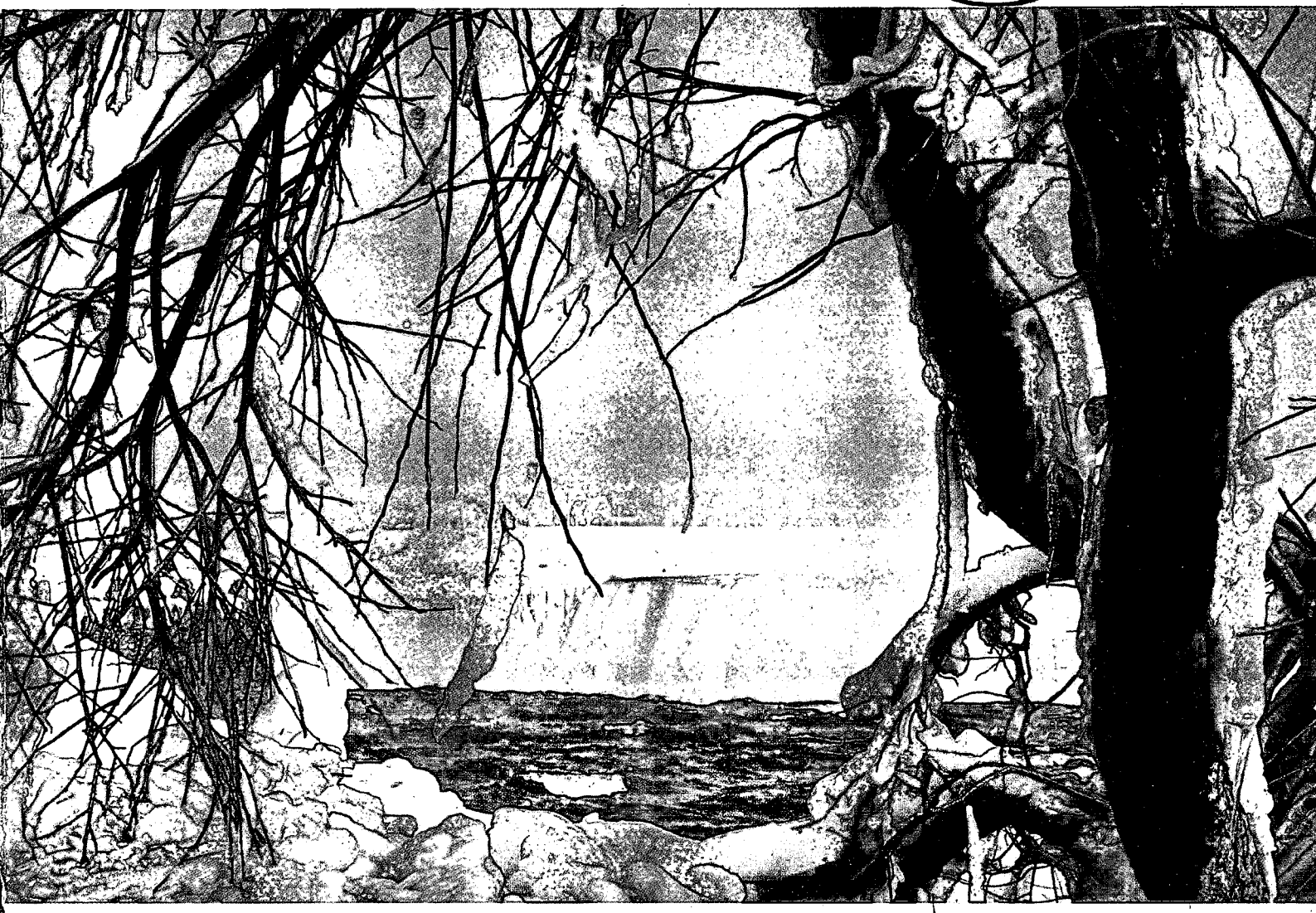
Environment Canada | Environnement Canada

Levels of Arsenic and Selenium in the Great Lakes Region

W.J. Traversy, R.D. Goulden, Y.M. Sheikh and J.R. Leacock



SCIENTIFIC SERIES NO. 58
(Résumé en français)

INLAND WATERS DIRECTORATE, ONTARIO REGION,
WATER QUALITY BRANCH,
BURLINGTON, ONTARIO, 1975.

Environment Canada
Environnement Canada

Levels of Arsenic and Selenium in the Great Lakes Region

W.J. Traversy, P.D. Goulden*, Y.M. Sheikh and J.R. Leacock

* P.D. Goulden is a member of the Analytical Methods Research Section, CCIW Branch, Burlington, Ontario.

SCIENTIFIC SERIES NO. 58
(Résumé en français)

INLAND WATERS DIRECTORATE, ONTARIO REGION,
WATER QUALITY BRANCH,
BURLINGTON, ONTARIO, 1975.

Cat. No.: En36-502/58

Contract No. 07KX.KL398-5-8029/A

THORN PRESS LIMITED

Contents

Tables

Illustrations

Abstract

Arsenic and selenium were determined in water, sediments and fish samples from the international Great Lakes, in water samples from international rivers and selected rivers in Ontario and in precipitation samples from the Great Lakes region, to assess their present levels and to provide base-line data for future reference.

Mean values for arsenic in lake waters varied from 0.23 μg/l for Lake Superior to 0.91 μg/l for Lake Ontario, and mean sediment values ranged from 2.03 μg/g for Lake Superior to 3.20 μg/g for Lake Erie. The mean arsenic fish value for lakes Erie and Ontario was 0.07 μg/g. Analyses of waters from the St. Marys and St Lawrence rivers showed mean arsenic values of 0.37 μg/l and 0.61 μg/l, respectively, and the mean value of other rivers in Ontario was 0.26 μg/l. The mean precipitation arsenic value was 0.72 μg/l.

Mean selenium values for lake waters were <0.1 μg/l for all of the Great Lakes and mean sediment values ranged from 0.63 μg/g for Lake Superior to 1.00 μg/g for Lake Ontario. Mean fish values from lakes Erie and Ontario were 0.05 μg/g and 0.06 μg/g, respectively. The St. Marys and St. Lawrence rivers showed mean selenium values of <0.1 μg/l, as did other rivers tested in Ontario. The mean precipitation selenium value was 0.29 μg/l.

Résumé

On a fait l'analyse de l'arsenic et du sélénium dans l'eau, les sédiments et le poisson des Grands lacs; dans l'eau de cours d'eau communs aux États-Unis et au Canada; dans l'eau d'autres cours d'eau choisis en Ontario et dans les précipitations de la région des Grands lacs, pour en déterminer les teneurs actuelles et pour obtenir des données de référence.

Pour l'arsenic, la teneur moyenne dans les eaux lacustres variait de 0.23 μg/l (lac Supérieur) à 0.91 μg/l (lac Ontario), et dans les sédiments, elle allait de 2.03 μg/g (lac Supérieur) à 3.20 μg/g (lac Érié). Dans le poisson, elle était de 0.07 μg/g pour les lacs Ontario et Érié. L'analyse des eaux de la rivière Sainte-Marie et du Saint-Laurent a donné des moyennes en arsenic de 0.37 μg/l et 0.61 μg/l respectivement, et la moyenne des autres rivières ontariennes était de 0.26 μg/l. Dans les précipitations, elle était de 0.72 μg/l.

Pour le sélénium, la teneur moyenne dans les eaux de tous les Grands lacs était inférieure à 0.1 μg/l, et dans les sédiments, elle allait de 0.63 μg/g (lac Supérieur) à 1.00 μg/g (lac Ontario). Dans le poisson, elle était de 0.05 μg/g (lac Érié) et de 0.06 μg/g (lac Ontario). Dans les cours d'eau ontariens, y compris la rivière Sainte-Marie et le Saint-Laurent, la teneur moyenne du sélénium était inférieure à 0.1 μg/l. Dans les précipitations, elle était de 0.29 μg/l.

Levels of Arsenic and Selenium in the Great Lakes Region

W.J. Traversy, P.D. Goulden, Y.M. Sheikh and J.R. Leacock

INTRODUCTION

In recent years, considerable attention has been focused on the pollution in the Great Lakes produced by the discharge of nutrients and other toxic and non-toxic substances from industries, municipalities and agricultural sources. Limited information is available on the distribution of arsenic and selenium in the Great Lakes basin, and because of their increasing use in various industries and agricultural products (1-4), arsenic and selenium have the potential of being an environmental concern. The purpose of this study is to assess the levels of arsenic and selenium in the Great Lakes basin to establish base lines for future reference.

Arsenic occurs widely in minerals, ores, coal and soil, with an average concentration of 2.0 ppm in the earth's crust (5). It is used commercially in the manufacture of glassware, ceramics, leather, dyes, metals and numerous chemicals, and has also been used in various insecticides.

Selenium is found in igneous rocks, sulphide deposits, some soils and is generally associated with volcanic activity. The burning of "fossil fuels" such as coal, coke, fuel oil, and gasoline, is a potential source of contamination of the atmosphere and surrounding land and water, since many of these fuels are known to contain high concentrations of selenium. More than 80% of the world's output of selenium is derived as a by-product of copper refining (4).

Selenium is used commercially in the manufacture of photoelectric cells, clarification of glass, photography, vulcanization of rubber, production of certain steels, petroleum-cracking catalysts, and in the manufacture of selenium rectifiers (4).

