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Water Resources Center
and
Department of Geology
THE OHIO STATE UNIVERSITY

Strontium Isotope Composition and Trace Element Concentrations in Lake Huron and Its Principal Tributaries

by

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August, 1967

Submitted to:
Office of Water Resources Research,
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Department of Geology
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ABSTRACT

Concentrations of the major cations: Na, K, Ca, Mg and Sr were determined for 64 samples of surface water from Lake Huron and for 17 of its major tributary rivers. For addition, isotopic compositions of strontium were measured for 30 samples of lake water and for 13 of the tributary rivers. Concentrations of dissolved iron and total phosphorus were determined for a small suite of lake and river water.

The data document important differences in the chemical composition of water discharged into Lake Huron by Lake Superior, Lake Michigan and tributary rivers. These differences are related to differences in the chemical and mineralogical composition of the bedrock underlying the Great Lakes drainage basin.

The strontium contributed to Lake Huron by water draining the Canadian Shield along its northern shore is enriched in radiogenic Sr^{87}. The average Sr^{87}/Sr^{86} ratio is 0.718. The rivers draining sedimentary rocks of Michigan and southwestern Ontario contribute strontium whose isotope composition is similar to that in the modern oceans and has a Sr^{87}/Sr^{86} ratio of 0.710.

A geochemical model is presented which attempts to represent the chemical composition of water in Lake Huron as a mixture of the different types of water discharged by different sources.

STATEMENT OF THE SIGNIFICANCE AND APPLICABILITY OF THE RESULTS

The information presented in this report emphasizes the close relationship of the chemical composition of the water in Lake Huron to the geology of its drainage basin. It is shown that the concentrations of several trace elements, such as sodium, calcium, and strontium, in Lake Huron are significantly increased by the rivers draining Michigan and southwestern Ontario, even though these rivers contribute less than 15 per cent of the total amount of water entering the lake. It is suggested, but not yet proved, that the above-mentioned elements are products of weathering of carbonate rocks and rock salt present in southwestern Ontario and Michigan.

In order to assess, in a quantitative way, the importance of this area as a source of pollution of Lake Huron, it is necessary to measure the chemical composition of the major rivers at regular intervals for several years. The information available now is not adequate to determine the total quantity of chemical elements discharged into Lake Huron annually.

The measurements of the concentration and isotope composition of strontium in Lake Huron and its tributaries are the first measurements of this kind in the Great Lakes. An understanding of the movement of strontium through the Great Lakes is of potential value to studies dealing with the dispersal of radioactive Sr^{90} produced as fall-out of atomic weapons tests.

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INTRODUCTION

The drainage basin of Lake Huron is underlain by two distinctly different types of rock. Figure 1 shows that the bedrock in northern Ontario consists of igneous and metamorphic rocks of Precambrian age. Numerous age determinations of biotite mica from these rocks have been published by Wanless et. al. (1967) who found dates ranging from about 800 m.y. (million years) to 2620 m.y. In addition, Lake Huron receives water from Lake Superior which also drains igneous and metamorphic rocks of Precambrian age.

The southern part of the drainage basin in Michigan and southwestern Ontario is underlain entirely by sedimentary rocks of Paleozoic age. These rocks consist of limestone, dolomite and shale as well as sequences of evaporite deposits containing rock salt, gypsum and anhydrite. Lake Huron also receives water from Lake Michigan which drains predominantly sedimentary rocks of Paleozoic age but does receive some water draining the Precambrian terrane of Wisconsin.

The chemical composition of the igneous and metamorphic rocks differs in several important respects from that of the sedimentary rocks. The difference arises primarily because of the presence of carbonate rocks and evaporites in the sedimentary sequences. Under temperate climatic conditions, such as those prevaling in the Great Lakes region, carbonate rocks are weathered by solution in dilute carbonic and humic acid. As a result, water draining areas underlain by such rocks are characterized by high concentrations of calcium, magnesium and strontium. Sodium or potassium may be contributed by solution of rock salt or

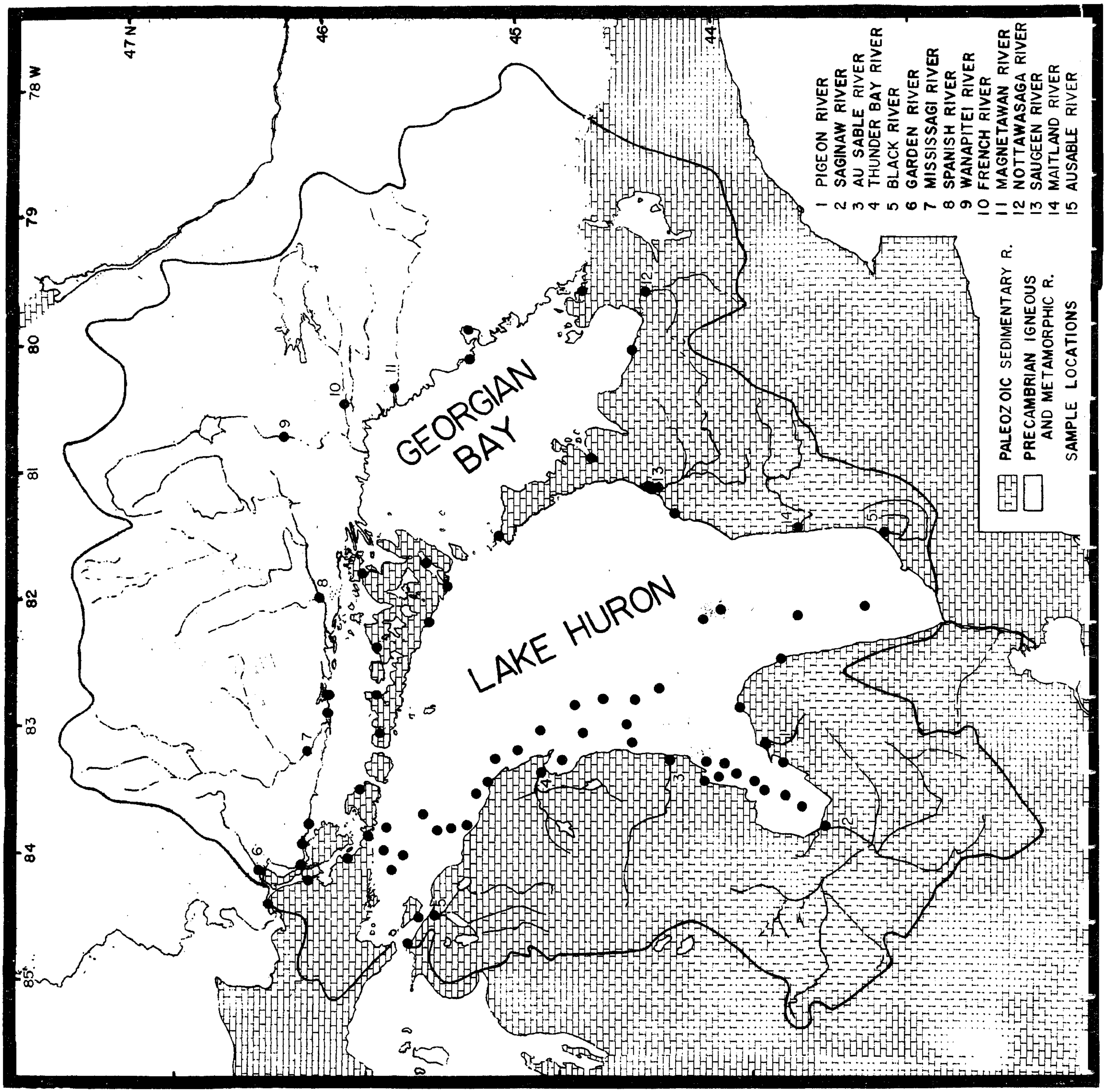

Figure 1. Lake Huron and its principal tributaries.

discharge of brines. It is to be expected, therefore, that the water contributed to Lake Huron by drainage of the regions underlain by sedimentary rocks differs in its chemical composition from water draining the Precambrian Shield. These two types of water mix during their passage through Lake Huron. The chemical composition of water samples from Lake Huron should reflect the progressive mixing of water derived from the Precambrian Shield with water draining sedimentary rocks.

In addition to differences in the chemical composition of the water, differences are also expected in the isotope composition of strontium derived from the Precambrian Shield as compared to strontium derived from the sedimentary rocks of Paleozoic age. The isotope composition of strontium in rocks and minerals changes continuously as a function of time by the addition of radiogenic Sr^{87}. This isotope is produced by radioactive decay of naturally-occurring Rb^{87} which decays by beta-decay with a half-life of 50×10^9 years. The ratio of Sr^{87} to the non-radiogenic and stable isotope Sr^{86} in a rock depends on the following parameters: a) the value of the Sr^{87}/Sr^{86} ratio at the time of formation of the rock or mineral; b) the ratio of Rb to Sr in the material; c) the length of time elapsed since the rock or mineral was formed. The igneous and metamorphic rocks of the Precambrian Shield are commonly enriched in rubidium relative to strontium and have existed for long periods of geologic time. They have therefore become enriched in radiogenic Sr^{87} which has accumulated within them by the continuous decay of Rb^{87}. The sedimentary rocks of southwestern Ontario and Michigan, on the other hand, are all less than 600 m.y. old and contain less rubidium relative to strontium than the rocks of the Precambrian Shield. This is particularly true of the carbonate rocks which have high strontium concentrations but contain very little rubidium (Turekian and Kulp, 1956 and Horstman, 1957). As a result, the strontium released by weathering of the rocks in southwestern Ontario and Michigan should have a lower Sr^{87}/Sr^{86} ratio than the strontium which originates on the Precambrian Shield. Measurements of the isotope composition of strontium extracted from water and mollusk shells in the Great Lakes region by Faure, Hurley and Fairbairn (1963) and Faure, Crocket and Hurley (1967) have confirmed the existence of this difference.

The objective of this study is to explore the feasibility of representing the chemical composition of water in Lake Huron in terms of a continuously varying mixture of two water types. To this end we have determined concentrations of Na, K, Ca and Mg in sixty water samples collected from Lake Huron, ten tributary rivers in Michigan and southwestern Ontario and seven rivers which drain the Precambrian Shield in northern Ontario. In addition, water samples from the other Great Lakes were analyzed for comparison.

Isotope compositions and concentrations of strontium were measured on all of the available river waters and for a representative number of samples from Lake Huron. These, as well as the chemical analyses, will be examined in detail to evaluate their usefulness in representing the chemical composition of water samples from Lake Huron as mixtures of two distinctly different water types.

Chemical analyses of water from Lake Huron and hydrologic studies have been reported by Allen (1964), Ayers, Anderson, Chandler and Lauff (1956), Livingstone (1963), Rodgers (1962) and Thomas and Gale (1965). No attempt has been made, to our knowledge, to construct a chemical model for Lake Huron along the lines we have proposed here.

In a related study Mr. René Eastin has measured concentrations of Na, K, Ca and Sr as well as isotope compositions of Sr, in water samples from the Scioto and Olentangy Rivers of Ohio. The water samples were collected at weekly intervals throughout 1966 and were analyzed as four-week composites. The objective of this study was to obtain information on the seasonal variations in the chemical compositions of these rivers. Excerpts from Mr. Eastin's dissertation are presented elsewhere in this report.

COLLECTION OF WATER SAMPLES

This study is based on water samples collected during September of 1963 and June and August of 1966. All samples are surface water and, except for the suite collected in August of 1966, were collected from shore. In August of 1966 Mr. Mason Christner was permitted to collect a suite of twenty-four samples from Lake Huron as a guest on The Kaho, operated by The Bureau of Commercial Fisheries.

At each station approximately two liters of water were collected and stored in two tightly-capped and sealed one-liter polyethylene bottles. Prior to analysis the water was filtered using either S 8 S 589 Blue Label filter paper or a Selas Fine B-4 inch filter attached to a vacuum pump.

ANALYTICAL METHODS

Concentrations of Na, K, Ca and Mg in water samples were determined by Miss Lois M. Jones. Na and K were measured by flame photometry using a Beckman DU-2 spectrophotometer with a flame attachment, Ca was determined by titration with EDTA, while Mg was measured by a spectrophotometric method using Titan Yellow. A small suite of samples was analyzed for total iron and dissolved in phosphorus.

Concentrations of strontium in water samples were measured by the method of isotope dilution using "spike solutions" enriched in Sr^{86}. The isotope composition of strontium was determined separately on unspiked strontium extracted from the water. The following is a summary of the analytical methods and procedures used in this study.

Determination of Sodium

Sodium was determined by flame photometry using the D-line at 589.6 $m\mu$. Data published by Dean (1960) indicate that no serious interference by other elements should occur in these water samples. Nevertheless, we demonstrated that 2.5 ppm Na could be detected without interference in the presence of 5 ppm K, 50 ppm Ca, 10 ppm Mg, 5 ppm Al, 5 ppm Fe^{+3}, 1750 ppm Cl^-, 20,000 ppm $SO_4^=$ and 30,000 ppm NO_3^-. According to Dean (1960, p. 166), the effects of carbonate and bicarbonate ions on the emission of Na is negligibly small. Phosphate interferes only at concentrations in excess of 500 ppm. It is unlikely that phosphate concentrations of this magnitude will be encountered in natural water samples.

Concentrations of Na in the water samples were determined from calibration curves or by the "bracketing" method in which the sample is compared to two standard solutions having slightly higher and lower known concentrations than the sample. Calibration curves showing Na concentration in ppm (parts per million) versus per cent transmission were constructed in ranges from 0 to 25 ppm, 0 to 5 ppm, and 0 to 1 ppm Na. These are shown as Figures 2, 3, and 4 respectively. Figure 2 shows the effect of increasing self-absorption with concentrations of Na in excess of about 10 ppm. Beyond this value the curve is distinctly non-linear. In the range 0 to 5 ppm Na (Figure 3) the calibration curve is a remarkably good straight line. The sensitivity of the instrument for the detection of Na is sufficient to produce a measurable response for less than 0.01 ppm of Na, as shown in Figure 4. Samples whose Na concentration exceeded 25 ppm were diluted with double-distilled and demineralized water to bring them into the range of the calibration curves.

Determination of Potassium

Potassium was determined by flame photometry using the resonance doublet at 766 and 769 mμ. A calibration curve in the range 0 to 2 ppm was established and was found to be linear as shown in Figure 5.

The emission of potassium at the 2 ppm concentration level was found to be unaffected by the presence of 50 ppm Ca, 10 ppm Mg, 1 ppm Fe, and 1 ppm Al. The presence of sodium, however, caused an enhancement of the potassium

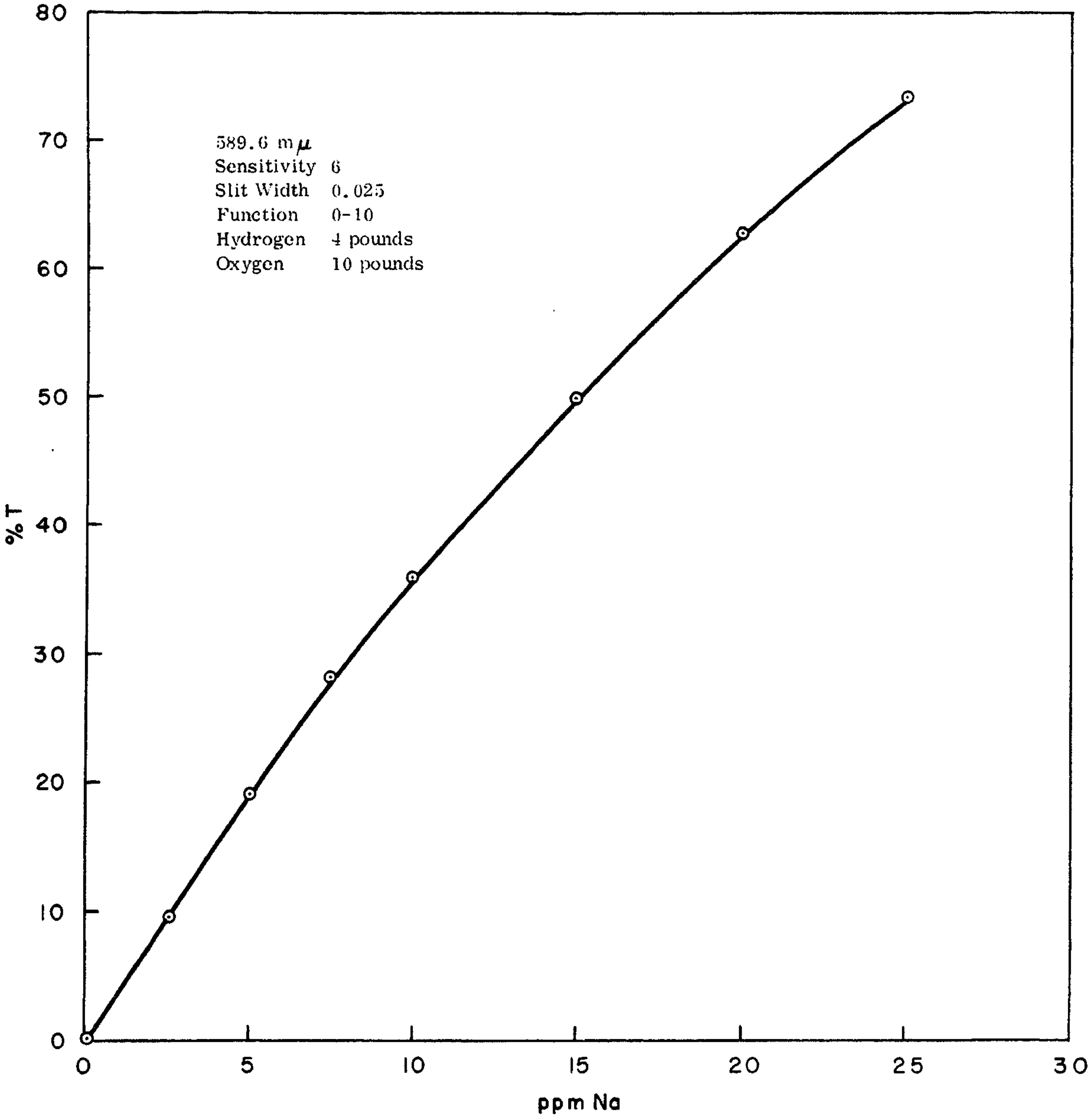

Figure 2. Relative intensity of sodium emission as a function of the sodium concentration.

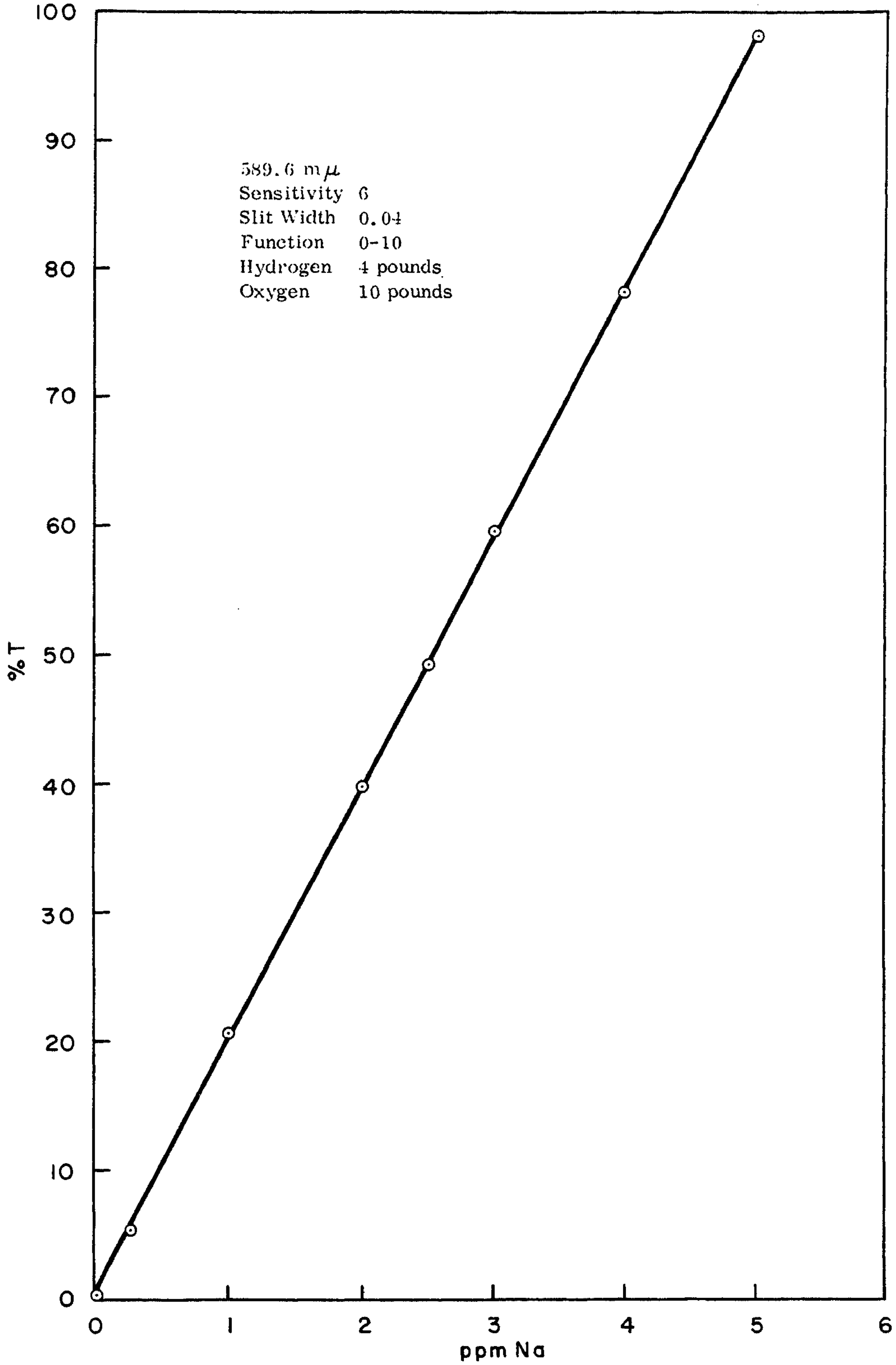

Figure 3. Relative intensity of sodium emission as a function of the concentration of sodium.

