Canadian Mineralogist
Vol. 14, pp. 73-90 (1976)

SEDIMENT GEOCHEMISTRY OF SUDBURY-AREA LAKES

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Abstract

Sixty-five lake-sediment samples were collected from the Sudbury-Temagami area (46°15′ - 47°30′N; 79°30′ - 81°30′W) during the summer of 1973. Sediment samples frozen in the field were freeze-dried and ground to 200 mesh for all chemical determinations. Sediment analyses included heavy metals (Ni, Cu, Zn, Pb, Cd, Fe, Mn), organic carbon, total Kjeldahl nitrogen, acid-extractable phosphorus, and particle-size distribution. Increasing concentration gradients towards Sudbury were observed for the heavy metals in the surface sediments, particularly Ni and Cu. Additional evidence for a point source of heavy metals at Sudbury was observed in the parallel behaviour of Ni:Cu and Cu:Zn ratios in both sediment and in atmospheric precipitation. The sediment material was determined to be a silty clay with a relatively high organic content, which is essentially typical of the surface sediments found in oligotrophic lakes. Acid-extractable sediment phosphorus formed approximately 50% of the total phosphorus and displayed a marked relationship to the sediment Fe concentration.

Résumé

Soixante-cinq échantillons de sédiments de lac ont été ramassés dans la région de Sudbury-Témagami (46°15′ - 47°30′N; 79°30′ - 81°30′W) pendant l'été 1973. Les échantillons de sédiments, gelés sur le terrain, ont été séchés à froid et moulus à des dimensions de 200 mailles pour toutes les déterminations chimiques. Les sédiments ont été analysés afin de connaître leur contenu en métaux lourds (Ni, Cu, Zn, Pb, Cd, Fe, Mn), en carbone organique, en nitrogène Kjeldahl total et en phosphore pouvant être extrait par l'acide. Une analyse granulométrique a aussi été effectuée. L'augmentation des gradients de concentration vers Sudbury ont été observer pour les métaux lourds dans les sédiments superficiels, particulièrement pour le Ni et le Cu. De nouvelles preuves concernant l'origine des métaux lourds ont été obtenues par le comportement parallèle de Ni:Cu et de Cu:Zn dans les deux sédiments et par la précipitation atmosphérique. Le matériel du sédiment s'est avéré être de l'argile limoneux avec un contenu organique relativement élevé qui est particulièrement typique des sédiments superficiels trouvés dans les lacs oligotrophiques. Le phosphore pouvant être extrait par l'acide contenu dans le sédiment formait presque 50% du phosphore total et démontrait un lien marqué avec la concentration de Fe du sédiment.

(Traduit par le journal)

Introduction

This study was initiated to define any deleterious effects associated with the mining and smelting industry at Sudbury, Ontario, on the oligotrophic lakes of the Precambrian Shield in this region. The study was deemed necessary in view of the sensitive and delicately-balanced chemical and biological status of such bodies of water (Conroy 1972) and in view of the levels of atmospheric pollutants presently being emitted from the smoke stacks at Sudbury (Kramer 1975).

Of particular concern is the concentration and degree of dispersion of the potentially toxic materials originating from Inco's 1250-foot smoke stack at Copper Cliff, Ontario. Table 1 summarizes the emissions data from this source for the period 1972 to 1974. It is apparent that heavy metals and acid-generating sulfur dioxide are loading the atmosphere at levels that may be hazardous to ecosystems in the surrounding area.

Lake sediments were selected as one means of defining these atmospheric inputs into the Sudbury lakes. Fine-grained sediments reflect the nature of overlying waters at the time of deposition because of their ability to incorporate organic and inorganic constituents during transport and deposition. Consequently, lake sediments can provide an accurate record of past

TABLE 1. QUANTITY OF MATERIAL EMITTED TO THE ATMOSPHERE FROM THE 1250 FT. STACK AT COPPER CLIFF*

Substance	Emission (10^6 g/day)	Substance	Emission (10^6 g/day)
SO_2	3970	Fe	5.46
SO_4	15.5	Ni	1.14
		Cu	1.56

* After Kramer (1975)

TABLE 2. STUDY LAKES AND THEIR LOCATIONS

Lake No.	Lake Name	Township(s)	Lake No.	Lake Name	Township(s)
1	Opikinimika	Moffat	34	Matagamasi	Mackelcan/Rathburn
2	Thor	Frechette/Lampman	35	Wanapitei	Norman/Maclennan/Scadding/Rathburn
3	Shoofly	Beulah/Marshay	36	Donald	McCarthy/Kelly
4	Barnet	Leask	37	Kukagami	Kelly/Rathburn
5	Welcome	Valin	38	Maskinonge	Kelly/McCarthy
6	Stull	McLeod/Ellis	39	Washigami	Davis/Wisner
7	Sunny Water	Gamble	40	Murray	Davis/Janes
8	Florence	Parker/Dundee	41	Sargesson	Janes
9	Laundrie	Howey	42	Pud	Pardo
10	Helen	Beaumont	43	Silver	Pardo
11	Frederick	Stobie	44	Wawiashkashi	McNish/Macbeth
12	Yortson	Seagram/Clary	45	Manitou	Clement
13	Laura	McConnell	46	Emerald	Afton
14	Chiniguchi	McConnell	47	Gull	Scholes
15	Telfer	Telfer	48	Obabika	Delhi/LeRoche/Belfast/Armagh
16	Fraleck	Fraleck	49	Sharp Rock Inlet	Canton/LeRoche
17	Bigwood	Kitchener	50	Diamond	Canton
18	Nelson	Bowell	51	Lady Evelyn	Leo/Medina
19	Joe	Wisner	52	Mountain	Best/Brigstocke
20	Capreol	Capreol	53	Rib	Gillies Limit
21	Whitson	Blezard	54	Lorrain	South Lorrain
22	Ramsey	McKim/Neelon	55	Temagami	
23	Whitewater	Snider/Rayside	56	Rabbit	Riddell/Eldridge/Askin
24	Fairbank	Fairbank/Trill	57	Jumping Caribou	Law/Olive
25	Whitefish	Waters	58	Fanny	Flett
26	Wavy	Eden	59	Red Cedar	McCallum
27	Millerd	Secord/Halifax	60	Marten	Gladman
28	Nepewassi	Hawley/Appleby/Hendrie/Burwash	61	McConnell	McAuslan
29	Hugel	Hugel	62	Valin	Mulock
30	Ratter	Ratter	63	Tomiko	Grant/Fell
31	Jackson	Street	64	Nipissing	
32	Ashigami	Davis/Scadding			
33	Bugg	Scadding			

climatic and geologic events. As an example of their potential value, lake sediments have recently been utilized as an exploration tool for metallic mineral deposits in the Canadian Precambrian Shield (Allan 1971; Allan *et al.* 1973). In addition, the sediments will evidence the cultural contamination associated with the presence of man in the surrounding watershed (Shrimp *et al.* 1971; Allan 1974; Schoettle & Friedman 1974).

METHOD AND RESULTS

Surface sediments in the study lakes were obtained with an Ekman dredge. Eh and pH measurements were recorded as soon after sample collection as possible. The sediment material was freeze-dried and ground to 200 mesh prior to all chemical analyses.

Total Kjeldahl nitrogen was determined by the method of Bremner (1965). Sediment phosphorus extractable in a dilute H_2SO_4/HCl solution

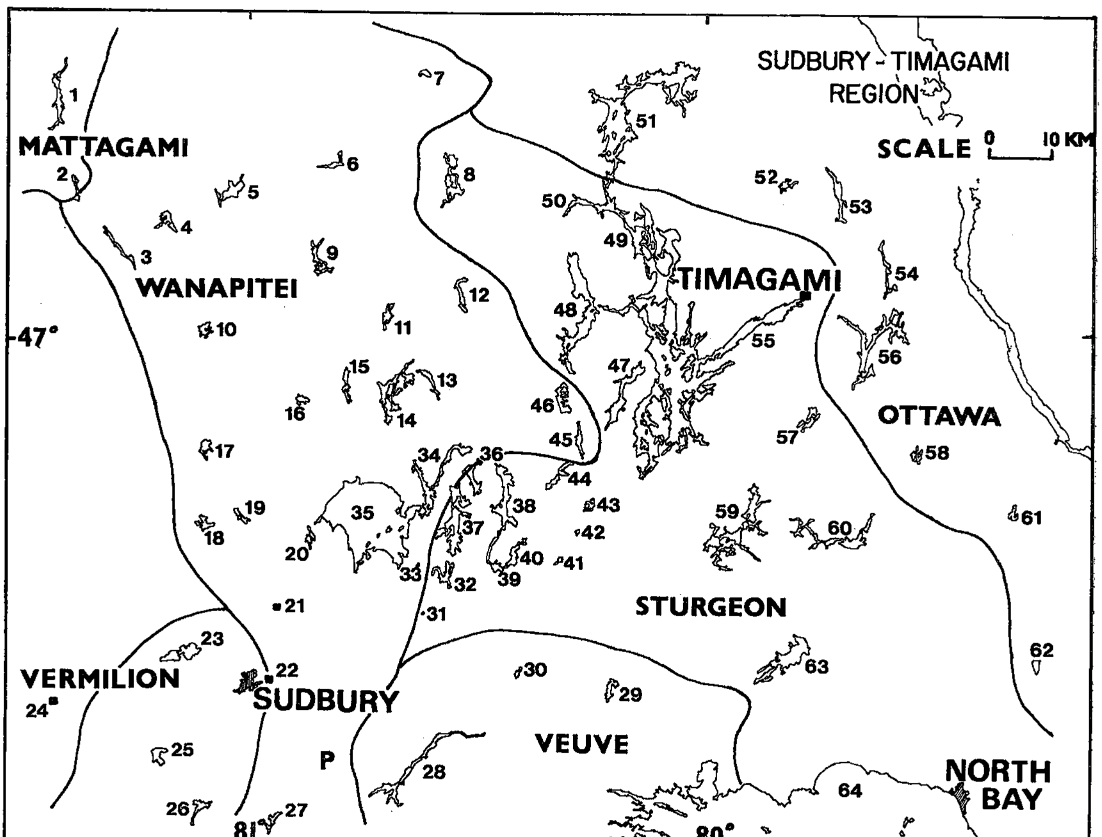


FIG. 1. Location of study lakes and the major drainage basins in the Sudbury area. (The Canadian Permanent Committee on Geographic Names approved a change from Timagami to Temagami, March 27, 1968 — *ed.*)