Arsenic and selenium are deposited into rivers and lakes through the dissolution of minerals and ores; industrial effluents associated with coal, metal mining, refining, and related chemical industries (1, 2); and agricultural and municipal runoffs. The incineration of solid wastes also results in stack emission of selenium into the atmosphere (6).

The toxic effects of arsenic (7) and selenium (8) have been known for quite some time. Both arsenic and selenium are cumulative in nature. Arsenic builds up in the body to a level that may cause systemic vascular, mitotic, and protoplasmic poisoning; skin diseases; and cancer (3, 9, 10). Ingestion and inhalation of selenium cause pallor, depression, nervousness, gastrointestinal disorders (4), carcinoma, and cirrhosis of the liver (11, 12). Unlike arsenic, selenium is an essential element required at trace levels for the normal growth of man and other warm-blooded animals. Deficiencies in the diet of animals can cause disease and retard growth, whereas toxic properties are exhibited by selenium when present in food sources at levels above 4 ppm (13). Selenium deficiencies appear to be more of a problem than selenium toxicity, particularly to farmers who have suffered losses because of animal pasturage low in selenium. In New Zealand, selenium is added to animal diets to guard against selenium deficiencies in sheep. This is necessary because the pasturage in much of New Zealand is low in selenium.

The Canadian Drinking Water Standards for arsenic and selenium are 50 μg/l and 10 μg/l, respectively, as maximum permissible limits, and 10 μg/l and <10 μg/l, respectively, as acceptable limits (14).

The development of a method for the determination of submicrogram levels of arsenic and selenium (15) made it possible to monitor their concentrations in the Great Lakes and in rivers in the Great Lakes basin. This paper presents information on the levels of arsenic and selenium in the Great Lakes region in different types of water, including the international Great Lakes, connecting channels, rivers, precipitation, sediments and fish.

A total of 782 water and sediment samples were collected at selected stations from lakes Superior, Huron, Erie, Ontario, and Georgian Bay, and from various rivers and precipitation monitoring stations in the Great Lakes region (Figs. 1-6). Forty-three fish samples were also taken from lakes Erie and Ontario (Figs. 7 & 8).

The St. Marys and St. Lawrence rivers were sampled more extensively than other rivers because of surveys underway during the course of this study. A total of 7 sampling ranges of 34 sampling stations covering a distance of 14 miles of the St. Marys River were sampled twice on three alternate days at different times of the year. The St. Lawrence River was sampled at 69 locations covering about 116 miles of the river from Kingston to Cornwall, Ontario. The river was divided into 6 sections of 4 to 7 ranges and was sampled twice at different times of the year on six consecutive days, each range being sampled once during that period. The details of these intensive surveys will be reported in a separate study in connection with programs related to the International Joint Commission.

ANALYTICAL METHODS

The water samples were analyzed by the automated atomic absorption technique developed by Goulden and Brooksbank (15). The method has a detection limit of 0.1 μg/l for both arsenic and selenium. In this procedure, the samples are pretreated by digestion with potassium persulphate and hydrochloric acid to break down organo-arsenic and organo-selenium compounds and to overcome the interferences from iron and nitrate which may be present. The arsenate and selenate, thus formed, are reduced to arsenite and selenite before the formation of their hydrides, which are then thermally decomposed to atomic arsenic and selenium for simultaneous atomic absorption measurement in a dual-channel spectrophotometer.

The sediment and fish samples were subjected to a slightly different digestion treatment from the water samples. For sediment samples, 1.0 g of the dried sample was weighed and placed in a 250-millilitre conical flask, to which 25 ml of deionized water, 25 ml of concentrated hydrochloric acid and a few glass beads were added, and the mixture was boiled down to approximately 10 ml. After the solution had cooled, 1 g of potassium persulphate and 50 ml of deionized water were added, and again the solution was boiled down to approximately 10 ml. Finally, the solution was cooled and made up to 100 ml. Analysis was made by the method of standard addition.

For fish samples, 1 g of ground whole fish sample was digested with 15 ml of deionized water, 25 ml of concentrated hydrochloric acid and 3 g of potassium persulphate in a conical flask. The mixture was boiled down to about 15 ml. If fish particles still remained, the digestion was repeated with further addition of 2 g of potassium persulphate and 10 ml of hydrochloric acid. Finally, the solution was cooled and made up to 100 ml. Analysis was carried out using the method of standard addition.

RESULTS AND DISCUSSION

Table 1 shows the average arsenic and selenium concentrations of all the various sample types analyzed, including maximum and minimum values. For statistical purposes, a value of 0.0 was given to samples containing less than detectable quantities.

Water

Great Lakes

Of the 243 water samples analyzed from the Great Lakes, detectable quantities (>0.1 μg/l) of arsenic were found in 93% of the samples, whereas only 34% showed similar detectable quantities of selenium. Sixty-five percent of the samples contained arsenic in the range 0.10-0.40 μg/l, and 32% showed selenium levels in the same range. The remaining samples having detectable quantities contained 0.5 μg/l or more of arsenic and selenium; the highest arsenic value was 1.20 μg/l and the highest selenium value, 0.80 μg/l. Figures 1 to 5 show the sampling locations on the Great Lakes for the work reported in this paper. Tables 2 to 6 show the details concerning the levels found in the Great Lakes including means, exact station location and number of samples analyzed.

The distribution of arsenic within each of the Great Lakes appears quite uniform, with Lake Ontario having the highest average concentration, 0.91 μg/l. The majority (75%) of the Lake Ontario samples were within the concentration range of 0.60-0.90 μg/l; the remaining samples were in the range of 1.00-1.20 μg/l. These higher levels occurred mostly in the western part of the lake. It is significant that none of the 24 samples analyzed from Lake Ontario showed arsenic to be less than 0.60 μg/l, whereas the other Great Lakes and Georgian Bay samples showed values <0.1 μg/l. Lake Huron had no minimum value of <0.1 μg/l.

Selenium values on the Great Lakes ranged from <0.1 μg/l to 0.80 μg/l. The lake-wide average concentration of <0.1 μg/l Se was common to all of the Great Lakes. The highest selenium value found was 0.80 μg/l at station 207 in the west end of Lake Superior near Duluth, Minnesota, and one sample, at station 89 near Marathon, Ontario, showed 0.50 μg/l. One other value of 0.50 μg/l occurred at station 35 located in the central part of Lake Ontario.

Table 1. Summary of Arsenic and Selenium Levels in the Great Lakes Region

Origin	Number of cruises or samplings	Total number of samples	Arsenic (As)			Selenium (Se)		
			Maximum	Minimum	Average*	Maximum	Minimum	Average*
Lakes								
Lake Superior	4	47	1.00 µg/l	<0.1 µg/l	0.23 µg/l	0.80 µg/l	<0.1 µg/l	<0.1 µg/l
Lake Huron	4	91	0.80	0.10	0.44	0.20	<0.1	<0.1
Georgian Bay	6	64	0.70	<0.1	0.35	0.20	<0.1	<0.1
Lake Erie	2	17	0.60	<0.1	0.25	0.20	<0.1	<0.1
Lake Ontario	2	24	1.20	0.60	0.91	0.50	<0.1	<0.1
Various rivers	8	108	1.40	<0.1	0.26	0.50	<0.1	<0.1
St. Marys River	2	160	1.00	<0.1	0.37	0.60	<0.1	<0.1
St. Lawrence River	2	132	1.00	<0.1	0.61	0.20	<0.1	<0.1
Precipitation at various locations	4	53	2.50	<0.1	0.72	1.00	<0.1	0.29
Sediments								
Lake Superior	1	15	8.00 µg/g	0.50 µg/g	2.03 µg/g	1.10 µg/g	0.20 µg/g	0.63 µg/g
Lake Huron	1	10	4.50	0.80	2.33	2.00	0.50	0.90
Lake Erie	1	10	5.50	2.00	3.20	1.30	0.20	0.79
Lake Ontario	1	8	14.00	1.50	4.06†	1.80	0.30	1.00
Fish								
Lake Erie	1	31	0.12	0.03	0.07	0.08	0.01	0.05
Lake Ontario	1	12	0.10	0.04	0.07	0.08	0.04	0.06

*Average value or result of one analysis if only one sample collected
†Average 2.64 µg/g, excluding a value of 14.00 µg/g

Table 2. Levels of Arsenic and Selenium in Water from Lake Superior

Station number	Latitude	Longitude	Number of samples	Arsenic (µg/l)			Selenium (µg/l)		
				Maximum	Minimum	Average*	Maximum	Minimum	Average*
34	47°50′00″	85°12′30″	3	0.40	0.10	0.20	<0.1	<0.1	<0.1
35	47°55′57″	85°16′09″	2	0.40	0.30	0.35	<0.1	<0.1	<0.1
38	47°48′30″	85°50′03″	3	0.30	<0.1	0.20	<0.1	<0.1	<0.1
45	46°51′36″	86°34′30″	4	0.40	0.10	0.25	<0.1	<0.1	<0.1
50	46°30′42″	86°34′06″	4	0.40	<0.1	0.20	<0.1	<0.1	<0.1
70	47°03′00″	88°18′00″	3	0.30	0.10	0.17	<0.1	<0.1	<0.1
80	47°35′00″	86°57′06″	1			0.50			0.10
89	48°42′00″	86°25′06″	4	0.50	0.10	0.25	0.50	<0.1	0.12
115	47°50′48″	87°27′24″	3	0.30	0.10	0.17	<0.1	<0.1	<0.1
133	48°17′00″	88°35′55″	4	0.30	0.10	0.20	<0.1	<0.1	<0.1
139	48°15′12″	88°11′00″	4	0.30	0.10	0.25	<0.1	<0.1	<0.1
189	46°50′54″	90°11′00″	4	0.30	0.10	0.25	<0.1	<0.1	<0.1
203	47°13′12″	91°12′18″	4	0.30	<0.1	0.18	<0.1	<0.1	<0.1
207	47°00′12″	91°30′54″	4	1.00	0.10	0.40	0.80	<0.1	0.20