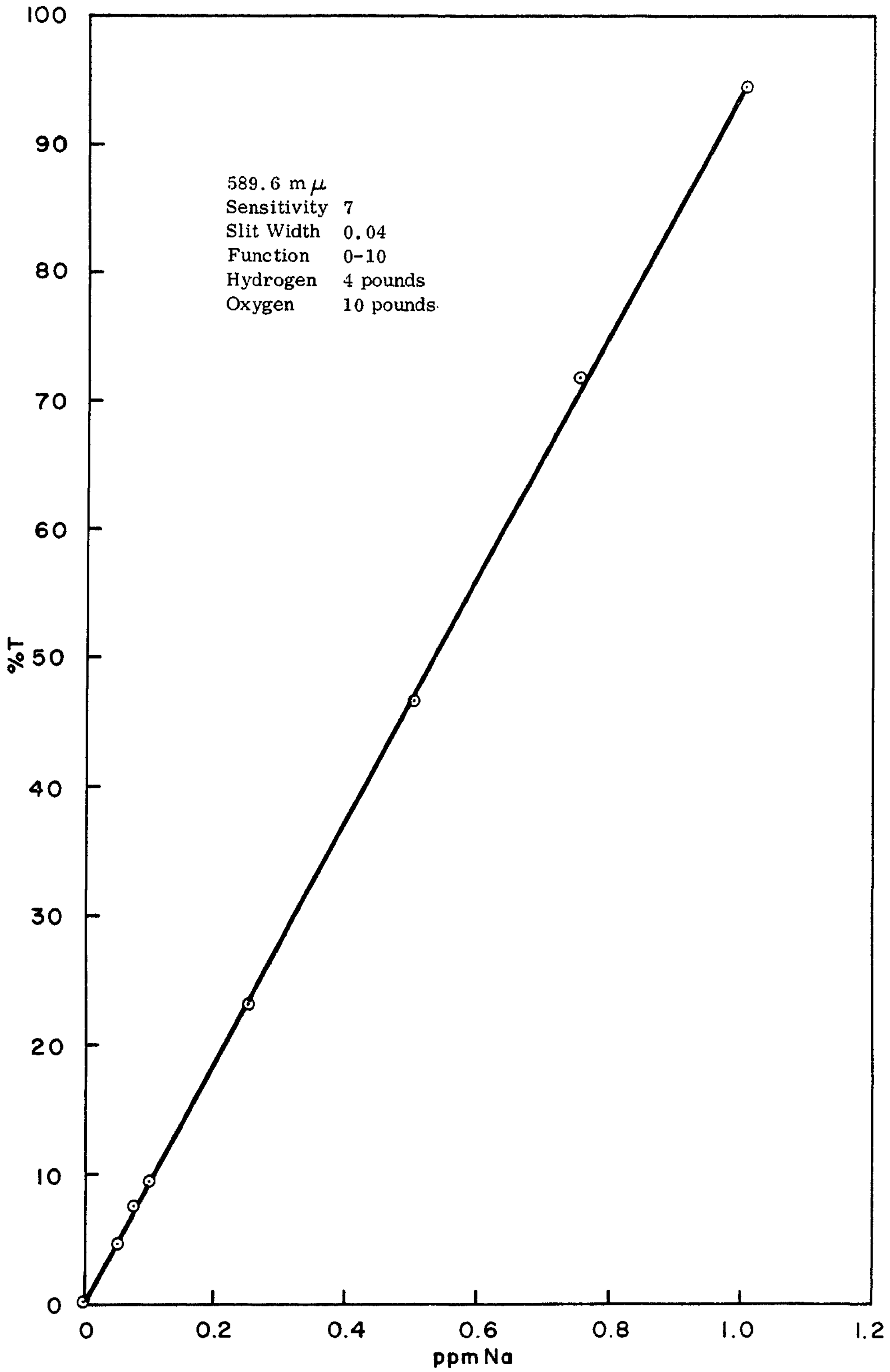

Figure 4. Relative intensity of sodium emission as a function of the sodium concentration.

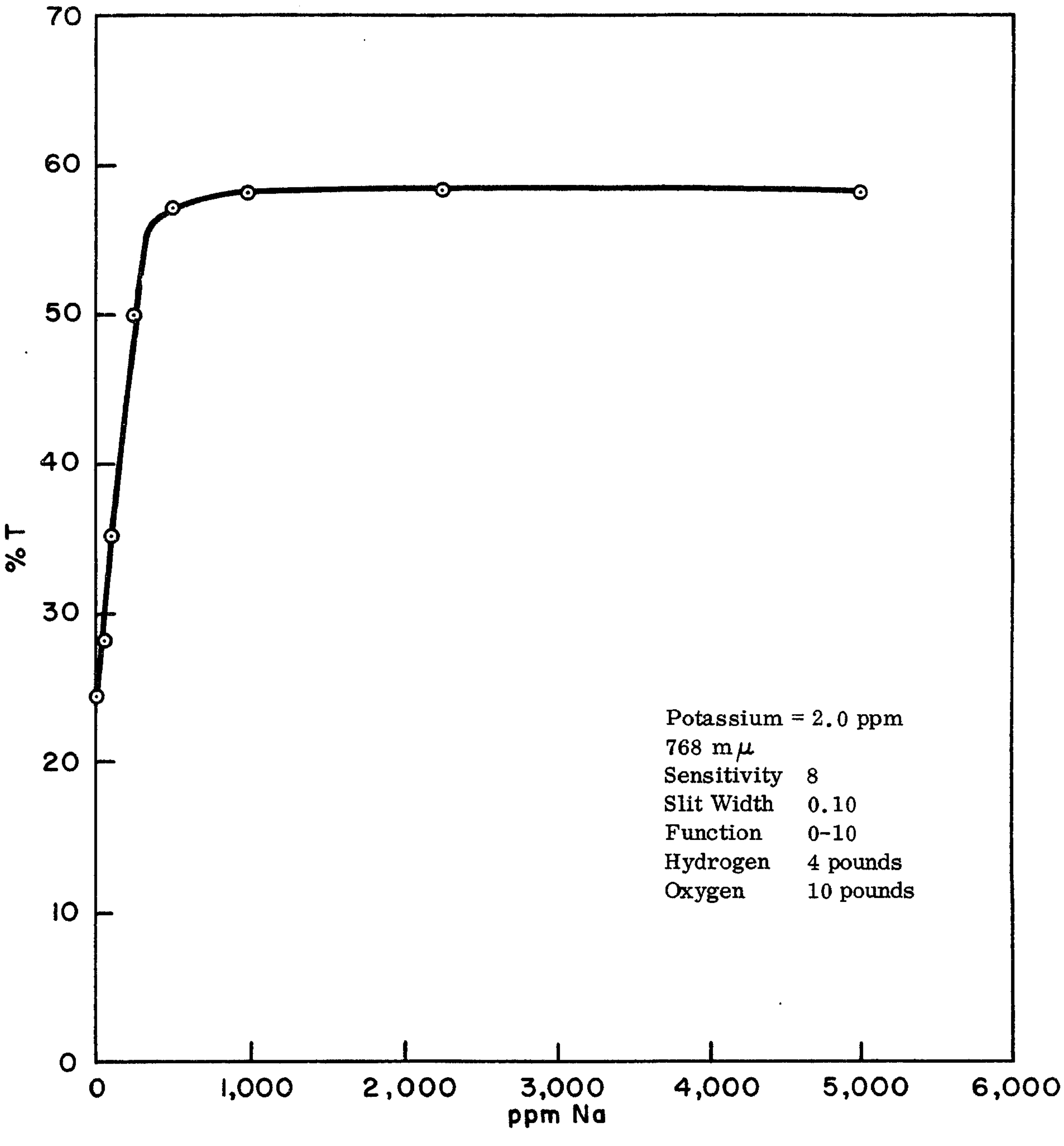

Figure 5. The effect of increasing sodium concentration on the emission of potassium.

emission. Figure 6 illustrates the increase in per cent transmission for 2 ppm K with increasing sodium concentration. It can be seen in Figure 6 that above a concentration of about 2000 ppm sodium, interference with potassium becomes constant. The interference of sodium in the emission of potassium was eliminated by the addition of solid reagent-grade NaCl to the samples to increase their sodium concentration above 2000 ppm. The high concentration of NaCl in the samples caused periodic blockage of the capillary tube in the burner of the flame photometer and detracted from the reproducibility of the potassium determinations.

Determination of Calcium

Calcium was determined by titration with EDTA (disodium (ethylenedinitrilo tetraacetate) at a pH $\geq$ 12. The indicator was Hydroxy Naphthol Blue A.R., marketed by Mallinckrodt Chemical Works. The color change of the indicator at the endpoint is sharp and is from red to blue. This color change can be easily determined visually. Interference caused by the presence of Al, Fe and other metals was eliminated by the addition of hydroxylamine hydrochloride and 2, 2', 2''-nitrilotriethanol. The pH of the water samples was adjusted to 12.0 to 12.5 with NaOH, the indicator was added and the solutions were then titrated visually with EDTA to a blue endpoint.

Efforts to determine calcium by flame photometry were abandoned when it became apparent that 1 ppm Al or 5 ppm Na depressed the emission of calcium by as much as 50 per cent.

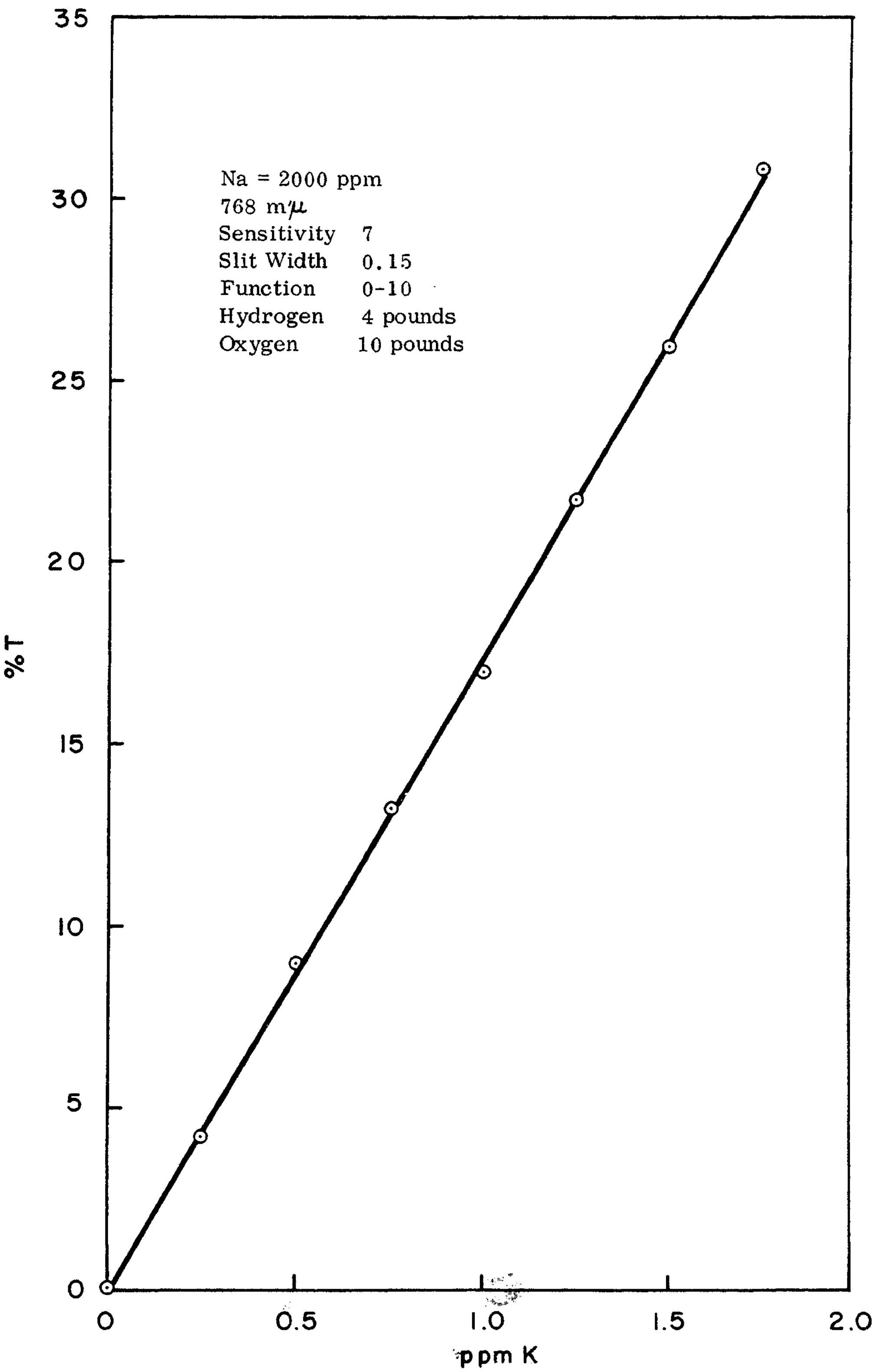

Figure 6. Emission of potassium as a function of concentration.

Determination of Magnesium

Concentrations of magnesium in the water samples were determined directly by a spectrophotometric method similar to that of Meyrowitz (1964). It involves the use of Titan Yellow and is relatively free of interference from other elements.

Magnesium was also determined indirectly by titration with EDTA at a pH of 10 followed by a calcium determination at pH ≥ 12. The magnesium concentration is then obtained by difference. This method was found to be unreliable and gave negative Mg concentrations for samples having high Ca/Mg ratios. All magnesium determinations reported here were made by the direct spectrophotometric method.

Determination of Total Phosphorus

Phosphorus was determined by the modified Heteropoly Blue method described by Boltz (1958). The precedure which we used determines the total dissolved phosphorus concentration of the samples.

Known volumes (500 to 1000 ml) of filtered water were evaporated to dryness in pyrex beakers, followed by wet oxidation of the residue with HNO_3 and HCl. The residue was then taken to fumes with $HClO_4$. The resulting solution was diluted to a known volume with double-distilled and demineralized water. Aliquots of this solution were taken for the determination of phosphorus and iron.

The phosphate concentration was determined by extracting the phosphomolybdate complex with isobutyl alcohol followed by reduction of the complex with stannous chloride. The alcohol layer was collected from a separatory funnel and diluted to a known volume with isobutyl alcohol. The absorbance of this solution at 725 mμ was measured in a Beckman Model DU-2 Spectrophotometer. The phosphate content of unknowns was determined by comparison to a calibration curve prepared from solutions containing known amounts of phosphate.

Determination of Total Iron

Total iron was determined in an aliquot of the solution prepared for the phosphorus analysis. After buffering the solution at pH=3.5 with sodium acetate, the iron was reduced with hydroxylamine hydrochloride and complexed with 1,10-phenanthroline. The absorbance was measured at 500 mμ and compared with a calibration curve prepared from solutions of known iron concentration.

Determination of Strontium

Concentrations of strontium were measured by the method of isotope dilution using a "spike" solution enriched in Sr^{86}. The principles on which this method is based were summarized by Webster (1960). The strontium spike used in this work was purchased from the Oak Ridge National Laboratory (Batch No. LH 1368 A). The isotopic composition of the spike was measured on a mass spectrometer and was found to be (in atom per cent): $Sr^{86} = 97.6$, $Sr^{88} = 1.69$, $Sr^{87} = 0.65$ and $Sr^{84} = 0.014$. The spike solution was added to known volumes of water by pipetting. The concentration of strontium of the spike solution was determined by separate isotope dilution experiments using a shelf solution of strontium of normal isotope composition and prepared from "spec-pure" $Sr(NO_3)_2$ marketed by Johnson, Mathy, and Co., Ltd.

The strontium in the samples was separated by cation exchange chromatography using Dowex 50W-X8, 200-400 mesh, packed in glass columns 25 cm long and about 1 cm wide. The passage of strontium through the columns was monitored by detecting the radioactivity of a small amount (less than 5 microcuries) of Sr^{89} added to the solutions. The eluant was 2 N HCl, predistilled in vycor glass.

The strontium fraction was evaporated to dryness and placed on the filament of a mass spectrometer for isotopic analysis. The mass range 86 to 88 was scanned 30 to 42 times and the ratio Sr^{86}/Sr^{88} was calculated from the heights of the peaks on the mass spectrum. The concentration of strontium in the water sample was then calculated from the measured 86/88 ratio of the mixture of normal and spike strontium.

Measurement of the Isotope Composition of Strontium

The isotope composition of strontium in the water samples was measured on a mass spectrometer built by Nuclide Corporation (Model 6-60-S). The strontium was extracted as described above from unspiked aliquots of the water samples. The strontium was applied as the chloride or nitrate to a pre-cleaned tantalum filament in the source of the mass spectrometer. Ion beams were produced by thermal evaporation and ionization of strontium from the single filament and measured by means of a Vibrating Reed Electrometer. From 40 to 60 consecutive scans were taken across the mass range from 86 to 88 and peaks were recorded on a 10 inch strip chart recorder. Peak heights were averaged in sets of six and the final Sr^{87}/Sr^{86} ratio for each run was calculated as the average of the ratios based on 6 to 10 sets of scans. A fractionation correction was applied to the measured Sr^{87}/Sr^{86} ratios based on the assumption that the Sr^{86}/Sr^{88} ratio has a value of 0.1194 and that fractionation is a function of mass differences (Faure and Hurley, 1963).

PRECISION AND ACCURACY

The precision of the chemical and isotopic analyses was evaluated for each element on the basis of duplicate or triplicate determinations. The accuracy was assessed by analysis of standards of known chemical composition and, in the case of calcium, by using two different methods of analysis.

Sodium

Out of a total of 103 samples which have been analyzed for sodium, 86 were determined in duplicate. Triplicate analyses were done whenever the duplicates appeared to be discordant. In this case the value we are reporting is the average of the two closest determinations. The differences between duplicate sodium determinations, expressed as a per cent of their mean, ranged from 0 to about 6 per cent, averaging 1.5 per cent. This indicates that duplicate sodium determinations differ from each other by 1.5 per cent, on the average.

The accuracy of the sodium determinations was checked by analyzing two rock standards: G-1 and W-1 for which numerous chemical analyses have been reported. Our analyses of G-1 and W-1 are presented in Table 1 and are compared there to the preferred values recommended most recently by Fleischer (1965). The agreement of our results with the recommended values is in all cases satisfactory, as can be seen by reference to Table 1.

Potassium

The reproducibility for potassium is not as good as for sodium. The differences between 83 duplicate analyses varied from 0 to about 29% of their means. On the average the difference is 5.4%.

The accuracy of the potassium determinations is satisfactory on the basis of our analyses of the rock standards G-1 and W-1, shown in Table 1.

Calcium

The reproducibility and accuracy of the calcium determinations is suggested by a set of 12 duplicate analyses, shown in Table 2. These samples were originally analyzed by Faure, Crocket and Hurley (1967) who used an EDTA titration procedure with a recording spectrophotometer and murexide as indicator. The same water was re-analyzed by Lois M. Jones using the method described earlier. The differences between these duplicate determinations range from 0 to 7.6% and average about 3%.

The results of our calcium analyses for the rock standards G-1 and W-1 are in satisfactory agreement with the recommended values.

Table 1

Analyses for Rock Standards G-1 and W-1 in Units of Weight Per Cent

	G-1		W-1	
	This Work	Recommended Fleischer (1965)	This Work	Recommended Fleischer (1965)
Na_2O	3.33	3.32	2.20	2.07
	3.39		2.17	
	3.38		2.22	
K_2O	5.47	5.45	0.66	0.64
	5.49		0.62	
	5.44		0.65	
CaO	1.19	1.39	10.91	10.96
	1.22		10.93	
	1.31		10.99	
MgO	0.34	0.41	6.46	6.62
	0.40		6.56	
	0.39		6.64	
Sr	254.8	250 ppm	187.8	180
	248.8		191.8	

Table 2

Comparison of Calcium Analyses of Identical Samples

Sample No.	Faure et al. (1967) µg/ml	This work. µg/ml
F - 63 - 5	33.0	31.6
F - 63 - 12	13.5	13.8
F - 63 - 14	13.9	15.0
F - 63 - 16	14.6	14.1
F - 63 - 22	14.6	14.2
F - 63 - 26	14.3	14.7
F - 63 - 27	19.5	20.0
F - 63 - 28	24.3	25.1
F - 63 - 39	14.6	14.1
F - 63 - 46	20.8	21.1
F - 63 - 51	24.5	24.3
F - 63 - 60	27.5	27.5

Magnesium

A total of 34 magnesium determinations were carried out in duplicate. The differences between duplicates range from 0 to 3% of their means and average about 0.6%.

The accuracy of the magnesium determinations of G-1 and W-1 (Table 1) are in satisfactory agreement with the recommended values.

Iron and Phosphorus

The reproducibility of the iron and phosphorus determinations is believed to be better than 5%, on the basis of past experience. No duplicate determinations were made.

The concentration of total iron is very sensitive to the presence of suspended mineral particles or organic matter in the water. Table 5 allows a comparison of the apparent total iron concentrations in filtered and unfiltered water samples. It is clear from the data that filtration (S + S, No. 589, Blue Ribbon) reduces the detectable iron concentration by as much as one order of magnitude.

Strontium

The concentrations of strontium in three water samples were determined in duplicate by Eastin (1967). The water samples were collected at different times from the Olentangy and the Scioto Rivers at Columbus, Ohio, during 1966. The results of Eastin's analyses are shown in Table 3. They indicate that duplicate

Table 5

Apparent Total Iron Concentration of Unfiltered and Filtered Water Samples

Sample Number	Locality	Unfiltered Fe, µg/ml	Filtered* Fe, µg/ml
C-66-1	Maumee River, Maumee, Ohio	0.44	0.058
C-66-4	Saginaw River, Bay City, Mich.	0.33	0.060
C-66-8	St. Mary's River, Sault Ste. Marie, Mich.	0.062	0.040
C-66-9	Garden River, Rte. 17, Ont.	0.13	0.11
C-66-10	Mississagi River, Rte. 17, Ont.	0.16	0.062
C-66-17	Wanapitei River, Rte. 69, Ont.	0.17	0.081
C-66-22	Nottawasaga River, Evendale, Ont.	0.48	0.058
C-66-23	Saugeen River, Port Elgin, Ont.	0.074	0.046
C-66-25	Aux Sables Grand Bend, Ont.	1.62	0.068
C-66-27	Lake Erie, Port Dover, Ont.	0.85	0.044
C-66-30	Lake Erie Dunkirk, Ohio	0.45	0.060

* Filtered using S+S, No 589 Blue Ribbon Filter Paper.

Table 3

Duplicate Determinations of the Concentrations of Strontium in Water from the Olentangy and Scioto Rivers at Columbus, Ohio (From Eastin, 1967, p. 41)

Sample Number	Sr, μg/ml
0 - 2	1.194
	1.185
0 - 3	0.817
	0.820
S - 1	2.120
	2.141

strontium determinations differ from each other by 0.4 to 1.0%, averaging 0.7%.

The accuracy of the analyses is indicated by duplicate strontium determinations of the rock standards G-1 and W-1 (Table 1) made by Kovach (1967) and Chandhuri (1966) in this laboratory.

