

THE UNIVERSITY OF MICHIGAN
COLLEGE OF ENGINEERING
Department of Meteorology and Oceanography

Technical Progress Report No. 3

- I. OCCURRENCE OF HALOGENS IN ATMOSPHERIC AEROSOLS AND PRECIPITATION
- II. AIR POLLUTION INPUTS OF TRACE METALS TO LAKE MICHIGAN WATER

John W. Winchester

ORA Project 08903

under contract with:

U. S. ATOMIC ENERGY COMMISSION
CHICAGO OPERATIONS OFFICE
CONTRACT NO. AT(11-1)-1705
ARGONNE, ILLINOIS

administered through:

OFFICE OF RESEARCH ADMINISTRATION

ANN ARBOR

May 1970

During the first three year period of this contract, June 1, 1967 to May 31, 1970, the major organizing principle guiding the research plan has been the question "What is the relationship between the composition of atmospheric particulates in the Great Lakes Basin, their natural and pollution sources, and the composition of waters of the Great Lakes?" Consequently the research of students and staff associated with the project has fallen into three areas:

- (1) Basic studies of aerosol composition building on previous work in marine aerosols.
- (2) Evaluation of the composition of air particulates in the urban-industrial area of Chicago and Northwest Indiana and in surrounding localities.
- (3) Tests of basic concepts of material balances for chemical substances in the Great Lakes.

At the present time we feel that useful techniques of neutron activation analysis have been perfected and that the groundwork has been laid for carrying out detailed studies on a much larger scale than has heretofore been possible and than has been possible with only the resources available under this project. The following report consists of a list of publications of work already completed under the contract and reprints of technical papers. In about May 1971 a supplementary report will be prepared containing additional reports still incomplete at the time of this writing.

ARTICLES

- John W. Winchester, "Halogens, Atmospheric Geochemistry of," 1968 Yearbook of Science and Technology, pp. 205-206, McGraw-Hill (1968); also in Encyclopedia of Science and Technology, McGraw-Hill (in press).
- Ronald H. Loucks, John W. Winchester, Wayne R. Matson and Mary A. Tiffany, "The Halogen Composition of Aerosol Particles Over Lake Michigan," Modern Trends in Activation Analysis, Conference Proceedings, U.S. National Bureau of Standards Special Publication 312, pp. 36-42 (1969).
- Mary A. Tiffany, John W. Winchester, and Ronald H. Loucks, "Natural and Pollution Sources of Iodine, Bromine, and Chlorine in the Great Lakes," Journal of the Water Pollution Control Federation, 41, 1319-1329 (1969).
- John W. Winchester, "Pollution Pathways in the Great Lakes," Limnos 2, No. 1, 20-24 (1969).
- Ronald H. Loucks and John W. Winchester, "Pollution Contributions to the Atmospheric Inventory of Chlorine and Bromine in Aerosols over Continental U.S.A.," Trace Substances in Environmental Health-III, Conference Proceedings, University of Missouri, June 1969 pp. 233-250.
- Mary A. Tiffany and John W. Winchester, "Surface Water Inputs of Iodine, Bromine, and Chlorine, to Lake Huron," Twelfth Conference on Great Lakes Research, Proceedings, 789-800, 1969.
- Ronald H. Loucks and John W. Winchester, "Some features of Chlorine and Bromine in aerosols," J. Geophys. Res. 75, 2311-2315, 1970.
- John W. Winchester and Gordon D. Nifong, "Water Pollution in Lake Michigan by Trace Elements from Pollution Aerosol Fallout," J. Air Pollution Control Assn. (submitted).
- R. Dams, J.A. Robbins, K.A. Rahn, and J.W. Winchester, "Nondestructive Neutron Activation Analysis of Air Pollution Particulates," Anal. Chem. (in press).
- R. Dams, K.A. Rahn, and J.W. Winchester, "Sampling Aerosols for Nondestructive Neutron Activation Analysis," Environmental Science and Technology (submitted).
- P.R. Harrison, K.A. Rahn, R. Dams, J.A. Robbins, J.W. Winchester, S.S. Brar, and D.M. Nelson, "Areawide Trace Metal Concentrations in Northwest Indiana as Determined by Multielement Neutron Activation Analysis: A One Day Study," J. Air Pollution Control Association (submitted).
- K.A. Rahn, R. Dams, J.A. Robbins, and J.W. Winchester, "Diurnal Variations of Aerosol Trace Element Concentrations as Determined by Nondestructive Neutron Activation Analysis," Atm. Environment (submitted).
- John W. Winchester, "Chemical Equilibria of Iodine in Great Lakes Waters," Thirteenth Conference on Great Lakes Research, Proceedings, 1970 (submitted).
- John A. Robbins, "A Model for Variations of Halogen Ion Ratios in Marine Aerosols with Particle Size", 1970 Precipitation Scavenging Meeting, June 1970, Richland Washington.

ABSTRACTS

- John W. Winchester, Douglas R. Sendelbach, and H. Göte Östlund, "Sea Salt Halogens as Natural Atmospheric Tracers in Hurricane Studies," *Trans. Am. Geophys. Union* 49, No. 1, 184 (1968) March.
- Mary A. Tiffany, John W. Winchester, and Ronald H. Loucks, "Natural and Pollution Sources of Iodine, Bromine, and Chlorine in the Great Lakes," 41st Annual Conference, Water Pollution Control Federation, Chicago, Illinois, September 22-27, 1968.
- John W. Winchester, "Selective Oxidation of Bromide in Aerosols," 154th Meeting, American Chemical Society, paper Y-32, September, 1967.
- Mary A. Tiffany and John W. Winchester, "Surface Water Inputs of Iodine, Bromine, and Chlorine to Lake Huron," 12th Conference on Great Lakes Research, Ann Arbor, Michigan, May 5-7, 1969.
- John W. Winchester, "Water Pollution in the Great Lakes by Trace Elements from Pollution Aerosol Fallout," 157th meeting, Am. Chem. Soc. paper WATR - 34, April 1969.
- R. H. Loucks, and J. W. Winchester, "Particle Size Distribution of Chlorine and Bromine in Mid-Continent Aerosols from the Great Lakes Basin," paper F-12, CACR Symposium on Atmospheric Trace Constituents and Atmospheric Circulation, Heidelberg, Germany, September 8-13, 1969.
- John W. Winchester, John A. Robbins, and Richard F. Dams, "Sources and sinks of air pollution trace metals in Lake Michigan," *Trans. American Nuclear Society*, 12, 484 (1969).
- John W. Winchester, "Chemical considerations in planning pollution-induced climate modification in the Lake Michigan Basin," Program, American Institute of Chemical Engineers 67th National Meeting, Atlanta, Georgia, 15-19 February 1970.
- Richard Dams, Kenneth A. Rahn, and John W. Winchester, "Sampling pollution aerosols for non-destructive neutron activation analysis," 159th meeting, American Chemical Society, February 1970.
- Richard Dams, John A. Robbins, Kenneth A. Rahn, and John W. Winchester, "Non-destructive neutron activation analysis of air pollution particulates," 159th meeting, American Chemical Society, February 1970.
- John W. Winchester, John A. Robbins, and Richard F. Dams, "Trace metals in air pollution from the Lake Michigan Basin," 159th meeting, American Chemical Society, February 1970.
- P. R. Harrison, K. A. Rahn, R. Dams, J. A. Robbins, J. W. Winchester, S. S. Brar, and D. M. Nelson, "Areawide atmospheric trace metal concentrations in Northwest Indiana as determined by multielement neutron activation analysis: a one day study," Am. Chem. Soc.-Canadian Institute of Chemistry, Toronto, 27 May 1970.
- Gordon D. Nifong and John W. Winchester, "Elemental Composition of Pollution Aerosols as a Function of Particle Size," Symposium on the Use of Nuclear Techniques in the Measurement and Control of Environmental Pollution, Salzburg, Austria, 26-30 October 1970, International Atomic Energy Agency (submitted).

Richard Dams, John A. Robbins, Kenneth A. Rahn, and John W. Winchester. "Quantitative Relationships Among Trace Elements in Air Particulates Over the Industrialized Area of Northwest Indiana." Symposium on the Use of Nuclear Techniques in the Measurement and Control of Environmental Pollution, Salzburg, Austria, 26-30 October 1970, International Atomic Energy Commission (submitted).

R. Dams, K. A. Rahn, G. D. Nifong, J. A. Robbins, J. W. Winchester, "Multi-element analysis of air pollution particulates by nondestructive neutron activation," 2nd International Air Pollution Conference of the International Union of Air Pollution Prevention Associations, December 6-11, 1970, Washington, D.C. (submitted).

REPORTS

John W. Winchester, "Occurrence of Halogens in Atmospheric Aerosols and Precipitation," Report COO-1705-1 (University of Michigan 08903-1-T) for U. S. Atomic Energy Commission Contract No. AT(11-1)-1705, Dept. of Meteorology & Oceanography, University of Michigan, March 1968.

John W. Winchester, "I. Occurrence of Halogens in Atmospheric Aerosols and Precipitation. II. Air Pollution Inputs of Trace Metals to Lake Michigan Water." Report COO-1705-2 (University of Michigan 08903-2-T) for U. S. Atomic Energy Commission Contract No. AT(11-1)-1705, Department of Meteorology and Oceanography, University of Michigan, March 1969.

Richard Dams and John A. Robbins (John W. Winchester, project director), "Non-destructive Activation Analysis of Environmental Samples," Special Report No. 48 of the Great Lakes Research Division, University of Michigan, Report COO-1705-6 (University of Michigan 08903-6-T) for U. S. Atomic Energy Commission Contract No. AT(11-1)-1705, Dept. of Meteorology and Oceanography, University of Michigan, May 1970.

John W. Winchester, "I. Occurrence of Halogens in Atmospheric Aerosols and Precipitation. II. Air Pollution Inputs of Trace Metals to Lake Michigan Water." Report COO-1705-7 (University of Michigan 08903-7-T) for U. S. Atomic Energy Commission Contract No. AT(11-1)-1705, Dept. of Meteorology & Oceanography, University of Michigan, May 1970.

THESES

Ronald Harold Loucks, Ph.D. September 1969, Department of Meteorology & Oceanography, University of Michigan, "Particle Size Distribution of Chlorine and Bromine in Mid-Continent Aerosols from the Great Lakes Basin."

Taro Yokoyama, M.S. January 1969, Department of Applied Chemistry, Keio University, Tokyo, Japan, "Selenium in the Great Lakes."

Gordon Dale Nifong, Ph.D. July 1970, Dept. of Environmental and Industrial Health, University of Michigan, "Particle Size Distributions of Trace Elements in Pollution Aerosols."

THE HALOGEN COMPOSITION OF AEROSOL PARTICLES OVER LAKE MICHIGAN

Ronald H. Loucks, John W. Winchester, Wayne R. Matson
and Mary A. Tiffany

*Department of Meteorology & Oceanography
University of Michigan
Ann Arbor, Michigan 48104*

I. Introduction

The halogen elements chlorine, bromine, and iodine are distributed in the atmosphere between particulate and gaseous phases and show evidence of chemical reactivity which affects the variation of chemical composition with particle radius in the stable aerosol range of 0.2 to 20 microns. Previously published analyses of naturally-occurring aerosols for halogens are restricted almost entirely to samples collected in coastal locations of the U.S. where local sources of sea salt are present [1-4]. In this investigation we are undertaking the first extensive sampling in the inland U.S. in regions where both natural and pollution sources of the halogens may be important. The results are to be compared with earlier studies of both naturally-occurring aerosols and aerosols containing lead of pollution origin [5-7].

High sensitivity means of chemical analysis are employed in order to permit sampling of cubic meter volumes of air which can be fractionated into particles of different sizes and permit sampling times of a few hours or less. The halogens are determined by neutron activation [8], and lead and certain other trace metals are determined using anodic stripping voltammetry [9,10]. Particle size sorting is accomplished using cascade impactors of six or more stages with polyethylene impaction surfaces suitable for activation analysis and for trace metal removal using ultrasonic vibration.

II. Experimental

As the principal objective of the sampling program, a field location was selected which would not have local sources of halogens, lead, and other trace metals of interest but with well-defined pollution sources at some distance removed as well as a regional natural distribution of these elements in the atmosphere. Sampling above the surface of Lake Michigan from the deck of the research vessel *Inland Seas* operated by

the University of Michigan was viewed as affording detection of air pollutants emanating from coastal locations, in particular the Chicago-Gary urban and industrial complex when winds were from the south, or the determination of the natural background of these elements, especially when the winds were from the north. During May 1968, a cruise was carried out where samples of aerosol particles were collected during two daylight traverses between Grand Haven, Michigan, and Chicago, Illinois, and during a continuous 24 hour sampling period overnight in the middle of the southern basin of Lake Michigan. During this time the winds varied from northerly to southerly.

Aerosol sampling was carried out using a Scientific Advances six-stage cascade impactor and an Andersen sampler, both devices resolving particles into groups differing by about a factor of two in radius in the stable aerosol range. Impaction on the surfaces of polyethylene inserts was judged to be efficient in the moist atmosphere over the lake. Possible contamination from the ship smoke-stack was monitored by Hi-Vol filter samplers operating in various places on the ship, and by the degree of darkening of some of the filters the impactor locations were selected so as to be free of contamination.

Chemical analysis for halogens was carried out by neutron activation of the polyethylene inserts, washing, and separation of I, Br, and Cl using solvent extraction followed by beta counting. Analysis for Pb, Cd, and Cu was performed by anodic stripping voltammetry using a composite mercury graphite electrode. Polyethylene inserts used in the Andersen sampler were cut into two portions, one for neutron activation and one for anodic stripping, the latter processed by desorbing the trace metal deposit into high purity aqueous NaCl solution using ultrasonic vibration. The sensitivity of both methods of analysis is adequate to determine these elements in all but the cleanest air using a few cubic meters of air volume passed through the impactor stages in several hours or less.

The locations and circumstances of the individual runs are given in Figure 1 and Table 1. Runs 8 and 9 were taken in the middle of the southern basin of Lake Michigan and runs 3 and 4 while the ship was at rest in a harbor of South Chicago, an urban and industrial location a few kilometers inland from the lake shore. The other samples were taken while the ship was underway over the stretches of water and during the times indicated.

III. Results and Discussion

A summary of the halogen results is given in Tables 2, 3, and 4. In all cases the six Scientific Advances cascade impactor stages and the backup filter were analyzed individually for 7 separate data points per sampling

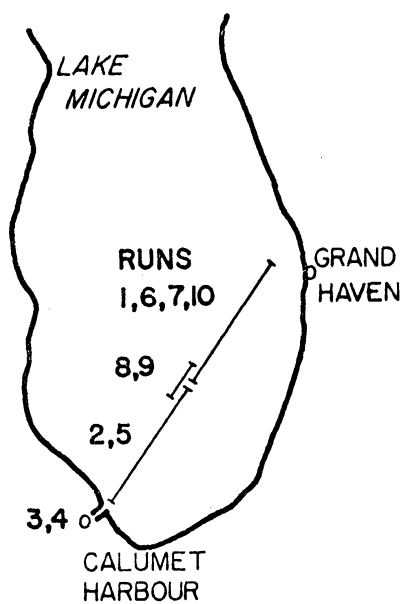


Figure 1. The ship's routes during the sampling runs.

Table 1. Circumstances of the runs.

Run ^a	Date, 1968	Time, EST	Wind, m/s	R.H., %	Clouds
1	May 20	0722-1156	NW @ 5	85	4/8
2	May 20	1225-1606	NW @ 5	80	4/8
3	May 20-21	1652-0224	NNW @ 5	75	0
4	May 21	0307-0559	W @ 5	95	0
5	May 21	0640-1102	SW @ 3	85	1/8
6	May 21	1124-1450	SW @ 3	85	1/8
7	May 22	0633-1033	SSE @ 3	98	7/8
8	May 22	1102-1912	SSE @ 2	80	fog
9	May 22-23	1940-0614	var. @ 3	98	8/8, rain
10	May 23	0650-0952	ENE @ 4	100	8/8

^aFor locations see Figure 1 and text.

run. Because of lack of space only a summary of these data is presented in the tables. The data for lead are not yet available at this writing.

Two major observations should be made in scanning the data for iodine in Table 2. (1) A large fraction of the iodine is held by particles of radius less than 0.25 micron without apparent systematic differences due to location, winds, or relative humidity. (2) The total iodine concentration does not vary with proximity to the Chicago-Gary urban-industrial area or with winds which could carry pollutants from that area to the sampling location, and the total iodine concentrations observed compare favorably with those observed in Hawaii and in polluted as well as unpolluted

Table 2. Iodine concentrations.

Run	Total concentration ng/m ³	Percent of total with radius <0.25 μm
1	7.4 ± 0.7	70
2	1.0 ± 0.4	65
3	7.3 ± 0.4	52
4	1.9 ± 0.5	37
5	<0.7	>90
6	5.0 ± 0.6	64
7	1.0 ± 0.4	>90
8	1.9 ± 0.4	32
9	0.9 ± 0.2	44
10	0.7 ± 0.3	>90
Mean:	3 ± 1	
Fairbanks background:	3.0 ± 0.3 ^a	
Fairbanks pollution:	3.9 ± 0.3 ^a	
Hawaii background:	≥ 1.7 ^b	

^a Means of 10 rural samples and 20 city samples collected by Millipore filter in and around Fairbanks, Alaska, during winter [6, 7].

^b Mean of 8 samples collected at the seashore by cascade impactor but without backup filter [4].

locations in Fairbanks, Alaska. Therefore, we do not observe iodine to have significant air pollution sources associated with urbanization.

The data for bromine in Table 3 indicate (1) that a large fraction of bromine is contained on particles of radius less than 0.25 micron, and there is no apparent systematic variation of this tendency with location, winds, or relative humidity. However, (2) the bromine values in Calumet Harbor are very much greater than the samples collected over the lake, strongly suggesting an urban pollution origin of much atmospheric bromine. The Fairbanks pollution average is not far from these values. The lake runs showed similar values independent of wind direction, but it should be borne in mind that the wind speeds were very mild during this sampling cruise. The similarity of these values with Fairbanks and Hawaii background values suggests that this bromine concentration is predominantly natural.

Table 3. Bromine concentrations.

Run	Total concentration ng/m ³	Percent of total with radius <0.25 μm	Percent of total with radius <0.5 μm
1	24 ± 3	91	94
2	11 ± 1	50	75
3	1380 ± 90	61	77
4	407 ± 20	29	64
5	22 ± 2	50	89
6	13 ± 2	80	80
7	27 ± 2	56	78
8	42 ± 2	45	68
9	31 ± 2	46	79
10	22 ± 1	51	74

Mean of runs 3 and 4: ~900

Mean of the other runs: 24 ± 4

Fairbanks background: 35 ± 3^a

Fairbanks pollution: 500 ± 50^a

Hawaii background: ~11^a

^aSee notes to Table 2.

The chlorine data, Table 4, (1) show negligible amounts held by particles smaller than 0.25 micron radius for the samples collected over the lake, and in the majority of cases at least a third of the chlorine is held by particles above 1 micron in radius without apparent correlation with the meteorological parameters of Table 1. (2) The two Calumet Harbor samples contrast by showing not only greatly higher concentrations than any of the other runs but a substantial fraction of chlorine in the smallest particle size fraction. A local pollution source is suggested, and because the concentration is so much greater than observed in the Fairbanks pollution study, we ascribe this tentatively to an industrial source other than automotive or other fuel combustion. (3) The average of lake samples is similar to the Fairbanks area background values, and these concentrations may represent natural chlorine aerosol levels.

Table 4. Chlorine concentrations.

Run	Total concentration $\mu\text{g}/\text{m}^3$	Percent of total with radius		
		$<0.25\ \mu\text{m}$	$<0.5\ \mu\text{m}$	$<1\ \mu\text{m}$
1	0.26 ± 0.04	<4	6	21
2	0.15 ± 0.02	<6	39	69
3	9.6 ± 1.0	58	83	89
4	12.2 ± 1.6	28	74	85
5	0.21 ± 0.03	<5	64	74
6	0.28 ± 0.03	<4	23	51
7	0.71 ± 0.04	<2	20	48
8	1.11 ± 0.06	<1	10	35
9	0.26 ± 0.02	<4	49	49
10	0.70 ± 0.05	<2	13	68

Mean of runs 3 and 4: ~ 11

Mean of the other runs: 0.5 ± 0.1

Fairbanks background: 0.5 ± 0.03^a

Fairbanks pollution: 1.4 ± 0.2^a

Hawaii background: $\sim 3.6^a$

^a See notes to Table 2.

In general, by comparison with the Hawaii and Fairbanks data, the Lake Michigan data suggest that natural concentration levels have been detected in many of the samples. The presumably natural bromine and iodine are carried to a great extent by the smallest size particles, in contrast to chlorine which is on mainly larger size particles. There is no evidence that iodine is a significant air pollutant associated with the urban or industrial areas tested, but both bromine and chlorine show anomalously high concentrations in the urban localities. The atmospheric input of bromine may be largely the result of burning leaded gasoline, but the inputs of chlorine may be from various urban and industrial sources. The question of atmospheric residence times and removal rates must await further sampling and analysis before answering.

IV. Acknowledgments

This work was supported in part by contract AT(11-1)-1705 with the U.S.A.E.C., grant AP-00585 from the U.S.P.H.S., facilities grant GA-811 from the N.S.F., and a grant from the Phoenix Memorial Fund of the University of Michigan. We are grateful for the use of the University of Michigan ship *Inland Seas*, and one of us (R.H.L.) is indebted to the Bedford Institute of Oceanography, Nova Scotia, for partial salary support to carry out this work.

V. References

- [1] Duce, R. A., Winchester, J. W., and Van Nahl, T. W., *J. Geophys. Res.* **70**, 1775 (1965).
- [2] Duce, R. A., Winchester, J. W., and Van Nahl, T. W., *Tellus* **18**, 238 (1966).
- [3] Winchester, J. W., and Duce, R. A., *Tellus* **18**, 287 (1966).
- [4] Duce, R. A., Woodcock, A. H., and Moyers, J. L., *Tellus* **19**, 369 (1967).
- [5] Lininger, R. L., Duce, R. A., Winchester, J. W., and Matson, W. R., *J. Geophys. Res.* **71**, 2457 (1966).
- [6] Winchester, J. W., Zoller, W. H., Duce, R. A., and Benson, C. S., *Atmospheric Environment* **1**, 105 (1967).
- [7] Winchester, J. W., and Duce, R. A., in *Nuclear Activation Techniques in the Life Sciences*, I.A.E.A., Vienna, 1967, pp. 631-43.
- [8] Duce, R. A., and Winchester, J. W., *Radiochim. Acta* **4**, 100 (1965).
- [9] Matson, W. R., Roe, D. K., and Carritt, D. E., *Anal. Chem.* **37**, 1594 (1965).
- [10] Matson, W. R., and Roe, D. K., *Analysis Instrumentation Vol. 4*, Plenum Publishing Corp., New York, 1967.

NATURAL AND POLLUTION SOURCES OF IODINE, BROMINE, AND CHLORINE IN THE GREAT LAKES

Mary A. Tiffany, John W. Winchester, and Ronald H. Loucks

The halogen elements chlorine, bromine, and iodine are of fundamental significance in the study of the chemical cycle of pollution trace elements in natural water. These elements, being very water soluble, essentially should be conservative properties of the water. Therefore, under natural conditions, efficient removal processes by biological uptake or sedimentation are not expected. The primary natural source of halogens in surface water is believed to be rainfall which derives these salt constituents ultimately from sea spray. Since these elements are not volatile when in the ionic form, they remain with lake water and are not affected by evaporation. Consequently, it should be possible to make a material balance model of halogen elements in a natural hydrologic situation and to use this model to assess pollution addition of these and other elements in polluted waters. The present work is a first step toward developing such a model for the Great Lakes. The approximate average concentrations for each of the lakes reported here not only are basic to formulation of a material balance model but also provide a valuable base line for comparison of future concentration measurements.

Mary A. Tiffany, John W. Winchester, and Ronald H. Loucks are, respectively, Assistant Research Oceanographer, Associate Professor, and Research Assistant, Department of Meteorology and Oceanography, University of Michigan, Ann Arbor, Mich.

The paper was presented at the 41st Annual Conference of the Water Pollution Control Federation, Chicago, Ill., Sept. 22-27, 1968.

The study by Beeton (1) of the eutrophication of the St. Lawrence Great Lakes showed that the abundant dissolved substances, Cl^- , SO_4^{2-} , Na^+ , and K^+ , have been rising in concentration for the past half century in the lower Great Lakes, but Lake Superior has not been changing and presumably is not polluted with these elements. As pointed out by Ownbey and Key (2), chloride levels in Lake Erie already are approaching levels considered deleterious to some industries, and the rise is attributed to pollution sources.

Bromide concentrations in fresh waters have been reported a few times in the literature (3) (4), but data for the Great Lakes are lacking. Very little is known about the biological importance of bromine or its significance as a pollutant. Bromide in fresh water is derived naturally from rainfall, but significant additions may be caused by the combustion of leaded gasoline containing ethylene dibromide. The relation between bromide and lead in atmospheric samples has been investigated by Winchester *et al.* (5), but the degree of water pollution potential from an atmospheric source has not been assessed.

Although iodine has been studied extensively in connection with goiter investigations (6), a systematic survey of the distributions of iodine in the Great Lakes has not been made. Goldschmidt (7) has held that the principal route of addition of iodine to soils and surface waters is through the atmosphere and ultimately from the sea surface. He believed that the

process of saturating soils with iodine from the atmosphere is a slow one, and that soils of the Great Lakes Basin and other recently glaciated regions still are deficient in iodine, not yet having recovered from removal of iodine-rich soils by glaciation. However, since the last glacial maximum 10,000 to 15,000 yr ago, the iodine concentrations in waters of the Great Lakes may be expected to have achieved steady-state values near that of their rainfall input. This steady-state condition would be expected if additional sources and efficient sedimentary or biological removal processes are not operative because mean residence times of the lake waters are at most a few hundred years.

Interest in iodine and thyroid function now has been broadened by the finding (8) that thyroid hyperplasia in some freshwater fish is linked with the low iodine content of lake water (~ 1 ppb) as compared to sea water (~ 60 ppb). The possibility exists (9) that thyroid disorders in alewife fish may have been a contributing factor to their massive die-off in Lake Michigan during 1967. Whether pollution-induced algae growth offers competition for available iodine is not established yet. Still, additional interest in the air and water chemistry of iodine has been stimulated by the addition of fission product iodine-131 to the environment. And very recently, Schaeffer (10) has reported evidence that iodine vapors may interact with atmospheric lead and other pollution particulates to form ice nuclei which may affect the weather.

The present study is an attempt to obtain average iodine, bromine, and chlorine concentrations significant to approximately a factor of two in each of the Great Lakes. It is recognized that inhomogeneities in water composition may exist for the halogens, for example, the chloride analyses reported by Kramer (11) for Lake Erie and by Allen (12) for Lake Huron.

However, for the purposes of these experiments, these variations are small and within the precision of the averages sought.

Sampling and Analysis

Water samples were collected in polyethylene bottles which were cleaned carefully with hot, concentrated nitric acid to eliminate contamination. Some samples were stored several months at room temperature before analysis and others were stored frozen. No differences in keeping qualities were detected. Believing the lakes to be sufficiently well-mixed for the purposes of this study, most water samples were collected at shore stations accessible by road, but additional samples also were taken from shipboard on Lake Michigan (Table I) (Figure 1).

Samples in the Lake Superior basin were collected both from the lake itself and from tributary streams in pollution-free localities. The streams, considered to be a natural integration of rainfall and fallout, were to provide an estimate of atmospheric halogen input more precise than could be provided by a direct rainfall and fallout measurement, unless a very large number of individual samples were taken. A comparison of tributary streams with Lake Superior water composition is a test for the hypothesis that Lake Superior is pollution free with respect to the halogens and derives these elements essentially from atmospheric sources.

Lake Michigan was sampled in both the northern and the southern basins, largely from shipboard. Samples were taken at depth as well as at the surface. Lake Huron was sampled only in the southern end. For this reason, the average composition may not be valid for the whole lake. However, a comparison of Lake Huron with Lake Michigan (discussed below) suggests that the true Lake Huron averages for

TABLE I.—Sample Descriptions

Sample Number	Location	Date Sampled	Sample Number	Location	Date Sampled
	LAKE SUPERIOR				
S-1	Porcupine State Park, Michigan	7-10-67	ST-22	Bullrush Lake, Ontario	7-14-67
			ST-23	Gravel River, Ontario	7-14-67
			ST-24	Betsy River, Michigan	3-24-68
S-2	Chequamegon Bay, Michigan	7-11-67	ST-25	Taquamenon River, Michigan	3-28-68
S-3	North of Duluth, Minnesota	7-11-67			
S-4	Near Gooseberry River, Minnesota	7-11-67	ST-26*	Knife River, goes through village of Knife River, Minnesota	7-11-67
S-5	Near Cascade River, Minnesota	7-12-67			
S-6	South of Kodonce River, Minnesota	7-13-67			
			LAKE MICHIGAN		
S-7	Nipigon Bay, Ontario	7-14-67	M-1	Hiawatha National Forest	7-9-67
S-8	Agawa Bay, Ontario	7-15-67	M-2	Mackinac State Forest	7-9-67
S-9	Batchawana Bay, Ontario	7-15-67	M-3	Six miles north of South Fox Island—surface water	7-19-67
S-10	Southeast of Whitefish Point, Michigan	3-28-68	M-4	Same location, 20 m	7-19-67
			M-5	Same location, 30 m	7-19-67
S-11	North of Whitefish Point, Michigan	3-29-68	M-6	Same location, 40 m	7-19-67
			M-7	Same location, 60 m	7-19-67
S-12	Near Taquamenon River, Whitefish Bay, Michigan	3-24-68	M-8	Same location, 80 m	7-19-67
			M-9	Same location, 90 m	7-19-67
			M-10	Same location, 100 m	7-19-67
			M-11	Same location, 110 m	7-19-67
			M-12	42°30'N, 87°00'W, 5 m	5-22-68
ST-1	Porcupine Mts. State Park, Michigan, Little Carp River	7-11-67	M-13	Same location, 55 m	5-22-68
			M-14	Same location, 85 m	5-22-68
ST-2	Porcupine Mts. State Park, Michigan, Presque Isle River	7-11-67	M-15	Same location, 115 m	5-22-68
	LAKE SUPERIOR TRIBUTARIES				
ST-2F	Foam from ST-2 site	7-11-67	H-1	Lakeport State Park, Michigan	6-10-68
ST-3	Tributary to Presque Isle River	7-11-67	H-2	Sarnia, 300 m south of Blue Water Bridge, Ontario	6-10-68
ST-4	Pond at Wakefield, Michigan	7-11-67	H-3	Kettle Point, Ontario	6-28-68
ST-5	Bad River, Wisconsin	7-11-67	H-4	Pinery Provincial Park, Ontario	6-28-68
ST-6	Iron River, Wisconsin	7-11-67			
ST-7	Gull Lake, Minnesota	7-12-67	H-5	Grand Bend, Ontario	6-28-68
ST-8	Cross River, Minnesota	7-13-67	H-6	Junction of highways 83 and 21, Ontario	6-28-68
ST-9	Loon Lake, Minnesota	7-13-67			
ST-10	Squint Lake, Minnesota	7-13-67			
ST-11	South Brule River, Minnesota	7-13-67			
			ST. CLAIR RIVER		
ST-12	Devil Track River, Minnesota	7-13-67	SCR-1	100 m south of Dow Chemical Co., Ontario	6-10-68
ST-13	Kodonce River, Minnesota	7-13-67	SCR-2	Clay Creek Provincial Park, Ontario	6-10-68
ST-14	Wolf River, Ontario	7-13-67			
ST-15	Nipigon River, Ontario	7-13-67			
			LAKE ST. CLAIR		
ST-16	Lake Nipigon, Macdiarimid, Ontario	7-14-67	SC-1	Lake Shore Drive and Vernier, Grosse Point Shores, Michigan	6-10-68
ST-17	Lake Nipigon, Leitch, Ontario	7-14-67	SC-2	St. Clair Shores, Michigan	6-10-68
ST-18	Blackwater River, Ontario	7-14-67			
ST-19	Orient Bay, Lake Nipigon, Ontario	7-14-67			
			DETROIT RIVER		
ST-20	Helen Lake, Nipigon River, Ontario	7-14-67	DR-1	Southfield Rd. and Jefferson, Detroit, Michigan	6-10-68
ST-21	Jackfish River, Ontario	7-14-67	DR-2	Jefferson and Livernois Rds., Detroit, Michigan	6-10-68

* Not used in computing average listed in Table V.

TABLE I.—Continued

Sample Number	Location	Date Sampled	Sample Number	Location	Date Sampled
DR-3	Windsor, 1 mile (1.6 km) south of Ambassador Bridge	6-10-68	E-10	Rayleigh-Dillon Road, Ontario	6-10-68
DR-4	Amherstburg, Ontario	6-10-68	E-11	Wheatley Provincial Park, Ontario	6-10-68
LAKE ERIE					
E-1	Willow Beach, Michigan	6-8-68	E-12	Kingsville, Ontario	6-10-68
E-2	Luna Pier, Michigan	6-8-68	E-13	Clark Beach, Ontario	6-10-68
E-3	Crane Creek State Park, Ohio	6-8-68	E-14	Holiday Beach, Ontario	6-10-68
E-4	Port Clinton, Ohio	6-8-68	LAKE ONTARIO		
E-5	East Harbor State Park, Ohio	6-8-68	O-1	Presqu'ile Provincial Park	8-19-68
E-6	Marblehead, Ohio	6-8-68	O-2	3 miles (4.8 km) west of Presqu'ile P. P.	8-18-68
E-7	North Bay State Park, Kelly's Island, Ohio	6-8-68	O-3	Colburne, Ontario	8-18-68
E-8	Boat dock, Kelly's Island, Ohio	6-8-68	O-4	Coburg, Ontario	8-18-68
E-9	Rondeau Provincial Park, Ontario	6-10-68	O-5	Bomanville, Ontario	8-18-68
			O-6	Darlington Provincial Park—bay	8-18-68
			O-7	Darlington Provincial Park—beach	8-18-68
			O-8	Scarborough Escarpment	8-18-68

Cl, Br, and I may be close to the values found in this work.

Because of the small number of

samples taken from the St. Clair River, Lake St. Clair, and the Detroit

River, and the evidence for great non-

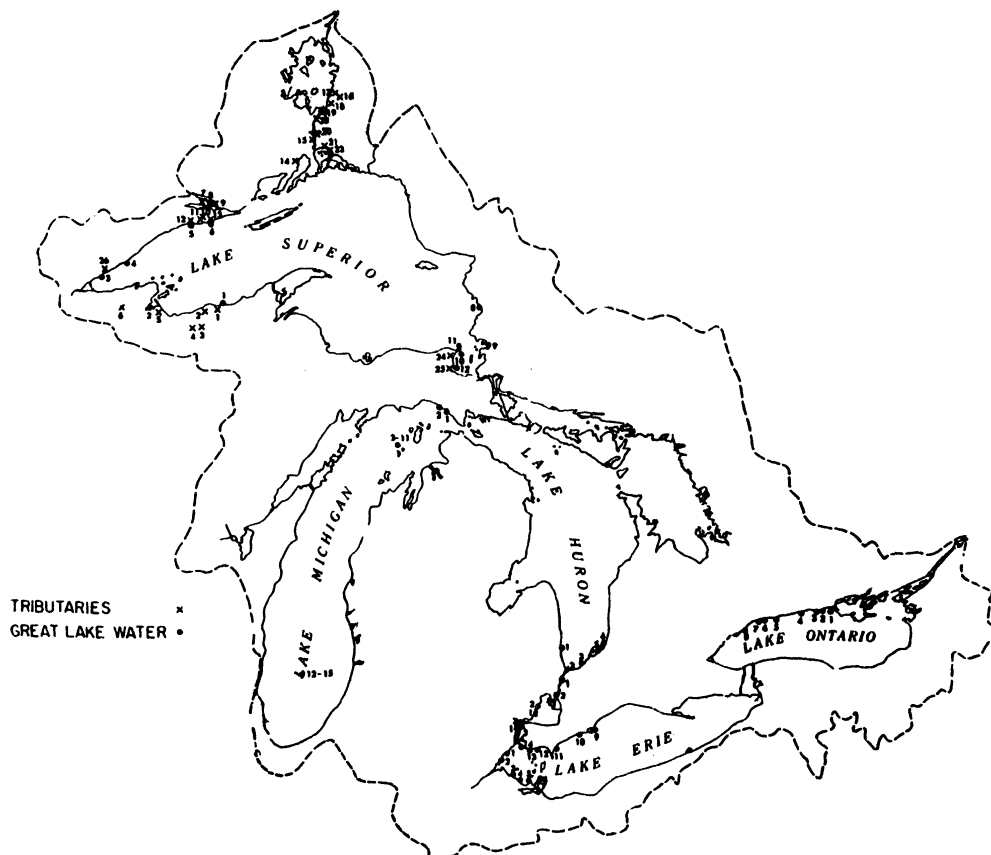


FIGURE 1.—This general map of the Great Lakes Basin shows the sample locations.

uniformity of composition in these rivers, averages for these groups can be no more than rough guides.

All Lake Erie samples were taken from the western basin, and some non-uniformity in composition near the shore is indicated by the data. Be-

TABLE II.—Halogen Concentrations in Lake Superior and Lake Superior Tributaries

Location	I (ng/ml)*	Br (ng/ml)	Cl (μ g/ml)
LAKE SUPERIOR			
S-1	1.3	12	1.1
S-2	2.2	12	1.2
S-3	1.3	15	1.8
S-4	1.6	11	1.6
S-5	0.8	12	1.2
S-6	0.8	7	0.5
S-7	0.7	9	1.5
S-8	0.4	7	1.3
S-9	0.8	8	1.7
S-10	1.0	33	2.8
S-11	0.5	9	0.7
S-12	1.5	18	1.5
LAKE SUPERIOR TRIBUTARIES			
ST-1	1.7	24	2.2
ST-2	2.3	13	1.7
ST-2F†	41	260	8.3
ST-3	1.4	18	1.7
ST-4	1.4	10	0.7
ST-5	1.2	11	1.4
ST-6	1.5	9	1.2
ST-7	1.3	8	0.7
ST-8	1.7	9	0.5
ST-9	2.1	10	0.5
ST-10	1.0	8	1.3
ST-11	1.7	10	0.4
ST-12	0.3	7	0.5
ST-13	0.9	9	0.5
ST-14	1.1	15	0.8
ST-15	0.8	7	1.6
ST-16	0.3	5	1.0
ST-17	1.0	10	2.3
ST-18	1.3	12	1.2
ST-19	1.6	9	1.6
ST-20	1.4	9	1.3
ST-21	1.2	25	2.3
ST-22	0.5	20	1.1
ST-23	0.3	11	1.1
ST-24	1.0	18	2.3
ST-25	1.3	9	0.7
ST-26†	1.1	51	5.1

* Measurement for I and Br in ng/ml, equal to 10^{-9} g/ml.

† Not included in averages in Table V.

TABLE III.—Halogen Concentrations in Lake Michigan and Lake Huron

Location	I (ng/ml)	Br (ng/ml)	Cl (μ g/ml)
LAKE MICHIGAN			
M-1	0.7	13	5.1
M-2	0.7	14	7.1
M-3	0.9	20	4.6
M-4	0.7	16	5.2
M-5	0.9	16	5.4
M-6	0.8	19	5.5
M-7	0.8	18	5.5
M-8	0.9	21	5.2
M-9	1.0	17	5.7
M-10	1.0	21	6.4
M-11	1.0	20	7.4
M-12	1.0	17	5.5
M-13	1.1	15	4.5
M-14	1.4	15	4.4
M-15	0.9	13	4.4
LAKE HURON			
H-1	0.9	25	5.6
H-2	—	18	5.7
H-3	2.1	18	5.4
H-4	1.1	29	5.3
H-5	1.3	13	4.3
H-6	1.3	20	6.4

cause of the study by Kramer (11), the eastern end of the lake is expected to be approximately 50 percent higher in halogen concentration. Lake Ontario was sampled only from the western half on the Canadian shore, both in the Toronto area and in rural areas.

All chemical analyses were performed using neutron activation by the Ford Nuclear Reactor at the University of Michigan and a radiochemical procedure by Duce and Winchester (13). The method is highly sensitive, requiring only five ml of water for each analysis; and errors because of contamination are controlled easily. Random analytical errors are usually 20 percent or less.

Results

Extensive sampling and testing yielded the data shown in Tables II, III, IV, and V, and Figures 2 through 10. An analysis of the data follows.

Lake Superior and its Tributaries

Tables II and V, Figures 2, 3, and 4:—(a) Although the distributions of the tributary data tend to be broader than the distributions of lake data, the means are nearly the same for all three halogen elements, thus supporting the view that the unpolluted atmosphere is still the only significant source for the halogens found in Lake Superior; (b) all three halogens appear to be conservative properties of the water and do not suffer significant

TABLE IV.—Halogen Concentrations in the St. Clair River, Lake St. Clair, Detroit River, Lake Erie, and Lake Ontario

Location	I (ng/ml)	Br (ng/ml)	Cl (μ g/ml)
ST. CLAIR RIVER			
SCR-1	1.4	39	82
SCR-2	3.1	19	16
LAKE ST. CLAIR			
SC-1	1.5	45	19
SC-2	2.1	55	22
DETROIT RIVER			
DR-1	1.7	28	22
DR-2	1.0	20	8
DR-3	1.5	22	6.8
DR-4	1.3	26	51
LAKE ERIE			
E-1	2.5	41	24
E-2	4.2	54	24
E-3	1.7	22	13
E-4	1.8	24	16
E-5	1.4	24	15
E-6	1.1	22	17
E-7	1.4	30	20
E-8	0.9	20	14
E-9	1.7	28	20
E-10	1.2	48	26
E-11	1.4	31	24
E-12	2.1	36	24
E-13	1.4	21	21
E-14	1.4	31	19
LAKE ONTARIO			
O-1	1.8	47	25
O-2	2.4	38	23
O-3	2.8	43	23
O-4	2.2	40	24
O-5	2.7	45	24
O-6	2.6	41	22
O-7	3.4	45	23
O-8	5.5	77	23

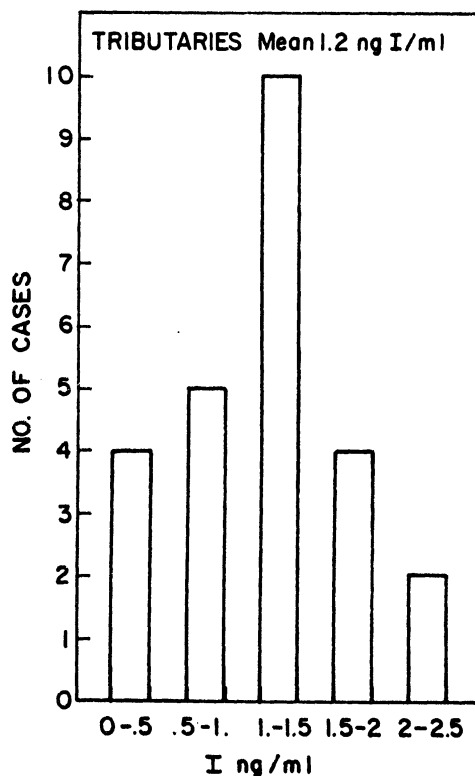
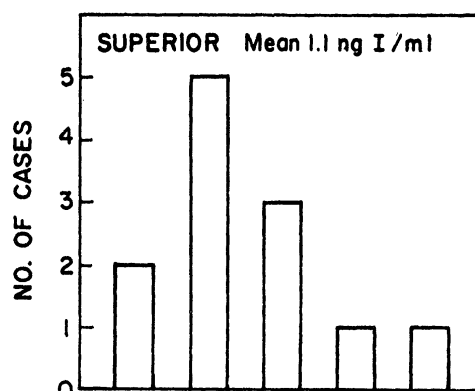


FIGURE 2.—Mean iodine concentrations found in Lake Superior and its tributaries are shown. (Note: $\text{ng} \times 10^9 = \text{g}$.)

removal by sedimentary or other processes; (c) the foam analysis, sample ST-2F, suggests that I and Br may be bound partially to surface active material of biological origin; and (d), sample ST-26, from a village stream which was observed during collection to be polluted, is high in Br and in Cl, although normal in I (an automotive fuel combustion source for the Br appears likely in this case).

TABLE V.—Halogen Concentration Averages for the Principal Sample Groups in the Great Lakes Basin

Location	No. of Samples	I (ng/g)	Br (ng/g)	Cl (μg/g)	Br/Cl × 10 ³	I/Cl × 10 ⁴
Lake Superior	12	1.1	13	1.4	9.3	0.8
Lake Superior tributaries	25	1.2	11	1.2	9.2	1.0
Lake Michigan	15	0.9	17	5.5	3.1	0.18
Lake Huron	6	1.3	21	5.4	3.9	0.24
St. Clair River	2	~2	~30	~50	~0.6	~0.04
Lake St. Clair	2	2	50	20	2.5	0.10
Detroit River	4	~1.4	~24	~20	~1.0	~0.07
Lake Erie	14	1.7	31	20	1.5	0.08
Lake Ontario	8	2.9	47	23	2.0	0.13

At the present time no systematic survey of I, Br, and Cl in rainfall of the Lake Superior basin has been

completed. However, for comparison the composition of unpolluted snow in inland Alaska has been reported (5) as 0.6 ng I/g, 4 ng Br/g, 0.2 μg Cl/g, and a Br/Cl ratio equal to 0.02. The factors which may account for the dif-

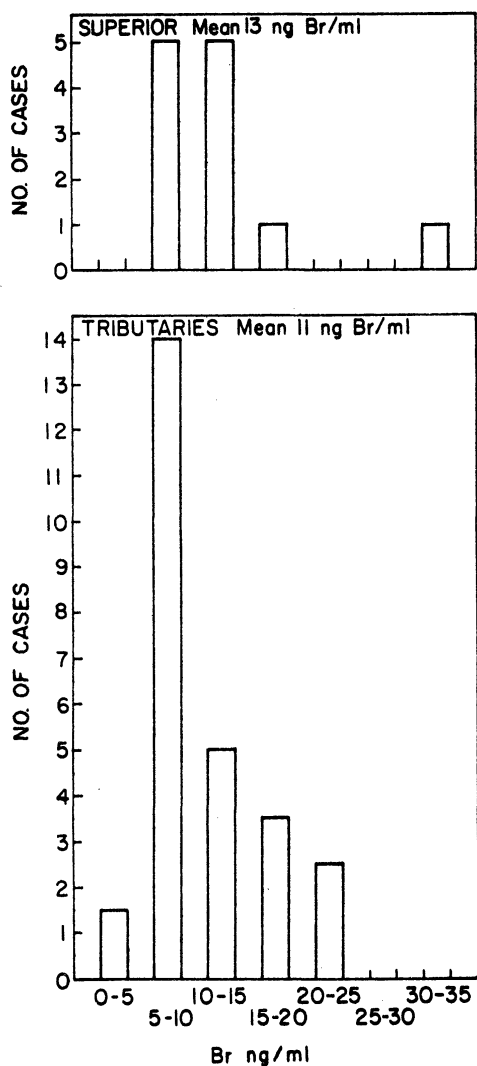


FIGURE 3.—Bromine data for Lake Superior and its tributaries are shown.

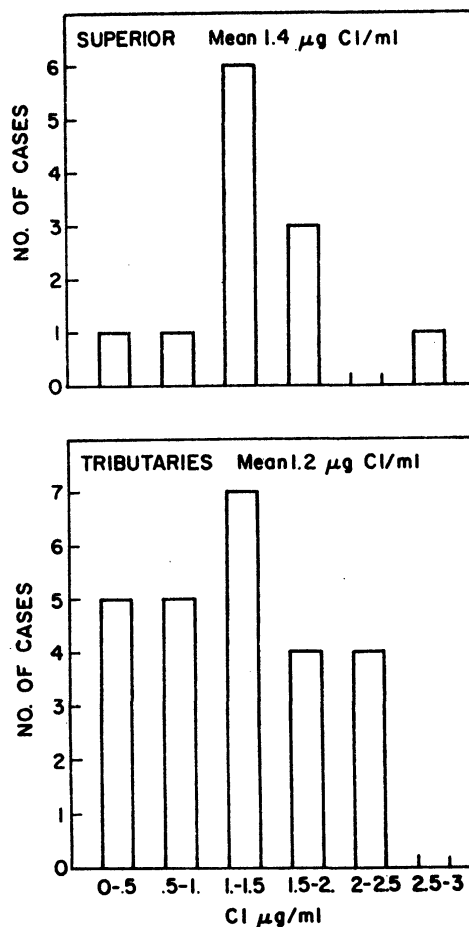


FIGURE 4.—The mean chlorine concentration for Lake Superior was found to be 1.4 μg Cl/ml.

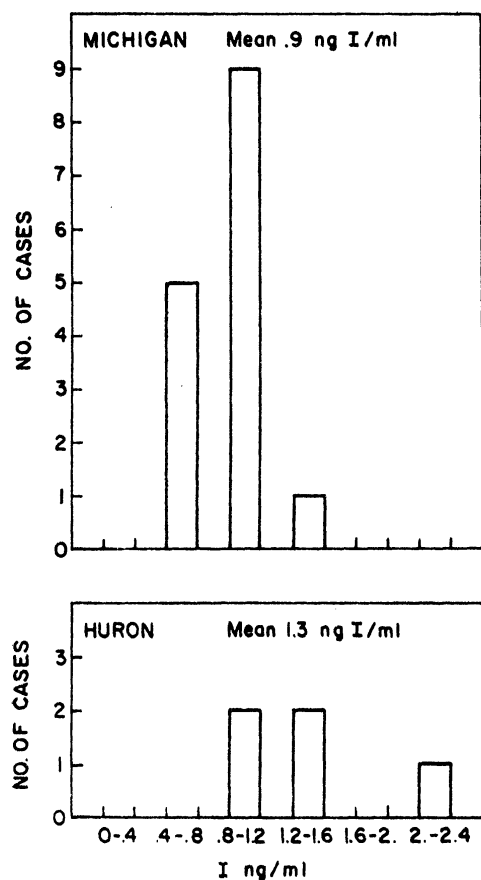


FIGURE 5.—Mean iodine concentrations found in Lake Michigan and Lake Huron are shown.

ferences are difficult to assess without actually sampling the Lake Superior rainfall.

Lake Michigan and Lake Huron

Tables III and V, Figures 5, 6, and 7:—Compared to Lake Superior, Lakes Michigan and Huron have (a) a 4-fold greater Cl concentration, (b) a Br concentration 1.5-fold greater, and (c) approximately the same I concentration. The differences in concentrations are attributed to pollution contributions to Lakes Michigan and Huron. Cl pollution is both absolutely and relatively greater than Br pollution, and I pollution is not detectable. However, the present rates of Cl, Br, and I pollution input are not necessarily in this order of importance.

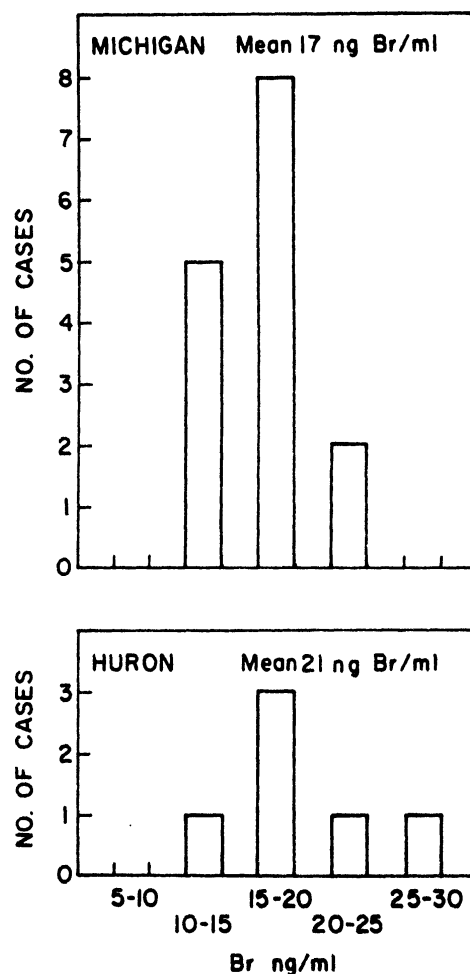


FIGURE 6.—Bromine data for Lake Michigan and Lake Huron are shown.

Lake Erie, Lake Ontario, and the Lake St. Clair Region

Tables IV and V, Figures 8, 9, and 10:—(a) The 4-fold rise in Cl concentration in Lake Erie relative to Lake Huron occurs to a great degree because of pollution sources in and south of the St. Clair River.

(b) Iodine in Lake Erie, Lake St. Clair, and the St. Clair and Detroit rivers is not high and can be accounted for largely by the natural atmospheric sources.

(c) Pollution sources of Br in the Lake St. Clair area appear to be significant. It is interesting to note, however, that Br is found in Lake St. Clair at higher concentrations than

those present in Lakes Erie or Ontario. If real, this result implies that the relative rates of Br and water addition to Lake St. Clair are greater than for Lakes Erie or Ontario. Such a situation could be the result of extensive fallout or rainout of Br-containing aerosols, derived from the combustion of automotive ethyl fluid in the Detroit area, into Lake St. Clair. Assuming that the volume-to-outflow ratio is approximately three years, Lake Erie gradually should assume concentrations of Br at least as great as those in Lake St. Clair over the period of a decade. By additional sampling in lakes St. Clair and Erie the Br concentration difference, if it exists, should be established with greater certainty. From these data, the Br pollution rates over the past few years can be determined.

(d) Pollution sources may be the cause of the higher I and Br concentrations in Lake Ontario compared to Lake Erie, although if evaporation

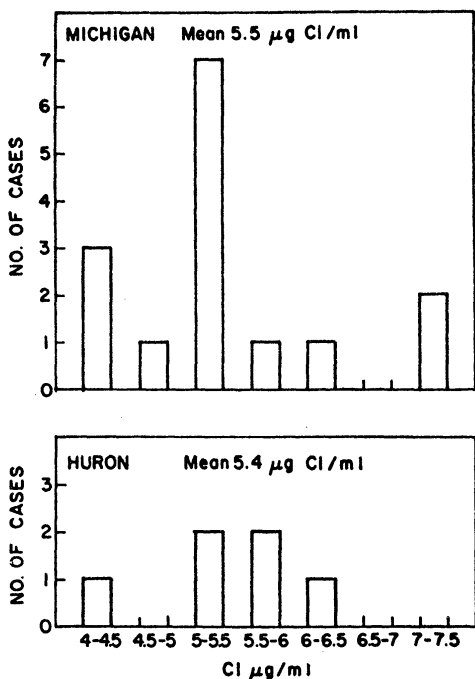


FIGURE 7.—The mean chlorine concentrations for Lake Michigan and Lake Huron were, respectively, 5.5 and 5.4 µg/ml.

