately 2 ppb. In the Kaminak area the highest concentrations found were of the order of 0.5 ppb in Kaminak Lake.

The major source of the Hg can only be the bedrock and/or sulphide and other mineralization contained in them. Mercury can penetrate permafrost to produce measurable dispersion haloes at the surface as shown by the work of Lehnert-Thiel and Vohryzka (1968) in Greenland about a tetrahedrite-galena-sphalerite deposit. Undoubtedly mercury is also penetrating extensive thicknesses of perennially frozen till in the Kaminak Lake area producing a distribution directly related to the bedrock geology.

Unfortunately, sufficient rock, mineral and soil samples are not available at this time to permit firm conclusions on the nature of the Hg occurrence and distribution in Kaminak and Hurwitz Group rocks. However, tentative conclusions are possible based on 37 samples of which 23 are representative rock types from formations within both groups. Concentrations obtained are similar to those tabulated by Jonasson and Boyle (1971) for normal igneous, sedimentary and metamorphic rocks.

An Hg content of 175 ppb was found in a greywacke from the upper Ameto Formation of the Hurwitz Group. Some other greywacke samples from the same formation ranged from 30 to 50 ppb. The elevated Hg content of this rock and its excellent exposure along most of the Hurwitz belt explains the good definition of the belt by the Hg anomaly map, Figure 4. Contrasting with the Hurwitz greywacke above, most of the representative Kaminak and Hurwitz Group rocks had visible sulphide mineralization. Soils overlying two sulphide gossans had approximately 300 ppb Hg, nearly three times the mean content of normal soils and equivalent to the mean of B horizon soils near known