Strontium Isotope Composition

The reproducibility of the Sr^{87}/Sr^{86} ratio was checked periodically by re-analyzing a strontium isotope standard ($SrCO_3$, Eimer and Amend, lot 492327). The results of fourteen isotopic analyses of this strontium are compiled in Table 4. The averages of the isotope ratios and their standard deviations are:

$$(Sr^{87}/Sr^{86}) = 0.7084 \pm 0.0004 \ (\delta)$$

$$Sr^{86}/Sr^{88} = 0.1180 \pm 0.0005 \ (\delta)$$

These values are in good agreement with results obtained by other investigators for this standard and provide an estimate of both the reproducibility and accuracy of these measurements.

Table 4

Analyses of the Isotopic Composition of Strontium of the Eimer and Amend, $SrCO_3$ (Lot #492327)

This work.

Date	(Sr^{87}/Sr^{86})*corr.	$Sr^{86}Sr^{88}$	Analyst
6/24/65	0.7084	0.1177	Faure
9/9/65	0.7080	0.1185	Chaudhuri
9/23/65	0.7084	0.1176	Chaudhuri
10/26/65	0.7089	0.1177	Chaudhuri
11/8/65	0.7074	0.1177	Chaudhuri
12/7/65	0.7083	0.1182	Faure
12/28/65	0.7084	0.1174	Kovach
5/25/66	0.7082	0.1180	Chaudhuri
6/13/66	0.7084	0.1189	Montigny
8/12/66	0.7084	0.1173	Montigny & Jones
2/8/67	0.7082	0.1179	Montigny
5/10/67	0.7090	0.1184	Fenton
5/25/67	0.7087	0.1182	Jones
6/19/67	0.7085	0.1181	Jones
Averages:	0.7084 ±0.0004	0.1180 ±0.0005	This work.

*Corrected to $Sr^{86}/Sr^{88} \simeq 0.1194$

PRESENTATION AND DISCUSSION OF THE RESULTS

The analytical data for Lake Huron and its major tributaries are compiled in Table 6. The discussion of their significance is illustrated by Figures 7, 8, 9, 10, and 11. The interpretation of the chemical characteristics of natural water samples has been reviewed by Hem (1959).

The data in Table 6 are grouped according to the source of the water samples, starting with the rivers draining rocks of the Precambrian Shield, rivers draining the sedimentary rocks of Paleozoic age from Michigan and southwestern Ontario, followed by the samples from the North Channel, the Georgian Bay, Saginaw Bay and the Central Area of Lake Huron. Concentrations of Na, K, Mg and Ca are expressed in units of micrograms per milliliter, while Sr is given in units of micrograms per liter. The isotope composition of strontium is represented by the ratio of Sr^{87}/Sr^{86}, corrected for isotope fractionation, as discussed in the previous section. The concentrations of iron and phosphorus are tabulated separately in Table 11.

The Tributary Rivers of Lake Huron

As noted in the Introduction, the tributary rivers of Lake Huron drain two distinctly different types of bedrock. Along the north shore water is discharged which drains igneous and metamorphic rocks of the Canadian Shield. The water draining Michigan and southwestern Ontario, on the other hand, drains sedimentary rocks which include carbonate rocks and evaporite sequences. The data com-

Table 6

Analytical Data for Water Samples from Lake Huron and its Major Tributaries

Sample Number	Locality	Collection Date	Na µg/ml	K µg/ml	Mg µg/ml	Ca µg/ml	Sr µg/l	Sr^{87}/Sr^{86}
Rivers draining igneous and metamorphic rocks of the Canadian Shield.								
F-63-12	St. Mary's R.	9/5/63	1.24	0.60	2.8	13.8	21.5	
C-66-8	Sault Ste. Marie	6/21/66	1.37	0.53	2.3	14.7		
F-63-42	Garden River	9/11/63	1.45	0.54	2.2	8.8	30.2	0.7191
C-66-9	Rte. 17, Ont.	6/21/66	1.24	0.44	1.3	8.6		
F-63-47	Mississagi R.	9/11/63	1.13	0.59	2.1	10.0	23.9	0.7179
C-66-10	Rte. 17, Ont.	6/21/66	1.03	0.45	1.3	8.9		
F-63-49	Spanish River	9/11/63	14.8	0.78	2.1	11.2	31.8	0.7209
C-66-12	Massey, Ont.	6/21/66	4.42	0.47	1.4	9.3	25.1	0.7199
C-66-17	Wanapitei R. Rte. 69, Ont.	6/23/66	1.24	0.56	2.2	11.3	27.7	0.7196
F-63-53	French R.	9/13/63	1.91	0.90	2.8	8.7	34.9	0.7157
C-66-18	Bon Air, Ont.	6/23/66	1.98	0.83	2.3	8.4		
F-63-54	Magnetawan R.	9/13/63	1.41	0.82	1.3	6.1	35.1	0.7126
C-66-19	Britt, Ont.	6/23/66	1.45	0.85	2.0	5.5	33.9	
Rivers draining sedimentary rocks of Paleozoic Age in Michigan.								
C-66-2	Black River Port Huron, Mich.	6/18/66	31.0	3.10	32.0	94.5	178.6	
C-66-3	Pigeon River Caseville, Mich.	6/18/66	17.7	2.15	31.8	97.2	415.3	0.7107
F-66-2	Saginaw River	9/4/66	59.0	10.2	22.8	95.1	2688	
C-66-4	Bay City, Mich.	6/19/66	100.0	5.95	21.5	125.5	1533	0.7088
C-66-5	Au Sable R. near Oscoda, Mich.	6/19/66	3.61	0.63	4.5	46.4	72.6	0.7102

Table 6 continued

Sample Number	Locality	Collection Date	Na µg/ml	K µg/ml	Mg µg/ml	Ca µg/ml	Sr µg/l	Sr^{87}/Sr^{86}
C-66-6	Thunder Bay R. Alpena, Mich.	6/20/66	4.58	0.77	12.9	54.8		0.7103
C-66-7	Black River Cheboygan, Mich.	6/20/66	3.27	0.77	12.3	44.2	102.5	
Rivers draining sedimentary rocks of Paleozoic Age in Southwestern Ontario								
C-66-22	Nottawasaga R. Evendale, Ont.	6/24/66	6.30	1.41	14.8	77.8	181.9	
F-63-59	Saugeen River Southampton, Ont.	9/14/63	3.98	1.25	25.7	62.6	1164	0.7109
C-66-23		6/24/66	3.70	1.62	25.4	56.9	537.1	
C-66-24	Maitland R. Goderich, Ont.	6/24/66	82.5	2.65	62.0	66.2	2791	0.7089
C-66-25	Aux Sable R. Grand Bend, Ont.	6/24/66	5.7	2.25	24.6	111.8	211.2	
Water from Lake Huron, North Channel Area								
F-63-43	Lake George, 1/2 mi. so. of Garden R., Ont.	9/11/63	1.37	0.52	4.5	14.1	22.3	
F-63-45	St. Joseph Channel at Ferry Dock, Ont.	9/11/63	1.25	0.53	2.6	14.2		
F-63-9	Munuscong Lake Raber, Mich.	9/5/63	1.24	0.53	3.1	14.8		
F-63-10	Lake Nicolet Neebish Island Ferry, Mich.	9/5/63	1.44	0.52	2.9	14.3	28.8	0.7151

Table 6 continued

Sample Number	Locality	Collection Date	Na µg/ml	K µg/ml	Mg µg/ml	Ca µg/ml	Sr µg/l	Sr^{87}/Sr^{86}
F-63-6	DeTour Passage, DeTour Village, Mich.	9/4/63	1.81	0.59	4.1	18.1	44.5	
F-63-7	East Side of Drummond Isl., Mich.	9/4/63	2.64	0.77	6.2	24.0		
F-63-46	Bruce Mine, Ontario	9/11/63	2.41	0.78	5.0	21.1	62.3	0.7123
F-66-11	Blind River, Ontario	6/21/66	1.97	0.63	3.2	18.2	48.4	0.7130
F-63-48	Algoma, Ont.	9/11/63	2.92	1.03	5.3	22.1	72.5	0.7113
F-63-50	Little Current, Ontario	9/12/63	2.66	0.86	5.3	23.4		0.7116
C-66-13		6/21/66	2.75	0.80	6.2	25.2	78.6	0.7111
F-63-51	Meldrum Bay Manitoulin Isl., Ontario	9/12/63	2.75	0.82	5.5	24.3	84.6	0.7118
C-66-31		6/22/66	2.41	0.72	5.4	22.2		
C-66-14	Gore Bay Manitoulin Is., Ont.	6/22/66	2.76	0.80	4.7	21.6	69.1	
C-66-15	Sheshegwaning Manitoulin Isl., Ont.	6/22/66	2.57	0.72	4.8	22.0	66.6	0.7112
Water from Lake Huron, Georgian Bay Area								
F-63-55	Snug Harbor, Shebeshekong, Ont.	9/13/63	2.46	0.80	5.0	22.5		0.7126
C-66-20	Parry Sound, Ontario	6/23/66	1.96	0.83	2.9	11.4	50.8	0.7109
C-66-21	Midland, Ont.	6/23/66	3.22	1.08	4.2	25.6	94.7	0.7108

Table 6 continued

Sample Number	Locality	Collection Date	Na µg/ml	K µg/ml	Mg µg/ml	Ca µg/ml	Sr µg/l	Sr^{87}/Sr^{86}
F-63-56	Craigleith, Ont.	9/13/63	2.67	0.88	5.4	27.1	90.6	0.7124
F-63-58	Colpeboy Bay, Ont.	9/14/63	2.51	0.79	5.7	23.5		0.7093
F-63-57	Tobermore, Ont.	9/14/63	3.00	0.88	6.6	26.2	94.6	0.7124
	Water from Lake Huron, Saginaw Bay Area							
F-63-1	Tawas City, Michigan	9/4/63	----	----	----	28.7	104.1	0.7101
C-66-57	2 mi. off-shore from Alabaster Pt., Michigan	8/31/66	3.56	0.86	6.6	27.4		
C-66-52	Lat. 43°45' Long. 83°44'	9/1/66	7.80	1.30	8.2	34.6	331.5	0.7106
C-66-58	Lat. 43°50' Long. 83°40'	9/ /66	7.98	1.27	7.8	33.2	213.0	0.7107
C-66-59	Lat. 43°57' Long. 83°37'	9/ /66	4.28	1.07	7.0	29.7		
C-66-60	Lat. 44°01' Long. 83°32'	9/ /66	4.24	0.99	6.7	29.5	133.4	0.7106
C-66-61	Lat. 44°06' Long. 83°30'	9/ /66	3.79	1.05	7.0	28.1		
C-66-62	Lat. 44°15' Long. 83°25'	9/ /66	3.44	0.77	6.4	27.5	108.0	0.7107

Table 6 continued

Sample Number	Locality	Collection Date	Na µg/ml	K µg/ml	Mg µg/ml	Ca µg/ml	Sr µg/l	Sr^{87}/Sr^{86}
C-66-63	Lat. 44°10' Long. 83°26'	9/ /66	4.02	0.83	6.4	28.2		
F-66-3	Bay Port, Mich.	3/18/66	13.4	1.53	10.4	25.4		
F-66-4	Port Austin, Mich.	3/18/66	14.2	3.21	21.0	69.0	149.7	
	Lake Huron, Central Area							
F-63-5	Mackinaw City Mich.	9/4/63	3.63	1.02	9.1	31.6	113.4	0.7113
C-66-16	South Baymouth, Manitoulin Isl., Ont.	6/22/66	2.71	0.85	8.1	29.6	97.9	0.7111
F-63-52	Providence Bay Manitoulin Isl., Ont.	9/12/63	2.83	0.78	6.7	28.0		0.7103
F-63-3	North Point, Presque Isle, Mich.	9/4/63	3.00	0.84	7.5	27.1		
F-63-60	Baie-du-dore, Ont.	9/14/63	3.27	0.88	7.0	27.5	110.0	0.7115
C-66-34	Lat. 45°54' Long. 83°53'	8/17/66	2.78	0.78	6.2	24.7		
C-66-35	Lat. 45°49' Long. 84°05'	8/18/66	2.93	0.82	6.6	26.1		
C-66-36	Lat. 45°51' Long. 84°09'	8/18/66	3.13	0.87	7.4	28.8	95.0	0.7102

Table 6 continued

Sample Number	Locality	Collection Date	Na µg/ml	K µg/ml	Mg µg/ml	Ca µg/ml	Sr µg/l	Sr^{87}/Sr^{86}
C-66-37	Lat. 45°54' Long. 84°02'	8/18/66	2.99	0.87	5.5	26.9		
C-66-38	Lat. 45°43' Long. 84°30'	8/21/66	3.13	0.98	7.1	26.6	93.5	
C-66-39	Middle of South Bay, Manitoulin Isl., Ont.	8/23/66	2.56	0.89	8.1	30.5		
C-66-40	About 1 mi. E. of Middle Isl., between Alpena & Calcite, Mich.	8/24/66	2.93	0.90	6.4	25.1	91.5	0.7099
C-66-41	About 2 mi. N. of Rogers City, 1 mi. offshore, Mich.	8/24/66	3.08	0.90	7.2	27.5		
C-66-42	Lat. 45°35' Long. 83°50'	8/25/66	3.00	0.96	6.6	26.9		
C-66-43	Lat. 45°31' Long. 83°50'	8/25/66	2.99	0.91	7.0	26.0		
C-66-44	Midway between Adams Pt. & Presque Isle, Mich., Light, 4 mi. offshore	8/25/66	3.04	0.93	7.0	27.0	91.8	0.7111
C-66-45	4 mi. offshore between Presque Isle & Middle Island, Mich.	8/25/66	2.89	0.88	6.3	25.4		
C-66-46	Lat. 44°52' Long. 83°02'	8/26/66	2.90	0.85	6.4	25.8	92.6	

Table 6 continued

Sample Number	Locality	Collection Date	Na µg/ml	K µg/ml	Mg µg/ml	Ca µg/ml	Sr µg/l	Sr^{87}/Sr^{86}
C-66-47	Lat. 44°51' Long. 83°13'	8/26/66	2.91	0.92	6.6	26.0		
C-66-48	Lat. 45°04' Long. 83°10'	8/27/66	2.93	0.83	6.5	26.0	94.5	0.7096
C-66-49	Lat. 45°40' Long. 83°45'	8/27/66	2.65	0.77	5.6	22.4		
C-66-50	Lat. 44°59' Long. 83°21'	8/29/66	2.96	0.81	6.4	26.0		
C-66-51	Lat. 44°37' Long. 83°15'	8/29/66	2.91	0.83	6.3	26.9		
C-66-53	Lat. 44°38' Long. 83°09'	8/30/66	2.91	0.79	6.2	26.4		
C-66-54	Lat. 44°37' Long. 83°00'	8/30/66	3.02	0.86	6.0	26.7		
C-66-55	Lat. 44°31' Long. 82°55'	8/30/66	3.07	0.82	6.3	27.3		
C-66-56	Lat. 44°45' Long. 82°57'	8/30/66	2.87	0.84	6.2	25.7	93.5	0.7109
C-66-64	Lat. 44°14' Long. 82°19'	9/ /66	3.08	0.73	6.5	26.9	99.6	0.7109
C-66-65	Lat. 44°08' Long. 82°17'	9/ /66	3.02	0.73	6.1	27.0		
C-66-66	Lat. 43°26' Long. 82°18'	9/ /66	3.28	0.77	6.1	27.1	105.4	0.7111

Table 6 continued

Sample Number	Locality	Collection Date	Na µg/ml	K µg/ml	Mg µg/ml	Ca µg/ml	Sr µg/l	Sr^{87}/Sr^{86}
C-66-67	Lat. 43°47' Long. 82°21'	9/ /66	3.28	0.75	6.6	27.0		
F-66-5	Harbor Beach, Mich.	3/18/66	9.1	1.21	9.0	15.2	Omitted from discussion.	

piled in Table 6 and summarized in Table 7 document the differences in the chemical composition of river water derived from the Canadian Shield and the southern drainage basin, respectively. In general, the river water from the Precambrian Shield is more constant in composition and more dilute than water from the southern drainage area.

The concentrations of sodium and potassium in the two types of river-water actually overlap. On the average, however, the rivers of Michigan and southwestern Ontario contain as much as ten times more sodium and five times as much potassium as the rivers on the Canadian Shield. Among the rivers in Michigan the Saginaw, the Pigeon and the Black River have unusually high sodium concentrations. High sodium concentrations occur also in the Maitland River of southwestern Ontario. These are tentatively attributed to the weathering of rock salt of the Salina formation of Silurean age which crops out in southwestern Ontario and along the edge of the Michigan Basin. Because of the great range of concentrations of sodium and potassium in the tributary rivers of Lake Huron and because of the overlap of the concentrations for rivers from the northern and southern part of the drainage basin, sodium and potassium are not useful in labelling water masses derived from either the Canadian Shield or the southern drainage basin of Lake Huron. On the other hand, the high concentration of sodium of certain rivers, such as the Maitland, may provide a useable parameter by which water from that river can be traced in the Lake.

Magnesium, calcium and strontium are consistently present at significantly lower levels of concentrations in the rivers of the Canadian Shield than in

Table 7

Comparison of the Chemical Compositions and Isotope Composition of Strontium in the Tributary Rivers of Lake Huron

Element	Precambrian Shield			Michigan and SW Ontario		
	Average		Range	Average		Range
Na	2.67	μg/ml	1.03 - 14.8	26.8	μg/ml	3.27 - 100.0
K	0.64	μg/ml	0.44 - 0.90	2.73	μg/ml	0.63 - 10.2
Mg	2.0	μg/ml	1.3 - 2.8	24.2	μg/ml	4.5 - 62.0
Ca	9.6	μg/ml	5.5 - 14.7	84.8	μg/ml	44.2 - 125.0
Sr	29.3	μg/l	21.5 - 35.1	897.7	μg/l	72.6 - 2791
Sr^{87}/Sr^{86}	0.7180		0.7126 - 0.7209	0.7100		0.7088 - 0.7109

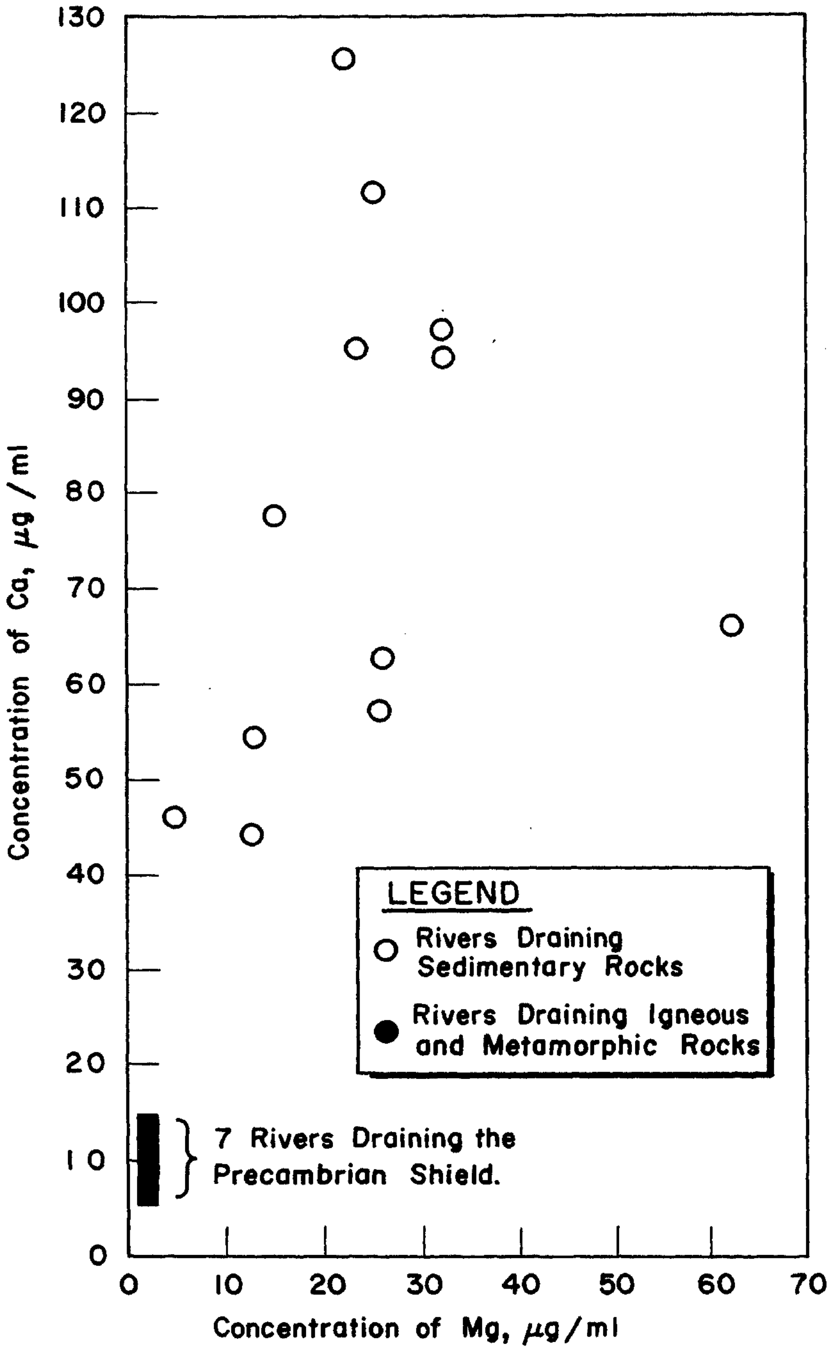

Figure 7. Concentrations of calcium versus magnesium for the major tributaries of Lake Huron.

the rivers of Michigan and southwestern Ontario. The concentrations do not overlap for any of the three elements. A direct comparison of the numerical values is best made by reference to Table 7. It can be seen there that when the concentrations of any two of the three elements are plotted, the two types of river water will form distinct clusters. Figure 7 is an example of such a plot and shows distribution of calcium and magnesium in the tributary rivers of Lake Huron. The data in Table 7 demonstrate that the rivers draining sedimentary rocks contain about 10 times more calcium and magnesium and about 30 times more strontium than the rivers of the Canadian Shield.

The isotope composition of strontium was determined for thirteen rivers. Of these, seven drain the Canadian Shield. The Sr^{87}/Sr^{86} ratios of these rivers vary from 0.7126 to 0.7209 and average 0.7180. The rivers draining sedimentary rocks of Paleozoic age, on the other hand, have lower Sr^{87}/Sr^{86} ratios ranging from 0.7088 to 0.7109 and have a mean of 0.7100. These data demonstrate the presence of excess radiogenic Sr^{87} in the water draining the Precambrian Shield.

Lake Huron

It is convenient for the purpose of this discussion to subdivide Lake Huron into the following regions:

1. North Channel, including Lake George, St. Joseph Channel, Lake Nicolet and Munuscong Lake.
2. Georgian Bay
3. Saginaw Bay
4. Central Region

The analytical data for the water samples from each of these four regions are compiled in Table 6.