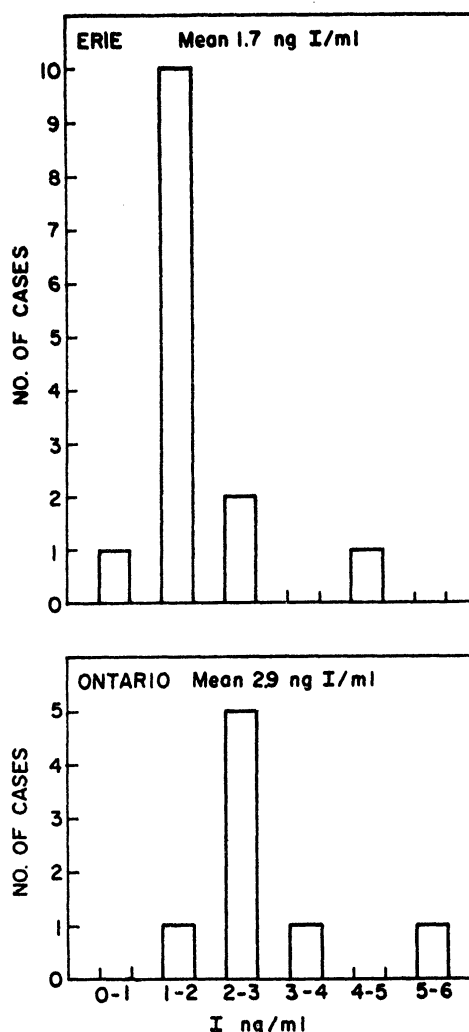


FIGURE 8.—The iodine in Lake Erie largely can be accounted for by natural atmospheric sources.

exceeds rainfall, this alone will contribute to an increase in concentration. Sample 0-8, exhibiting especially high values for both I and Br, was taken near Toronto and suggests that local pollution in this locality, while important for both elements, apparently is not significant for Cl. Lake Ontario appears to be the only lake to exhibit observably greater I concentrations than can be accounted for readily by natural sources.

Discussion

These preliminary survey data indicate that both Br and Cl are in-

creasing in the Great Lakes by pollution as well as by natural sources. Iodine, however, does not appear to be a serious pollutant in the Great Lakes, except possibly in Lake Ontario. Future research should be directed to determining more precisely not only the present total accumulated pollution component of these elements but also the present pollution addition rates. To a limited extent the data reported in this paper suggest that the relative Br/Cl pollution rate has increased in recent years and varies strongly with locality in the lower Great Lakes. By more detailed sampling, especially from shipboard away from shore, and higher precision analysis, especially for the ratio Br/Cl, areal inhomogeneities may be detected which may allow more quantitative estimates of present pollution rates.

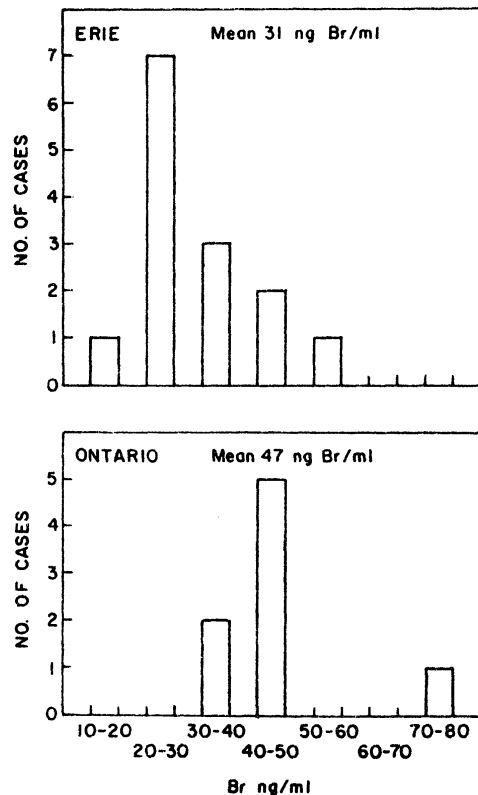


FIGURE 9.—The mean bromine concentration for Lake Erie was found to be 31 ng/ml; that for Lake Ontario, 47 ng/ml.

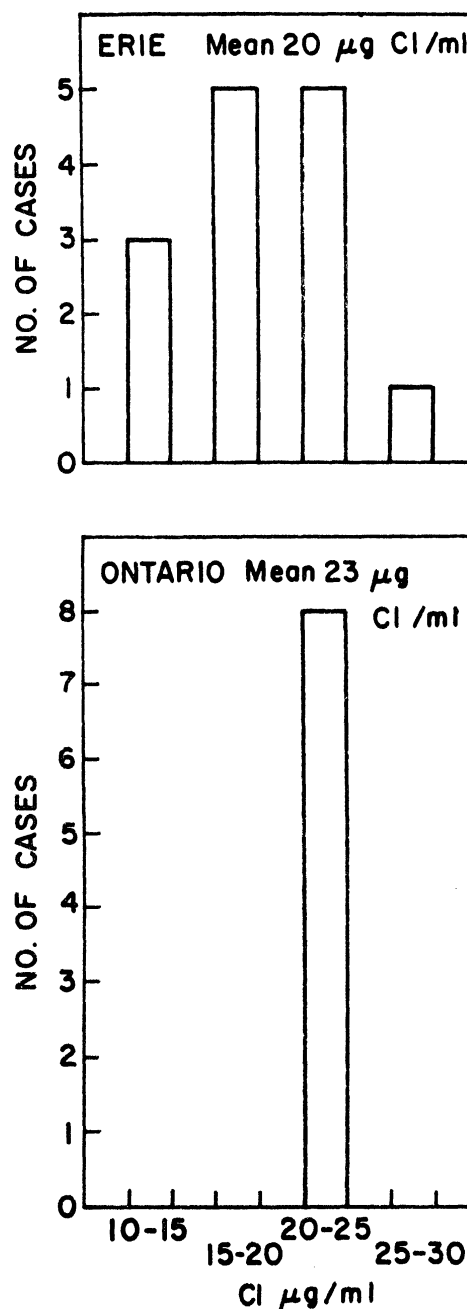


FIGURE 10.—Chlorine data from Lake Erie and Lake Ontario are shown.

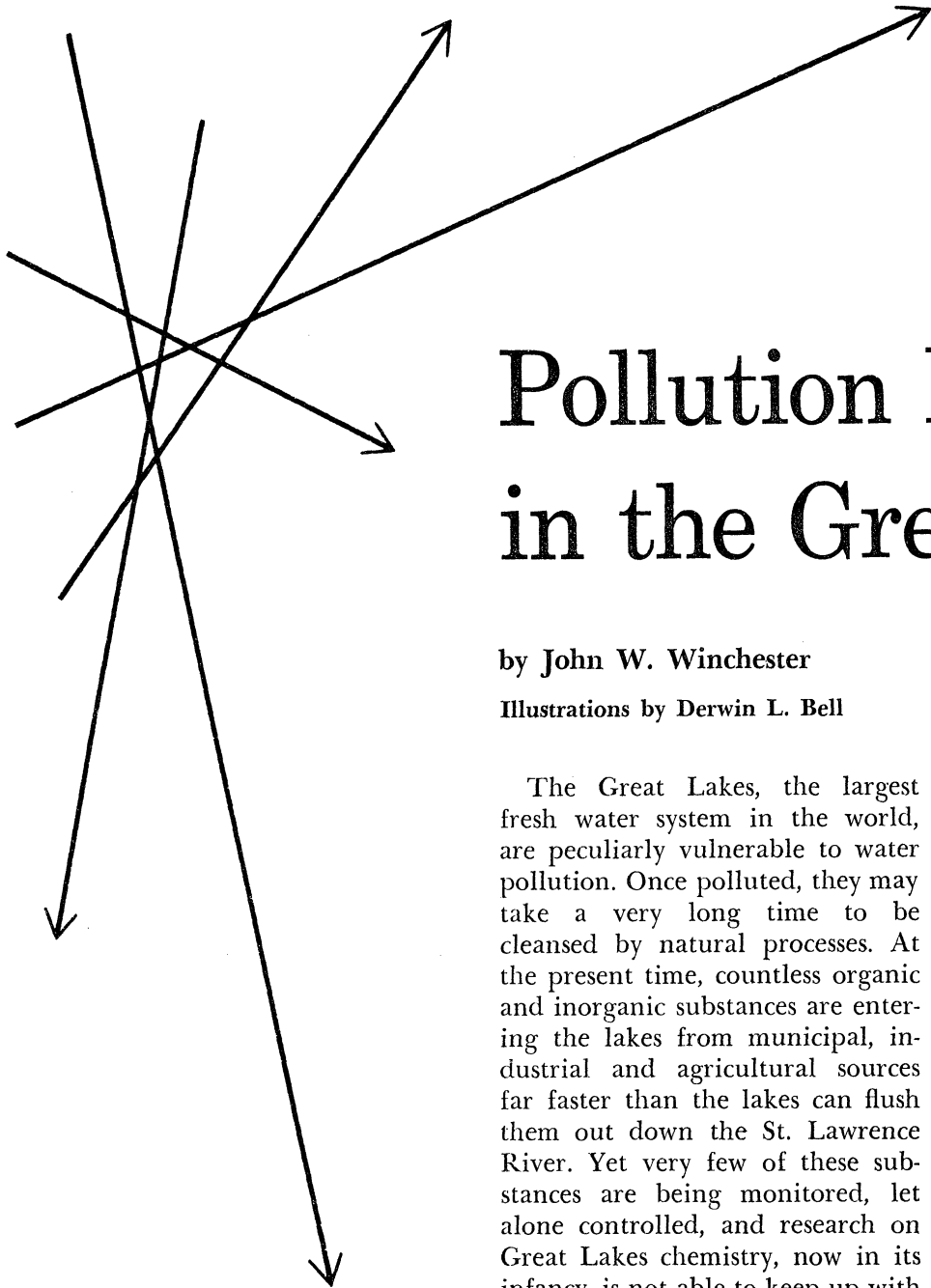
Finally, future investigations should be made of the chemical states of the halogens in lake water, e.g., organic vs. inorganic and iodate vs. iodide. This question may be particularly important in studies of iodine uptake by lake organisms which have become adapted from sea water.

Acknowledgments

The assistance provided by the Great Lakes Research Division of The University of Michigan, by the captain and crew of the ship R. V. Inland Seas, and by J. L. Hough for aiding measurably in obtaining samples of Lake Michigan water from shipboard is acknowledged gratefully. Additional samples in Lake Superior were obtained with the assistance of E. W. Marshall, and technical assistance in the analytical laboratory was given by Lawrence Timte and Tania Weiss. This work was supported in part by a grant from The University of Michigan Phoenix Memorial Fund and by USAEC contract AT(11-1)-1705. This paper is recorded as Publication No. 151, Department of Meteorology and Oceanography, University of Michigan.

References

1. Beeton, A. M., "Eutrophication of the St. Lawrence Great Lakes." *Limnol. & Oceanog.*, **10**, 240 (1965).
2. Ownbey, C. R., and Key, D. A., "Chlorides in Lake Erie." Proc. 10th Conf. Great Lakes Res., Intl. Assn. Great Lakes Res., Ann Arbor, Michigan (1967).
3. Hutchinson, G. E., "A Treatise on Limnology." John Wiley & Sons, Inc., New York, N. Y. (1957).
4. Bowen, H. J. M., "Trace Elements in Biochemistry." Academic Press, New York, N. Y. (1966).
5. Winchester, J. W., Zoller, W. H., Duce, R. A., and Benson, C. S., "Lead and Halogens in Pollution Aerosols and Snow From Fairbanks, Alaska." *Atmos. Environ.* **1**, 105 (1967).
6. "Geochemistry of Iodine." Chilean Iodine Educational Bureau, London, England (1956).
7. Goldschmidt, V. M., "Geochemistry." Clarendon Press, Oxford, England (1954).
8. Robertson, O. H., and Chaney, A. L., "Thyroid Hyperplasia and Tissue Iodine Content in Spawning Rainbow Trout: A Comparative Study of Lake Michigan and California Sea-run Trout." *Physiol. Zool.*, **26**, 328 (1953).
9. Smith, S. H., "The Alewife." *Limnos*, **1**, 12 (1968).
10. Schaeffer, V. J., "Ice Nuclei From Automobile Exhaust and Iodine Vapor." *Science*, **154**, 1555 (1966).
11. Kramer, J. R., "Chemistry of Lake Erie." Proc. 4th Conf. Great Lakes Res., Great Lakes Res. Div., Univ. of Michigan, Publ. **7**, 27 (1961).
12. Allen, H. E., "Chemical Characteristics of South-Central Lake Huron." Proc. 7th Conf. Great Lakes Res., Great Lakes Res. Div., Univ. of Michigan, Publ. **11**, 45 (1964).
13. Duce, R. A., and Winchester, J. W., "Determination of Iodine, Bromine, and Chlorine in Atmospheric Samples by Neutron Activation Analysis." *Radiochim. Acta*, **4**, 100 (1965).



Pollution Pathways in the Great Lakes

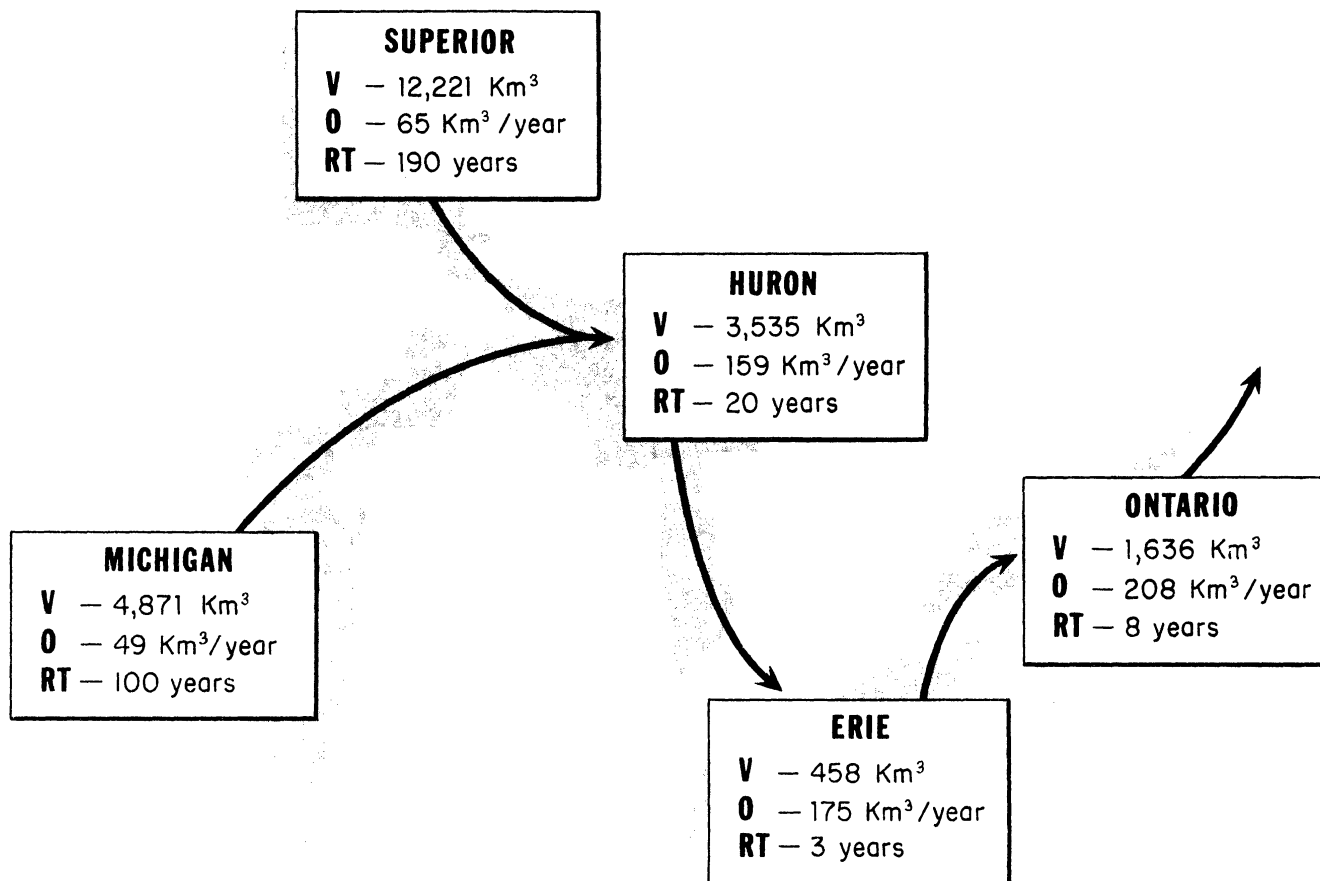
by John W. Winchester

Illustrations by Derwin L. Bell

The Great Lakes, the largest fresh water system in the world, are peculiarly vulnerable to water pollution. Once polluted, they may take a very long time to be cleansed by natural processes. At the present time, countless organic and inorganic substances are entering the lakes from municipal, industrial and agricultural sources far faster than the lakes can flush them out down the St. Lawrence River. Yet very few of these substances are being monitored, let alone controlled, and research on Great Lakes chemistry, now in its infancy, is not able to keep up with the enormous task of studying the biological, economic, and aesthetic consequences of pollution of the Great Lakes.

The lakes contain very large volumes of water, and we sometimes think of them as being almost unlimited for dilution of any contaminant we care to throw into the water. However, the lakes lie in small drainage basins where

rainfall onto the lakes and onto the land surrounding the lakes is a relatively small trickle. If the lakes were suddenly completely drained of all their water, they would take a very long time to fill by the rainfall in the Great Lakes Basin. Figure 1 shows this situation more clearly. Lake Superior has a volume of 12,221 cubic kilometers and the water outflow into Lake Huron through the Soo Locks is 65 cubic kilometers per year. Normally the water level in Lake Superior is held constant because rain falls into the drainage basin of the lake at the same rate as water is lost by outflow and evaporation, and the net inflow of this water over evaporation is also 65 cubic kilometers per year. By dividing the volume by the outflow, or net inflow, we obtain the time of 190 years. This "residence time" represents the time required for the lake to fill by the rainfall if it were initially empty or the time for it to empty by outflow if the rain were stopped.



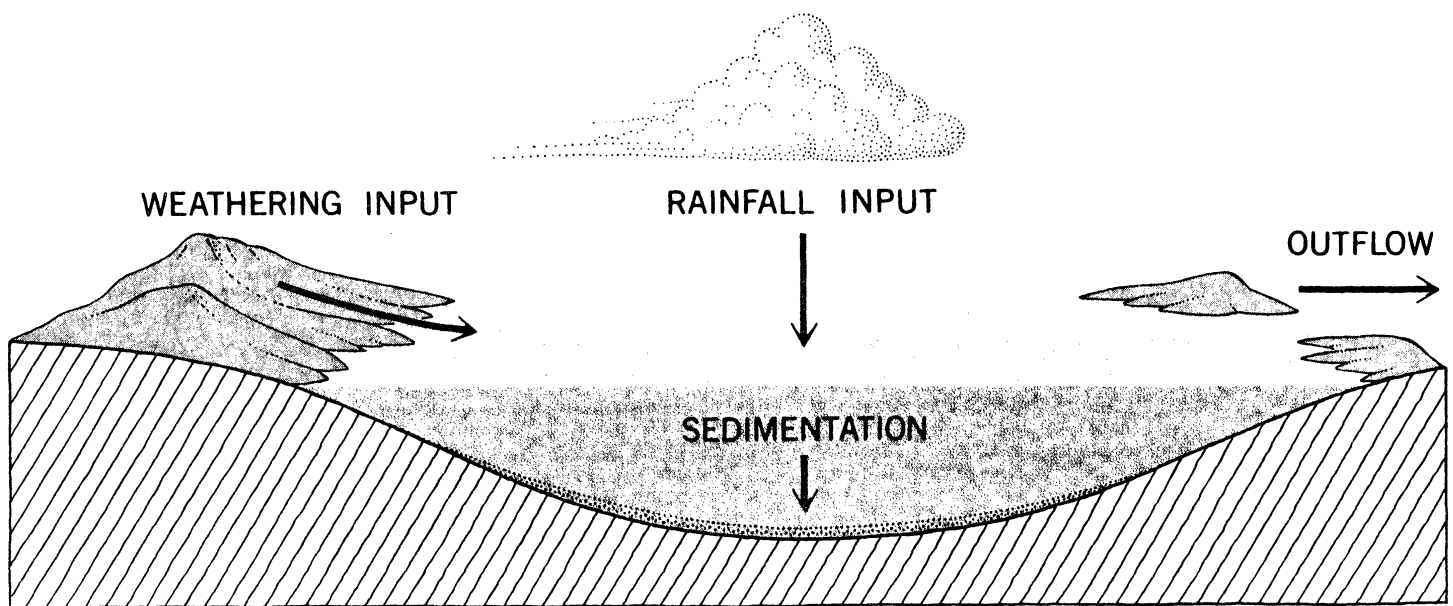
RESIDENCE TIMES OF WATER SOLUBLE SUBSTANCES, $RT=V/O=volume/outflow$, may be very long. Once polluted, the Great Lakes will be slow to cleanse themselves by outflow.

It also represents the average time water and substances dissolved in the water spend in the lake before they flow out through the Soo Locks during the normal constant level condition of the lake.

Figure 1 shows the volumes of the other four lakes in the Great Lakes system to be smaller than Lake Superior, and the residence times of dissolved substances to be shorter. However, compared to the times during which we have witnessed large changes in population and industry in the Great Lakes Basin, these residence times are

still quite long. Water stays in Lake Michigan for perhaps 100 years before it flows through the Straits of Mackinac into Lake Huron, and this time may actually be longer because the exact value of the outflow rate is not well known. Lake Huron also holds its water and dissolved materials for a long time, about 20 years, before passing them on to Lake Erie. In Lake Erie, however, the residence time is only 3 years because this lake actually has a rather small volume. Even though on a map Lake Erie appears fairly large compared with the other

Great Lakes, it is only 17 meters deep on the average, in contrast to Lake Superior which averages 148 meters deep, and the flow through Lake Erie is also three times as great. In a sense Lake Erie is a wide river which dumps its polluted waters fairly quickly, by Great Lakes standards, over Niagara Falls into Lake Ontario. There, after 8 years on the average the waters are passed out of the Great Lakes Basin into the St. Lawrence River and on to the Atlantic Ocean. The lakes contain a great deal of water which is only slowly replaced if it



MANY CHEMICAL ELEMENTS ARE ADDED NATURALLY to lake water by rainfall and by the weathering of rocks and soils. These are removed naturally by sedimentation and outflow to maintain a steady-state composition of lake water.

should become contaminated, especially in Lakes Superior, Huron, and Michigan.

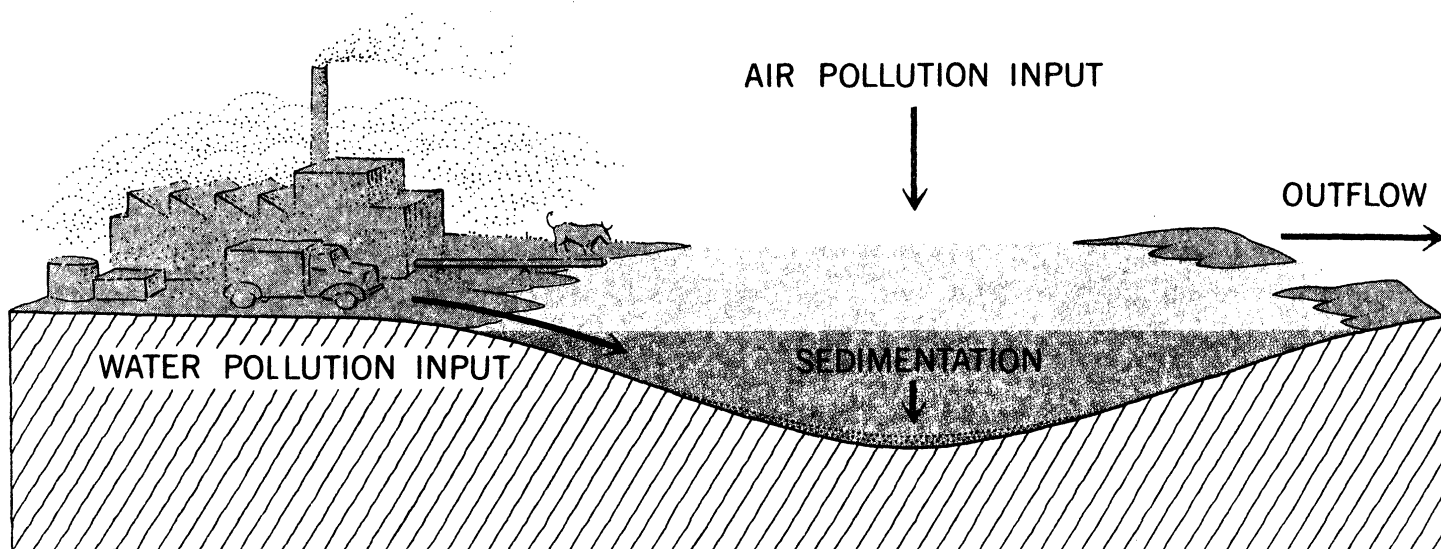
Less than two centuries ago explorers and settlers of the Great Lakes Basin described their waters as crystal clear and pure. Small amounts of dissolved inorganic substances were being supplied, as shown in Figure 2, by rainfall and by the weathering of rocks and soils. At the same time sedimentation removed the less soluble components to the bottom and outflow drew off the more soluble materials causing a steady state concentration level to be maintained. All five of the Great Lakes were probably about equally pure containing some 30 parts per million of calcium, about 15 parts per million of sulfate, and between 5 and 10 parts per million each of chloride and sodium. Lake Superior water tends

to be somewhat "purer" than this because its basin contains rocks somewhat more resistant to weathering, but to the explorers all the lakes contained delightfully clean water.

Today, except for Lake Superior, the Great Lakes show unmistakable signs of rising concentrations of these soluble substances, especially since 1920. For example, Lakes Erie and Ontario contain 4 times the chloride concentration they had prior to 1920. Part of the increase is due to pollution from streams carrying polluted water to the lakes, as illustrated in Figure 3. Municipal and industrial sources supply wastes from urbanized areas, and agricultural sources may contribute chemicals as well as larger quantities of natural weathering products because of farming activity. In addition, the air pollution

products of combustion of coal and petroleum fuels, of industrial processes, and of atmospheric chemical reactions of pollution and natural gaseous constituents of the atmosphere are brought down with rainfall into the Great Lakes Basin and contribute to the water pollution of the lakes.

The contribution of air pollution to water pollution is now under investigation at the University of Michigan, especially for certain trace metals which are abundant in air pollution. Figure 4 shows how prevailing winds may very efficiently blow air pollution from the major population centers over various parts of the Great Lakes Basin. Those of us who live in the Basin are familiar with the frequent rain and snow, especially on the leeward side of a lake. This precipitation scavenges the air of



BECAUSE OF MAN'S ACTIVITY, *air pollution and water pollution inputs bring new materials to the lakes. In time these may be removed by sedimentation and outflow.*

small particles of pollution dust which serve as condensation nuclei for formation of raindrops and snowflakes. Since the large population and industrial centers of Chicago and Detroit lie upwind from Great Lakes water bodies, transfer of their air pollutants into lake water by rainout seems virtually assured.

The changing water quality of the Great Lakes poses many challenges to environmental geochemists and to the people in charge of water quality management. Some 40 million people of the United States and Canada live in the Great Lakes Basin, and the public health and industrial vigor of both countries depend on water purity. Nevertheless, many things are unknown or are too imperfectly known to evaluate quantitatively, and action to preserve our

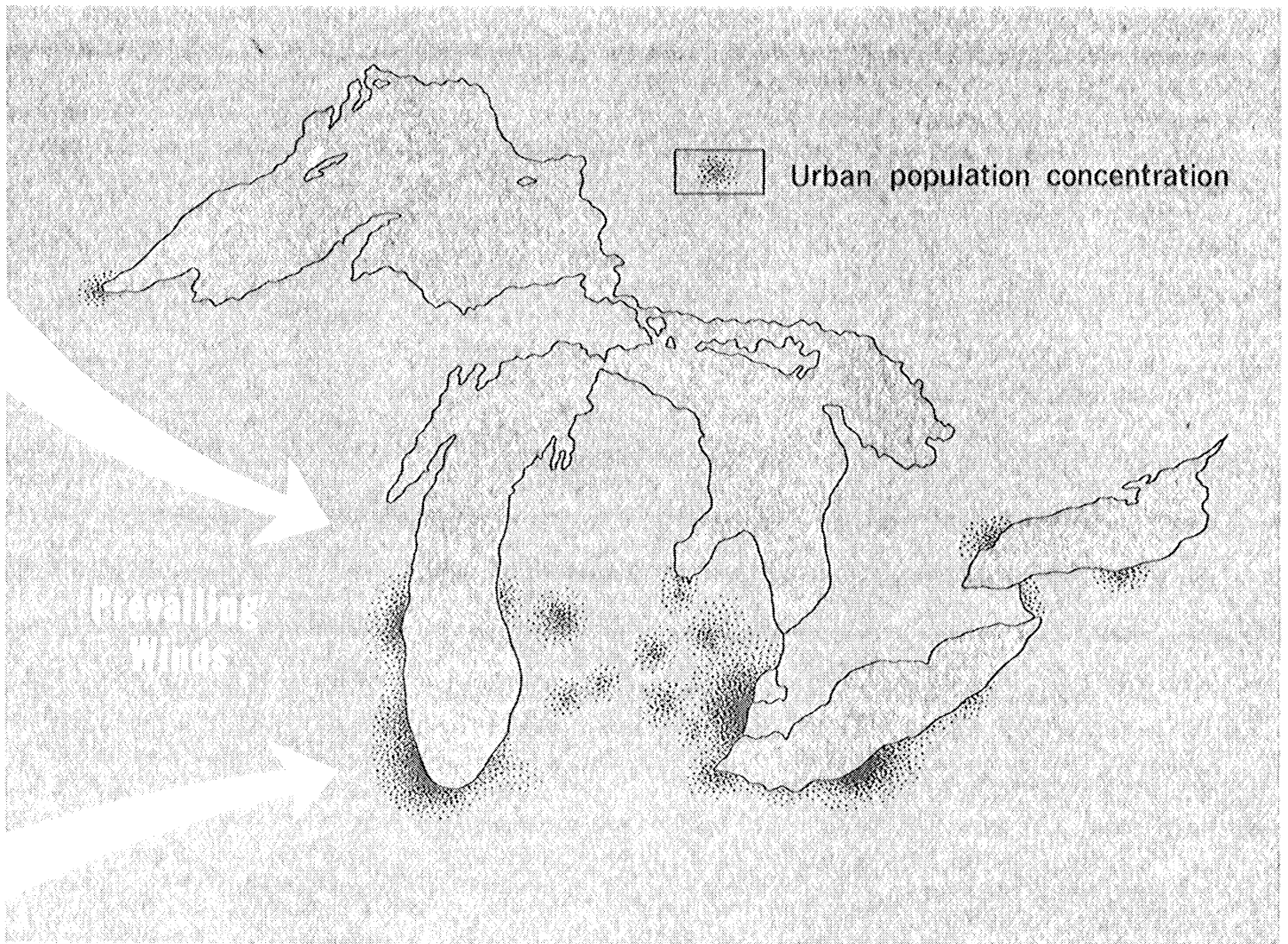
health and economic well-being is slow in coming. Some of the imponderables are these:

(1) Although chloride and certain other common dissolved materials have shown striking increases in the lower Great Lakes during the past 50 years, the majority of elements of the periodic table have not even been measured a single time in any water sample of the Great Lakes. Some of these may be increasing rapidly, but we have not yet made an attempt to monitor these increases.

(2) New and bizarre organic chemicals are created each year by industry, and some of these certainly find their way into lake water and present a pollution hazard. Since it is impossible to anticipate what new pollutants may be discovered in waters of the Great Lakes in forthcoming years, a bank

of systematically collected and preserved water samples taken each year for future analysis may provide the means to judge rates of increase of water pollution levels. Yet apparently no such sampling is being carried out in the Great Lakes, and no collection of old water samples taken in years past for even one lake is known to us to be available for chemical analysis.

(3) Chemical composition is closely tied to biological activity in the lakes, but the biological effects of most of the elements of the periodic table as well as of many organic compounds currently added as water pollutants is essentially unknown. Some substances are very water soluble and do not affect plants and animals living in the water in any direct way. Other substances are concentrated by organisms and thereby removed from



PREVAILING WINDS FROM THE WEST cause air pollutants from urban centers to move across the Great Lakes and be added to the lakes by rainfall and fallout.

the water to act as possibly poisonous agents to the growth of the organisms. It is the poisons which concern us the most, but these are the least often measured components of waters in the Great Lakes Basin. For example, chloride is frequently measured by water pollution experts, but this is essentially a non-toxic substance. Selenium, on the other hand, has apparently never been measured in lake water even though it is poisonous and is known to be a common air pollutant which may find its way to lake water during rainfall.

(4) Most people intuitively feel that the large-scale pollution of the Great Lakes would be highly unfortunate, but few can estimate the cost in dollars of that catastrophe. On strictly economic grounds the Great Lakes are necessary for cooling water in manufacturing processes and power plants, for transportation by ship, and for convenient water supply of cities. If the water quality should be damaged by gradual pollution or by a large industrial accident, it is not clear that the cooling water and transportation uses would be impaired,

or that shipping in drinking water from a more remote location would significantly increase the cost of living. But for aesthetic as well as practical reasons the number of people who would leave the Great Lakes Basin for other parts of the country because of waters rendered unsightly and unhealthy through pollution is an unknown probably greater than all the knowns. Good judgement would indicate that any mistake made now in water quality control of the Great Lakes may be a tragedy lasting for decades to centuries.

POLLUTION CONTRIBUTIONS TO THE ATMOSPHERIC
INVENTORY OF CHLORINE AND BROMINE IN AEROSOLS
OVER CONTINENTAL U. S. A.

Donald H. Loucks and John W. Winchester

Department of Meteorology and Oceanography
University of Michigan
Ann Arbor, Michigan 48104

ABSTRACT

Continental aerosols in the U. S. A. contain halogens derived from both pollution and natural sources. Particle size distributions of Cl and Br in continental aerosols, determined by sampling with cascade impactors and analyzing by neutron activation, show marked differences from fresh marine aerosols. A calculation of major sources shows most of the Cl in continental aerosols to be derived from the sea, but most of the Br appears to be derived from the combustion of ethyl fluid. About 95% of total U. S. bromine production, about 100,000 metric tons of Br per year, is converted to ethylene dibromide and burned with tetraethyl lead. Most of the Br contained in the lead halide aerosol appears to be volatilized in the atmosphere and may react further, e. g. by bromination of organic materials. The toxicological significance of these reactions is not yet known.

INTRODUCTION

The halogen elements are especially useful objects for investigation in the field of air and water pollution because both natural and pollution sources may be significant. Thus, a detailed comparison of the abundances of Cl and Br in environmental samples and a knowledge of natural sources may lead to quantitative estimates of the prevalence and dispersion characteristics of pollution substances. Furthermore, the halogens are not without important environmental chemical properties of their own. For example, chloride and bromide are highly water soluble and tend to be conservative properties of water bodies. In the atmosphere heterogeneous gas-particle chemical reactions of the halogens may cause transfer of the elements from one group of particles to another. Cloud droplet nucleation may operate more effectively with some particle substrates than with others, and halogens may prove to be convenient tracers for details of this process. Overall atmospheric residence times and removal efficiencies of pollution and natural aerosols produced near the earth's surface may be

estimated from data on the halogen composition of aerosols and precipitation. With these possibilities in mind, we have begun an investigation of bromine and chlorine occurrences in aerosols from the Great Lakes Basin where pollution sources are large and the oceanic source is remote.

Some typical particle size distributions of Br and Cl are presented in Figure 1. Aerosol particles are collected by cascade impactor of either of two designs, Andersen Sampler (AS) or Scientific Advances (SA), and the horizontal scale of impactor stage ranges from largest particles (stage A) to smallest particles (stage F, G, or in-line backup filter, Z). Particle sizes collected on each stage depend on the inertia of the particles, and smaller and smaller particles are caused to impact on successive stages because the linear air flow is increased as the air is passed through smaller and smaller orifices in the device. Particle size, shape, and density determine the stage on which a particle will impact if the device is operated at a carefully controlled flow rate, but one often speaks of equivalent particle radius for spheres of unit density. Within these limitations, the effective particle radius ranges represented by the data of Figure 1 are given in Table I (2, 9, 19).

TABLE I. Ranges of Effective Radii for Particle Collection by Cascade Impactor Stages.

<u>Stage</u>	<u>Effective Radius range, microns</u>	
	<u>SA Impactor</u>	<u>AS Impactor</u>
A	$r > 8$	$r > 4.6$
B	$8 > r > 4$	$4.6 > r > 2.9$
C	$4 > r > 2$	$2.9 > r > 1.6$
D	$2 > r > 1$	$1.6 > r > 0.9$
E	$1 > r > 0.5$	$0.9 > r > 0.5$
F	$0.5 > r > 0.25$	$0.5 > r > 0.3$
G		$0.3 > r > 0.1$
Z		$0.1 > r$

Neutron activation analysis is used to analyze each stage of the cascade impactor for Cl and Br. Normally the impaction surface is a 95 mm disk of thin polyethylene or Mylar plastic to which adhere particles of the appropriate size range. For example, the Andersen Sampler, which has

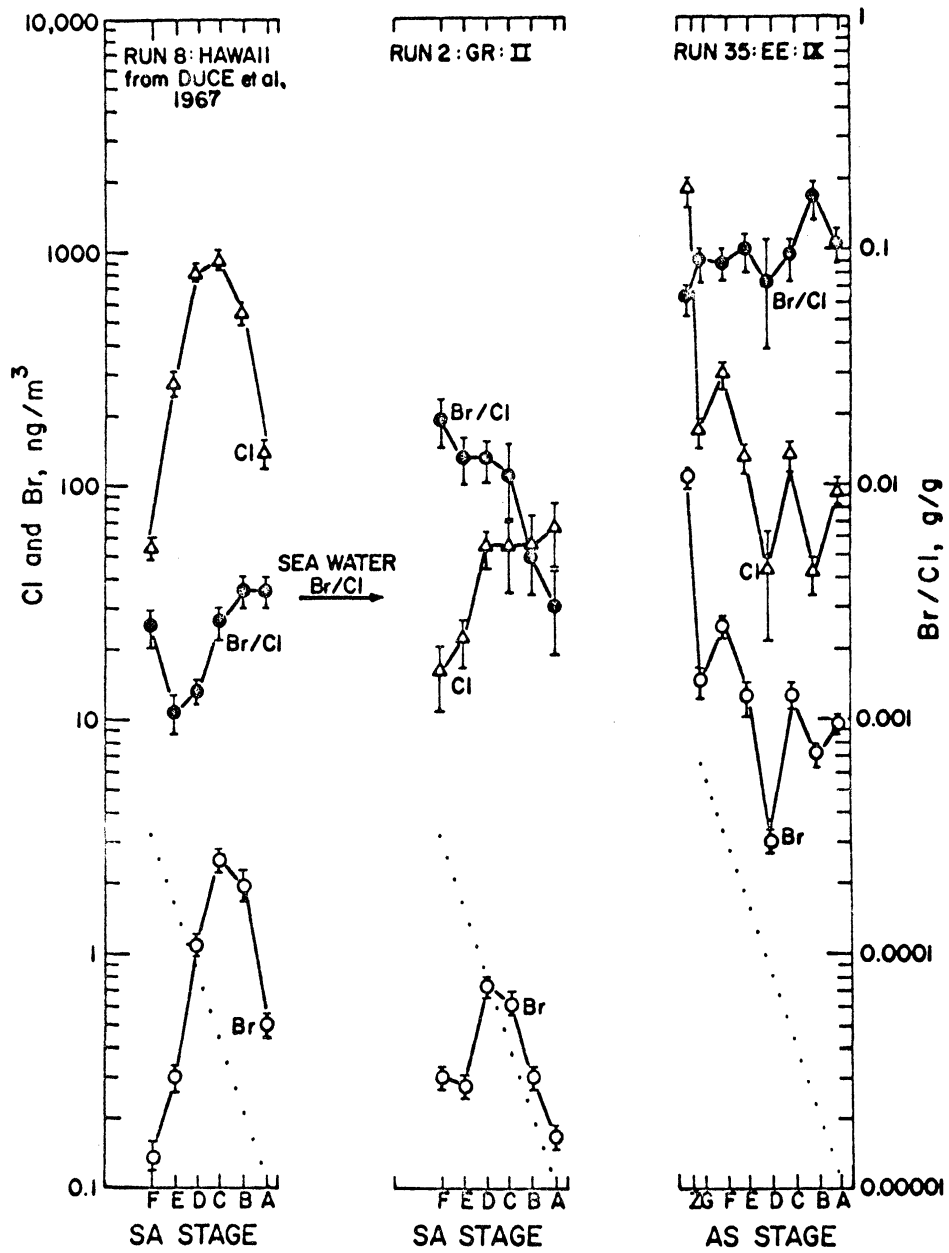


Figure 1. Size distributions of aerosol Cl and Br from Hawaii (1 run) and Michigan (2 runs).

a large number of orifices per stage, operates at a flow rate of 1 cfm ($2 \text{ m}^3/\text{hr}$) and usually in a few hours dark spots of particulate material are visible below each orifice. The disk is removed and packaged in a capsule for neutron irradiation after which the induced radioactivity is leached from the surface and counted, usually following a radiochemical separation step (5). In Figure 1 the total amount of Cl and Br found on particles of each impactor stage, expressed as concentration in the air mass sampled, is plotted against impactor stage, i. e. particle size. Because particle radii differ by approximately a factor of 2 for successive impactor stages, the figure is essentially a plot of mass of the element on a logarithmic scale versus logarithm of particle radius for aerosols containing the element. It would also be of interest to know the concentration of the element in the particles themselves, but, owing to the experimental difficulty of determining total mass of particulate material on each stage, this has not been attempted in the present investigation. Because of the great sensitivity of neutron activation analysis for certain elements but not others, it is actually easier to measure individual elements than total mass of particles. Nevertheless, it is sometimes possible to make inferences about composition of the particles themselves from the systematics of elemental distribution among the size fractions collected by the cascade impactor.

The data in Figure 1 illustrate the contrasts which are found between Cl and Br size spectra characteristic of aerosols fresh from the sea and those of inland localities. Duce et al. (7) found aerosols of the Hawaiian marine atmosphere to carry most of the Cl and Br in particles of a few microns radius but most of the I on much smaller particles. The ratio Br/Cl, however, showed significant variation around the sea water value, as can be seen on the left side of Figure 1.

The center and right hand portions of Figure 1 show two of the Cl and Br spectra we determined in samples of aerosols collected in the Great Lakes Basin near Ann Arbor, Michigan. These inland data, collected under different meteorological circumstances, reflect the variability which we find to be typical far from the sea. For Run 2:GR:II, from a rural area in southeastern Michigan, the winds were from the northwest

and trajectory analysis indicates the air to have traveled from the North Atlantic around Hudson Bay. The implication is that a major source upwind was the ocean. However, the data of Run 2:GR:II differ from those of Run 8:Hawaii in several respects. Concentrations, especially of Cl, are reduced in Run 2:GR:II and the Cl distribution is shifted toward giant ($r > 1\mu$) particles. The mass ratio Br/Cl does have approximately the sea water value on Stages A and B but rises far above this in the smaller particles.

For Run 35:EE:IX, from the roof-top of the East Engineering Building in the city of Ann Arbor, the winds were from southerly to easterly and the major sources upwind probably included important air pollution components. The tendency of the Br/Cl ratios of Run 2:GR:II to exceed the sea water ratio is strengthened in Run 35:EE:IX where Br/Cl ratios are uniformly high. The Cl distribution tends to be weighted toward the small particles in contrast to Run 8:Hawaii, although the Cl concentrations in these two runs are comparable. The Br distribution in Run 35:EE:IX has a shape similar to the Cl distribution, and the Br concentrations vastly exceed those in the other two runs.

In this paper we wish to develop a perspective over-view of the sources and modifying atmospheric processes for aerosol Cl and Br in order to account for some of the contrasts illustrated by Figure 1. (A discussion of intricacies of the complete set of inland Cl and Br aerosol distributions will be presented elsewhere (17).) We shall begin by analysis of the sources and removal processes for atmospheric Cl and Br guided both by information in the literature and by the present data.

SOURCES OF AEROSOL Cl AND Br

a. The ocean is the greatest natural source for aerosol Cl and Br although in arid areas salt crystals from the soil may also become airborne (8). The production mechanism for oceanic aerosols involves breaking waves giving rise to air bubbles in the water; the airborne sea spray particles are produced as droplets ejected by the breaking bubbles (3). On the average, the particles produced have a mass ratio, Br/Cl, approximately equal to the sea water ratio, 0.0034 (7). Most of the aerosol mass is found in the large particle ($0.1 < r < 1\mu$) and giant particle ($1 < r < 10\mu$) size

ranges (7). Aitken particles ($r < 0.1\mu$), though they have not been analyzed for Cl and Br, are judged not to include a significant sea salt component (14).

b. Ethyl fluid, the automobile gasoline additive containing tetraethyl lead, also contains ethylene dibromide and ethylene dichloride with the mass ratio Br/Cl = 1.15 and a ratio Br/Pb = 0.39. Upon combustion the halogens form PbBrCl which is relatively volatile. This salt is dispelled in the exhaust and thus Pb, Br and Cl are scavenged from the combustion chamber and added to the atmosphere. Stipp (24) reports that 95% of Br produced in the U. S. is used in ethyl fluid. The circumstances of combustion of ethyl fluid satisfy the requirements for formation of a condensation aerosol (10). The volatile halide salt is heated to high temperature and then rapidly cooled in the exhaust conduits. High supersaturation leading to the formation of small ($r < 0.1\mu$) particles is expected. Subsequently coagulation would probably transfer some of this material to larger particle sizes (14).

The aerosol particles from automobile exhaust have Br/Cl ranging from 0.1 to 0.9 initially but decreasing with time due to preferential volatilization of Br (26). Figure 2 shows the results of an experiment designed to test the hypothesis of selective volatilization of Br from lead halide pollution aerosols, formulated on the basis of our earlier analyses of environmental samples. The ratio Br/Cl found in the smallest aerosol particles, viz. those which are caught on the Z filter stage after passing through seven impaction stages of the Andersen Sampler, are plotted against time during the experiment. For a two hour period ambient air was sampled in Ann Arbor in an open garage. Then the garage was closed, an automobile engine was run for 10 minutes, and the Andersen Sampler was operated in the garage simultaneously. Immediately after the engine was stopped another Andersen sample was taken for 10 minutes to sample aerosols which ranged in "age" from 0 to 20 minutes. A third Andersen sample was taken from 30 to 65 minutes after stopping the engine and a fourth was taken from 80 to 145 minutes after the end of engine operation and aerosol generation. The Br/Cl ratios in the finest particles are plotted in Figure 2 against aerosol age and show a marked decrease in Br relative to Cl in the first half hour but thereafter a constant low value some 50 times lower

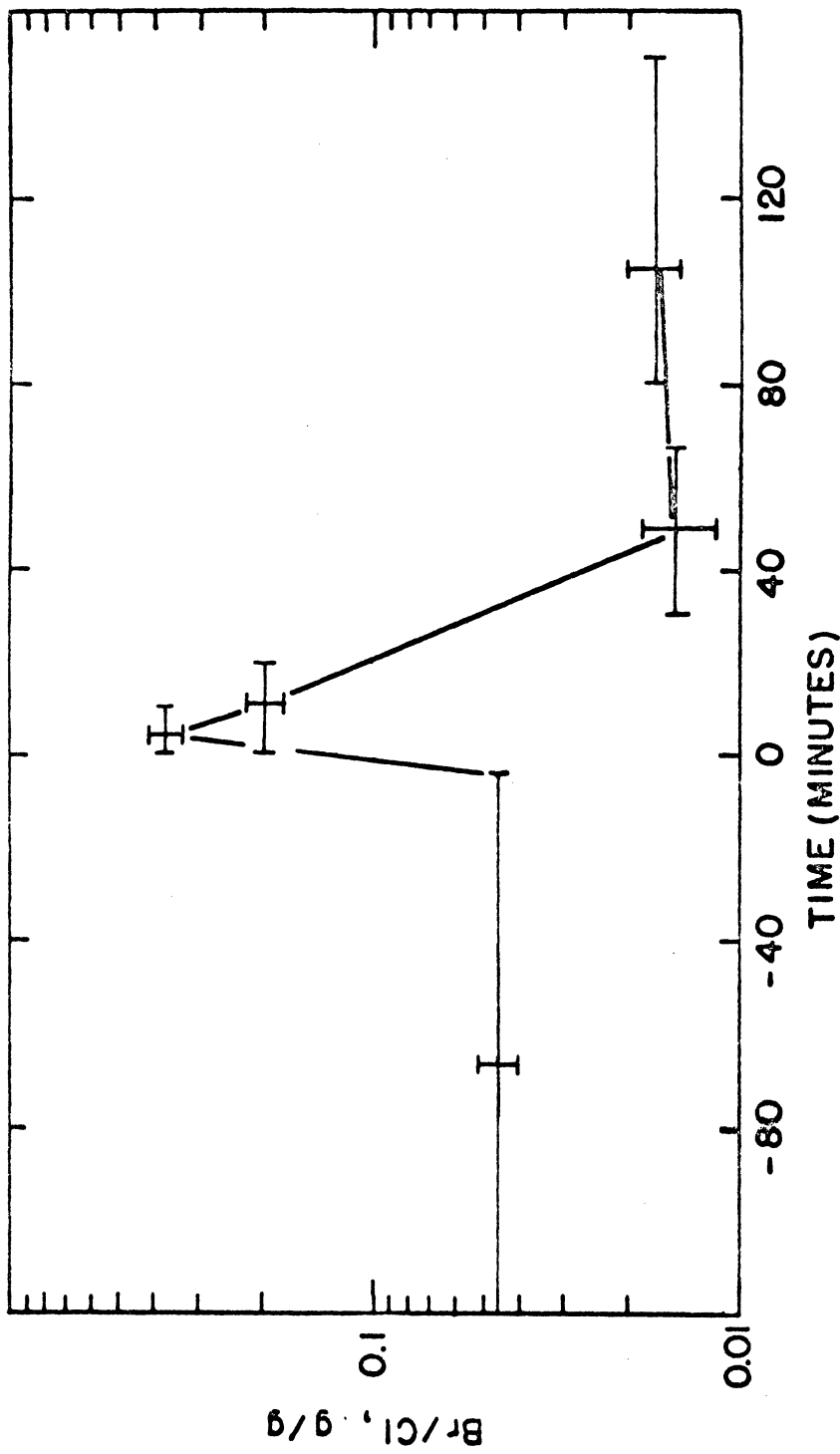


Figure 2. The time variation of the Br/Cl ratio in very small automobile exhaust particles introduced fresh at time zero.

than the ethyl fluid ratio. The somewhat higher ratio observed before the experiment started we attribute to nearby automobile traffic and the possibility of some aerosols less than a half hour in age being sampled in the open garage. The selective loss of Br we believe to be due to selective oxidation of bromide ion, compared to the more stable chloride ion, by oxidants in the atmosphere, and the reaction apparently proceeds readily in the low light intensities of our garage experiment. Evidence in hand (17) suggests that the volatile product, perhaps Br_2 , may be reactive and combine with unsaturated organic matter contained in other aerosol particles. It is important to note that the Br and Cl were detected only on the Z filter stage of the garage experiment, (e. g. Z-stage Br > 98% of total Br during engine operation) indicating that the combustion product is very fine particles.

c. In fuel oil Cl is present in trace amounts. While a small sized condensation aerosol with a Cl component would be expected to be produced on combustion, fly-ash or dispersion aerosol would not be expected. The Br/Cl ratio is taken to be that of sea water (23).

d. Coal contains a few parts per thousand of Cl and the Br/Cl ratio may be near the sea water ratio, 0.0034 (23). On combustion, a small sized condensation aerosol would be expected. In addition, condensation onto less volatile constituents, mechanically dispersed by combustion, would produce a Cl component in fly-ash and dust-fall. Thus it is likely that Cl-rich particles of all aerosol size ranges, from Aitken ($r < 0.1\mu$) to giant ($r > 1\mu$) are produced.

ESTIMATION OF Cl AND Br AEROSOL SOURCE STRENGTHS

Useful upper and lower bounds on the masses of Cl and Br from the major sources contributing to inland aerosols can be estimated.

a. The Ocean. For the upper bound we note that Eriksson (8) reports an estimate of 5.4 kg of sea slats, or 3 kg Cl, transported per day across each meter of windward Hawaiian sea coast in projection perpendicular to the wind. This result is based on measurements of Amman (1) and Woodcock (27). It is consistent with results of Duce et al. (7) who find approximately $3\mu\text{g Cl/m}^3$ at a few meters altitude. Assuming uniform mixing to an altitude of 2 kilometers and an average wind speed of 10 m/sec,

this is equivalent to a resultant transport of 5 kg Cl/(m-day). As both these estimates may underestimate storm conditions which enhance sea salt transport inland, we choose 1.5 times Eriksson's estimated flux of chloride and apply it along a projected windward coastline of 4000 km to obtain 7×10^{12} g Cl/yr as an upper bound for the annual natural Cl input over the continental United States. Taking $\text{Br/Cl} = 0.0034$, an upper bound for the annual natural Br input is 2×10^{10} g Br/yr.