*Average value or result of one analysis if only one sample collected

Table 3. Levels of Arsenic and Selenium in Water from Lake Huron

Station number	Latitude	Longitude	Number of samples	Arsenic (μg/l)			Selenium (μg/l)		
				Maximum	Minimum	Average	Maximum	Minimum	Average
1	43° 09′ 30″	82° 20′ 30″	4	0.60	0.40	0.50	0.20	0.10	0.13
3	43° 48′ 30″	82° 32′ 30″	2	0.60	0.50	0.55	0.10	0.10	0.10
5	44° 05′ 18″	83° 04′ 54″	6	0.60	0.20	0.40	0.20	<0.1	<0.1
6	43° 51′ 30″	83° 40′ 15″	3	0.20	0.10	0.17	0.20	0.20	0.20
7	44° 12′ 24″	83° 23′ 00″	2	0.60	0.60	0.60	0.20	0.10	0.15
9	44° 44′ 48″	83° 08′ 12″	2	0.50	0.40	0.45	<0.1	<0.1	<0.1
11	44° 52′ 25″	82° 12′ 00″	6	0.50	0.30	0.42	0.20	<0.1	<0.1
12	45° 14′ 00″	82° 25′ 00″	7	0.60	0.30	0.43	0.10	<0.1	<0.1
18	45° 18′ 54″	83° 24′ 12″	5	0.60	0.30	0.50	0.20	<0.1	<0.1
20	45° 43′ 42″	83° 17′ 48″	2	0.50	0.40	0.45	0.10	0.10	0.10
24	45° 41′ 00″	83° 42′ 54″	2	0.80	0.60	0.70	0.10	0.10	0.10
25	45° 30′ 00″	83° 52′ 00″	3	0.50	0.30	0.40	0.20	0.20	0.20
26	45° 32′ 24″	84° 05′ 12″	6	0.70	0.30	0.51	0.20	<0.1	<0.1
28	45° 43′ 12″	84° 30′ 00″	2	0.50	0.50	0.50	0.10	0.10	0.10
30	45° 46′ 40″	84° 55′ 00″	3	0.60	0.30	0.40	0.20	0.10	0.13
32	45° 50′ 00″	84° 38′ 30″	6	0.60	0.30	0.47	0.20	<0.1	<0.1
35	46° 02′ 30″	83° 51′ 42″	2	0.40	0.40	0.40	0.20	0.20	0.20
36	46° 04′ 42″	84° 01′ 42″	4	0.70	0.30	0.45	<0.1	<0.1	<0.1
38	46° 14′ 00″	83° 44′ 48″	2	0.50	0.50	0.50	0.10	<0.1	<0.1
46	46° 07′ 24″	82° 53′ 00″	5	0.40	0.20	0.32	0.20	<0.1	<0.1
51	46° 05′ 30″	82° 33′ 24″	4	0.50	0.30	0.35	0.20	<0.1	<0.1
53	46° 00′ 18″	82° 23′ 18″	2	0.40	0.30	0.35	0.10	<0.1	<0.1
56	46° 03′ 12″	81° 59′ 06″	2	0.40	0.30	0.35	0.20	0.10	0.15
59	45° 22′ 54″	81° 56′ 06″	5	0.60	0.30	0.46	0.20	<0.1	<0.1
65	45° 21′ 06″	81° 44′ 42″	4	0.50	0.40	0.48	<0.1	<0.1	<0.1

Table 4. Levels of Arsenic and Selenium in Water from Georgian Bay

Station number	Latitude	Longitude	Number of samples	Arsenic (μg/l)			Selenium (μg/l)		
				Maximum	Minimum	Average	Maximum	Minimum	Average
1	44°37′24″	80°55′24″	5	0.50	0.20	0.36	0.10	<0.1	<0.1
2	44°43′03″	80°51′24″	5	0.50	0.20	0.32	0.10	<0.1	<0.1
3	44°48′30″	80°52′18″	5	0.60	0.10	0.36	0.10	<0.1	<0.1
5	44°36′30″	80°24′30″	5	0.50	0.20	0.36	0.10	<0.1	<0.1
12	44°57′06″	80°08′06″	6	0.50	0.30	0.37	0.10	<0.1	<0.1
13	44°52′36″	80°55′48″	5	0.50	<0.1	0.28	0.20	<0.1	0.10
14	45°03′18″	80°11′30″	5	0.40	0.20	0.34	0.10	<0.1	<0.1
23	45°14′42″	80°52′30″	5	0.40	0.20	0.34	0.20	<0.1	<0.1
28	45°25′30″	81°04′00″	5	0.40	0.20	0.32	0.20	<0.1	<0.1
32	45°46′36″	80°45′06″	5	0.40	0.20	0.30	0.20	<0.1	<0.1
36	45°28′42″	81°23′00″	3	0.70	0.20	0.47	<0.1	<0.1	<0.1
52	45°43′00″	81°22′30″	6	0.50	0.30	0.40	0.20	<0.1	<0.1
53	45°53′00″	81°06′30″	3	0.60	0.20	0.37	0.20	0.10	0.13

Table 5. Levels of Arsenic and Selenium in Water from Lake Erie

Station number	Latitude	Longitude	Number of samples	Arsenic (μg/l)			Selenium (μg/l)		
				Maximum	Minimum	Average*	Maximum	Minimum	Average*
2	42°50′18″	78°55′42″	1			<0.1			0.10
4	42°47′18″	79°06′18″	2	0.20	<0.1	0.10	0.10	0.10	0.10
12	42°51′06″	79°31′12″	1			<0.1			0.10
13	42°49′05″	79°31′09″	1			0.20			0.10
14	42°47′24″	79°33′24″	2	<0.1	<0.1	<0.1	0.10	0.10	0.10
24	42°40′12″	80°01′06″	1			0.50			0.20
33	42°26′30″	80°14′12″	1			0.50			0.10
35	42°19′00″	80°37′48″	2	0.40	0.30	0.35	<0.1	<0.1	<0.1
37	41°55′42″	80°54′42″	1			0.50			0.20
39	42°30′00″	81°05′36″	1			0.30			0.10
42	42°31′54″	81°28′48″	1			0.60			0.20
104	41°50′06″	83°06′00″	1			0.20			0.20
117	41°58′00″	83°03′12″	1			0.20			0.10
121	42°39′24″	80°16′12″	1			0.30			0.10

*Average value or result of one analysis if only one sample collected

Table 6. Levels of Arsenic and Selenium in Water from Lake Ontario

Station number	Latitude	Longitude	Number of samples	Arsenic (μg/l)			Selenium (μg/l)		
				Maximum	Minimum	Average*	Maximum	Minimum	Average*
2	43°34′24″	79°24′00″	1			1.0			<0.1
3	43°17′18″	79°24′00″	1			1.1			<0.1
5	43°17′36″	79°24′30″	1			0.80			<0.1
6	43°21′36″	78°43′48″	1			0.60			<0.1
9	43°34′54″	78°47′18″	1			1.20			<0.1
10	43°42′24″	79°13′06″	1			0.70			<0.1
12	43°49′48″	78°51′00″	1			1.20			<0.1
15	43°57′00″	78°03′00″	2	1.20	0.80	1.00	0.10	<0.1	<0.1
19	43°35′24″	78°00′42″	1			0.90			0.30
20	43°39′30″	78°48′00″	1			0.80			0.10
22	43°23′00″	88°59′24″	1			0.70			0.10
25	43°39′06″	78°30′00″	1			0.80			0.10
26	43°21′30″	76°57′18″	1			0.90			0.10
29	43°34′06″	76°59′42″	1			0.90			0.10
30	43°45′42″	78°17′00″	1			0.80			<0.1
32	43°48′00″	77°02′24″	1			0.80			<0.1
35	43°26′24″	77°54′00″	1			1.20			0.50
40	43°39′06″	77°36′00″	1			0.90			0.10
45	43°39′00″	77°18′00″	1			0.90			<0.1
50	43°39′00″	77°00′00″	1			0.90			<0.1
55	43°30′24″	76°42′00″	1			0.90			0.10
60	43°43′42″	76°24′00″	1			0.90			<0.1
65	44°00′18″	76°48′00″	1			0.90			<0.1

*Average value or result of one analysis if only one sample collected

Rivers

Figure 6 indicates the sampling location of the rivers in the region that were considered in this study. It may be noted that a few samples were collected outside the Great Lakes basin for data comparison purposes. Table 7 presents the details concerning the levels of metals found at the river stations.