North Channel

In the North Channel of Lake Huron water from Lake Superior is discharged by the St. Mary River mainly through the St. Joseph Channel. In addition, water from the Canadian Shield is discharged by several rivers, including the Garden and Spanish Rivers which were sampled for this study. This water mass mixes with surface run-off from Manitoulin, Cockburn, Drummond, and St. Joseph Islands all of which are underlain by sedimentary rocks of Paleozoic age.

The chemical composition of the water in the North Channel changes progressively from west to east and north to south. Table 8 summarizes the variation in chemical composition and isotope composition of strontium for the North Channel area. The concentrations of sodium, potassium, magnesium and calcium increase by about a factor of two, while strontium increases almost four fold in concentration. The higher values occur generally along the north shore of the islands and increase in an easterly direction.

The north-south variation is illustrated by a comparison of the chemical composition of water at Blind River (C-66-11) and Meldrum Bay (C-66-31) which lie on opposite sides of the North Channel. The concentrations of all elements which we analyzed are higher at Meldrum Bay than they are at Blind River. The Sr^{87}/Sr^{86} ratio is 0.7130 on the north side, but only 0.7118 on the south side.

Table 8

Chemical Composition and Isotope Composition of Strontium in the North Channel of Lake Huron

Element	High	Low
Na μg/ml	2.92	1.24
K μg/ml	1.03	0.52
Mg μg/ml	6.2	2.6
Ca μg/ml	25.2	14.1
Sr μg/l	84.6	22.3
Sr^{87}/Sr^{86}	0.7151	0.7111

The variation of the chemical composition of water from Lake Huron is illustrated by Figures 8, 9, and 10. The samples from the North Channel are shown as the solid circles. Figures 8 and 9 show the relationships between the concentrations of calcium and magnesium and calcium and strontium, respectively. Approximately linear trends are suggested in both cases for all the samples, but are especially well developed for the water from the North Channel. The best linear relations relationship is displayed by calcium and strontium, shown in Figure 9. The linearity of this plot can be interpreted as being the result of progressive mixing of the two types of water discharged into Lake Huron.

The isotope composition and concentration of strontium are plotted in Figure 10. There is a marked negative correlation between the Sr^{87}/Sr^{86} ratio and the concentration of strontium. This effect can be attributed to the mixing of water from the Precambrian Shield, having high Sr^{87}/Sr^{86} ratios but low strontium concentrations, with water draining Paleozoic carbonate rocks which has a low Sr^{87}/Sr^{86} ratio but high strontium concentration. This fact is documented by the data summarized in Table 7. The lowering of the Sr^{87}/Sr^{86} ratio in surface water by strontium derived by weathering of marine carbonate rocks will be called the "limestone effect." Faure, Hurley and Powell (1965) have suggested that the limestone effect is largely responsible for controlling the isotope composition of strontium in the oceans.

Georgian Bay

The Georgian Bay receives water from the Canadian Shield along its

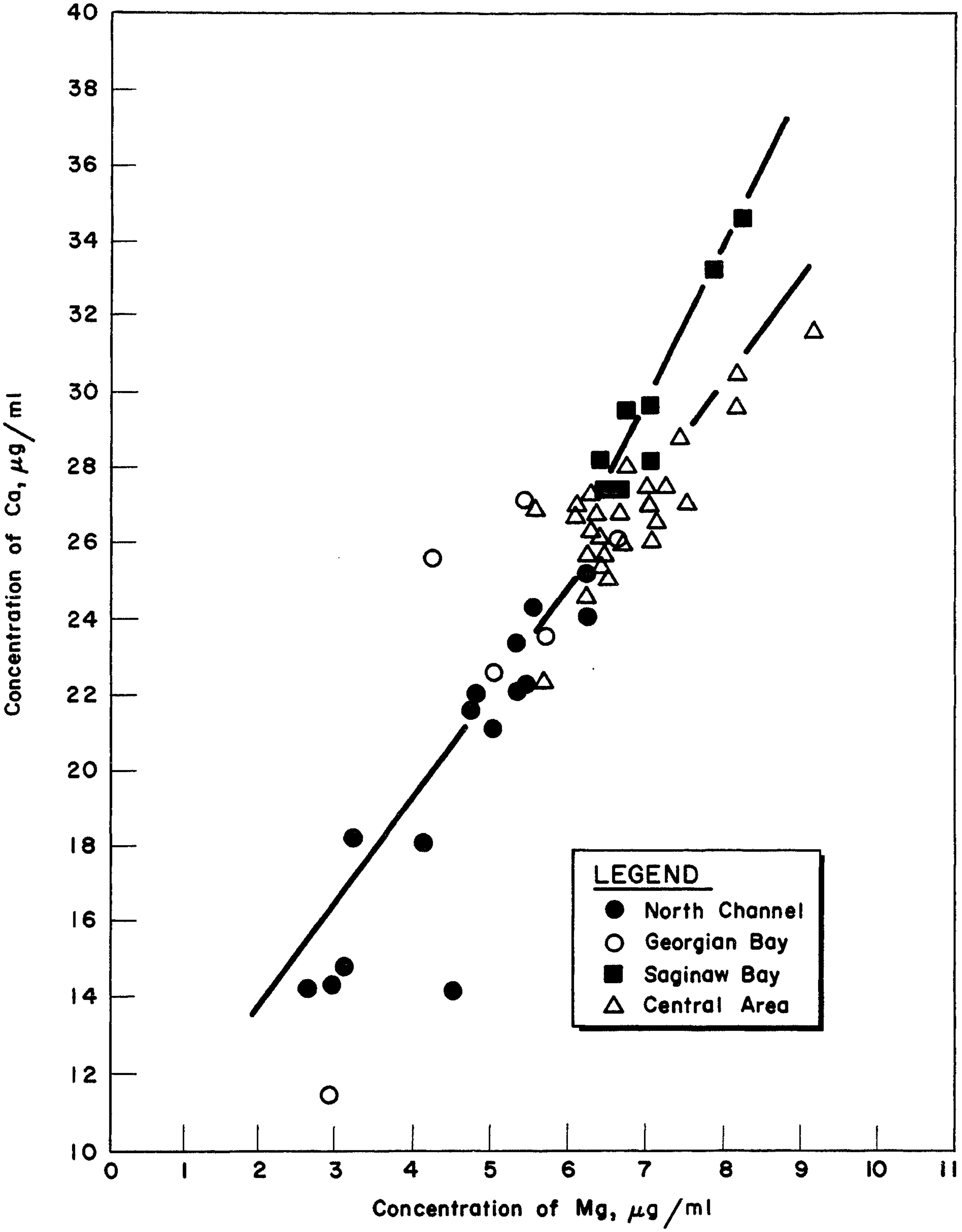

Figure 8. Concentrations of calcium and magnesium in Lake Huron.

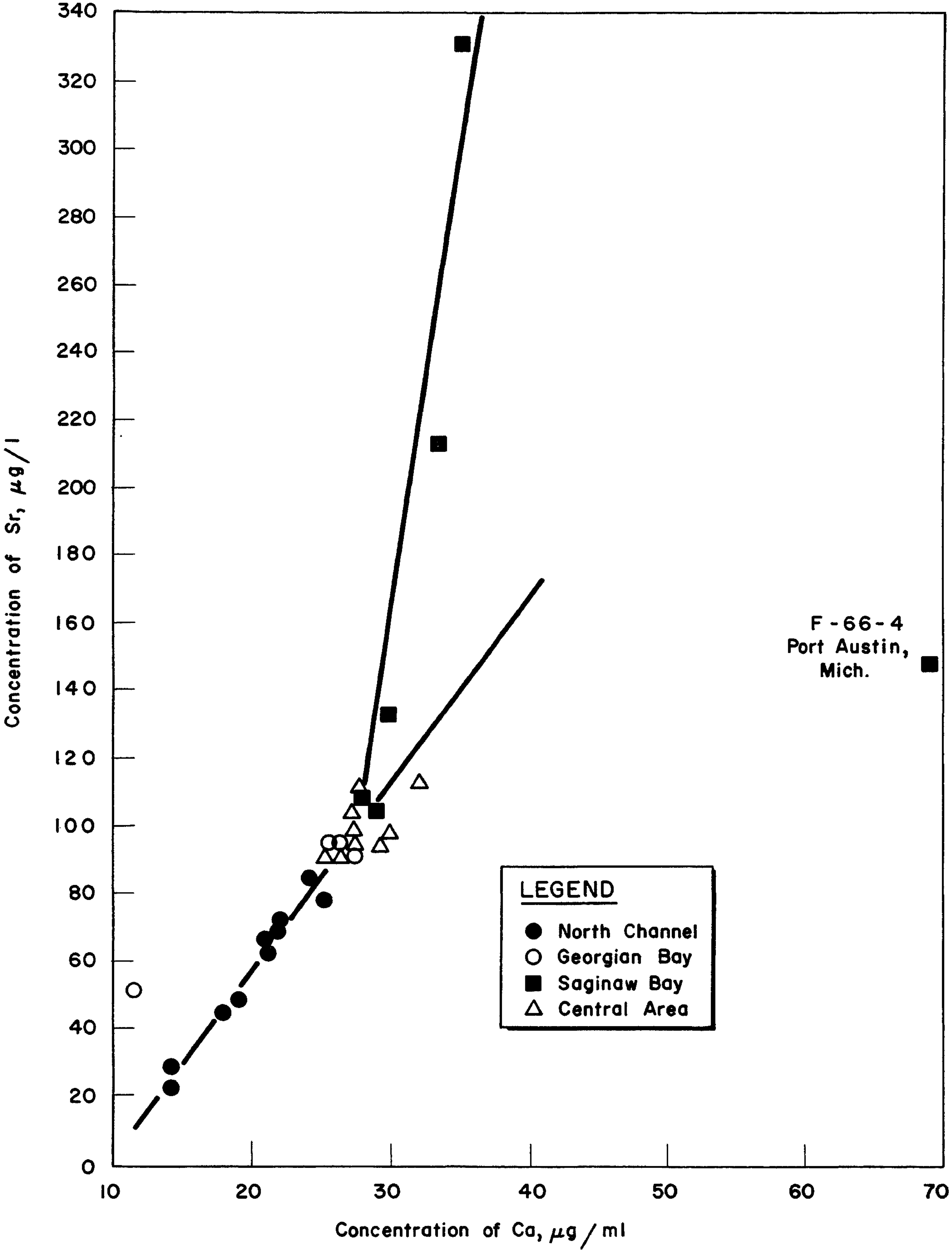

Figure 9. Concentrations of strontium and calcium in Lake Huron.

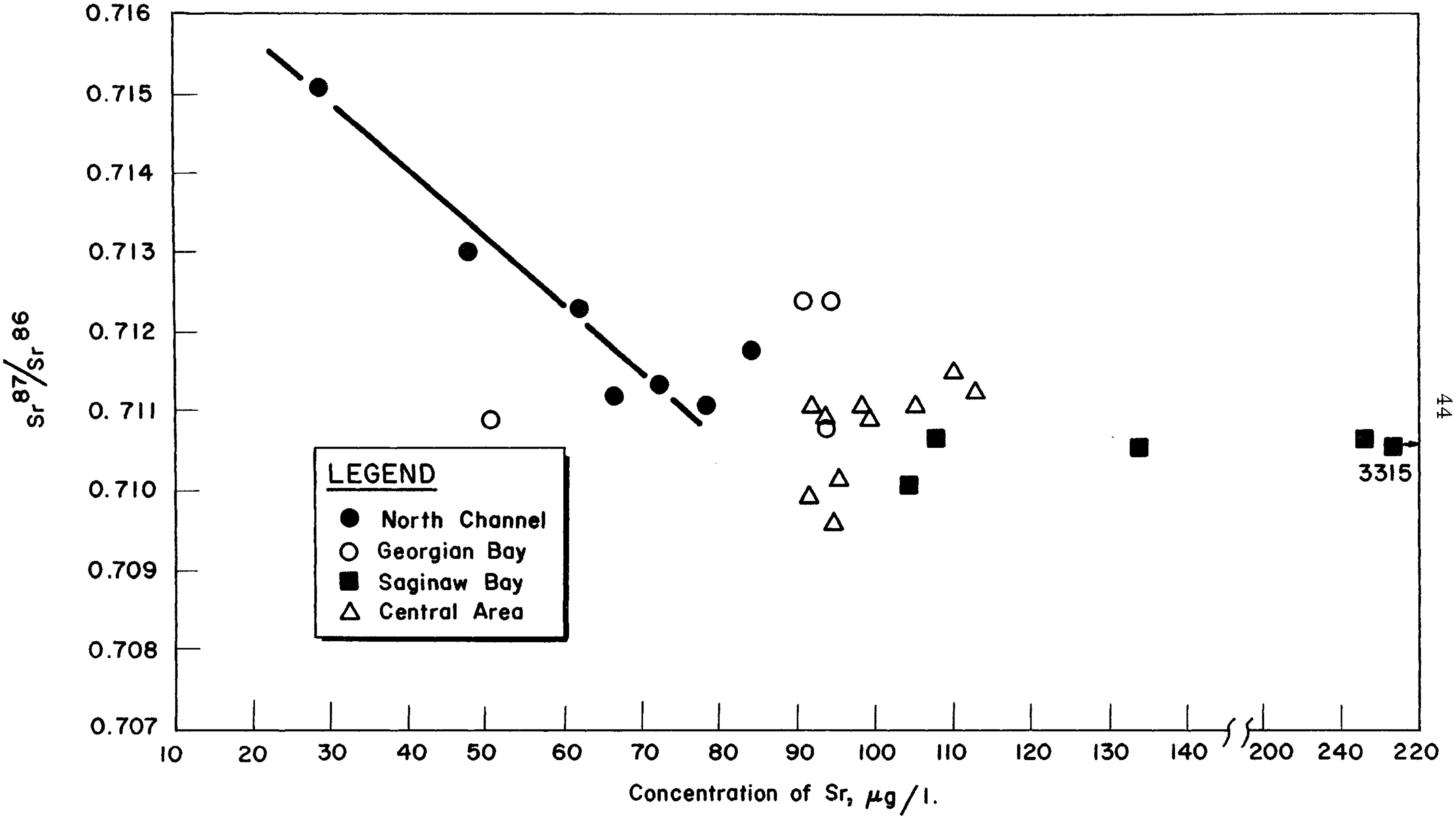

Figure 10. Isotope composition and concentration of strontium in Lake Huron.

northern and eastern shore. On the south and west it is bounded by the Bruce Peninsula and Manitoulin Island which are underlain by sedimentary rocks. The six samples of water from this region are not sufficient to describe adequately the chemical composition of this body of water.

In Figures 8, 9, and 10 water from the Georgian Bay is shown as open circles. The points seem to have a tendency to cluster but generally do continue the linear trends so well displayed by the water from the North Channel.

Saginaw Bay

The chemical composition of the water in Saginaw Bay is strongly affected by the discharge of the Saginaw River at Bay City. This river is far more concentrated than the water in the central region of Lake Huron. The result is that in Saginaw Bay one can document a continuous change in the chemical composition as the water from the Saginaw River mixes with the water from the central region of the lake. Chemical compositions of water from Saginaw Bay and south-central Lake Huron were published by Allen (1964) who also listed references to earlier studies of the chemical composition of the water of Lake Huron.

Table 9 is a compilation of the high and low values for sodium, potassium, magnesium, calcium and strontium observed in the ten samples from Saginaw Bay included in this study. Specimen F-66-4 collected along the shore at Port Austin was not included because its composition deviates appreciably from the pattern established by the other samples.

The water samples from Saginaw Bay are plotted as solid squares in

Table 9

Chemical Composition and Sr^{87}/Sr^{86} Ratios of Water from Saginaw Bay

Element	High	Low
Na µg/ml	13.4	3.44
K µg/ml	1.53	0.77
Mg µg/ml	10.4	6.4
Ca µg/ml	34.6	25.4
Sr µg/l	331.5	104.1
Sr^{87}/Sr^{86}	0.7107	0.7101

Figures 8, 9, and 10. Both Figures 8 and 9 suggest that calcium and magnesium and calcium and strontium from linear arrays which are distinctly different from those formed by the water from other regions of Lake Huron. This characteristic of water from Saginaw Bay is especially well shown for strontium and calcium plotted in Figure 8. It is very probably caused by the unusually high strontium concentration of the Saginaw River compared to all other rivers in Michigan included in this study. Only the Maitland River of Ontario approaches the Saginaw River in its concentration of strontium.

The isotope composition of strontium in water from Saginaw Bay is constant within experimental errors and has an average Sr^{87}/Sr^{86} ratio of 0.7105.

Central Region of Lake Huron

Thirty two samples of water from the central region of Lake Huron have been analyzed. Table 10 shows the averages and ranges of concentration for this part of the lake. The data are also plotted as open triangles in Figures 8, 9 and 10. It can be seen by reference to these figures that the concentrations of calcium, magnesium and strontium tend to cluster and thereby suggest that this part of the lake is relatively better mixed than the North Channel or Saginaw Bay. The average concentrations of the elements analyzed in this study are: Na = 2.99 ± 0.20 mg/ml; K = 0.85 ± 0.07 mg/ml; Mg = 6.7 ± 0.8 mg/ml; Ca = 26.9 ± 1.7 mg/ml; Sr = 98.2 ± 7.5 mg/l; $Sr^{87}/Sr^{86} = 0.7107 \pm 0.0006$. The errors are one standard deviation calculated from the data. Our average

Table 10

Chemical Composition and Isotope Composition of Strontium in the Central Region of Lake Huron

Element	Mean ± σ *	High	Low
Na µg/ml	2.99 ± 0.20	3.63	2.56
K µg/ml	0.85 ± 0.07	1.02	0.73
Mg µg/ml	6.7 ± 0.8	9.1	5.5
Ca µg/ml	26.9 ± 1.7	31.6	22.4
Sr µg/l	98.2 ± 7.5	113.4	91.5
Sr^{87}/Sr^{86}	0.7107 ± 0.0006	7113	0.7096

* Standard deviation

values for potassium and calcium are in excellent agreement with those of Allen (1964). Our average sodium concentration is approximately 10 per cent higher than that of Allen who reported an average of 2.67 and a median of 2.54 ppm of sodium. No previous analyses of the concentration and isotope composition of strontium have been reported for Lake Huron.

Figure 11 shows histograms for the concentrations of sodium, potassium, magnesium, and calcium from the central region of Lake Huron. To a first approximation all of the distributions are considered normal, although some skewness is shown by magnesium. The approximately normal distribution of the concentrations supports the validity of the average concentrations calculated in Table 10 and suggests again that the water in the central part of Lake Huron is relatively well mixed. In a later section of this report a model calculation will be made which will permit a more quantitative interpretation of the degree of mixing of water in Lake Huron.

Iron and Phosphorus in Lake Huron and its Tributaries

Concentrations of dissolved iron and phosphorus were determined for twelve tributary rivers of Lake Huron. Phosphorus only was measured in seven water samples from the North Channel and the Georgian Bay. Three analyses of water from Lake Erie were made for comparison. All data are compiled in Table 11.

The observed concentration of iron was found to be very sensitive to the presence of suspended mineral and/or organic matter. This problem was

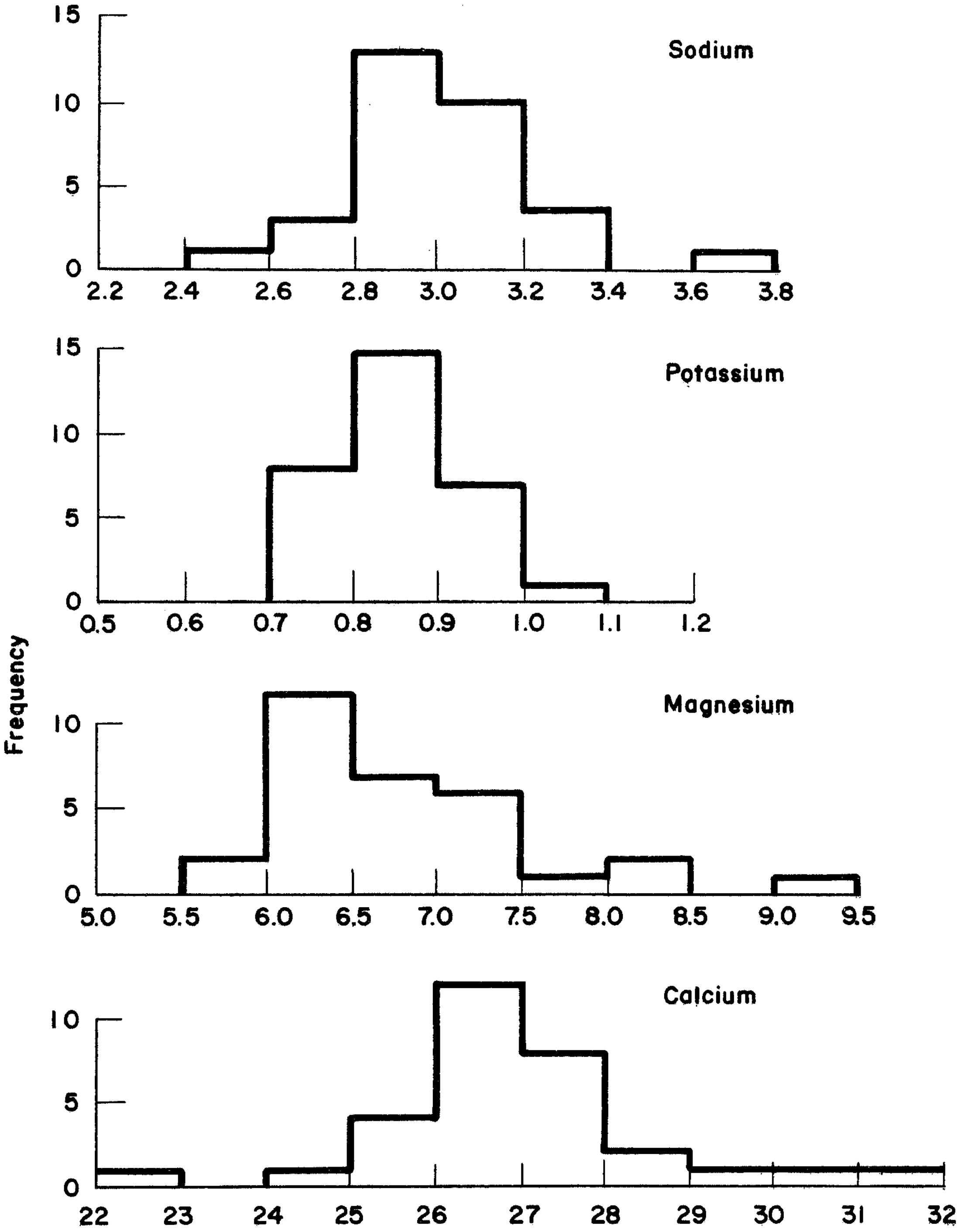

Figure 11. Histograms showing the distribution of Na, K, Mg and Ca in Central Lake Huron, in units μg/ml.