For the lower bounds, Eriksson (8), using Woodcock's data, finds the rate of salt transport at Pompano Beach, Florida, and at various places in the Caribbean to be as little as half the rate found for Hawaii. If, in addition, the transport extends over as little as 1000km of projected coastline then a lower bound for natural Cl input is 1/8 the values calculated above, viz. 8×10^{11} g Cl/yr. For Br the lower bound estimate is 3×10^9 g Br/yr.

b. Ethyl Fluid. For the upper bound, May (18) reports the bromine sold by primary producers in the U. S. in that year to amount to 133×10^6 kg. If 95% of this is used as ethylene dibromide in ethyl fluid (24), then 12.5×10^7 kg of Br was so consumed in 1967. From data presented by Hirschler et al. (12) we infer that up to 100% of the lead halides being consumed might be emitted and of these 75% might remain airborne during country driving. Therefore the annual Br input from automobile exhaust might be as high as 9×10^{10} g Br/yr.

With $\text{Br/Cl} = 1.15$, the annual Cl input from this source, as an upper bound, is 0.8×10^{11} g Cl/yr.

For a lower bound, Hirschler et al. (12) suggest that in city driving only about 40% of the lead halide material may be emitted of which 50% remains airborne. Consequently, lower bounds on inputs from the automobile source are 2.5×10^{10} g Br/yr and 2×10^{10} g Cl/yr.

c. Fuel Oil. For the upper bound, Kirby and Moore (16) report that 6.75×10^{11} kg of fuel oil were consumed in the U. S. A. in 1967. Smith (21) finds from 1 to 5 grams of particles produced by the firing of 1 kilogram of oil. Moreover in the only analysis reported, the particles were found to be 0.5% Cl (21). We estimate as an upper limit for Cl input from the combustion of fuel oil 2×10^{10} g Cl/yr. Assuming $\text{Br/Cl} = 0.0034$, we estimate as an upper limit 6×10^7 g Br/yr.

For the lower bound, we suggest the particulate production to be one gram per kilogram of fuel oil fired and the Cl content of the particulates to be only 0.05%. Consequently we find at least 4×10^8 g Cl/yr and 1×10^6 g Br/yr to be emitted by fuel oil combustion.

c. Coal. Young and Gallagher (29) report the consumption of coal in the U. S. A. during 1967 to be 5×10^{11} kg. Smith and Gruber (22) find the Cl content of several American coals to lie between 0.5% and 0.01% and Cuffe and Gerstle (4) find between 3% and 25% of the fly-ash to escape collection and be emitted to the atmosphere while Jones (13) reports electrostatic precipitators to be approximately equally efficient in the collection of particles of all size ranges. Therefore let us assume that equal masses of fly-ash and smaller particles are produced and emitted. These particles should include the Cl component because it is not rapidly oxidized by combustion. The upper bounds for Cl and Br aerosol production (assuming Br/Cl = 0.0034) are 6×10^{11} g Cl/yr and 2×10^9 g Br/yr. The corresponding lower bounds are 1.5×10^9 g Cl/yr and 5×10^6 g Br/yr.

Table II summarizes the calculations of upper and lower bounds for Cl and Br inputs to the atmosphere from the major natural and pollution sources. Quite clearly Cl which is deposited over the U. S. A. comes overwhelmingly from the ocean, although local exceptions may be observed in highly polluted areas. However, for Br the situation is quite different. Although the Br contained naturally in fuel oil and coal contributes only in a minor way, the Br originating from ethyl fluid combustion appears to be the major source, exceeding oceanic Br probably many-fold.

TABLE II. Estimated Atmospheric Cl and Br Inputs to Continental U. S. A.

Source	Cl, 10^9 g/yr		Br, 10^9 g/yr	
	Maximum	Minimum	Maximum	Minimum
Ocean	7000	800	20	3
Ethyl Fluid	80	20	100	20
Fuel Oil	20	0.4	0.06	0.001
Coal	600	1.5	2	0.005

NUMBERS OF AEROSOL PARTICLES GENERATED

In meteorology the number of particles produced by a source may be more important than total particulate mass. Visibility through haze is reduced by particle-scattering and depends upon the number as well as the sizes of the particles (14). Rain drops and ice crystals are formed around nucleating particles (20). Size, solubility and numbers of particles are important factors in nucleation. Human intake of atmospheric aerosols depends on particle size; e. g. larger aerosols may be deposited in the respiratory tree but smaller aerosols may enter in the alveoli and be retained (28). In spite of the practical importance of knowing the sizes of particles which contain different chemical elements and compounds and the numerical abundance of these particles, most air pollution measurements are of total particle mass without distinction as to particle size distribution.

Any serious attempt to estimate the total number of particles generated by all important processes operating in the U. S. A. is met with formidable difficulties mainly because of the scarcity of information on sizes of particles generated. Nevertheless, it is informative to make the attempt based on our data for Cl to at least deepen our appreciation for the difficulties of the task. Beginning with the source strength estimates of the previous section, we may estimate numbers of particles if we make certain assumptions for particle size, density, and fractional content of Cl in the particles.

For sea salt, average particle radii range from 0.5 to 5μ (7), density is close to 2 g/cm^3 (NaCl) and the Cl fraction is 0.6. For ethyl fluid, particle radii may range from 0.05 to 0.5μ (28), density may be 6 g/cm^3 (PbClBr) and the Cl fraction, 0.1 (26). For fuel oil, the condensation aerosol particles are expected to range in radius from 0.05 to 0.5μ with density about 1 g/cm^3 and Cl content, 0.005 (21). For coal, the condensation aerosol particles with radius range from 0.05 to 0.5μ may be most important numerically. Their density may be about 1 g/cm^3 and Cl content, 0.5 (taking Smith and Gruber's (22) 0.5% Cl in coal and assuming 1% ash).

Now the Cl mass strength, $M \text{ g Cl/yr}$, particle radius, $r \text{ cm}$, particle density, $\rho \text{ g/cm}^3$, and fractional Cl content, f , can be combined as

$$\frac{M}{(4/3)\pi r^3 \rho f} = N \text{ particles/yr}$$

where the upper bound for M (Table II) and lower bound for r give an upper bound for N and vice versa. The numbers of particles generated, so estimated, are listed in Table III.

TABLE III. Numbers of Aerosol Particles Generated as Inferred from Calculated Chloride Inputs.

Source	log (Particles/yr)		log (Particles/cm ³)	
	Maximum	Minimum	Maximum	Minimum
Ocean	25	21	1.8	-3.2
Ethyl Fluid	26.3	22.8	3.1	-1.4
Fuel Oil	27.8	23	4.6	-1.2
Coal	27	21.3	3.8	-2.9

Particle concentrations may be estimated only after we have knowledge of dilution volumes. Very crudely, we may view the $7.8 \times 10^{16} \text{ km}^2$ area of continental U. S. A. as covered with air uniformly mixed to an altitude of 2 km and replenished with "clean" air 10 to 100 times per year. By dividing the particle generation rate by the air replenishment rate, $10^{8.2}$ to $10^{9.2} \text{ km}^3/\text{yr}$, we arrive at an estimate of steady state particle concentration for the different sources. These results are also shown in Table III.

The results of Table IV were inferred from cascade impactor data. Estimates of numbers of particles were obtained by assuming the average density and fractional Cl content to be $P = 2 \text{ g/cm}^3$ and $f = 0.5$ respectively for marine aerosols and $P = 3 \text{ g/cm}^3$ and $f = 0.1$ respectively for pollution aerosols. However the Cl concentration was measured over several hours rather than estimated for continental U. S. A. over a year.

Comparison of Table IV with Table III shows those aerosols probably of marine origin to have numbers comparable to the average in Hawaii (1 run) (7) and to be in low abundance inland compared to the average, while the pollution particles may exceed the average concentration. These conclusions are consistent and suggest that, in spite of the crude estimation and resulting wide separation, the limits (Table III) do encompass the true average particle concentration due to each major Cl source.

TABLE IV. Concentrations of Aerosol Particles as Inferred from Measurements of Cl (17).

<u>Location</u>	<u>Approximate Particle Radius (μ)</u>	<u>log (Particles/cm³)</u>	
		<u>Maximum</u>	<u>Minimum</u>
Hawaii (7) (ocean, 1 case)		0.5	
S. E. Michigan (probable ocean aerosol, 3 cases)	4	-3.7	-4.7
(high concentration pollution, 5 cases)	0.05	+3.9	+3.0
S. Chicago (high concentration pollution, 2 cases)	0.05	+4.3	+4.2

The results suggest that a substantially greater concentration of particles on the average over the U. S. A. arise from pollution sources than from the ocean. The calculations of Table III consider only particles containing Cl, a major component of marine aerosols but a component not common to all pollution aerosols. Additional pollution aerosols may exist, and the relative importance of pollution sources of particles may be greater than shown in Table III.

ATMOSPHERIC REMOVAL PROCESSES

The cycle of halogens in aerosols is closed by their return to the earth's surface by wet or dry fallout. Eriksson (8) has made an especially valuable analysis of data taken by Junge and Werby (15) on the Cl content of rains primarily due to sea salt, which portrays the extent of transport of marine aerosols inland. Figure 3 shows that Cl deposition in kg/hectare-yr diminishes with increasing distance from the sea coast and enables us to estimate the mean Cl deposition velocity for the U. S. A. Since the contours are logarithmically spaced, we can estimate the mean travel distance of aerosol Cl to be about 200 km near the coast to 1000 km far from the coast. If air masses move 400 Km/day (5 m/sec), an atmospheric residence time of $(4-20) \times 10^4$ sec is implied. A single mean deposition velocity of 1 cm/sec would account for this range of residence times if the mean altitude for atmospheric Cl varied from 400 meters near the coast to 2000 meters inland. Eriksson (8) cites other evidence indicating that 1 cm/sec is not an unreasonable deposition velocity for sea salt aerosols.

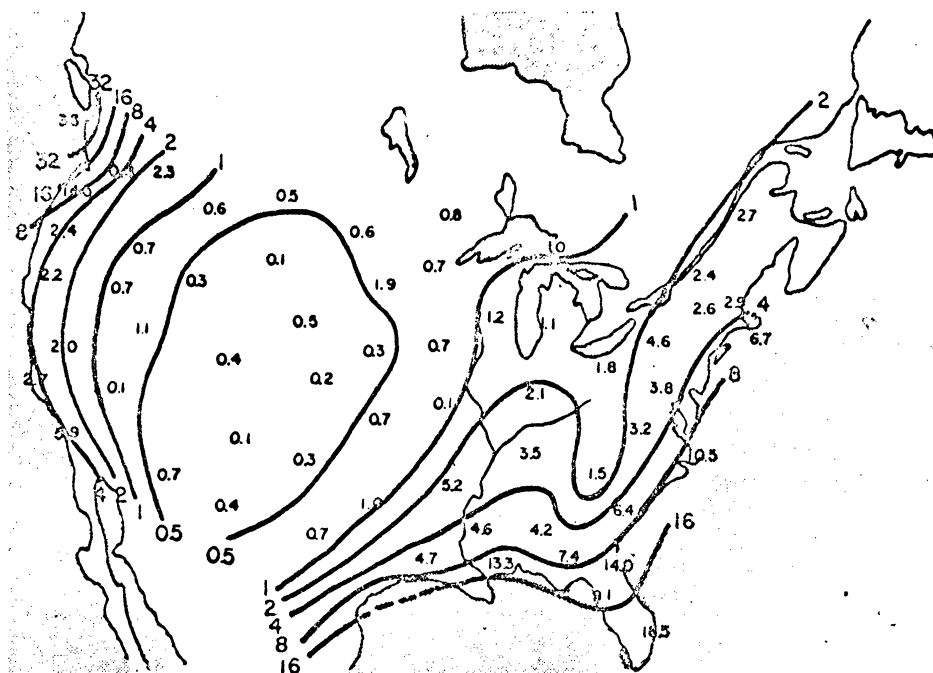


Figure 3. Chloride in precipitation over the U. S. A. in kg/(hectare-yr), computed from concentrations of chloride in precipitation (Junge and Werby, 15) and rainfall data (from Eriksson, 7).

By inspection of Figure 3, the mean deposition may lie in the range 1-4 kg Cl/hectare-yr by wet precipitation. Eriksson (8) argues that dry deposition may exceed wet precipitation by two-fold, i. e. 2-8 kg Cl/hectare-yr, and total deposition becomes 3-12 kg Cl/hectare-yr or $(1-4) \times 10^{-12}$ g Cl/cm² sec. Over the 7.8×10^8 hectares of continental U. S. A., deposition totals $(2-10) \times 10^{12}$ g Cl/yr. This value is not in disagreement with the source strength estimate given in Table II.

A further check may be made by calculating the product to total Cl found in Run 2:GR:II (Figure 1), about $0.3 \mu\text{g Cl/m}^3$ and deposition velocity, 1 cm/sec. This result, 0.3×10^{-12} g Cl/cm² sec, is not far from the above estimate based on Eriksson's analysis.

Deposition of natural Br can be estimated from the ratios Br/Cl = 0.0034 for sea water, and Br/Cl = 0.01 for uncontaminated surface waters near Lake Superior (25). Assuming the higher ratio is typical far from the sea (6), wet removal of Br may be 10-14 g Br/hectare-yr. Dry deposition of Br may not be as efficient as that for Cl owing to the small particle

size for inland Br found in this work. Accordingly, the range 10-40 g Br/hectare-yr or $(8-30) \times 10^9$ g Br/yr over the U. S. A. for total wet and dry deposition of natural Br is our best estimate. This result agrees with Table II.

Locally much greater ratios Br/Cl have been observed in rain water as well as aerosols, by ourselves and others (11). If the removal characteristics of pollution aerosols resemble those of natural aerosols, such that mean transport distances are much shorter than continental dimensions, then the total removal of pollution Br and Cl is approximated by the pollution generation rate. Consequently the total input rates presented in Table II also represent reasonable estimates of removal rates.

SUMMARY AND CONCLUSIONS

Several broad perspectives emerge from the foregoing discussion. The ocean is the strongest source for mass of aerosol Cl over the continental U. S. A. and exceeds the strength of pollution sources. Combustion of ethyl fluid as a source for mass of aerosol Br is stronger than the natural source. While the natural aerosol has a Br/Cl ratio of approximately 0.003, the pollution aerosol has a much greater Br/Cl ratio, sometimes 0.1 or larger. The pollution sources considered, combustion of ethyl fluid, fuel oil and coal, exceed the oceanic production for numbers of overland particles. The estimated inputs of aerosol Cl and Br generally agree with the outputs due to wet and dry precipitation.

Finally, some interpretation of the data in Figure 1 is feasible. While Run 8:Hawaii (7), our reference for marine aerosols, has the size distributions of a dispersion aerosol and Br/Cl values approximately equal to the ratio in sea water, Run 35:EE:IX, collected in Ann Arbor, Michigan, during a period of southeasterly winds and thundershowers, has Br and Cl mass concentrated in small particles (condensation aerosol) and Br/Cl thirty times greater than the sea water ratio. The total Cl concentrations in Runs 8:Hawaii and 35:EE:IX are comparable but the total Br concentration is greater in Run 35:EE:IX. These features all suggest that the aerosol sampled in Run 35:EE:IX was of pollution origin.

Run 2:GR:II, collected in southeastern Michigan during an intrusion of Arctic and Atlantic Ocean air, shows some characteristics intermediate

between the extremes of the other two runs. The Br distribution and Br/Cl values suggest the giant particles to be of marine origin and the smaller particles of pollution origin. Precipitation en route from the Arctic may have been responsible for reducing the concentration and modifying the size distribution of the Cl-rich aerosols of Run 2:GR:II (17).

Both natural and pollution aerosols may be transported and modified in the atmosphere. Thus, depending upon meteorological conditions, the prevalence inland of one or the other of these classes leads to wide variations in the characteristics of the aerosols observed there.

LITERATURE CITED

1. Amman, E., 1957: Upper air data for Project Shower. Tellus, 9, 569-580.
2. Andersen, A. A., 1966: A sampler for respiratory health hazard assessment. J. Amer. Ind. Hyg. Assoc., 27, 160-165.
3. Blanchard, D. C. and A. H. Woodcock, 1957: Bubble formation and modification in the sea and its meteorological significance. Tellus, 9, 145-158.
4. Cuffe, S. T. and R. W. Gerstle, 1967: Emissions from coal-fired power plants. U. S. Dept. of Health, Education and Welfare, Public Health Service Publication No. 999-AP-35, Cincinnati, Ohio.
5. Duce, R. A. and J. W. Winchester, 1965: Determination of iodine, bromine and chlorine in atmospheric samples by neutron activation. Radiochim. Acta., 4, 100-104.
6. Duce, R. A., J. W. Winchester and T. W. VanNahl, 1965: Iodine, bromine and chlorine in the Hawaiian marine atmosphere. J. Geophys. Res., 70, No. 8, 1775-1799.
7. Duce, R. A., A. H. Woodcock and J. L. Moyers, 1967: Variation of ion ratios with size among particles in tropical oceanic air. Tellus, 19, No. 3, 369-379.
8. Eriksson, E., 1959: The yearly circulation of chloride and sulphur in nature; meteorological, geochemical and pedological implications. Part I; Tellus, 11, 375-403; Part II, Tellus, 12, 63-109.
9. Flesch, J. P., C. H. Norris and A. E. Nugent, Jr., 1967: Calibrating particulate air samplers with monodisperse aerosols. J. Amer. Ind. Hyg. Assoc., 28, 507-526.

10. Fletcher, N. H., 1963: The Physics of Clouds, University Press, Cambridge, 390 pp.
11. Harriss, R. C. and H. H. Williams, 1969: Specific-ion electrode measurements on Br, Cl and F in atmospheric precipitation. J. Applied Meteor., 8, No. 2, 299-301.
12. Hirschler, D. A., L. F. Gilbert, F. W. Lamb and L. M. Niebylski, 1957: Particulate lead compounds in automobile exhaust gas. Ind. Eng. Chem., 49, 1131.
13. Jones, H. H., 1962: Electrostatic precipitators. Air Sampling Instruments, 2nd edition, Amer. Conf. Governmental Industrial Hygienists.
14. Junge, C. E., 1963: Air Chemistry and Radioactivity, Academic Press, 382 pp.
15. Junge, C. E. and R. T. Werby, 1958: The concentration of chloride, sodium, potassium, calcium, and sulphate in rain water over the United States, J. Meteorol., 15, 417-425.
16. Kirby, J. G. and B. M. Moore, 1967: Crude Petroleum and petroleum products. Minerals Yearbook, I-II, U. S. Dept. of the Interior, Bureau of Mines, 837-948.
17. Loucks, R. H. and J. W. Winchester: Particle size distribution of chlorine and bromine in mid-continent aerosols from the Great Lakes Basin. To be presented at the Symposium on Atmospheric Trace Constituents and Atmospheric Circulation Sponsored by the International Association of Meteorology and Atmospheric Physics, Heidelberg, Germany, September 8-13, 1969.
18. May, T. C., 1967: Bromine, Minerals Yearbook, I-II, U. S. Dept. of the Interior, Bur. Mines., 249-252.
19. Mitchell, R. I. and J. M. Pilcher, 1959: An improved cascade impactor for measuring aerosol particle sizes. Ind. and Eng. Chem., 51, No. 9, 1039-1042.
20. Schaefer, V. J., 1969: The inadvertent modification of the atmosphere by air pollution. Bull. Amer. Meteor. Soc., 50, No. 4, 199-206.
21. Smith, W. S., 1962: Atmospheric emissions from fuel oil combustion. U. S. Dept. of Health, Education and Welfare, Public Health Service Publication No. 999-AP-2, Division of Air Pollution, Cincinnati, Ohio.

22. Smith, W. S., and Gruber, C. W., 1966: Atmospheric emissions from coal combustion - an inventory guide. U. S. Dept. of Health, Education and Welfare, Public Health Service Publication No. 999-AP-24, Division of Air Pollution, Cincinnati, Ohio.
23. Stenger, V. A., 1964: Bromine. Kirk-Othmer Encyclopedia of Chemical Technology, 3, Interscience, 750-766.
24. Stipp, H. E., 1960: Bromine, Mineral facts and problems. U. S. Bur. Mines Bull. 585, 149-154.
25. Tiffany, M. A., J. W. Winchester and R. H. Loucks: Natural and pollution sources of iodine, bromine and chlorine in the Great Lakes. J. Water Pol. Cntrl. Assoc., May, 1969 (in press).
26. Winchester, J. W., W. H. Zoller, R. A. Duce and C. S. Benson, 1967: Lead and halogens in pollution aerosols and snow from Fairbanks, Alaska. Atmospheric Environment, 1, 105-119.
27. Woodcock, A. H., 1957: Atmospheric sea salt nuclei data for Project Shower. Tellus, 9, 521-524.
28. The Working Group on Lead Contamination, 1965: Survey of lead in the atmosphere of three urban communities. U. S. Dept. Health, Education and Welfare, Public Health Service Publication No. 999-AP-12, Division of Air Pollution, Cincinnati, Ohio.
29. Young, W. H. and J. J. Gallagher, 1967: Coal--Bituminous and Lignite. Minerals Yearbook, I-II, U. S. Dept. of the Interior, Bur. Mines, 331-356.

SURFACE WATER INPUTS OF IODINE, BROMINE, AND CHLORINE TO LAKE HURON¹

Mary A. Tiffany and John W. Winchester

*Department of Meteorology and Oceanography and Great Lakes
Research Division, University of Michigan, Ann Arbor*

Abstract. Surface waters were systematically sampled and analyzed for chlorine, bromine, and iodine by neutron activation for material balance calculation of inputs and outflows for Lake Huron. 42 Saginaw River basin samples from autumn 1968 showed marked halogen pollution, also detected in 11 Saginaw Bay samples. River water from 16 northern Michigan and Ontario locations was less polluted. Using these and our previously published analyses, together with available rainfall and river discharge data, we calculated total input/outflow ratios for Lake Huron: Cl, 1.04 ± 0.08 ; Br, 1.73 ± 0.19 ; I, 1.15 ± 0.16 . Cl and I are apparently near a steady state, but inflow of Br significantly exceeds outflow. If present inputs continue, the Br concentration will rise in Lake Huron, but Cl and I will remain roughly constant. Reducing Saginaw River halogen pollution, which supplies nearly half the Cl and Br input, should cause decreasing Lake Huron Cl concentration and arresting of Br concentration increase.

INTRODUCTION

In his important paper "Eutrophication of the St. Lawrence Great Lakes," A. M. Beeton (1965) published graphs showing that the concentrations of the major dissolved ions Cl^- , SO_4^{2-} , Ca^{++} , Na^+ and K^+ , have tended to increase over the past 50 years in each of the Great Lakes with the exception of Lake Superior. Therefore, is a rise in the concentrations of these and other components of the water of an individual Great Lake expected in the future? Figure 1 (Beeton, 1965) indicates an apparent increase in mean chloride concentration in Lake Huron of 3.5 g/m^3 , from 4.0 to 7.5 g/m^3 , in the 30 years, 1930 to 1960. However, scatter of the individual points precludes making an estimate of the present

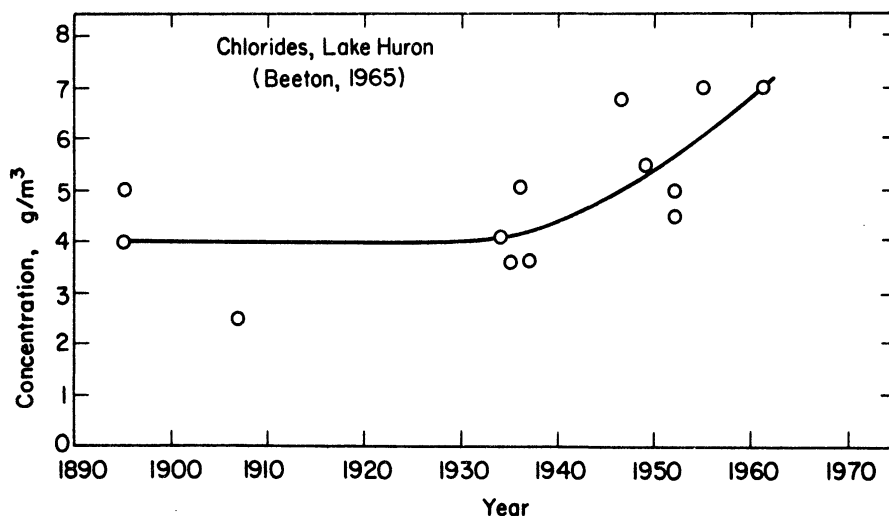


FIG. 1. Chloride contents reported for Lake Huron waters.

¹This work was supported in part by the U.S. Atomic Energy Commission under contract AT (11-1)-1705. Publication No. 158 from the Department of Meteorology and Oceanography and Contribution No. 108 from the Great Lakes Research Division, University of Michigan.

rate of concentration increase. Furthermore, large recent changes in input rate might be expected because of growth in population, increases in industrial activity, or because of regulation of water quality in rivers that feed Lake Huron. Consequently, determination of present rates of increase in concentration of a substance in a particular Great Lake requires knowledge of input and outflow rates by measuring its flux through all possible sources and sinks for that Lake, and noting the net balance or imbalance.

Dissolved substances are removed from the Lakes primarily by outflow and have a mean residence time in each Lake defined by the ratio of volume to water discharge rate. The Great Lakes have large volumes relative to their discharges, hence residence times are relatively long. In their natural states, the fluxes of dissolved substances into and out of a Great Lake are equal, and steady state concentrations are realized in each one. An increase in input rate of a substance to a Lake, on a time scale short compared to the residence time, will result in an increasing concentration, but it will require a duration of several mean residence times for the Lake to approach a new steady state concentration with respect to that substance.

Ownbey and Kee (1967) were able to demonstrate that Lake Erie is currently at a steady state with respect to chloride. They showed that the known chloride inputs are equal to the measured outflow at the Niagara River to within 3%. About 75% of the total chloride input comes from the Detroit River. Lake Erie, whose mean residence time of about 2.6 years is the shortest of the Great Lakes, is analogous to a wide river due to its shallowness and consequent small volume. It may be expected to respond rather quickly to changes in input rate of a dissolved substance.

The mean residence time of Lake Huron is longer—about 20 years—long enough that the steady state concentrations may not yet have been reached if the input of dissolved materials has increased substantially in the past few decades. A study of the inputs of dissolved halogens to Lake Huron was made for several reasons: an increase in chlorine concentration has been documented (Beeton, 1965); Lake Huron possesses only a few large sources and sinks of these elements so that a material balance study is feasible and can be undertaken as a short term project; and the concentrations of these three elements are relatively conservative properties of the water. That is, the uptake of chlorine, bromine and iodine by biota and loss to the sediments is not expected to be significant in the total material balance in a Great Lake.

The study of halogen material balance in Lake Huron leads to a model for the study of more complex materials in the Great Lakes which have sources and sinks that are more difficult to define or measure: e.g. nitrogen, phosphorus, trace metals and pesticides. Such substances may have long hold-up times in organisms or annual recycling within the Lake; others may rapidly enter the sediments or otherwise present a more difficult problem than the halogens for an attempt at a material balance.

SAMPLING AND ANALYSIS

Figure 2 is a schematic diagram of the sources and sinks of halogens in Lake Huron considered in this study. The Saginaw River basin, as a major pollution source of halogens, was sampled extensively.

Michigan rivers to the north of the Saginaw River and rivers in Ontario were sampled, but less extensively, in order to obtain a mean halogen inflow from these less polluted regions. Lake Superior and Lake Michigan compositions are taken from Tiffany et al. (1969), and precipitation input is estimated as described below. Outflow is calculated from a previous Lake Huron study

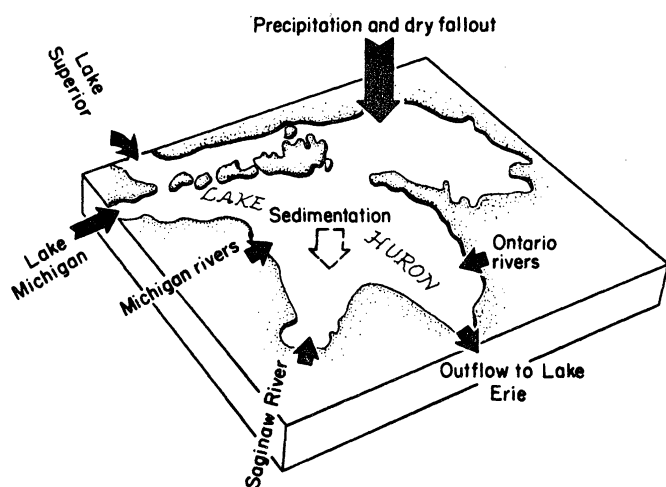


FIG. 2. Sources and sinks of dissolved ions in Lake Huron.

(Tiffany et al, 1969). Omitted from the final material balance calculation are air pollution fallout and sedimentation, neither of which appears to be large.

The water samples analyzed in this study were taken from streams in Michigan and Ontario and from shore locations along Saginaw Bay. All streams were sampled from bridges by lowering a clean polyethylene bucket and transferring the water to a polyethylene bottle, previously cleaned with nitric acid

and rinsed with river water. The Saginaw Bay samples were taken at beaches, usually 20-30 m from the shore. Samples were stored, chilled for up to 48 hr and then frozen for permanent storage. Prior to analysis the samples were thawed completely, an aliquot was taken, and the remainder was refrozen. Analysis for halogens was by neutron activation using the Ford Nuclear Reactor at the University of Michigan and employing a radiochemical procedure described in Appendix 2.

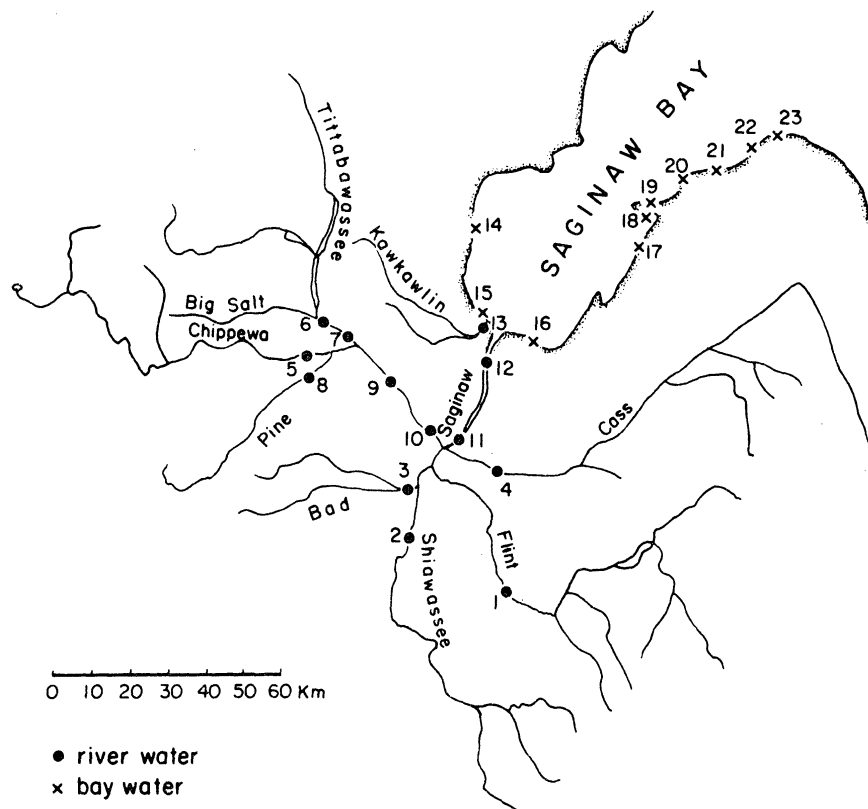


FIG. 3. Sample locations in the Saginaw River basin and Saginaw Bay.

HALOGEN FLUX FROM THE SAGINAW RIVER BASIN

Sampling locations are shown in Fig. 3 and are described in Appendix 1. Pollution of the streams in the Saginaw Basin is very localized and is probably correlated with brine wells or with chemical industry of the area. Consequently, a network of sampling stations was decided upon which took advantage of stream gauging data and which would give an indication of halogen pollution source locations.

TABLE 1. Tittabawassee River, mean November flow, 1936-1960.^a

Water year ^b	ft ³ /sec	m ³ /sec
1937	655	18.6
1938	831	23.5
1939	573	16.2
1940	594	16.8
1941	1,143	32.4
1942	2,537	73.3
1943	1,746	49.4
1944	1,053	29.8
1945	592	16.8
1946	1,753	49.6
1947	644	18.2
1948	747	21.2
1949	684	19.4
1950	493	14.0
1951	629	17.8
1952	2,785	78.9
1953	862	24.4
1954	670	19.0
1955	1,073	30.4
1956	730	20.7
1957	625	17.7
1958	2,260	64.0
1959	1,373	38.9
1960	2,154	61.0
Mean	1,136	32.2

a Near sampling location 9 (Fig. 2), U. S. Geological Survey Station 4-1560, (U. S. Geological Survey, Water Supply Papers 1307 and 1727).

b Water year 1937 is 1 Oct., 1936 to 30 Sept., 1937, and similarly for other water years given.

TABLE 2. Tittabawassee River mean daily flow, 1968.^a

	ft ³ /sec	m ³ /sec
Nov. 1	830	23.5
Nov. 8	729	20.6
Nov. 22	1,664	47.1
Dec. 12	1,184	33.5
Mean	1,102	31.2

a Water year 1969, same location as in Table 1, Midland, Mich., (Dow Chemical Co. pers. comm.)

The most direct way to obtain a total halogen input to Lake Huron from the Saginaw Basin is to multiply the concentrations at the Saginaw River mouth by the flow rate of this river. However, the flow rate for this river is not determined accurately except during floods, owing to its great breadth and small gauge height fluctuations. Consequently, it was necessary to estimate the flow rate from the gauge data on tributary streams and to support the halogen flux calculation with more detailed information on halogen flow through the tributaries. This procedure is developed in the following tables.

Table 1 presents the mean November flow gage data over a 24 year period for the Tittabawassee River, the principal source of halogen pollution of the Saginaw River. Table 2 gives the actual flow data for this river during the period of sampling in this study, and the mean flow is very close to the mean November gauge data of Table 1. If it is assumed that the flow is determined by rainfall in the area, then, flows of other streams tributary to the Saginaw River were estimated to be at rates close to their mean November values (Table 3), since actual flow data for these streams were not available.

Table 4 shows the concentrations measured at 13 stations in the Saginaw River region. Note that concentrations vary over the three to five sampling times, but a pattern of regional variation in concentration can, nevertheless, be seen with reference to the locations shown in Fig. 3. A particularly strong source appears upstream of Location 8 on the

TABLE 3. Rivers of Saginaw Basin, mean November flows^a.

River	Years of record	U.S.G.S. station no.	Mean Flow	
			ft ³ /sec	m ³ /sec
1. Cass	1939-59	4-1515	249	7.05
2. Flint	1940-59	4-1490	443	12.5
3. Shiawassee	1931-59	4-1445	204	5.78
4. Bad	1949-58	4-1455	43.5	1.23
5. Tittabawassee	1936-59	4-1560	1,136	32.2
6. Chippewa	1947-59	4-1545	352	10.0
7. Pine	1949-59	4-1555	230	6.51
Sum 1-5			2,076	58.8

^a Locations near sampling locations (Fig. 2), (U. S. Geological Survey, Water Supply Papers 1307 and 1727).

Pine River and causes the Tittabawassee concentrations at Locations 9 and 10 to exceed those at Locations 6 and 7 by a large factor. Locations 1-7 all are upstream of the strongest local sources, but their concentrations are nevertheless greater than those found in streams of Michigan rivers further north and Ontario rivers (Table 5), and in the Lake Superior basin (Tiffany et al. 1969). Halogen pollution on a more regional scale in the Saginaw River basin is indicated by these data.

In Table 6 we calculate the fluxes of iodine, bromine, and chlorine from the Tittabawassee River where we have stream gauge data for the period of sampling. In spite of variations of concentration and of stream flow rates over the 6 week interval, the halogen fluxes appear consistent and imply a relatively more constant rate of halogen input than of water. From the dispersion of the individual halogen flows we calculate the standard deviations of the means as shown in the last line of Table 6.

In Table 7 we combine this information with that for the other rivers tributary to the Saginaw River. It is seen that their contribution is small but significant. Therefore, the lack of stream flow data for the period of sampling for these other streams is probably not a major source of error in the calculation.

Also shown in Table 7 is the estimate of the Saginaw Basin area drained by streams for which flow rates were not available. From this another water flow is estimated, assuming proportionality between land area and rainfall input of water. Calculation of halogen fluxes through the Saginaw River used the measured concentration means from Locations 11 and 12. These fluxes are somewhat greater than those from the major tributaries studied, an expected result because of the additional pollution sources downstream of Station 10 in the heavily urban and industrial area.

The concentrations measured in the Saginaw Bay are shown in Table 8. Although most of these samples were taken at another season of the year, they are several-fold greater than the concentrations for southern Lake Huron, reflecting the great halogen input to the Saginaw Bay documented above.

HALOGEN MATERIAL BALANCE FOR LAKE HURON

Table 9 is a summary of estimates for sources of iodine, bromine, and chlorine to Lake Huron. This table refers specifically to November and December, 1968, but may have general validity. The Saginaw Basin inputs are those

TABLE 4. Measured halogen concentrations in the Saginaw Basin.

Station & River	Date 1968	I g/m ³	Br g/m ³	Cl g/m ³	Br/Cl x10 ³	I/Cl x10 ³	I/Br
1. Flint	Nov. 1	0.0110	0.098	60	1.6	0.18	0.11
	Nov. 3	0.022	0.146	48	3.0	0.46	0.15
	Nov. 8	0.019	0.195	63	3.1	0.30	0.10
	Nov. 22	0.0107	0.142	48	3.2	0.22	0.08
	Dec. 12	0.0089	0.138	53	3.1	0.17	0.064
	Av.	0.0143	0.144	54	2.7	0.26	0.10
2. Shiawassee	Dec. 12	0.0047	0.064	29	2.2	0.16	0.073
3. Bad	Dec. 12	0.0046	0.124	52	2.4	0.088	0.037
4. Cass	Nov. 1	0.0046	0.086	53	1.6	0.087	0.053
	Nov. 8	0.0073	0.147	54	2.7	0.13	0.050
	Nov. 22	0.0042	0.127	63	3.2	0.067	0.033
	Dec. 12	0.0079	0.168	34	5.0	0.23	0.047
	Av.	0.0060	0.132	51	2.6	0.12	0.045
5. Chippewa	Nov. 1	0.0064	0.152	35	4.4	0.18	0.042
	Nov. 8	0.0045	0.136	34	4.0	0.13	0.033
	Nov. 22	0.0046	0.114	34	3.3	0.14	0.040
	Dec. 12	0.0059	0.221	32	6.9	0.18	0.026
	Av.	0.0053	0.156	34	4.6	0.16	0.034
6. Tittabawassee	Nov. 1	0.0049	0.085	16.7	5.1	0.29	0.059
	Nov. 8	0.0114	0.080	18.6	4.3	0.61	0.143
	Nov. 22	0.0026	0.054	13.5	4.0	0.19	0.048
	Av.	0.0063	0.073	16.3	4.5	0.39	0.086
7. Tittabawassee	Nov. 1	0.0058	0.063	19.4	3.4	0.30	0.092
	Nov. 8	0.0052	0.062	18.6	3.3	0.26	0.084
	Nov. 22	0.0036	0.136	38	3.6	0.10	0.026
	Av.	0.0049	0.087	25.3	3.4	0.20	0.056
8. Pine	Nov. 1	0.048	2.96	782	3.8	0.061	0.016
	Nov. 8	0.082	5.34	720	7.4	0.11	0.015
	Nov. 22	0.045	2.36	389	6.1	0.12	0.019
	Dec. 12	0.066	5.53	364	15.2	0.18	0.012
	Av.	0.060	4.05	564	7.2	0.11	0.015
9. Tittabawassee	Nov. 1	0.065	1.74	353	4.9	0.18	0.037
	Nov. 8	0.084	2.10	364	5.8	0.23	0.040
	Nov. 22	0.035	1.30	294	4.4	0.12	0.027
	Dec. 12	0.074	1.36	241	5.6	0.31	0.054
	Av.	0.065	1.62	313	5.2	0.21	0.040
10. Tittabawassee	Nov. 1	0.060	1.85	402	4.6	0.15	0.032
	Nov. 8	0.061	1.83	298	6.1	0.20	0.033
	Nov. 22	0.034	0.81	170	4.8	0.20	0.042
	Dec. 12	0.076	1.82	295	6.2	0.26	0.042
	Av.	0.058	1.58	291	5.4	0.20	0.037
11. Saginaw	July 24 ^a	0.058	2.35	268	8.8	0.22	0.025
	Nov. 1	0.026	1.38	197	7.0	0.13	0.019
	Nov. 8	0.053	1.33	212	7.2	0.40	0.025
	Nov. 22	0.025	1.37	196	7.0	0.13	0.018
	Dec. 12	0.050	1.14	162	7.0	0.31	0.044
	Av.	0.038	1.30	192	6.8	0.20	0.029
12. Saginaw	July 24 ^a	0.035	1.60	240	6.7	0.14	0.022
	Nov. 1	0.030	0.80	184	4.4	0.16	0.037
	Nov. 8	0.046	1.04	226	4.6	0.20	0.044
	Nov. 22	0.026	1.14	184	6.2	0.14	0.023
	Av.	0.034	1.00	198	5.0	0.17	0.034
13. Kawkawlin	Nov. 22 ^b	0.0066	0.574	220	2.6	0.030	0.012

a Not included in means.

b Outside Saginaw River drainage basin. Irregular flow during November.

TABLE 5. Measured halogen concentrations in rivers of Ontario and of Michigan north of the Saginaw Basin.

Station & River	Date 1969	I g/m ³	Br g/m ³	Cl g/m ³	Br/Cl x10 ³	I/Cl x10 ³	I/Br
<i>Michigan</i>							
24. Rifle	April 8	0.00077	0.0504	6.62	7.6	0.12	0.015
25. AuGres	"	0.00108	0.0358	8.64	4.1	0.13	0.032
26. Tawas	"	0.00101	0.0337	2.70	12.5	0.37	0.030
27. Sand Creek	"	0.00105	0.0481	5.02	9.6	0.21	0.022
28. AuSable	"	0.00121	0.0373	3.06	12.3	0.40	0.032
29. Thunder Bay	"	0.00082	0.0134	1.72	7.8	0.48	0.061
30. Ocqueoc	"	0.00095	0.137	6.22	22.0	0.15	0.007
31. Cheboygan	"	0.00126	0.0274	2.03	13.5	0.62	0.046
Average		0.00102	0.048	4.5	10.7	0.23	0.021
<i>Ontario</i>							
32. Nottawasaga	April 16	0.00109	0.0172	3.56	4.8	0.31	0.063
33. Wye	"	0.00107	0.0534	3.59	14.9	0.30	0.020
34. Six Mile Lake	"	0.00095	0.0458	6.69	6.8	0.14	0.027
35. Gibson	"	0.00105	0.063	1.58	40.0	0.67	0.017
36. Muskoka	"	0.00052	0.065	1.38	47.0	0.38	0.008
37. Moon	"	0.00075	0.085	2.23	38.1	0.34	0.009
38. Severn	April 17	0.00064	0.0206	1.25	16.5	0.51	0.031
Average		0.00088	0.050	2.9	17.2	0.30	0.017

TABLE 6. Calculation of mean halogen flux from Tittabawassee River to Saginaw River.

Date, 1968	Flow, m ³ /sec	Station	I, g/sec	Br, g/sec	Cl, g/sec
Nov. 1	23.5	9	1.53	40.8	8,300
		10	1.41	43.5	9,450
Nov. 8	20.6	9	1.73	43.3	7,500
		10	1.26	37.7	6,140
Nov. 22	47.1	9	1.65	61.2	13,850
		10	1.60	38.1	8,010
Dec. 12	33.5	9	2.48	45.6	8,070
		10	2.55	61.0	9,880
Mean	31.2		1.77 ±0.17	46.4 ±3.4	8,900 ± 816

given in Table 7, where it is implicitly assumed that the halogen fluxes found during the sampling period are typical. The error estimates are based on dispersion of the samples analyzed and do not include estimates of errors in the stream flow data, believed to be smaller than other uncertainties. Summing the mean annual discharges from all gauged streams (U.S. Geological Survey, Papers 1307 and 1727) and adding contributions from ungauged streams in proportion to the areas drained, provides an estimate of the mean annual flow rate of other Michigan rivers. This is in close agreement with the contours of runoff per unit area given by Browzin (1966). Ontario river concentrations (Table 5) were measured in a few resort locations draining into Georgian Bay and were found to be greater than in unpolluted streams of Lake Superior. Our best estimate of a mean halogen flux from all regions of

TABLE 7. Calculation of mean halogen flux from the Saginaw Basin to Lake Huron.

River	Basin area, km ²	Mean Nov. flow, m ³ /sec	Cl, g/sec	Br, g/sec	I, g/sec
Cass	2,200	7.05	360	0.93	0.042
Flint	2,900	12.5	675	1.80	0.179
Shiawassee	1,650	5.78	168	0.37	0.027
Bad	230	1.23	64	0.15	0.057
Tittabawassee ^a	6,220	32.2	8,900	46.4	1.77
Sum	13,200	58.8	10,200	49.7	2.08
Ungaged ^b	2,700	12.0			
Total ^c	15,900	71	13,800	81.4	2.55

a Mean Cl, Br, and I inputs calculated according to Table 6.

b Estimated from sum of river drainage basin areas and total area of Saginaw Basin, 15,900km², assuming uniform rainfall distribution.

c Saginaw River is not regularly gauged except during floods. Mean concentrations from Table 4: 195 gCl/m³, 1.15 gBr/m³, 0.036 gI/m³.

TABLE 8. Measured halogen concentrations in Saginaw Bay.

Station	Date 1968	I g/m ³	Br g/m ³	Cl g/m ³	Br/Cl x10 ³	I/Cl x10 ³	I/Br
14	July 24	0.0086	0.270	49	5.5	0.18	0.032
15	"	0.0070	0.160	23	7.0	0.30	0.044
15	Nov. 22	0.0043	0.081	28	2.9	0.15	0.053
16	July 24	0.0048	0.230	25	9.2	0.19	0.021
17	"	0.0054	0.230	39	5.9	0.14	0.023
18	"	0.0045	0.170	32	5.3	0.14	0.026
19	"	0.0082	0.230	37	6.2	0.36	0.022
20	"	0.0063	0.190	29	6.6	0.21	0.033
21	"	0.0044	0.170	27	6.3	0.16	0.026
22	"	0.0040	0.150	19	7.9	0.21	0.027
23	"	0.0018	0.120	13	8.1	0.14	0.015

Ontario into Lake Huron is the average of these concentrations and those found for the unpopulated localities around Lake Superior (Tiffany et al. 1969), inasmuch as about half of the Ontario area in question is very sparsely populated. The uncertainty assigned to the mean concentration brackets the range of the extremes. The halogen inputs from Lakes Superior and Michigan are based on the mean concentrations reported in Tiffany et al. (1969) and flow rates given by Powers and Ayers (1960) for Lake Michigan and by Chandler (1964) for Lake Superior. The outflow of water from Lake Huron (Hough, 1958) multiplied by the concentrations of halogens in the southern end of the Lake (Tiffany et al. 1969) gives the halogen outflow to the uncertainty indicated.

Natural precipitation sources, neglecting air pollution, are estimated from the chloride concentration of rainfall in this region to be 0.004 meq. Cl⁻/l given by Junge and Werby (1958). Assuming that the Br and I contents of the rainfall are in the same proportions as found in the streams of unpopulated localities around Lake Superior (Tiffany et al. 1969) we arrive at the Br and I concentrations as indicated. A rainfall rate over Lake Huron of 31 in/yr (787 mm/yr) was assumed.

TABLE 9. Sources and sinks of halogens in Lake Huron.

	Water flow m ³ /sec	Mean Concentration, g/m ³			Mass Flow, g/sec		
		Cl	Br	I	Cl	Br	I
Lake Superior	2,067	1.1	0.013	0.0010	2,280 ±	26.9 ±	2.7 ± 0.2
Lake Michigan	1,560	5.5	0.017	0.0009	8,580 ±	26.5 ±	2.7 ± 0.14
Saginaw Basin	71	195	1.150	0.036	13,800 ±	81.4 ±	10 ± 0.2
Other Michigan Rivers	~220	4.5	~0.048	~0.0010	990 ±	250 ±	2.7 ± 0.05
Ontario Rivers	~1,200	~2	~0.03	0.0009	2,400 ±	1,000 ±	36 ± 24
Natural Precipitation	~1,500	0.14	0.0012	0.00014	210 ±	40 ±	1.8 ± 0.4
Total Sources ^a					28,300 ±	1,600 ±	183 ± 28
Lake Huron Outflow	5,027	5.4	0.021	0.0013	27,200 ±	1,350 ±	105.6 ± 12.0

^a Air pollution sources are not included.

In the material balance calculation, air pollution sources were neglected. It is believed that this neglect may be most serious for Br, but we can arrive at an estimate of the upper limit of its contribution in two ways. First, assuming that 10^6 automobiles contribute 10^9 g Br/yr to Lake Huron, or about 30 g Br/sec, this is almost within the uncertainty of the calculation of total Br input of 15%. Second, the maximum ratio of Br/Cl seen in rainfall in Ann Arbor, Michigan (Loucks, pers. comm.) is about 0.1, i.e. 10 times greater than the ratio Br/Cl we feel is typical of natural rainfall over Lake Huron, and this implies no more than 20 g Br/sec by polluted rainfall. Therefore, in the case of Lake Huron, which derives its halogen inputs from relatively unpolluted areas, except for the Saginaw River basin, air pollution sources are probably not large. The same may not necessarily be assumed for other Great Lakes, however.

A sink for halogens not considered in this calculation is sedimentation. Although this is difficult to assess quantitatively, we can set an upper limit by the following reasoning. The ratio I/Br has been measured in a wide variety of sedimentary materials by Walters (1967) and has been found to be of the order of unity where most of the I and a significant fraction of Br are apparently surface bound with organic matter on the sediment particles. An exploratory measurement of Great Lakes sediment, done as part of the present research, was consistent with this finding. If the sedimentary sink of I is of the order of or less than 1 g I/sec in Lake Huron, as judged by the data of Table 9, then we do not expect sedimentary removal of Br to be more than a few g Br/sec, a small amount compared to the outflow rate of Br.

The material balance calculation indicated the following ratios for input/outflow for the halogens in Lake Huron:

Cl: 1.04 ± 0.08

Br: 1.73 ± 0.19

I: 1.15 ± 0.16

We conclude that neither Cl nor I appear to be increasing in Lake Huron at the present time but that Br is increasing.

The very large contribution of the Saginaw River basin to the halogens of Lake Huron indicates that a great reduction of this pollution source would cause the input of Cl to be less than the outflow. Therefore, without the Saginaw basin source, the waters of Lake Huron would progressively become lower in chloride concentration with a time constant of the order of the residence time of 20 years. For Br and I, however, a reduction of the Saginaw basin source would not lead to a progressive lowering of these concentrations in the Lake, but an approximate steady state would be maintained as can be determined by the data of Table 9.

REFERENCES

- BEETON, A. M. 1965. Eutrophication of the St. Lawrence Great Lakes. *Limnology and Oceanography*, 10: 240-254.
- BROWZIN, B. S. 1966. Annual runoff in the Great Lakes-St. Lawrence Basin. Proc. Ninth Conf. on Great Lakes Research, University of Michigan Great Lakes Research Division Publication 15: 203-219.
- CHANDLER, D. C. 1964. The St. Lawrence Great Lakes. *Verh. International Verein. Limnology*, XV: 59-75.
- DUCE, R. A. and J. W. WINCHESTER. 1965. Determination of iodine, bromine, and chlorine in atmospheric samples by neutron activation. *Radiochim. Acta*, 4:100-104.
- HOUGH, J. L. 1958. *Geology of the Great Lakes*, University of Illinois Press.
- JUNGE, C. E. and R. WERBY. 1958. The concentration of chloride, sodium, potassium, calcium and sulfate in rain water over the United States. *J. Meteorology*, 15: 417-425.

- OWNBEY, C. R. and D. A. KEE. 1967. Chlorides in Lake Erie. *Proceedings, Tenth Conference on Great Lakes Research*, 382-389.
- POWERS, C. F. and J. C. AYERS. 1960. Water transport studies in the Strait of Mackinac Region of Lake Huron. *Limnology and Oceanography*, 5: 81-85.
- TIFFANY, M. A., J. W. WINCHESTER and R. H. LOUCKS. 1969. Natural and pollution sources of iodine, bromine and chlorine in the Great Lakes. *Journal of Water Pollution Control Federation*, 41: 1319-1329.
- U.S. GEOLOGICAL SURVEY. Water Supply Paper 1307, *Compilation of Records of Surface Waters of the United States through September 1950*, part 4, St. Lawrence River Basin.
- U.S. GEOLOGICAL SURVEY. Water Supply Paper 1727, *Compilation of Records of Surface Waters of the United States October 1950 to September 1960*, part 4. St. Lawrence River Basin.
- WALTERS, L. 1967. *Bound halogens in sediments*, Ph.D. Thesis, Mass. Inst. of Tech.

APPENDIX 1. Sampling locations for Lake Huron and tributary streams.

<u>Station</u>	<u>Location</u>
1.	Flint River, Main Street Bridge, Flushing, Michigan.
2.	Shiawassee River, Chesaning, Michigan, M-57 Bridge.
3.	Bad River, St. Charles, Michigan, M-47 Bridge.
4.	Cass River, Dixie Highway Bridge, 1 km downstream from Bridgeport, Michigan.
5.	Chippewa River, Meridian Road.
6.	Tittabawassee River, Sanford, Michigan.
7.	Tittabawassee River at Midland, Michigan, Currie Parkway Bridge.
8.	Pine River, Meridian Road, 10 km downstream from St. Louis, Mich.
9.	Tittabawassee River at Freeland, Michigan.
10.	Tittabawassee River at M-46.
11.	Saginaw River at M-46, Saginaw, Michigan.
12.	Saginaw River, Bay City, M-25 bridge.
13.	Kawkawlin River, Kawkawlin, Michigan, U.S. 23 Bridge.
14.	Saginaw Bay, adjacent to Pinconning Road.
15.	Saginaw Bay, Bay City State Park.
16.	Saginaw Bay, Vanderbilt County Park.
17.	Saginaw Bay, Bay Port, Michigan.
18.	Saginaw Bay, South shore, Sand Point.
19.	Saginaw Bay, North shore, Sand Point.
20.	Saginaw Bay, 11 km west of Sleeper State Park.
21.	Saginaw Bay, Sleeper State Park.
22.	Saginaw Bay, McGraw Roadside Park.
23.	Saginaw Bay, Port Austin Harbor.
24.	Rifle River, Omer, Michigan, U.S. 23.
25.	Au Gres River, Au Gres, Michigan, U.S. 23.
26.	Tawas River, Tawas, Michigan, U.S. 23.
27.	Sand Creek, M-55 Bridge.
28.	Au Sable River, one lane bridge just off U.S. 23 in Oscoda, Mich.
29.	Thunder Bay River, Alpena, Michigan, U.S. 23.
30.	Ocqueoc River, U.S. 23.
31.	Cheboygan River, Bridge at Lincoln Avenue and Main Street, 2 km. upstream from mouth, Cheboygan, Michigan.
32.	Nottawasaga River, Edenville, Ontario, Highway 26.
33.	Wye River, Midland, Ontario, Highway 12.
34.	Six Mile Lake, 12 km north of Port Severn, Ontario.
35.	Gibson River, Highway 103.
36.	Muskoka River, Highway 103.
37.	Moon River, Highway 103, 10 km south of Footes Bay, Ontario.
38.	Severn River, Severn Bridge, Ontario, Highway 11.