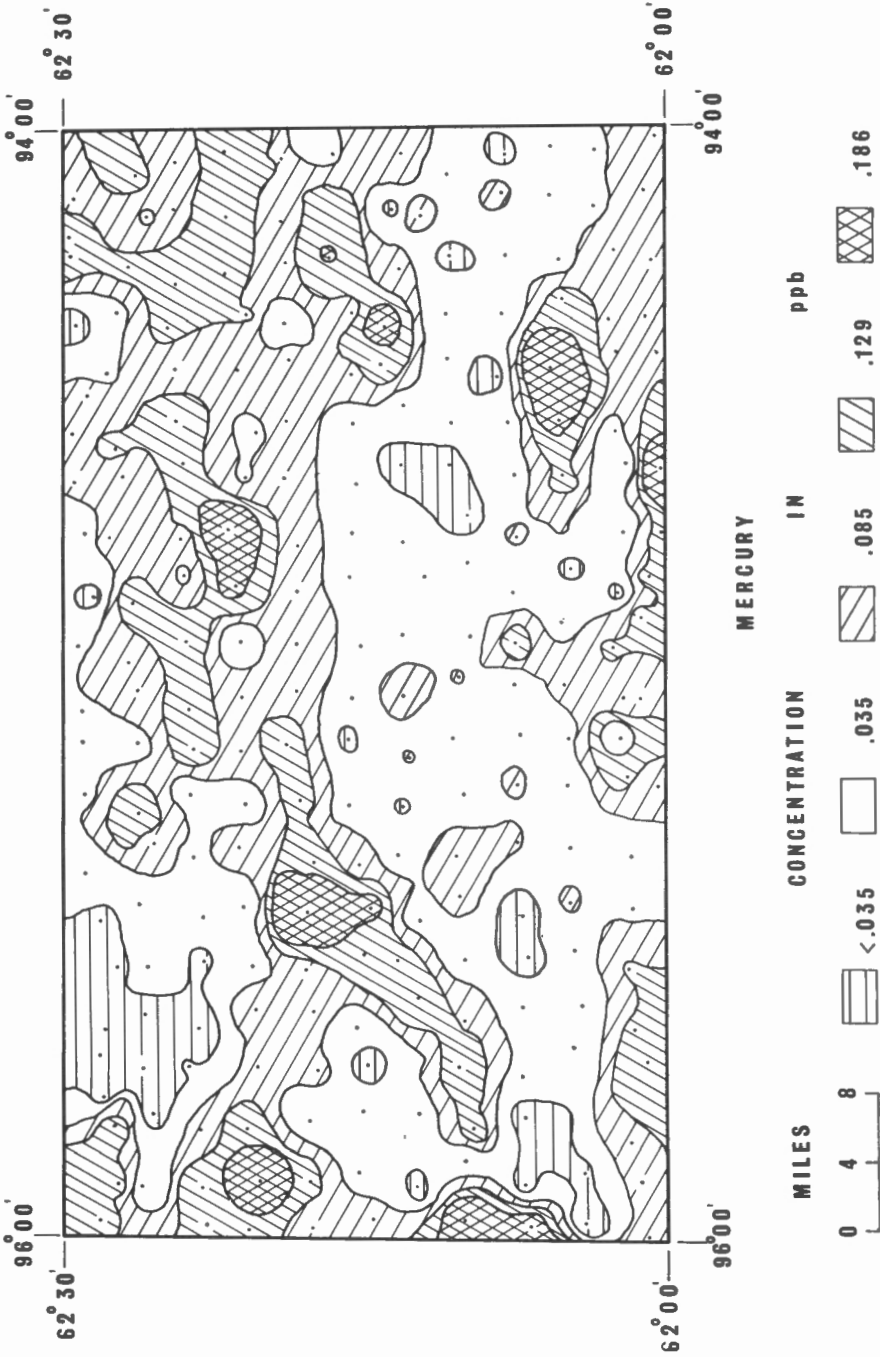


Figure 4. Regional hydrogeochemical mercury anomaly map: Kaminak Lake area; Northwest Territories. Sample density - one sample per 10 square miles.

disseminated polymetallic deposits as tabled by Jonasson and Boyle (1971). In sulphide mineralization from the area, Hg appears to be concentrated in galena and sphalerite (850 ppb) relative to its lower content in pyrrhotite, pyrite and possibly chalcopyrite (70 ppb). This is in agreement with similar findings of Webber and Horska (1970). Whether or not the Hg dispersion haloes detected in the natural waters of the area originate from gaseous sources, disseminated sulphides, country rock, or a combination of these, has not been determined. Available data indicate that the Hg haloes originate from either country rock or widely disseminated sulphides in the rocks and that the broad areal dispersion haloes may be modified locally by the presence of sulphide gossans. The superimposition of the mercury anomalies (Fig. 4) on the Kaminak Lake complex structure (Fig. 2), therefore, probably reflects the Hg content, whatever its chemical form, of the Kaminak and Hurwitz Group rock types.

The distribution of mercury in lake waters, which is seemingly controlled by the chemical nature of the underlying rock types, is of some relevance to environmental scientists. These scientists seek first to establish, and then to determine the effects of such controls on the natural distribution of mercury in order to ascertain just what may be termed "natural" or "normal" levels and so deduce what contributions man subsequently makes to the further contamination of such an area. It is also significant that commercial fishing is carried out in Kaminak Lake where there is no other industrial or agricultural activities and where the only mercury present in the lake waters is due to natural sources.

CONCLUSIONS

The current effectiveness of the Hg technique at a sampling density of one sample per ten square miles is sufficient to delineate major structures and discriminate between granitic plutons and the volcanic and sedimentary rocks present in complexes. Future work will attempt to determine if the technique can discriminate between mafic and felsic volcanic rocks and sedimentary rocks and perhaps describe anomalies that can be related specifically to sulphide mineralization. This can be tested, for example, by increasing the sample density. Mercury hydrogeochemical surveys could be beneficial in the mapping and mineral exploration of other till covered complexes in the Ennadai-Rankin belt, such as the Wallace River complex, where the exposure of bedrock is less than that in the Kaminak Lake complex. Similar mercury surveys could also serve to define those areas in the Canadian Shield that are enriched in mercury and are therefore of interest to both environmental scientists and exploration geochemists.