Table 11

Concentrations of Dissolved Iron and Phosphorus in Lake Huron and its Tributaries

Sample Number	Location	Fe µg/ml	P µg/ml
Rivers draining igneous and metamorphic rocks.			
C-66-8	St. Mary's River, Sault Ste. Marie	0.040	----
C-66-9	Garden River, Rte. 17, Ontario	0.110	----
C-66-10	Mississagi River, Rte. 17, Ontario	0.062	----
C-66-12	Spanish River, Massey, Ontario	----	0.190
C-66-17	Wanapitei River, Rte. 69, Ontario	0.081	0.080
C-66-18	French River, Britt, Ontario	----	0.150
Rivers draining sedimentary rocks.			
C-66-4	Saginaw River, Bay City, Michigan	0.060	----
C-66-22	Nottawasaga River, Evendale, Ontario	0.058	0.410
C-66-23	Saugeen River, Southampton, Ontario	0.046	0.160
C-66-24	Maitland River, Goderich, Ontario	----	0.200
C-66-25	Aux Sables River, Grand Bend, Ontario	0.068	0.120

Table 11 continued

Sample Number	Location	Fe µg/ml	P µg/ml
Water from Lake Huron.			
C-66-13	Little Current, Ontario	----	0.068
C-66-31	Meldrum Bay, Ontario	----	0.036
C-66-14	Gore Bay, Ontario	----	0.028
C-66-15	Sheshegwaning, Ontario	----	0.180
C-66-16	South Baymouth, Ontario	----	0.016
C-66-20	Parry Sound, Ontario	----	0.070
C-66-21	Midland, Ontario	----	0.015
Water from Lake Erie and its Tributaries.			
C-66-1	Maumee River, Maumee, Ohio	0.058	----
C-66-26	Lake Erie, Port Stanley, Ontario	----	0.014
C-66-27	Lake Erie, Port Dover, Ontario	0.044	0.070
C-66-30	Lake Erie, Dunkirk, Ohio	0.060	0.113

discussed earlier and a comparison of the apparent iron concentrations in filtered and unfiltered water samples was made in Table 5.

The phosphorus content of natural water is normally controlled by the dissolution of the mineral apatite ($Ca_3(PO_4)_2$) and by biological activity. However, industrial and municipal waste disposal may significantly raise the phosphate ion concentration of lake and river water. Because the exact ionic species present in natural waters is not known, we have expressed concentrations in terms of total phosphorus in solution.

The average concentrations of iron and phosphorus in rivers draining the Canadian Shield are: Fe = 0.07 μg/ml and P = 0.12 μg/ml. The value for iron is in good agreement with the average of five analyses from the St. Mary's River at Sault Ste. Marie reported by Leverin (1947) and quoted by Livingstone (1963). Leverin obtained 0.06 ppm dissolved iron.

The rivers draining sedimentary rocks of Michigan and southwestern Ontario contain on the average 0,06 μg/ml Fe and 0.22 μg/ml P. The concentration of phosphorus in these rivers is, on the average, about twice that found in the rivers on the Canadian Shield. The higher phosphorus content may be due to pollution by detergents or phosphate fertilizer. The average iron concentration of the rivers draining sedimentary rocks is similar to that of rivers on the Canadian Shield.

The phosphorus content of Lake Huron in the North Channel and the Georgian Bay averages 0.06 μg/ml. This relatively low value is probably explained by the fact that the water in the North Channel and the Georgian Bay is derived largely from the Canadian Shield which is more thinly populated and has less industry than Michigan and southwestern Ontario. No iron determinations were made on these samples.

The concentrations of iron and phosphorus in three samples of Lake Erie do not differ appreciably from those of Lake Huron and its tributaries.

FORMULATION OF A MODEL FOR THE CHEMICAL COMPOSITION OF LAKE HURON

Introduction

Lake Huron receives water from a number of sources which are readily identified. These include:

1. Lake Superior draining through St. Mary's River.
2. Surface run-off draining igneous and metamorphic rocks along the north shore and the Georgian Bay of Lake Huron.
3. Lake Michigan draining through the Straights of Mackinac.
4. Surface run-off draining the sedimentary rocks of Michigan and south-western Ontario.
5. Precipitation of water from the atmosphere as rain or snow.
6. Inflow of groundwater along the shores of the lake.

The last two sources listed above are not considered to be important in determining the chemical composition of water in Lake Huron. To a first approximation rain and snow will act merely as dilutants and will not change the composition of the salts dissolved in the water. On the other hand, the chemical composition of groundwater is probably similar to that of surface water discharged by rivers. Inflow of groundwater therefore should not be an important parameter in the description of the chemical composition of the lake.

In the following we will calculate average concentrations of Na, K, Ca, Mg, and Sr in Lake Huron, weighted in accordance to the average annual discharge of water from each of the four sources listed above. For each source approximate chemical compositions will be assumed, based on our analyses or derived from the literature. The ultimate objective will be to compare the chemical composition of water samples from Lake Huron to this model composition and to obtain thereby a more precise estimate of the degree of mixing of the water in different parts of Lake Huron.

Lake Superior

Five samples of water collected from shore along the circumference of Lake Superior have been analyzed. The data are summarized in Table 12. The average concentrations are: Na = 1.24 ± .06 μg/ml, K = 0.56 ± .07 μg/ml, Mg = 2.4 ± .2 μg/ml, Ca = 14.4 ± .4 μg/ml, Sr = 21.8 ± .6 μg/ml, and Sr^{87}/Sr^{86} = 0.7162 ± .0015. Our analyses agree resonably well with those of Leverin (1947) as quoted by Livingstone (1963). The only major discrepancy appears to be the concentration of magnesium. Leverin reported 3.7 ppm, while we find only 2.4 μg/ml, on the average. Since we determined magnesium directly and independent of calcium, we have confidence in the accuracy of our value for magnesium in Lake Superior. The strontium determinations listed in Table 12 were published by Faure, Crocket, and Hurley (1967). They differ only slightly from two strontium determinations by Hart and Tilton (1966).

According to data by Hough (1958), the average annual outflow of water from Lake Superior through St. Mary's River is 73,700 ft^3/sec.

Surface Run-off From the North Shore of Lake Huron

Chemical analyses of water from seven rivers (including St. Mary's River) are tabulated in Table 6 and summarized in Table 7. Because of the remark-

Table 12

Chemical Composition of Water from Lake Superior

Sample Number	Location	Collection Date	Na µg/ml	K µg/ml	Mg µg/ml	Ca µg/ml	Sr µg/l	Sr^{87}/Sr^{86}
F-63-14	Whitefish Pt., Michigan	9/5/63	1.22	0.56	2.4	15.0	21.2	0.7161
F-63-16	Copper Harbor, Michigan	9/6/63	1.24	0.56	2.1	14.1	22.0	0.7181
F-63-22	Tofte, Minnesota	9/8/63	1.23	0.49	2.4	14.2	22.9	0.7147
F-63-26	Silver Islet, Ontario	9/8/63	1.24	0.48	2.4	14.7	21.4	
F-63-39	Mamainse Pt., Ontario	9/10/63	1.16	0.67	2.4	14.1	21.6	0.7153
F-63-12	St. Mary's R.	9/5/63	1.24	0.60	2.8	13.8	21.5	
C-66-8	Sault Ste. Marie	6/21/66	1.37	0.53	2.3	14.7		
Average Lake Superior Water:			1.24	0.56	2.4	14.4	21.8	0.7161
Standard Deviation:			0.06	0.07	0.2	0.4	0.6	0.0015

able uniformity in chemical composition, the unweighted averages of Table 7 are taken to be representative of the composition of water draining this part of the Canadian Shield.

An estimate of the discharge derived from this region can be made from a knowledge of the surface area which is drained and the average discharge per unit area for this region. Figure 12 is a plot of the average annual discharge and the size of the drainage basin of tributary rivers draining igneous and metamorphic rocks. The data on which this plot is based were taken from Water Resources Paper No. 119 of the Department of Northern Affairs and Natural Resources, Canada.

The average discharge per square mile, calculated by least squares regression of the data points, is 1.09 $ft^3/sec/mile^2$. The surface area of this part of the drainage basin is 26,300 $miles^2$. The average annual discharge from the Canadian Shield to Lake Huron is therefore approximately 28,700 ft^3/sec.

Lake Michigan

The chemical composition of water entering Lake Huron from Lake Michigan is best represented by sample F-63-5 (Table 6) from Mackinaw City, Michigan. This sample contains 3.63 $\mu g/ml$ Na, 1.02 $\mu g/ml$ K, 9.1 $\mu g/ml$ Mg, 31.6 $\mu g/ml$ Ca, and 113.4 $\mu g/l$ Sr. The composition of this water is fairly typical for "Straits Water", which is a mixture of water from Lake Michigan and Lake Huron. (Ayers et al., 1956). Lake Michigan water, studied by Ayers, et. al., (1958) is characterized by calcium concentrations up to about 34.5 ppm at

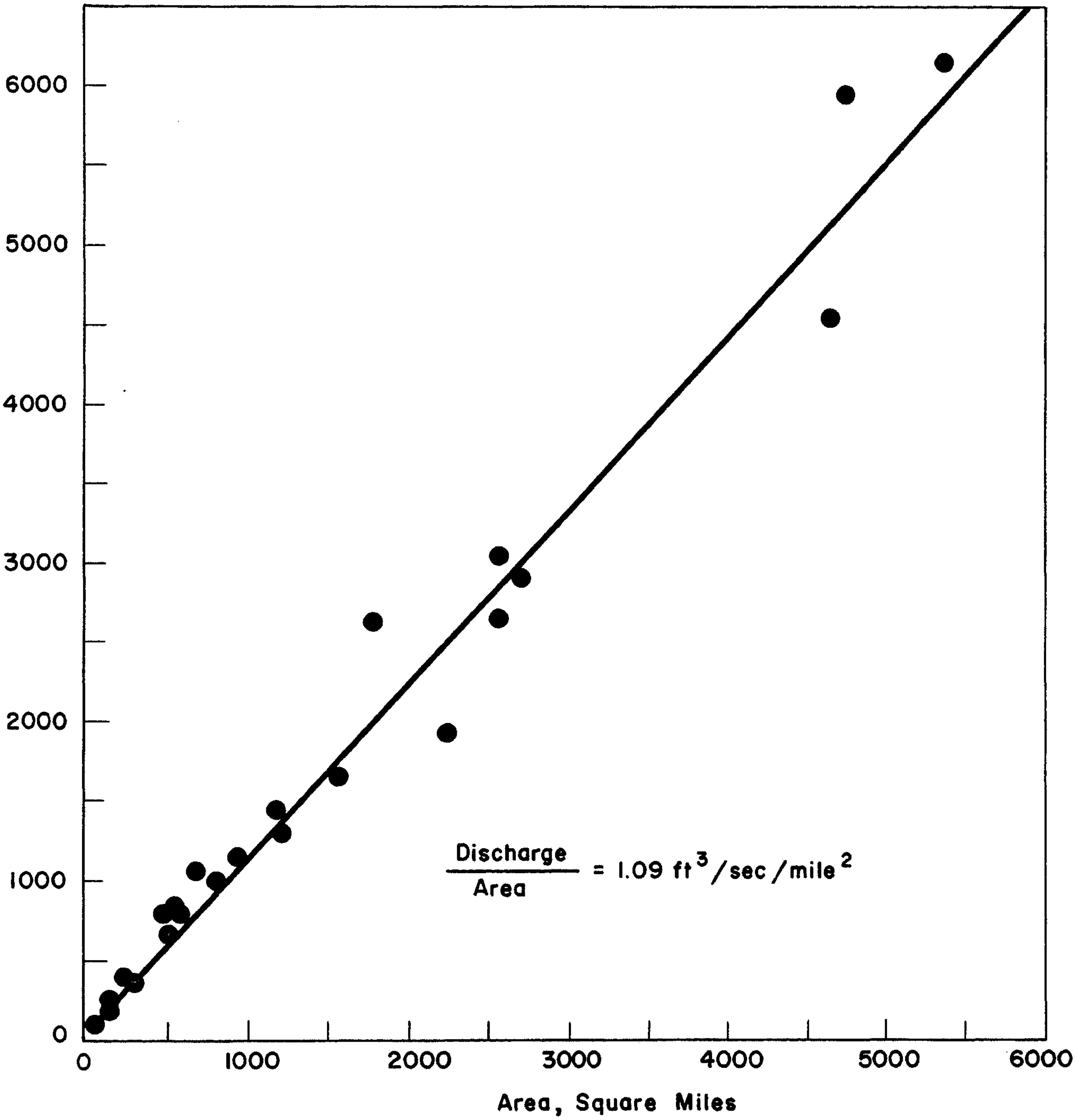

Figure 12. Plot of discharge versus drainage area for tributaries of Lake Huron which drain igneous and metamorphic rocks of the Canadian Shield.

the surface and magnesium concentrations of about 10.5 ppm. Nevertheless, for the purposes of this report we will assume that the water entering Lake Huron from Lake Michigan has a composition represented by sample F-63-5 in Table 6.

The net average annual discharge of Lake Michigan into Lake Huron is 55,000 ft^3/sec, according to Hough (1958).

Surface Run-off From Michigan and Southwestern Ontario into Lake Huron

The chemical composition of the water draining the sedimentary rocks of Michigan and southwestern Ontario is represented by the ten rivers included in this study. Because of the great differences in composition of these rivers, it is necessary to weight each river by a factor which is calculated from the relative magnitude of its average annual discharge. These calculations are carried out in Table 13. The values of the average annual discharge were taken from U. S. Geological Survey Water-Supply Paper 1707. The weighted average chemical composition of water draining Michigan and southwestern Ontario is: 40.0 μg/ml Na, 3.80 μg/ml K, 23.6 μg/ml Mg, 78.2 μg/ml Ca, and 1230 μg/l Sr.

The average annual discharge from this part of the drainage basin was estimated as before from the average discharge per unit area. These estimated are based on the data plotted in Figures 13 and 14 for Michigan and southwestern Ontario, respectively. A summary of the data used to make these estimates is presented in Table 14.

The discharge per unit area of rivers in Michigan on which gauging stations are located is 0.67 ft^3/sec/mile^2. This is approximately one half the rate

Table 13

Calculation of a Weighted Average Chemical Composition of Tributaries of Michigan and Southwestern Ontario

River	Avg. Ann. Discharge ft^3/sec.	f*	Na µg/ml	Naf µg/ml	K µg/ml	Kf µg/ml	Mg µg/ml	Mgf µg/ml	Ca µg/ml	Caf µg/ml	Sr µg/l	Srf µg/l
Michigan												
Black River	309	.026	31.0	.806	3.10	.081	32.0	.816	94.5	2.41	178.6	4.64
Pigeon River	33	.003	17.7	.053	2.15	.006	31.8	.085	97.2	.262	415.3	1.25
Saginaw River	4,303	.356	79.5	28.3	8.10	2.88	22.2	7.90	110.3	39.2	2110	751
Aux Sable R.	1,475	.122	3.61	.440	0.63	.077	4.5	.548	46.4	5.66	72.6	8.86
Thunder Bay R.	739	.061	4.58	.279	0.77	.047	12.9	.788	54.8	3.35	(90)**	5.49
Black River at Cheboygan	1,198	.099	3.27	.324	0.77	.076	12.3	1.22	44.2	4.38	102.5	10.1
Ontario												
Nottawasaga R.	376	.031	6.3	.195	1.41	.044	14.8	.458	77.5	2.40	181.9	5.64
Saugeen River	1,980	.164	3.84	.629	1.43	.235	25.6	4.19	59.8	9.79	850	139
Maitland River	1,283	.106	82.5	8.75	2.65	.281	62.0	6.79	66.2	7.02	2791	296
Aux Sable R.	395	.033	5.7	.186	2.25	.074	24.6	.801	111.8	3.69	211.2	6.97
Totals	12,091	1.001		40.0		3.80		23.6		78.2		1230

*f is the fraction of the total discharge of the rivers included in the study.

**Sr concentration was estimated.

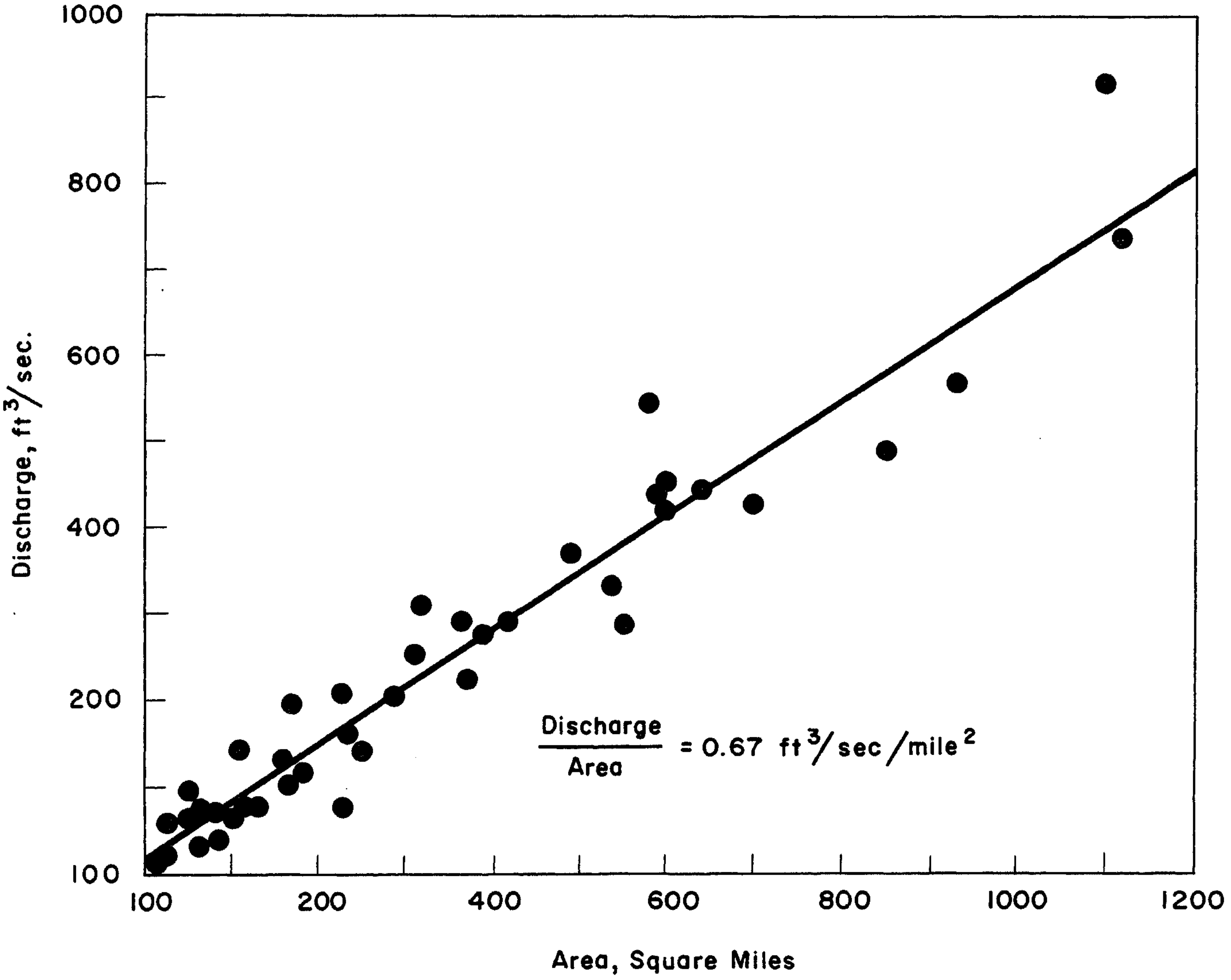

Figure 13. Plot of discharge versus drainage area for tributaries of Lake Huron which drain sedimentary rocks of Michigan.

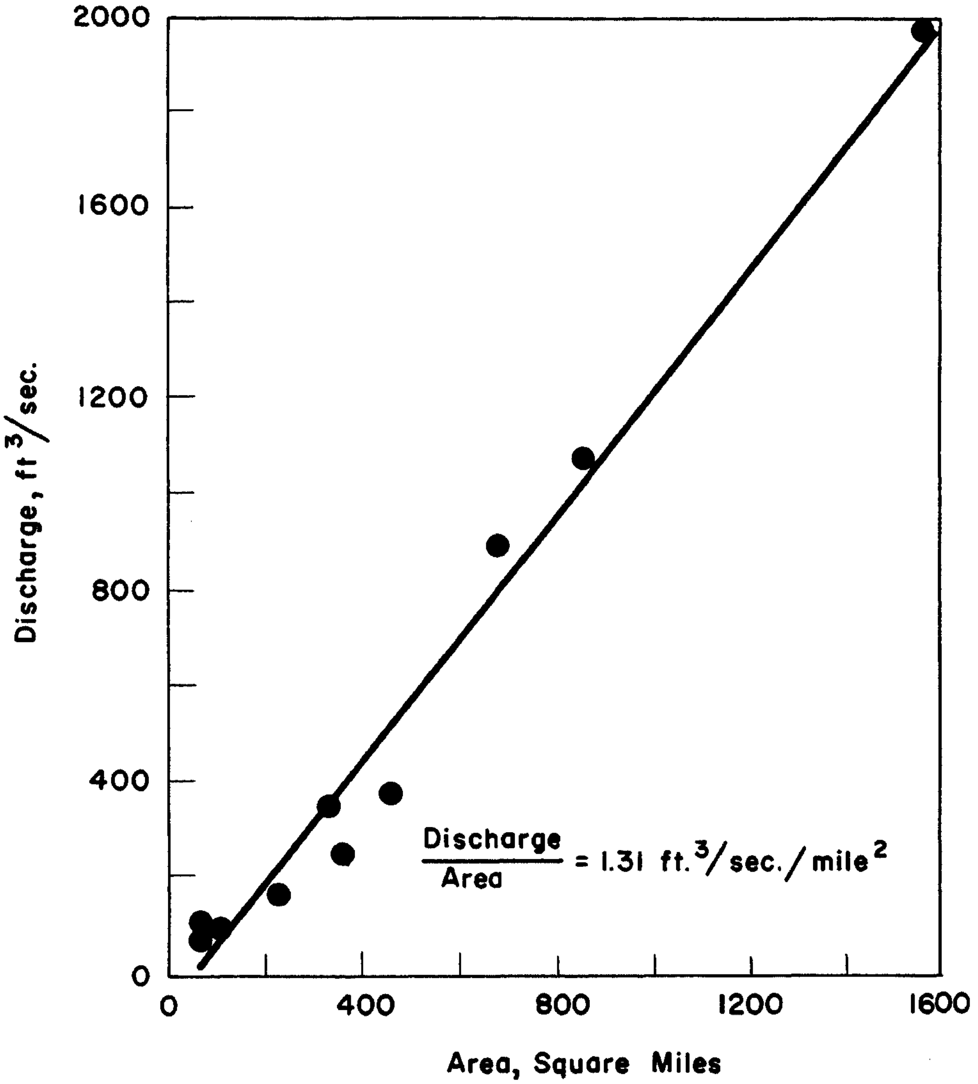

Figure 14. Plot of discharge versus drainage area for tributaries of Lake Huron which drain sedimentary rocks of Ontario.