APPENDIX 2. Analytical procedure.

Neutron activation analyses of the water samples of this study were carried out in the following way. Three water samples of about 4 ml each were irradiated together in the pneumatic tube facility of the Ford Nuclear Reactor at the University of Michigan in a neutron flux of about 2×10^{12} n/cm² sec for 30 min. Iodine was extracted as I₂ from a 2 or 3 ml aliquot by CCl₄ and precipitated as AgI following the procedure of Duce and Winchester (1965) and beta counted for 25 min (I-128). Using a separate 0.1 to 1 ml aliquot, Br and Cl were precipitated as AgCl-AgBr mixture and beta counted for 37 min Cl-38 and 4.5 hr Br-80m + 18 min Br-80; the decay curve was resolved graphically for the Br and Cl components. By analyzing I, Br, and Cl standard solutions in separate irradiations, the relation between counting rate and halogen mass was established. However, because small differences in neutron flux occur between irradiations, chloride was determined independently in those water samples having the highest concentrations by a Mohr titration using a silver chromate endpoint. For these samples the I, Br, and Cl activation analyses were corrected by the titration/activation Cl ratio. The summary of data shown in Table 10 indicates the degree of variation of specific neutron-induced radioactivity to be no more than a few per cent in most cases. Therefore, samples with lower concentrations were analyzed by activation only, without titration correction. All analyses are judged to be uncertain to a standard deviation of about 10%.

TABLE 10. Comparison of titration and activation analysis for chloride.

Station, Date	Cl, g/m ³		Ratio
	Titration	Activation	
1, Dec. 12	56	53.2	1.06
1, Nov. 1	69	60	1.15
8, Nov. 1	782	830	0.94
8, Nov. 22	395	389	1.02
8, Dec. 12	413	364	1.13
9, Nov. 1	353	364	0.97
9, Nov. 22	294	280	1.05
9, Dec. 12	241	221	1.09
10, Nov. 1	402	410	0.98
10, Nov. 22	170	179	0.95
10, Dec. 12	295	250	1.18
11, Nov. 1	197	168	1.18
11, Nov. 22	196	182	1.08
11, Dec. 12 ^A	162	149	1.09
11, Dec. 12 ^B	154	---	---
12, Nov. 1	186	187	1.01
12, Nov. 8	226	232	0.97
12, Nov. 22	184	188	0.98
13, Nov. 22	220	237	0.93

SOME FEATURES OF CHLORINE AND BROMINE IN AEROSOLS¹

Ronald H. Loucks² and John W. Winchester
Dept. of Meteorology & Oceanography and
Great Lakes Research Division, University
of Michigan, Ann Arbor, Michigan 48104

Abstract. Size fractions of inland aerosols collected by cascade impactor have been analyzed for Cl and Br by neutron activation. Br mass shows an approximately inverse radius dependence with impactor size range, corresponding to a distribution proportional to total surface area of particles in each size range. A decrease in abundance observed in intermediate size fractions, compared to smaller particles, during precipitation is interpreted to reflect the lower size limit for particles nucleating cloud droplets or crystals. The low ratio of Br/Cl found in larger particles and precipitation, compared to smaller particles, suggests that Cl-rich particles are activated and removed from the atmosphere by precipitation more efficiently than are Br-rich particles.

1. Contribution No. 168 from the Department of Meteorology & Oceanography and No. 113 from the Great Lakes Research Division, University of Michigan.
2. Present address: Atlantic Oceanographic Laboratory, Bedford Institute, Dartmouth, Nova Scotia, Canada.

Introduction

Measurements of the halogen composition of marine aerosols have shown variation with respect to particle size. Winchester and Duce [1966] suggested that the greater ease of oxidation of iodide and bromide, compared to chloride, may lead to the separation of these elements by volatility and their possible reassociation with other particles through chemical reaction. Duce et al. [1967] have analyzed size fractions of marine aerosols from Hawaii collected by cascade impactor and found that the ratio I/Cl increases markedly with decreasing impactor size range and that the ratio Br/Cl exhibits a minimum value less than the sea water ratio at intermediate sizes. Aerosols from inland locations may differ from marine aerosols because of transformations of marine-derived components during transport over land and additions of terrestrial components. Over continental U.S.A. atmospheric bromine may be principally derived from the combustion of leaded gasoline [Loucks and Winchester, 1969] and the initial lead halide aerosol may undergo loss of bromine in the atmosphere [Lininger et al., 1966; Winchester et al., 1967; Pierrard, 1969; Pitts, 1969]. In this paper we report briefly some neutron activation analyses of aerosol size fractions collected in Michigan and near Chicago for bromine and chlorine. These aerosols, through their occurrence together with precipitation, form a special case among a collection of aerosol samples from the Great Lakes region. Their origins and trajectories are discussed elsewhere (Loucks, 1969); they are interpreted to be largely of pollution origin (loc. cit.).

Analytical and Sampling Conditions

Cascade impactors of two designs were used: A six-stage impactor (SA) with a single orifice per stage, obtained from Scientific Advances, Columbus, Ohio, is described by Mitchell and Pilcher [1959] and is identical to the impactor used by Duce et al. [1967]. A seven-stage impactor (AS) with many

orifices per stage, obtained from Andersen Air Samplers, Salt Lake City, Utah, is described by Flesch et al. [1967]. A thin polyethylene insert was placed in each stage as the impaction surface and later given neutron irradiation for halogen analysis. Determinations of Br and Cl were carried out either by the radiochemical and β -counting procedure of Duce and Winchester [1965] or by a modified procedure and γ -counting using a NaI(Tl) detector. In both devices particles of constant density are separated into fractions (A to F or G) differing in radius by roughly a factor of 2 in the range of "large" and "giant" aerosols [Junge, 1963]. In addition, in-line backup filters (stage Z) collected particles of radii smaller than about 0.3 μm (SA) or 0.1 μm (AS). Although care was taken to operate the impactors as prescribed by the instructions, no attempt was made to determine the actual sizes of the particles collected in each fraction, and the impactor size ranges are primarily of relative significance.

We report here the results of samples taken at two locations: LM - on Lake Michigan between Grand Haven and Chicago aboard the research vessel Inland Seas during May 1968 using the SA impactor; EE - on the roof of the East Engineering Building, University of Michigan, Ann Arbor during November and December 1968 using the AS impactor.

The LM series was four samples taken sequentially under a rain shield during May 22-23 for the air volumes and time intervals as indicated:

Run 21:LM:V, 3.0 m^3 , 0633-1033 hours

Run 22:LM:V, 6.1 m^3 , 1102-1912 hours

Run 23:LM:V, 7.9 m^3 , 1940-0614 hours

Run 24:LM:V, 2.3 m^3 , 0650-0952 hours

On the synoptic scale during the sampling period, air was moving slowly over southern Lake Michigan from the east and southeast. Run 21 was collected under conditions of smudge-colored haze, then overcast and light fog. During Run 22 the fog thickened, and fog and rain were experienced during Run 23. The fog was dissipating and there was no rainfall during Run 24.

The EE series was two samples taken for the air volumes and times as indicated:

Run 43:EE:XI, 80 m³, 28 Nov./0530-30 Nov./1450 hours

Run 44:EE:XII, 100 m³, 4 Dec./1050-7 Dec./0850 hours

Rain was collected concurrently with Run 43 and snow was collected just before the period of Run 44. During both runs strong low pressure systems were controlling the weather in southeastern Michigan, and during about half the hours in each sampling period precipitation was recorded at Willow Run Airport, 15 km east of Ann Arbor.

Results and Discussion

Figure 1 presents the mass of Cl and Br, and the mass ratio Br/Cl, found for each impactor stage for the Lake Michigan runs. The linear abscissa in stage designation approaches a logarithmic scale of particle radius to the extent that cut-off radii of adjacent stages differ by a factor of 2, particle density remains constant, and dispersion characteristics are the same for all stages. The dotted lines represent the approximate trend of $dM/d(\log r) \sim r^{-1}$ as an aid in the interpretation of the Br data.

The distribution patterns of Cl and Br differ from each other regularly in this series of four runs. Br appears to exhibit a pattern which approximates an inverse radius dependence. For reasons enlarged upon elsewhere [Loucks, 1969], we suggest that Br in some polluted air may have become

attached from the vapor phase to aerosols by chemical reaction. If the aerosols themselves display a "Junge" number distribution, $dN/d(\log r) \sim r^{-3}$, the trend approximated by the Br data suggest a Br content of each impactor size range proportional to the total surface area of particles in that range.

The Cl distribution patterns are quite unlike those of Br, and the ratios Br/Cl increase more or less steadily with decreasing impactor size range. The dips in the Cl patterns are more pronounced in the later runs, and an especially deep dip occurs in both the Br and Cl patterns for Run 23 when rain was falling for part of the time. Br/Cl is also highest for this run. In these observations we may have evidence for cloud nucleation processes among larger particles, as commented upon further below.

Figure 2 presents similar data for two runs in Ann Arbor when considerable rain or snow was falling, and minima in the lower curves are a striking feature. It should be emphasized that these patterns are averages over an extended period of time only part of which precipitation was falling at the sampling location, and an exact interpretation of aerosol-precipitation relationships cannot be made with these data alone. Nevertheless, we observe that approximately equal contents of Br and Cl are found in intermediate size ranges so that the ratio Br/Cl is close to unity. (Close agreement with the ethyl fluid ratio Br/Cl ~ 1.15 is probably fortuitous.) For larger particles, however, the ratio Br/Cl is considerably less and approaches, with increasing size range, the ratios found for the rain and snow samples, indicated by the arrows.

The minima are consistent with models of Mordy [1959] and Neiburger and Chien [1960], discussed by Fletcher [1962] and by Junge [1963, p. 136, Fig. 31]. Vapor pressure lowering by dissolved salts in giant aerosols would permit

growth to larger sizes, but enhancement of vapor pressure by surface tension effects in smaller aerosols would inhibit their growth, and a minimum in abundance of intermediate sized particles is expected. The observed minimum occurs near the predicted value of the order of a micron according to these models. The increased abundance of larger particles is suggested to arise from activation of the much more numerous intermediate sized nuclei. However, it appears that Cl is removed by this process more efficiently than is Br and less effective cloud nucleation by aerosols rich in Br is suggested. (Lower water solubility of organic or inorganic compounds in these Br aerosols may account for this difference.) This implies that coagulation was far from complete even in a case (Run 23:LM:V) where the aerosol was removed from its sources and resident in the atmosphere for at least an hour; the Cl-rich and Br-rich aerosol subpopulations may remain distinguishable.

Acknowledgements. We are indebted to John A. Robbins for a critical reading of the manuscript. This research was supported in part by contract AT(11-1)-1705, U.S. Atomic Energy Commission, and by grants AP-00585, U.S. Public Health Service, and GA-811, National Science Foundation. One of us (R.H.L.) is grateful for financial aid from Bedford Institute, Dartmouth, N.S., Canada.

References

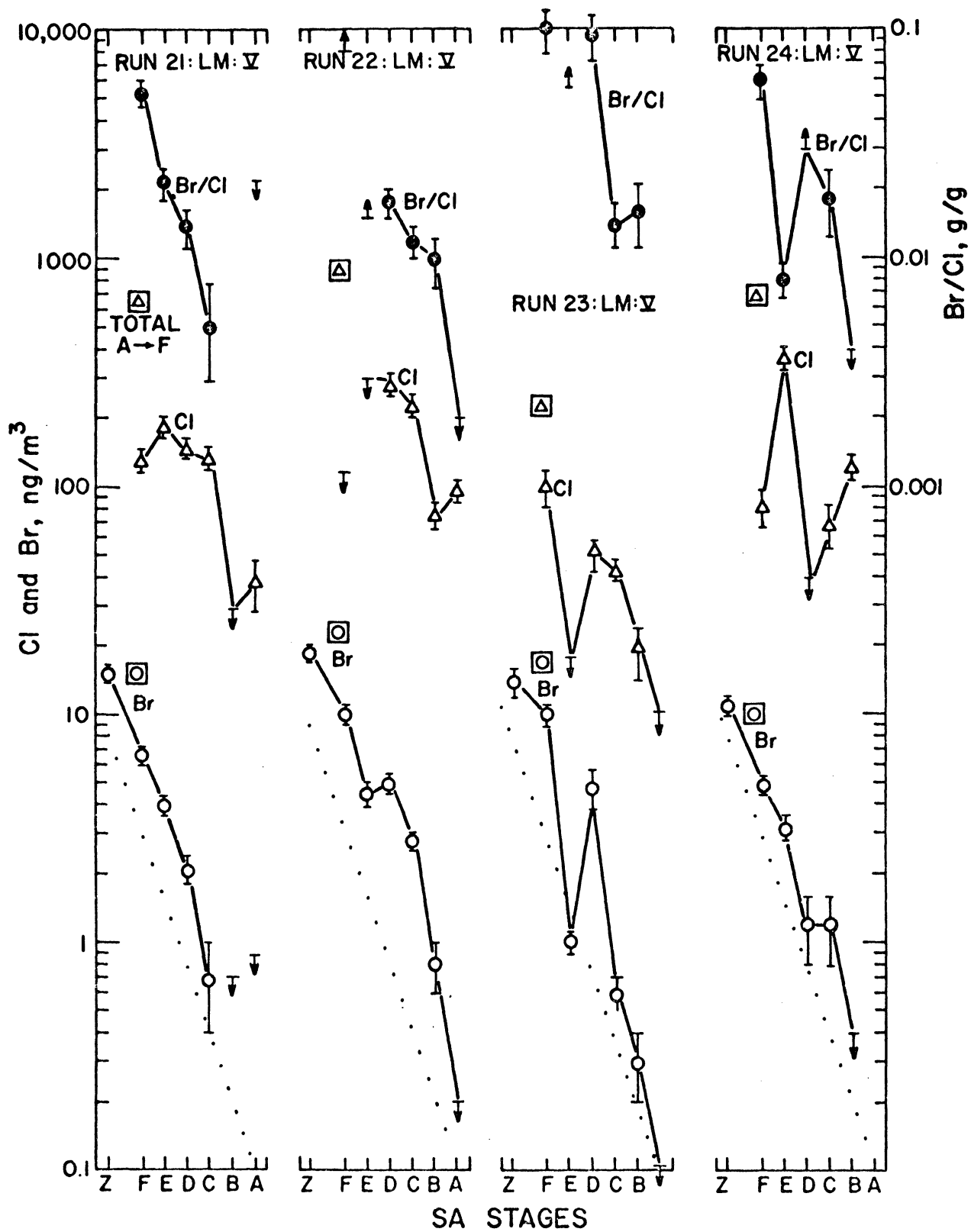
- Duce, R. A., and J. W. Winchester, Determination of iodine, bromine, and chlorine in atmospheric samples by neutron activation analysis, Radiochim. Acta, 4, 100-104, 1965.
- Duce, R. A., A. H. Woodcock, and J. L. Moyers, Variation of ion ratios with size among particles in tropical oceanic air, Tellus, 19, 369-379, 1967.
- Flesch, J. P., C. H. Norris, and A. E. Nugent, Jr., Calibrating particulate air samplers with monodisperse aerosols, J. Amer. Indus. Hyg. Assoc., 28, 507-516, 1967.
- Fletcher, N. H., The Physics of Clouds, Cambridge University Press, 1962.
- Junge, C. E., Air Chemistry and Radioactivity, Academic Press, 1963.
- Lininger, R. L., R. A. Duce, J. W. Winchester, and W. R. Matson, Chlorine, bromine, iodine, and lead in aerosols from Cambridge, Massachusetts. J. Geophys. Res., 71, 2457-2463, 1966.
- Loucks, R. H., Particle Size Distribution of Chlorine and Bromine in Mid-Continent Aerosols from the Great Lakes Basin, Ph.D. thesis, University of Michigan, 1969.
- Loucks, R. H., and J. W. Winchester, Pollution contributions to the atmospheric inventory of chlorine and bromine in aerosols over continental U.S.A., Proc. 3rd Conf. Trace Substances in Environmental Health, Columbia, Missouri, June 1969 (in press).
- Mitchell, R. I., and J. M. Pilcher, An improved cascade impactor for measuring aerosol particle sizes, Ind. Eng. Chem., 51, 1039-1042, 1959.
- Mordy, W. A., Computations of the growth by condensation of a population of cloud droplets, Tellus, 11, 16-44, 1959.

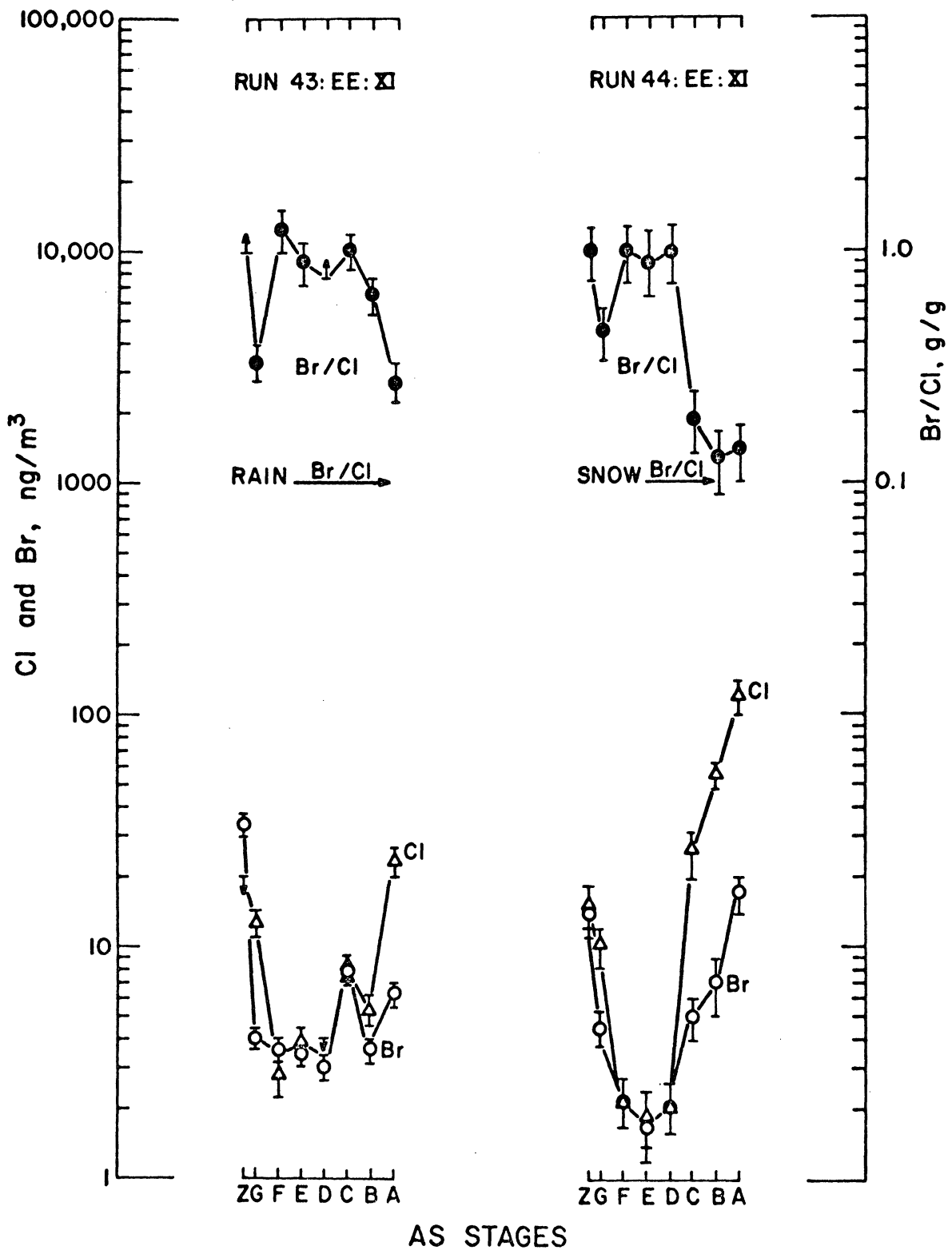
- Neiburger, M., and C. W. Chien, Computations of the growth of cloud drops by condensation using an electronic digital computer, in Physics of Precipitation, Geophysical Monograph No. 5, Amer. Geophys. Un., 1960.
- Pierrard, J. M., Photochemical decomposition of lead halides from automobile exhaust, Environ. Sci. Technol., 3, 48-51, 1969.
- Pitts, J. N., Environmental appraisal: oxidants, hydrocarbons, and oxides of nitrogen, J. Air Pollution Control Assn., 19, 658-667, 1969.
- Winchester, J. W., and R. A. Duce, Coherence of iodine and bromine in the atmosphere of Hawaii, northern Alaska, and Massachusetts, Tellus, 18, 281-286, 1966.
- Winchester, J. W., W. H. Zoller, R. A. Duce, and C. S. Benson, Lead and halogens in pollution aerosols and snow from Fairbanks, Alaska, Atmos. Environ., 1, 105-119, 1967.

Figure Captions

Figure 1. Distribution of Cl and Br with impactor size range for the Lake Michigan runs.

Figure 2. Distribution of Cl and Br with impactor size range for the East Engineering Building runs.





WATER POLLUTION IN LAKE MICHIGAN BY TRACE
ELEMENTS FROM POLLUTION AEROSOL FALLOUT*

John W. Winchester**

and

Gordon D. Nifong***

The University of Michigan
Ann Arbor, Michigan 48104

*Contribution No. 161 from the Department of Meteorology and Oceanography and No. 110 from the Great Lakes Research Division, University of Michigan. Supported in part by USAEC contract AT(11-1)-1705 and by a USPHS air pollution traineeship for one of us (G.D.N.)

**Now at: Dept. of Oceanography, Florida State University, Tallahassee, Florida 32306.

***Now at: Bethlehem Steel Corp., Bethlehem, Pennsylvania.

Abstract.

Certain trace elements which are strongly associated with air pollution sources in the Lake Michigan basin may be contributing significantly to lake water pollution by an atmospheric fallout route. In this paper a partial inventory of air pollution emissions for 30 trace elements is presented for the Chicago, Milwaukee, and northwest Indiana metropolitan areas, based on available published information, and compared with natural and pollution stream trace element inputs. Evidence indicates that the atmosphere may be the major source of Zn in Lake Michigan, and atmospheric inputs of Cu and Ni are also considerable. Moreover, the evidence suggests that air pollution probably exceeds expected unpolluted stream inputs for many additional elements in Lake Michigan, highlighting the need for more comprehensive chemical data to quantify the evaluation.

A chemical model for the trace element composition of a Great Lake, where sources and sinks of each element are evaluated and compared with the observed concentrations in the lake, must consider atmospheric as well as surface water sources. For Lake Michigan atmospheric inputs may be especially important since surface water inputs from the heavily populated and industrialized southern shore have been minimized by the construction of artificial drainage channels in the Chicago area (1). Consequently, air pollution, which is carried from the southern and western shore by prevailing westerly winds over the lake, may be a relatively large source of water pollution by fallout, impaction, rainout, or rainfall washout of the atmospheric aerosol over the lake itself.

A quantitative calculation of the air pollution contribution to lake water pollution requires an accurate estimate of trace element inputs to the atmosphere from various sources, but such an emissions inventory does not appear in the literature. It is possible, however, to construct a table of trace element emissions resulting from the major air pollution sources in the Chicago area by combining published data on the composition of different particulate emissions with expected total emissions from the different sources. In this paper, such a preliminary trace element emissions inventory is presented, and its significance for Lake Michigan water pollution is discussed.

Air Pollution Sources.

In Table 1 the populations are presented for three Standard Metropolitan Statistical Areas important in this study (2). In the Chicago SMSA the population density is high, and air pollution from vehicular traffic and electric power production is considerable. Northwest Indiana has the largest concentration of iron and steel industry, and important inputs of trace elements characteristic of this type of source are expected. Milwaukee is a population center with a relative emission composition perhaps resembling that of Chicago.

The major sources of air pollution which contribute trace elements to the atmosphere over southern Lake Michigan are:

- (1) Coal burned for electrical and heating uses.
- (2) Emissions from coke ovens in the manufacture of metallurgical coke.
- (3) Fuel oil burned for electrical and heating needs.
- (4) Automotive fuel burned for transportation.
- (5) Emissions from iron and steel manufacturing facilities.
- (6) Emissions from cement manufacturing plants.

The consumption of coal, fuel oil, and automotive fuel in the region of interest here is assumed to be 4% of the national consumption, in proportion to the estimated 1969 population of the region, where total U.S. annual consumption is estimated as (3): coal, 540 million short tons* (not including coal for coke production); fuel oil, 1200 million barrels (200 million short tons); automotive fuel, 830 gallons per year by each of 95 million automobiles (79 billion gallons). Coke production is estimated to be 21% of the national production of 77 million tons, based on the fraction of total U.S. iron and steel produced in the region (4). Emissions from blast furnaces, sinter plants,

*Because source data are available only in the English system of units, calculations have been carried out largely in terms of short tons of 2000 pounds (0.907 metric ton).

open hearth furnaces, and basic oxygen furnaces (4), as well as cement plant emissions (5), are based on production figures for the region. It should be pointed out that emissions based on production figures and listed in this report are conservative; that is, emissions from major sources were considered, but not inputs from minor sources, e.g. chemical industry, galvanizing, tinning, and trash.

The best available information on the composition of particulate emission from coal combustion appears to be contained in two recent reports of the U. S. Public Health Service (6,7). For some common elements analyses of fly ash itself are presented (6) but for the less common elements the data are presented (7) as grains of the element per standard cubic foot of flue gas for several types of boiler firing. The same reference presents the total amount of fly ash in the same units, as well as further data, which permits an estimate of emissions to be calculated as approximately 20 pounds of fly ash per short ton of coal used in electric power production, and 25 pounds of fly ash per short ton of coal burned for purposes other than generation of electricity. The weighted average is about 22 pounds of fly ash per short ton of coal consumed as a mean of the types of boiler firings considered. Fly ash emitted to the atmosphere comprises about 10% of the total ash produced. Table 2 summarizes calculations of the composition of particulate emission from coal combustion using this information. The selenium content is estimated by assuming 2.4% sulfur in the coal, a ratio $Se/S = 10^{-4}$ (8,9), and 10% of the Se appearing in the particulate emission, in line with an assumed 90% collection efficiency. (Se emissions may exceed this estimate since the expected compound, SeO_2 , is a vapor above 315° C.) Coke oven emissions are assumed to have the same relative elemental composition as the particulates from coal combustion and are estimated to be 20,000 short tons per year, 1.5 times the value published for northwest Indiana alone (10).

Table 3 represents very roughly the composition of particulate emissions from fuel oil combustion, based on two tests reported (11), and an assumed value of $Se/S = 10^{-4}$, although the elemental composition varies widely with the source of the crude oil. The reported value (12) of 0.2% of the weight of fuel oil burned which appears as airborne particulates is taken, or 16,000 short tons of particulate from this source per year in the region.

Calculations of trace elements in particulate emissions for the iron and steel industry require a detailed examination of the several sources involved, and the considerations which went into such calculations include the following:

In the nation, approximately 82 million short tons of pig iron per year are produced from iron ore, coke, and limestone, and 130 million tons of raw steel are produced (4,13). Very nearly 21% of the steel, or 27 million tons, is made in the Chicago and northwestern Indiana area. Thus it was assumed that 21% of total pig iron was also produced in the area, or 17 million tons. About 2/3 of this area production actually arises from plants in northwestern Indiana, and 1/3 from plants in northeastern Illinois (3,4).

Emissions from blast furnaces during pig iron production are fairly well controlled, but about 13,000 tons/year are emitted for the entire area (10,12) as a minimum. Emissions from sinter plants are considerably higher, and were arrived at by separate methods for northwestern Indiana and the remainder of the study area. Sinter plant emissions for northwestern Indiana have been published (10); sinter plant emissions for Chicago were calculated from the tons of iron processed, and an emission of 3.5 pounds particulate emitted per ton processed (12). Thus yearly atmospheric emissions of 88,000 tons from northwestern Indiana sinter production, and 10,000 tons from Chicago sinter plants were obtained, for a total of approximately 100,000 tons. Table 4 gives the composition of emissions from sinter plants and blast furnaces (14).

Regarding the production of raw steel, about half is made in open hearth furnaces, and, although a small amount is produced in electric furnaces, it was assumed for purposes of calculation that half is made in the basic oxygen furnace. Again, particulate emissions for northwestern Indiana were available for both processes (10) -- 67,000 tons from the open hearth and 500 tons from the basic oxygen furnace (BOF). In northeast Illinois, emissions from steel manufacturing had to be calculated from tons of product (12,13). Assuming emission control devices in operation, 7.5 pounds/ton are emitted from the open hearth process, and 0.4 pounds/ton from the BOF, or, per year, 17,000 tons from the open hearth and 1,000 tons from the BOF for northeastern Illinois. Thus total particulate emission for the entire region from open hearth were 84,000 tons/year, and from BOF, 1500 tons/year. Elemental composition of open hearth and BOF emissions (13) are also given in Table 4.

Particulate emissions from the manufacturing of portland cement could be conservatively estimated as 40,000 tons/year, based on production figures for the area (5). This corresponds to about 13 pounds of dust emitted per ton of cement produced. Of this total, about 27,000 tons of dust are emitted per year in northwestern Indiana (10). The emission was assumed to have the same approximate composition as the finished product (15); hence its composition was determined and is listed in Table 5.

The emissions of five elements were estimated from burning leaded gasoline in internal combustion engines. The number of gallons of gasoline consumed in the study area was estimated from census data regarding number of motor vehicles (2) and annual gasoline consumption per vehicle (12). Sulfur and selenium emissions could be calculated as 7,000 tons/year (12) and 1 ton/year (8,9) respectively. Lead, chlorine, and bromine emissions could be calculated as 2,000 tons/year, 700 tons/year, and 800 tons/year, respectively, assuming 25%

of lead and halogen product eventually becomes airborne (16). Partial fuel composition is listed in Table 6.

Calculated and Measured Air Pollution Composition.

Table 7 presents a summary of emissions into the atmosphere of trace elements from the major sources in the Chicago, Milwaukee, and northwestern Indiana metropolitan areas. As a test of the adequacy of our air pollution estimates, let us compare this calculated composition with analyses of air pollution particulates by the National Air Sampling Network (17). Spectrographic analyses were performed on standard high volume filter samples taken throughout 1964 in one central location in each of the cities Chicago, East Chicago, and Milwaukee. In Chicago the sampling location was considerably to the north of some important industrial sources. Likewise, in East Chicago the location was generally upwind of industrial sources and far enough away for some local fallout to occur between source and sampler, and we expect some bias as a result. However, for the distributed sources of coal, oil, and gasoline combustion, all three sampling locations may be representative.

Let us first compare our inventory with average elemental composition of suspended particulate matter during 1964 for Chicago, East Chicago, and Milwaukee, Table 8 (17). Also given is our inventory normalized to Pb = 1. Note that the Pb content of suspended particulate matter is approximately equal to $1 \mu\text{g}/\text{m}^3$. Hence it might be expected that similar ratios exist between concentrations of elements as found in the analyses of suspended particulate matter and that determined in the inventory. Indeed, within an order of magnitude, this is generally the case.

The elements Fe, Mn, Cu, and Zn are seen by our inventory in Table 7 to come primarily from the iron and steel industry, and their ratios may be compared with mean measured values in the three locations, indicated in Table 9. Agreement is satisfactory for the ratios Fe/Mn/Cu for all three locations but for Fe/Zn only approximately in one location, Milwaukee. The very high observed Zn values for Chicago and East Chicago suggest an additional pollution source not considered in our inventory.

A further test is a comparison of the content of elements in the inventory due mainly to coal, coke, and fuel oil combustion with observed particulate composition, Table 10. Normalizing to Cr = 100, apparently the most accurate value reported by the NASN, the contents of As and Sn are greater than expected whereas Ti is much less than expected. The elements Ni and V, due mainly to fuel oil, are also lower than expected.

Finally, a comparison may be made between key elements for each major source type: Pb (automotive), Fe (iron and steel), and Cr (coal). Table 11 indicates Pb/Cr predicted by the inventory is close to the observed values in all three locations, but Fe/Pb is predicted some ten-fold higher than generally observed at the NASN sampling sites. The agreement for Pb/Cr is reassuring, for both elements originate in distributed sources and the NASN sampling site is expected to be fairly representative for the city in each case. However, bias in sampling against emissions from the ferrous metal industry for Chicago and East Chicago may be considerable and may be the cause of the discrepancy in Fe/Pb. It is important to look for agreement between calculated and observed element abundances relative to one element whose atmospheric input can be estimated with the greatest reliability, e.g. Pb, as this serves a criterion for evaluating the reliability of our quantitative elemental inventories.

Water Pollution From Aerosol Fallout.

To answer the question of whether fallout of air pollution is a significant source of water pollution we must estimate the efficiency of air pollution transfer to the water surface. In constructing a model we may visualize the following steps: (1) emission from the various sources of the region into the atmosphere to various altitudes depending on the source; (2) local fallout of some components in the immediate vicinity of the source outside the Lake Michigan drainage basin; (3) long range fallout over the surface of Lake Michigan or its drainage basin. The efficiency of the long range fallout will depend on the wind direction and speed, altitude at which air pollutants are found, and effectiveness of removal of the air pollutants from the atmosphere by clear air deposition and precipitation scavenging. We emphasize that quantitative treatment of our model is premature at this time without knowing more precisely the exact locations of sources of each element and details on local winds near specific sources, winds which are affected by lake breezes and ^{which} may be important in bringing local fallout from shore-side industries into the lake. Quantitative evaluation of clear air deposition likewise requires knowledge of particle size distributions of trace metals, and precipitation scavenging may also be affected by water solubility of aerosols. At this time our paper will attempt only to evaluate qualitatively whether overall transfer of air pollution to Lake Michigan may be sufficiently large to warrant further consideration of this source of water pollution.

To begin with, although wind directions have not been measured systematically at all pollution sources, data for Midway Airport, Chicago, may serve as a useful guide. The 10-year averages shown in Figure 1 (18) indicate that winds blow from NW to S about 2/3 of the time in a direction generally from

the pollution sources toward Lake Michigan. Local wind circulation nearer the lakeshore may be altered by lake breeze effects, but it remains likely that much of the air pollution in this region finds its way to the air over the lake.

The processes of removal of particulates from the atmosphere are intricate and depend, among other factors, on particle size. For Chicago area pollutants, particle size information is not generally available, but we may estimate that gravitational settling may be rapid for some industrial pollutants, e.g. Fe, such that a large fraction of that which is blown toward the lake soon enters the lake. On the other hand, some elements, e.g. Pb, which are components of much smaller particles, may enter the lake with a lower efficiency depending on frequency of rainfall or likelihood of impaction with the water surface.

In this connection, the deposition velocity of ^{131}I from the British Windscale nuclear reactor accident has been estimated (19) to be 0.3 to 0.4 cm/sec. Eriksson (20) estimates 0.7 cm/sec as reasonable for deposition of sea salt aerosols over the open ocean. Both estimates refer to clear air deposition near the ground, for iodine vapors and for giant aerosols having radius $>1 \mu$. Consequently, we may estimate 0.5 cm/sec for average pollution aerosol deposition velocity, implying that particles carried initially to 100 meters altitude near the source would probably reach the water surface in

20,000 seconds (5.6 hours). If carried by a 5 meter/sec wind, the expected travel distance would be 100 km, a distance close to the mean east-west distance across Lake Michigan. By this simple logic it is not unreasonable to expect a large degree of clear air aerosol fallout over Lake Michigan regardless of particle size. (Additional air scavenging by rainfall may also occur.) To obtain more quantitative estimates, we believe these matters should be explored experimentally, but 10% transfer efficiency to the lake is not unlikely.

The significance of air pollution as a source of water pollution cannot be decided until we evaluate inputs of trace elements from other sources, especially streams. Unfortunately, the published literature does not include comprehensive studies of Lake Michigan tributary stream composition with respect to trace metals, but a recent report of the Federal Water Pollution Control Administration(21) presents stream analyses for Cu, Ni, and Zn. In Table 12 we compare our inventory with their observed concentrations and a calculated total inflow rate based on the composition of each stream and its gaged annual flow rate. The air pollution inventories of all three elements Cu, Ni, and Zn are in excess of the actual stream inputs and that for Zn exceeds the stream input 6-fold. However, we have already pointed out that our Zn inventory appears to be low when compared to Fe, Mn, and Cu (Table 9). Taking this into consideration, the possibly much greater than 6-fold excess of pollution input of Zn to the atmosphere near Lake Michigan, compared to actual stream input of Zn, suggests that Zn may indeed enter Lake Michigan primarily from the atmosphere. On the average for all of Lake Michigan, Cu and Ni probably do not enter the lake mainly from the atmosphere, but for the southern basin, which lies near the air pollution source and has limited river inflow, the principal sources of these elements may likewise be from air pollution fallout. Data of a similar sort for additional toxic trace elements would be desirable.

Let us now compare air pollution with estimated natural (unpolluted) stream inputs to Lake Michigan. Even though its tributary streams may no longer be unpolluted, Turekian's (22) recent compilation of stream data for other locations allows us to estimate expected pre-industrial trace metal inputs to Lake Michigan. Table 13 shows the results for those elements included in our inventory. For those marked "X" in the last column, air pollution emissions exceed calculated natural water inputs by a factor of 10 (8 for Co), those marked "?" are in question for reasons apparent from the table, and (X) signifies two cases, Zn and Se, where we suspect our inventory underestimates actual emissions for reasons discussed in the text. Compared to natural stream inputs, and assuming an air pollution efficiency of transfer to the lake of 10%, air pollution appears to be an important water pollution source for 7 to 14 of the 31 elements listed. We should point out that the chemical behavior of air pollution fallout into the lake may differ from stream carried material with respect to solubility, sedimentation, and biological activity, and these factors may affect residence times in the water or water and sediment systems.

It is interesting to note (Table 12) that measured stream inputs of Cu and Ni exceed the estimated natural stream inputs (Table 13) by 12 and 76 times, respectively, but Zn is close to our estimate of its natural stream input. Zn appears not to be a stream pollutant in the Lake Michigan basin, but overall pollution of the basin by Zn, including atmospheric, appears to be considerable.

Finally, another way of looking at our air pollution inventory is to ask how long it would take to raise lake concentrations by an ecologically significant increment through fallout. Again, quantitative treatment of the question must await further information on actual Lake Michigan composition

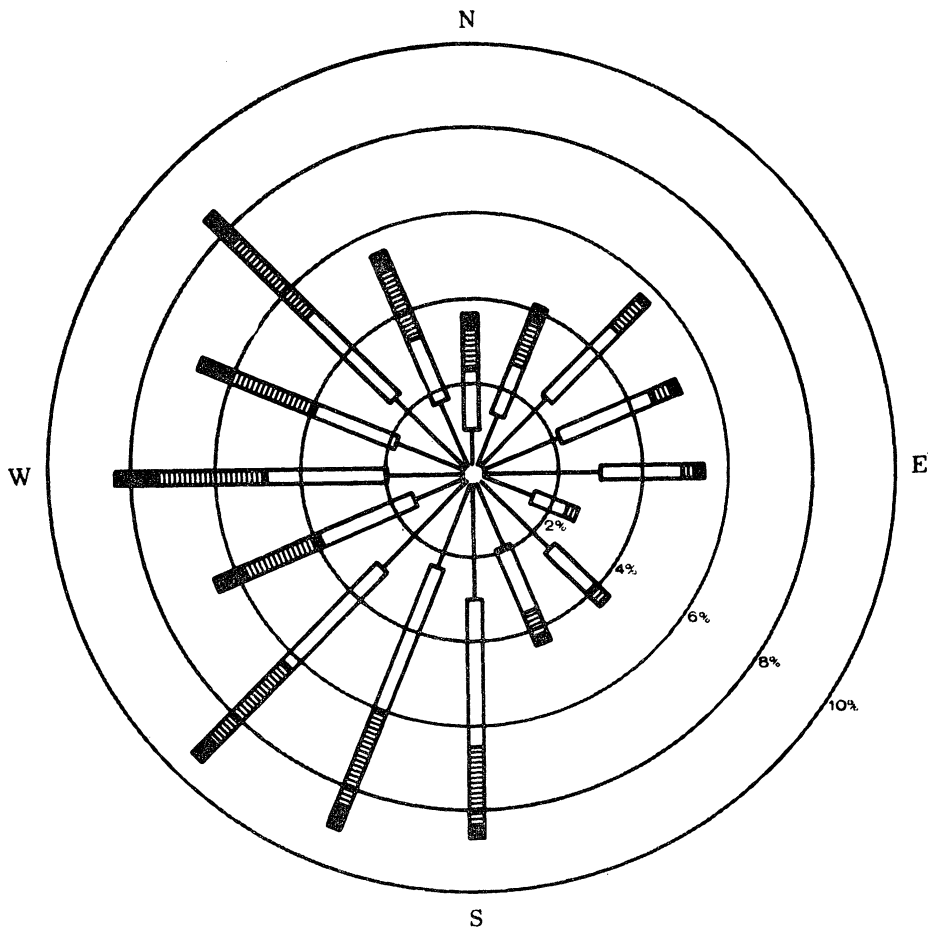
and ecology. However, very crudely we may suggest that air pollution in general enters the lake with 10% efficiency, and 0.1 $\mu\text{g}/\text{l}$ is a significant concentration increase. Taking the volume of Lake Michigan to be 4900 km^3 , we have constructed Table 14 for 11 elements. Of these, 8 elements are shown to raise the concentration by the stated amount in times much shorter than the water outflow residence time (100 years). If sedimentation residence times for these elements are sufficiently long, then as a result of air pollution we may observe an increase in steady state water concentration for these elements. Otherwise, the pollution component should be manifested in high trace metal concentrations in uppermost lake sediment layers. Further investigation of this question should be carried out.

Conclusions.

In this paper we have attempted to evaluate from published information in the literature whether air pollution along the southwestern shores of Lake Michigan can be a significant source of trace element contamination of the lake. In spite of the extremely fragmentary nature of available data on air and water composition and on meteorological factors, air pollution appears to be an important water pollution source for certain elements. More importantly, this study highlights the need for more comprehensive information in order to formulate exact chemical models for inputs and outputs of contaminants to a Great Lake.

Figure Caption.

Fig. 1. Percentage frequency of wind direction and speed, Midway Airport, Chicago, average 1950-1959 (18).



ANNUAL

Average Speed: 10.2
Percent Calms: 0.7

Wind Speeds (mph)

1 - 7	———
8 - 12	▬▬▬▬
13 - 18	▤▤▤▤▤▤▤▤
19 +	▢▢▢▢

**From U. S. Weather
 Bureau Monthly Weather
 Data Summary for
 Midway Airport (1950-1959)**

Table 1. 1960 Census Data for Standard Metropolitan Statistical Areas
Considered in this Study

<u>SMSA</u>	<u>Population, Millions</u>	<u>Percent</u>
Chicago	6.25	78
Northwestern Indiana	0.575	7
Milwaukee	<u>1.20</u>	15
Total	8.025	

Table 2. Composition of Particulate Emission from Coal Combustion

<u>Element</u>	<u>Parts Per Thousand</u>	<u>Element</u>	<u>Parts Per Thousand</u>
Al	140	Mn	0.24
As	0.16	Mo	0.16
Ba	0.6	Na	4
Be	0.018	Ni	0.4
Ca	40	Pb	1.2
Cd	0.04	Se	0.02
Co	0.09	Si	200
Cr	0.3	Sn	0.05
Cu	0.4	Ti	9
Fe	70	V	0.8
Mg	8	Zn	0.9

Table 3. Composition of Particulate Emission from Fuel Oil Combustion

<u>Element</u>	<u>Parts Per Thousand</u>	<u>Element</u>	<u>Parts Per Thousand</u>
Al	50	Mn	0.3
Ag	0.20	Mo	0.2
B	0.25	Na	15
Ba	2.5	Ni	60
Ca	4	Pb	1.8
Co	1.5	Se	1.0
Cr	1.2	Si	24
Cu	1.6	Sr	0.3
Fe	25	Ti	0.3
K	1.0	V	25
Mg	3	Zn	0.5

Table 4. Composition of Particulate Emission from the Iron and Steel Industry

<u>Element</u>	<u>Content in Parts Per Thousand</u>		
	<u>Blast Furnaces & Sinter Plants</u>	<u>Open Hearth Furnaces</u>	<u>Basic Oxygen Furnaces</u>
Al	35	12	1
Ca	90	17	12
Cu	30		
Fe	220	560	570
Mg	20	13	3
Mn	35	12	31
P		2	1
Si		10	7
Zn	35		

Table 5. Composition of Particulate Emission from Cement Manufacturing

<u>Element</u>	<u>Parts Per Thousand</u>
Al	25
Ca	440
Fe	27
Mg	12
Si	100

Table 6. Partial Composition of Leaded Gasoline

<u>Element</u>	<u>Grams Per Gallon</u>
Br	0.8
Cl	0.7
Pb	2
S	2
Se	0.0002

Table 7. Calculated Particulate Emission of Trace Elements From Air Pollution Sources in Chicago, Milwaukee, and Northwest Indiana Considered in this Study

Element	Calculated Source Emission, Short Tons Per Year						Total, Short Tons Per Year	Total, Kilograms Per Year (x10 ³)
	Coal	Coke	Fuel Oil	Iron & Steel	Cement	Transportation		
Ag			3				3	
Al	40,000	2,800	955	4,950	1,000		50,000	45,000
As	46	3					49	44
B			4				4	4
Ba	176	12	45				230	210
Be	5.0	1					6	5
Br						800	800	725
Ca	10,600	760	74	11,600	17,600		41,000	37,000
Cd	12	1					13	12
Cl						700	700	635
Co	25	2	28				55	50
Cr	80	6	22				110	100
Cu	109	8	28	3,400			3,500	3,200
Fe	19,500	1,400	450	73,000	930		95,000	86,000
K			16				16	15
Mg	2,090	150	56	3,360	500		6,100	5,500
Mn	67	5	6	5,000			5,100	4,600
Mo	45	3	3.4				51	46
Na	1,120	80	274				1,500	1,400
Ni	109	8	1,030				1,100	1,000
P				170			170	150
Pb	328	24	33				2,400	2,200
*S	550,000	40,000	150,000	1,000		2,000	750,000	680,000
Se	5.5	0.4	15				22	20
Si	55,800	4,000	433	850	4,000	1	65,000	59,000
Sn	13	1					14	13
Sr			6				6	5
Ti	2,390	170	6				2,600	2,400
V	209	15	450				670	610
Zn	247	18	9	4,000			4,300	3,900

*Sulfur included in order to calculate selenium.

Table 8. Ambient Air Concentrations of Elements and Comparison with Calculated Emission Inventory

<u>Element</u>	<u>Concentration in $\mu\text{g}/\text{m}^3$, 1964</u> <u>Arithmetic Mean</u>			<u>Inventory</u> <u>(Adjusted to Pb = 1)</u>
	<u>Chicago</u>	<u>E. Chicago</u>	<u>Milwaukee</u>	
(Total particulate)	176	218	146	80
Ag				0.001
Al				21
As	0.03	0.04	0.02	0.02
B				0.002
Ba				0.10
Be	<0.001	<0.005	<0.001	0.003
Br				0.3
Ca				17
Cd	< 0.05	< 0.04	<0.01	0.005
Cl				0.3
Co	<0.006	<0.011	<0.006	0.02
Cr	0.014	0.033	0.01	0.05
Cu	0.04	0.12	0.06	1.5
Fe	1.6	5.5	1.9	40
K				0.007
Mg				2.5
Mn	0.07	0.28	0.12	2.1
Mo	<0.01	<0.16	< 0.03	0.02
Na				0.6
Ni	0.42	0.123	0.023	0.5
P				0.07
Pb	0.9	0.9	0.5	(1)
S				300
Se				0.01
Si				30
Sn	0.02	0.06	0.01	0.006
Sr				0.003
Ti	0.02	0.05	0.05	1.1
V	0.03	0.04	0.004	0.3
Zn	0.95	2.57	0.16	1.8

Table 9. Ratios of Elements in Air Pollution Particulates
 Estimated to Originate Mainly From the Iron And
 Steel Industry, Compared With NASN Means of 1964,
 Normalized to Fe = 100

<u>Element</u>	<u>Our Inventory</u>	<u>Chicago</u>	<u>East Chicago</u>	<u>Milwaukee</u>
Fe	100	100	100	100
Mn	5.4	4	5	6
Cu	3.7	2.5	2	3
Zn	4.5	56	47	8

Table 10. Ratios of Elements in Air Pollution Particulates
 Estimated to Originate Mainly From Coal, Coke, and
 Fuel Oil Combustion, Compared With NASN Means of 1964,
 Normalized to Cr = 100

<u>Element</u>	<u>Our Inventory</u>	<u>Chicago</u>	<u>East Chicago</u>	<u>Milwaukee</u>
As	44	200	120	200
Cr	100	100	100	100
Sn	13	140	180	100
Ti	2,400	140	150	500
Ni	1,000	300	370	230
V	610	200	120	40

Table 11. Ratios of Key Elements in Air Pollution Particulates Estimated From Different Major Sources Compared With NASN Means of 1964, Normalized to Pb = 100

<u>Element</u>	<u>Major Source</u>	<u>Our Inventory</u>	<u>Chicago</u>	<u>East Chicago</u>	<u>Milwaukee</u>
Pb	automotive	100	100	100	100
Fe	iron & steel	4,000	180	600	380
Cr	coal	4.5	1.6	3.7	2.0

Table 12. Comparison of Air Pollution Inventory with River Inflow of Trace Elements to Lake Michigan, metric units

	<u>Cu</u>	<u>Ni</u>	<u>Zn</u>
Air pollution emissions inventory, tons/year	3,200	1,000	3,900 ^a
Lake Michigan rivers approx. mean conc., 1963-1964, micrograms/liter	90	40	30
Inflow to Lake Michigan, tons/year ^b	2,700	760	~500

^aInventory appears to be low by ~10X; additional sources may be present.

^bEstimated for total Lake Michigan drainage basin from contents and flow rates of individual rivers, reference 21.

Table 13. Expected Natural Stream Inputs to Lake Michigan, metric units

<u>Element</u>	<u>Stream conc.^a µg/l</u>	<u>Input^b tons/yr</u>	<u>Air Pollution Inventory tons/yr</u>	<u>Ratio^c ≥10?</u>
Ag	0.3	10	3	
Al	400	13,000	45,000	
As	2	65	(44)	?
B	10	330	4	
Ba	10	330	210	
Be	-	-	5	?
Br	20	650	725	
Ca	15,000	490,000	37,000	
Cd	-	-	12	?
Cl	7,800	250,000	635	
Co	0.2	6.5	50	X
Cr	1	33	100	
Cu	7	230	3,200	X
Fe	(670)	(22,000)	86,000	?
Ga	0.09	3	(4.4)	
K	2,300	75,000	15	
Mg	4,100	134,000	5,500	
Mn	7	230	4,600	X
Mo	1	33	46	
Na	6,300	200,000	1,400	
Ni	0.3	10	1,000	X
P	20	650	150	
Pb	3	100	2,200	X
S	5,600	180,000	680,000	
Se	0.2	6.5	(20)	(X)
Si	1,350	44,000	59,000	
Sn	-	-	13	?
Sr	60	2,000	5	
Ti	3	100	2,400	X
V	0.9	29	610	X
Zn	20	650	(3,900)	(X)

^aStream data from reference 22. 1 µg/l = 1 ton/km³

^bEstimated average stream flow into Lake Michigan = 32.6 km³/yr.

^cIf the ratio air pollution inventory/stream input $\gg 10$, there is reason to expect a major input to the lake by the atmospheric route. Such cases are indicated by "X"; "?" denotes elements where data are lacking or uncertain.

Table 14. Years Required to Raise Lake Michigan Water Concentrations by 0.1 Microgram/Liter from Fallout of Chicago Area Air Pollution with 10% Efficiency

<u>Element</u>	<u>Years</u>
Cd	500
Cr	55
Cu	1.6
Fe	0.06
Mn	1.1
Ni	5.5
Pb	2.4
Se	73
Ti	2.5
V	9
Zn	1.3

Literature Cited

- (1) Bacon, V. W., and Dalton, F. E., "Professionalism and Water Pollution Control in Greater Chicago," Journal Water Pollution Control Federation, 40: 1586, 1968.
- (2) U. S. Bureau of the Census, U. S. Censuses of Population and Housing: 1960, Census Tracts, U. S. Government Printing Office, Washington, D. C., 1961.
- (3) The World Almanac and Book of Facts 1968, Newspaper Enterprise Association, Inc., New York, 1967.
- (4) "Raw Steel Production," from "Market Outlook," Steel, 163, 1968.
- (5) Kreichelt, T. E., Kemnitz, D. A., and Cuffe, S. T., Atmospheric Emissions from the Manufacture of Portland Cement, Publication No. 999-AP-17, National Center for Air Pollution Control, U. S. Department of Health, Education, and Welfare, Cincinnati, Ohio, 1967.
- (6) Smith, W. S., and Gruber, C. W., Atmospheric Emissions from Coal Combustion - An Inventory Guide, Publication No. 999-AP-24, Division of Air Pollution, U. S. Public Health Service, U. S. Department of Health, Education, and Welfare, Cincinnati, Ohio, 1966.
- (7) Cuffe, S. T., and Gerstle, R. W., Emissions from Coal-Fired Power Plants: A Comprehensive Summary, Publication No. 999-AP-35, National Center for Air Pollution Control, U. S. Department of Health, Education, and Welfare, Cincinnati, Ohio, 1967.
- (8) Hashimoto, Y., and Winchester, J. W., "Selenium in the Atmosphere," Environmental Science and Technology, 1: 338, 1967.
- (9) Thomas, C., unpublished data from the Western New York Nuclear Research Center, Buffalo, N. Y., 1969.
- (10) Ozolins, G., and Rehmann, C., Air Pollutant Emission Inventory of Northwest Indiana, A Preliminary Survey, 1966, Publication No. APTD-68-4, National Center for Air Pollution Control, U. S. Department of Health, Education, and Welfare, Durham, N. C., 1968.
- (11) Smith, W. S., Atmospheric Emissions from Fuel Oil Combustion, An Inventory Guide, Publication No. 999-AP-2, Division of Air Pollution, Public Health Service, U. S. Department of Health, Education, and Welfare, Cincinnati, Ohio, 1962.
- (12) Duprey, R. L., Compilation of Air Pollutant Emission Factors, Publication No. 999-AP-42, National Center for Air Pollution Control, U. S. Department of Health, Education, and Welfare, Durham, N. C., 1968.