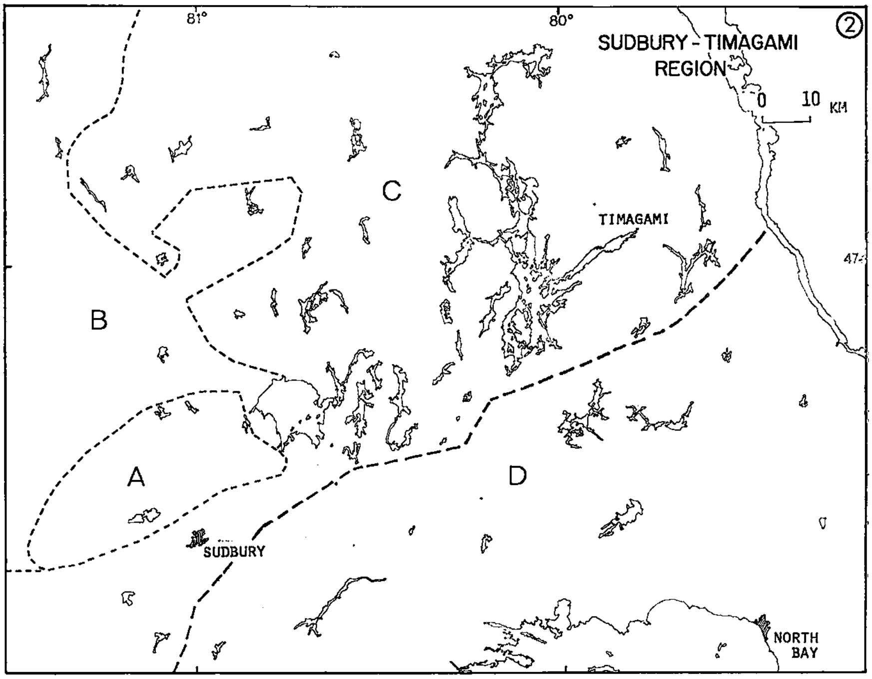


FIG. 2. Bedrock geology of the study area: (A) Sudbury Nickel Irruptive, (B) felsic and mafic igneous rocks, (C) Huronian metasediments-Nipissing diabase, (D) Grenville clastic siliceous metasediments and felsic igneous rocks.

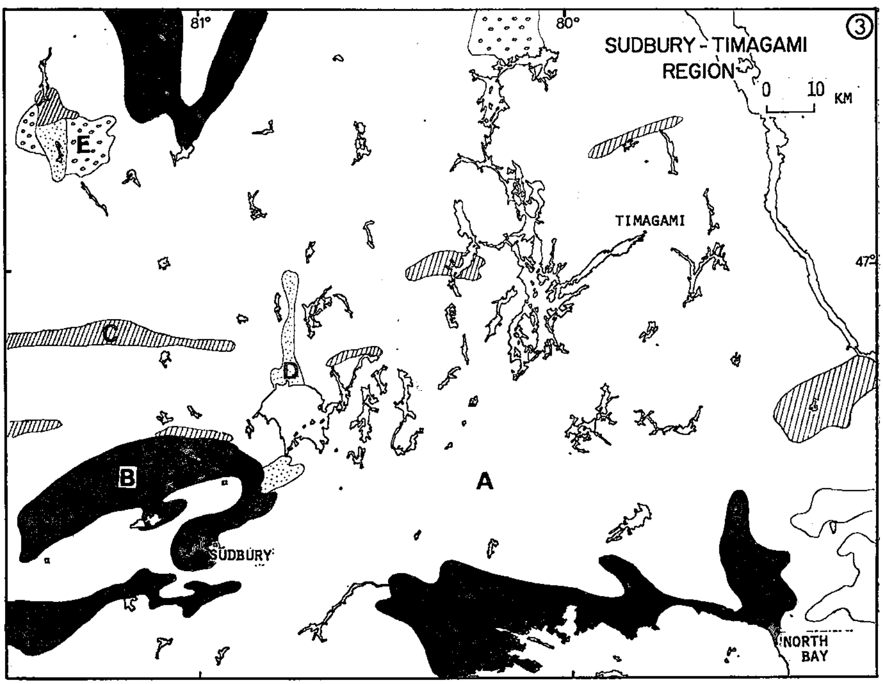


FIG. 3. Pleistocene geology of the study area: (A) ground moraine — silty to sandy till; (B) lacustrine deposits — varved or massive clay, silt, fine sand, sand; (C) end moraine, interlobate moraine — sand, gravel and boulders; (D) esker, esker complex, kame-sand, gravel, boulders; (E) outwash deposits — sand, fine sand, gravel.

was analyzed following the technique of Olsen & Dean (1965). Organic carbon was analyzed by combustion in a Leco WR-12 Carbon Determinator. Heavy metals Ni, Cu, Fe, Mn, Pb, Zn and Cd, were measured by atomic absorption after the sediment material had been digested with aqua regia and filtered through a 0.45μ Millipore filter paper. The particle-size distribution of some of the bottom sediments was recorded using a Micrometrics Instrument Corp. Model 5000 Particle Size Analyzer.

Location of the Study Lakes

The location of the study lakes in the Sudbury area is indicated in Figure 1. Individual lake names and the townships in which the lakes are found are given in Table 2. The Sudbury lakes are contained within six major drainage basins, as outlined in Figure 1: 1) Wanipitei-Lake Huron; 2) Mattagami-Moose River; 3) Sturgeon - Lake Nipissing; 4) Vermillion - Lake Huron; 5) Ottawa - St. Lawrence; 6) Veuve - Lake Nipissing.

Geology of the Lake Basins

The lakes in the study area lie in a wide range of rock types that comprise the Precambrian Shield (Semkin 1975).

For simplicity, this region has been divided into four geological settings as is indicated by Figure 2. The Grenville Front, running SW-NE across the map separates Archean metavolcanics, metasediments and felsic intrusive rocks and Nipissing diabase-Huronian Supergroup rocks of the Southern and Superior provinces from clastic siliceous metasediments and felsic igneous rocks of the Grenville Province. The Nickel Irruptive is considered as a separate grouping because of the unique rock types found here. Basin geology from the individual lakes in the Sudbury-Temagami area is described by Semkin (1975).

Pleistocene glacial processes have scoured and eroded the bedrock and deposited a thin, discontinuous mantle of till in the Sudbury-Temagami area. Moraine, glaciofluvial, and glaciolacustrine deposits formed during the retreat of the Wisconsin ice sheet some 10,000 years ago occur locally. The distribution and history of formation of these surficial deposits are given by Boissoneau (1965), and are summarized in Figure 3.

Recent deposits include fluvial sands and gravels and organic accumulations in the numerous swamps that cover the Shield rocks.

TABLE 3. PARTICLE-SIZE DISTRIBUTION OF 27 SUDBURY LAKE SEDIMENTS

Lake	Sand %	Silt %	Clay %	Lake	Sand %	Silt %	Clay %
Sharp Rock Inlet	-	50.4	49.6	Nepewassi	0.8	47.7	51.5
Diamond	-	43.2	56.8	Murray	2.5	35.7	61.8
Sunny Water	-	52.1	47.9	Millerd	2.1	39.1	58.8
Florence	6.4	56.2	37.4	Ratter	-	37.2	62.8
Lady Evelyn	-	40.1	59.9	Mountain	-	77.2	22.8
Obabika	1.0	44.4	54.6	Jumping Caribou	-	61.3	38.7
Laundrie	2.4	24.1	73.5	Rabbit	-	72.4	27.6
Welcome	-	53.0	47.0	Frederick	-	61.1	38.9
Stull	1.1	33.4	65.5	Red Cedar	3.7	52.7	43.6
Rib	-	58.0	42.0	Kukagami	4.2	83.3	12.5
Fanny	3.1	11.7	85.2	Emerald	-	96.7	3.3
Opikinimika	13.6	69.3	17.1	Fraleck	-	79.9	20.1
Hugel	-	52.2	47.8	Thor	-	83.1	16.9
Helen	3.7	32.5	63.8				

TABLE 4. STATISTICAL SUMMATION OF HEAVY-METAL DATA FROM THE SUDBURY LAKE SEDIMENTS

Element	No. of Samples	Mean	Standard Deviation	Range
Ni	66	120	105	30 - 630
Cd	66	8.6	4.1	0.5 - 19.4
Pb	66	116	61	34 - 290
Cu	66	101	79	37 - 515
Zn	66	152	51	46 - 270
Fe	66	32,256	22,166	5,250 - 133,900
Mn	66	1,450	1,815	135 - 8,900

Sediment data recorded in ppm.