Table 14

Summary of Data Used to Estimate Average Annual Run-off for Drainage Basin of Lake Huron

	North Shore Area	Michigan	SW Ontario
Discharge/Area $ft^3/sec/mile^2$	1.09	0.67	1.31
No of Data Points	23	42	10
Lin. Corr. Coeff.	0.986	0.981	0.991
Total Area Drained $miles^2$	26,300	16,800	10,600
Est. Run-off ft^3/sec	28,700	11,300	13,900

found for rivers in southwestern Ontario where the apparent rate is 1.31 ft^3/sec/mile^2. The difference appears to be real and may be related to differences in total precipitation received by the areas. Data on the precipitation in the Great Lakes Region compiled by Browzin (1963) show that the region west of Lake Huron receives less than 750 mm of precipitation annually while the eastern side receives from 750 to 950 mm of precipitation.

The area of the drainage basin in Michigan is 16,800 miles^2 which suggests an average annual run-off of 11,300 ft^3/sec. The drainage area in southwestern Ontario is 10,600 miles^2 while the estimated run-off is 13,900 ft^3/sec.

Calculation of the Average Chemical Composition of Lake Huron

In the preceeding section all of the data have been assembled which are necessary to calculate an average chemical composition for water in Lake Huron, assuming it to be well mixed. It is expected that the actual chemical composition of any given water sample from any given spot in the lake will deviate from the idealized composition.

The calculations required to arrive at the chemical composition of well-mixed water in Lake Huron are carried out in Table 15. The concentrations are in each case weighted by a factor "f" which is the fraction of the discharge from a given source relative to the total discharge received by Lake Huron from all sources.

It is apparent from the data in Table 15 that approximately 40 per cent of the water entering Lake Huron originates in Lake Superior, while 56 per cent of

Table 15

Calculation of the Composition of Well-mixed Lake Huron Water

	Discharge ft^3/sec.	f	Na	Naf	K	Kf	Mg	Mgf	Ca	Caf	Sr	Srf
Lake Superior	73,700	.404	1.24	.501	0.56	.226	2.4	.970	14.4	5.82	21.8	8.81
North-shore	28,700	.157	2.67	.419	0.64	.100	2.0	.314	9.6	1.51	29.3	4.62
Lake Michigan	55,000	.301	3.63	1.09	1.02	.307	9.1	2.74	31.6	9.51	113.4	34.1
Michigan and SW Ontario	25,200	.138	40.0	5.52	3.80	.524	23.6	3.26	78.2	10.8	1230	170
Totals	182,600	1.000		6.5		1.16		7.28		27.64		217.5

the water is derived from drainage of the igneous and metamorphic rocks of the Canadian Shield, including the drainage of Lake Superior. Approximately 30 per cent of the water originates in Lake Michigan and the remaining 14 per cent are derived from the drainage basin in Michigan and southwestern Ontario. The total rate of flow into Lake Huron is estimated at 182,600 ft^3/sec.

The weighted average chemical composition of this water displays several discrepancies. The concentrations for sodium (6.5 μg/ml) and strontium (217.5 μg/l) appear to be unreasonably high when compared to actually observed values in the lake. Table 10 shows that the average observed concentrations of sodium and strontium in the central region of Lake Huron are only 2.99 ± 0.20 μg/ml and 98.2 ± 7.5 μg/l, respectively. These values are only about one half the predicted average concentrations. On the other hand, the predicted average concentrations for magnesium and calcium are reasonable compared to the actual measurements summarized in Table 10, while potassium appears to be somewhat high.

Part of the explanation for the discrepancies is to be found in the seasonal variations of the chemical composition of rivers and the resulting difficulty in obtaining a meaningful average chemical composition of river water. The samples of river water available for study were collected either in June or in September with a three-year delay between them. Reference to Table 6 will show that in the case of the rivers draining the Precambrian Shield the differences in concentration are small and in all but one case much less than a factor of two. Because of the apparent constancy in composition of any given river and the limited differences in the composition of different rivers, there is little doubt about the composition of water draining this area as a whole.

A very different picture emerges for the rivers draining the sedimentary rocks of Michigan and southwestern Ontario. The two largest rivers in this region are the Saginaw River of Michigan and the Saugeen River of Ontario. Both were sampled at two different times. The analyses in Table 6 show that in the Saginaw River the concentrations of sodium, potassium and strontium differ by almost a factor of two. The calcium concentrations differ by about 30 per cent, while the magnesium concentrations of the two samples are virtually identical. In the case of the Saugeen River only the concentration of strontium varies by a factor of two while the other elements appear to be approximately constant.

These considerations cast serious doubt on the estimates of the average chemical composition of water draining Michigan and southwestern Ontario which are compiled in Table 13. It appears that seasonal variations of discharge and the concentration of elements in these rivers must be considered in order to obtain a more representative estimate.

Eastin (1967) studied the seasonal variation in the chemical composition of the Olentangy and Scioto Rivers of Ohio. Both rivers drain sedimentary rocks and are believed to be sufficiently similar to the rivers of Michigan and southwestern Ontario to make a comparison meaningful. Eastin observed that the concentrations of strontium varied by a factor of about three in both rivers in the course of one year. The highest concentrations occurred in September and October while the lowest occurred in June and December. The concentrations of sodium, potassium and calcium varied similarly by factors ranging from two to almost four. More details of Eastin's work are presented elsewhere in this report.

The preceeding discussion makes clear that the estimation of the average chemical composition of river water draining Michigan and southwestern Ontario is not a simple matter and will require analyses of water samples collected over the period of one year from several of the major rivers in this area. It is clear, however, that these rivers collectively are introducing significant amounts of sodium, calcium and strontium into Lake Huron and that the chemical composition of this Lake is appreciably changed as a result.

Summary and Evaluation

In the preceeding section a model was developed for the chemical composition of water in Lake Huron, based on the fact that water of differing chemical compositions is contributed to Lake Huron from several different sources. The composition of well-mixed Lake Huron water was calculated as an average, weighted in accordance with the fraction of the total discharge contributed by each source. These calculations were only partially successful because of the difficulty in specifying the average chemical composition of the surface run-off draining Michigan and S.W. Ontario. Although this source contributed only about 14 per cent of the total amount of water received by Lake Huron, it is a major contributor of dissolved salts to Lake Huron.

The concentrations of sodium, strontium and potassium predicted by the calculations in Table 15 are too high by about a factor of two compared to the observed average concentrations of these elements in the central region of Lake Huron. Only the predicted calcium and magnesium concentrations appear to be in satisfactory agreement with observed values.

Figure 15 is a plot of the average concentrations of calcium and magnesium of the four major sources of water in Lake Huron. On a plot of this type the sources of water should form the corners of a polygon. Water samples from the lake should plot inside this polygon. In the case shown in Figure 15 the polygon is virtually collapsed to a straight line represented by the equation:

$$\mathrm{Ca} \simeq 3.0\ \mathrm{Mg} + 6$$

The predicted concentrations of calcium and magnesium for well-mixed lake water and the average observed concentrations are in satisfactory agreement. In the right half of Figure 15 the regions are outlined into which samples from different parts of the lake will fall. It is clear that the samples from the North Channel and Saginaw Bay are approaching the average composition of the Central Region from opposite directions. The Central Region of Lake Huron appears to be quite well mixed.

In the case of calcium and magnesium the model is successful and gives a reasonably accurate picture of the degree of mixing achieved in different parts of the lake.

Figure 16 is a similar plot for the concentrations of calcium and strontium. On the left side of Figure 16 the polygon of mixing is outlined and the predicted and observed average concentrations for calcium and strontium are plotted. It is evident that the actual average concentration is barely within the polygon which

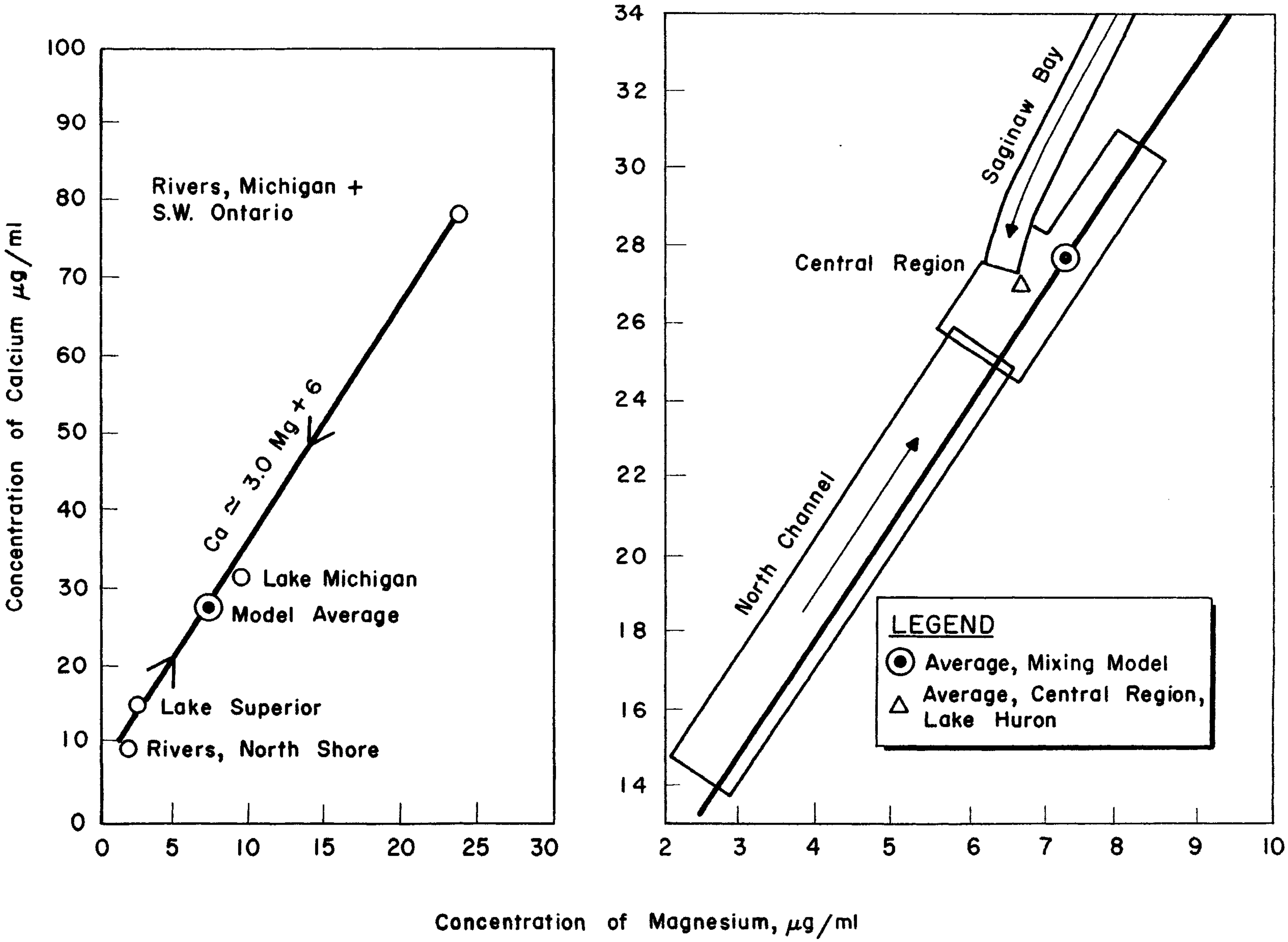

Figure 15. Mixing of calcium and magnesium in Lake Huron.

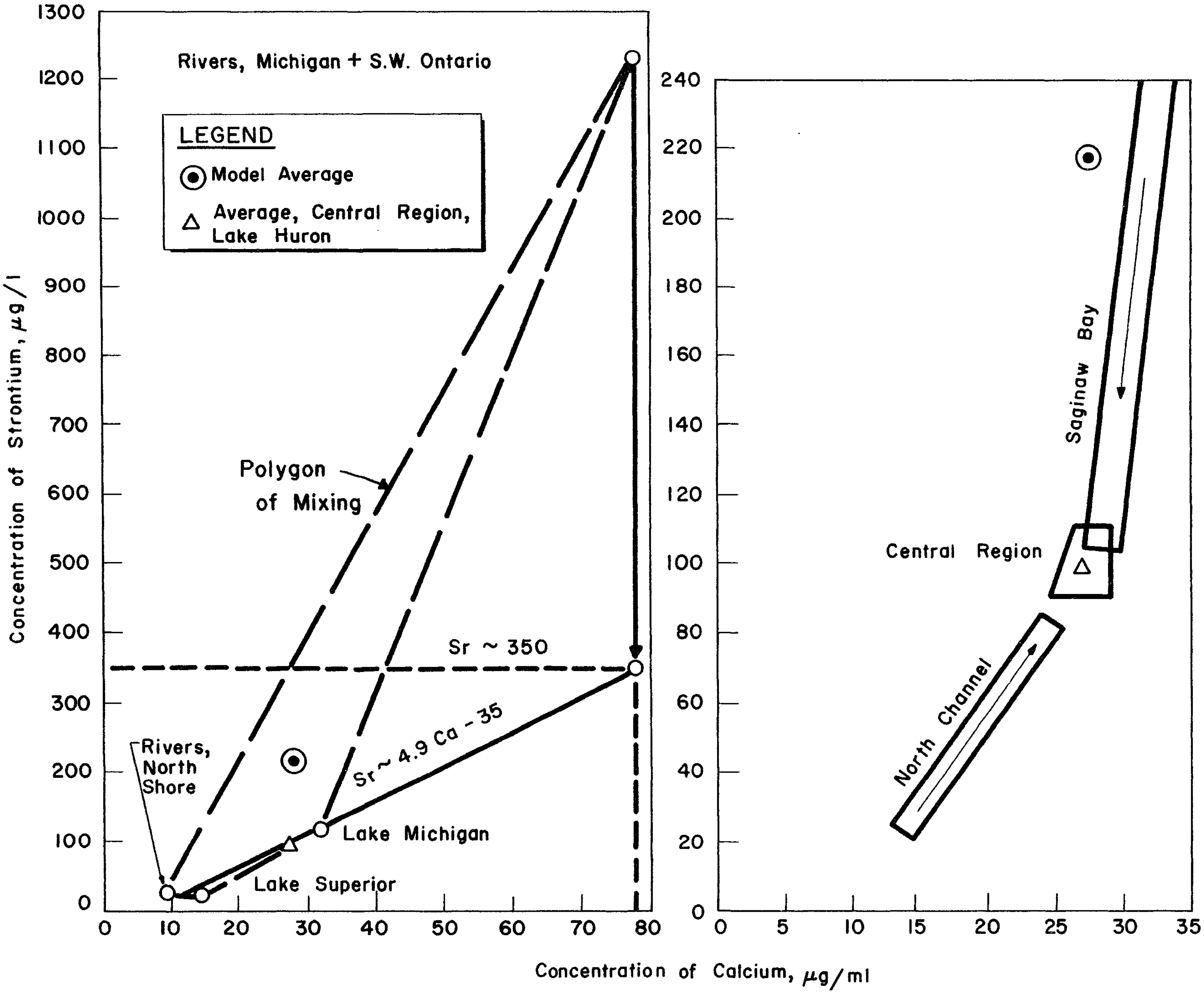

Figure 16. Mixing of strontium and calcium in Lake Huron.

is greatly distorted by the point representing the rivers draining Michigan and southwestern Ontario. The fit of the model to the data can be improved by the following rationalization: We assume that the polygon of mixing will, in this case, approach a straight line, as it appears to do in the case of magnesium and calcium. A straight line can then be drawn to fit the remaining four points. The approximate equation of this line is:

$$\mathrm{Sr} \simeq 4.9\ \mathrm{Ca} - 35$$

where Sr is in units of μg/l and Ca is in units of μg/ml. When this line is extrapolated to where it intersects the calcium concentration of the rivers of Michigan and southwestern Ontario, the corresponding strontium concentration can be read from the graph. The value so obtained is Sr = 350 μg/l.

On the right-hand plot in Figure 16 concentrations of strontium and calcium for different regions of Lake Huron are again outlined. The pattern is very similar to the one obtained in Figure 15 and illustrates the progressive changes in composition of water from the North Channel and Saginaw Bay. The Central Region of Lake Huron is found to be remarkably homogeneous with respect to strontium and calcium.

Calcium and potassium in Lake Huron and its major sources of water are shown in Figure 17. Again, the observed average composition of water in the lake is barely within the polygon of mixing. Using the same procedure as before, it is shown that the concentration of potassium in water discharged by rivers of Michigan and Southwestern Ontario should be reduced from 3.80 to about 2.0 μg/ml.

The pattern of distribution of calcium and potassium in the North Channel,

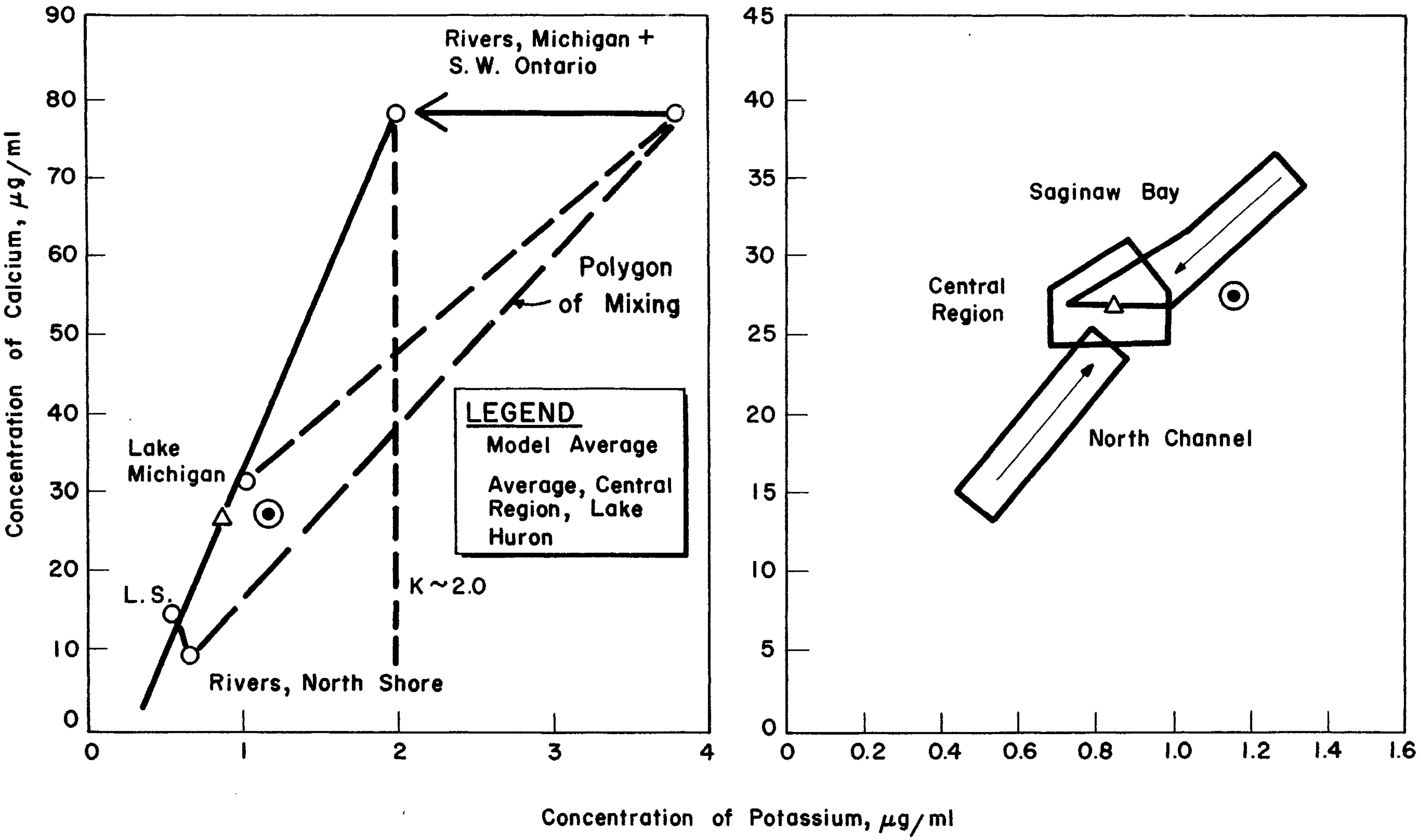

Figure 17. Mixing of calcium and potassium in Lake Huron.

Saginaw Bay and the Central Region of Lake Huron is similar to those observed in Figures 15 and 16.

THE ISOTOPE COMPOSITION OF STRONTIUM IN THE GREAT LAKES

Introduction:

The drainage basin of the Great Lakes and the St. Lawrence River is underlain by rocks ranging in age from early Precambrian to late Paleozoic. Compositionally the bedrock includes the igneous and metamorphic rocks of the Precambrian Shield as well as sedimentary rocks of Paleozoic age, including limestone, dolomite, and evaporite deposits. Because of these differences in age and mineral as well as chemical composition of the bedrock, the isotope composition of strontium which is released into solution during chemical weathering of the bedrock will show wide variations. Generally, the strontium coming from the rocks on the Canadian Shield will be enriched in radiogenic Sr^{87} relative to the strontium weathering out of the marine carbonate rocks of the Paleozoic sediments. As a result, the Sr^{87}/Sr^{86} ratio in the Great Lakes-St. Lawrence River drainage should exhibit variations on a regional scale and these variations should be related to the sources of the strontium which is discharged into the drainage system at different points.