- (13) Schueneman, J. J., High, M. D., and Bye, W. E., Air Pollution Aspects of the Iron and Steel Industry, Publication No. 999-AP-1, Division of Air Pollution, Public Health Service, U. S. Department of Health, Education, and Welfare, Cincinnati, Ohio, 1963.
- (14) Sebesta, W., "Ferrous Metallurgical Processes," Air Pollution, Stern, A. C., ed., III: 143, Academic Press, New York, 1968.
- (15) "Cement," Encyclopaedia Britannica, 5: 153, 1968.
- (16) The Working Group on Lead Contamination, Survey of Lead in the Atmosphere of Three Urban Communities, Publication No. 999-AP-12, Division of Air Pollution, Public Health Service, U. S. Department of Health, Education, and Welfare, Cincinnati, Ohio, 1965.
- (17) Air Quality Data from the National Air Sampling Networks and Contributing State and Local Networks, 1964-1965, Division of Air Pollution, Public Health Service, U. S. Department of Health, Education, and Welfare, Cincinnati, Ohio, 1966.
- (18) Managing the Air Resource of Northeastern Illinois, Technical Report No. 6, Northeastern Illinois Planning Commission, Chicago, August, 1967, p. 25.
- (19) Chamberlain, A. C., "Deposition of Iodine-131 in Northern England in October 1957," Quart. J. Roy. Meteor. Soc., 85: 350, 1959.
- (20) Eriksson, E., "The yearly circulation of chloride and sulfur in nature; meteorological, geochemical, and pedological implications, 1," Tellus, 11: 375, 1959; ibid. 12: 63, 1960.
- (21) "Water Quality Investigations, Lake Michigan Basin, Physical and Chemical Quality Conditions," U. S. Department of the Interior, Federal Water Pollution Control Administration, Chicago, January, 1968.
- (22) Turekian, K. K., "Elements, hydrosphere distribution of," 1969 Yearbook of Science and Technology, McGraw-Hill, New York, 1969.

NONDESTRUCTIVE NEUTRON ACTIVATION ANALYSIS OF AIR POLLUTION PARTICULATES

R. Dams, J. A. Robbins, K. A. Rahn, and J. W. Winchester

Dept. of Meteorology & Oceanography and Great Lakes

Research Division, University of Michigan, Ann Arbor,

Michigan 48104

Abstract. A nondestructive and computer assisted neutron activation analytical procedure for the determination of up to 33 elements in air pollution particulates has been designed and tested in studies of samples taken in and near the Northwest Indiana industrial area. Samples are counted after (1) 3 minutes, (2) 15 minutes, (3) 20-30 hours, and (4) 20-30 days following neutron irradiation for (1) Ca, Ti, V, Cu, Al, S, (2) Na, Mg, Mn, In, Cl, Br, I, (3) K, La, Sm, Eu, Cu, Zn, W, Au, Ga, As, Sb, Br, (4) Sc, Ce, Th, Cr, Fe, Co, Ni, Ag, Zn, Hg, Sb, Se using a Ge(Li) detector.

Introduction.

Elemental analysis of pollution aerosols requires a precise yet sensitive method if the results are to be used for study of source identification or atmospheric transport processes. For studies involving large numbers of samples speed and ease of analysis are necessary, and selectivity in the detection of many elements at the nanogram to microgram level is desirable in order to permit sampling of only a few cubic meters of air. Zoller and Gordon (1) have presented a discussion of the principles and merits of nondestructive neutron activation analysis in this application, together with an outline of a procedure and results of several analyses of Cambridge, Massachusetts, air pollution particulate samples for more than 20 elements. In this paper we present a procedure which extends the method to 33 elements and utilizes a computer data processing technique offering a good compromise between speed, accuracy, and economy. A thorough test of

reproducibility of the procedure is presented by the results of replicate determinations of samples taken in East Chicago, Indiana, and Niles, Michigan.

The National Air Sampling Network (2) has used an emission spectrographic technique to analyze for 16 elements -- Be, Bi, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Sn, Ti, V, Zn -- using a procedure involving ashing and extracting in nitric acid. The method requires skilled operators, is not highly sensitive, and is often limited by high blank values for several elements. Of the reported values 45% are given only as upper limits. When the high neutron fluxes of nuclear reactors are used, neutron activation analysis is an extremely sensitive method and no blanks due to chemical reagents are introduced. Several authors (3, 4, 5) have applied NaI γ -spectrometry coupled to radiochemistry or automatic resolution of the γ spectra to the determination of several elements in aerosols. High resolution Ge(Li) detectors greatly extends the scope of nondestructive activation analysis so that a very large number of isotopes can be counted simultaneously. If computer assisted, this technique can be made almost completely automated. Several authors (1, 6, 7, 8) have used Ge(Li) detectors for destructive or nondestructive analysis of aerosols.

Sampling procedure.

Aerosols may be sampled by passing air through a filter which allows a high flow rate and at the same time has good particle retentivity down to 0.1 μ m size. Glass fiber filters have often been used for the analysis of organics, sulfate, nitrate, and total particulate, but this filter must be ruled out for nondestructive activation analysis because of its high concentrations of trace metals. Although it is not an ideal filter, polystyrene (9) was used in the present investigation, combining a good filtering performance with fairly low blank values. However, the sensitivity of a number of elements, such as Cl, Na, Al, Ca, Mn, Zn, and Sb, is still limited by the magnitude of the blank (9), and values for Cl are not reported in the test results described below for this reason.

Insofar as pumps are concerned, those in common use for air pollution monitoring are low vacuum, high volume types used with 20x25 cm (8x10 inch) filters. In the present investigation, however, high vacuum, low free air capacity pumps equipped with 25 mm (or 47mm) diameter holders were also used. Where the high volume pumps generate a flow rate of 4.5 l/min-cm^2 the high vacuum pumps and 25 mm holders reach 12 l/min-cm^2 . In spite of the fact that the latter holder has an unexposed waste zone at the edge of the filter (25% of the total area) which decreases the signal to blank ratio somewhat, this figure is still twice as high as for the high volume samplers.

Nondestructive neutron activation analysis.

A procedure for the nondestructive analysis of air pollution particulate matter for up to 33 elements in solid form has been developed, though it can also be used for the analysis of other types of environmental samples as well

For the analysis of elements giving rise to short-lived isotopes, each sample in our procedure is packaged in a polyethylene vial, then placed in a rabbit which carries it through a pneumatic tube to a position near the core of the Ford Nuclear Reactor on the campus of the University of Michigan, where it is irradiated for 5 minutes at a flux of 2×10^{12} neutrons/cm²sec. At the end of this period it rapidly returns to the laboratory where it is manually transferred to a counting vial and carried to the counting room. At 3 minutes after irradiation a count of 400 seconds live-time duration is begun, and this is followed by a count of 1000 seconds live-time starting 15 minutes after irradiation. Both these and subsequent counts are performed on a 30 cm³ Ge(Li) detector coupled to a 4096 channel analyzer. The detector is housed in an iron shield and operated in an air conditioned room at gain settings of 1 kev/channel. The observed resolution is 2.5 kev FWHM for the Co⁶⁰ 1332 kev photopeak and a peak to Compton

ratio of 18/1. Table 1 shows the isotopes determined by the first two counts.

All spectra are recorded on 7 track magnetic tape for future data analysis and can also be printed on paper tape. Conversion of counting rates under the various peaks to concentrations is accomplished by subjecting a few standard solutions containing well-known mixtures of these same elements to the same irradiation and counting sequence. To avoid possible errors due to coincidence summing or to broadening of peaks at high counting rates, sample sizes are generally adjusted to make counting rates of sample and standard of comparable magnitude.

Though all the short irradiations are performed at the same site in the reactor and under conditions of nearly constant power, small corrections for variations of both the neutron flux and rabbit placement from irradiation to irradiation are accomplished by co-irradiation of a titanium metal foil flux monitor with each sample. It is counted for 20 seconds at 13 minutes after the end of irradiation, between the two sample counts. If the analysis rate does not exceed one sample in 40 minutes, the same flux monitor may be used repeatedly, with less than 1% of the original 5.8-minute ^{51}Ti remaining in the next count. Net counting rates of the sample spectrum are normalized to an arbitrary Ti activity, equivalent to a reference neutron flux. Experimentally we have found that during one 20-day reactor operating cycle the standard deviation of the flux as determined by means of this flux monitor was 3%. However, variations of up to 8% were experienced between the neutron flux at the irradiation site during different reactor cycles.

The same sample, or another portion of the same air filter, is then irradiated at a higher flux (1.5×10^{13} neutrons/cm²sec) for 2-5 hours in the reactor core. Each is individually heat sealed in a polyethylene tube and irradiated together with 8 others plus a standard mixture of elements in a polyethylene bottle, 4 cm diameter, lowered into the reactor pool. Cooling of the samples during irradiation

is achieved by allowing the pool water to circulate through several holes cut in the container bottle. Standards are prepared by depositing 100 μ l each of two well-balanced mixtures of the appropriate elements onto a highly pure substrate (ashless filter paper) and allowing to dry, then sealing immediately inside polyethylene tubes. After irradiation, the samples and standards are transferred to clean containers and counted once for 2000 seconds live-time after 20-30 hours of cooling and then for 4000 seconds live-time after 20-30 days of cooling.

Table 2 shows elements determined from these counts. Horizontal and vertical flux gradients at the irradiation site in the core have been measured, and errors due to thermal neutron flux gradients over the bottle dimensions appear to be less than 5% providing the samples are confined to a single horizontal layer of vertically oriented tubes at the bottom of the bottle and the bottle is rotated 180° at half of the irradiation time. Fast neutron flux gradients at this site are about twice as large as thermal gradients, but the only fast neutron reaction used in our procedure is in the determination of nickel, $^{58}\text{Ni} (n,p) ^{58}\text{Co}$.

The entire irradiation and counting procedure is illustrated in Figure 1, and Tables 1 and 2 list the γ transitions used. Sometimes the most prominent photopeak of an isotope cannot be used because of interferences by neighboring peaks of other isotopes. Examples of unusable peaks include 844 keV of ^{27}Mg (846 keV ^{56}Mn) and 559 keV of ^{76}As (555 keV ^{82}Br and 564 keV ^{122}Sb). The monoenergetic ^{203}Hg (279.1 keV) is interfered with by ^{75}Se (279.6 keV), but a correction based on the spectrum of pure ^{75}Se can be applied because the interference is usually less than 20% of the ^{203}Hg activity in the air pollution samples we have analyzed so far. Zoller and Gordon (1) apparently overlooked this possibility. The measurement of ^{64}Cu (511.0 keV) is interfered with by external pair production of high energy γ -rays. In typical samples 15-hour ^{24}Na is the most important source of high energy γ -rays after a decay period of 20 hours, and a correction, usually less than 10%, can be applied to the apparent ^{64}Cu activity.

The ratio of thermal to fast neutron flux was determined at both irradiation sites using the reactions $^{31}\text{P} (n, \gamma) ^{32}\text{P}$ and $^{32}\text{S} (n, p) ^{32}\text{P}$. The ratios obtained were 7.5 for pneumatic tube and 4.5 for pool irradiation sites. Interferences by threshold reactions were calculated and checked experimentally, with the finding that in typical aerosol samples the only reaction affecting a calculated concentration by more than 2% is $^{27}\text{Al} (n, p) ^{27}\text{Mg}$. Once the aluminum concentration is known, the appropriate correction can be applied to the magnesium concentration.

Automated data reduction.

In order that our nondestructive neutron activation analysis procedure should be applicable to large numbers of samples, such as in routine monitoring, some sort of automatic data reduction is necessary. We feel that accuracy as well as speed is increased by elimination of many human errors, but we have also found that human judgement should be retained in the examination of the data and in devising procedures for checking data quality.

In the present investigation a computer program was developed and used to do the following: (1) qualitatively determine the presence of isotopes, (2) calculate net peak areas, (3) convert areas to weights of trace elements, (4) subtract analytical blanks due to filter materials, (5) calculate concentrations of trace elements in the originally sampled air.

The program.

The magnetic tape on which up to 100 γ -ray spectra, each of 4096 channels, are stored is submitted to the IBM 360/67 computer together with a Fortran IV program typed on cards. The program makes an inventory of the tape and creates a new compact error-free version, providing a list with position and tagword of each spectrum on the final tape.

Initially an approximate energy calibration of the spectrometer is required. On this basis the program can refine and update the calibration for each spectrum by comparing the observed positions of some prominent peaks with the true γ -ray

energies, present as a data library in the program. This calibration fit can in principle be a polynomial of any order, but usually a linear or at most quadratic fit suffices.

The main program for obtaining trace element concentrations from spectra requires a data set specifying γ transition energies of expected peaks. From this and the above energy calibration an approximate peak location is computed. The channel with the greatest number of counts is sought in a 7 channel interval centered on this calculated location. If this channel occurs at the end of the search interval, such as if the expected peak is masked by the edge of a nearby large peak, it fails to qualify as a peak and the program moves on to the next peak search; otherwise it is taken as the actual peak location. The net peak area is evaluated by summing counts over an interval of 7 channels centered about the actual peak position and subtracting baseline counts. The estimate of the baseline under peaks is accomplished by a regression technique as described by Ralston and Wilcox (10). Not all maxima found within the scan interval are associated with real peaks. Included in the output is a measure of the statistical significance of each net peak area which enables the user to assess data quality at a glance.

Further data sets are provided in the program. For the short counts (Table 1) these include conversion factors from peak areas to concentrations (calculated from standard short lived spectra), and for the longer count data (Table 2) they include concentrations of the elements in the standards, filter blank values, and isotope half lives. Apart from the above data sets the program requires only one card per spectrum, containing information about the irradiation and count type, filter type and fraction of sample irradiated, whether the sample is a standard, flux monitor, or unknown, and finally factors used in converting weights of elements to concentrations in air, expressed in any desired units.

If the spectrum is a flux monitor, only one net peak area is determined (320 keV ^{51}Ti). This value is used to normalize all peak areas of the unknown (400 and 1000 second counts) to a reference neutron flux. In an unknown sample the peak areas are converted to weights. If the spectrum is from a long count (2000 or 4000 seconds), peak areas are compared to those of the standard and after decay corrections (arising because sample and standard are not counted at the same time after irradiation) weights of the trace elements are calculated. Appropriate blanks are subtracted, followed by division by volume of air sampled to give concentrations. A detailed error analysis gives standard deviations of concentrations based on counting statistics and uncertainties in blank and standard values. Figure 2 shows schematically the outline of the computer program.

In its present form the program does not resolve doublets. A Gaussian fit treating these cases has been tried successfully in some cases but the increased running time and consequent expense does not justify its inclusion as a permanent feature of the program. For similar reasons the computer technique is supplemented by manual calculations for ^{76}As , ^{72}Ga , ^{122}Sb , and ^{187}W where very small photopeaks are located on tails of neighboring large peaks. Processing of one 4096 channel spectrum takes about 15 seconds of computer time, and the turnaround time at the University of Michigan Computing Center for a full magnetic tape of several spectra may be as short as 1 hour.

Sensitivity.

The sensitivity for the different elements is often determined by the composition of the sample because it may be limited by the degree of interference from other substances. Column 3 of Table 3 shows the sensitivity obtained by the present procedure for the analysis of typical inland aerosol samples, expressed in weights of the elements. The sensitivity obtained by the National Air Sampling Network (2) applying emission spectrography and using 90 cm^2 (14 inch^2) of a 24-hour high volume sample is expressed in concentrations of the elements in urban air (column 5). For convenience the sensitivities obtained by the present neutron

activation technique were also converted to concentrations in urban air (column 4) when counting irradiated samples after the decay times indicated, where 0.8, 0.8, 1.6, and 13 cm² of the filter were used for the four counts, respectively, corresponding approximately to 5, 5, 10, and 80 m³ of air collected during 24 hours by a high volume sampler. The sensitivities obtainable in non-urban areas are better for both methods. It should be borne in mind that the sensitivities given are not fixed values for all urban aerosols because they also depend to a certain extent on the composition of the sample.

Application.

We have applied our procedure to a study of the composition of aerosols collected in the southern Lake Michigan basin. As an example the data given in Tables 4 and 5 are drawn from results of a one-day area-wide survey of the Northwest Indiana region, June 11, 1969, a full account of which will be published separately. Each sample was 24 hours in length, taken on a polystyrene 20x25 cm (8x10 inch) filter. The East Chicago, Indiana, location was chosen to be illustrative of a heavily polluted industrial area, whereas the Niles, Michigan, station is in a rural location some 100 km to the ENE. During the sampling period the sky was generally overcast (0.6-0.9 fractional cloud cover), and scattered traces of rain fell in the metropolitan area but not at the rural location. Winds were nearly constant from the south at 5-10 m/sec during the 24 hours.

Tables 4 and 5 show that the concentrations of 30 elements in total were investigated, and 4 of these (Cu, Zn, Sb, Br) were duplicated in different counts. Each analysis was replicated from two to four times. Standard deviations are given both for the single measurements as returned by the computer (based on counting statistics and uncertainties in blanks and standards) and for the mean of the values reported (based on the dispersion of the replicate analyses).

Discussion.

Tables 4 and 5 show the 29 elements can be determined, even though some of these are present only in very low concentrations. Although a much smaller amount of the filter is used, the sensitivities compare favorably with those

obtained by emission spectrography as performed by the National Air Sampling Network (2). For most elements at least ten times better sensitivity is obtained; exceptions are Ti and Ni. In another application, which will be published elsewhere, we found that, after a sampling time of only 90 minutes in a rural location, 15 elements could routinely be determined. In an industrial or urban area the same number of elements may be detected after a much shorter sampling time.

For some elements the sensitivity is limited by the purity of the filter paper, e.g. Cl, Br, Na, and Zn. For at least 15 elements the sensitivity is affected by the composition of the sample. The abundant elements Al, Na, and Br give rise to a large amount of radioactivity, and other elements may be difficult to detect in their presence. It appears that the large amount of V found by Zoller and Gordon (1) in their samples caused a limitation on sensitivity in their short runs. A destructive technique involving chemical separations may improve the sensitivity for some elements, e.g. Cu, Zn, Ga, As, Se, Ce, Sm, Eu, W, Au, Hg, but the nondestructive sensitivities for these elements appear to be adequate for the 24-hour samples from urban and rural areas we have examined. Some increase in sensitivity may be achieved by increasing the counting time or the neutron dose, although some chemical separations may still be required to detect elements such as Sr, Mo, Cd, I, and additional rare earths.

By close examination of Tables 4 and 5 it can be seen that, although only trace quantities are determined, from 10^{-3} to 10^{-10} grams, the reproducibility of the determinations is quite adequate, for the differences are generally within the calculated standard deviations (67% confidence level) of the single values. These standard deviations are high ($> 40\%$) only when the concentrations determined are near the limit of detection. In cases where the determination of an element is duplicated in different counts or in irradiations of different portions of the air filter sample, good agreement is usually obtained. This includes the reproducibility of the chemical analysis, the accuracy in measurement of the filter

area taken for analysis and the possible nonuniform air-flow through the filter. We conclude that for the determination of most elements an accuracy of 25% can readily be obtained from one analysis. This is sufficient for many monitoring purposes.

A test of the adequacy of the analytical precision obtained is given in Table 6 showing the ratios of concentrations found in East Chicago to those in Niles, together with the standard deviations of the ratios. In nearly every case the ratio is significantly greater than unity, and in general the ratio is not statistically the same for every element. A study involving a number of sampling locations over a wide area may lead to the identification of local sources characteristic for each element or group of elements. Such an investigation is now in progress in our laboratory.

Acknowledgements.

We are grateful to Dr. S. S. Brar of the Argonne National Laboratory and to personnel of the division of air pollution control of the city of East Chicago, Indiana, for collection of the sample described in Table 4. This work was supported in part by U.S.A.E.C. contract AT(11-1)-1705, U.S.P.H.S. grant AP-00585, N.S.F. grant GA-811, and the University of Michigan. Contribution No. ____ from the Department of Meteorology and Oceanography and No. ____ from the Great Lakes Research Division, University of Michigan.

References.

- (1) W.H. Zoller and G.E. Gordon. Anal. Chem. 42, 256 (1970).
- (2) U.S. Public Health Service, Air Quality Data from the National Air Sampling Networks and Contributing State and Local Networks, 1966 Edition, Durham, N.C. (1968).
- (3) S.S. Brar, D.M. Nelson, E.L. Kanabrocki, C.E. Moore, C.D. Burnham and D.M. Hattori, Proceedings 1968 International Conference "Modern Trends in Activation Analysis", Gaithersburg, Maryland, p. 43 (1969).
- (4) R.M. Loucks, J.W. Winchester, W.R. Matson and M.A. Tiffany, Proceedings 1968 International Conference "Modern Trends in Activation Analysis", Gaithersburg, Maryland, p. 36 (1969).
- (5) J.R. Keane and E.M.R. Fisher, Atmospheric Environment 2, 603 (1968).
- (6) N.D. Dudey, L.E. Ross, V.E. Noshkin, Proceedings 1968 International Conference "Modern Trends in Activation Analysis", Gaithersburg, Maryland, p. 55 (1969).
- (7) G.L. Hoffman, R.A. Duce and W.H. Zoller, Environmental Science and Technology 3, 1207 (1969).
- (8) K.K.S. Pillay and C.C. Thomas, Jr., Report WNY-046, Western New York Nuclear Research Center, Buffalo, 1969.
- (9) R. Dams, K. Rahn, J.W. Winchester, Environmental Science and Technology (submitted).
- (10) H.R. Ralston and G.E. Wilcox, Proceedings 1968 International Conference "Modern Trends in Activation Analysis", Gaithersburg, Maryland, p. 1238 (1969).

Table 1. Nuclear properties and measurement of short-lived isotopes.

Element	Isotope	Half-life	$t_{\text{irradiate}}$	$t_{\text{cool.}}$	$t_{\text{count.}}$	Gamma-rays used Key
Al	^{28}Al	2.31 min.	5 min.	3 min.	400 sec.	1778.9
S	^{37}S	5.05 min.	"	"	"	3102.4
Ca	^{49}Ca	8.8 min.	"	"	"	3083.0
Ti	^{51}Ti	5.79 min.	"	"	"	320.0
V	^{52}V	3.76 min.	"	"	"	1434.4
Cu	^{66}Cu	5.1 min.	"	"	"	1039.0
Na	^{24}Na	15 hr.	"	15 min.	1000 sec.	1368.4; 2753.6
Mg	^{27}Mg	9.45 min.	"	"	"	1014.1
Cl	^{38}Cl	37.3 min.	"	"	"	1642.0; 2166.8
Mn	^{56}Mn	2.58 hr.	"	"	"	846.9; 1810.7
Br	^{80}Br	17.6 min.	"	"	"	617.0
In	$^{116\text{m}}\text{In}$	54 min.	"	"	"	417.0; 1097.1
I	^{128}I	25 min.	"	"	"	442.7

Table 2. Nuclear properties and measurement of long-lived isotopes.

Element	Isotope	Half-life	$t_{\text{irradiate}}$	$t_{\text{cool.}}$	$t_{\text{count.}}$	Gamma-rays used Kev
K	^{42}K	12.52 hr.	2-5 hr.	20-30 hr.	2000 sec.	1524.7
Cu	^{64}Cu	12.5 hr.	"	"	"	511.0
Zn	$^{69\text{m}}\text{Zn}$	13.8 hr.	"	"	"	438.7
Br	^{82}Br	35.9 hr.	"	"	"	776.6; 619.0; 1043.9
As	^{76}As	26.3 hr.	"	"	"	657.0; 1215.8
Ga	^{72}Ga	14.3 hr.	"	"	"	630.1; 834.1; 1860.4
Sb	^{122}Sb	2.75 day	"	"	"	564.0; 692.5
La	^{140}La	40.3 hr.	"	"	"	486.8; 1595.4
Sm	^{153}Sm	47.1 hr.	"	"	"	103.2
Eu	$^{152\text{m}}\text{Eu}$	9.35 hr.	"	"	"	121.8; 963.5
W	^{187}W	24.0 hr.	"	"	"	479.3; 685.7
Au	^{198}Au	2.70 day	"	"	"	411.8
Sc	^{46}Sc	83.9 day	"	20-30 day	4000 sec.	889.4; 1120.3
Cr	^{51}Cr	27.8 day	"	"	"	320.0
Fe	^{59}Fe	45.1 day	"	"	"	1098.6; 1291.5
Co	^{60}Co	5.2 yr.	"	"	"	1173.1; 1332.4
Ni	^{58}Co	71.3 day	"	"	"	810.3
Zn	^{65}Zn	245 day	"	"	"	1115.4
Se	^{75}Se	121 day	"	"	"	136.0; 264.6
Ag	$^{110\text{m}}\text{Ag}$	253 day	"	"	"	937.2; 1384.0
Sb	^{124}Sb	60.9 day	"	"	"	602.6; 1690.7
Ce	^{141}Ce	32.5 day	"	"	"	145.4
Hg	^{203}Hg	46.9 day	"	"	"	279.1
Th	^{233}Pa	27.0 day	"	"	"	311.8

Table 3. Sensitivities for determination of trace elements in aerosols

Element	Neutron Activation			Emission Spectrography
	Decay Time*	Detection Limit (µg)	Minimum Detectable Concentration in Urban Air (µg/m ³) 24 hours sample	Minimum Detectable Concentration in Urban Air (µg/m ³) 24 hours sample
Al	3 min.	0.04	0.008	----
B	"	25.0	5.0	----
Ca	"	1.0	0.2	----
Cl	"	0.2	0.04	0.0024
Cu	"	0.001	0.002	0.0032
K	"	0.1	0.02	0.01
La	15 min.	0.2	0.04	----
Mg	"	3.0	0.6	----
Mn	"	0.5	0.1	----
Ni	"	0.003	0.0006	0.011
Pb	"	0.02	0.004	----
Pm	"	0.0002	0.00004	----
Rb	"	0.1	0.02	----
Sr	20-30 hr.	0.075	0.0075	----
Ta	"	0.05	0.005	0.01
Ti	"	0.2	0.02	0.24
V	"	0.025	0.0025	----
W	"	0.04	0.004	----
Xe	"	0.01	0.001	----
Yb	"	0.03	0.003	0.040
Zr	"	0.002	0.0002	----
Am	"	0.00005	0.000005	----
Eu	"	0.0001	0.00001	----
Nd	"	0.005	0.0005	----
Au	"	0.001	0.0001	----
Sc	20-30 day	0.003	0.000004	----
Cr	"	0.02	0.00025	0.0064
Fe	"	1.5	0.02	0.084
Co	"	0.002	0.000025	0.0064
Ni	"	1.5	0.02	0.0064
Zn	"	0.1	0.001	0.24
Se	"	0.01	0.0001	----
Ag	"	0.1	0.001	----
Sb	"	0.08	0.001	0.040
Ce	"	0.02	0.00025	----
Hg	"	0.01	0.0001	----
Th	"	0.003	0.00004	----

*Decay time before counting. See Tables 1 and 2.

Table 4. Elements detected in suspended particulate from East Chicago, Indiana, ng/m³.

Element	1st Anal. ^a	2nd Anal. ^a	3rd Anal. ^a	4th Anal. ^a	Mean ^b
Ca	7700(1200)	6600(1000)	6650(1000)		7000(700)
Ti	225(60)	165(55)	170(60)		190(40)
V	20(1.4)	16.1(1.2)	18.2(1.3)		18.1(1.5)
Cu	1020(100)	1050(100)	1140(100)		1070(80)
Al	2370(150)	1980(130)	2200(150)		2175(170)
S	11,000(9,000)	----	15,000(9,000)		13,000(8,000)
Na	485(36)	405(35)	470(40)		455(40)
Mg	2600(750)	1650(700)	2850(800)		2400(600)
Mn	245(14)	222(12)	305(17)		255(40)
In	0.13(0.07)	0.06(0.06)	0.11(0.07)		0.10(0.05)
Br	81(9)	74(9)	94(10)		83(9)
K	1510(100)	1380(70)	1600(160)	1210(120)	1415(150)
La	5.8(0.7)	6.0(0.5)	6.5(0.6)	5.6(0.7)	5.9(0.4)
Sm	0.53(0.06)	0.35(0.04)	0.47(0.04)	0.39(0.05)	0.41(0.05)
Eu	0.165(0.03)	0.12(0.03)	0.17(0.05)	0.10(0.03)	0.135(0.02)
Cu	1150(150)	1125(150)	1200(150)	1100(150)	1150(100)
Zn	1440(150)	1370(140)	1420(140)	1365(140)	1400(100)
W	7.6(2)	5.0(1)	5.6(1)	5.2(2)	5.8(1)
Ga	1.3(0.7)	1.4(0.6)	1.2(0.8)	1.3(0.7)	1.3(0.4)
As	14.5(0.7)	8(2.5)	14(2)	12.5(3)	12(3)
Sb	25(3)	24(3)	30(3)	23(4)	25(2)
Br	63(7)	68(6)	77(8)	60(7)	67(4)
Sc	3.8(0.3)	3.2(0.5)	2.1(0.2)		3.1(0.5)
Ce	15.2(2.0)	14.2(2.0)	8.6(1.5)		13(3)
Th	1.4(0.3)	1.2(0.5)	----		1.3(0.4)
Cr	137(10)	112(15)	88(10)		113(20)
Fe	17,000(1200)	13,500(1000)	10,500(1000)		13,800(3000)
Co	3.35(0.3)	2.6(0.2)	1.9(0.2)		2.6(0.6)
Ni	----	<60	----		<60
Ag	3.1(2.5)	1.8(2.0)	2.2(2.4)		2.4(1.5)
Zn	2210(240)	1450(150)	1430(140)		1690(300)
Hg	5.3(1.4)	4.4(1.3)	----		4.8(1.0)
Sb	43(4)	28(3)	23(3)		32(9)
Se	3.0(0.8)	4.6(1.4)	----		3.8(1.0)

^aStandard deviations are based on counting statistics of sample, blank, and standard.

^bStandard deviations are based on dispersion of replicate analyses.

Table 5. Elements detected in suspended particulate from Niles, Michigan, ng/m³.

Element	1st Anal. ^a	2nd Anal. ^a	3rd Anal. ^a	4th Anal. ^a	Mean ^b
Ca	600(200)	1100(300)	1150(280)		1000(200)
Ti	105(35)	105(35)	150(40)		120(25)
V	5.0(0.5)	5.2(0.5)	4.9(0.5)		5.0(0.3)
Cu	250(30)	290(35)	325(37)		290(30)
Al	1100(100)	1240(80)	1280(85)		1200(70)
S	9,000(6,000)	9,000(6,000)	16,000(8,000)		11,000(5,000)
Na	140(18)	180(20)	175(20)		170(20)
Mg	350(400)	680(400)	----		500(300)
Mn	58(3)	62(4)	67(5)		62(4)
In	0.04(0.03)	0.04(0.03)	0.03(0.03)		0.04(0.03)
Br	34(4)	28(4)	34(5)		32(3)
K	740(40)	930(50)	660(30)	700(30)	750(100)
La	1.4(0.2)	1.7(0.2)	1.1(0.2)	1.0(0.2)	1.3(0.3)
Sm	0.26(0.01)	0.30(0.01)	0.21(0.02)	0.20(0.02)	0.24(0.03)
Eu	0.05(0.017)	0.065(0.021)	0.045(0.009)	0.06(0.010)	0.055(0.008)
Cu	260(35)	260(35)	245(35)	305(35)	270(25)
Zn	124(33)	186(40)	132(20)	113(20)	140(20)
W	0.4(0.2)	0.2(0.2)	0.55(0.2)	0.4(0.2)	0.4(0.1)
Ga	1.1(0.6)	1.0(0.6)	0.7(0.4)	0.9(0.4)	0.9(0.4)
As	4.4(2)	5.2(2)	4.8(2)	4.0(2)	4.6(2)
Sb	5.4(1)	7.0(1)	5.7(1)	4.7(0.8)	5.8(0.6)
Br	46(2)	55(3)	35(2)	38(2)	43(5)
Sc	1.2(0.1)	1.2(0.1)			1.2(0.1)
Ce	0.77(0.1)	0.86(0.1)			0.82(0.10)
Th	0.28(0.04)	0.26(0.04)			0.27(0.03)
Cr	9.1(0.8)	10.0(0.8)			9.5(0.8)
Fe	1900(100)	1840(100)			1900(100)
Co	1.0(0.1)	0.90(0.08)			0.95(0.10)
Ni	----	----			----
Ag	<1	<1			<1
Zn	185(10)	172(10)			180(10)
Hg	2.0(0.6)	1.7(0.6)			1.9(0.3)
Sb	6.6(0.7)	6.1(0.5)			6.3(0.5)
Se	2.5(0.6)	2.5(0.6)			2.5(0.5)

^aStandard deviations are based on counting statistics of sample, blank, and standard.

^bStandard deviations are based on dispersion of replicate analyses.

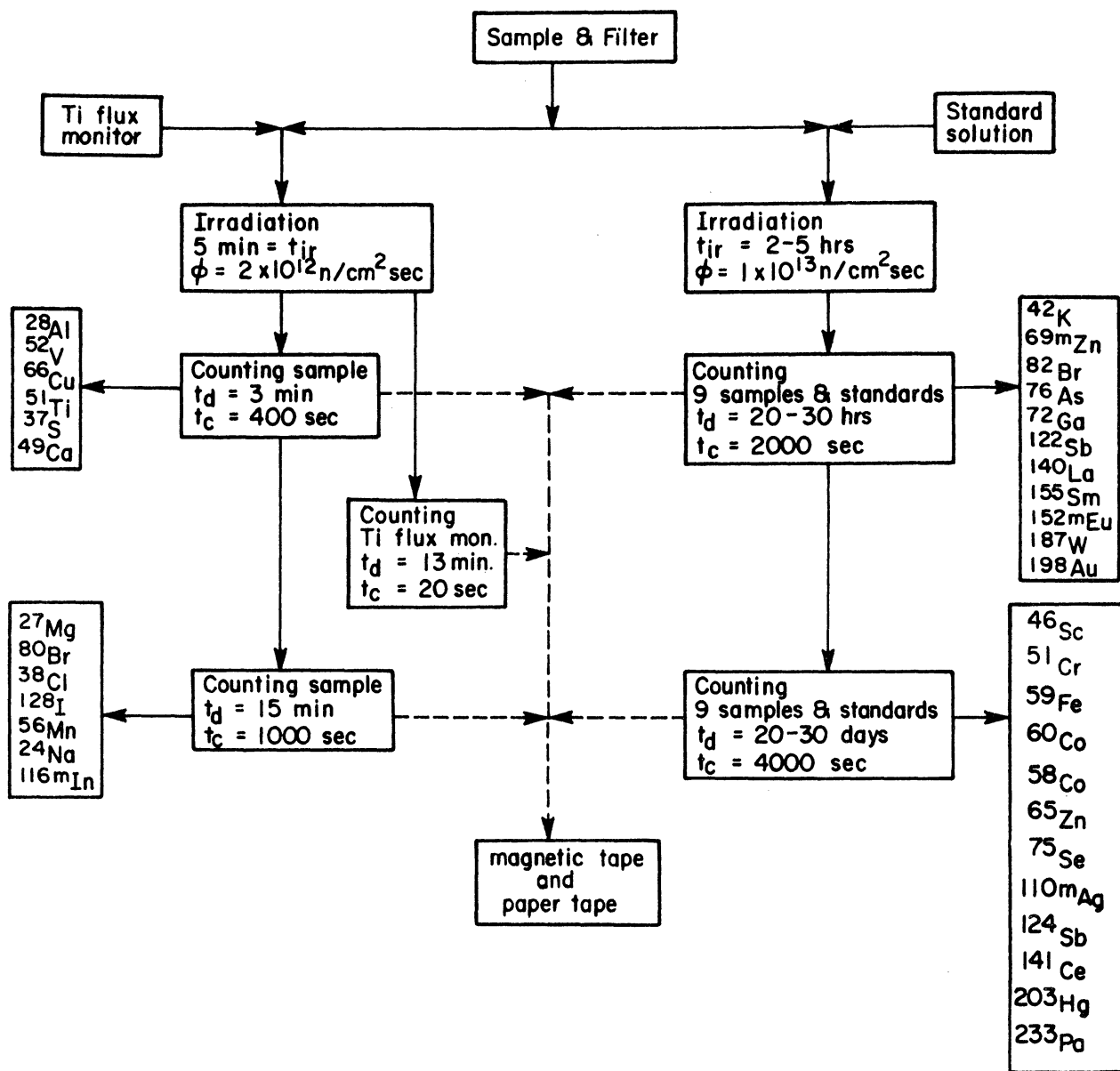
Table 6. Ratios of concentrations found, East Chicago/Niles.

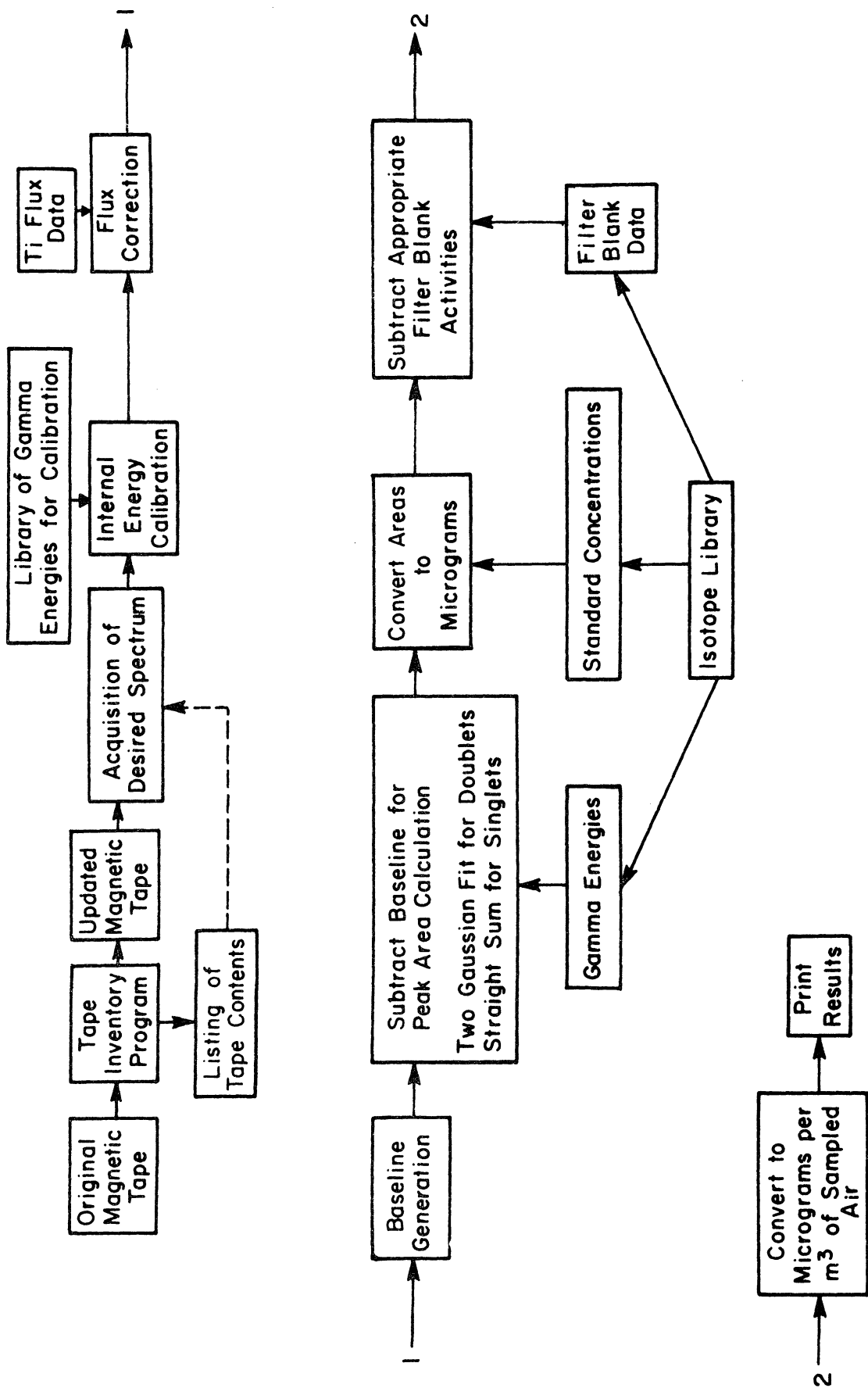
3 & 15 min. decay		20-30 hr. decay		20-30 day decay	
Ca	7.0 ± 1.5	K	1.9 ± 0.3	Sc	2.6 ± 0.4
Ti	1.6 ± 0.6	La	4.5 ± 1.2	Ce	16.0 ± 4.0
V	3.6 ± 0.4	Sm	1.7 ± 0.3	Th	4.8 ± 1.4
Cu	3.7 ± 0.4	Eu	2.5 ± 0.4	Cr	12.0 ± 2.0
Al	1.8 ± 0.2	Cu	4.3 ± 0.6	Fe	7.3 ± 1.6
S	1.1 ± 0.8	Zn	10.0 ± 2.0	Co	2.7 ± 0.6
Na	2.7 ± 0.3	W	14.5 ± 4.5	Ag	2.4 ± 1.5
Mg	4.8 ± 3.0	Ga	1.4 ± 0.7	Zn	9.4 ± 1.7
Mn	4.1 ± 0.7	As	2.6 ± 1.3	Hg	2.5 ± 0.7
In	2.5 ± 2.0	Sb	4.3 ± 0.5	Sb	5.1 ± 1.5
Br	2.6 ± 0.4	Br	1.5 ± 0.2	Se	1.5 ± 0.5

List of Figures

Figure 1. Irradiation-Counting Scheme.

Figure 2. A simplified flow diagram of automated spectrum analysis.





Sampling Aerosols for Nondestructive Neutron Activation Analysis

K. Dams, K. A. Rahn, and J. W. Winchester
Dept. of Meteorology & Oceanography and
Great Lakes Research Division
University of Michigan
Ann Arbor, Michigan 48104

Abstract

Ten filter materials were tested for suitability for atmospheric particulate sampling and elemental analysis by nondestructive neutron activation using Ge(Li) γ -ray spectroscopy. Trace element contents in most materials are high and are often the principal limitation in analytical sensitivity. Of the commercially available filters tested, Whatman 41 cellulose has the lowest analytical blanks but may clog during prolonged sampling. For some elements Millipore membrane filters have low blanks but tend to disintegrate during neutron irradiation. Polystyrene fiber filters appear to be the most suitable if they could be made available from commercial suppliers with uniformly low blank levels.

Short Abstract

Nondestructive neutron activation analysis has been used to detect 33 elements in urban air particulates. Sensitivity of the method is limited primarily by the availability of filter materials with low analytical blanks. Of 10 filters tested, Whatman 41 cellulose is usable. However, if clean polystyrene fiber filters were commercially available, the method would be improved.

Recent years have seen an increasing interest in studies of the trace element content of aerosols, both natural and pollution derived. Their extremely complex composition, however, places great importance on sampling techniques and analytical procedure.

Because of the very low mass-mixing ratios of aerosols (10^{-5} to 10^{-8}) an important concentration must be effected before analysis becomes feasible. Therefore large volumes of air are filtered through an appropriate material and the particulate matter collected. A number of vacuum pump - filter combinations are presently used where the main variables are pump vacuum, free air capacity, filter size, particle retentivity, impurity level, and flow rate. One type of pump, the modified vacuum cleaner type used with typical 20x25 cm (8x10 inch) high volume filter holders, provides high flow rates with a relatively small vacuum if loaded with low resistivity filters. The other type, such as is used with 25 and 47 mm diameter filter holders, provides higher vacuum but has a smaller free air capacity, yielding lower flow rates. For this second type, even though the total flow rate is much lower, the higher vacuum provides a greater flow rate per surface area, which for equal sampling times allows a greater signal/blank ratio. Moreover, this type can be equipped with high resistance filters.

A number of different filter materials have been used, common ones being either the fibrous type, employing cellulose or synthetic organic fibers, and the membrane type. An excellent study of the physical characteristics of a large number of filter media was made by Lockhart and Patterson (1964) and Keane and Fisher (1968) using nondestructive neutron activation analysis and NaI(Tl) γ -ray spectroscopy, have determined 7 inorganic impurity levels in a number of the commoner types. In the present work several of these filters were tested more extensively for

their inorganic element content, with a view toward nondestructive neutron activation analysis of the sample collected on them.

In urban and rural air individual trace element components of aerosols usually have very low concentrations (10^{-2} - 10^{+3} ng/m³ of air), and a combination of high filtration rate and sensitive analytical technique is needed in order to reduce sampling times to reasonable levels. Because of the chemical complexity of the collected sample, simultaneous determination of many elements becomes especially important. In addition, large numbers of samples generally must be analyzed before valid conclusions may be drawn. These three conditions (chemical complexity, low concentrations, large sample numbers) call for an instrumental approach, allowing rapid analysis to be performed routinely by an essentially unskilled operator. Until recent times mainly a spectrographic method has been used for the determination of metals, some fifteen in number (USPHS, 1968). The sensitivity of this method, however, is often not high enough. Therefore neutron activation analysis is becoming more and more recognized as a powerful tool in aerosol trace element studies (Brar et al. 1969, 1970). It is extremely sensitive, very selective when high resolution gamma-ray spectrometry is used, and can be performed nondestructively, resulting in an almost completely automated analysis.

Nondestructive Neutron Activation Analysis

A nondestructive activation analysis procedure for the simultaneous determination of a large number of elements on an aerosol filter sample has been developed (Dams et al., in prep.). Filter samples are packed in polyethylene and irradiated twice in the Ford Nuclear Reactor at the University of Michigan, once for 5 minutes at a neutron flux of 2×10^{12} neutrons/cm²-sec, then later for 5 hours at a 5 times higher flux. Each sample is counted 4 times with a 30 cm³ high resolution germanium-lithium γ -ray diode coupled to a 4096 channel analyzer, at respectively 3 minutes

and 15 minutes, or 20 hours and 20 days after the irradiations, allowing detection of isotopes with half lives ranging from minutes to years. The gamma spectra are stored on magnetic tape for computer assisted analysis. This automatic data reduction process calculates elemental ambient air concentrations by comparison of the decay rates of isotopes in the sample with those in a standard, subtraction of filter blank values, and division by the appropriate volume of air. Aliquot parts of the filter used ranged from 1 to 20 cm², depending on the volume of air sampled and the pollution level of the site. Table I shows that up to 33 elements can be determined from a single sample, after which it is still available for other investigations. For those elements determined from the short irradiation the time between receipt of sample and calculation of concentrations may be less than 1 hour, especially important for general monitoring where results may be used as a warning of critically high pollution levels. Column 5 of this table illustrates the sensitivity of the method. Comparison of these detection limits with some typical rural (Niles, Michigan) or heavily polluted (East Chicago, Indiana) concentrations shows that for a number of elements sample sizes can be reduced to some m³ of air, requiring only short collection times if high flow rates can be effected.

The reproducibility of the method is adequate (10%) when concentrations several times higher than the detection limit were determined.

Analysis of Filter Media

The ultimate sensitivity of a nondestructive technique of analysis, especially activation analysis, is in practice limited by the presence in the filter material of interfering elements such as metals and halogens. There presently exists a large stockpile of particulate samples taken at the local, state, and national level, the vast majority of which are on 20x25 cm (8x10 inch) glass fiber filters. Though glass fiber filters from different manufacturers may differ in their content of various inorganic materials, all of them introduce high blanks into ordinary

destructive analysis. For nondestructive neutron activation analysis they are completely unusable because of the presence of minor constituents such as Na, Al, Ca, V, K, Mn, Mg, and Ba. Therefore our search for a commercially available filter suitable for nondestructive analysis emerged as a problem of prime importance.

The above results from Niles and East Chicago were obtained using a small supply of a reference polystyrene filter not now commercially available and whose reserves are now nearly depleted.

Experimental

Using the review of Lockhart and Patterson (1964) as a guide, we selected a number of filters whose physical properties were suitable and which were expected to contain only low concentrations of inorganic materials. These included a commercially available polystyrene (Delbag Microsorban), a tightly packed cellulose (Whatman #41), a loosely woven cellulose-base, and various halogen-free membranes of pore size 0.45 μm and 0.8 μm . Table II summarizes these materials and their manufacturers. Impurity levels of several elements were determined in each of these materials. The results, summarized in Table III, can be compared to the concentrations in the reference polystyrene(PS). Elements not mentioned have concentrations below the detection limit of the method. Membrane filters EHWPO47 and GA-6 were only analyzed for elements with short lived isotopes.

Flow Rates

To ensure a high sensitivity, a filter should not only contain low concentrations of interfering elements, but also allow a high flow rate. As mentioned earlier, flow rates depend both on the resistivity of the filter, on the pump vacuum and on the free air capacity. The use of small filter holders and a pump with high vacuum but low free air capacity often yields a higher signal/blank ratio. For highly sensitive analytical methods such as neutron activation, this "purity" of signal obtained with the high vacuum pumps may be of greater importance than the greatly increased but less "pure" signal from high volume pumps. For

research purposes then, sampling may often be performed better and at lower cost on the smaller filters. However, the effective surface area of these filters is much smaller than their nominal area. The unexposed zones at the edge represent 25% of the total for a 25 mm filter, and 45% for the 47 mm size. Samples to be analyzed from 20x25 cm filters can be cut wholly from the exposed portion, resulting in 100% efficiency.

Experimental

In the present work flow rates were measured in the 20x25 cm format (when filters were available), using the recommended General Metal Works high volume pump (model GMWL 2000). For the 25 and 27 mm sizes, flow rates were measured with a Gelman Twin Cylinder pump (model NO) with a free air capacity of 68 ft^3/min and a maximum vacuum of 66 cm Hg. Table IV shows the results as flow rates over the "effective" surface of the filter.

Filtering Performances of the Materials

A filter should have a high particle retentivity down to a radius of 0.1 μm and a small decrease in flow rate due to dust loading.

Filter retentivity depends on a number of properties of the filter itself, such as pore size, total thickness, density, and ease of production of electrostatic charges by the flowing air. Besides the obvious dependence on particle size, retentivity varies also with the linear velocity of the particles, which dependence differs significantly among the filter types considered here. Lockhart and Patterson (1964) found that with increasing air velocities membrane filters show an increase in penetration, Whatman #41 shows a decrease, and polystyrene shows a slight maximum at medium velocities. Table IV gives the percentage penetration of a 0.3 μm dioctyl phthalate (DOP) aerosol, as measured by these authors at the air velocity obtained through a 25 mm diameter disc and a 20x25 cm filter.

Decrease in flow rate from dust loading becomes important for collection times of 24 hours or more. The same authors measured this loss. Table IV

gives the number of cubic meters of air filtered per cm^2 of filter area needed to cause a 10% reduction in flow rate. These numbers of course depend largely on atmospheric particulate loading, a function of site and season.

Experimental

Because some elements may be preferentially found on small particles it is also of interest to determine the degree of penetration, element by element, of actually occurring aerosols. An experiment was performed with two 20x25 cm polystyrene filters placed on top of each other, a primary (upper) and backup (lower) filter. Only 5% of the Zn, 2.5% of the Br, 5% of La and Sm and 1% of the Al were found on the backup filter. The other elements could not be detected on the backup filter. It appeared, however, that the sheets of this filter medium were not very homogeneous, differences in thickness of a factor of two being not uncommon. Also the effect of dust loading was investigated on Whatman #41, Cellulose-base and HAWPO47 in Ann Arbor, Michigan. Figure 1 and Table IV show the results. It is obvious that airflow readings should be taken at intervals throughout a long sampling period if a filter is used which has a high tendency to plug due to dust loading.

Discussion

A figure of merit incorporating several of the previous factors, namely the impurity levels per total 25mm filter, the plugging, and the flow rates per effective surface, is the length of sampling time necessary to collect an amount of a given element equal to the amount present as impurity within the filter. Table V gives these numbers, for both a rural concentration (Niles, Michigan) and a heavily polluted concentration (East Chicago, Indiana).

Table III showed that the reference polystyrene contains large concentrations of Ba and Cl, precluding the nondestructive determination of both elements. Fortunately neither has a high enough neutron cross section to strongly interfere with the measurement of other isotopes. The radioactivity induced in the Ba

impurity may be used as an internal standard to correct for differences in thickness of the material and may thus allow the subtraction of (adjusted) blank values for the other elements. Comparison of columns 2 and 3 of Table V illustrates that the sensitivity of determination for several elements collected on polystyrene is limited by the filter impurity levels rather than by the inherent sensitivity of the procedure, examples being Cl, Br, Na, Cu, Al, Mn, Zn and Sb. This condition also obtains for various elements in each of the other filters.

From a comparison of the impurity levels of the other filters with this polystyrene it first appears that the cellulose base and the membrane filters EHWPO47 and GA-6 have much higher blanks, restricting their application to sampling in highly polluted areas. Delbag Microsorban contains important amounts of Cl, Br, Cu, and Zn, which not only preclude a sensitive determination of these elements but due to the high neutron cross section of Br also increase the detection limit of at least 15 other elements by an order of magnitude. (Columns 4 and 11 of Table V do not take into account this additional interference.) The membrane filters HA and AA have blank values quite similar to the polystyrene, but with slightly higher concentrations of Na, Cr, and Cu. However, their lower flow rates raise the minimum sampling times considerably (Table V). All the blank values of Whatman #41 compare favorably with polystyrene, especially the Cl concentration (30 times lower).