Arsenic and selenium in rivers tested in Ontario were within the concentration range of <0.1-1.40 μg/l and <0.1-0.50 μg/l, respectively (Table 7). The rivers in the northern part of Ontario outside the Great Lakes basin showed lower concentrations of arsenic and selenium (<0.1-0.35 μg/l and <0.1-0.10 μg/l, respectively) than the rivers situated in the southern portion of the Province (0.10-1.10 μg/l and <0.1-0.50 μg/l), which is perhaps indicative of industrial activities in this part of the region. A value of 1.40 μg/l As in the English River was observed, although there is no known industrial source in the region. The mean concentration of selenium in the rivers tested was <0.1 μg/l. The mean concentrations of arsenic were 0.37 μg/l and 0.61 μg/l for the St. Marys and St. Lawrence rivers, respectively, whereas the mean concentration for selenium was <0.1 μg/l for both rivers.

In general, the water samples from the Great Lakes and most rivers in the Great Lakes basin are within the concentration ranges of <0.1-1.40 μg/l As and <0.1-0.80 μg/l Se. These results are considerably lower than arsenic levels reported for other parts of the world, some of which are tabulated in Table 8.

The river data reported by Kopp and Kroner (18) appear to be up to 70 times higher than our findings. Yet it must be realized that the spectrographic method of analysis used by Kopp and Kroner is much less sensitive (about 50 μg/l) than the method used for this report (0.1 μg/l). In addition, the data reported by Kopp and Kroner represent the mean concentration of positive occurrences only, and arsenic was found in less than 6% of all of the samples tested.

The United States Geological Survey (21) shows a median river water value for arsenic of less than 10 μg/l, the lower limit of detection of their method. Twenty-two percent of the samples analyzed did show detectable amounts, mostly in the lower range of detection, 10-20 μg/l.

The selenium values we obtained are in general agreement with those shown in Table 8. The nine rivers in the United States reported by Kharkar, Turekian and Bertine (20) have an average selenium value of 0.2 μg/l.

Precipitation

Atmospheric pollution is one of the sources which contributes considerably toward the pollution of rivers and lakes (22). The atmospheric pollutants are deposited in the surface waters, either by dry fallout or by wet precipitation. The analytical data on the precipitation constituents could indicate the nature of industrial activities in a particular area, as well as in adjoining regions depending on meteorological conditions.

The precipitation samples used for this study were collected at 18 permanent sampling locations (Fig. 6) and showed values that ranged from levels found in the lakes to a high of 2.50 μg/l As and 1.00 μg/l Se (Table 9). The high arsenic and selenium values were observed at or near highly industrialized locations, such as Toronto, Sarnia and Hamilton. The precipitation samples collected aboard research vessels during monitor cruises on lakes Superior, Erie and Ontario showed more or less the same concentration ranges as those found in the lake waters.

The average concentration of selenium in precipitation was found to be 0.29 μg/l, which is in general agreement with the value of 0.2 μg/l reported by Hashimoto and Winchester (23). The average concentration of arsenic in precipitation was 0.72 μg/l, and no other data could be located in the literature for comparison. The highest arsenic level in precipitation was 2.50 μg/l from the station at Toronto Island, and the lowest value, <0.1 μg/l, was from Guelph, Ontario.

It is interesting to note that considerably higher arsenic and selenium values occurred in precipitation, as compared to the values found in lakes and rivers. This indicates that precipitation may be a significant source of these pollutants. Copeland (8) has shown that the selenium concentration in Lake Michigan zooplankton increases as one approaches Chicago from the lake. This could be related to the smoke from fossil fuel combustion being carried by prevailing winds blowing from the southwest and taking most of the smoke over Chicago and out over the southern end of the lake. Copeland also noted that the selenium is apparently very quickly taken up by zooplankton rather than accumulating in the bottom sediments.

Sediments

The sediment samples analyzed for this study were collected as a part of the geochemical and sedimentological studies on the Great Lakes from 1968 to 1973. The samples were collected by a Shipek grab sampler, and the top 3 cm of the sediment was subsampled and retained for geochemical analysis.

Table 7. Levels of Arsenic and Selenium in Water from Rivers in the Great Lakes Region

Rivers	Latitude	Longitude	Number of samples	Arsenic (μg/l)			Selenium (μg/l)		
				Maximum	Minimum	Average	Maximum	Minimum	Average
Michipicoten	47°55′	84°46′	4	0.35	0.10	0.22	<0.1	<0.1	<0.1
Mississagi	46°12′04″	83°01′32″	4	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
French	46°03′01″	80°34′26″	4	0.20	0.10	0.13	<0.1	<0.1	<0.1
Severn	44°51′25″	79°32′30″	5	0.30	0.20	0.24	0.30	<0.1	<0.1
Lake Huron	43°00′07″	82°25′10″	7	0.50	0.10	0.26	0.10	<0.1	<0.1
St. Clair	42°39′28″	82°30′29″	8	0.70	0.10	0.29	0.50	<0.1	<0.1
Thames	42°32′42″	81°58′04″	3	0.50	0.20	0.30	0.30	<0.1	0.10
Detroit	42°19′42″	82°58′46″	6	0.20	0.10	0.18	<0.1	<0.1	<0.1
Detroit	42°07′20″	86°06′53″	7	0.50	0.10	0.29	0.10	<0.1	<0.1
Grand	43°07′56″	80°16′01″	3	0.60	0.20	0.43	0.10	<0.1	<0.1
Niagara	43°09′25″	79°02′50″	3	0.60	0.10	0.37	0.10	<0.1	<0.1
Trent	44°22′14″	77°46′42″	4	1.00	0.20	0.43	<0.1	<0.1	<0.1
Napanee	44°16′39″	76°55′43″	5	0.20	<0.1	<0.1	<0.1	<0.1	<0.1
St. Lawrence	45°00′21″	74°47′43″	6	1.10	0.30	0.60	0.10	<0.1	<0.1
Rainy	48°38′30″	93°20′00″	8	0.30	0.10	0.15	0.10	<0.1	<0.1
English	50°35′00″	93°27′15″	3	1.40	0.30	1.00	0.10	<0.1	<0.1
Kénogami	49°54′56″	86°29′17″	2	0.20	0.10	0.15	<0.1	<0.1	< 0.1
Moose	50°48′50″	81°17′40″	3	0.30	0.20	0.23	<0.1	<0.1	<0.1
Abitibi	50°36′00″	81°25′00″	2	0.30	0.30	0.30	0.10	<0.1	<0.1
Winisk	54°31′	87°14′	3	0.20	<0.1	0.10	<0.1	<0.1	<0.1
Albany	51°19′30″	83°52′20″	2	0.20	0.20	0.20	<0.1	<0.1	<0.1
Goulais	at Search Mount		7	0.20	<0.1	<0.1	0.10	<0.1	<0.1
N. Magnetawan	at Pickerel Lake		4	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
St. Marys*	at various locations		160	1.00	<0.1	0.37	0.60	<0.1	<0.1
St. Lawrence*	at various locations		132	1.00	<0.1	0.61	0.20	<0.1	<0.1

*Intensive surveys

Table 8. Published Arsenic and Selenium Levels in Fresh Water

Origin and location	Average or concentration range		Reference
	Arsenic (μg/l)	Selenium (μg/l)	
Illerkanal, Germany	3.0 (± 10%)	0.22 (± 10%)	(16)
Donau, Ulm, Germany	3.3 (± 10%)	0.15 (± 10%)	(16)
Donau, Böfingerhalde, Germany	2.2 (± 10%)	0.12 (± 10%)	(16)
Lech Kanal, Gersthofen, Germany	8.1 (± 10%)	1.20 (± 10%)	(16)
Lech Kanal, Langweid, Germany	4.5 (± 10%)	1.50 (± 10%)	(16)
Water reservoir, U.K.	1.0	12.00 (± 10%)	(17)
St. Lawrence River, Massena, U.S.A.	38.	–	(18)
Schuylkill River, Philadelphia, U.S.A.	69.	–	(18)
Allegheny River, Pittsburgh, U.S.A.	70.	–	(18)
Columbia River, Wenatchee, U.S.A.	46.	–	(18)
Subsurface waters, France	–	10-20	(19)
Nine rivers, U.S.A.	–	0.11-0.34 (Average 0.2)	(20)