In the following section we will describe the variations in the isotope composition and concentrations of strontium in the Great Lakes and the St. Lawrence River. The pertinent data are summarized in Table 16. In order to illustrate this discussion we have plotted the isotope composition and concentration of strontium as a profile through the Great Lakes and the St. Lawrence River. The position on this profile of each sample was determined by projecting it at

Table 16

Isotope Composition and Concentration of Strontium in the Great Lakes and the St. Lawrence River

Sample Number	Location	Collection Date	Sr µg/l	(Sr^{87}/Sr^{86})* corr.	Approximate Distance from Duluth, Minn. Miles
Lake Superior					
C-4355	Ashland, Wisconsin	1961	clam	0.7152	50
F-63-22	Tofte, Minnesota	9/8/63	22.9	0.7147	80
F-63-16	Copper Harbor, Michigan	9/6/63	22.0	0.7181	220
F-63-39	Mamainse Pt., Ontario	9/10/63	21.6	0.7153	380
F-63-14	Whitefish Pt., Michigan	9/5/63	21.2	0.7161	390
Lake Huron					
F-63-10	Lake Nicolet, Neebish Isl. Ferry	9/5/63	28.8	0.7151	460
F-63-5	Mackinaw City, Michigan	9/4/63	113.4	0.7113	480
C-66-44	Adams Pt. & Presque Isl., Michigan	8/25/66	91.8	0.7111	515
C-66-48	Lat. 45°04' Long. 83°10'	8/27/66	94.5	0.7096	525
F-63-52	Providence Bay Manitoulin Isl.	9/12/63	----	0.7103	545

Table 16 continued

Sample Number	Location	Collection Date	Sr µg/l	(Sr^{87}/Sr^{86})* corr.	Approximate Distance from Duluth, Minn. Miles
C-66-40	Middle Isl., Michigan	8/24/66	91.5	0.7099	535
C-66-16	South Baymouth Manitoulin Isl.	6/22/66	97.9	0.7111	560
C-66-56	Lat. 44°45' Long. 82°57'	8/30/66	93.5	0.7109	580
C-66-64	Lat. 44°14' Long. 82°19'	9/ /66	99.6	0.7109	640
C-66-66	Lat. 43°26' Long. 82°18'	9/ /66	105.4	0.7111	710
Lake Erie					
F-67-1	Detroit River, Windsor, Ontario	4/28/67	155.1	0.7099	790
C-66-26	Port Stanley, Ontario	6/25/66	162.2	0.7097	950
Lake Ontario					
C-66-28	Grimsby Beach, Ontario	6/25/66	172.9	0.7093	1115
C-66-29	Olcott, New York	6/26/66	178.4	----	
F-67-14	Wellington, Ontario	5/2/67	168.4	0.7096	1215
St. Lawrence River					
F-67-17	Montreal, Quebec	8/7/67	----	----	1460

Table 16 continued

Sample Number	Location	Collection Date	Sr µg/l	(Sr^{87}/Sr^{86})* corr.	Approximate Distance from Duluth, Minn. Miles
C-4334	L'Islet, Quebec	1961	clam	0.7120	1670
C-4333	Trois Pistoles, Quebec	1961	clam	0.7115	1765

* Corrected for fractionation assuming $Sr^{86}/Sr^{88} = 0.1194$

right angles to a line bisecting the lakes. This line generally coincides with the International Boundary. Each sample was then plotted as a function of its distance, in miles, from Duluth, Minnesota, as measured along the bisecting line. The resulting profile of the isotope composition and concentration of strontium is shown in Figure 18.

Lake Superior

The isotope composition of strontium in Lake Superior shows the expected enrichment in radiogenic Sr^{87}. The Sr^{87}/Sr^{86} ratios of five strontium samples range from 0.7147 to 0.7181. This much variation in the Sr^{87}/Sr^{86} ratio is surprising and seems incongruous with the remarkably uniform concentration of strontium of 21.8 µg/l. Sample C-4355 is the shell of a modern pelecypod collected along the beach at Ashland, Wisconsin. This shell was previously analyzed in duplicate by Faure, Hurley and Fairbairn (1963) who reported an average Sr^{87}/Sr^{86} ratio of 0.7176. This value is in excellent agreement with the new analysis reported in Table 16, when a correction of -0.0024 is applied to the earlier analyses. This correction is the difference between the Sr^{87}/Sr^{86} ratios of the Eimer and Amend $SrCO_3$ Isotope Standard reported by Faure, Hurley, and Fairbairn (1963) and the value obtained by the present authors. Hart and Tilton (1966) reported three isotope analyses of two strontium samples collected near the bottom of Lake Superior. Their Sr^{87}/Sr^{86} ratios range from 0.715 to 0.718. Hart and Tilton felt that 0.718 was the best value. It is conceivable that variations in the isotope composition occur near shore and that the scatter which we have observed is real. More analyses are needed to clarify this point.

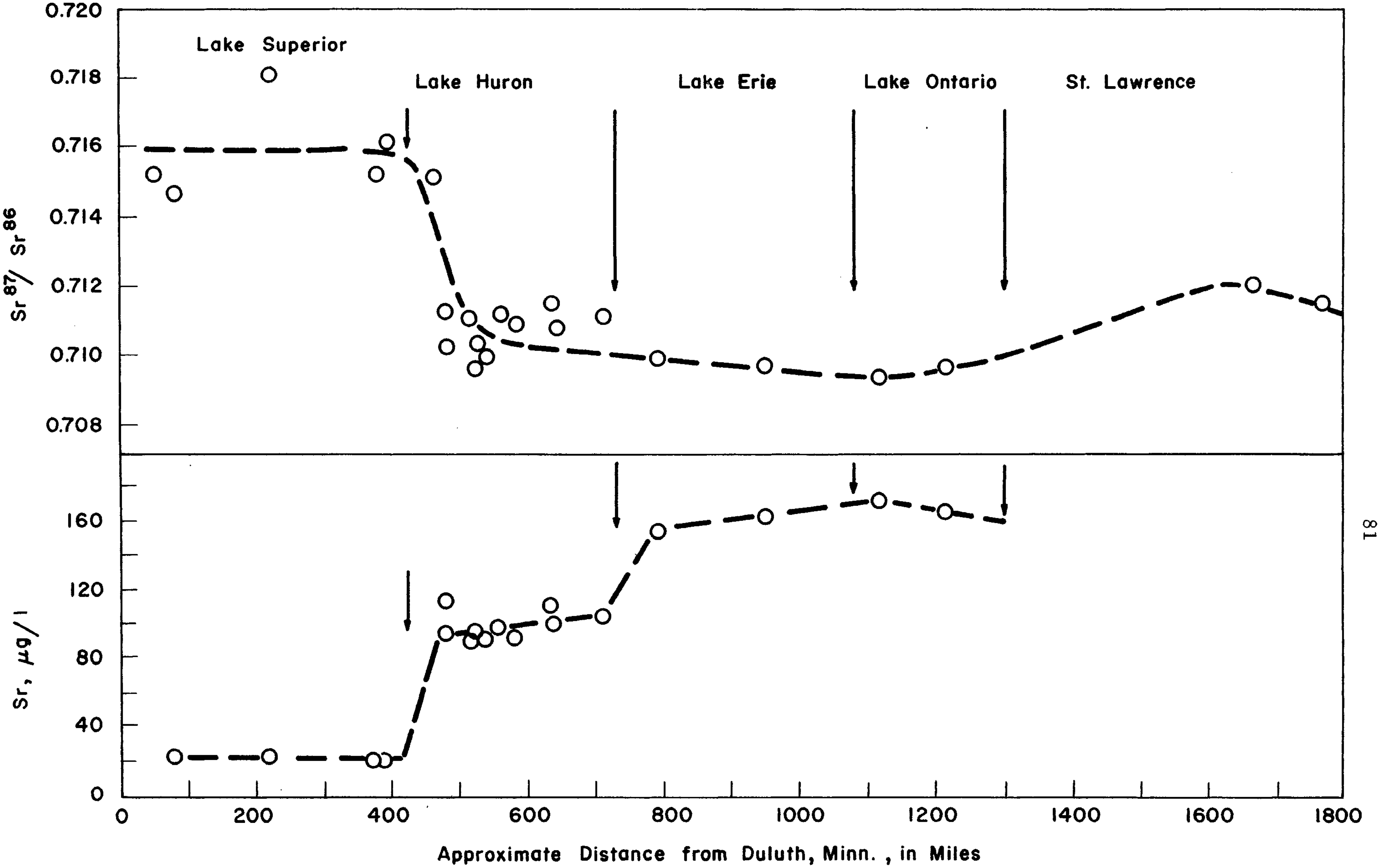

Figure 18. Isotope composition and concentration of strontium in The Great Lakes and the St. Lawrence River.

Lake Huron

As the water overflows from Lake Superior and enters Lake Huron via St. Mary's River a drastic change occurs in the isotope composition and concentration of strontium. This point is best made by reference to Figure 18. It can be seen that the Sr^{87}/Sr^{86} ratio drops sharply and ranges from 0.710 to 0.711, while the concentration rises to about 95 μg/l.

This sudden change is due to the "marine limestone effect" which was defined earlier. In the north end of Lake Huron water from the Precambrian Shield mixes with water which drains the sedimentary rocks of Michigan and southwestern Ontario. Data compiled in Table 7 show that the rivers draining the Canadian Shield have a high Sr^{87}/Sr^{86} ratio (0.7180) but a low concentration of strontium (29.3 μg/l). The rivers draining the Paleozoic rocks have a low average Sr^{87}/Sr^{86} ratio of 0.7100, but the concentrations vary from 72.6 up to 2791 μg/l. The result of mixing these two types of water is, therefore, a sharp lowering of the Sr^{87}/Sr^{86} ratio accompanied by an increase in the total strontium concentration of water entering Lake Huron from Lake Superior.

The concentration continues to rise slowly as the water moves toward the south in Lake Huron. The Sr^{87}/Sr^{86} ratios are scattered, but average 0.7107 ± 0.0006 in the Central Region of Lake Huron.

Lakes Erie and Ontario

Figure 18 shows that the Sr^{87}/Sr^{86} ratio continues to decline slowly through Lake Erie and reaches a minimum value of 0.7093 in the west end of

Lake Ontario. At the same time the concentration of strontium rises to about 173 μg/l. In the eastern end of Lake Ontario the Sr^{87}/Sr^{86} has a slightly higher value of 0.7096, while the concentration drops to 168 μg/l. These differences are small and hardly reproducible. Nevertheless, these changes may be caused by the discharge of water draining the Precambrian rocks of the Frontenac axis near Kingston, Ontario.

St. Lawrence River

The data for the St. Lawrence River are incomplete, but show clearly that the Sr^{87}/Sr^{86} ratio continues to rise after the water leaves Lake Ontario. This rise is due to the entry of water from the Canadian Shield via the Ottawa River and other rivers draining northern Quebec. At L'Islet, about 50 miles downstream from Quebec City, the Sr^{87}/Sr^{86} ratio is 0.7120. At Trois Pistoles, 150 miles from Quebec City, we obtained a value of 0.7115. Although this difference is not significant on the basis of these two measurements, it suggests a slow decrease in the Sr^{87}/Sr^{86} ratio in the Gulf of St. Lawrence down to 0.7093, which is the value of this ratio in the open ocean.

SUMMARY AND CONCLUSIONS

The chemical composition of water in Lake Huron is determined by the mixing of two types of water originating as run-off on the Canadian Shield and from the sedimentary rocks of Michigan and southwestern Ontario. The concentrations of the major cations in these two types of water were determined by analysis of water from the major tributaries of Lake Huron.

The water which drains the Canadian Shield and enters Lake Huron along its north shore was found to be dilute and uniform in composition. The strontium in this water is enriched in radiogenic Sr^{87} and has a Sr^{87}/Sr^{86} ratio of about 0.718. The radiogenic Sr^{87} is produced in the rocks of the Precambrian Shield by decay of naturally-occuring Rb^{87}.

The rivers draining Michigan and southwestern Ontario contain higher concentrations of the major cations and are far more variable in composition. The greatest differences in composition of these rivers occur in the concentrations of sodium, strontium and potassium. These variations in concentration are the result of the inhomogeneous distribution of the sources of these elements in this part of the drainage basin. It is very likely, although not yet demonstrated, that sodium and potassium are contributed to certain rivers by the weathering or exploitation of deposits of rock salt. Similarly, the exceptionally high strontium concentrations of several rivers in this area may be due to the weathering of celestite ($SrSO_4$).

The isotope composition of strontium in the rivers of Michigan and southwestern Ontario is very similar to that of strontium in the modern oceans. The average value of the Sr^{87}/Sr^{86} ratio was found to be 0.710. This observation indicates that a major portion of the strontium in these rivers originates as a weathering product of carbonate rocks or celestite deposits of marine origin.

The chemical composition of water in Lake Huron shows regional variations which are caused by the progressive mixing of the two types of water described above. These regional variations can be documented for the North Channel and Saginaw Bay. The number of samples from the Georgian Bay is insufficient to define a definite trend, although it may well exist. The water in the central part of Lake Huron, south of Manitoulin Island, is quite well mixed. Nevertheless, a slight increase in the concentrations of strontium and calcium can be discerned in the southern end of the Lake.

The isotope composition of strontium in Lake Huron varies within fairly narrow limits. The most pronounced differences occur in the North Channel area, while the strontium in Saginaw Bay appears to have constant isotope composition. In the central area of the lake the Sr^{87}/Sr^{86} ratios are somewhat scattered but do not correlate well with strontium concentration. On the average, the Sr^{87}/Sr^{86} ratio in the central area of Lake Huron has a value of 0.7107 ± 0.0006.

An attempt to calculate the chemical composition of well-mixed water in Lake Huron was only partially successful because of the difficulty in obtaining representative concentrations of the major cations in the rivers of Michigan and southwestern Ontario. Calcium and magnesium concentrations predicted by the model agree well with observed values. However, the predicted values for sodium, potassium and strontium are too high by a factor of about two.

The concentration and isotope composition of strontium in the Great Lakes and the St. Lawrence River vary in an opposite sense along a profile from Lake Superior to the Gulf of St. Lawrence. While the concentration rises from Lake Superior to Lake Ontario, the Sr^{87}/Sr^{86} ratio decreases. In the east end of Lake Ontario and the St. Lawrence River this pattern is reversed by the influx of dilute water from the Canadian Shield. The Sr^{87}/Sr^{86} ratios rise to a value of 0.712, but decline again as the water of the St. Lawrence River mixes with seawater.

This study has demonstrated the feasibility of representing the chemical composition of water in Lake Huron as a mixture of two (or more) types of water of differing chemical compositions. These differences in composition are related to the geology of the drainage basin.

The isotope composition of strontium in Lake Huron is limited in its usefulness as a tracer of water masses by the large amounts of strontium originating as weathering products of carbonate rocks and evaporite deposits in Michigan and southwestern Ontario.

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GEOCHEMICAL ASPECTS OF THE SCIOTO AND OLENTANGY RIVERS AT COLUMBUS, OHIO (1)

by Rene Eastin

INTRODUCTION

Water samples from the Olentangy and Scioto Rivers at Columbus were collected at weekly intervals during 1966 in order to study the seasonal variation of the chemical composition of these rivers. Composites of these samples were analyzed for sodium, potassium, calcium, strontium, and the strontium isotope composition. The resulting data were then analyzed to determine the influences of stream discharge and the geology of the drainage basin on the relative chemical composition of the two rivers.

GEOLOGY

The basins of the Olentangy and upper Scioto Rivers, shown in Figure 1, are underlain by nearly flat-lying sedimentary rocks dipping gently to the east. The rocks range from Upper Silurian dolomites and Devonian limestone and shales, of marine origin, to Lower Mississippian sandstone and shale, which are in part deltaic in origin.

The upper Scioto River basin is almost entirely underlain by carbonate rock such as the Tymochtee dolomite of the Bass Islands Group, the Greenfield dolomite, the Columbus limestone, and the Delaware limestone. (Stout, 1941).

The Olentangy River basin is largely underlain by the Ohio, Olentangy, and Bedford shales, and the Berea sandstone. The Columbus and Delaware limestones crop out only in the western part of the Olentangy basin.

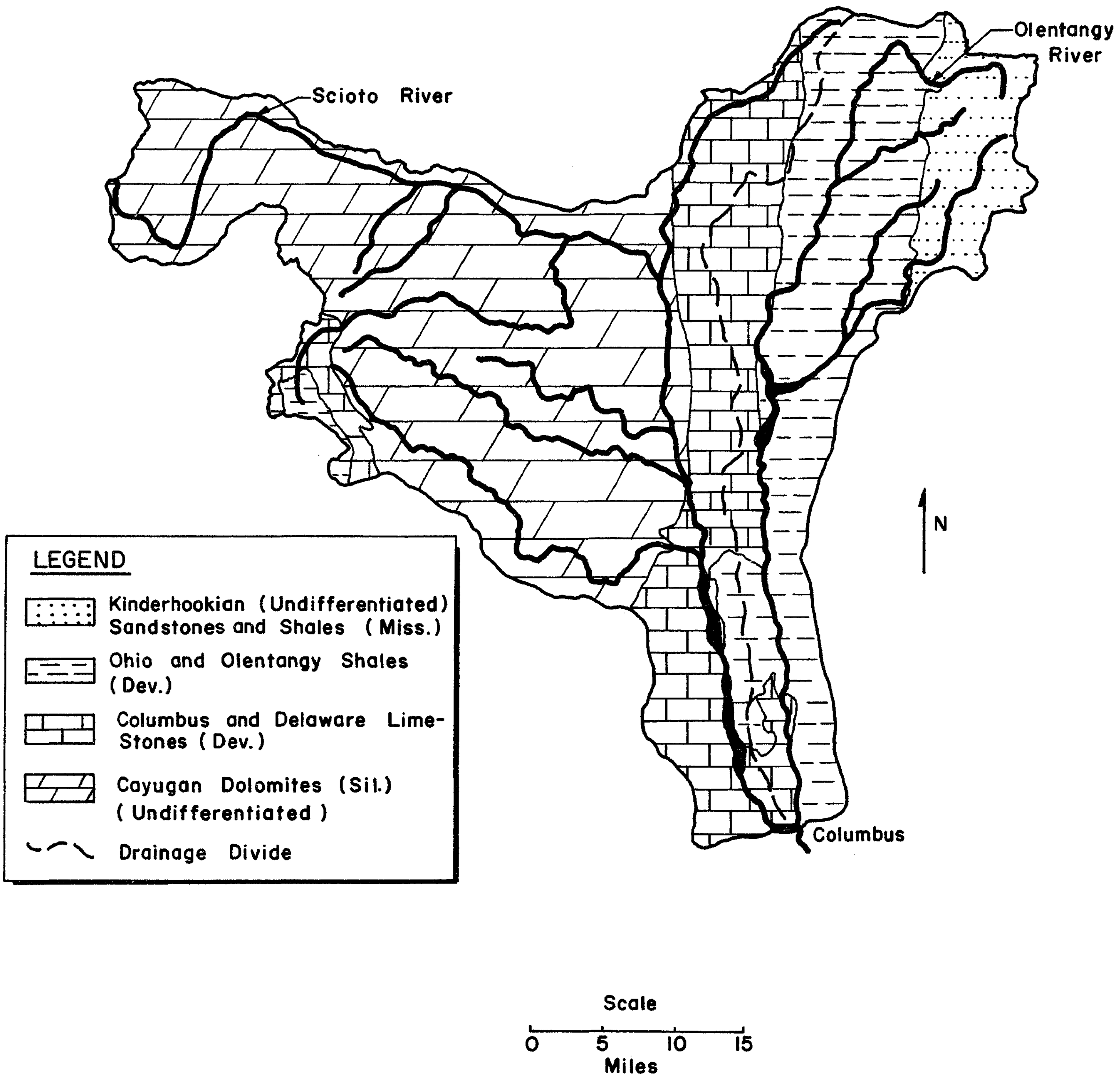

Figure 1. Geologic map of the Olentangy and Scioto River drainage basins.

Bedrock in Central Ohio is covered, in most places, by Pleistocene glacial deposits. The Olentangy and upper Scioto river basins are primarily covered with deposits of Wisconsin age. Illinoin drift occurs only as a fine sand, filling deep buried valleys.

The till and gravel sequence which covers central Ohio is well exposed along Rocky Fork Creek in Gahanna. The Bedford shale there is overlain by the early Wisconsin Rocky Fork Till and Lockbourne Gravel, and the late Wisconsin Darby Till. The four end moraines which loop across the Olentangy and upper Scioto river basins consist of Hiram Drift, which is of Cary (?) age (15,000 B.P.) (Goldthwait and Forsythe, 1965).

The Ground moraines average about 50 feet in thickness. Pebble lithology (primarily dolomite) and fabric indicate that the late Wisconsin glacier came from the north-northwest.

ANALYTICAL PROCEDURES

Water samples were taken at weekly intervals during 1966. The Olentangy River was sampled on the Ohio State University campus. The Scioto River samples were collected just below Griggs Reservoir, in Columbus.

Temperature and pH determinations were made on these samples at the time of collection. Composites were made by combining samples from each four-week period. The composites were filtered and analyzed for Na and K by flame photometry, for Ca by titration with EDTA, and for Sr by isotope dilution. In addition the isotope composition of Sr was measured by mass spectrometry.

DISCUSSION

A complete listing of measurements made on the Olentangy and Scioto river samples at Columbus during 1966 is presented in Tables 1 and 2. This data is summarized in Figure 2 for the Olentangy River and in Figure 3 for the Scioto River.

The data on streamflow were taken from stream gauges operated by the U. S. Geological Survey about ten miles upstream from the sampling sites. The Delaware Reservoir on the Olentangy River and the O'Shaughnessy Reservoir on the Scioto River affect the streamflow data and limit its application to this study. During 1966 there were four periods of low flow: January-February, April, June-July, and September-October.

River water should be chemically most concentrated during periods of low flow when highly mineralized ground water is the source of streamflow and contributions by dilute surface runoff are minimal. The concentrations of sodium, calcium, and strontium in the Olentangy and Scioto Rivers show this pattern. Potassium, however, seems to steadily increase throughout the year to a maximum level in October.

The range of concentrations of sodium, potassium, calcium, and strontium measured in water samples from the Olentangy and Scioto Rivers is presented in Table 3. Ohio rivers contain primarily hard waters whose dominant ions are calcium, magnesium, bicarbonate, and sulfate (Hubble and Collier, 1960). Differences in the chemical composition of Ohio rivers are related to the sources of the dissolved elements namely: bedrock, till, soil, and waste disposal.

Table 1. Complete listing of measurements on water samples of the Olentangy River during 1966. (Concentration in units of μg per ml; temperature in ^{o}C; bracketed values are not included in the mean).

Date	Temp	pH	Composite	Na	Mean Na	K	Mean K	Ca	Mean Ca	Sr	Mean Sr	$\frac{Sr x 10^3}{Ca}$	$\frac{Sr^{87}}{Sr^{86}}$
Jan. 4	3			30.3	30.3	3.12	3.2	81.2	81.2				
11	1			30.3		3.18							
18	1		1			3.28							
25	1					3.00							
						3.37							
Feb. 1	1	7.90		38.3	38.5	3.10	2.9	92.3	92.3	1.194	1.190	12.9	0.7116
8	0	7.88		38.7		2.97				1.185			±0.0005
15	2	7.80	2			[3.28]							
22	1	7.85				2.75							
						2.93							
Mar. 1	4	7.75		[29.2]	21.7	2.33	2.2	79.3	79.3	0.817	0.819	10.3	
8	3	7.95		23.2		2.11				0.820			
15	8.9	7.80	3	20.2		2.24							
22	9.0	8.30				2.20							
Mar. 30	7.5	8.55		29.7	29.7	2.75	2.6	71.9	71.9	1.208	1.208	16.8	
Apr. 5	7.0	8.50		29.7		2.42							
12	7.2	8.20	4			2.60							
19	15.6	8.30											
Apr. 27	13.6	8.20		18.5	18.6	2.55	2.4	71.5	71.5	0.725	0.725	10.1	0.7086

Table 1. Continued.