Table IV displays a sharp contrast between fibrous and membrane filters. The latter generally show high flow resistance, not only resulting in low flow rates through 47 and 25 mm discs, but also rendering them unusable with the 20x25 cm high volume samplers, where the available vacuum is smaller. They have extremely high retentivities, even for small particles at high velocities. Flow rates decrease reasonably fast due to dust loading, but not enough to be a problem. Since retentivities are so nearly equal between the two pore sizes investigated, the 75% greater flow rate of the 0.8 μm type represents a real sampling advantage over the 0.45 μm size. It should also be pointed out that the handling of samples

collected on membrane filters is very difficult, especially after irradiation.

Complete recovery of the membrane filter and sample for counting after irradiation requires dissolution in an organic solvent such as acetone. The procedure is then no longer nondestructive, and the sample is lost for further investigation.

Of the fibrous filter group, the polystyrenes (PS and DMS) combine high flow rates, high retentivities, and a very small tendency to plug. Even at lower velocities (20x25 cm sampling) elements such as Br and Zn, often found predominantly on the smaller particles, are retained with greater than 95% efficiency.

The Whatman #41 filter also allows high flow rates but has a lower overall retentivity than the polystyrenes. This difference is insignificant at high particle velocities (such as obtained through a 25 mm filter) but at the lower velocities typical of 20x25 cm high volume systems the penetration of small particles may be troublesome in critical air sampling studies. When samples of 24 hours or longer are taken in heavily polluted areas the decrease in flow rates from dust loading may cause a problem. If the flow rate decrease is almost linear with time over the sampling period, an average value between initial and final readings may be sufficiently accurate.

The cellulose filter allows a very high flow rate but has a poor filtering performance because of the very low retentivity of small particles. It can profitably be used for less critical general monitoring and control purposes, especially in heavily polluted areas where its virtual freedom from clogging may be employed to greatest advantage.

Conclusions

1) It is clear that there is no single ideal filter medium compatible with all objectives of air sampling. The availability of a homogeneous filter with the performance characteristics of polystyrene (glass fiber) but with lower concentrations of Cl, Br, Cu, and Zn than presently available is highly desirable.

Such a filter could be routinely used both for control and research purposes, and workers in both these fields could freely exchange samples, a decided advantage over the present situation. Not only would needless duplication of sampling efforts be eliminated, but filter stockpiles of the new material would become open to survey type trace metal studies by the more sensitive methods such as nondestructive neutron activation analysis.

2) From the presently commercially available and investigated filter materials Whatman #41 can for 20x25 cm high volume sampling fairly satisfactorily replace the reference polystyrene. It has very low impurity levels, a low flow resistance, is inexpensive, easy to handle and is obtainable in reproducible and homogeneous thickness and quality. Two important disadvantages are the high degree of penetration of small particles and decrease of flow rate due to dust loading. The penetration can however be drastically reduced either by the use of two layers or by higher flow rates. In heavily polluted areas where dust loading may be a problem also the use of two layers of cellulose can be considered. For research purposes sampling with much smaller filter sizes, especially the 25 mm diameter disc, may often be advisable. The choice between Whatman #41 and 0.8 μm pore size Millipore membrane should be resolved by the objective of the sampling.

References

- S.S. Brar, D.M. Nelson, E.L. Kanabrocki, E.E. Moore, C.D. Burnham, and D.M. Hattori, Proceedings 1968 Int. Conf. "Modern Trends in Activation Analysis", Gaithersburg, Maryland, 43 (1969).
- S.S. Brar, D.M. Nelson, E.L. Kanabrocki, E.E. Moore, C.D. Burnham, and D.M. Hattori, Environ. Sci. Technol., 4, 50 (1970).
- R. Dams, J.A. Robbins, K.A. Rahn, and J.W. Winchester (in preparation).
- J.R. Keane and E.M.R. Fisher, Atmospheric Environment, 2, 603 (1968).
- L.B. Lockhart and R.L. Patterson, NRL Report 6054, U.S. Naval Research Laboratory, Washington, D.C. (1964).
- U.S. Public Health Service, Air Quality Data from the National Air Sampling Networks and Contributing State and Local Networks, 1966 Edition, Durham, N.C. (1968).

This work was supported in part by the U.S. Atomic Energy Commission under Contract No. AT(11-1)-1705. We are highly indebted to Dr. S.S. Brar of Argonne National Laboratory for providing us with the reference polystyrene filter material. Contribution No. from the Department of Meteorology and Oceanography and No. from the Great Lakes Research Division, University of Michigan.

Figure caption: Fig. 1 Effect of dust loading on flow rate during continuous air sampling at Ann Arbor, Michigan, for three filter materials.

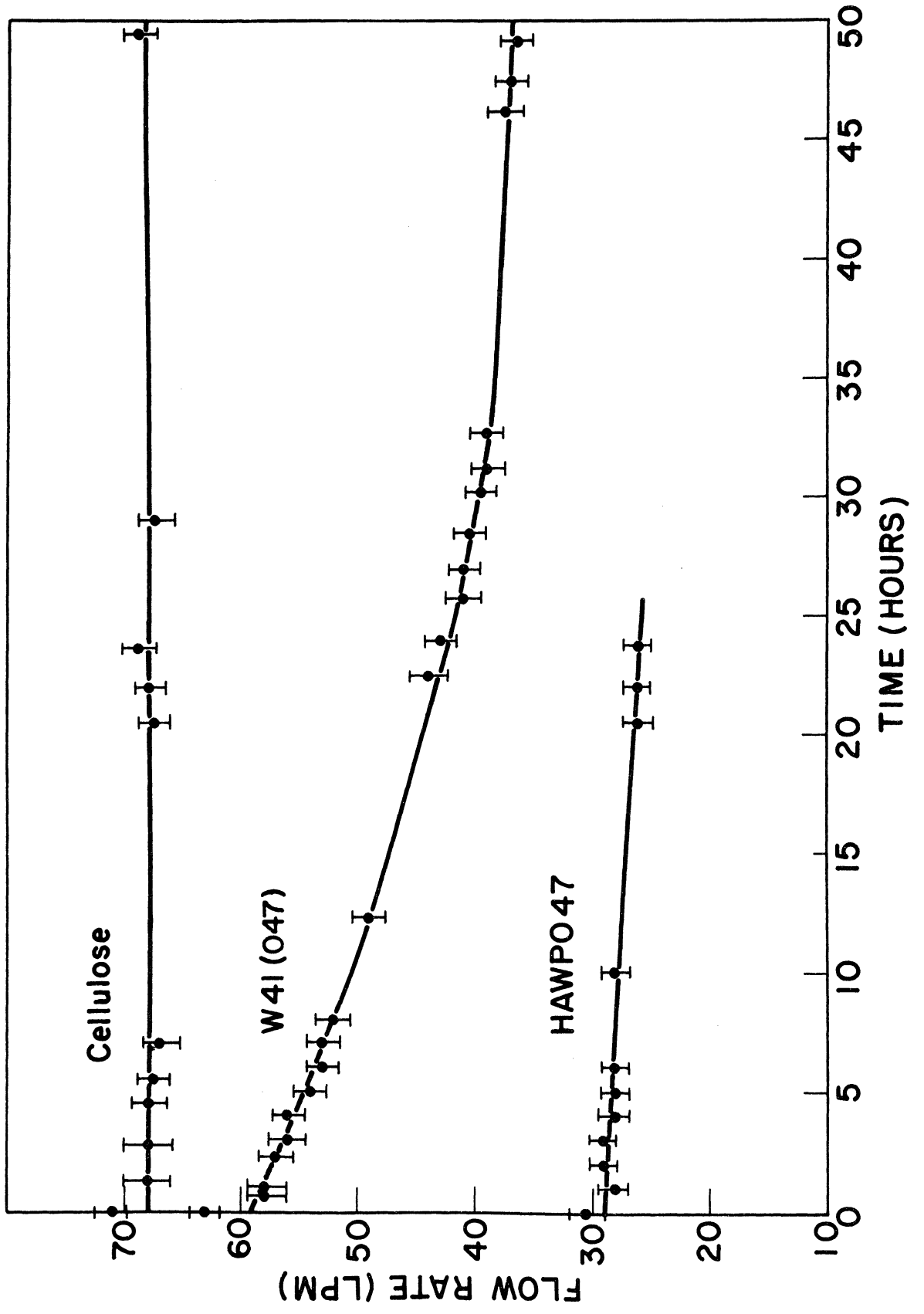


Table I: Nondestructive Activation Analysis of Aerosols

Element	$t_{\text{irradiation}}$	t_{cooling}	t_{counting}	Detection limit, ng	Concentration, ng/m ³ air	
					Niles, Michigan*	East Chicago, Indiana**
Al	5 min.	3 min.	400 sec.	40	800	1,000
V	"	"	"	1	3	10
Cu	"	"	"	100	30	900
Ti	"	"	"	200	100	100
S	"	"	"	25,000	---	10,000
Ca	"	"	"	1,000	900	4,000
Mg	"	15 min.	1000 sec.	3,000	800	1,000
Br	"	"	"	20	70	50
Cl	"	"	"	500	---	---
Mn	"	"	"	3	30	100
Na	"	"	"	200	200	300
In	"	"	"	0.2	0.02	0.05
K	5 hours	20-30 hours	2000 sec.	75	400	1,000
Zn	"	"	"	200	50	3,000
Br	"	"	"	25	50	70
As	"	"	"	40	0.05	10
Ga	"	"	"	10	---	1
La	"	"	"	2	1	6
Sm	"	"	"	0.05	0.1	0.4
Eu	"	"	"	0.1	0.04	0.1
Sb	"	"	"	30	1	30
W	"	"	"	5	---	6
Au	"	"	"	1	0.1	---
Sc	"	20-25 days	4000 sec.	0.3	0.5	3
Cr	"	"	"	20	10	100
Co	"	"	"	2	0.3	3
Fe	"	"	"	1,500	600	10,000
Ni	"	"	"	1,500	---	---
Zn	"	"	"	100	60	2,000
Se	"	"	"	---	---	2
Ag	"	"	"	10	---	3
Sb	"	"	"	8	2	30
Ce	"	"	"	20	2	10
Hg	"	"	"	10	---	4
Th	"	"	"	3	0.4	1

* Average concentrations over 36 hours, 21-22 August 1969, 1-5 m above ground, wind variable < 1 m/sec. at rural location 5 km from Niles, Michigan.

** Average concentrations over 24 hours, 11 June 1969, 3 m above ground, wind south 5-10 m/sec, in industrial area ~1 km from Lake Michigan.

Table II: Filter Material Investigated

Filter Material	Manufacturer's Name	(Key)	Specifications	Manufacturer
Polystyrene	----	(PS)	----	----
"	Microsorban	(DMS)	----	Delbag Luftfilter (Germany)
Cellulose- organic binder	Whatman 41	(W41)	----	W. and R. Balston Ltd. (England)
Cellulose	----	(C)	----	C.H. Dexter and Son (U.S.A.)
Membrane cellulose esters	MF-Millipore	(HAWPO25)	Pore size 0.45 μm , diameter 25 mm	Millipore Filter Corp. (U.S.A.)
"	MF-Millipore	(HAWPO47)	Pore size 0.45 μm , diameter 47 mm	"
"	MF-Millipore	(AAWPO25)	Pore size 0.8 μm , diameter 25 mm	"
"	MF-Millipore	(AAWPO47)	Pore size 0.8 μm , diameter 47 mm	"
Membrane cellulose acetate	Cellotate	(EHWPO47)	Pore size 0.5 μm , diameter 47 mm	"
Membrane cellulose triacetate	Metrical	(GA-6)	Pore size 0.45 μm , diameter 47 mm	Gelman Instrument Co. (U.S.A.)

Table III: Filter Impurity Levels (ng/cm²)

	PS	DMS	W41	C	HAWPO25	HAWPO47	AAWPO25	AAWPO47	EHWPO47	GA-6
Cl	3,000	27,000	100	300	1,000	1,000	1,700	1,000	1,800	600
Br	25	1,000	5	20	4	3	< 5	< 2	6	4
S	---	+30,000	---	6,000	---	---	4,800	---	---	---
Na	80	90	150	700	600	330	520	400	1,800	2,200
K	20	8	15	200	130	100	120	100	---	---
Mg	< 200	< 1,500	< 80	2,400	< 300	< 200	400	200	---	---
Ca	300	300	140	3,800	670	250	500	370	570	1,250
Ba	7,000	< 500	< 100	< 100	< 100	< 100	< 100	< 100	---	---
Al	20	20	12	200	20	10	15	10	60	740
Sc	0.04	< 0.01	< 0.05	0.2	< 0.05	< 0.01	< 0.01	< 0.05	---	---
Ce	< 0.4	< 1	< 0.5	< 0.3	< 0.5	< 1	< 0.5	< 0.3	---	---
La	< 0.2	< 0.1	< 0.2	< 0.3	< 0.1	< 0.2	< 0.5	< 0.2	---	---
Ti	10	70	10	50	15	5	10	< 10	---	---
Fe	100	85	40	300	40	< 300	80	40	---	---
Mn	1	2	0.5	80	7	2	2.5	2	6	2
Co	0.2	0.2	0.1	0.8	0.2	< 1	0.4	0.1	---	---
Ni	25	< 25	< 10	60	< 8	< 50	14	< 20	---	---
Ag	< 2	< 2	2	3	< 4	---	< 3	< 1	---	---
Cu	10	320	< 4	90	20	40	85	60	25	30
Zn	60	515	< 25	30	25	20	10	7	---	---
Sb	2.5	1	0.15	0.5	0.5	3	0.4	1	---	---
Cr	5	2	3	12	15	14	20	15	---	---
Hg	3	1	0.5	3	< 0.4	< 1	< 1	0.5	---	---
V	0.06	< 0.6	< 0.03	0.5	< 0.06	0.09	< 0.2	< 0.05	< 0.05	< 0.05

(-) not determined

Table IV: Flow Rates, Retentions and Loading Losses of Filters

Filter material	PS	DMS	W41	C	HAWPO25	HAWPO47	AAWPO25	AAWPO47	EHWPO47	GA-6
Flow rate (l-min. $\frac{-1}{-1}$ cm $^{-2}$) 20x25 cm (effective surface 400 cm 2)	4.5	4.5	4.5	6	---	---	---	---	---	---
Flow rate (l-min. $\frac{-1}{-1}$ cm $^{-2}$) 47mm diameter (effective surface 9.62 cm 2)	6.5	6.5	6.5	7	---	2.6	---	4.8	2.6	2.6
Flow rate (l-min. $\frac{-1}{-1}$ cm $^{-2}$) 25mm diameter (effective surface 3.68 cm 2)	12	13	13	17	4.3	---	7.3	---	---	---
Retention (%) of 0.3 μ m D.O.P. aerosol (25mm diameter) Determined by Lockhart and Patterson (1964)	99.96	99.95	99.7	---	>99.98	---	99.97	---	---	---
Retention (%) of 0.3 μ m D.O.P. aerosol (20x25 cm) Determined by Lockhart and Patterson (1964)	99.8	99.7	91	80**	---	---	---	---	---	---
Volume filtered at 10% reduction in flow - (m 3 air/cm 2 filter) Determined by Lockhart and Patterson (1964)	48	35	2.0	>50*	4.1*	4.1*	6.3	6.3	---	---
			2.8*							

*Determined by the authors in Ann Arbor, Michigan

**Determined by Brar et al. (1969) for total particulate by weight in Chicago

Table V: Sampling Times to Equal Blank Values or Detection Limits

Element	Sampling time at Niles in hours on 25mm filter disc to equal:				Sampling time at East Chicago in hours on 25 mm filter disc to equal:									
	Detection Limit	PS Blank	DMS Blank	W41 Blank	C Blank	HAWPO25 Blank	AAWPO25 Blank	Detection Limit	PS Blank	DMS Blank	W41 Blank	C Blank	HAWPO25 Blank	AAWPO25 Blank
Cl	2	60	500	1.7	4	50	50	1.2	35	300	1	2.5	30	30
Br	0.15	0.8	29	0.15	0.4	0.35	---	0.15	0.8	29	0.15	0.4	0.35	---
Na	0.5	1	0.9	1.5	5	18	9	0.3	0.5	0.5	0.9	3	10	5
K	0.1	0.1	0.04	0.085	0.8	2.2	1	0.025	0.03	0.01	0.02	0.2	0.55	0.3
Mg	1.5	---	---	---	4	---	1.5	1	---	---	---	2.5	---	1
Ca	0.5	0.7	0.6	0.25	5.5	3.8	1.7	0.15	0.15	0.15	0.065	1.5	0.9	0.4
Al	0.02	0.05	0.04	0.025	0.3	0.15	0.06	0.01	0.03	0.025	0.015	0.2	0.075	0.035
Ti	0.6	0.2	1	0.1	0.5	0.7	0.35	0.8	0.3	1.5	0.20	0.75	1.0	0.5
Fe	1	0.3	0.25	0.1	0.6	0.35	0.4	0.04	0.015	0.010	0.005	0.025	0.015	0.02
Mn	0.05	0.08	0.15	0.035	4	1.5	0.3	0.01	0.015	0.025	0.006	0.7	0.25	0.05
Co	2.8	1.5	1	0.6	3.3	3.5	4	0.3	0.15	0.15	0.07	0.4	0.4	0.5
Cu	2	1	25	---	5	5	12	0.05	0.02	0.4	---	0.12	0.1	0.3
Zn	0.7	2.5	18	---	0.75	2.5	0.6	0.02	0.06	0.45	---	0.02	0.065	0.015
Sb	2	3.5	1.5	0.2	0.5	2	1	0.1	0.15	0.05	0.009	0.02	0.08	0.04
Cr	0.8	1	0.35	0.5	1.5	7.8	6	0.08	0.1	0.35	0.05	0.15	0.78	0.6

(-) If for the blank value only a higher limit was found or if it was not determined.

AREAWIDE TRACE METAL CONCENTRATIONS IN NORTHWEST INDIANA AS

DETERMINED BY MULTIELEMENT NEUTRON ACTIVATION ANALYSIS:

A ONE DAY STUDY

P.R. Harrison^a, K.A. Rahn^{*}, R. Dams^b, J.A. Robbins, and J.W. Winchester^c

Department of Meteorology and Oceanography
and
Great Lakes Research Division
University of Michigan
Ann Arbor, Michigan 48104

S.S. Brar and D.M. Nelson
Divisions of Biology and Radiological Physics
Argonne National Laboratory
Argonne, Illinois 60439

- a) Present address: Dept. of Environmental Control, 320 N. Clark St., Chicago, Illinois 60610.
- b) Present address: Institute for Nuclear Sciences, University of Ghent, Belgium.
- c) Present address: Dept. of Oceanography, Florida State University, Tallahassee, Florida 32306.

*Please direct inquiries and reprint requests to Mr. K.A. Rahn, Dept. of Meteorology & Oceanography, University of Michigan, Ann Arbor, MI 48104.

ABSTRACT

A suite of 24 hour high volume air particulate samples, collected June 11-12, 1969 at 25 locations in the Northwest Indiana area, has been analyzed by nondestructive neutron activation analysis for 30 trace elements. The use of Ge(Li) gamma-ray spectrometry and computer assisted data reduction, combined with 2-4 replications of each analysis, yielded precise results which allowed a study of the geographical distribution patterns of the elements. Some elements, such as Na, K, Ti, Al, Sm, and Eu, show only minor concentration variations over the area, while others, such as Cu, W, Cr, Zn, Sb, Ga, Br, Ag, Fe, and Ce, show large variations, indicative of important local sources. Similar distribution patterns and high correlation coefficients suggest common sources for several elements. The variations of most heavy elements significantly exceed previously reported variations of total particulate, indicating the latter to be an unsatisfactory guide for elemental distribution, especially near pollution sources. Three representative locations for measurement of elemental abundances in the area are suggested. The influence of meteorological conditions and the potential Lake Michigan pollution hazard are discussed.

INTRODUCTION

Extensive monitoring of atmospheric pollutants has until recent years been generally limited to trace gases and total suspended particulate, with the elemental composition of the latter being left undetermined. While knowledge of total particulate may be adequate to assess nuisance levels, evaluation of any more serious potential hazards requires explicit concentrations of individual pollutants. Since a number of trace elements are strongly suspected to be toxic when inhaled in sufficient concentrations, typical exposures for representative individuals derived from ambient trace element concentrations constitute significant basic data.

Because of their integrated chemical nature total suspended particulate levels should show smaller spatial fluctuations than should those of individual elements, especially in industrialized regions containing strong point sources of different chemical compositions. Areawide simultaneous multiple-point sampling such as reported here may be effective in delineating the elemental concentration patterns and the degree to which they may differ from the pattern of suspended particulate.

Areawide sampling is not new indeed; local control agencies routinely sample gases and particulate at up to a dozen locations, depending on the size of the community. One of the most extensive areawide studies was performed in Nashville (1), with 119 sampling locations in and around the city. Results from measurements of sulfur dioxide, soiling index, dustfall and total particulate have provided useful guidelines for the planning of future studies of these parameters, but no aerosol trace elements were determined. Though the National Air Sampling Network, with some 250 urban and nonurban stations, generally uses only one site per city, large urban complexes may contain more than one, creating loose networks. These filters are analyzed for 16 elements in addition to total particulate, but the single sampling point per city, though perhaps satisfying some receptor criteria,

may not reveal the full range of concentrations to which various individuals are exposed.

A limited number of investigations have been reported where simultaneous samples from a closely spaced grid were given multielement analysis (2,3,4,5,6). One of these, an elaborate study in the Detroit, Michigan-Windsor, Ontario area by the International Joint Commission (2), included 24-hour particulate sampling during 6 weeks at 31 stations in Detroit. Mean suspended particulate levels varied smoothly from station to station over a factor of 2.9. 22 elements were determined spectroscopically, with concentrations tending toward uniformity over the network, except for one or two stations per element with higher values. These stations, though typically near industrialized areas, were not always the same for the different elements, and presumably reflected specific sources.

More recently Munn et al. (3) found from a 7 station network in the Windsor area that the distribution of suspended iron did not coincide with the distribution of the total suspended particulate. While the particulate measurements pointed toward the central Detroit urban area, the iron concentrations increased toward the major steel mills farther to the south. Using a 3 station network in New York City, Kneip et al. (5) derived some positive and negative correlations between the concentrations of 8 trace elements in airborne particulates and various factors such as temperature, atmospheric stability and windspeed. The study by Brar et al. (6) involving sampling at twenty stations distributed over the Chicago urban area disclosed important spatial variations in the concentrations of several trace elements out of twenty determined. While most of the elements correlated highly with total particulate, the distributions of vanadium, mercury and cobalt showed larger concentration gradients and lower correlations.

LOCATION AND SAMPLING

A detailed study of the behavior of atmospheric pollutants in the southern Lake Michigan area is highly desirable from several points of view (Fig. 1).

The Hammond-East Chicago-Gary-Whiting metropolitan complex area is one of the nation's largest industrial areas, with three large steel mills and four large petroleum refineries situated along the shoreline dominating the area. Other important industries are foundries, steel fabricators and chemical plants, as well as a large cement manufacturing plant and two large power utilities. The "Air Pollution Inventory" (18) of the area shows that particulate emission from industrial processes contributes 76 percent of the total particulate matter emitted in the area. This compact clustering of major sources might provide both high concentrations and strong spatial variations of trace elements. Furthermore the variety of source processes should tend to maximize the number of detectable trace elements, a situation perhaps not desirable for standard analytical procedures but quite manageable with the application of multielemental neutron activation analysis.

A point of additional significance for the study of this area is the relationship between the source locations and the lake. As shown in Figures 1 and 2 the metropolitan area is located at the southwest corner of the lake, while the prevailing winds are also out of the southwest, so that on the average, air passing over this region undergoes a fairly long overwater trajectory before again meeting land. This attaches added importance to the question of the fate of the large particle aerosol component immediately following emission. Under the usual geographic conditions particles would fall out onto the surrounding land at varying distances downwind from the source, but for the Chicago-Northwest Indiana area, the lake is the downwind zone about 50 percent of the time on annual basis. With Lake Michigan water having approximately a 100 year residence time (12), soluble pollutants falling into the lake will have a long period in which to accumulate in the water, the biological material or the sediments before removal by natural flow into the downstream lakes (Huron, Erie, Ontario). By determining which elements have strong source regions in N.W. Indiana and localizing these regions

relative to the lake shore, an areawide survey can thus serve as a first step toward evaluation of the water pollution potential of the air pollution particulates.

Elements having strong sources near the lake should be expected to be transferred into the water more effectively than those simply present in the "background" both because of their locally high concentrations and possibly because of particle size distribution weighted heavily toward the larger, faster settling sizes. No particle size measurements from N.W. Indiana are included in the present work, but samples taken both on land and at various locations on the lake itself are under analysis in our laboratory, the results of which will be reported later.

For the purposes of this study a multistation inter-city sampling network was established by combining the already present facilities operated by the local communities of East Chicago, Hammond, Gary, Whiting, Lake County, Porter County, and Michigan City, at which SO₂ and suspended particulate are normally sampled. Figure 3 shows the location and numerical designation for each of these 24 sites. Table I shows their areas of jurisdiction and names. Where possible, the stations are 2-3 stories above ground, but at least for station 6 this was not the case. In an effort to obtain a measure of the more distant background, a sample was taken at a rural station (#30, Niles, Michigan), located on a farm some 100 km ENE of the metropolitan area. The sampler here was 1.5 meters above ground, over short grass.

All filters were 20x25 cm (8x10 in), exposed for 24 hours starting June 11, 1969, usually at 0000 hrs but in some cases at 0900 hours. In an effort to reduce trace element impurities in the filter to a minimum, a polystyrene material (Microsorban) was used which combines high flow rate, low analytical blanks, and ease of handling (13). It is, however, rather delicate, and its loosely woven cottonlike constitution causes a certain portion of the unexposed edge area to be retained on the high volume filter holder at removal, precluding exact weighing. For this reason no suspended particulate measurements are available for this day.

Figure 4 shows the surface weather map for 7 AM, June 11. A strong southerly flow would be expected, and was generally observed during the period at all reporting meteorological stations in the area (Fig. 3). Other meteorological data of interest are listed in Table II. As expected from the strong pressure gradient and 0.9 fractional cloud cover, the wind traces at East Chicago reveal primarily mechanical turbulence accompanied by small longer period variations of speed and direction, hourly extremes of these being 6-18 mph and 180-220°, respectively.

CHEMICAL ANALYSIS OF THE SAMPLES

Because of the low atmospheric concentration of most trace elements (10^{-3} - 10^4 ng/m³) a highly sensitive analytical method is a necessity for a study of this type. In addition, the great variety of elements present in the atmosphere places a premium on techniques which are both multielemental and highly specific.

Emission spectroscopy is used by the National Air Sampling Net work for analysis of 16 metals, but because of limited sensitivity only 9 are detected at more than 50% of the sampling sites, and several of these elements could never be detected in particulate matter collected in urban areas (17). No estimate of uncertainties in the results is included, and there is a time lag of more than one year between sample collection and analysis.

Several authors have initiated the use of neutron activation analysis for the determination of the inorganic content of airborne particulates (6,7,8,9,10, 11). We feel that this technique is a potentially powerful tool in air pollution studies, especially in light of the recent advent of extremely high resolution solid-state Ge(Li) gamma-ray detectors. These crystal diodes add much greater specificity to the already established sensitivity of activation analysis, reducing elemental interferences to levels low enough that chemical manipulations of the filter sample may often be entirely eliminated. This not only speeds the analysis rate but also opens the possibility of near automation of the technique. At the conclusion of a nondestructive analysis, the chemically unchanged sample is

available for analysis by other techniques. With this in mind we developed a procedure which allows the determination of up to 33 elements in air particulates by nondestructive neutron activation analysis, employing high resolution Ge(Li) gamma-ray spectrometry in combination with computer assisted data reduction. Because a detailed outline of this procedure has been given elsewhere (14) only a brief description will be given here.

Various sized sections of each filter sample were irradiated three times (Ford Nuclear Reactor, University of Michigan) and counted four times, according to the sequence of Table III. Because of the ease of sample handling and high degree of reproducibility of both sample placement in the reactor and actual length of irradiation offered by pneumatic tubes, a fixed cooling and counting sequence was adopted for the short lived isotopes, using a flux monitor for small corrections due to variations in neutron flux. Once standards were run with the flux monitor, only the monitor itself accompanied the samples on later runs, substantially reducing counting times.

In this study the two longer irradiations were run separately, usually for respective times of 2 and 5 hours, but can easily be combined into a single 3-5 hour irradiation. Each irradiation consisted of 6-8 samples in heat sealed polyethylene tubes, accompanied by 1-2 standards, similarly sealed.

At the conclusion of each count the spectrum was recorded on 7 track magnetic tape for subsequent computer-assisted analysis. The program determines masses of elements by a comparison of decay rates between unknown sample and known standard, then subtracts filter blanks and divides by the appropriate volume of air, giving the final results element by element as nanograms per cubic meter of air.

The accuracy of the determinations was tested by running well-known standards as unknown samples. Four elements (Cu, Sb, Br, Zn) are independently determined from two different isotopes, usually from a different part of the filter and a different irradiation and always from different counts, and compared to different

standards. A good agreement of these different determinations points again towards a good accuracy of the analytical result.

It appeared from the actual analyses that when maximum accuracy is desired replication of analyses is advantageous. Because of the pilot study nature of this application and the desire to try to evaluate realistically all possible sources of error, every analysis was performed from two to four times, on different sections of the filter, and the numbers of Table IV represent mean values of these replications. Standard deviations given in parentheses were determined from the dispersion of these individual analyses, rather than from simple counting statistics alone, and represent approximately the 60-70% confidence level. Uncertainties contributing to the reported deviations include filter subdivision, spatial neutron flux variation during irradiation, counting geometry, and statistics, filter impurity inhomogeneities, and possible inhomogeneity of air flow through the filter.

RESULTS

Twenty-eight elements have been detected in nearly all the samples collected at 25 stations, while 2 other elements (Ag and Ni) could only be detected in a limited number of samples. Table IV summarizes the mean values by element and station with standard deviations. No values for Cl are given because of prohibitively high impurity levels in the polystyrene filter used, while the concentrations of the elements I and Au were below the detection limit of urban samples (13,14). In subsequent sampling on Whatman 41 filter paper and in less polluted areas both Cl and I have been regularly determined. The concentration of the elements detected ranges from 18,000 ng/m³ for S down to 0.04 ng/m³ for In. In order of decreasing maximum concentration the list reads: S, Fe, Co, Cu, Al, Mg, K, Zn, Na, Mn, Br, Ti, Cr, Sb, V, Ce, As, La, W, Ag, Hg, Se, Ga, Sc, Co, Th, Sm, Eu, and In. It can be seen that the chemical properties of the elements detected cover a wide spectrum, ranging from light alkali metals (Na, K) over rare earths (La, Sm) and heavy metals (Hg, Th) to non-metals (S, Se) and a halogen (Br). It must however be

pointed out that in its present form the procedure does not allow the measurement of some important elements such as Be, Cd and Pb.

Adequate signal for most elements determined is provided by the customary 24-hour sampling period in conjunction with a high volume pump--pure polystyrene filter combination. Indeed, sensitivities are great enough to allow drastic reductions in sampling time when required. Reproducibilities are reflected in the standard deviations of Table IV, generally in the 10-30% range but larger for elements whose concentrations were in the neighborhood of the urban detection limit (S, In, W, Ga, As, Mg, Ag, Ni). Further information about sensitivities and reproducibilities is given elsewhere (14).

DISCUSSION

The results can be considered under the following five topics.

1) Which elements have significant sources in Northwest Indiana and how well can their sources be located from the obtained concentration patterns?

A study of the concentration maps for 24 elements (Figs. 5-28) will reveal subjective differences in the areawide distributions (results for Ga, In, W, As, Ti, and Ni, having large uncertainties, were not plotted). As an aid to visualizing patterns and comparing element to element, concentration isopleths have been drawn in a geometric series at 50% of the maximum concentration, 25%, 12%, 6%, and 3%. From these and from Table IV it can be seen that some elements such as K, Ti, Al, Na, Eu, and Sm show only minor concentration variations throughout the entire 25 station network, reflected in isopleths having little pattern regularity. On the other hand, certain others such as Cu, Fe, Zn, Sb, Cr, W, and Br show much larger variations, with their isopleths revealing well-defined and often similar concentration patterns. This correlation of large concentration variations with patterned isopleths suggests that the latter group of elements may possess distinct sources in N.W. Indiana.

In an attempt to make these arguments more objective, Figure 29 shows a double plot of the ratio of maximum to minimum concentration (control station excluded) for each element, as listed in Table V. These give an idea of relative concentration gradients over the N.W. Indiana area, and seem to suggest a classification of the elements into four moderately defined groups:

- a) The single element Cu, clearly different from the others by a factor of 8, with at least one obvious source in East Chicago. The concentration maps suggest that this source may be unique for Cu. The magnitude of these gradients, the absolute concentrations, and the location of the maximum are all confirmed by Harrison (16), whose 6-day study was conducted with samples taken 1 year earlier.
- b) The other 9 elements with large concentration ratios (W, Cr, Zn, Sb, Ga, Br, Ag, Fe, Ce). These elements probably have local sources, mostly in the East Chicago area.
- c) A transitional group (Th, La, Mn, Hg, As, S, Co, Se, Mg, Ca, V) whose concentration gradients are smaller than the previous groups but probably large and consistent enough to indicate sources in the area. These sources may be more numerous but weaker than for the above groups, having a less localized and less significant net effect.
- d) A final group (Sm, Eu, Sc, Na, K, Al, Ti) whose distributions are too smooth to give definite indications of sources large relative to the background levels of the area.

It is interesting to note that among the elements showing pronounced enrichment in the area, only a limited number of different concentration patterns are found, indicating that although different sources are present, a given group of sources may be primary for several elements. This is clearly seen in Figure 30 where the elements are plotted next to the location of their maximum concentration. Most of the elements with large concentration gradients have their maximum at

station 6 in East Chicago, near which the heaviest industry is located, in particular two large steel mills. Indeed maxima for Fe, Zn, Cr, W, As, and Co, which might be linked with the steel production, are found in this location, with Sb and Ag having maxima in the immediate neighborhood. The Ca maximum and the high Mg concentration at this station may originate from the large amounts of dolomite used in the steel production as well as from a neighboring cement plant. The elements Ga, Hg, Mn, Ce, La, Sc and Th also had high concentrations at this location. At station 13 in Gary in the immediate vicinity of another steel mill, several of the latter elements show a secondary maximum, examples being Fe, Cr, As, Co, W, Ce, Mn, Ca and Mg. Station 1 in Hammond, situated near the shoreline, shows a primary maximum for Mn, Mg, Sc, Na, K, and Ti and a secondary maximum for Al, La, Sm, Eu, Ce, Th, Ca, Mg, Co, Fe, S, and Se. It is not obvious to which industrial process the very high copper concentration in the East Chicago area can be linked. A secondary copper maximum is experienced at station 23 in Chesterton.

Repeated subsequent smaller-scale sampling (15) in this area has revealed considerably higher concentrations for several of the above elements at stations 6 and 9 and nearer the shoreline steel mills. Two suggestions follow:

- a) Absolute concentration maxima reported here may be lower than the average for this area. The reasons for this may be twofold. The unusually steady and brisk south-southwest wind during the sampling period caused a situation of high ventilation, producing lower than normal concentrations of those elements having nearby sources. Secondly, the wind direction was such as to transport a large fraction of the shoreline steel and cement plant emissions directly out over the lake, making downwind sampling impossible. Since the steel and cement manufacturing industries emit respectively about 85% and 12.5% of the industrial particulate emissions in this area (18), this wind direction may have caused the observed concentrations to be significantly lower than normal.

b) Higher concentrations found in the immediate neighborhood of open hearth and sintering plants confirm the previous suggestion that the source of several elements is linked with the steel production.

Inspection of the concentration maps for those elements with large variations often reveals a solitary maximum surrounded by stations all having much lower values, with no clear-cut plume. This pattern is not shared by the total particulate and presumably reflects a point source for the element in question. The presence of such large concentration changes between stations often separated by as little as 2 km may be attributed in part to the extremely steady prevailing wind during the sampling period, but more probably represents the grosser features of a permanent fine structure on a scale smaller than that revealed by the present network. A follow-up study with more closely spaced stations is being planned, in an attempt to further delineate the qualitative and quantitative features of these concentration gradients.

One useful byproduct of such a study would be the more precise location of sources, especially in the center of East Chicago where sources must be other than the steel mills.

2) What are the differences between approximate minimum sampling requirements for trace elements vs. total particulate in Northwest Indiana, and how does the present network meet each of these?

Station distribution requirements for a network are determined by the goal of the sampling. For suspended particulate, where the variation over the entire region may often be a small factor, establishment of a suitable mean value may be the major goal, with monitoring of variations at individual locations somewhat secondary. Because the individual elements are much more likely to vary by factors of the order of 5-10, requirements for representative sampling here should be more stringent than for total particulate. "Hot spots" of biologically active or harmful elements may be the most important consideration, and any proposed trace element

network should do more than establish mean values; it must as well adequately define maximum concentrations of the region. Because of the apparent association of high elemental concentrations and industry found here, a closer spacing of stations in industrial zones would be implied. As mentioned above, there is some evidence that the present network could be profitably made more dense, particularly in East Chicago and Gary.

On the other hand, the network seems more than adequate for suspended particulate. Stalker et al. (1) offer the following formula as a guide for station planning when estimation of the mean is the goal:

$$N = \frac{(CV)^2 t^2}{p^2}$$

where:

N = minimum number of stations required

t = student "t" for specified confidence

CV = coefficient of variation in per cent (std dev/meanx100)

p = allowable percent departure from the true mean

Though suspended particulate values are not available for June 11-12, 1969, the distribution can be approximated from that of June 6, 1968, a day of similar wind (16). These data, shown in figure 31, reveal a maximum variation of 2.4X over the network, but a somewhat anomalous maximum near station 2 in Hammond. (Inspection of the data from other days (16) commonly reveals broad maxima centered over northern East Chicago or vicinity, the region here found to contain the maxima of most individual elements. These data also suggest that the range of total particulate may vary from about 1.5-4 over the network.). From the coefficient of variation for this day (26%) it follows that

- 1) the present 24 station network determines the daily mean to within 11% at the 95% confidence level, and

- 2) 4 randomly chosen stations could determine the daily mean to about 25% at the 95% confidence level.

Practical considerations concerning trace element monitoring must involve compromise, because of the combination of large numbers of stations ideally needed (more than in the present network) and increased work load per station due to the more sophisticated multielemental analysis. One possible solution would consist of single point sampling both in regions of greatest population density and/or highest pollutant concentrations, together with a comparison (control) station at lower pollutant levels. For the Northwest Indiana area these various criteria may partially overlap, because the two regions of greatest population density (1960 census) are near stations 6(or 9) and 13, where most elements have concentration maxima. Since most of the remaining population lives in Hammond, a station located near 2 or 3 would simultaneously represent lower levels of the region and the remaining population exposure. A minimum trace element network would then consist of 3 stations, near the present locations 2(or 3), 6(or 9), and 13.

This conclusion is in close agreement with that of Stalker et al. (1), who show that for Nashville a two station total particulate network (one high pollution urban and one suburban) gives the same yearly, seasonal, and monthly (most months) means as a 4 station urban network. Even daily mean estimates of the two networks were reasonably close.

For other industrial areas the critical establishment of trace element sampling locations should be determinable after a multistation survey of the area. A similar sequence is also recommended in the Nashville report (1).

An objection could be raised here about the drawing of a large conclusion from a study of only a single day's sampling. Results from further days would be better, but the those of Harrison (16), who has measured Pb, Cu, and Cd over this network during 6 days, show remarkably little day to day

variation either in location of maxima or geographical concentration patterns.

3) Are the observed concentration patterns consistent with meteorological variables such as wind direction and speed, thermal stability, etc.?

It is extremely doubtful whether significant meteorological effects can be noted in a one-day study. Also, as previously noted, the wind direction was such as to blow the greatest mass of particulate material over the lake where downwind effects could not be studied. In spite of this hindrance, however, some effect of wind direction may be evident in the general N-NE orientation of isopleths of elements which show large concentration gradients, such as Cu, Zn, Cr, Sb, and Fe.

It is of course impossible on the basis of a 1-day study to rule out the possible coincidental lining up of sources of these elements with the wind. There is some hint of strong concentration gradients on the downwind side of sources, especially for Cu, but this is not clearly defined.

The presence of strong maxima in steel-related elements at stations 6, 9, and 13, which for this day were upwind of the mills, is here tentatively interpreted as arising from re-entrainment of surface dust previously originating from the mills. Turbulent backwash of the plumes seems highly unlikely both because of the stack heights and distance scales involved.

Originally it was hoped that the "control" station (30, Niles, Michigan, rural) would be of some value in assessing longer range effects such as differential transport, but relatively high concentrations were found there for S, Se, Cu, Sb, As, and Ga. These may be partially ascribed to the influence of South Bend, Indiana, some 15 km to the south, but may more generally represent normal variations in the trace element background of the region.

4) How does the areawide behavior correlate or differ among the elements?

It was pointed out previously that a first view to the isopleths reveals that a number of elements which are expected to have common sources in East Chicago show very similar distribution patterns. It is interesting to note that

the distributions, as reflected in the isopleths, of Cr, Fe, and Ce are quite similar, as well as those of Sb and Zn, Sc and Co, Sm and Eu. It may also be worthwhile to compare the distribution of the elements S and Se which are known to have common sources (burning of coal and fuel oil). Although the analytical results for sulfur are of a low quality and bear a large uncertainty, the isopleths show some similarity. To find possible correlations between the elements, their source and their atmospheric behavior, a statistical analysis of the data is in preparation and will be published later. Preliminary linear correlation coefficients between the elements, calculated from their distribution patterns over the 25 stations are given in Table VI. Some significant correlations might be Sc-Co-Th, Fe-Cr, Sb-Zn, and Na-K-Sm-Eu for the background elements.

5) For which elements might air pollution contributions to water pollution of the lake be significant?

Though the total air pollution input to Lake Michigan cannot be calculated from the present experiment, an important indication can be found in the fact that the three stations (1, 6, and 13) with maximum concentrations for most of the elements investigated are located near the shoreline. The large amounts of air pollution particulates produced in these areas may thus easily be carried over Lake Michigan by the prevailing winds from the southwest. Their removal by fall-out, impaction, or precipitation seems to be a real potential hazard for the pollution of the lake waters, although the real significance can only be decided after quantitative evaluation of the inputs and comparison with trace element inputs from other sources, especially streams. From the elements investigated in this work, significant contributions due to air pollution might exist for Cu, Fe, Zn, Sb, Cr, W, Br, Ag, Ce, and to a lesser extent Th, La, Mn, Hg, As, S, Co, Se, Mg, Ca, and V.

Acknowledgements. Cooperation of the local air pollution control agencies of Northwest Indiana and of Mr. C. L. Haslett of Niles, Michigan are gratefully acknowledged. This work was supported in part by USAEC contract AT(11-1)-1705.

REFERENCES

- (1) W.W. Stalker, R.C. Dickerson, G.D. Kramer, D.M. Keagy and C.E. Zimmer, J. Air Poll. Control Assoc. 11, 270 (1961); 12, 111 (1962); 12, 170 (1962); 12, 361 (1962).
- (2) Report of the International Joint Commission United States and Canada on the Pollution of the Atmosphere in the Detroit River Area, Washington (1960).
- (3) R.E. Munn, D.A. Thomas and A.F.W. Cole, Atmos. Environ. 3, 1 (1969).
- (4) E.C. Tabor and W.V. Warner; A.M.A., Arch. Ind. Health 17, 141 (1958).
- (5) T.J. Kneip, J.M. Eisenbud, C.D. Strehlow and P.C. Freudenthal; J. Air. Poll. Control Assoc. 20, 3, 144 (1970).
- (6) S.S. Brar, D.M. Nelson, E.L. Kanobrocki, C.E. Moore, C.D. Burnham and D.M. Hattori, Proc. 1968 Int. Conf. "Modern Trends in Activation Analysis". Gaithersburg, Maryland, p. 43 (1969); Environmental Science and Technology 4, 50 (1970).
- (7) G. Lee and R.E. Jervis, Amer. Nucl. Soc. Trans. 11, 50 (1968).
- (8) J.R. Keane and E.M.R. Fisher, Atmos. Environ. 2, 603 (1968).
- (9) W.M. Zoller and G.E. Gordon, Anal. Chem. 42, 256 (1970).
- (10) K.K.S. Pillay and C.C. Thomas, Jr., Report WNY-046, Western New York Nuclear Research Center, Buffalo, 1969.
- (11) N.D. Dudey, L.E. Ross, V.E. Noshkin, Proc. 1968 Int. Conf. "Modern Trends in Activation Analysis", Gaithersburg, Maryland, p. 55 (1969).
- (12) J.W. Winchester, Limnos 2, No. 1, 20 (1969).
- (13) R. Dams, K.A. Rahn, and J.W. Winchester, Environ. Sci. and Tech., submitted (1970).
- (14) R. Dams, J.A. Robbins, K.A. Rahn, and J.W. Winchester, Anal. Chem., submitted (1970).
- (15) G.E. Nifong private communication.
- (16) P.R. Harrison, Ph.D. Thesis, University of Michigan (1970).
- (17) "Air Quality Data, from the National Air Sampling Networks and Contributing State and Local Works" 1966 Edition, U.S. Department of Health, Education, and Welfare, Durham, N.C. (1968).
- (18) G. Ozolins and C. Rehmann, "Air Pollutant Emission Inventory of Northwest Indiana, A Preliminary Survey, 1966", National Center for Air Pollution Control Publication APTD-68-4, (1968).

TABLE I. Station Key

HAMMOND

- 1 Water Works
- 2 Goldblatt's
- 3 City Hall

WHITING

- 4 Fire Station
- 5 South Side School

EAST CHICAGO

- 6 Marktown
- 7 Central Fire Station
- 8 Roxanna School
- 9 Field School
- 10 Franklin School

GARY

- 11 Airport
- 12 Ivanhoe
- 13 Fire Station
- 14 Williams School
- 15 Kuny School
- 16 Wirt

LAKE COUNTY

- 17 Highland
- 18 Hobart
- 19 Crown Point

PORTER COUNTY

- 21 Ogden Dunes
- 22 South Haven
- 23 Chesterton
- 24 Valparaiso

OTHER

- 26A Michigan City
- 30 Niles, Michigan

TABLE II. Summary of Meteorological Data

Location	Sky Cover*	Average Wind Speed		Prevailing Direction**	T _{max.} °C	T _{min.} °C	Precipitatio mm
		mph	m/s				
O'Hare Field	.9-.9	10.4	4.6	170	31	16	1
University of Chicago	---	----	---	---	33	17	-----
Midway	.9-.8	13.6	6.1	180	33	18	Trace
East Chicago	----	10.7	4.8	200	--	--	-----
Michigan City	---	10.8	4.8	170	--	--	-----

* Sunrise-sunset and sunset-sunrise

**Measured in degrees East of North

TABLE III. Irradiation and Counting Scheme

Filter Area (cm ²)	Air Volume (m ³)	T _{irr}	Reactor Location	Flux (n/cm ² -sec)	T _{cool}	T _{count}	Isotopes Measured
0.8	5	5 min.	Pneum.	2x10 ¹²	3 min.	400 sec.	28 ^{Al} ; 52 ^V ; 66 ^{Cu} ; 51 ^{Ti} ; 37 ^S ; 49 ^{Ca} ;
1.6	10	2-5 hrs.	Core	1.5x10 ¹³	15 min.	1000 sec.	27 ^{Mg} ; 80 ^{Br} ; 38 ^{Cl} ; 128 ^I ; 56 ^{Mn} ; 24 ^{Na} ; 116 ^m In
13.0	80	2-5 hrs.	Core	1.5x10 ¹³	18-36 hrs.	2000 sec.	42 ^K ; 64 ^{Cu} ; 69 ^m Zn; 82 ^{Br} ; 76 ^{As} ; 72 ^{Ga} ; 122 ^{Sb} ; 140 ^{La} ; 153 Sm ; 152 ^m Eu; 187 ^W ; 198 ^{Au} ;
		2-5 hrs.	Core	1.5x10 ¹³	20-30 days	4000 sec.	46 ^{Sc} ; 51 ^{Cr} ; 59 ^{Fe} ; 60 ^{Co} ; 58 ^{Co} ; 65 ^{Zn} ; 75 ^{Se} ; 110 ^m Ag; 124 ^{Sb} ; 141 ^{Ce} ; 203 ^{Hg} ; 233 ^{Pa}

TABLE IV. Trace Element Concentrations in Nanogram/m³ of Air Sampled at 25 Stations.

Station Number	1	2	3	4	5	6	7	8	9	10
S*	15(6)	11(6)	16(10)	8(5)	14(8)	13(8)	9(6)	14(7)	11(7)	7(5)
Ca	5450(600)	3000(1000)	4700(600)	3100(800)	3000(600)	7000(700)	5300(800)	2300(400)	3050(500)	5000(1100)
Al	2450(300)	2250(500)	2350(300)	1550(200)	1800(200)	2175(170)	2120(270)	1400(90)	1375(70)	1450(200)
V	9.8(0.9)	8.2(1)	9.1(1)	16.8(3.0)	11.3(1.0)	18.1(1.5)	9.8(1.0)	6.3(1.0)	6.2(0.5)	5.2(0.7)
Cu	130(20)	33(15)	93(10)	195(20)	100(15)	1100(100)	210(15)	3100(200)	3100(200)	4000(250)
Ti	280(50)	170(35)	200(40)	135(50)	155(35)	190(40)	185(40)	190(35)	260(40)	155(30)
In	0.12(0.06)	0.08(0.05)	0.11(0.05)	0.07(0.04)	0.12(0.05)	0.10(0.05)	0.09(0.06)	0.04(0.04)	<0.05	0.04(0.03)
Br	180(20)	170(30)	180(25)	95(15)	75(8)	75(8)	130(15)	67(5)	55(7)	40(4)
Mn	390(50)	150(30)	177(30)	215(40)	300(45)	255(40)	208(12)	125(6)	105(12)	83(5)
Mg	1500(700)	1500(500)	1200(400)	900(400)	1300(500)	2400(600)	1750(500)	780(300)	1250(400)	1650(400)
Na	500(50)	370(100)	300(40)	225(18)	270(55)	455(55)	335(50)	210(15)	215(50)	160(20)
Sm	0.46(0.06)	0.48(0.06)	0.36(0.05)	0.37(0.04)	0.38(0.03)	0.41(0.08)	0.32(0.04)	0.22(0.04)	0.27(0.03)	0.26(0.04)
Zn	750(70)	350(25)	255(25)	740(70)	390(35)	1540(150)	1120(100)	250(20)	460(70)	320(50)
Sb	14(1)	6.5(1)	5.2(0.5)	28(5)	15(2)	28(4)	32(3)	7.0(0.7)	13(3)	5.3(0.5)
W	<0.8	0.8(0.3)	0.5(0.3)	0.8(0.3)	0.7(0.3)	5.6(1)	1.0(0.3)	0.5(0.25)	0.7(0.3)	0.5(0.3)
Ga	<1.0	0.9(0.3)	<0.5	0.8(0.4)	0.8(0.4)	1.3(0.4)	1.3(0.5)	0.7(0.4)	0.8(0.4)	0.8(0.4)
Eu	0.14(0.02)	0.11(0.04)	0.095(0.03)	0.115(0.015)	0.10(0.01)	0.135(0.02)	0.10(0.015)	0.10(0.02)	0.08(0.015)	0.07(0.02)
As	3(2)	3(1)	3(2)	7(3)	2(1)	12(3)	8.5(2)	2(1)	6.8(1.5)	3.5(1.2)
K	1860(200)	1500(150)	1370(130)	1200(150)	1260(160)	1415(150)	1390(150)	1040(140)	990(70)	800(40)
La	4.4(0.3)	5.2(0.8)	3.5(0.6)	3.2(0.4)	3.7(0.5)	5.9(0.4)	2.7(0.5)	2.5(0.5)	2.3(0.3)	2.5(0.3)
Co	2.4(0.2)	1.2(0.1)	1.35(0.15)	1.65(0.1)	1.4(0.15)	2.6(0.6)	1.8(0.2)	0.92(0.10)	1.5(0.1)	1.3(0.1)
Fe	9900(400)	4550(200)	5500(300)	7300(400)	7250(400)	13,800(3000)	8300(600)	4000(600)	6000(300)	4000(200)
Sc	3.1(0.3)	1.85(0.1)	2.0(0.2)	2.3(0.2)	2.2(0.2)	3.1(0.5)	1.9(0.2)	1.3(0.1)	2.0(0.1)	1.7(0.1)
Cr	66(4)	26(3)	38(4)	58(3)	69(5)	113(20)	55(5)	21(2)	79(4)	79(4)
Hg	4.9(0.9)	3.5(1)	2.8(1)	1.4(0.4)	1.9(0.6)	4.8(1.0)	1.5(0.5)	2.8(1.0)	1.9(0.5)	2.0(0.4)
Se	2.9(0.6)	3.6(1.3)	2.4(1.0)	2.3(0.5)	3.4(0.6)	3.8(1.0)	2.9(0.6)	1.8(0.5)	2.1(0.5)	1.8(0.3)
Th	0.85(0.25)	0.48(0.1)	0.62(0.10)	0.58(0.10)	0.70(0.10)	1.3(0.4)	0.48(0.10)	0.28(0.10)	0.46(0.05)	0.45(0.06)
Ce	10.7(1.0)	8.3(0.5)	7.2(1.0)	8.1(1.0)	7.6(0.8)	13(3)	5.5(0.5)	5.1(1.0)	2.5(0.2)	2.1(0.2)
Ag	1.7(1.5)	1.4(1.3)	1.3(1.1)	2(1.5)	1.7(1.2)	2.4(1.5)	<2	3.0(1.2)	5(2)	3(2)
Ni	<50	<40	25(25)	30(20)	<50	<40	<80	30(25)	<30	<20

*µg/m³

TABLE IV. (cont.)