Table 9. Levels of Arsenic and Selenium in Precipitation Samples

Station number and location	Latitude	Longitude	Number of samples	Arsenic (μg/l)			Selenium (μg/l)		
				Maximum	Minimum	Average*	Maximum	Minimum	Average*
1 Isle Royale	47°55′	89°12′	4	1.40	0.30	0.65	0.10	<0.1	<0.1
2 Thunder Bay	48°22′27″	89°18′38″	4	0.50	<0.1	0.30	<0.1	<0.1	<0.1
3 Copper Harbour	47°28′	87°55′	4	1.40	0.40	0.90	0.60	<0.1	0.20
4 Ney's Park	48°46′38″	86°35′12″	4	0.80	0.40	0.55	0.10	0.10	0.10
5 Caribou Island	47°19′30″	85°49′48″	4	1.90	0.70	1.38	0.70	0.10	0.40
6 Gore Bay	45°53′06″	82°34′28″	2	0.80	0.60	0.70	0.30	0.10	0.20
7 Wiarton	44°44′48″	81°06′46″	2	0.40	0.30	0.35	0.10	0.10	0.10
8 Trenton	44°06′40″	77°32′38″	1			0.30			0.50
9 Kingston	44°13′05″	76°35′46″	2	1.20	0.80	1.00	0.50	0.50	0.50
10 Main Duck Island	43°55′28″	76°36′39″	2	0.90	0.70	0.80	1.00	0.50	0.75
11 Toronto Island	43°37′54″	79°23′48″	3	2.50	0.50	1.60	1.00	0.50	0.67
12 Woodbridge	43°47′36″	79°34′08″	3	0.90	<0.1	0.30	0.50	0.40	0.47
13 CCIW, Burlington	43°17′56″	79°47′58″	5	0.90	0.10	0.46	0.50	0.30	0.36
14 Guelph	43°38′04″	80°06′52″	1			<0.1			0.40
15 Ancaster	43°10′31″	79°57′00″	1			1.90			0.60
16 Port Stanley	42°40′14″	81°13′28″	2	0.90	0.80	0.85	0.40	0.20	0.30
17 Sarnia	42°59′48″	82°18′25″	2	1.90	0.80	1.35	0.70	0.30	0.50
18 Pelee Island	41°45′02″	82°41′13″	1			1.20			0.80
Lake Superior†	47°42′00″	89°00′00″							
	47°10′54″	86°07′48″	2	0.20	<0.1	0.10	<0.1	<0.1	<0.1
	47°10′54″	86°07′48″							
	46°30′30″	84°37′30″							
Lake Erie†	42°36′48″	79°13′12″							
	42°50′24″	78°53′12″	2	0.50	0.40	0.45	0.20	0.20	0.20
	42°40′12″	80°01′06″							
Lake Ontario†	43°24′42″	79°24′30″							
	43°36′12″	79°21′24″	2	0.20	<0.1	0.10	<0.1	<0.1	0.1
	43°42′	77°18′							

*Average value or result of one analysis if only one sample collected
†Samples were collected during monitor cruises on lakes Superior, Erie and Ontario

Data and other details pertaining to levels of arsenic and selenium in sediments from the Great Lakes are given in Tables 10 to 13. It should be noted that in this study sediment data are reported on a dry basis and fish data, on a wet basis.

The average lake-wide concentrations of arsenic in the sediments were 2.03 μg/g, 2.33 μg/g, 3.20 μg/g and 2.64 μg/g (excluding a single high value of 14 μg/g at station L-35, Lake Ontario) for lakes Superior, Huron, Erie, and Ontario, respectively. These results are considerably lower than other sediment data reported by Schramel, Samsahl and Pavlu (16) (Table 14). Ruch, Kennedy and Shimp (24) reported from 5-30 ppm As in Lake Michigan sediments. The highest sediment value observed in the present study was 7.0 ppm in Lake Superior near Duluth, Minnesota.

For selenium in sediments, the average lake-wide concentrations were 0.63 μg/g, 0.90 μg/g, 0.79 μg/g and 1.00 μg/g for lakes Superior, Huron, Erie and Ontario, respectively. These results are higher than the 0.5 ppm selenium content of the sediments in Lake Michigan near Chicago reported by Copeland, although 4 of the 15 sediment samples analyzed for this study from Lake Superior showed selenium values <0.5 ppm. They are in agreement with values reported in Table 14 for Lake Mendota in the United States, and Markt Redwitz in Germany.

Fish

The fish samples analyzed for this study were collected in 1971 as part of a pesticide residue study (Figs. 7 & 8). The fish had been retained in a frozen state. The analyses carried out on portions of ground whole fish showed a concentration range of 0.03-0.12 μg/g and 0.01-0.08 μg/g for arsenic and selenium, respectively. Data and other details pertaining to levels of arsenic and selenium in fish from lakes Erie and Ontario are shown in Tables 15 and 16. If the values for arsenic and selenium in this report are compared to the data published elsewhere (Table 17), the values are from 2 to 4 times higher for arsenic and 50 to 100 times higher for selenium

Table 10. Levels of Arsenic and Selenium in Sediments from Lake Superior

Basin	Station	Latitude	Longitude	Arsenic μg/g (dry)	Selenium μg/g (dry)
Duluth	I-7	47° 11.4′	91° 14.10′	7.0	0.2
	I-9	47° 12.1′	90° 58.80′	0.8	0.7
Thunder Bay	G-34	47° 05.0′	87° 55.90′	5.0	0.8
	I-20	47° 14.6′	89° 30.90′	1.0	0.6
	I-41	47° 16.4′	87° 08.50′	8.0	0.2
	M-41	47° 38.0′	87° 08.00′	0.5	0.6
	N-56	47° 42.9′	85° 08.00′	0.8	0.9
	P-48	47° 53.6′	86° 12.40′	2.0	0.2
	Q-22	47° 58.1′	89° 17.10′	0.7	0.8
	R-23	48° 03.9′	89° 08.90′	0.5	1.1
	R-33	48° 04.8′	88° 04.20′	0.7	0.8
	S-25	48° 09.3′	88° 53.00′	0.5	0.8
	S-41	48° 10.0′	87° 08.10′	0.5	0.8
	T-25	48° 15.06′	88° 53.20′	2.0	0.2
	T-28	48° 15.4′	88° 36.60′	0.5	0.7

Table 11. Levels of Arsenic and Selenium in Sediments from Lake Huron

Basin	Station	Latitude	Longitude	Arsenic μg/g (dry)	Selenium μg/g (dry)
Mackinac	H-30	45° 39.6′	83° 49.50′	4.0	0.5
Manitoulin	S-25	43° 14.2′	82° 23.80′	1.5	0.5
	V-22	44° 58.1′	82° 00.90′	2.0	2.0
	W-19	44° 41.3′	81° 54.00′	1.5	0.7
Port Huron	S-5	43° 26.3′	82° 21.20′	2.0	0.9
	S-7	43° 37.0′	82° 21.80′	2.0	0.7
	S-9	43° 47.8′	82° 22.20′	2.0	1.0
Goderich	V-6	43° 31.8′	81° 59.50′	3.0	0.9
	V-10	43° 53.5′	81° 59.50′	4.5	0.9
	V-12	44° 04.2′	82° 00.00′	0.8	0.9

Table 12. Levels of Arsenic and Selenium in Sediments from Lake Erie

Basin	Station	Latitude	Longitude	Arsenic μg/g (dry)	Selenium μg/g (dry)
Sandusky	B-8	41° 32.58′	82° 33.50′	3.5	0.6
Central	E-12	41° 49.10′	82° 05.00′	2.0	1.0
	E-15	41° 49.28′	81° 43.35′	2.5	1.3
	G-19	42° 00.18′	81° 14.48′	5.5	1.1
	H-22	42° 05.63′	80° 52.73′	3.5	0.4
Eastern	M-31	42° 32.25′	79° 46.93′	4.0	0.9
	N-33	42° 37.50′	79° 32.20′	2.0	0.9
	P-35	42° 48.10′	79° 17.30′	2.0	0.2
Western	F-6	41° 54.70′	82° 48.20′	3.0	0.6
	V-40	41° 50.80′	83° 13.70′	4.0	0.9

Table 13. Levels of Arsenic and Selenium in Sediments from Lake Ontario

Basin	Station	Latitude	Longitude	Arsenic μg/g (dry)	Selenium μg/g (dry)
Niagara	B-3	43° 17.2′	79° 36.00′	2.0	0.8
	B-7	43° 17.3′	79° 12.10′	3.5	0.8
	D-5	43° 25.7′	79° 24.30′	2.5	1.1
Mississauga	D-16	43° 25.8′	78° 17.80′	4.0	1.8
	E-14	43° 30.2′	78° 30.00′	2.0	0.5
	F-20	43° 34.4′	77° 54.00′	3.0	1.7
Rochester	E-27	43° 30.0′	77° 12.10′	1.5	1.0
Kingston	L-35	44° 00.5′	76° 24.00′	14.0	0.3

Table 14. Published Arsenic and Selenium Levels in Sediments

Origin and location	Concentration range μg/g (dry)				Reference
	Arsenic		Selenium		
Markt Redwitz, Germany	51-59	(± 10%)	0.8-0.9	(± 10%)	(16)
Faulschlamm, GroBlappen, Germany	15.6	(± 10%)	7.1	(± 10%)	(16)
Bodenschlamm, Imm, Germany	24.5	(± 10%)	1.4	(± 10%)	(16)
Isorwerk Kanal, Munchen, Germany	10.9	(± 10%)	2.9	(± 10%)	(16)
Southern Lake Michigan, U.S.A.	5-30		–		(24)
Lake Mendota, Dane County, U.S.A.	–		0.5-1.8		(25)
Lake Crystal, Vilas County, U.S.A.	–		3.5		(25)
Lake Waubesa, Dane County, U.S.A.	–		2.2		(25)