Nature of the Sediments

In the Sudbury lakes, sediments range in colour from brown to brownish-green, and in consistency from a silty sand to a gelatinous suspension. Water content in the sediments was exceedingly high. Sediments having a "semi-suspended" nature were also described in a study of Ontario Precambrian and Paleozoic lakes by Kleerekoper (1957), who attributed their formation to the precipitation of humic substances ("humossols") with Fe, Al, Ca and Mg ions.

Although most of the sediments appeared to be quite flocculent and without any well-defined interface, Emery (1973), in a detailed study of two Precambrian Shield lakes in Algonquin Park, observed exactly the opposite features. Emery recorded that the sediment surface was not smooth, but had many small ridges and valleys and that the sediments were of a jelly-like nature. He also noted that they showed deep crevasses, and that upright chironomid tubes, fungal mats and other animals were firmly emplaced in the sediment substrate.

The sediments of the study lakes generally contained an abundance of organic debris in an inorganic matrix of clayey silt. Table 3 indicates tthe particle-size distribution for 27 lake-sediment samples. An average particle-size distribution for the Sudbury lake sediments was estimated to be 53.6% silt, 44.7% clay and 1.7% sand.

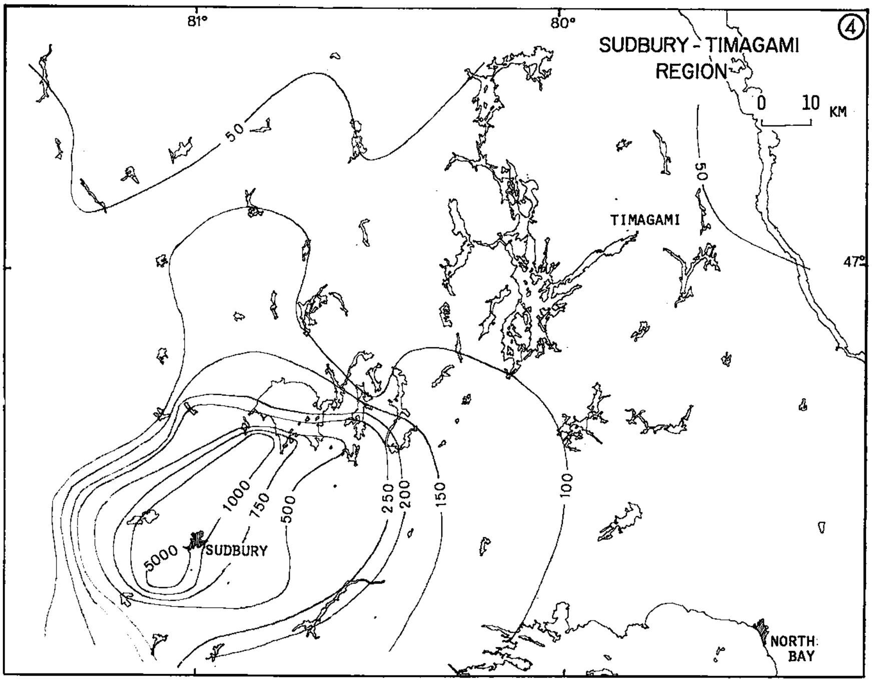


Fig. 4. Distribution of Ni (μg/g dry wt.) in bottom sediments of the study lakes. The elliptical decrease in Ni relative to Sudbury is parallel to that in the lake waters.

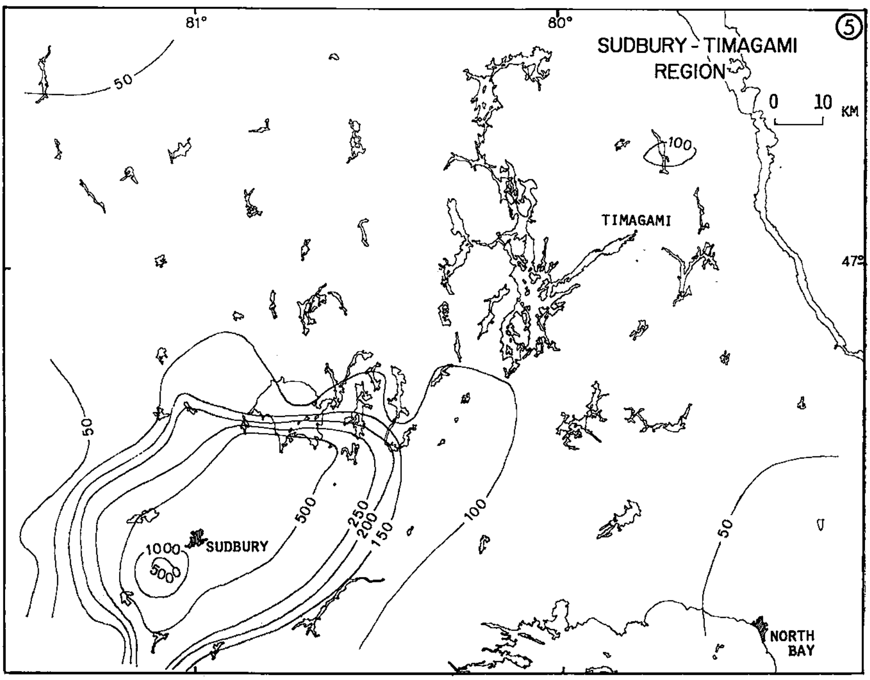


Fig. 5. Distribution of Cu (μg/g dry wt.) in bottom sediments of the study lakes, showing an increasing concentration gradient towards Sudbury.

Sediment Nitrogen

Analyses for total Kjeldahl nitrogen in the lake sediments indicated a mean of 0.84% dry weight and a range of 0.12 to 3.28% dry weight. This is comparable to the data collected from other Shield and very dilute lakes (Semkin 1975) and well within the range of 0.1% to 4.0% outlined by Keeney (1973) for surface sediments in general.

Sediment Organic Carbon

Analyses of organic carbon in the sediments revealed a mean carbon concentration of 10.4% dry weight and a range of 1.2 to 36.3% dry weight. These values are comparable to sediment organic C contents found in other soft-water lakes (Semkin 1975). In hard-water lakes, the precipitation of carbonates and deposition of calcite-bearing organisms in the sediments may have a diluting effect on the concentration of organic C, so that values less than those encountered in oligotrophic Shield lakes can be expected.

Lakes such as Opikinimika, Thor and McConnell all showed relatively high levels of standing algal crop as indicated by chlorophyll *a* (Semkin 1975). Predictably, concentrations of organic carbon in the sediments of these lakes were well above the average. In addition, the shallow lakes — Pud, Valin and Jackson — were noted to have abundant bottom-growing flora, a feature reflected in the very high concentrations of sediment organic carbon: Pud 21.9%, Valin 32.5%, Jackson 36.3% dry weight.

Sediment Phosphorus

The quantity of phosphorus in the lake sediments that was acid-extractable averaged 161 μg/g P dry weight and showed a range of 1.8 to 550 μg/g P dry weight. This is comparable to the acid-available phosphorus levels of 230 μg/g P and 350 μg/g P dry weight found by Kleerekoper (1957) for two Precambrian and thirteen Paleozoic enclosed lakes in Ontario. Lakes approaching eutrophic conditions will tend to have higher amounts of extractable phosphorus; for example, St. John (1972, 1973) found an average P content (extractable in 1*N* HCl) of 836 μg/g P dry weight for five lakes in the Okanagan Valley in British Columbia.

In an attempt to define what percentage of total phosphorus that the acid-available phosphorus represents, the ratios total phosphorus/acid-extractable phosphorus and total P/inorganic P (assuming that the acid-available phosphorus will be essentially inorganic in nature) were tabulated from other lake sediment studies (Semkin 1975). Results showed an average ratio value of 2.2. Therefore, it may not be incorrect to suggest that the phosphorus released by acid-extraction approximates 50% of the total phosphorus present in lake sediments.

Heavy Metals

Table 4 is a statistical tabulation of heavy-metal data for lake sediments in the Sudbury study area. For comparative purposes, concentrations of heavy metals in other lake and river sediments and in soils and rocks of the Precambrian Shield have been assembled in Table 5.