Station Number	11	12	13	14	15	16	17	18	19
S*	9(4)	8(3)	15(7)	8(4)	9(3)	6(4)	10(5)	6(4)	3(3)
Ca	2900(300)	1700(200)	3600(1000)	2100(100)	2250(250)	1500(300)	4330(400)	1430(400)	1410(200)
Al	2200(250)	1675(150)	2400(300)	1900(250)	2600(250)	1650(150)	2090(150)	1770(140)	1590(100)
V	5.5(0.4)	5.3(1.5)	8.6(1.0)	4.3(1.2)	6.6(0.5)	4.0(1.0)	17.3(0.8)	4.5(0.4)	4.8(0.3)
Cu	170(10)	32(10)	75(15)	240(60)	150(40)	75(10)	32(10)	26(5)	182(15)
Ti	185(35)	130(30)	190(50)	150(30)	240(35)	150(50)	145(25)	150(25)	120(25)
In	0.07(0.04)	0.05(0.04)	0.15(0.06)	0.04(0.03)	<0.05	<0.05	0.04(0.03)	0.04(0.03)	0.04(0.03)
Br	45(6)	57(8)	300(30)	68(7)	52(7)	51(6)	37(5)	26(3)	35(5)
Mn	112(10)	92(12)	270(40)	98(10)	130(10)	92(15)	101(10)	85(5)	63(3)
Mg	700(400)	1000(400)	2700(400)	620(400)	1000(500)	1000(500)	1350(400)	800(300)	530(300)
Na	300(20)	270(30)	380(40)	255(20)	305(25)	225(50)	360(30)	305(15)	290(20)
Sm	0.28(0.04)	0.44(0.05)	0.42(0.03)	0.25(0.03)	0.23(0.04)	0.17(0.02)	0.45(0.05)	0.33(0.02)	0.38(0.02)
Zn	100(12)	160(30)	290(25)	135(20)	115(20)	130(15)	315(20)	135(20)	280(20)
Sb	2.25(0.4)	3.8(0.6)	4.1(0.5)	2.5(0.5)	3.0(0.8)	3.0(0.5)	11.5(1.0)	2.2(0.3)	2.7(0.4)
W	0.25(0.2)	1.2(0.4)	1.2(0.5)	<0.4	0.4(0.3)	0.3(0.3)	0.5(0.3)	0.5(0.5)	<0.5
Ga	0.7(0.3)	1.8(1.0)	0.25(0.15)	0.55(0.3)	0.5(0.3)	3.5(1.0)	0.8(0.3)	0.9(0.4)	0.7(0.4)
Eu	0.085(0.015)	0.085(0.010)	0.09(0.01)	0.08(0.01)	0.08(0.02)	0.06(0.01)	0.095(0.01)	0.07(0.01)	0.085(0.015)
As	4(3)	6.5(3)	7(3)	4(2)	3.5(1.5)	4(3)	3(2)	3(2)	2.7(2)
K	905(65)	1300(150)	1090(60)	1000(60)	990(110)	730(90)	1250(70)	1050(85)	1320(80)
La	1.7(0.3)	2.2(0.4)	2.4(0.3)	1.8(0.3)	1.5(0.3)	0.9(0.1)	4.4(0.4)	2.2(0.2)	2.6(0.2)
Co	0.47(0.10)	0.84(0.08)	1.15(0.15)	0.60(0.1)	0.55(0.06)	0.70(0.10)	1.3(0.1)	0.8(0.1)	0.90(0.07)
Fe	2025(150)	2940(250)	12,000(1000)	2050(200)	1420(120)	2290(300)	3300(300)	2700(180)	3000(150)
Sc	0.92(0.1)	1.4(0.2)	1.8(0.2)	1.1(0.2)	0.95(0.1)	1.1(0.1)	1.9(0.1)	1.3(0.1)	1.4(0.11)
Cr	9(1)	13(0.7)	33(4)	10.2(2)	6.2(0.8)	8.6(0.8)	18(1.5)	8.7(0.5)	9.0(0.6)
Hg	0.8(0.3)	1.5(0.4)	1.5(0.6)	1.6(1.0)	1.5(0.5)	1.2(0.3)	0.9(0.5)	0.8(0.4)	1.8(0.5)
Se	0.8(0.5)	2.3(1.0)	1.1(0.4)	1.7(0.3)	1.5(0.6)	1.8(0.5)	1.4(0.5)	1.1(0.4)	1.5(0.3)
Th	0.17(0.02)	0.42(0.04)	0.43(0.10)	0.25(0.05)	0.22(0.04)	0.34(0.04)	0.52(0.04)	0.42(0.06)	0.47(0.04)
Ce	2.4(0.2)	4.2(0.8)	7.2(1.0)	3.0(0.3)	2.5(0.4)	3.1(0.6)	3.3(0.2)	1.8(0.2)	1.8(0.1)
Ag	<1	<1	<1.5	<1	<1	0.9(0.8)	<1.5	<1	<1
Ni	<20	<20	14(15)	<30	<20	<20	<25	<25	16(12)

* $\mu\text{g}/\text{m}^3$

TABLE IV. (cont.)

Station Number	21	22	23	24	26A	30
S*	17(8)	7(6)	10(8)	18(10)	15(7)	11(5)
Ca	3900(1000)	2260(400)	1950(400)	3400(1000)	2650(600)	1000(200)
Al	3000(600)	2260(400)	1960(150)	3100(300)	1850(150)	1200(70)
V	8.2(1.0)	6.9(1.0)	6.2(0.8)	10.2(1.0)	5.9(0.4)	5.0(0.3)
Cu	95(15)	75(30)	860(60)	43(15)	290(25)	280(25)
Ti	265(80)	195(35)	180(35)	225(50)	165(25)	120(25)
In	0.09(0.06)	0.04(0.04)	0.08(0.06)	0.05(0.04)	0.05(0.03)	0.04(0.03)
Br	70(12)	32(7)	27(6)	61(12)	75(7)	37(6)
Mn	145(20)	115(20)	82(10)	160(20)	106(7)	62(4)
Mg	1150(500)	1200(600)	800(600)	1350(600)	800(400)	500(300)
Na	325(60)	275(70)	230(40)	405(30)	255(40)	170(20)
Sm	0.65(0.20)	0.31(0.03)	0.36(0.06)	0.43(0.07)	0.38(0.05)	0.24(0.03)
Zn	195(15)	135(15)	260(40)	190(15)	190(20)	160(20)
Sb	5.2(0.5)	5.0(0.8)	4.6(1.1)	5.9(0.7)	5.0(0.5)	6.0(0.5)
W	1.3(0.7)	0.5(0.2)	1.2(0.6)	0.75(0.3)	0.8(0.3)	0.4(0.2)
Ga	2.9(1.3)	0.8(0.3)	0.7(0.4)	0.65(0.25)	1.0(0.3)	0.9(0.4)
Eu	0.17(0.03)	0.08(0.02)	0.10(0.02)	0.10(0.01)	0.08(0.02)	0.055(0.010)
As	8(4)	5(2.5)	6(3)	8(3)	3.5(1.0)	4.6(2.0)
K	1810(110)	1190(100)	1025(70)	1510(150)	1110(130)	750(100)
La	3.6(0.5)	1.8(0.2)	0.9(0.3)	2.6(0.5)	2.1(0.3)	1.3(0.3)
Co	1.6(0.15)	0.76(0.1)	0.7(0.3)	1.35(0.20)	1.0(0.1)	0.95(0.10)
Fe	5375(200)	2050(200)	2050(200)	3150(250)	2300(100)	1900(100)
Sc	2.55(0.15)	1.25(0.15)	1.1(0.2)	1.7(0.2)	1.3(0.1)	1.2(0.1)
Cr	18.2(0.8)	10.3(1.5)	9.6(1.6)	13.3(1.8)	11.5(0.6)	9.5(0.8)
Hg	3.45(0.5)	2.1(0.6)	4.8(1.4)	3.5(1.0)	2.0(0.4)	1.9(0.3)
Se	4.4(1.2)	2.5(0.5)	3.4(2.0)	2.8(1.0)	2.5(0.3)	2.5(0.5)
Th	0.68(0.07)	0.29(0.10)	0.28(0.10)	0.40(0.10)	0.29(0.03)	0.27(0.03)
Ce	7.0(0.6)	2.9(0.4)	2.3(0.8)	4.5(0.5)	1.4(0.1)	0.82(0.10)
Ag	<0.5	<1	<4	1.7(1.0)	<1	<1
Ni	<15	<30	<15	250(250)	20(15)	<25

* $\mu\text{g}/\text{m}^3$

TABLE V. Concentrations at Maximum, Minimum and Control Station.

Element	Concentrations ng/m ³			Concentration Ratios	
	Maximum	Minimum	Niles	Max./Min.	Max./Niles
S	18,000(10,000)	3,000(3,000)	11,000(5,000)	6(6)	1.6(1.0)
Fe	13,000(3,000)	1,420(120)	1,900(100)	9.7(3)	7.3(2.0)
Ca	7,000(700)	1,410(200)	1,000(200)	5.0(0.7)	7.0(1.5)
Cu	4,000(200)	25(4)	280(20)	160(30)	14(1.5)
Al	3,100(300)	1,375(70)	1,200(70)	2.3(0.3)	2.6(0.3)
Mg	2,700(1,000)	530(300)	500(300)	5.1(3)	5.4(3)
K	1,860(110)	730(90)	720(50)	2.5(0.4)	2.4(0.3)
Zn	1,550(200)	100(12)	160(20)	16(2)	9.6(1.4)
Na	500(50)	160(20)	170(20)	3.1(0.4)	2.9(0.4)
Mn	390(50)	63(3)	62(3)	6.2(1)	6.3(1.0)
Br	300(30)	26(2)	38(6)	12(1.5)	8.1(2)
Ti	280(50)	120(25)	120(25)	2.3(0.7)	2.3(0.7)
Cr	113(20)	6.2(0.8)	9.5(0.8)	18(3)	12(2)
Sb	31(3)	2.2(0.2)	6.0(0.3)	14(2)	5.3(0.7)
V	18.1(1.5)	4.0(1.0)	5.0(0.3)	4.5(1.2)	3.6(0.4)
Ce	13(1.5)	1.4(0.1)	0.82(0.06)	9.3(1)	16(4)
As	12(2)	2(1)	4.6(2)	6(4)	2.6(1.2)
La	5.9(0.4)	0.9(0.3)	1.3(0.3)	6.6(2.5)	4.5(1.0)
W	5.6(1)	0.3(0.3)	0.4(0.2)	19(19)	14(7)
Ag	5(2)	<0.5	<1	>10	>5
Hg	4.9(0.9)	0.8(0.3)	1.8(0.3)	6.1(3)	2.6(0.7)
Se	4.4(1.2)	0.8(0.5)	2.5(0.5)	5.5(3)	1.5(0.6)
Ga	3.5(1.0)	0.25(0.15)	0.9(0.4)	14(10)	3.9(1.2)
Sc	3.1(0.3)	0.92(0.1)	1.2(0.1)	3.4(0.4)	2.6(0.3)
Co	2.6(0.6)	0.47(0.06)	0.95(0.1)	5.5(1)	2.7(0.7)
Th	1.3(0.4)	0.17(0.02)	0.27(0.08)	7.6(2)	3.1(1.0)
Sm	0.65(0.20)	0.17(0.02)	0.24(0.03)	3.8(1.5)	2.0(0.4)
Eu	0.17(0.03)	0.06(0.01)	0.055(0.02)	2.8(0.5)	3.0(0.5)
In	0.15(0.06)	0.03(0.03)	0.04(0.03)	5(5)	3.7(3)

TABLE VI. Linear Correlation Coefficients ($\times 10^2$)*

	S	Fe	Ca	Cu	Al	Mg	K	Zn	Na	Mn	Br	Ti	Cr	Sb	V	Ce	As	La	W	Ag	Hg	Se	Ga	Sc	Co	Th	Sm	Eu	In									
S	--																																					
Fe	74	--																																				
Ca	74	74	--																																			
Cu	--	--	--	--																																		
Al					--																																	
Mg	82	74	74	--	--																																	
K	80	75	75	--	--	74																																
Zn	80	75	75	--	--	74																																
Na	82				72																																	
Mn										--																												
Br										--	--																											
Ti												--																										
Cr	78	76											--																									
Sb													72	--																								
V													72	--	73																							
Ce	84															--																						
As																	--																					
La																		--																				
W																			--																			
Ag																				--																		
Hg																					--																	
Se																																						
Ga																																						
Sc	82	79																																				
Co	83	84																																				
Th	80	75																																				
Sm																																						
Eu																																						
In	76																																					

*Blanks indicate coefficients less than 70%.

List of Figures

- Fig. 1. Map of southern Lake Michigan.
- Fig. 2. Wind rose for the Chicago-Northwest Indiana area.
- Fig. 3. Map of sampling area with numbers and locations of sampling sites and wind direction for 11 June 1969.
(10.7 mph = 4.8 meters/sec)
- Fig. 4. Weather map of northeast U.S.A. for 0700 11 June 1969.
- Fig. 5. Concentration distribution of copper.
- Fig. 6. zinc.
- Fig. 7. antimony.
- Fig. 8. bromine.
- Fig. 9. silver.
- Fig. 10. iron.
- Fig. 11. chromium.
- Fig. 12. cerium.
- Fig. 13. lanthanum.
- Fig. 14. thorium.
- Fig. 15. manganese.
- Fig. 16. mercury.
- Fig. 17. sulfur.
- Fig. 18. selenium.
- Fig. 19. cobalt.
- Fig. 20. scandium.
- Fig. 21. magnesium.
- Fig. 22. calcium.
- Fig. 23. vanadium.
- Fig. 24. samarium.
- Fig. 25. europium.

List of Figures, continued.

Fig. 26. Concentration distribution of sodium.

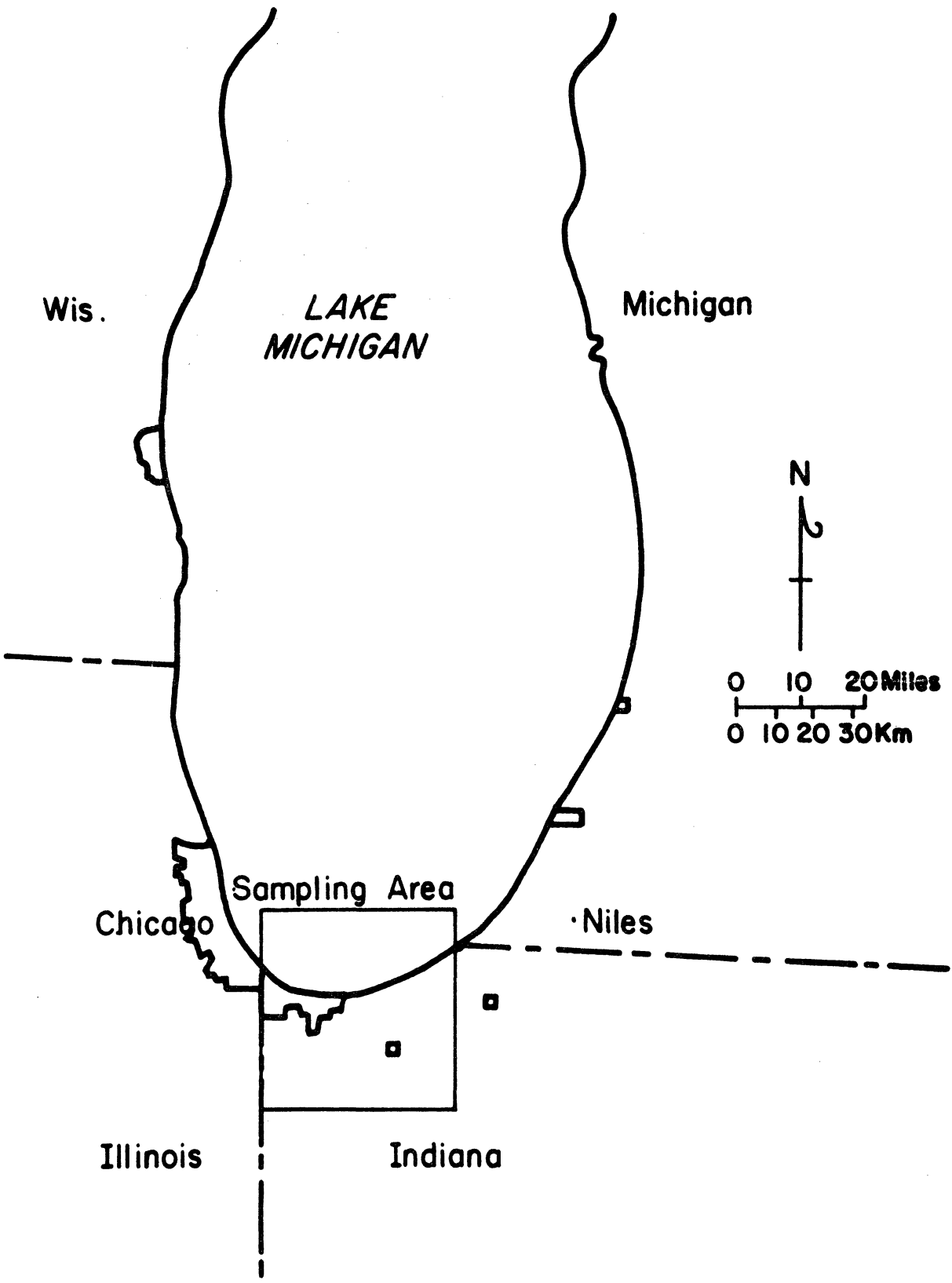
Fig. 27. potassium.

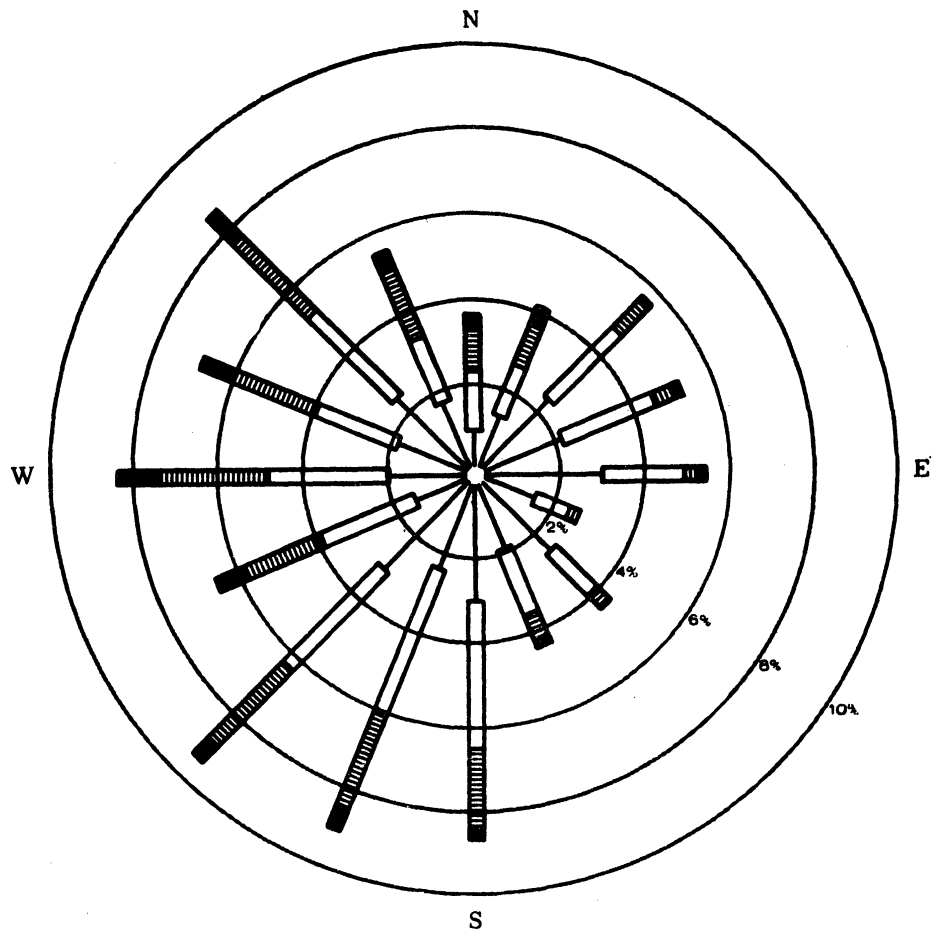
Fig. 28. aluminum.

Fig. 29. Concentration ratios of maximum to minimum stations.

Fig. 30. Locations of maximum concentrations of the elements.

Fig. 31. Concentration distribution of suspended particulate
and wind direction for 6 June 1968. (8 mph = 3.6 meters/sec;
3.8 mph = 1.7 meters/sec)

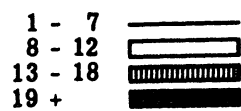




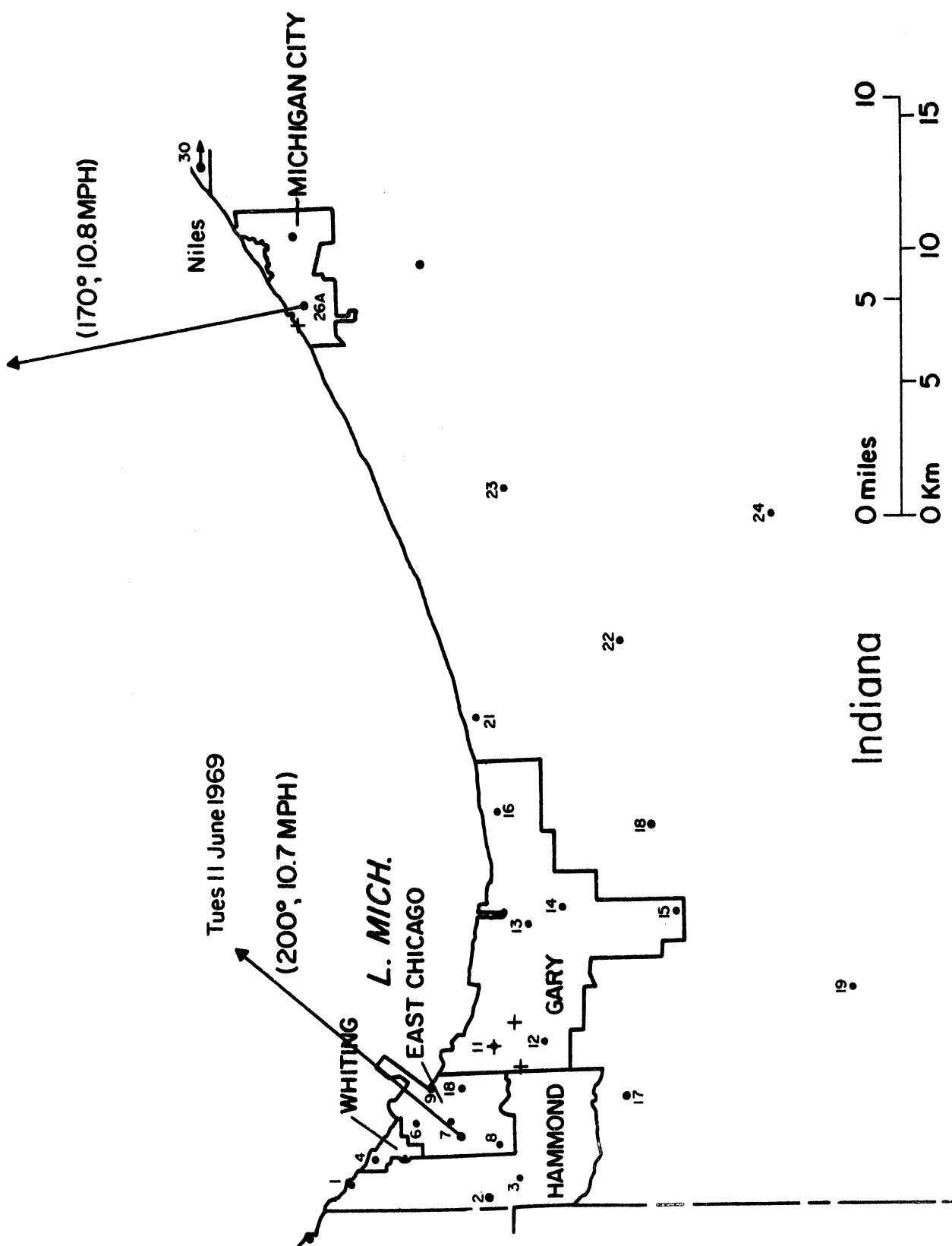
ANNUAL

Average Speed: 10.2
Percent Calms: 0.7

Wind Speeds (mph)



**From U. S. Weather
 Bureau Monthly Weather
 Data Summary for
 Midway Airport (1950-1959)**



Tues 11 June 1969

(200°, 10.7 MPH)

(170°, 10.8 MPH)

Niles

MICHIGAN CITY

WHITING

L. MICH.

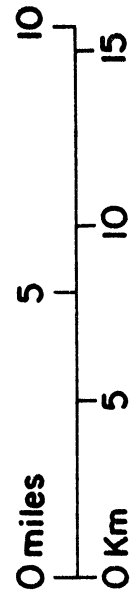
EAST CHICAGO

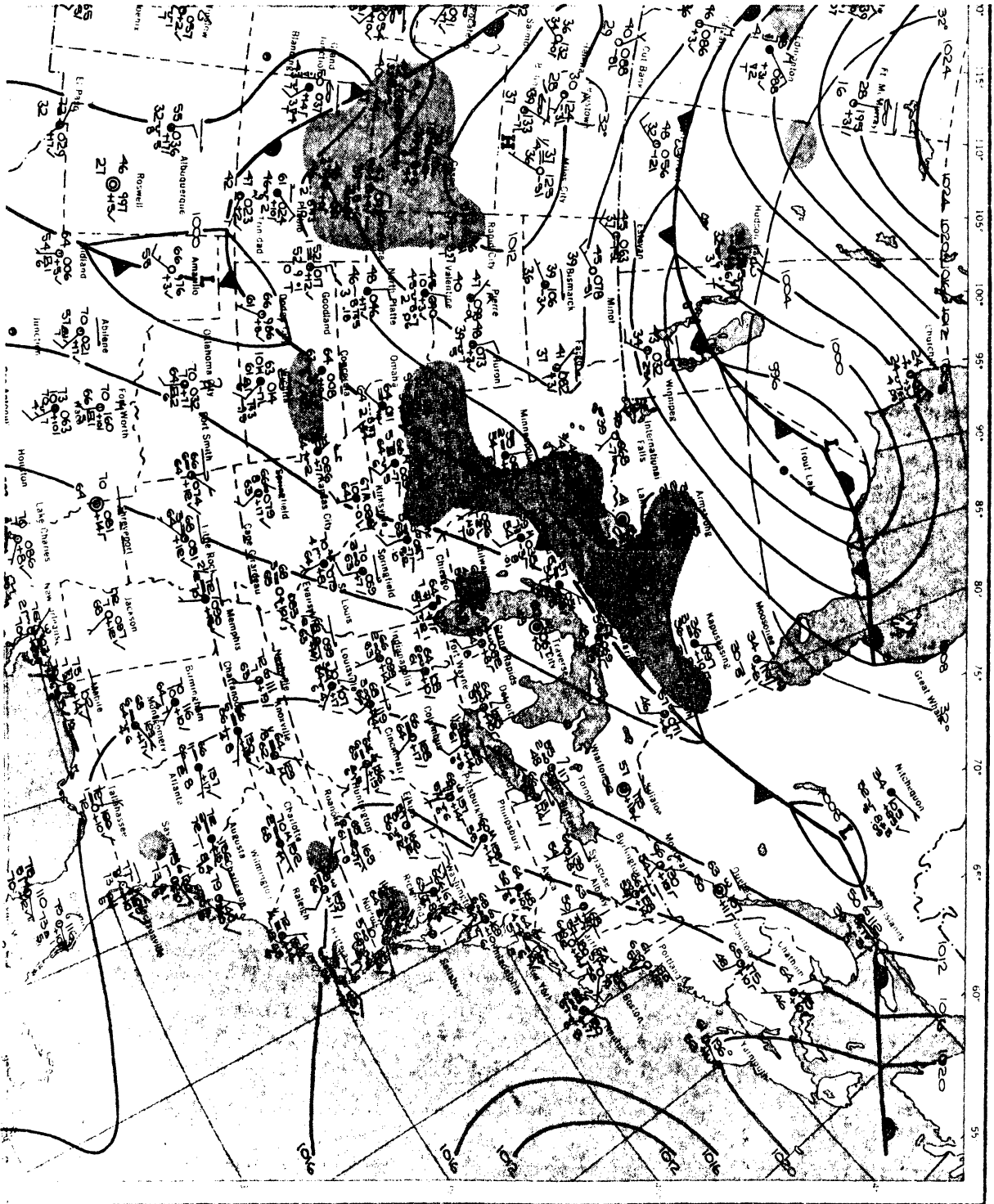
HAMMOND

GARY

19

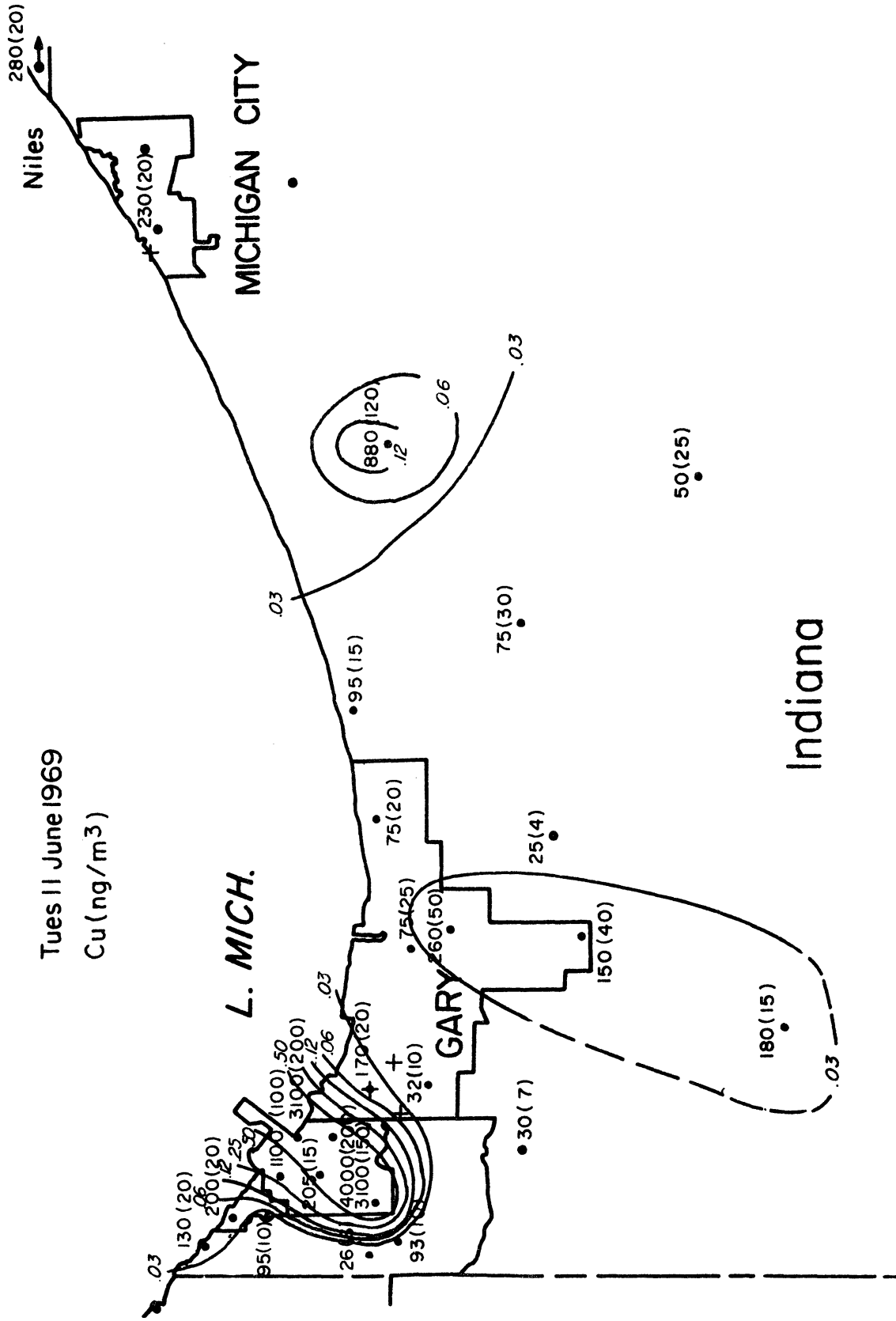
Indiana



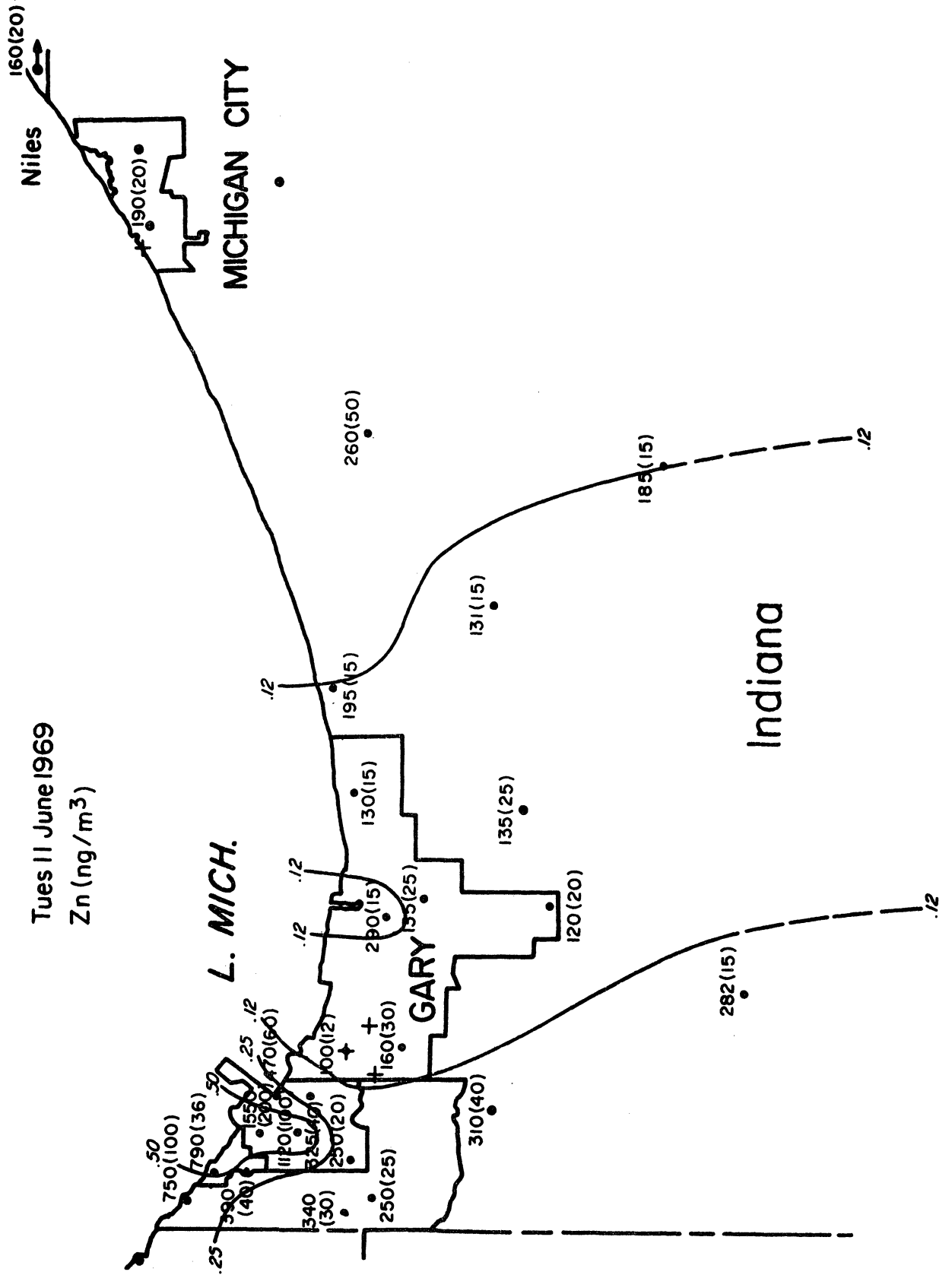


Tues 11 June 1969

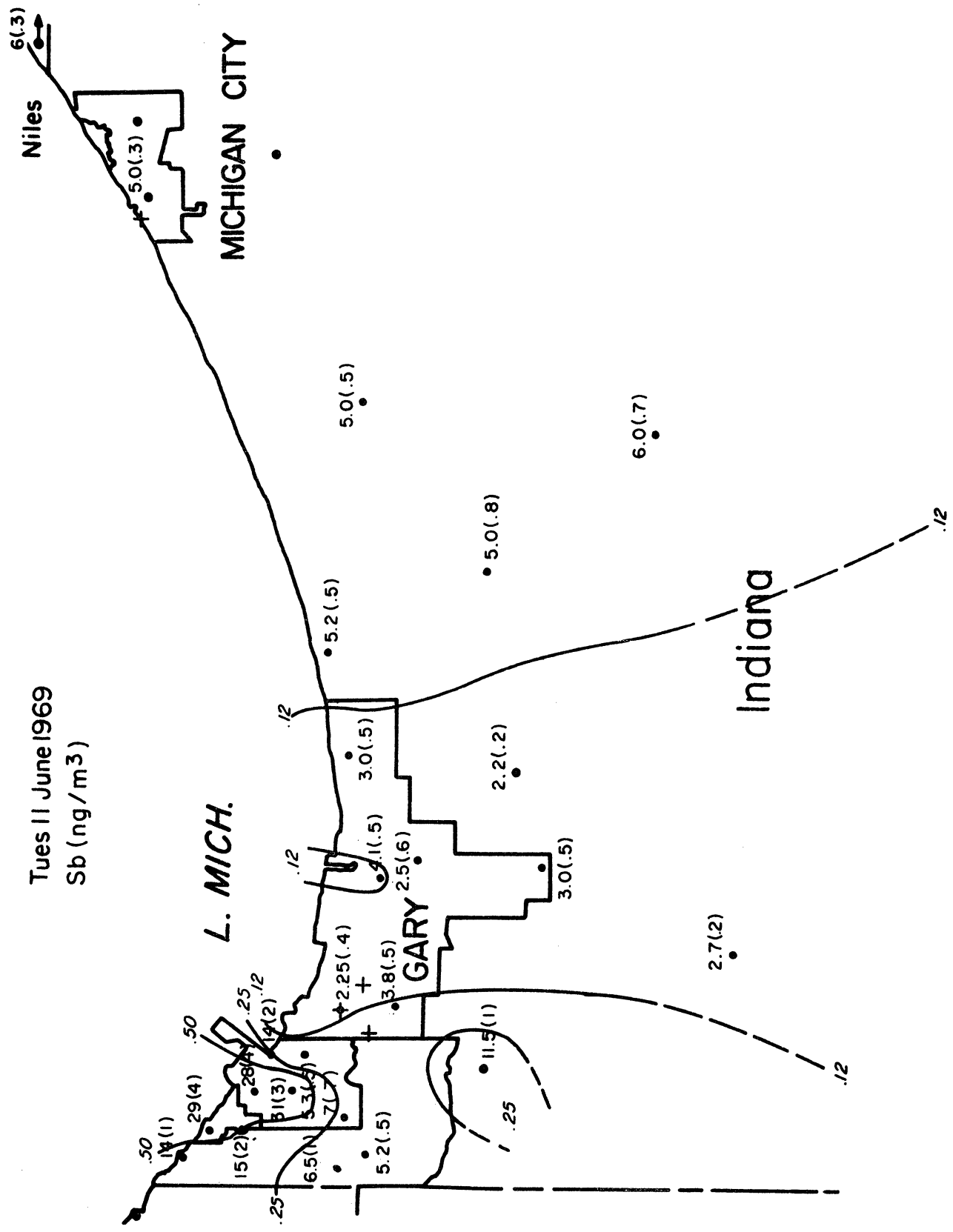
Cu (ng/m³)



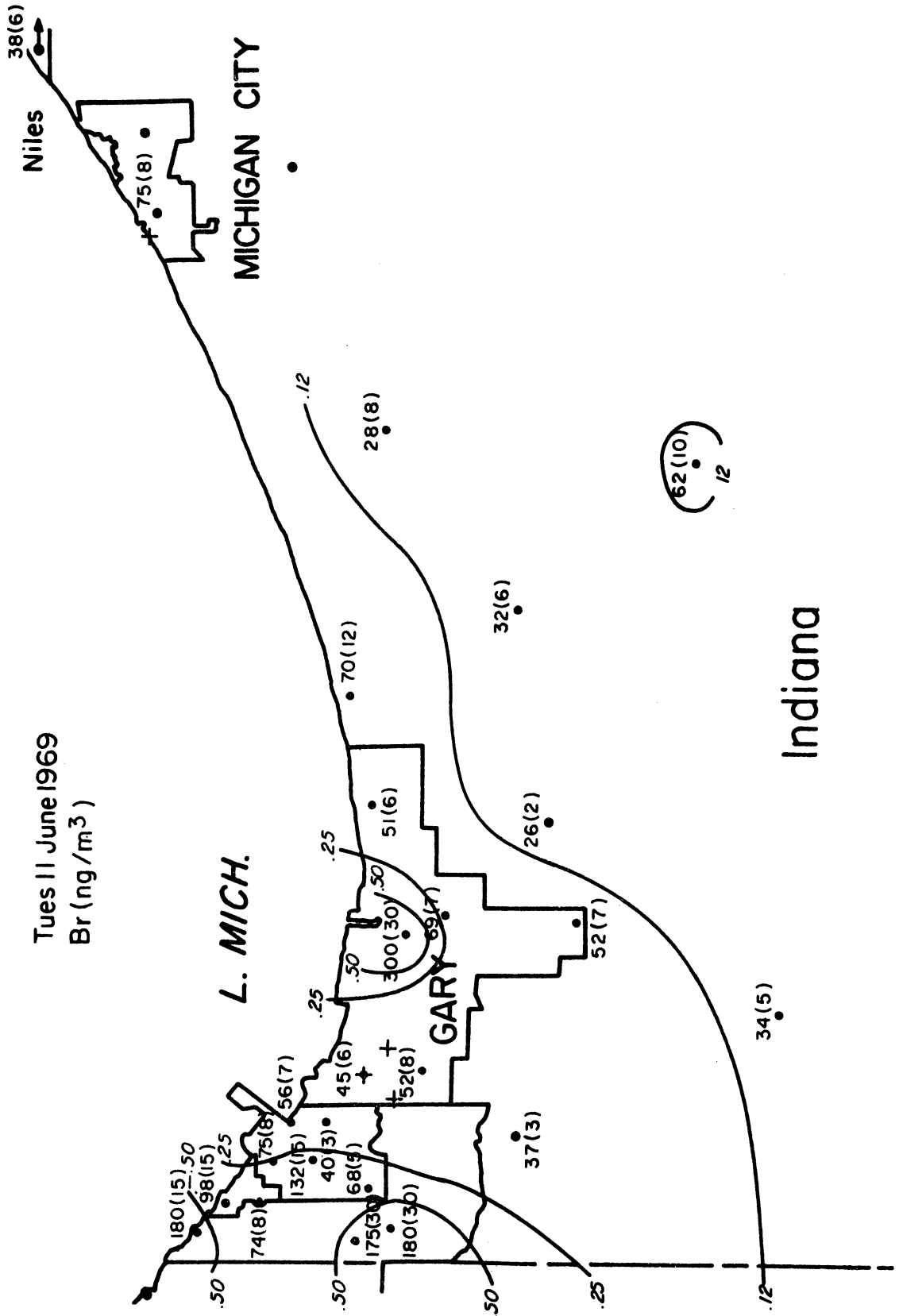
Tues 11 June 1969
Zn (ng/m³)



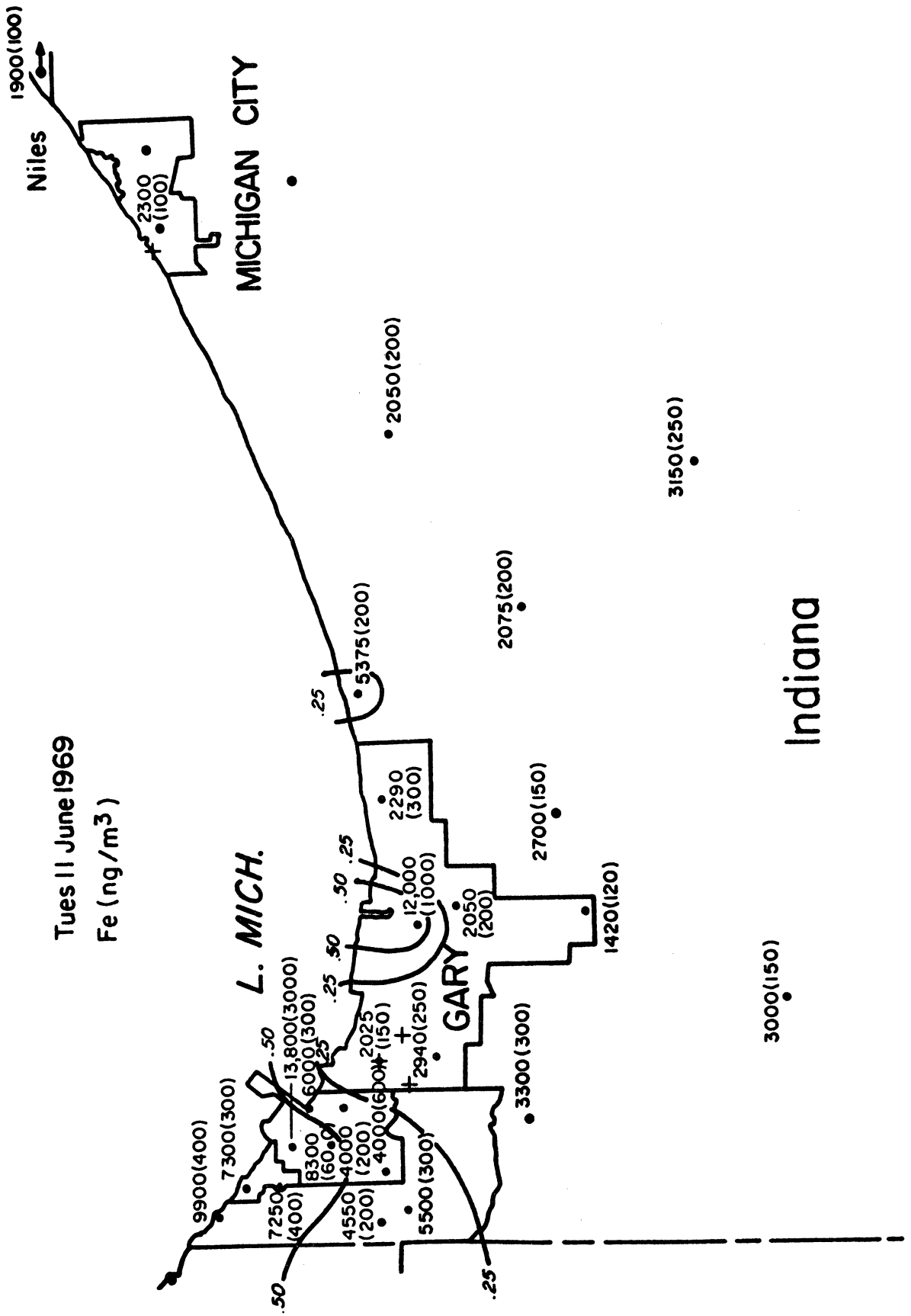
Tues 11 June 1969
Sb (ng/m³)



Tues 11 June 1969
Br (ng/m³)

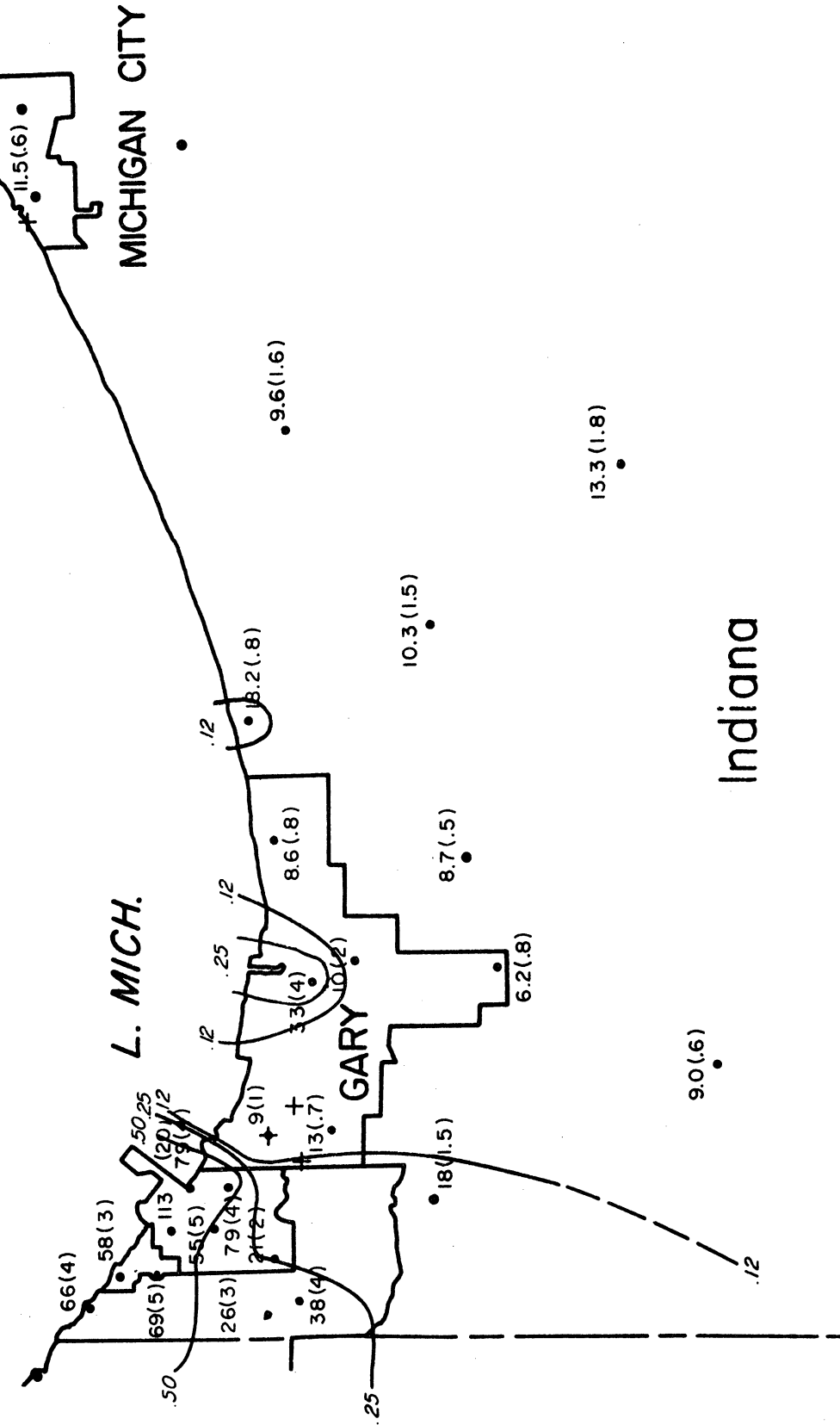


Tues 11 June 1969
Fe (ng/m³)



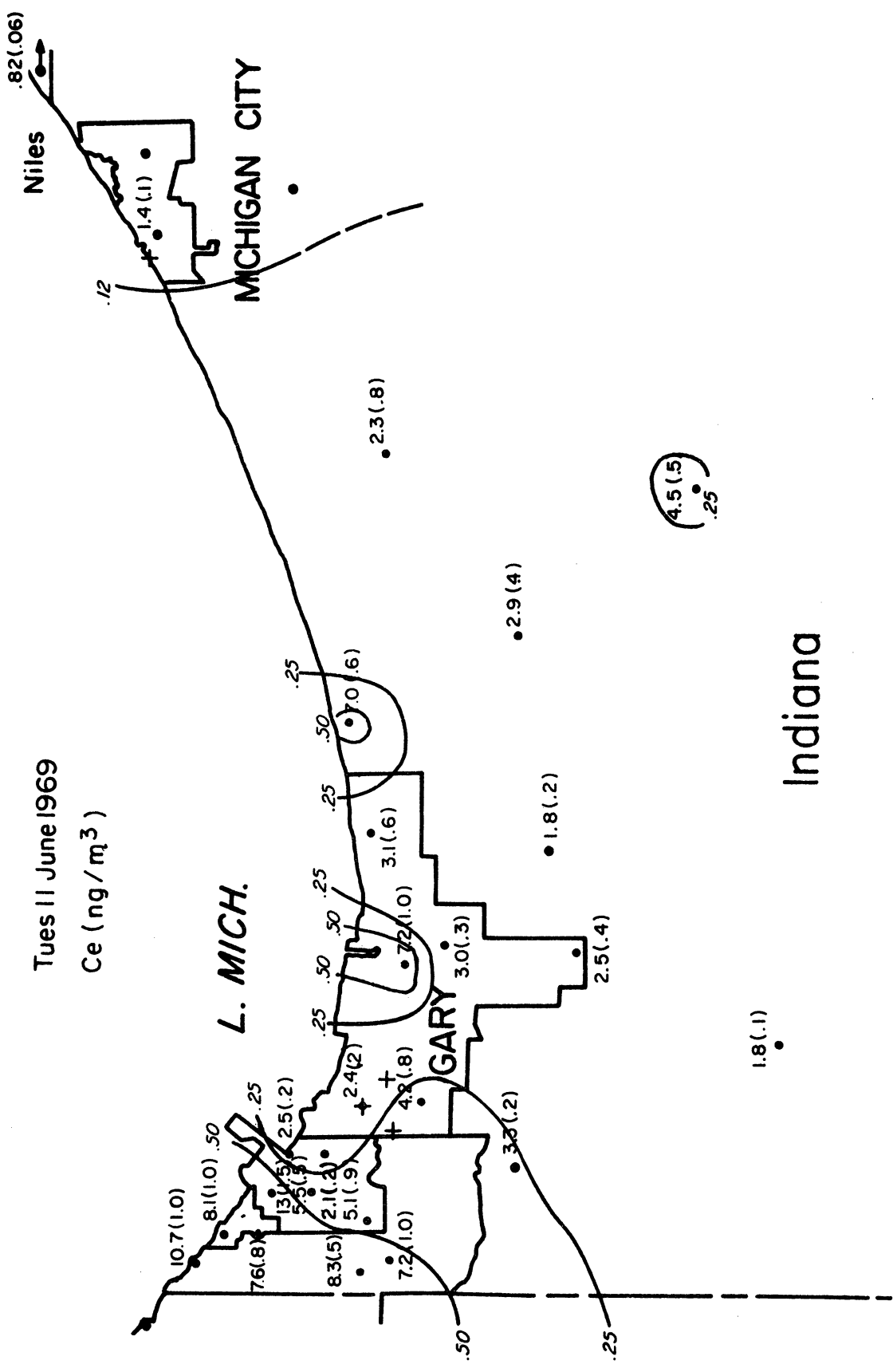
9.5(8)

Niles



Tues 11 June 1969

Ce (ng/m³)



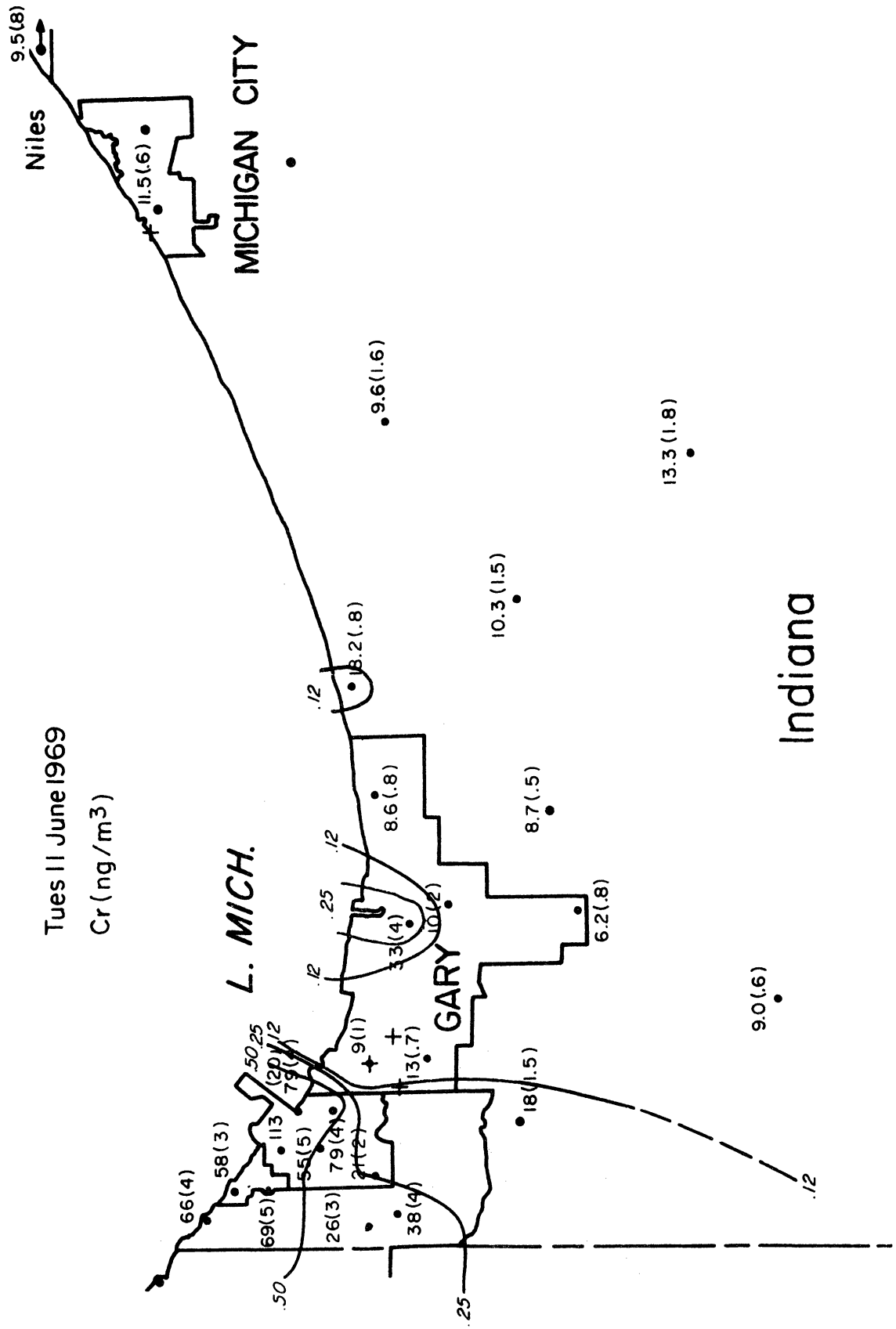
L. MICH.