Table 15. Levels of Arsenic and Selenium in Fish from Lake Erie

Station number	Latitude	Longitude	Species	Number of samples	Arsenic μg/g (wet)			Selenium μg/g (wet)		
					Maximum	Minimum	Average*	Maximum	Minimum	Average*
1	42°50′00″	79°34′00″	white bass	2	0.08	0.07	0.075	0.06	0.03	0.045
			yellow perch	3	0.09	0.05	0.067	0.07	0.03	0.047
4	42°34′00″	79°44′06″	perch	1			0.060			0.060
			chub	1			0.070			0.060
5	42°28′48″	79°47′30″	barbote	1			0.030			0.010
			clams	1			0.070			0.050
			smelt	1			0.120			0.050
			perch	1			0.080			0.060
			chub	1			0.070			0.050
6	42°23′30″	79°51′30″	carp	1			0.120			0.050
			yellow pickerel	1			0.100			0.050
			catfish	1			0.090			0.030
			g. shad	1			0.100			0.040
			drum	1			0.070			0.060
			smelt	1			0.040			0.050
			yellow perch	1			0.070			0.020
			clams	1			0.050			0.030
7	42°18′18″	79°54′42″	perch	1			0.060			0.040
			chub	1			0.070			0.030
			clams	1			0.070			0.040
8	42°13′00″	79°58′00″	drum	1			0.060			0.050
			perch	1			0.100			0.040
			chub	1			0.070			0.040
11	42°03′00″	81°47′24″	perch	1			0.030			0.060
12	41°57′12″	81°45′18″	perch	1			0.060			0.060
19	41°45′00″	82°56′06″	yellow perch	1			0.090			0.040
			drum	1			0.030			0.040
20	41°38′12″	82°53′18″	clams	1			0.100			0.080

*Average value or result of one analysis if only one sample collected

Table 16. Levels of Arsenic and Selenium in Fish from Lake Ontario

Station number	Latitude	Longitude	Species	Number of samples	Arsenic μg/g (wet)			Selenium μg/g (wet)		
					Maximum	Minimum	Average*	Maximum	Minimum	Average*
1	43°37′00″	79°27′00″	alewife	1			0.04			0.07
			smelt	1			0.04			0.07
5	43°18′30″	78°56′30″	smelt	1			0.09			0.05
6	43°56′48″	77°48′00″	alewife	2	0.05	0.05	0.05	0.06	0.06	0.06
7	43°52′48″	77°48′00″	smelt	2	0.07	0.06	0.065	0.05	0.04	0.04
			alewife	1			0.07			0.05
			sculpin	1			0.06			0.05
13	43°22′30″	77°48′00″	alewife	1			0.10			0.08
			sculpin	1			0.09			0.04
15	44°04′00″	76°34′00″	rock bass	1			0.07			0.08

*Average value or result of one analysis if only one sample collected

Table 17. Published Arsenic and Selenium Levels in Fish

Origin and location	Average or concentration range		Reference
	Arsenic (μg/g)	Selenium (μg/g)	
Isar (fish-meat), Germany	0.4 (± 10%)	2.0 (± 10%)	(16)
Salzach (fish-meat), Germany	0.2-0.4 (± 10%)	1.0-4.6 (± 10%)	(16)
10 different species, lakes Superior and Michigan	0.003-0.043	0.0001-0.0020	(26)
7 different species, lakes Erie and Ontario	–	0.12-0.75	(27)

than the data of Lucas, Edgington and Colby (26). The results in a more recent publication (27) on the levels of selenium are from 5 to 40 times higher than the results we obtained for the same species within the same lake. These published data indicate a large variability, particularly for selenium concentrations in fish from the Great Lakes, and also probably reveal a need for method standardization.

Toxic substances present in the aquatic environment are assimilated by the organisms and are carried through the lower members of the food chain to the higher members, such as zooplankton and eventually to fish. Selenium, as reported by Copeland for southern Lake Michigan, is taken up very quickly and accumulated by zooplankton reaching a level of 7 ppm, which is considerably higher than the selenium in the sediment which is always less than 0.5 ppm in that part of the lake. Copeland mentioned that 7 ppm selenium is approaching a dangerous limit insofar as foodstuffs are concerned. Data reported in our study show that the concentration of selenium in fish from lakes Ontario and Erie is on an average 10 to 20 times less than the level found in sediments, and therefore does not apparently indicate a magnification from sediments to fish in those lakes. Further investigation is needed to determine if high levels of selenium are present in zooplankton in other parts of the Great Lakes.

The selenium content of the fish illustrates bioconcentration of selenium representing about a 1000-fold increase over the level found in the waters of the same lakes.

Much of the arsenic as arsenate is taken up by the phosphate transport system of many organisms (28, 29). Data reported in our study show that the concentration of arsenic in fish from lakes Ontario and Erie is on an average about 50 to 60 times less than the level found in sediments from those lakes. Again, as with selenium, this indicates no apparent magnification of arsenic concentration from sediments to fish in lakes Ontario and Erie.

The arsenic content of the fish shows a bioconcentration of arsenic representing about an 80-fold to 300-fold increase over the level found in the waters of the same lakes.

CONCLUSIONS

Presented here is a summary of the major conclusions involving the concentrations of arsenic and selenium found in the Great Lakes region.

Arsenic and selenium levels in the waters of the Great Lakes, Georgian Bay and in the rivers tested in the Ontario region are in the ranges of <0.1-1.40 μg/l and <0.1-0.80 μg/l, respectively. Selenium levels found are generally in agreement with the levels of selenium found by others in lakes, rivers and reservoirs elsewhere in the world. Arsenic levels, however, are considerably lower than the levels generally reported in these areas in other parts of the world.

Arsenic and selenium levels in the precipitation samples are in the ranges of <0.1-2.50 μg/l and <0.1-1.00 μg/l, respectively. The results indicate that precipitation may be a significant source of these two toxic elements to the environment. High arsenic and selenium concentrations in precipitation samples were generally found near industrial locations.

Arsenic and selenium levels in the sediments of the Great Lakes are in the ranges of 0.5-14.0 μg/g and 0.2-2.0 μg/g, respectively.

Arsenic and selenium levels in fish from lakes Ontario and Erie are in the ranges of 0.03-0.12 μg/g and 0.01-0.08 μg/g, respectively. The results indicate no apparent magnification of either element from sediments to fish in lakes Ontario and Erie.

No water samples that were analyzed showed arsenic or selenium concentrations over the permissible limits of the Canadian Drinking Water Standards.

ACKNOWLEDGMENTS

The authors wish to thank Dr. R.L. Thomas, Canada Centre for Inland Waters, for supplying the sediment samples used for this study, and Dr. Y.K. Chau and

Mr. M.T. Shiomi, for their valuable suggestions and comments.

REFERENCES

1. Anon. 1968. *Merek Index — an Encyclopedia of Chemicals and Drugs*. 8th ed. Rahway, N.J.: Merek & Co. Inc.
2. Browning, E. 1961. *Toxicity of Industrial Metals*. London, England: Butterworths.
3. Luh, M.D., R.A. Baker and D.E. Henley. 1973. "Arsenic Analysis and Toxicity — a Review," *Sci. Total Environ.*, Vol. 2, pp. 1-12.
4. Lymburner, B.D. 1972. *Selenium Production and Use in the Canadian Economy*. CCIW Internal Report, pp. 9, 31-38.
5. Fleischer, M. 1973. "Natural Sources of Some Trace Elements in the Environment," *Proceedings* of Environmental Resources Conference, "Cycling and Control of Metals," October 31 - November 2, 1972, Columbus, Ohio, pp. 3-10.
6. Johnson, H. 1970. "Determination of Selenium in Solid Wastes," *Environ. Sci. Technol.*, Vol. 4, No. 10, pp. 850-853.
7. Grimett, R.E.R. and I.G. McIntosh. July 1940. "Occurrence of Arsenic in Soils and Water in the Waiotapu Valley and its Relation to Stock Health," *Water Pollut. Abs.*, Vol. 13.
8. Copeland, R. 1970. "Selenium: The Unknown Pollutant," *Limnos*, Vol. 3, No. 4, pp. 7-9.
9. Neubauer, O. 1947. "Arsinecal Cancer, a Review," *Br. J. Cancer*, Vol. 1, p. 192.
10. Stocks, P. 1960. "On the Relations between Atmospheric Pollution in Urban and Rural Localities and Mortality from Cancer, Bronchitis and Pneumonia with Particular Reference to 3..4 Benzopyrene, Beryllium, Molybdenum, Vanadium and Arsenic," *Br. J. Cancer*, Vol. 14, p. 397.
11. Fitzhugh, O.G., A.A. Nelson and C.I. Bliss. 1944. "Chronic Oral Toxicity of Se," *J. Pharmacol.*, Vol. 80, pp. 289-299.
12. Vilenkina, G.Y.A. and C.A. Cherkes. 1966. "Nucleic Acid Content in the Liver of Rats Fed a Diet Containing Selenium," *Vopr. Pitan.*, Vol. 25, No. 1, pp. 30-33.
13. Lakin, H.W. 1973. "Selenium in Our Environment. Trace Elements in the Environment," *Advances in Chemistry Series 123*, American Chemical Society, Washington, D.C., p. 96.
14. Department of National Health and Welfare. 1968. *Canadian Drinking Water Standards and Objectives*. Ottawa, Ontario.
15. Goulden, P.D. and P. Brooksbank. 1974. "Automated Atomic Absorption Determination of Arsenic, Antimony, and Selenium in Natural Waters," *Anal. Chem.*, Vol. 46, pp. 1431-1435.
16. Schramel, P., K. Samsahl and J. Pavlu. 1973. "Some Determinations of Hg, As, Se, Sb, Sn and Br in Plants, Sediments and Fishes in Bavarian Rivers," *Int. J. Environ. Stud.*, Vol. 5, pp. 37-40.
17. Hamilton, E.I. 1974. "The Chemical Elements and Human Morbidity, Water, Air, and Places — a Study of Natural Variability," *Sci. Total Environ.*, Vol. 3, pp. 3-85.
18. Kopp, J.F. and R.C. Kroner. 1967. *Trace Metals in Waters of the United States — a Five Year Summary*. Federal Water Pollution Control Administration.
19. Morette, A. and J. Divin. 1965. "Sur le sélénium des eaux — analyse et résultats," *Ann. Pharm. Fr.*, Vol. 23, No. 3, p. 169.
20. Kharkar, D.P., K.K. Turekian and K.K. Bertine. 1968. "Stream Supply of Dissolved Silver, Molybdenum, Antimony, Selenium, Chromium, Cobalt, Rubidium and Cesium to the Ocean," *Geochim. Cosmochim. Acta*, Vol. 32, p. 285.
21. Durum, W.H., J.D. Hem and S.G. Heidel. 1971. "Reconnaissance of Selected Minor Elements in Surface Waters of the United States," *Geological Survey Circular No. 643*, United States Department of the Interior.
22. Shiomi, M.T. and K.W. Kuntz. 1973. "Great Lakes Precipitation Chemistry: Part 1. Lake Ontario Basin," *Proceedings* of 16th Annual Great Lakes Research Conference, IAGLR, Huron, Ohio, April 16-18, pp. 581-602.
23. Hashimoto, Y.K. and J.W. Winchester. 1967. "Selenium in the Atmosphere," *Environ. Sci. Technol.*, Vol. 1, No. 4, pp. 338-340.
24. Ruch, R.R., E.J. Kennedy and N.F. Shimp. 1970. "Distribution of Arsenic in Unconsolidated Sediments from Southern Lake Michigan," *Environ. Geol. Notes, Ill. State Geol. Surv.*, Vol. 37.
25. Wiersma, J.H. and G.F. Lee. 1971. "Selenium in Lake Sediments — Analytical Procedure and Preliminary Results," *Environ. Sci. Technol.*, Vol. 5, No. 12, pp. 1203-1205.
26. Lucas, H.F., Jr., D.N. Edgington and P.J. Colby. 1970. Concentrations of Trace Elements in Great Lakes Fishes," *J. Fish. Res. Board Can.*, Vol. 27, No. 4, pp. 677-684.
27. Beal, A.R. 1974. *A Study of Selenium Levels in Fresh Water Fishes of Canada's Central Region*, Tech. Report CEN/T-74-6, Department of the Environment, Fisheries and Marine Service.
28. Jung, C. and A. Rothstein. 1965. "Arsenate Uptake and Release in Relation to the Inhibition of Transport and Glycolysis in Yeast," *Biochem. Pharmacol.*, Vol. 14, p. 1093.
29. Strauss, R. 1971. "Résistance du *Chara fragilis* Desvaux aux effets toxiques des composés arsenicaux," *C. R. Acad. Sc. Paris, Série D*, Vol. 272, p. 827.