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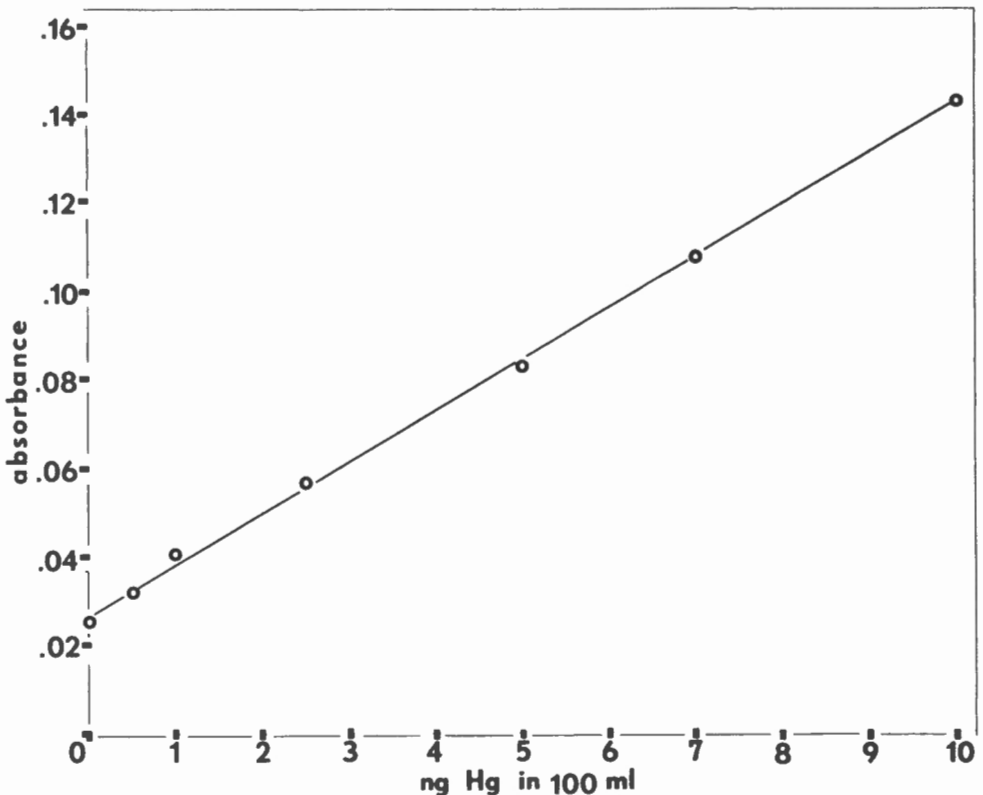
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APPENDIX: ANALYTICAL PROCEDURE

The analytical technique adopted for this study is now known as the cold vapour atomic absorption method. Essentially, mercury (I) or (II) ions are reduced by acidic tin (II) ions and the elemental mercury thus produced is flushed from the system by a stream of air and conducted into the light path of an atomic absorption spectrometer (Poluektov et al, 1963 and Hatch and Ott, 1968).

Certain modifications to established procedures have been made in these laboratories to enable an absorption cell of one metre path length to be used. A full description of the analytical methods used for mercury in water, sediments, rocks and ores is the subject of another paper at present in preparation (Jonasson and Lynch, G.S.C. laboratories).

For the purposes of this work, a 100 ml water sample is treated. A minimum concentration of 0.005 ng/ml (ppb) total mercury can then be measured. A standard curve is presented in Figure 5.



Instrument: Techtron AA5; Cell length: 1 metre;
Slit Width: 100 μ ; Wavelength: 253.7 nm;
Lamp Current: 4 ma.; Scale Expansion x 5.

Figure 5. Standard Curve for Mercury Analysis of Water Samples.

TREATMENT OF SAMPLES

Water samples were collected, without filtration, in polypropylene bottles. Waters from the Kaminak Lakes region are characteristically clean and clear in appearance with no visible sediment in most cases.

Samples were acidified with nitric acid to make the solution 0.015M in hydrogen ions. Mercury analyses were not made on the sample until some four months after collection. It is often reported (Beněs, 1969; Beněs and Rajman, 1970) that mercury in natural water samples will disappear from the bulk solution to the walls of the containing vessel in a relatively short time, so methods were devised to recover the adsorbed mercury prior to analysis.