Date	Temp.	pH	Composite	Na	Mean Na	K	Mean K	Ca	Mean Ca	Sr	Mean Sr	$\frac{Sr\times10^3}{Ca}$	$\frac{Sr^{87}}{Sr^{86}}$
May 3	13.8	7.95		18.7		2.23							
11	10.4	8.08	5			2.40							
18	15.9	8.00											
25													
May 25	14.4	8.18		24.0	24.3	3.05	3.0	81.2	81.2	0.624	0.624	7.4	
June 1	23.2	7.90		24.6		2.89							
8	23.5	7.87	6			3.00							
14	26.0	8.33				3.05							
June 21	26.7	8.61		30.2	30.3	3.40	3.3	81.7	81.7	1.542	1.542	18.9	0.7105
27	32.5	8.35		30.4		3.28							
July 5	28.0	7.85	7			3.20							
12	24.8	7.82				3.30							
July 19	24.6	7.72		17.0	17.1	3.74	3.7	54.4	54.4	0.907	0.907	15.4	0.7103
26	32.4	8.90		17.2		2.73							
Aug. 2	24.1	8.06	8			[3.50]							
9	24.6	8.60				3.75							
Aug. 16	26.7	7.77		20.3	20.1	3.79	3.7	63.8	63.6	0.979	0.979	15.4	0.7103
23	25.6	8.54		[25.1]		3.66		63.3					
30	31.5	7.10	9	19.9		3.45							
Sept. 6	24.0	7.30				3.99							
						3.53							
Sept. 13	21.7	8.10		31.8	31.8	4.01	4.0	74.0	74.0	1.575	1.575	21.3	

Table 1. Continued

Date	Temp.	pH	Composite	Na	Mean Na	K	Mean K	Ca	Mean Ca	Sr	Mean Sr	$\frac{Srx10^3}{Ca}$	$\frac{Sr^{87}}{Sr^{86}}$
20	17.8	7.50		31.7		4.09							
27	18.6	8.60	10			[3.69]							
Oct. 4	16.2	8.58				4.03							
Oct. 11	16.0	8.58		34.5	34.6	4.95	4.9	80.1	80.1	1.733	1.733	21.6	
18	13.0	7.70		34.6		4.95							
25	12.0	7.85	11			[4.79]							
Nov. 2	7.5	7.65				4.90							
Nov. 8	9.0	7.70		[20.5]	22.4	4.15	4.1	71.0	71.0	0.835	0.835	11.8	
17	9.5	7.86		22.4		4.21							
23	7.5	7.79	12	22.3		3.83							
29	5.0	7.90				4.40							
						4.06							
Dec. 6	2.0	8.05		16.7	16.6	3.23	3.2	69.0	69.0	0.618	0.618	9.0	
14	4.0	7.73		16.4		3.11							
21	3.0	7.25	13			[2.78]							
27	1.0	8.05				3.20							
Jan. 3	1.0	8.00			—	3.19	3.1	101.8	101.5	1.405	1.405	13.8	
10	1.0	8.07				2.98		101.2					
17	1.0	7.95	14										
24	5.0	7.98											

Table 2. Complete listing of measurements on water samples of the Scioto River during 1966. (Concentration in units of $\mu g/ml$; temperature in ^{o}C; bracketed values are not included in the mean.)

Date	Temp.	pH	Composite	Na	Mean Na	K	Mean K	Ca	Mean Ca	Sr	Mean Sr	$\frac{Sr x 10^3}{Ca}$	$\frac{Sr^{87}}{Sr^{86}}$
Mar. 1	3	7.70		14.0	14.1	2.45	2.5	90.6	90.6	2.120	2.121	23.5	0.7094
8	4	8.08		14.1		2.63				2.141			
15	7.6	8.10	1										
22	11.0	8.20											
Mar. 30	7.4	8.20		[16.5]	15.9	2.50	2.2	96.2	96.2	2.694	2.694	28.0	
Apr. 5	8.9	8.40		15.8		2.20							
12	6.7	8.10	2	16.0		1.81							
19	10.8	8.45				2.10							
Apr. 27	14.6	8.66		12.5	12.4	3.25	2.9	85.1	85.1	2.136	2.136	25.1	0.7092
May 3	14.2	7.90		[11.7]		2.93							
11	12.5	7.80	3	12.3		2.50							
18	14.5	8.00				2.72							
May 25	19.3	8.20		14.3	13.3	[3.23]	2.7	84.5	84.5	2.113	2.113	25.0	
June 1	22.8	8.15		12.3		[2.98]							
8	22.7	8.35	4			2.68							
14	25.5	8.60				2.70							
June 21	27.4	8.63		15.4	15.6	3.30	3.4	74.0	74.0	2.530	2.530	34.2	
27	28.9	8.20		15.7		3.40							
July 5	28.9	7.73	5										
12	26.3	8.10											

Table 2. Continued.

Date	Temp.	pH	Composite	Na	Mean Na	K	Mean K	Ca	Mean Ca	Sr	Mean Sr	$\frac{Sr \times 10^3}{Ca}$	$\frac{Sr^{87}}{Sr^{86}}$
July 19	27.1	7.80		5.6	5.8	3.77	3.9	53.2	53.2	0.954	0.954	17.9	
26	29.5	8.78		6.0		3.95							
Aug. 2	26.7	8.01	6										
9	24.5	7.90											
Aug. 16	26.5	8.31		13.4	13.5	4.00	4.2	70.6	70.6		2.268	32.1	0.7096
23	25.2	8.60		13.6		4.30							
30	29.4	7.23	7										
Sept. 6	25.0	7.65											
Sept. 13	22.0	8.15		17.6	17.6	3.90	4.1	68.0	68.0	2.426	2.426	35.7	
20	19.8	7.73		17.6		4.22							
27	18.5	8.17	8										
Oct. 4	14.6	7.56											
Oct. 11	16.5	8.66		20.1	20.3	3.95	4.0	72.3	72.3	2.793	2.793	38.6	
18	13.8	7.94		20.5		3.95							
25	16.0	8.62	9										
Nov. 2	6.5	7.75											
Nov. 8	9.2	8.00		14.4	14.6	4.85	5.0	79.1	79.1	2.108	2.108	26.7	
17	9.0	7.82		14.7		5.15							
23	9.5	7.75	10										
29	7.5	7.84											

Table 2. Continued

Date	Temp.	pH	Composite	Na	Mean Na	K	Mean K	Ca	Mean Ca	Sr	Mean Sr	$\frac{Sr\times10^3}{Ca}$	$\frac{Sr^{87}}{Sr^{86}}$
Dec. 6	5.0	8.05		8.4	8.7	4.13	3.9	74.3	74.3	1.365	1.365	18.4	
14	4.0	7.75		8.9		[4.31]							
21	4.0	7.67	11			3.96							
27	3.0	8.00				3.88							
Jan. 3	3.5	7.85				3.18	3.1	95.7	95.7	1.965	1.965	20.5	
10	2.5	7.92				2.98							
17	2.5	7.84	12										
24	5.5	7.75											

Sodium

Sodium varied from 16.6 to 38.5 μg/ml in the Olentangy River and from 5.8 to 20.3 μg/ml in the Scioto River. Comparing simultaneous samples, the Olentangy River contained about two to three times as much sodium as the Scioto River. This difference could be related to the bedrock composition of the two river basins. The shales of the Olentangy River basin contain more sodium than do the dolomite and limestone of the Scioto River basin (Stout, 1941, samples 92, 93, 208, 209, 15, 244, and Lamborn, et. al., 1938, pp. 20, 34, 49).

However, the relatively high sodium content of the Olentangy River is more probably related to waste disposal. Oil production began in Morrow and Delaware counties in 1961. By 1966 an estimated 16,000,000 barrels of salt water were produced and disposed of. Much of the brine was dumped or evaporated in unlined pits and extensively contaminated ground water in the Olentangy River basin.

In an unpublished Master's Thesis at the Ohio State University in 1966, J. E. Shaw mapped this brine contamination and traced the movement of brine from well of pit toward the nearest stream.

Two analyses of the Olentangy River at Columbus in 1956 and 1957 showed only 10 and 11 ppm sodium, respectively (Hubble and Collier, 1960, p. 201). These samples had relatively high concentrations of the other elements present and could thus be expected to contain a near maximum of sodium concentration.

For 1966 the sodium concentrations shown in Table 3 are significantly higher than those recorded in 1956 and 1957. The increased sodium content of the Olentangy River in 1966 may be due to brine contamination from the oil wells.

Table 3. Range of Concentrations of Na, Ca, and Sr in the Olentangy and Scioto Rivers (In units of μg/ml).

Element	Olentangy River	Scioto River
Sodium	16.600 - 38.500	5.800 - 20.300
Potassium	2.200 - 4.900	2.200 - 5.000
Calcium	54.400 - 101.500	53.200 - 96.200
Strontium	0.604 - 1.733	0.954 - 2.793

Potassium

Potassium varied from 2.2 to 4.9 μg/ml in the Olentangy River and from 2.2 to 5.0 μg/ml in the Scioto River. The annual pattern of potassium concentration in both rivers is very similar (see Figures 2 and 3). Because potassium concentrations seem to show no relationship to streamflow, potassium probably has an artificial source, still undetermined, but perhaps related to agriculture.

Calcium

Calcium concentrations in the two rivers were essentially equal: 54.4 to 101.5 μg/ml in the Olentangy River and 53.2 to 96.2 μg/ml in the Scioto River. If bedrock were the primary source of dissolved calcium, then the Scioto River should have had a higher calcium content than the Olentangy River.

A more likely source of calcium is the limestone and dolomite rock fragments in the till covering both river basins. Glacier transport from dolomite and limestone outcrops to the north and northwest has made the till lithology over both basins largely carbonate rock. Solution of the carbonate rock in this till would then result in nearly equal calcium concentrations in the two rivers.

Strontium

Strontium in the Scioto River varied from 0.954 to 2.793 μg/ml; the range of strontium in the Olentangy River was 0.604 to 1.733 μg/ml. Comparing simultaneous samples, the Scioto River had up to 3 times the strontium content of the Olentangy River. According to Stout and Lamborn analyses of the bedrock in the two basins, there is 0.01 per cent of SrO in the Tymochtee dolomite of the Scioto basin, but none in the shales of the Olentangy basin. Bedrock composition might, therefore, account for the greater concentration of strontium in the Scioto River.

However, the measured concentrations of strontium in both rivers is very high compared to other rivers and lakes of North America (Odum, 1957; Skougsted and Horr, 1963). The magnitude of the strontium content in the Olentangy and Scioto rivers makes it unlikely that the bedrock is the primary source of strontium.

In the Bass Islands-Sandusky area, in northwestern Ohio, the Upper Silurian dolomites contain up to 3.56 per cent of SrO (Stout, 1941). The strontium is present in the mineral celestite ($SrSO_4$), which is found as small crystals lining cavities or as distinct granules throughout the rock. The celestite occurs with gypsum beds in a hypersaline facies. The strontium was most common in the Tymochtee, Greenfield, and Lockport dolomites.

It is very likely that the till in the Scioto and Olentangy river basins contains celestite which was glacier-transported from outcrops in the Sandusky area. The celestite would then supply strontium to both the Olentangy and Scioto rivers. The Scioto River basin, because of its relative proximity to the celestite source area, may have received more celestite than did the Olentangy River basin. This might explain the higher strontium content of the Scioto River relative to the Olentangy River.

In addition, there is other evidence that the dissolved strontium is derived from celestite. The $Sr/Ca \times 10^3$ ratios measured in the Scioto and Olentangy Rivers range from 17.9 to 38.6. These values are much higher than the Sr/Ca

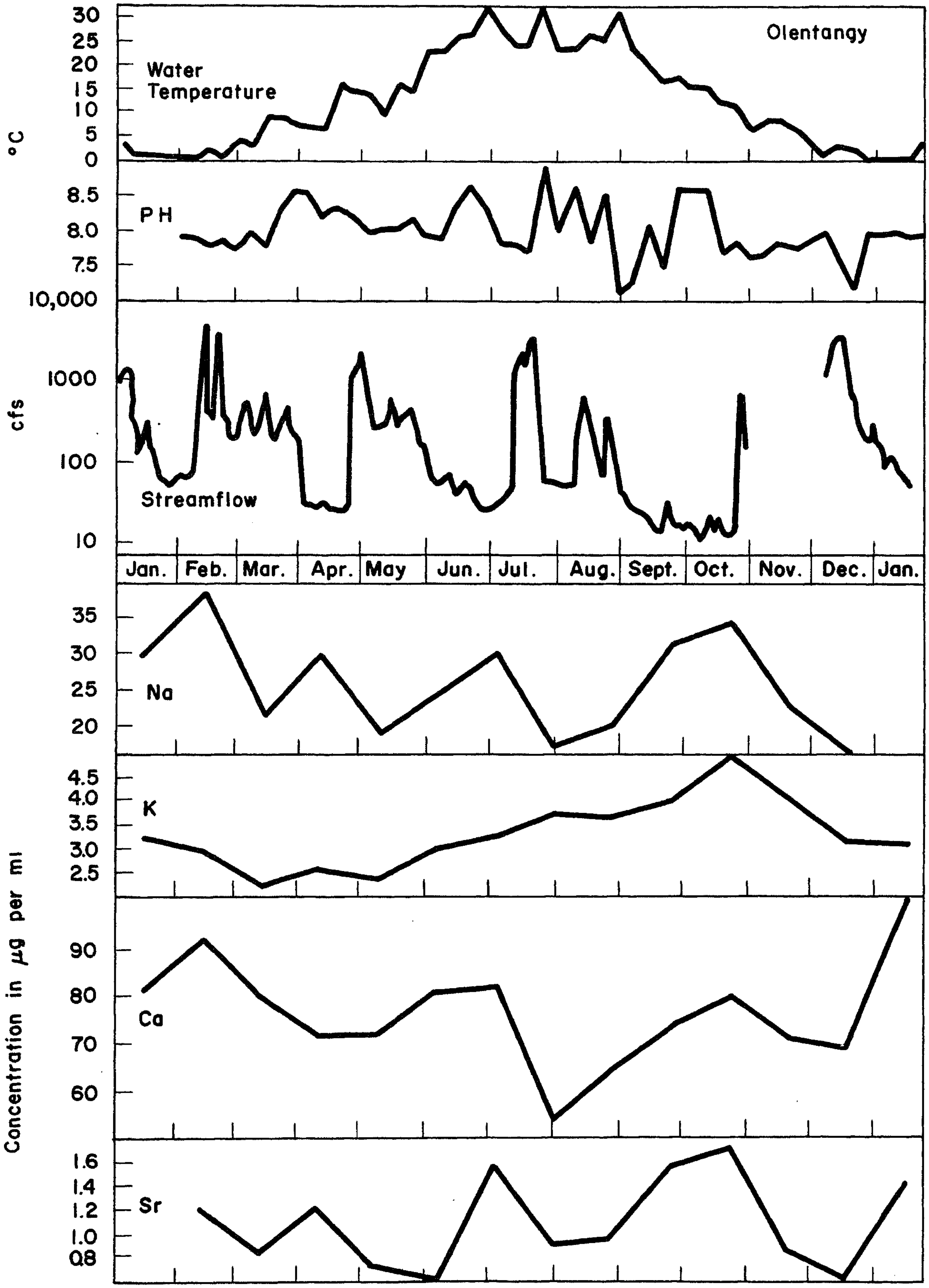

Figure 2. Summary of data for the Olentangy River.

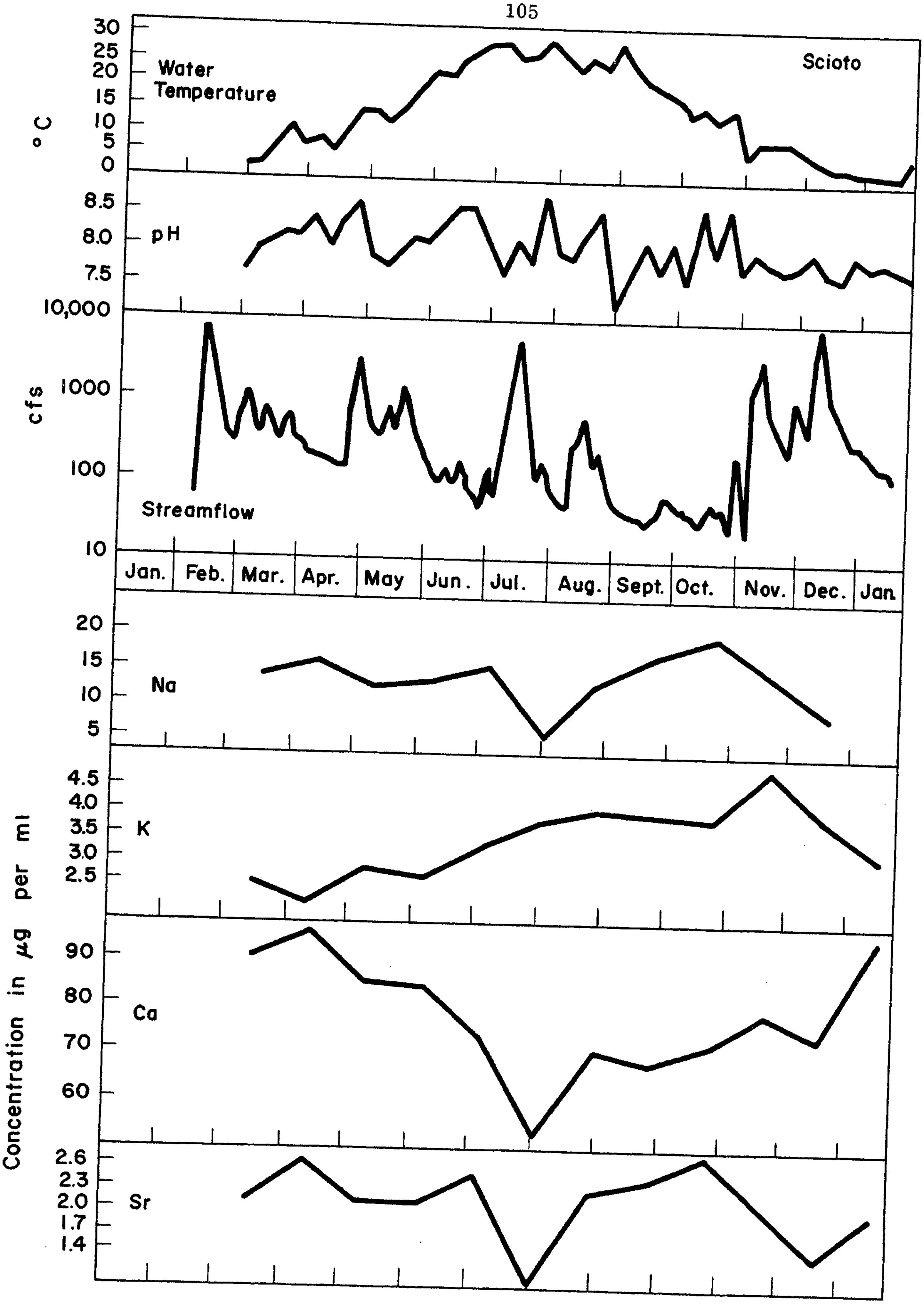

Figure 3. Summary of data for the Scioto River.

x 10^3 ratios of most streams (Turekian, 1964, p. 1492) and are only explained if the strontium is derived from strontium minerals.

In a study of high strontium concentration in the surface and ground water of Champaign County, Ohio, Feulner and Hubble (1960) concluded that the strontium was derived from the Upper Silurian dolomite bedrock in Champaign County and also from glacier-transported celestite present in the local till.

MEASURED Sr^{87}/Sr^{86} RATIOS

Measurements of the isotopic composition of strontium in samples from the Olentangy and Scioto rivers are shown in Table 4. The corrected Sr^{87}/Sr^{86} values varied from 0.7116 to 0.7086 for the Olentangy River, and from 0.7096 to 0.7088 for the Scioto River.

The isotope measurements for the Scioto River are identical within the limits of experimental error. The mean Sr^{87}/Sr^{86} ratio for the Scioto was 0.7093 ± 0.0003, identical to the ratio for modern oceans, and perhaps related to the marine origin of the celestite.

The variation of the Sr^{87}/Sr^{86} ratio in the Olentangy River may be real and may indicate that the strontium is derived from more than one source, each source having a characteristic Sr^{87}/Sr^{86} ratio. The igneous and metamorphic rock in local till could provide old strontium, having a higher Sr^{87}/Sr^{86} ratio. This old strontium might affect the Sr^{87}/Sr^{86} ratio in the Olentangy River, where less celestite strontium is present compared to the Scioto River. The variation in the Sr^{87}/Sr^{86} ratio of the Olentangy River may be related to the relative distribution and hydrologic environment of celestite-rich till and till having a high

Table 4. Isotopic composition of strontium in the Olentangy and Scioto Rivers and in the Columbus limestone.

Period	Sr^{86}/Sr^{88}	Sr^{87}/Sr^{86}	(Sr^{87}/Sr^{86}) corrected
Olentangy			
Feb. 1 - Feb. 22	0.1191 ±0.0003	0.7125 ±0.0014	0.7116 ±0.0005
Apr. 27 - May 18	0.1186	0.7110	0.7086
June 21 - July 12	0.1193	0.7108	0.7105
Aug. 16 - Sept. 6	0.1185	0.7130	0.7130
Scioto			
Mar. 1 - Mar. 22	0.1195	0.7091	0.7094
Apr. 27 - May 18	0.1197	0.7083	0.7092
June 21 - July 12	0.1195	0.7086	0.7088
Aug. 16 - Sept. 6	0.1205	0.7064	0.7096
Columbus			
Limestone	0.1200	0.7082	0.7099 ±0.0017

igneous and metamorphic rock content.

CONCLUSIONS

Concentrations of sodium, calcium and strontium in the Olentangy and Scioto Rivers in 1966 varied inversely with discharge. Potassium concentrations increased to a maximum in October, independent of discharge.

Relative concentrations of sodium and potassium in the two rivers could not be related to basin geology because of the influence of waste disposal. The relative concentrations of calcium and strontium present in the Olentangy and Scioto may indicate that glacial till overlying both drainage basins is the primary source of these elements. The unusually high strontium concentrations in both rivers are attributable to the presence of detrital celestite in the till deposits.

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