Figures 1 to 8

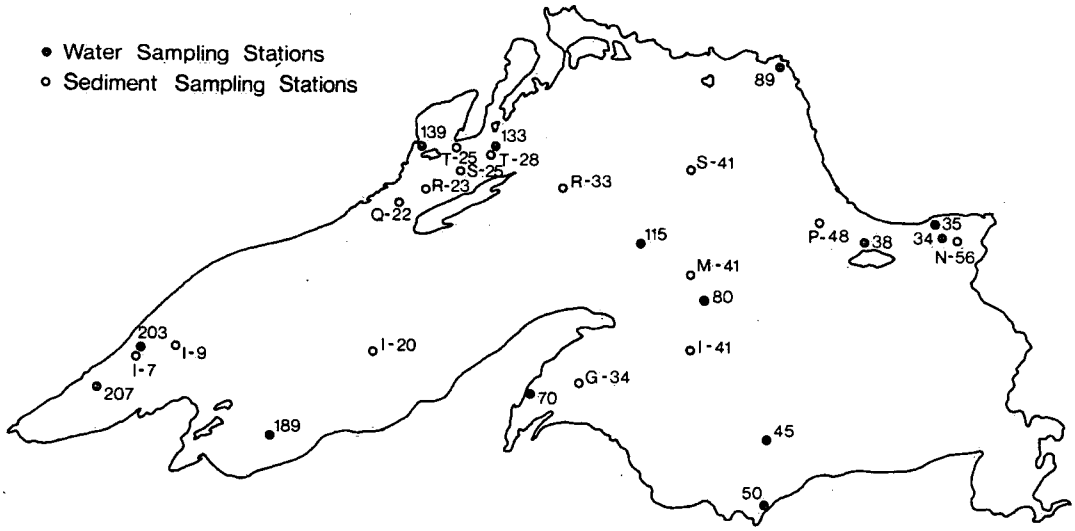


Figure 1. Lake Superior sampling locations.

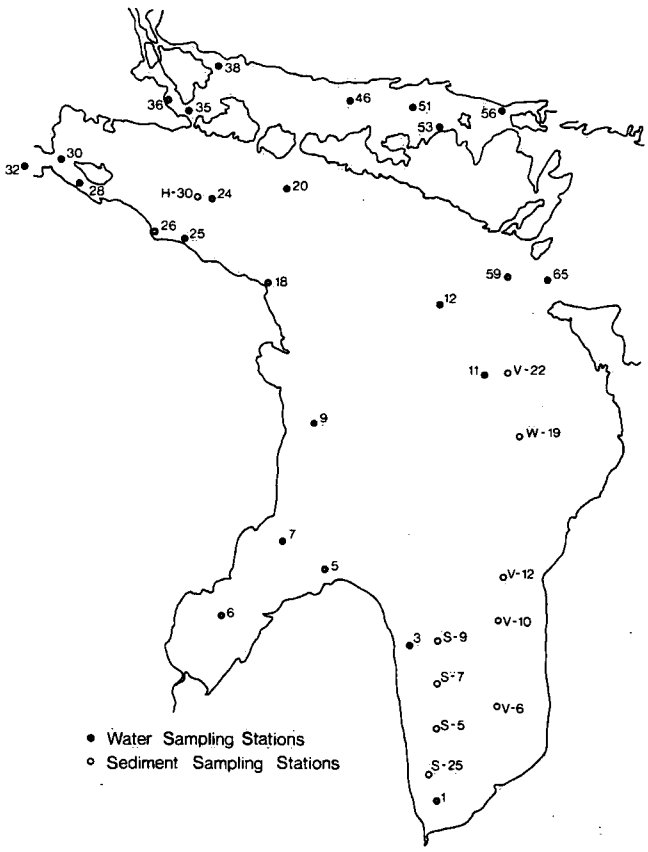


Figure 2. Lake Huron sampling locations.

Figure 3. Georgian Bay sampling locations.

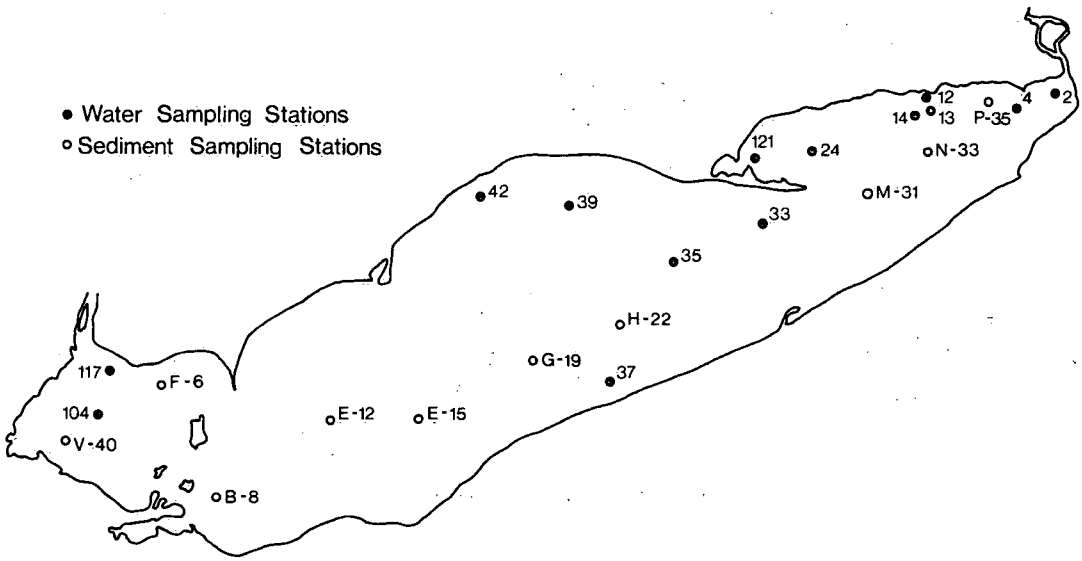


Figure 4. Lake Erie sampling locations.