TABLE 5. COMPARATIVE SUMMARY OF THE HEAVY-METAL CONTENT IN SOIL, SEDIMENT AND ROCK MATERIALS[1]

Sediments	Ni	Cu	Zn	Pb	Cd	Fe	Mn	Reference
1. Ottawa R.	22	28	84	26	--	9200	118	Oliver & Kinrake (1972)
Rideau R.	23	24	86	42	--	12700	241	Oliver & Kinrake (1972)
2. Okanagan Mainstem Lakes, B.C.	29.6	136.4	59.8	33.5	0.9	--	--	St. John (1972)
3. Lake Michigan[2]	34	37	206	88	--	14100	560	Frye & Shimp (1973)
	35	20	66	20	--	12450	390	Frye & Shimp (1973)
4. Lake Superior (northern part)	82	118	133	--	--	43700	2108	Mothersill & Fung (1972)
5. ELA lakes, NW Ontario	90	--	130	--	--	41500	900	Brunskill et al. (1971)
6. Bear-Slave Provinces, NW Canadian Shield	23.3	19.6	31.8	12.9	--	21800	89	Cameron & Durham (1974)
Soils								
7. Average, United States Range	20 <5-700	25 <1-300	54 <25-2000	20 <10-700	--	25000 100-<100,000	560 <1-7000	Shacklette et al. (1971)
8. North of study area								
a) 'B' soil horizon	38	8	25	--	--	--	--	O.D.M. Prelim. Maps P.938;935;934 (1974),
b) glacial till	70	17	21	--	--	--	--	Halliday, Midlothian Twps.
9. Avg. Precambrian Canadian Shield	23	14	--	--	--	30900	530	Shaw et al. (1967)
10. Crustal abundance	75	55	70	12.5	0.2	--	950	Levinson (1974)
Model A[3]	37	32	63	15	0.15	34300	670	Turekian (1972)
Model B[4]	72	58	82	10	0.18	58000	1000	Turekian (1972)

1. All sediment data recorded in μg/gm (ppm). 2. Two sets of Lake Michigan sediment data: a) top interval 0-15 cm, b) all intervals greater than 15 cm but less than 100 cm. 3. Model A crustal abundance: 0.25% ultramafic, 18% basaltic, 39% high Ca-granitic, 39% low Ca-granitic and 3.75% syenitic rocks. 4. Model B crustal abundance: 50% basaltic and 50% high Ca-granitic rocks.

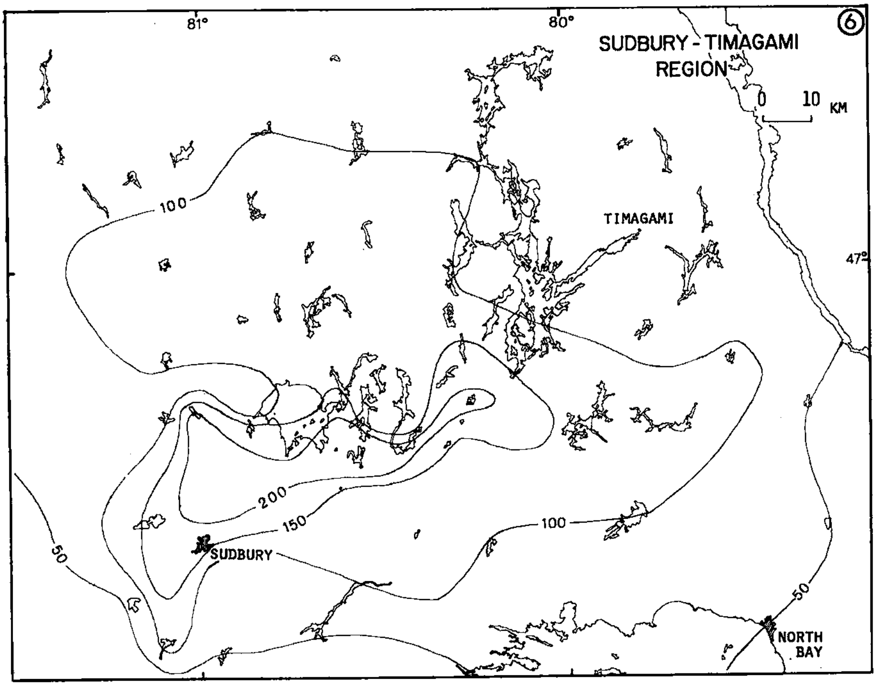


Fig. 6. Distribution of Pb (μg/g dry wt.) in bottom sediments of the study lakes. Note the increased levels north and northeast of Sudbury, possibly reflecting the predominant wind direction in this region.

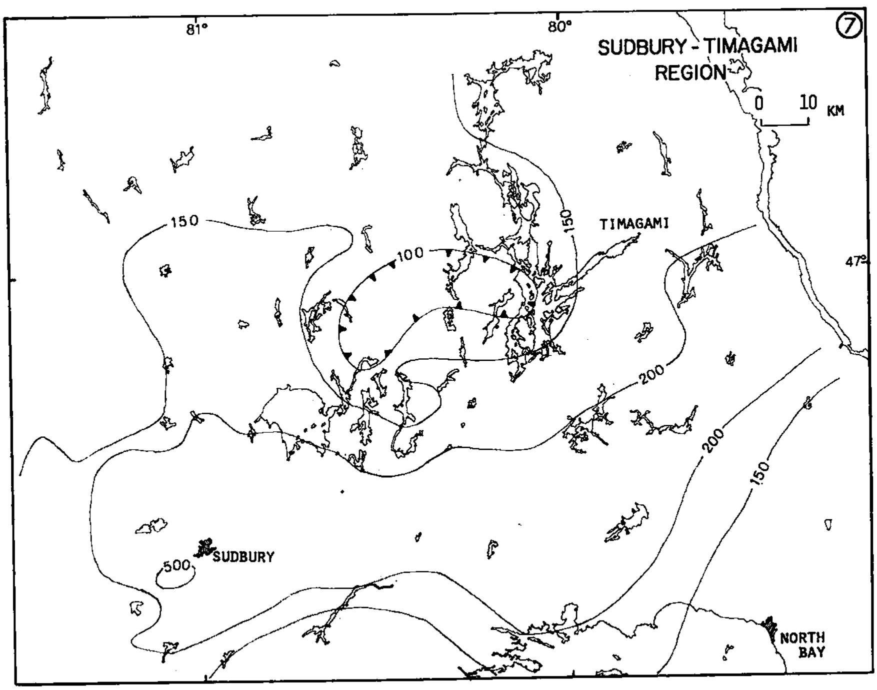


Fig. 7. Distribution of Zn (μg/g dry wt.) in bottom sediments of the study lakes. The wide easterly-trending band of high Zn probably reflects naturally high levels of Zn in the local geology.

From these two tables, it is apparent that several anomalous metal concentrations are contained within the Sudbury lake sediments. In particular, Ni, Pb, and Cd occur at higher levels in the sediments than normally found in natural environments.

Figures 4 to 10 outline the regional distribution of the heavy metals relative to Sudbury. Increasing concentration gradients in the sediments toward the mining centre are recorded for Ni and Cu — a concentration pattern quite similar to that found in the lake waters for these elements (Semkin 1975). Pb and Zn display increasing levels toward Sudbury as well, but with the centres of highest concentration focused north and northeast of Sudbury. High sediment Zn values extend in an easterly-trending band and somewhat parallel the distribution recorded in the lake waters (Semkin 1975). The anomalous Zn concentrations observed in lake waters northeast of Sudbury are not reflected in the sediments of these lakes, a fact possibly attributed to increased solubilization (and hence decreased precipitation) of Zn at the lower pH values found in such lake waters. This distribution of metals in the sediments and general similarity to the heavy-metal pattern recorded in the lake waters does suggest an external input, *e.g.*, atmospheric precipitation, as opposed to any natural geological source.

Of all the sediment metals analyzed, only Fe and Mn do not define the point source at Sudbury in terms of their concentration gradients. This is in spite of the fact that concentrations of these elements in atmospheric precipitation and in lake waters (Semkin 1975) do outline the significance of Sudbury as a source of metal emissions in this region.

TABLE 6. ATMOSPHERIC-PRECIPITATION SAMPLES IN THE STUDY AREA

Station	No. of Samples	Sampling Period	Station	No. of Samples	Sampling Period
1	41	June/70 - December/73	8	41	June/70 - December/73
2	10	February/73 - December/73	9	41	June/70 - December/73
3	41	June/70 - December/73	10	3	May/74 - October/74
4	31	June/70 - February/73	11	7	June/73 - May/74
5	41	June/70 - December/73	12	7	June/73 - May/74
6	10	February/73 - December/73	13	3	May/74 - October/74
7	10	February/73 - December/73	14	3	June/74 - October/74

Atmospheric Precipitation

The locations of the atmospheric precipitation monitoring stations in the Sudbury lakes area are shown in Figure 11 and Table 6 outlines the number of samples collected per site and date of the sampling periods.

A compilation of selected chemical data from the precipitation study that is ongoing at McMaster University is provided in Table 7. Several significant observations can be made from this information regarding the nature and composition of the atmospheric precipitation in the vicinity of Sudbury. These are: (1) the precipitation is very acidic, with a mean pH of 4.26; (2) high levels of sulfate (mean is 5.7 mg/l SO_4) are recorded; (3) a notably high content of Fe, Ni, Cu and Zn is found in the precipitation; (4) variation in the chemical nature of the heavy metals, for example, total Fe, Ni and Cu, record a very high particulate concentration, whereas Zn is primarily in a filterable form (where filterable is defined as passing through a 0.45 micron filter paper).

The areal distribution of the heavy metals in atmospheric precipitation is presented in Figures 11 to 16. All metals show increasing concentration gradients towards Sudbury. A generally-high metal concentration extends northeastward from Sudbury, reflecting a predominant wind direction in this region.

Discussion

There is no obvious direct geological control of trace elements in the Sudbury lake sediments.