It was considered that most of the mercury present would be bound by organic material, soluble or suspended, which would have to be destructively oxidised to produce mercuric ions.

The ideal oxidant would fulfil this requirement and in the process take the organically bound mercury from the walls of the container back into solution.

Several oxidants were tested, viz., acidic permanganate solution, acidic persulphate solution and ozone gas.

Multiple samples were treated with the various oxidants and yielded results as displayed in Table 1. For comparison, unoxidised samples are included in which the only mercury detected was presumed to be inorganic or in some other chemical form reducible by tin (II) ions (See Table 2).

TABLE 1

EFFECT OF DIFFERENT OXIDANTS ON MEASURED MERCURY CONTENTS OF LAKE WATER SAMPLES

Samples (100ml)	Acidic Permanganate 10 ml 0.03% (1)	Ozone Gas 550 mg. (2)	Acidic Persulphate 1.0 g (3)
1	0.065	0.040	0.065
2	0.040	0.033	0.032
3	0.057	0.040	0.070
4	0.033	0.015	0.025
5	0.108	0.125	0.171
6	0.033	0.020	0.060
7	0.180	0.175	0.255
8	0.105	0.103	0.163

- Notes: 1. Permanganate solution is made up in M/2 sulphuric acid. Samples are shaken for 15 hours at room temperature.
2. Ozone gas was bubbled through the acidified (0.015M) sample solution for one hour. Flow rate 550 mg/hr.
3. One gram of $K_2S_2O_8$ was added to the sample solution made M in nitric acid. Solution was brought up to near boiling for 1 minute and allowed to cool to room temperature.
4. All mercury concentrations quoted are in units of nanogram per ml., i.e., in parts per billion.

TABLE 2

RECOVERY OF MERCURY IN THE ANALYSIS OF AGED SAMPLES

Sample	No oxidant added to 100 ml sample	Oxidant + 100 ml sample	Oxidant + 100 ml sample in original container
1	0.5	1.3	3.0
2	<0.5	2.3	3.5
3	<0.5	0.8	6.0
4	<0.5	3.8	8.0
5	<0.5	3.5	16.4
6	<0.5	5.0	11.0
7	<0.5	2.0	12.0
8	<0.5	5.0	8.7
9	<0.5	3.5	21.0
10	<0.5	2.0	68.9
11	<0.5	2.0	9.5

- Notes: 1. Mercury recovered is expressed as nanograms Hg in 100 ml sample.
2. For true comparisons the quantity of mercury recovered must be distributed over the total volume of sample initially collected to enable original mercury content of the sample to be calculated.
3. The example data presented indicate clearly that mercury losses to the walls of the container were considerably greater in cases where original mercury content was high. Anomalous values, therefore, are suppressed and often obliterated when bulk solution data only is viewed.

Both permanganate and persulphate proved to be quite effective as oxidants. Ozone is less convenient to use but does offer the advantage of not increasing the salt content of the solution (unimportant for mercury analysis but significant if say, copper or nickel were being analyzed by conventional extraction and atomic absorption procedures). Although ozone frees most of the mercury, it apparently does not destroy the host organic material as completely as does permanganate. Final flushing of mercury vapour from the sample solution was slower when ozone was used than when either of the other two oxidants were used, indicating perhaps that some complexing species remain after ozone attack. Permanganate was selected as the reagent to be used. Because of its intense colour a rough estimate of the organic content of the waters could be made in terms of the amount of manganese (VII) consumed. This was found to be $\leq 20 \mu\text{g Mn}$ per 100 ml lake water. The mercury contents ultimately measured for all of the samples bore no correlation with the estimated organic content.

The amount of mercury lost during storage (4 months) of the samples cannot be judged. Initial acidification with nitric acid would be expected to suppress losses which may have resulted from elemental mercury formation, bacterial or otherwise. Acidity was sufficiently high to effectively hydrolyse any of the low molecular weight dialkyls which may have been originally

present upon collection. Losses from the system are, therefore, considered to be negligible and to have an insignificant effect on the data presented or on the interpretive conclusions drawn from them.

Further work is underway to study any possible effects that aging of fresh natural water samples may have on their measurable mercury contents.