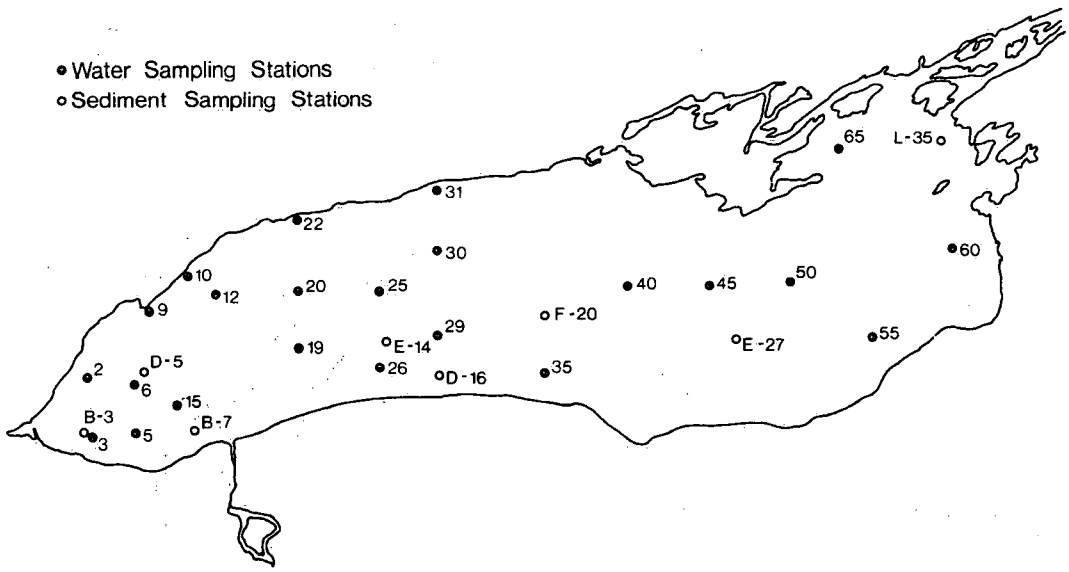


Figure 5. Lake Ontario sampling locations.

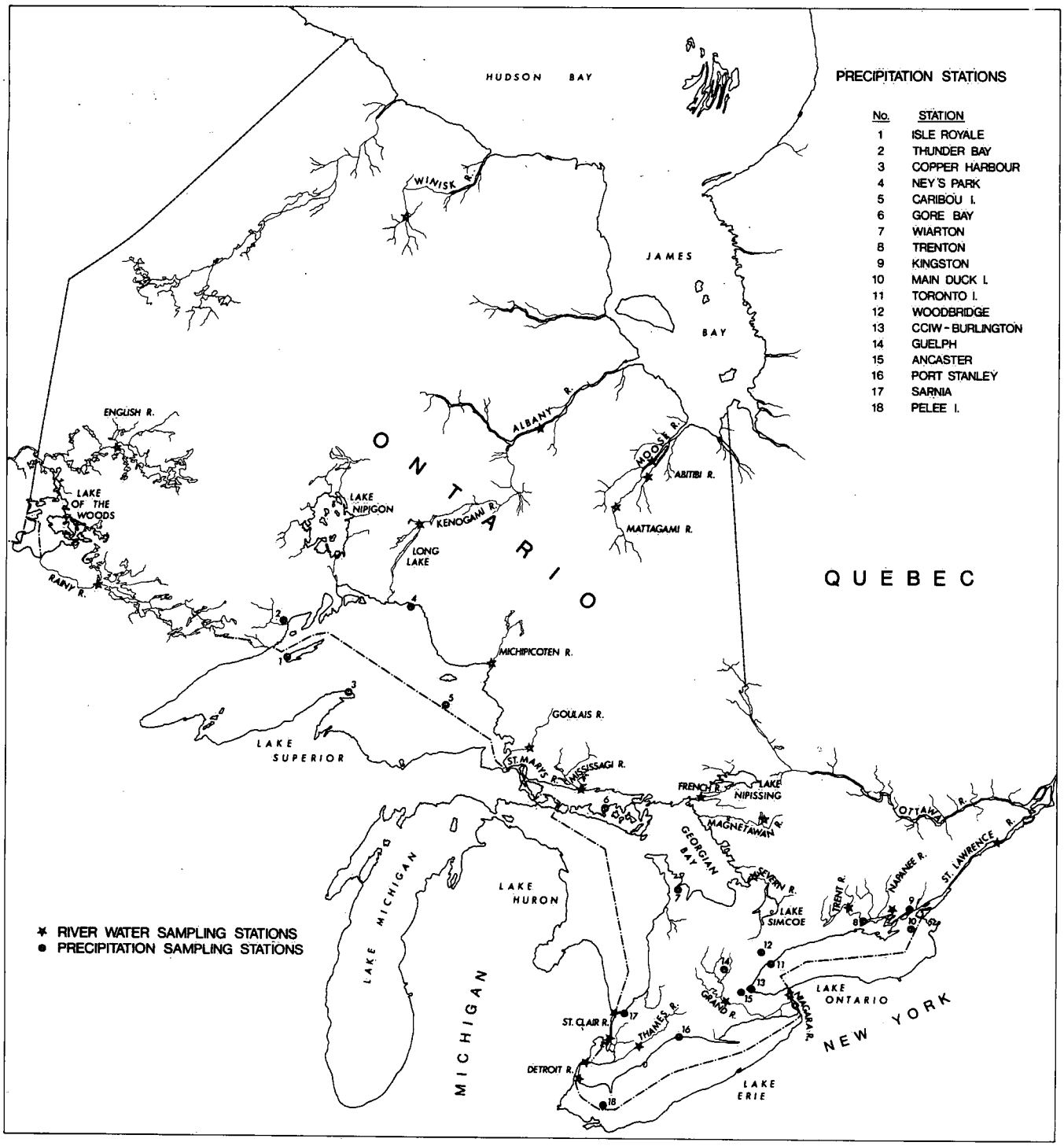


Figure 6. Location of precipitation and surface water stations.

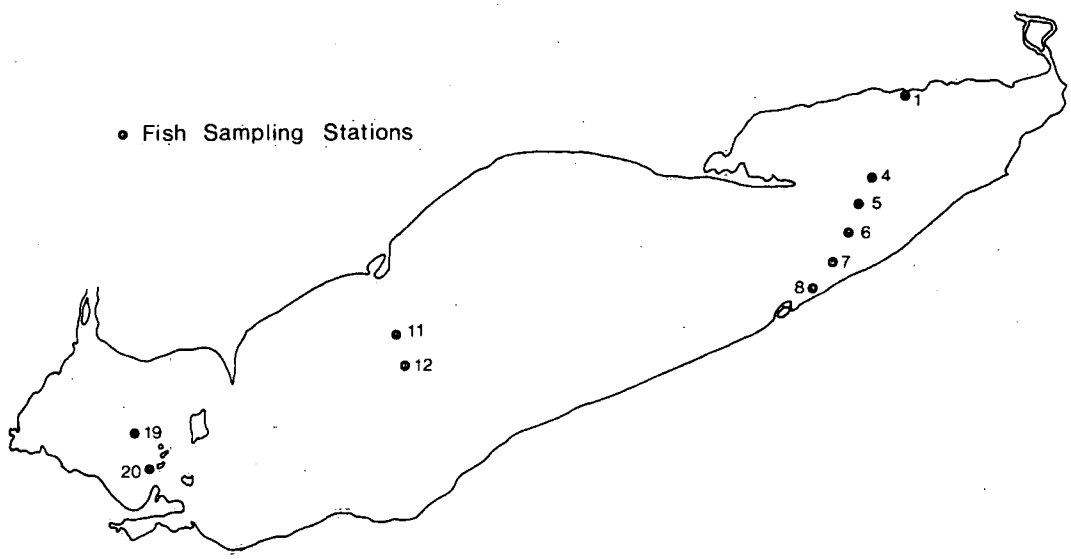


Figure 7. Lake Erie fish sampling locations.

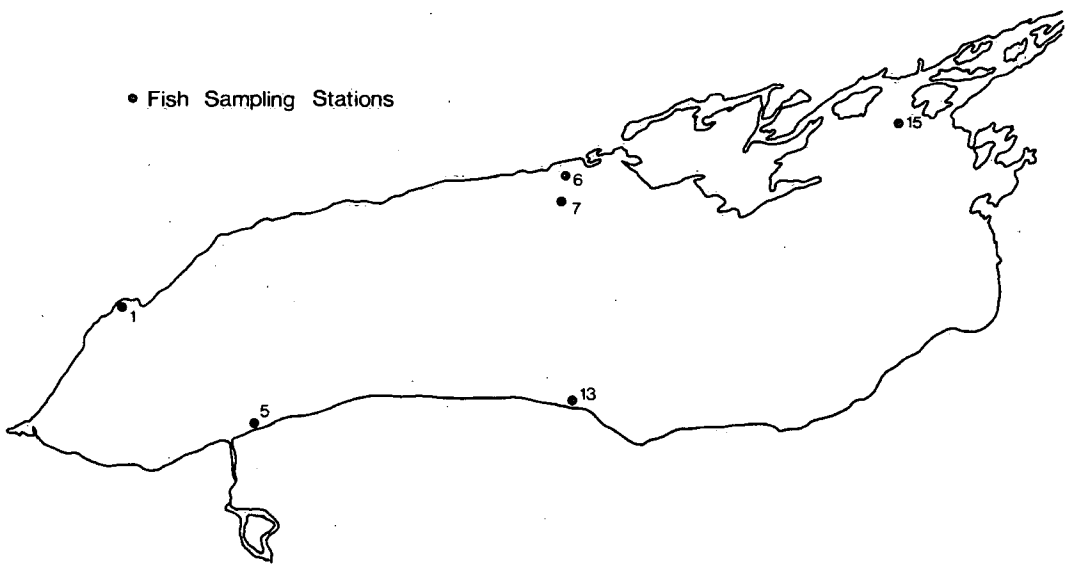


Figure 8. Lake Ontario fish sampling locations.