TABLE 7. SUMMARY OF SELECTED CHEMICAL PARAMETERS FOR ATMOSPHERIC PRECIPITATION IN THE STUDY LAKES AREA*

Station	pH	SO_4	Ni_T	Ni_F	Cd_T	Cd_F	Pb_T	Pb_F	Zn_T	Zn_F	Cu_T	Cu_F	Fe_T	Fe_F
1	4.31	5.6	15.5	9.0	1.1	1.0	23.5	18.0	138.0	107	23.9	15.3	268	30
2	4.47	10.0	227.0	72.0	3.6	2.3	53	36	266	150	307	142	1350	49
3	4.31	7.2	202.0	92.0	2.1	1.5	47	33	223	197	187	88	790	108
4	4.57	6.4	-	-	-	-	20	-	-	210	-	-	-	-
5	4.10	7.6	154.0	50.0	2.8	1.8	46	26	333	247	195	87	1000	224
6	4.23	6.2	7.0	5.0	0.9	0.5	27	22	145	97	38	7	308	35
7	4.26	4.5	14.0	3.0	0.6	0.7	14	10	79	52	18.6	4.1	79	52
8	4.26	4.0	12.0	3.0	0.6	0.8	27	29	68	91	18.6	7.7	302	49
9	4.34	6.5	10.0	3.5	2.4	1.1	35	23	150	134	22	11	526	59
10	4.23	4.3	12.7	6.2	0.7	1.2	11.5	8.8	138	109	11.2	4.8	174	22.5
11	4.22	4.2	24.6	10.6	1.9	1.4	34.6	18.9	105	99	63.4	24.8	500	28
12	4.24	5.0	17.7	11.1	0.8	1.3	24.5	20.0	159	154	28.3	23.5	237	44
13	4.08	3.9	26.3	10.8	0.7	0.7	14.3	6.5	93.3	80.7	39.8	17.0	165	3
14	4.03	4.2	25.8	10.0	3.2	3.3	17.0	12.3	112	102	30.8	11.5	202	11.3

* Concentration units: SO_4 mg/l; heavy metals μg/l

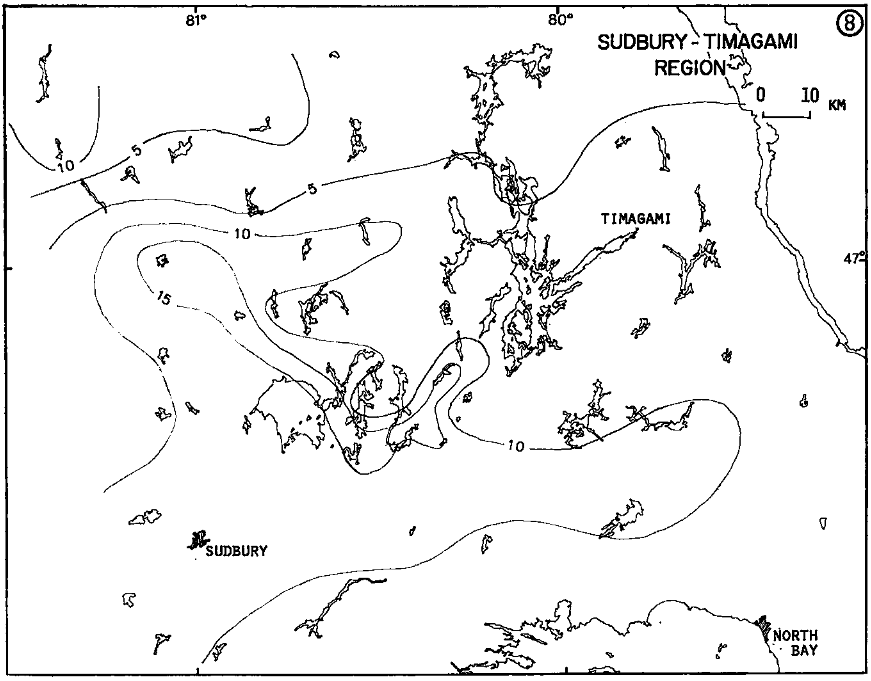


FIG. 8. Distribution of Cd (μg/g dry wt.) in bottom sediments of the study lakes. Note the increased levels of Cd in lake sediments north and northeast of Sudbury, reflecting the predominant wind direction in this region.

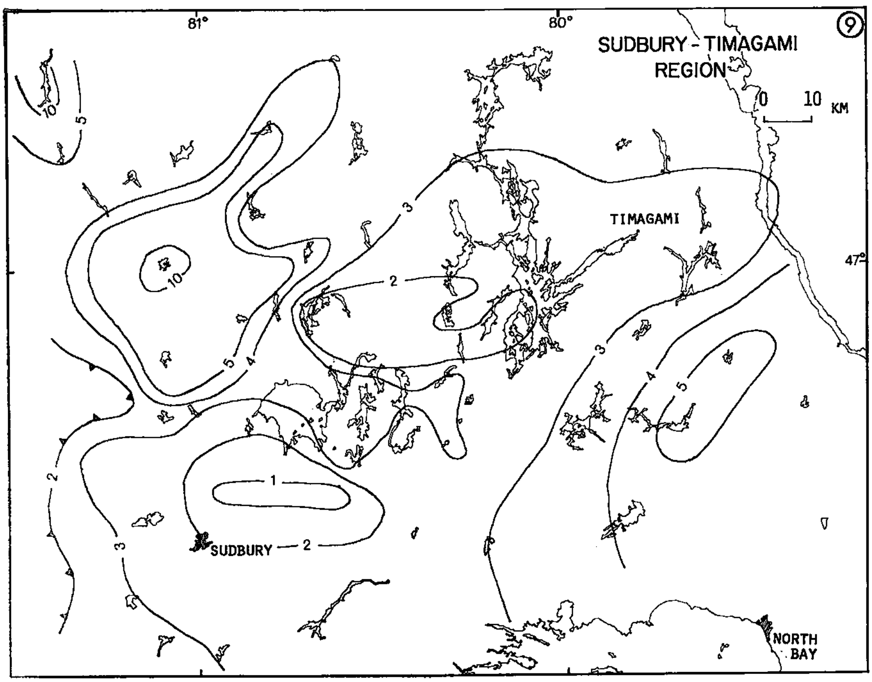


FIG. 9. Distribution of Fe (% dry wt.) in bottom sediments of the study lakes. Note that Fe concentrations appear to be controlled by geological factors as opposed to atmospheric precipitation.

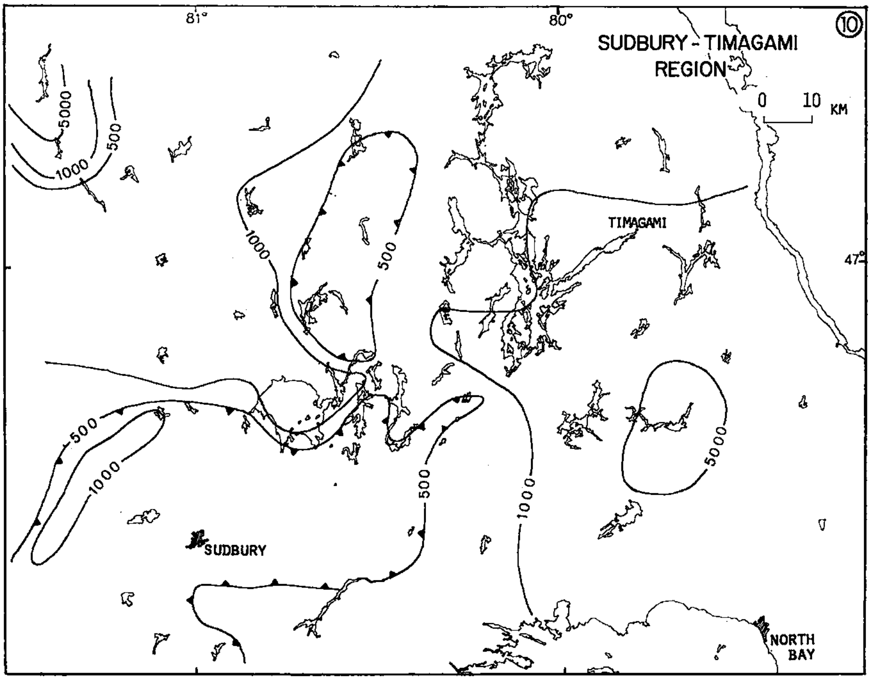


FIG. 10. Distribution of Mn (µg/g dry wt.) in bottom sediments of the study lakes. Note that Mn behaves geochemically in a manner similar to that of Fe.

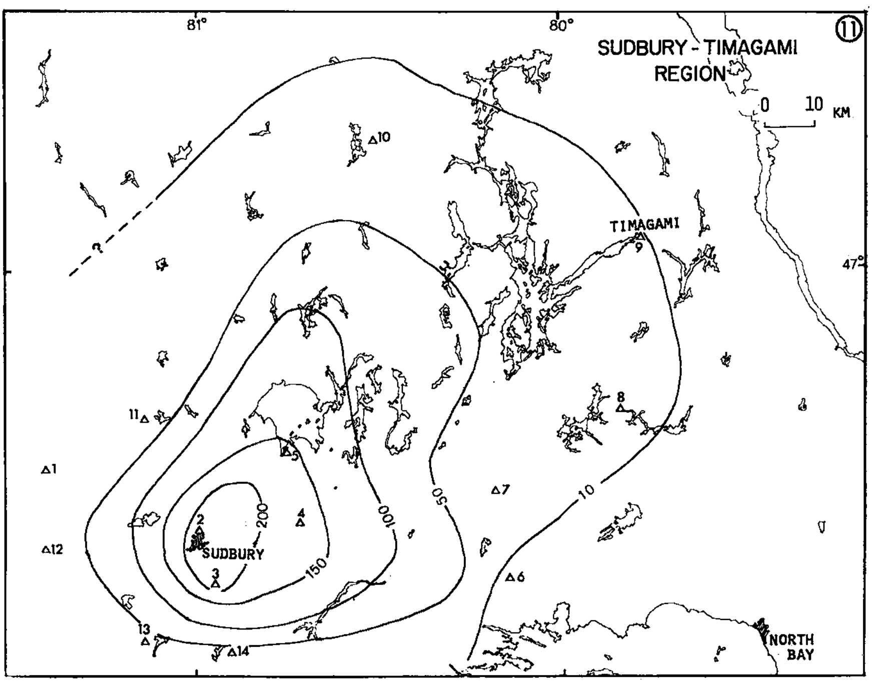
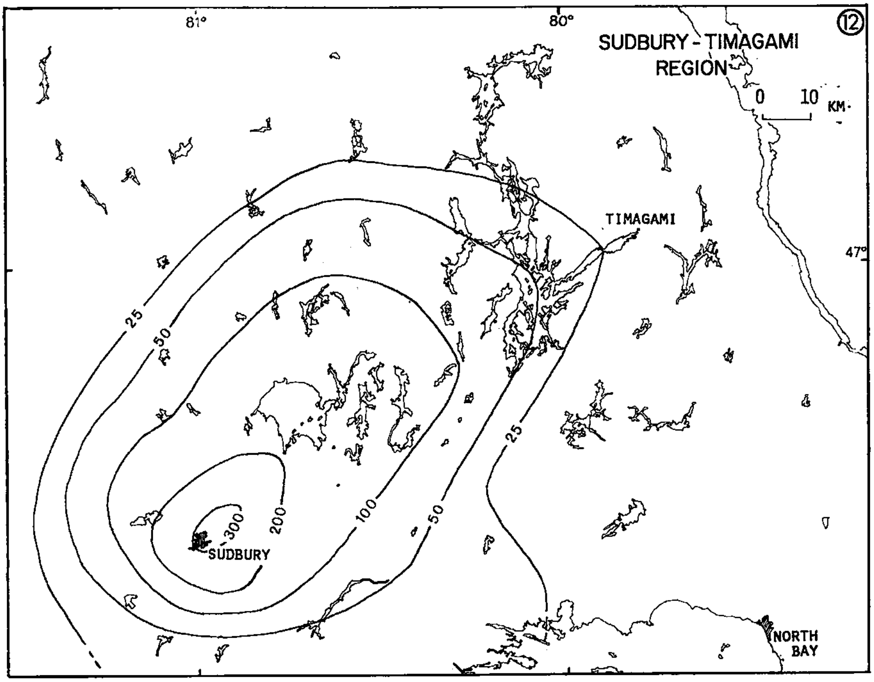
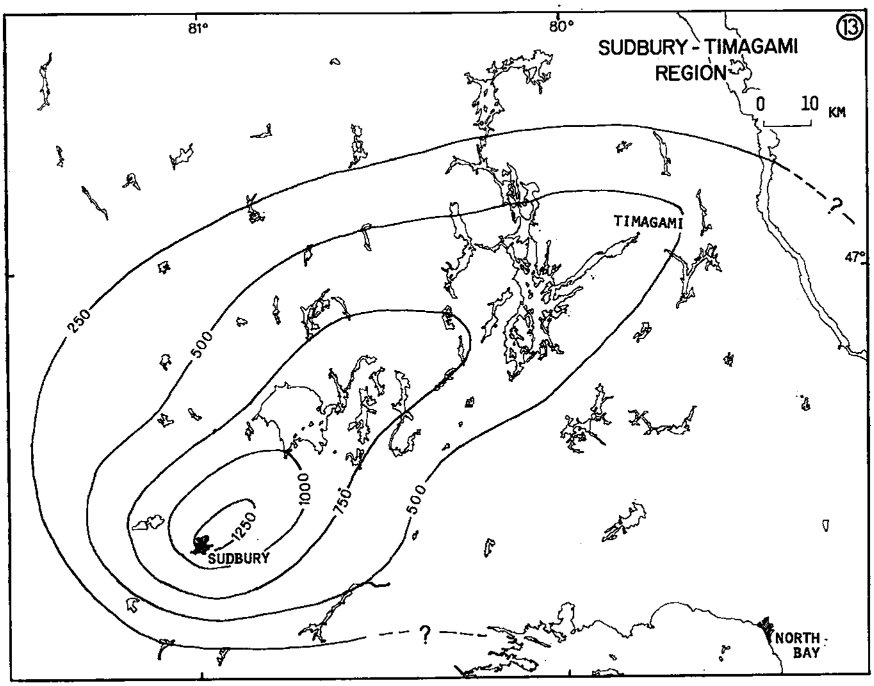
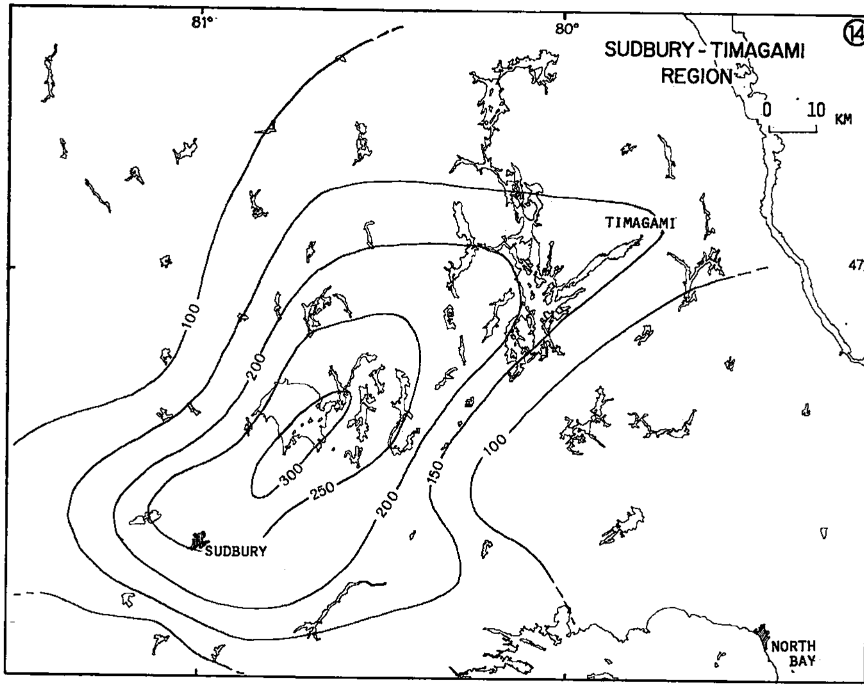


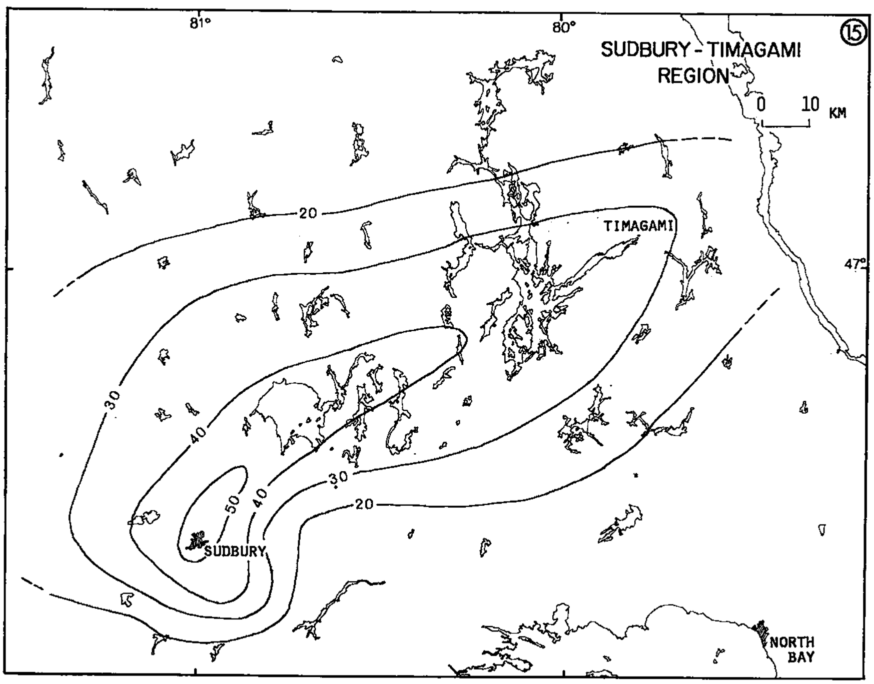
FIG. 11. Location of atmospheric precipitation stations and distribution of Ni (µg/1) in atmospheric precipitation, showing an increasing concentration gradient towards Sudbury.





FIGS. 12, 13. Distribution of Cu (Fig. 12) and Fe (Fig. 13), μg/l, in atmospheric precipitation, showing an increasing concentration gradient towards Sudbury.





FIGS. 14, 15. Distribution of Zn (Fig. 14) and Pb (Fig. 15), μg/l, in atmospheric precipitation showing an increasing concentration gradient towards Sudbury.

Geochemical factors generally accepted to be involved in the deposition of metals are rather insignificant in the study lakes. The relationship between concentrations of trace elements and/or organic carbon and levels of Fe and Mn in the sediments, a feature commonly reported by other investigators (Shrimp *et al.* 1971; Allan 1971) is lacking (Semkin 1975). What is evident from the aerial distribution of heavy metals (with the exception of Fe and Mn), from the maximum concentration of metals at Sudbury, and from the knowledge of the prevailing wind direction is that the sediment trace elements have an external, *i.e.*, atmospheric, source.

A comparison between the distribution of sediment Fe and the geology of the study area reveals the importance of basin geology in characterizing the concentrations of Fe in the lake sediments. Sediments of lakes located in the Sudbury Irruptive, Huronian metasediments, and Nipissing diabase contain the lowest levels of Fe; Grenville clastic siliceous metasediments have intermediate levels, and Archean felsic and mafic intrusive rocks have the highest Fe contents. Petrological evidence from the various rock units supports this "geological" distribution in that Card (1973) classified the Archean mafic rocks as having a mineralogy similar to Nipissing diabase, but showing a higher total-iron content. In addition, the behaviour of Mn parallels that of Fe in the lake sediments, further supporting a geological source for the sediment Fe.

The rather high levels of sediment Fe in lakes enclosed by Grenville metasediments cannot be easily related to lithology due to the variety and complexity of these rocks. However, on the geological compilation map for this area (Card 1969), numerous occurrences of Cu, Ni and Fe have been outlined.

An association of acid-extractable P with Fe in the lake sediments was observed in this study, as is indicated in Figure 17. The literature supports the existence of a short-range order Fe-inorganic P complex, resulting from the sorption of orthophosphate by hydrated iron oxides. (Li *et al.* 1972; Williams *et al.* 1971). Fe/P atomic ratios (Semkin 1975) are generally too high to consider the formation of such iron-phosphorus minerals as strengite, $FePO_4 \cdot 2H_2O$, or vivianite, $Fe_3(PO_4)_2 \cdot 8H_2O$. Factors also precluding strengite formation are the low phosphorus concentrations and the reducing nature of the sediment environment (Nriagu 1972). Vivianite may form under reducing conditions, but this reaction also requires very high phosphate concentrations, particularly in a sulfide-generating anoxic environment as may occur in the Sudbury lake sediments (Nriagu 1972). That sulfide species are present is evident from the black laminations of pyrite observed in many of the sediment samples.

The importance of atmospheric loadings of trace elements into lake systems in areas of industrial build-up, particularly where metal smelting and refining are involved, cannot be underestimated. In a study of 30 trace elements in an industrialized section of Lake Michigan, Winchester & Nifong (1971) concluded that airborne emissions were more significant for Zn and comparable to the watershed drainage in inputs of Cu and Ni to the lake. In the same region, Robbins *et al.* (1972) calculated that the atmosphere contributed high concentrations of Fe, Mn, Cu, Ni and Zn to Lake Michigan using the assumption that at least 20% of the daily air emissions had entered the lake waters. Andelman (1973) tabulated the data in Table 8 from three regional drainage basins in the United States and showed comparable levels of trace elements in surface waters and in atmospheric precipitation.

The fact that the atmosphere is heavily loaded with trace elements in the vicinity of Sudbury is well-documented. Kramer (1973, 1975) recorded high levels of Ni, Cu, Fe and Zn throughout the study region.

In this present investigation, metal contours for atmospheric precipitation, lake waters (Semkin 1975) and lake sediments generally showed the same increasing concentration gradient towards Sudbury. In view of this, considering the wide variations in lake basin geology, lake morphometry and particularly the variable physicochemical nature of air, water and sediments, it is readily apparent that the atmosphere is a

TABLE 8. COMPARISON OF MEAN CONCENTRATIONS OF SEVERAL TRACE ELEMENTS IN SOME U.S. SURFACE WATERS AND PRECIPITATION*

Element		Basin		
		Northeast	Western Gulf	Pacific Northwest
Pb	Precipitation	50 - 90	0 - 4	0 - 4
	Surface	17	4	15
Zn	Precipitation	40 - 70	0 - 30	0 - 30
	Surface	96	92	40
Mn	Precipitation	2 - 19	2 - 4	2 - 19
	Surface	4	10	3
Cu	Precipitation	16 - 55	5 - 15	5 - 15
	Surface	15	11	9
Ni	Precipitation	0 - 5	3 - 5	0 - 8
	Surface	8	10	10

* Data from Andelman (1973). Concentrations in μg/l.

major source of heavy metals for the land and water around Sudbury. Additional evidence for this phenomenon is provided by the following points:

(a) factor analysis of water and lake sediment chemical data indicated a very strong relationship between Cu and Ni, the major elements emitted at Sudbury

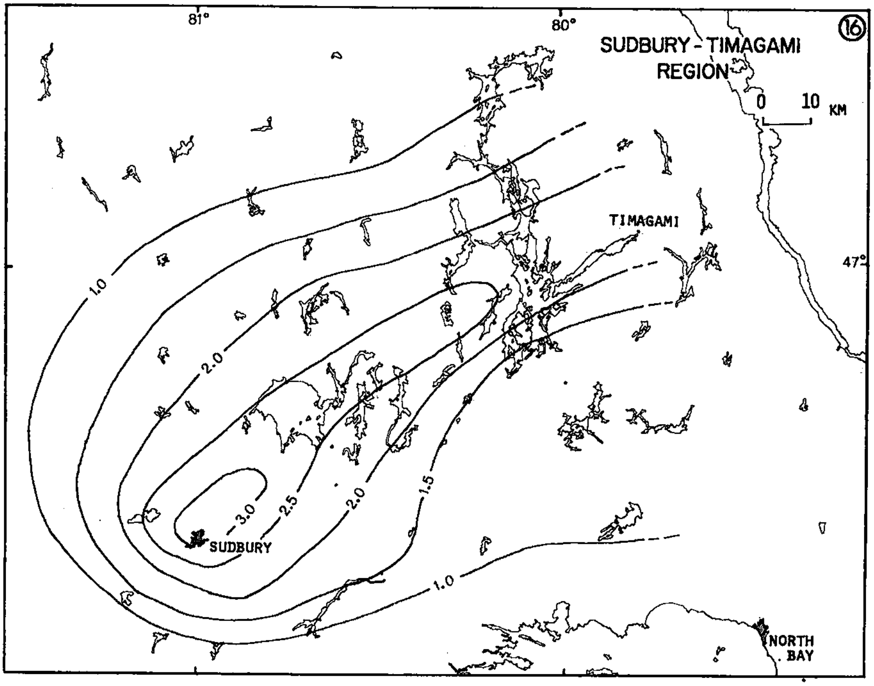


FIG. 16. Distribution of Cd (μg/l) in atmospheric precipitation showing an increasing concentration gradient towards Sudbury.

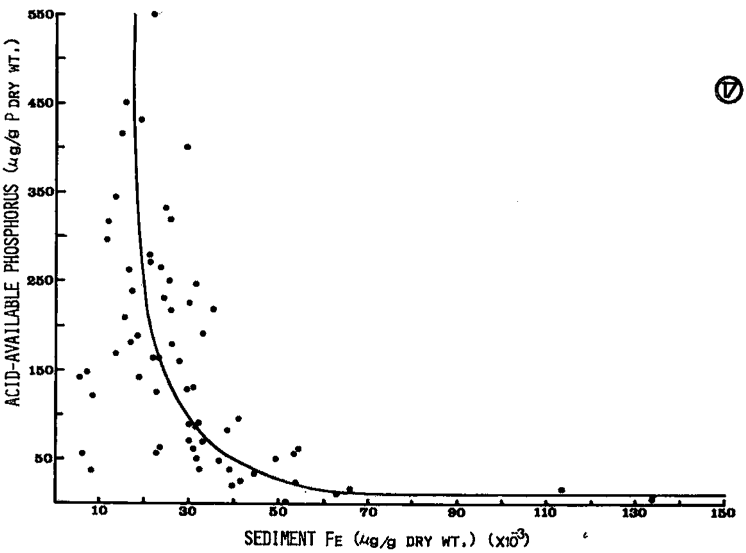


FIG. 17. Relationship between acid-available phosphorus and total iron in lake sediments.

(Air Management Branch, Ministry of the Environment, 1974), and a less pronounced relationship between these elements and the distance from Sudbury (Semkin 1975).

(b) Ni:Cu and Cu:Zn ratios in atmospheric precipitation and in lake sediments (Figs. 18 and 19) showed similar distribution patterns relative to the distance from Sudbury. In addition, these graphs revealed parallel rates of deposition of the three trace elements in the precipitation and sediments, *i.e.*, Ni deposited before Cu, which was deposited before Zn. This rate of deposition sequence was the same as that found by Kramer (1975) in a more intensive program of atmospheric monitoring in northern Ontario. Kramer attributed the variation in deposition rates to size differences, with Ni being primarily in a particulate form in the atmosphere and the other metals occurring in a finer size spectrum.

(c) Hutchinson & Whitby (1973) showed that concentrations of heavy metals in soils decreased sharply with distance from the now-defunct smelting operation at Coniston, 9 miles (14 km) east of Sudbury. Ni, Cu and Co particularly appeared as surface contaminants in that their concentrations were correlated with both distance from the point source of metallic emissions at Coniston and depth in the soil column.

(d) Sediment cores collected by Allan (1974) from 25 lakes close to Sudbury revealed an accumulation of heavy metals (with the exception of Fe and Mn) in the surface section, decreasing down the sediment cores.

The depth at which the background value for the sediment metals first appears and a knowledge of the sedimentation rate in the Sudbury lakes can be used to outline the history of the smelting industry at Sudbury. Huhn (1974) defined a recent sedimentation rate of from 3 to 5 years/cm in a study of two lakes, Loon Lake and Lake K45, near Sudbury. Using this sedimentation rate, it is apparent that lakes close to Sudbury, such as Kelley (Allan 1974), first recorded high Cu and Ni values in the sediments approximately 50 years ago. This would correspond roughly to the time when the mining industry at Sudbury discontinued using

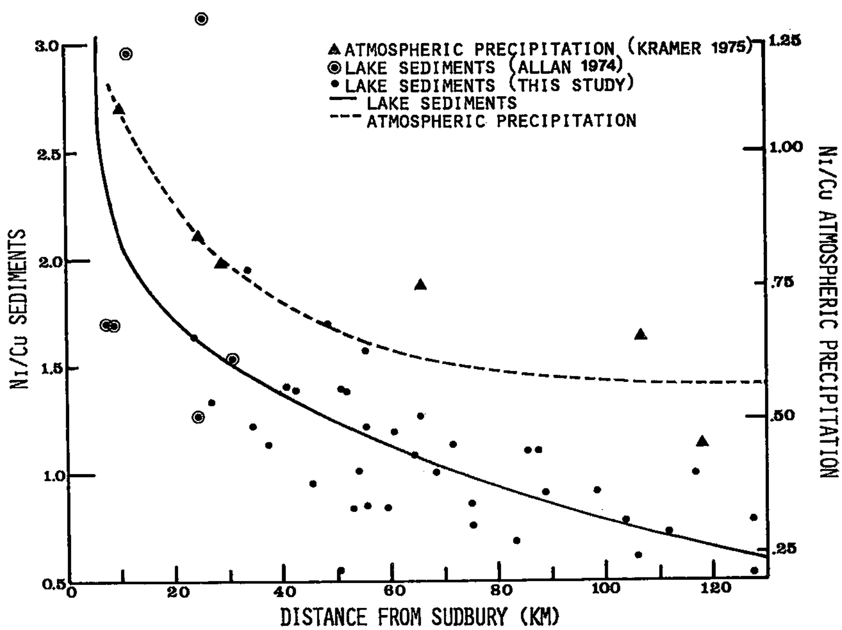


FIG. 18. Parallel trend of Ni:Cu ratios in atmospheric precipitation and in lake sediments. Note the increased deposition of Ni relative to Cu in close proximity to Sudbury.

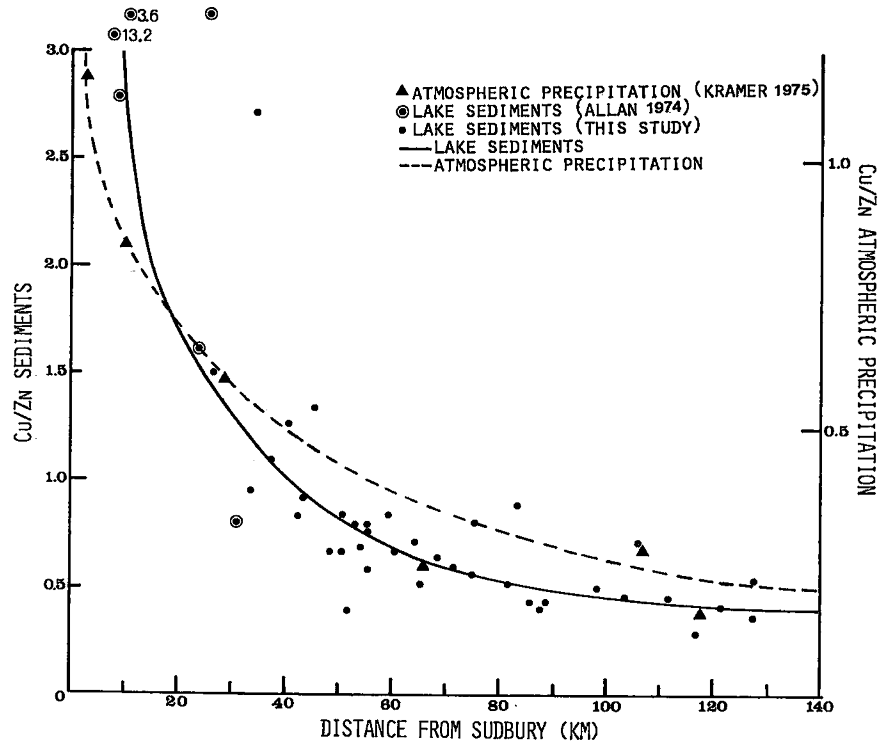


FIG. 19. Parallel trend of Cu:Zn ratios in atmospheric precipitation and in lake sediments. Note the increased deposition of Cu relative to Zn in close proximity to Sudbury.

roasting beds as a method of reducing sulfur in the sulfide ores and built a 510-foot (170m) stack and sulfur-recovery plant at Copper Cliff (Huhn 1974). With this new development, the output of Ni and Cu in Canada (and, therefore, at Sudbury) sharply increased as is indicated by the metal production curves in Figure 20. In lakes at greater distances from Sudbury, normal background-metal concentrations appear in the sediment cores at about 5-cm depths, a depth which represents a period of 15 to 25 years of sedimentation. From the graphs in Figure 20, it is observed that the year 1950 marked the rise of extensive Cu and Ni production in Canada. This expansion of Sudbury's metal industry subsequently became well-documented in the sediment record of the surrounding lakes.

Allan's work also shows that metal values in lake sediments of "pre-smelter" time are quite similar for lakes in the Sudbury Nickel Irruptive and in lakes not in this peculiar geological setting. The presence of economic concentrations of Ni and Cu in the Irruptive rocks does not reveal itself in the lake sediments, as might be expected.

SUMMARY

The sediments of the Sudbury-area lakes effectively act as a sink for heavy metals that have been introduced via atmospheric precipitation. Evidence for this phenomenon has been well-substantiated by observing heavy-metal trends in both lake sediment and atmospheric fall-out. Results indicated: 1) similar metal ratios in both media; 2) increasing concentration gradients for the trace elements in sediment and atmospheric precipitation toward the mining-smelting centre; and 3) significant correlations of the sediment parameters, suggesting a point-source emission of heavy metals. The role of lake-basin geology in characterizing sediment metals content has been overshadowed (excepting Fe and Mn) by the effects of atmospheric input.

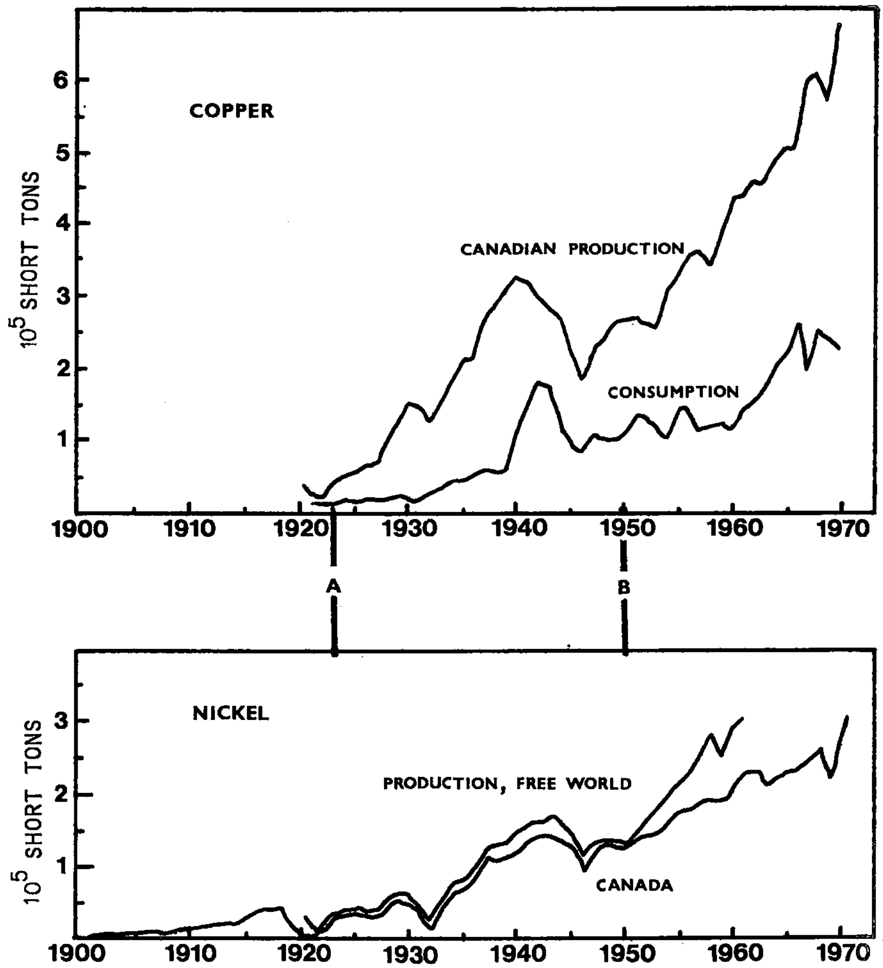


FIG. 20. Trend of nickel and copper production in Canada. (Adapted from Huhn 1974).
(A) Anomalous heavy-metal concentrations in sediments first recorded in lakes close to Sudbury.
(B) Anomalous heavy-metal concentrations in sediments first recorded in lakes at greater distances from Sudbury.

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Manuscript received August 1975, emended December 1975.