GARY

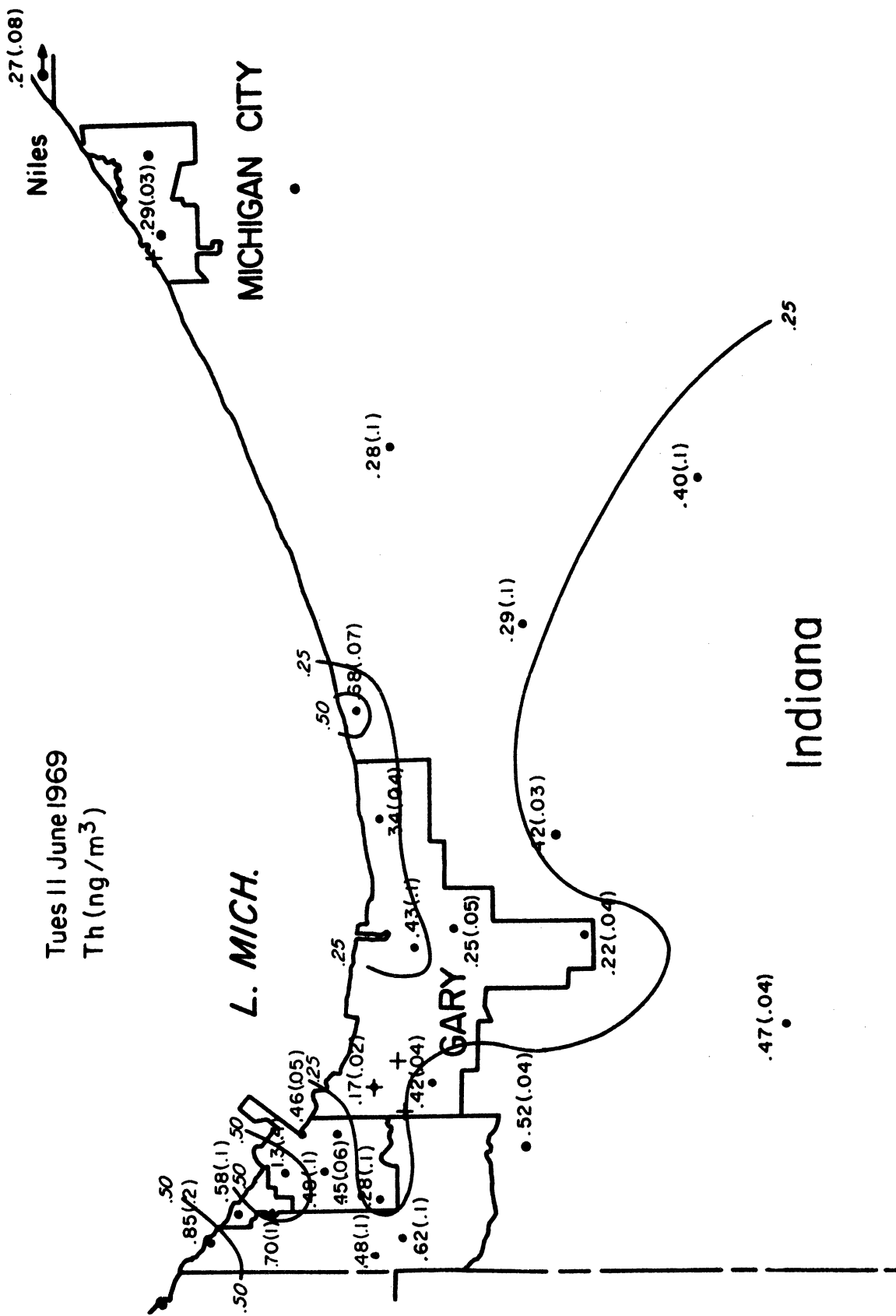
MICHIGAN CITY

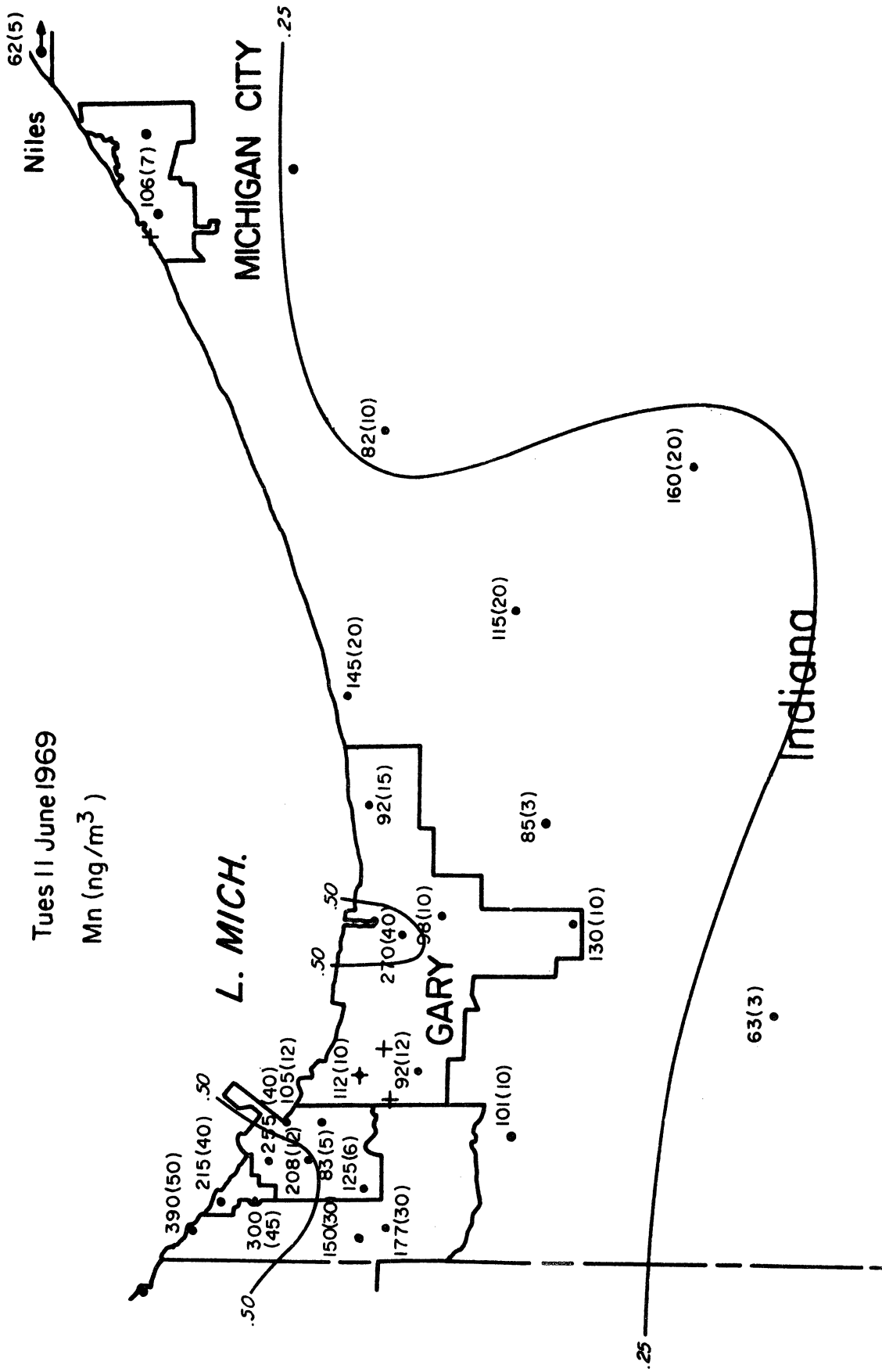
Niles

Indiana



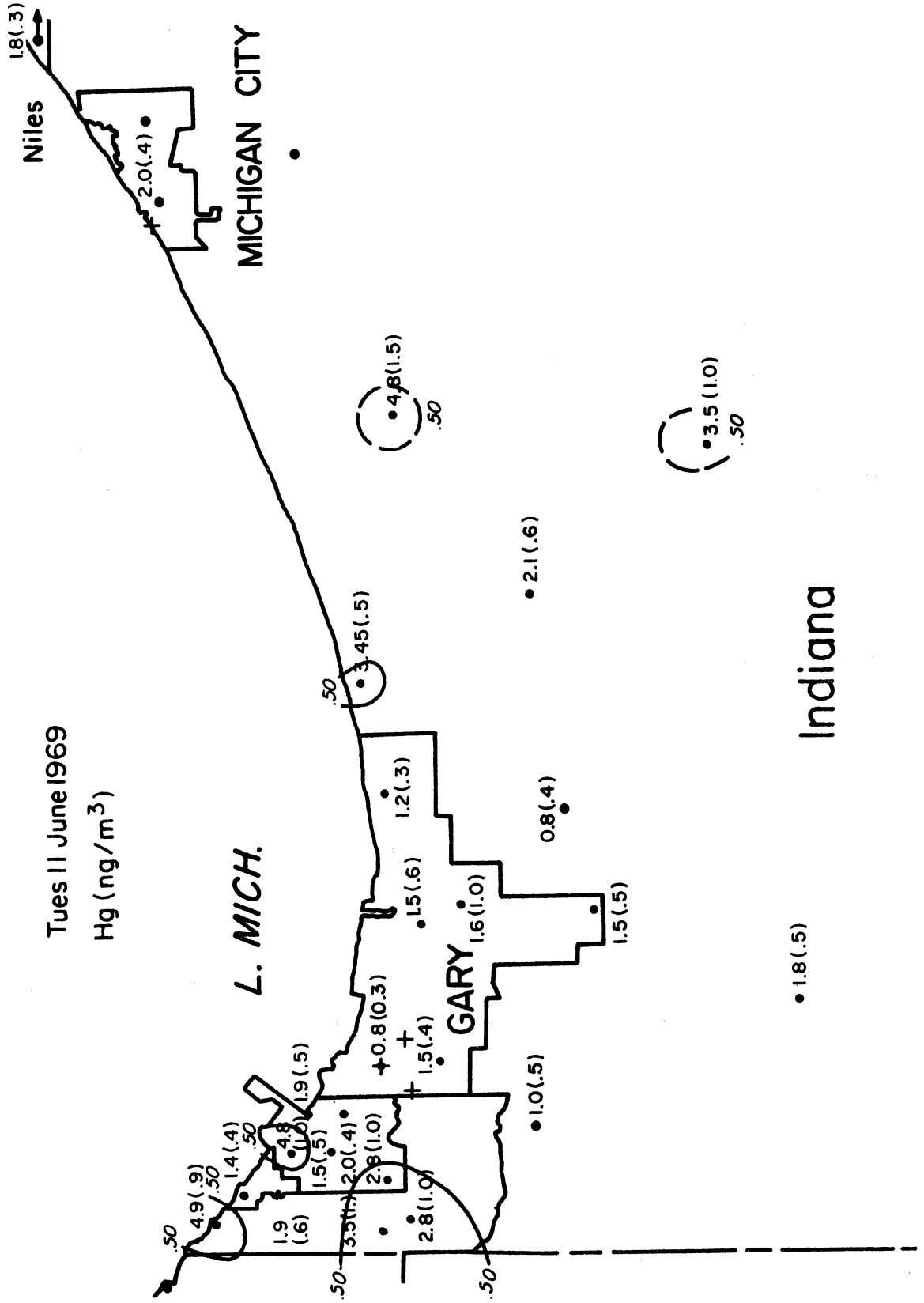
Tues 11 June 1969
Th (ng/m³)



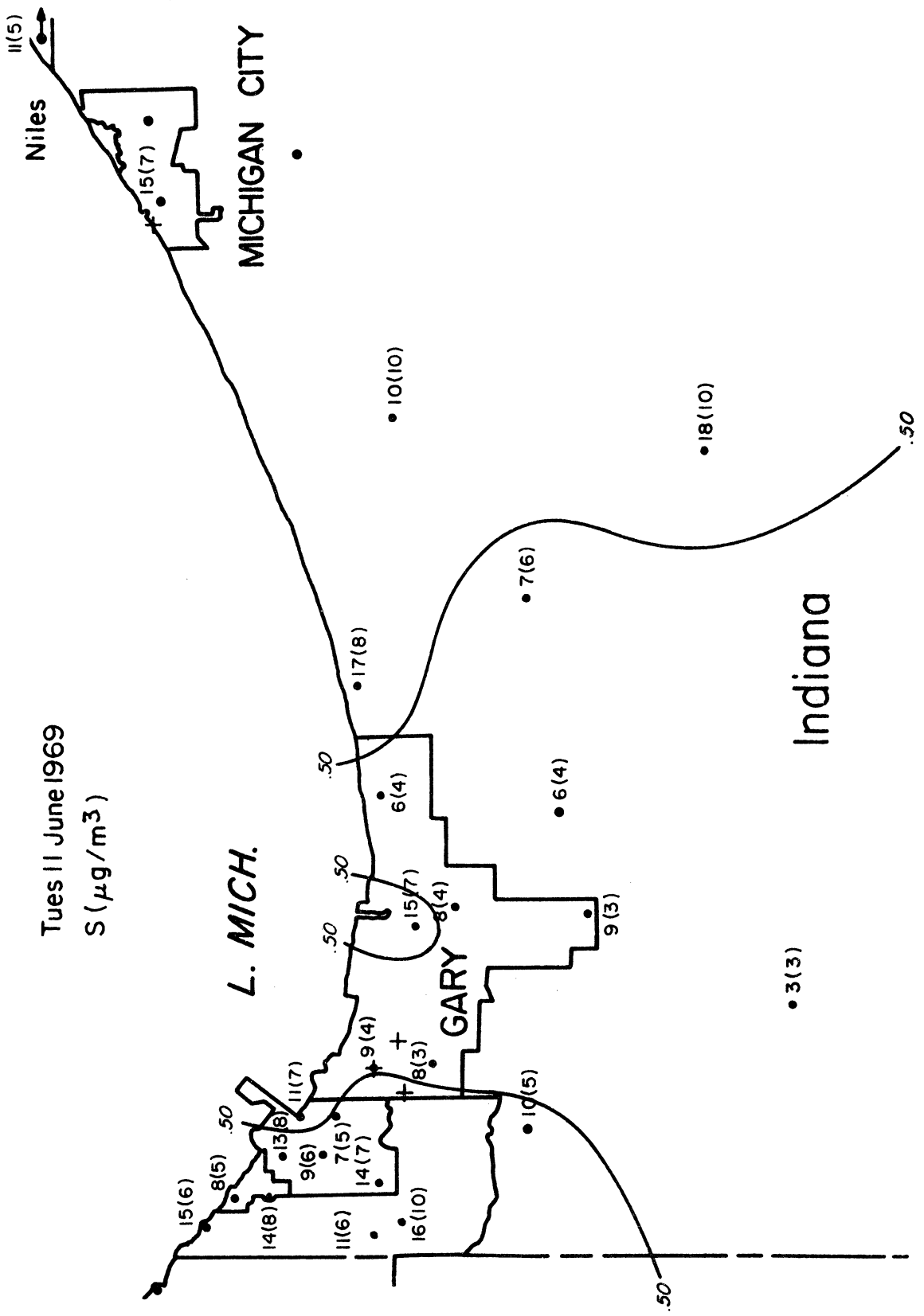


Tues 11 June 1969

Hg (ng/m³)

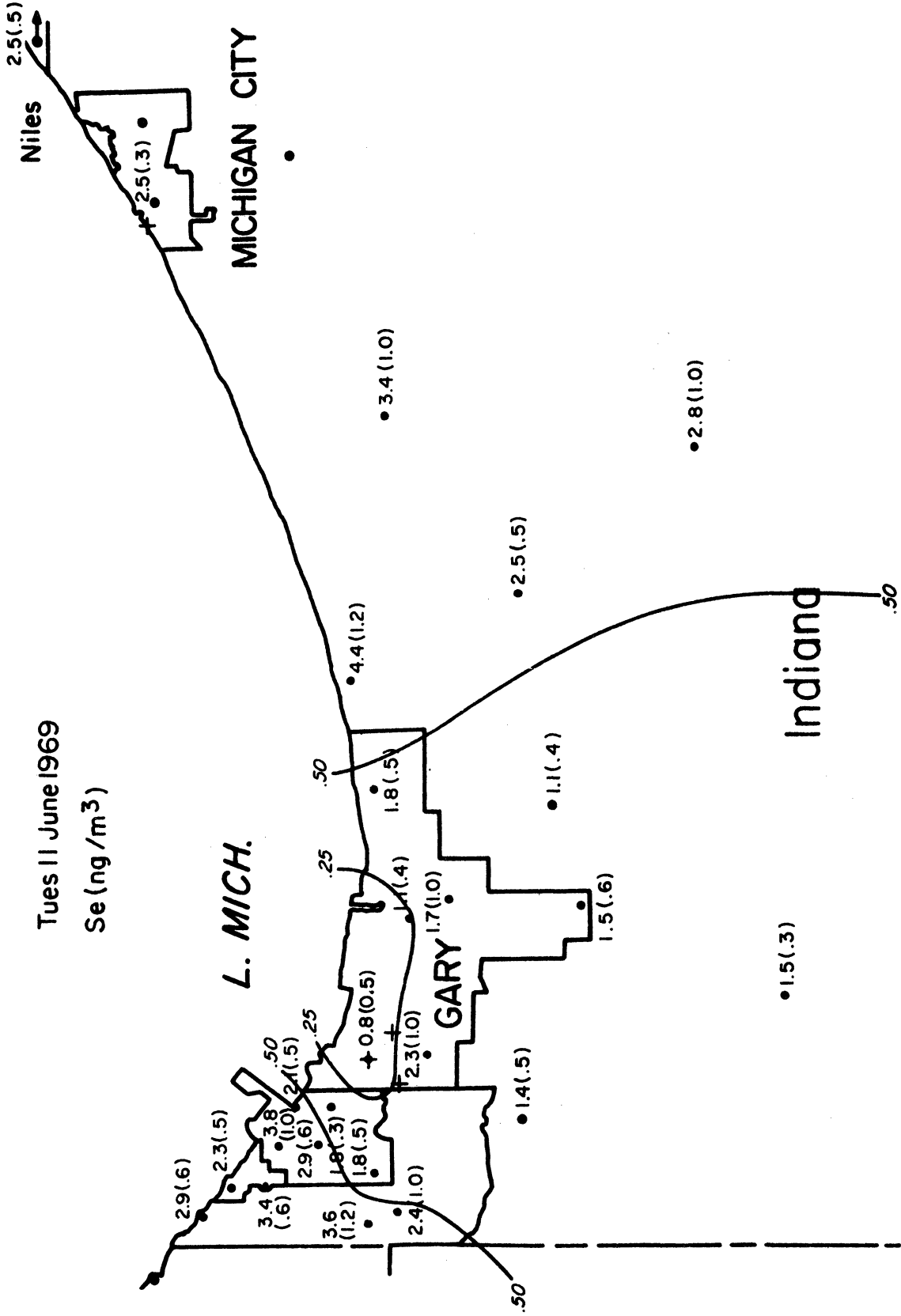


Tues 11 June 1969
S ($\mu\text{g}/\text{m}^3$)



Tues 11 June 1969

Se (ng/m³)



Niles

.95 (.1)



1.0 (.1)

MICHIGAN CITY

Tues 11 June 1969

Co (ng/m³)

L. MICH.

.50

.50

.25

.25

.25

.25

.25

.25

.25

.25

.25

.25

.25

.25

.25

.25

.70 (.15)

.76 (.10)

1.35 (.20)

.50

.50

.25

.25

.25

.25

.25

.25

.25

.25

.25

.25

.25

.25

.25

.25

.25

.70 (.10)

.8 (.1)

1.5 (.15)

.6 (.1)

.55 (.06)

.47 (.06)

.84 (.08)

1.35 (.15)

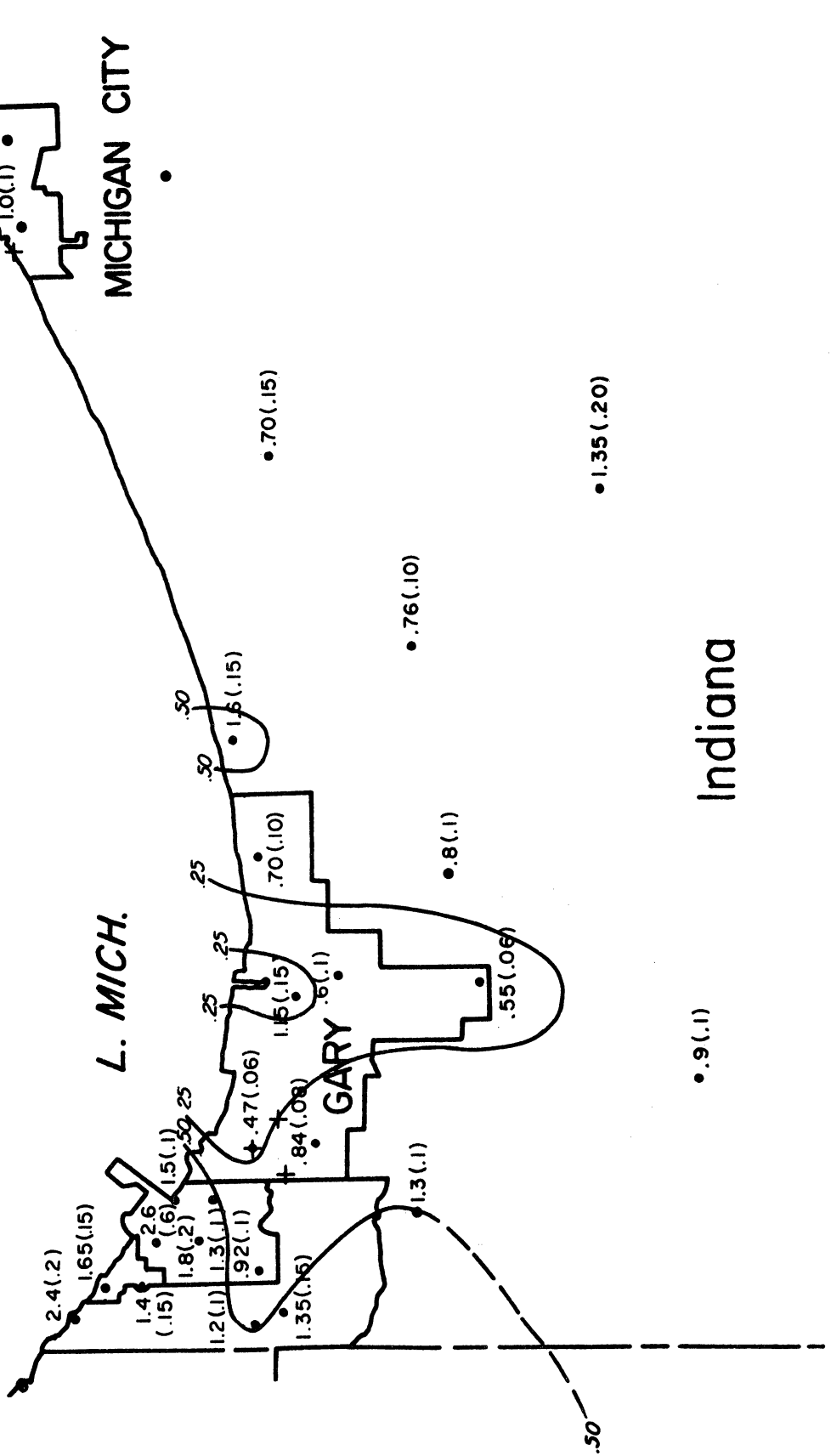
1.3 (.1)

GARY

.9 (.1)

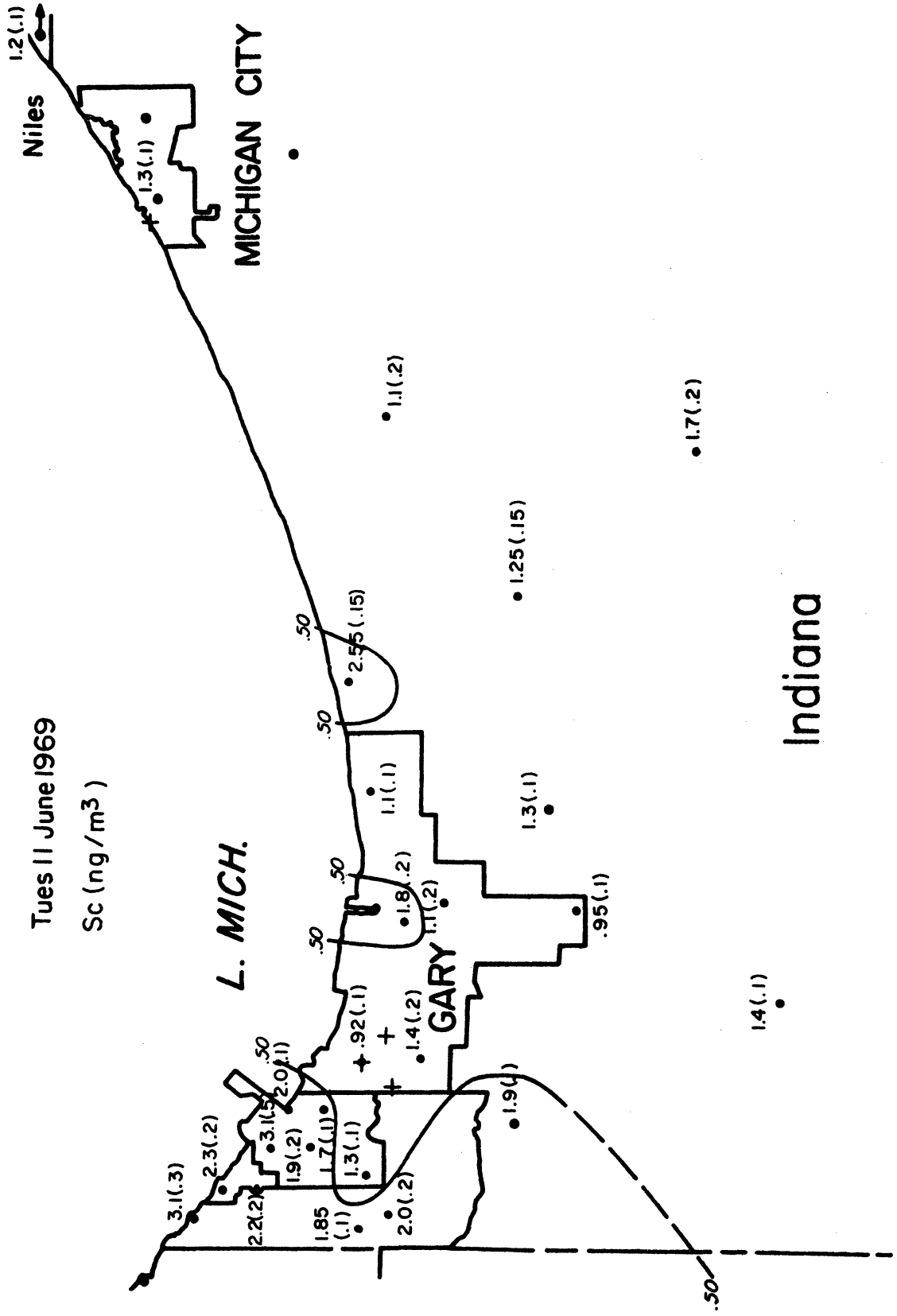
Indiana

.50

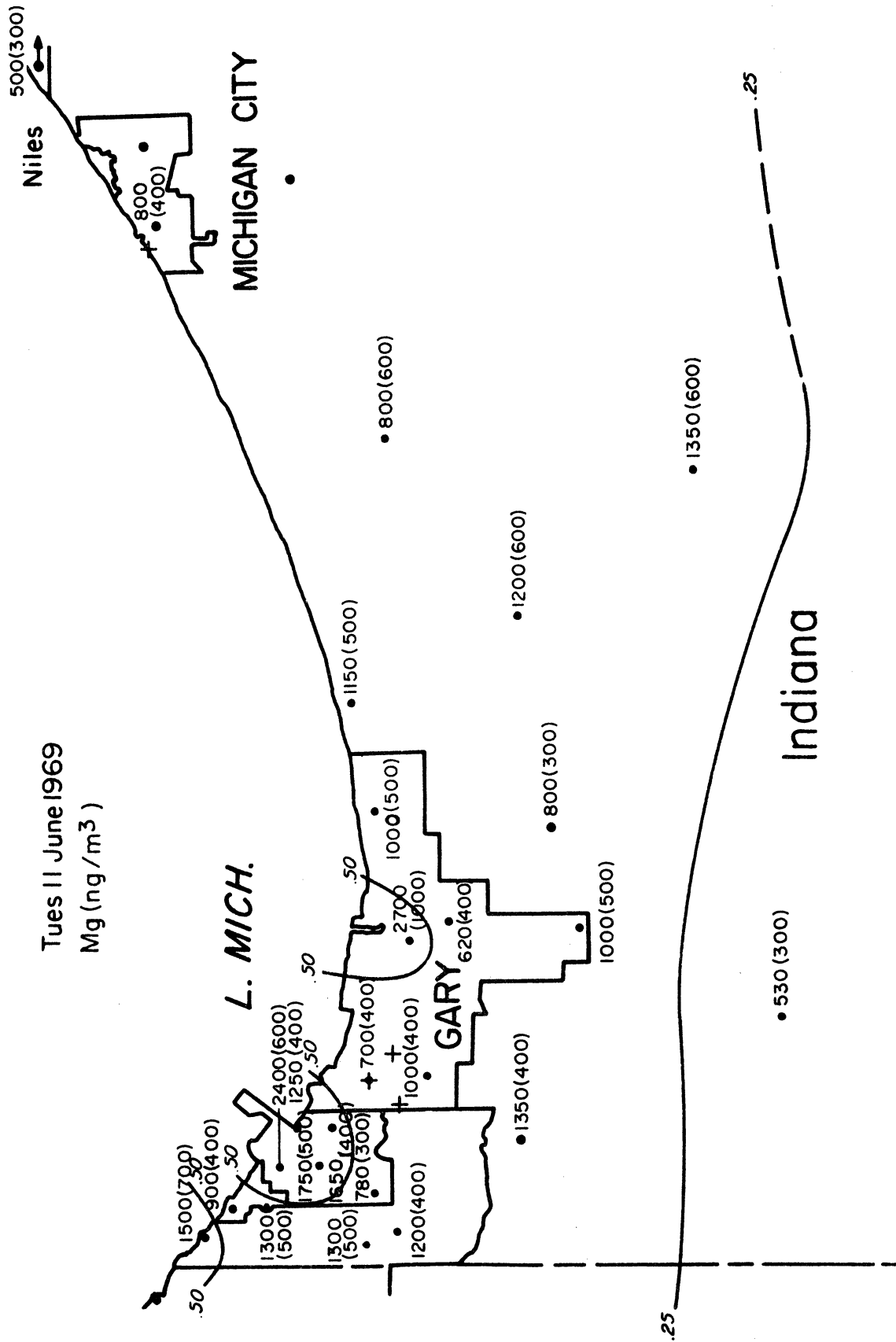


Tues 11 June 1969

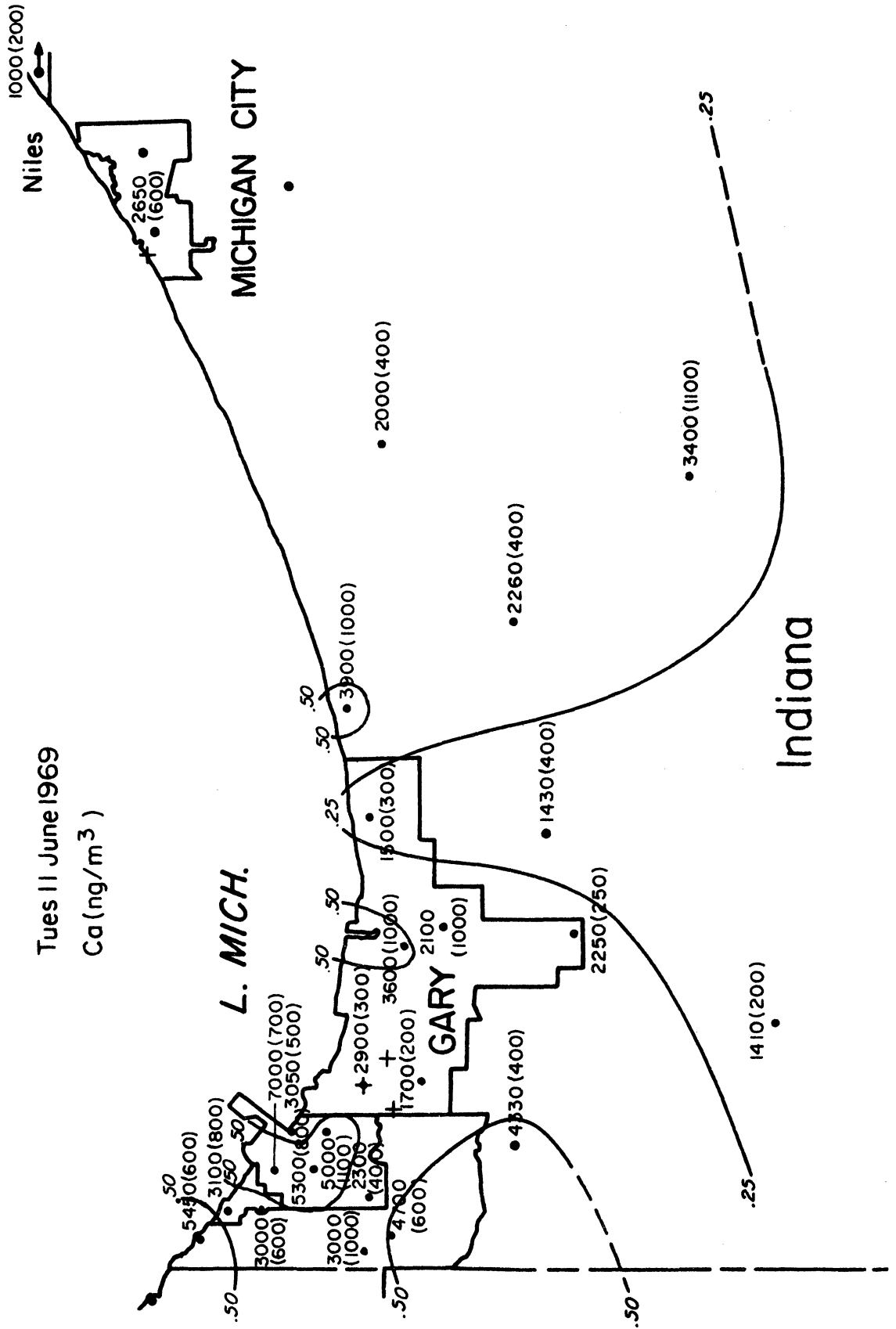
Sc (ng/m³)



Tues 11 June 1969
Mg (ng/m³)

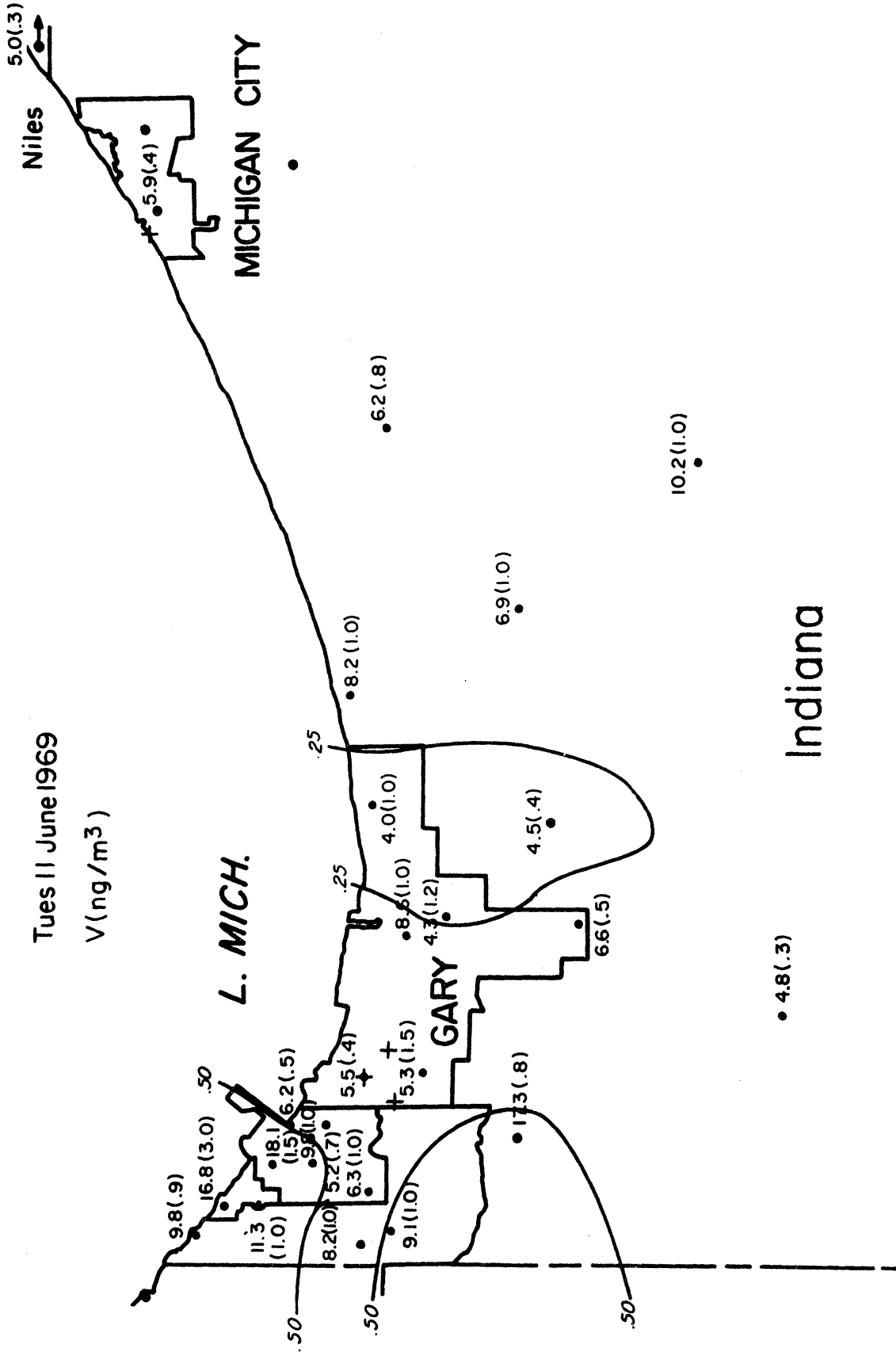


Tues 11 June 1969
Ca (ng/m³)



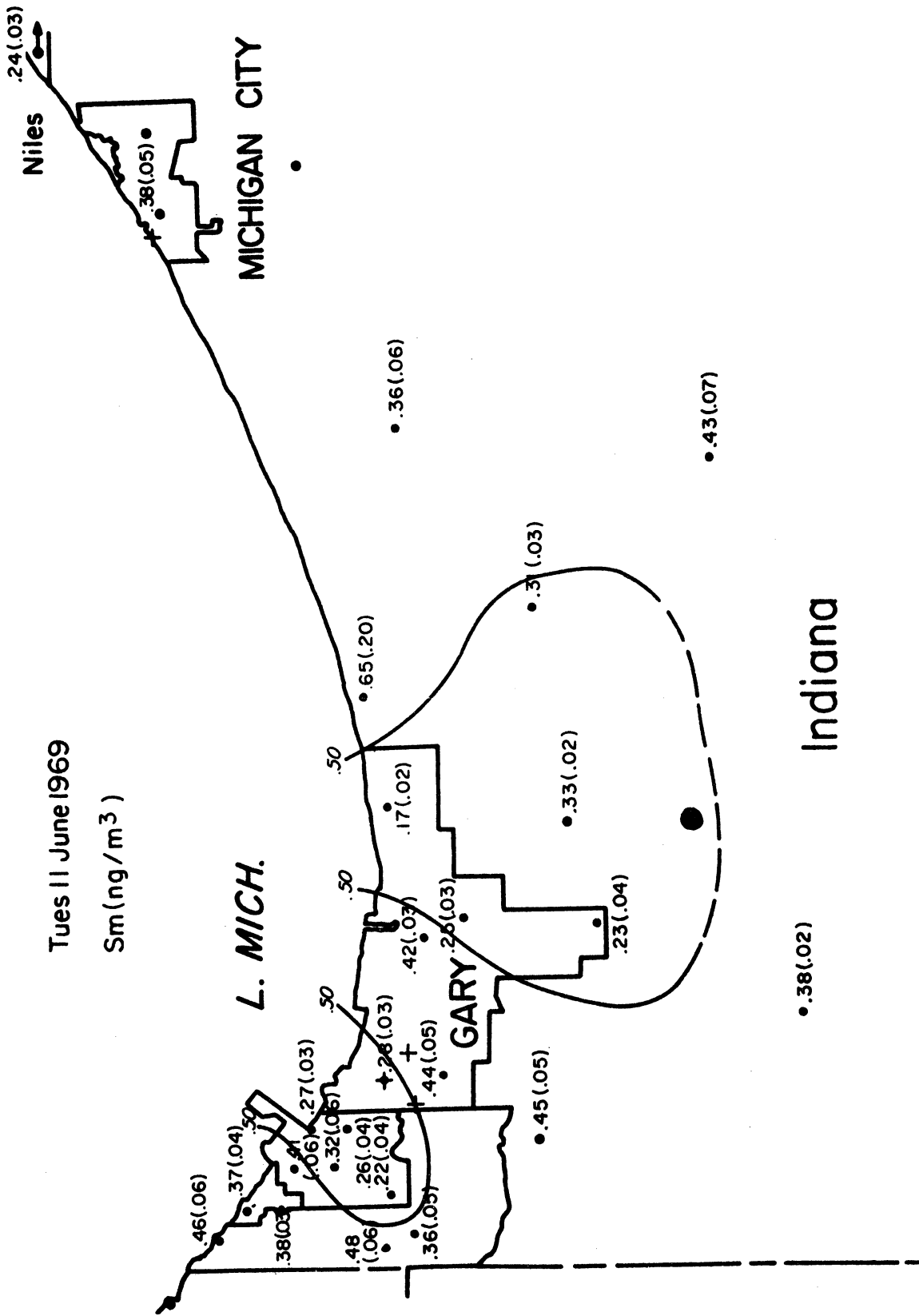
Tues 11 June 1969

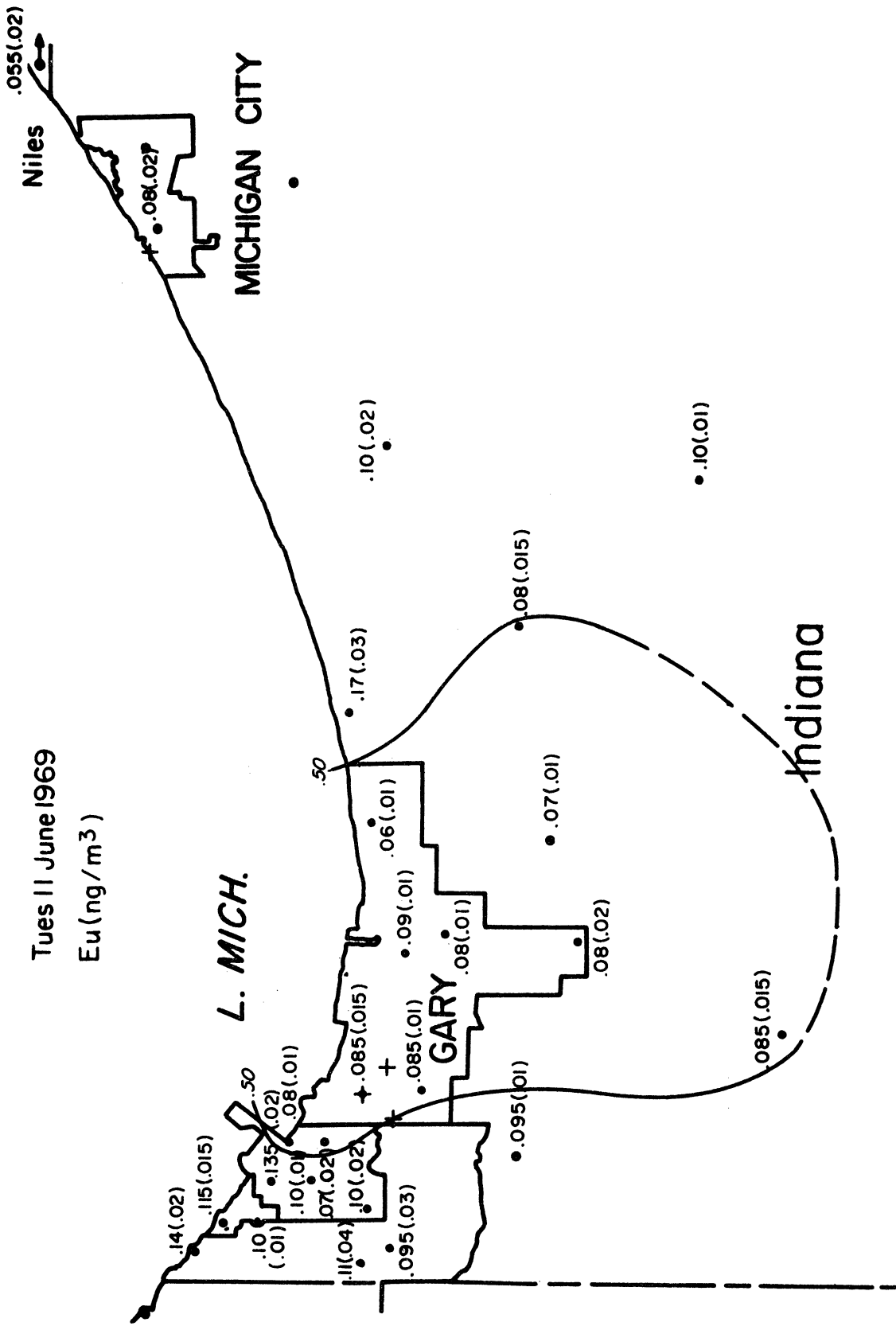
V (ng/m³)



Tues 11 June 1969

Sm (ng/m³)





Niles 170(20)

Tues 11 June 1969

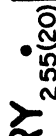
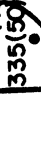
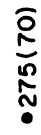
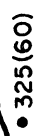
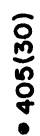
Na (ng/m³)

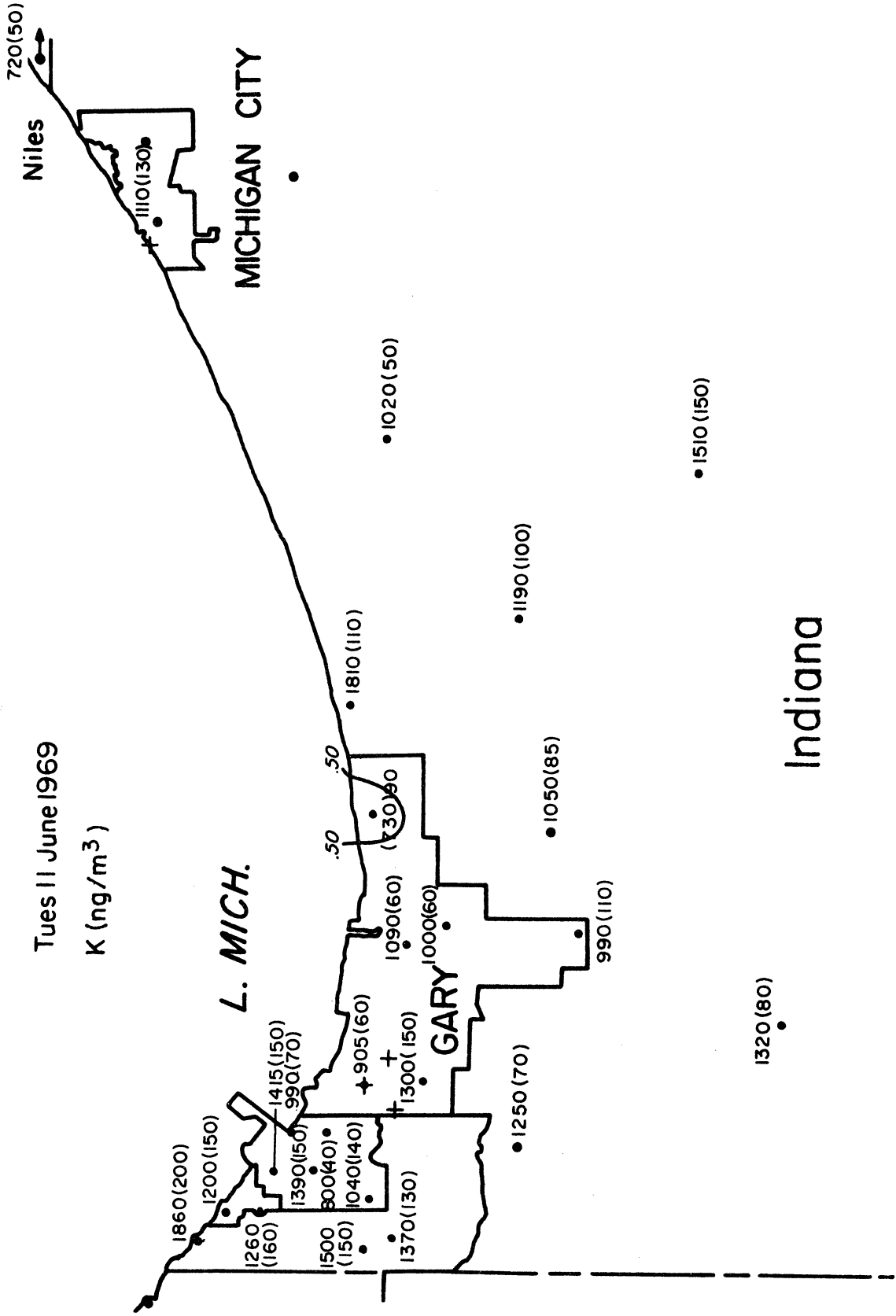
MICHIGAN CITY

L. MICH.

GARY

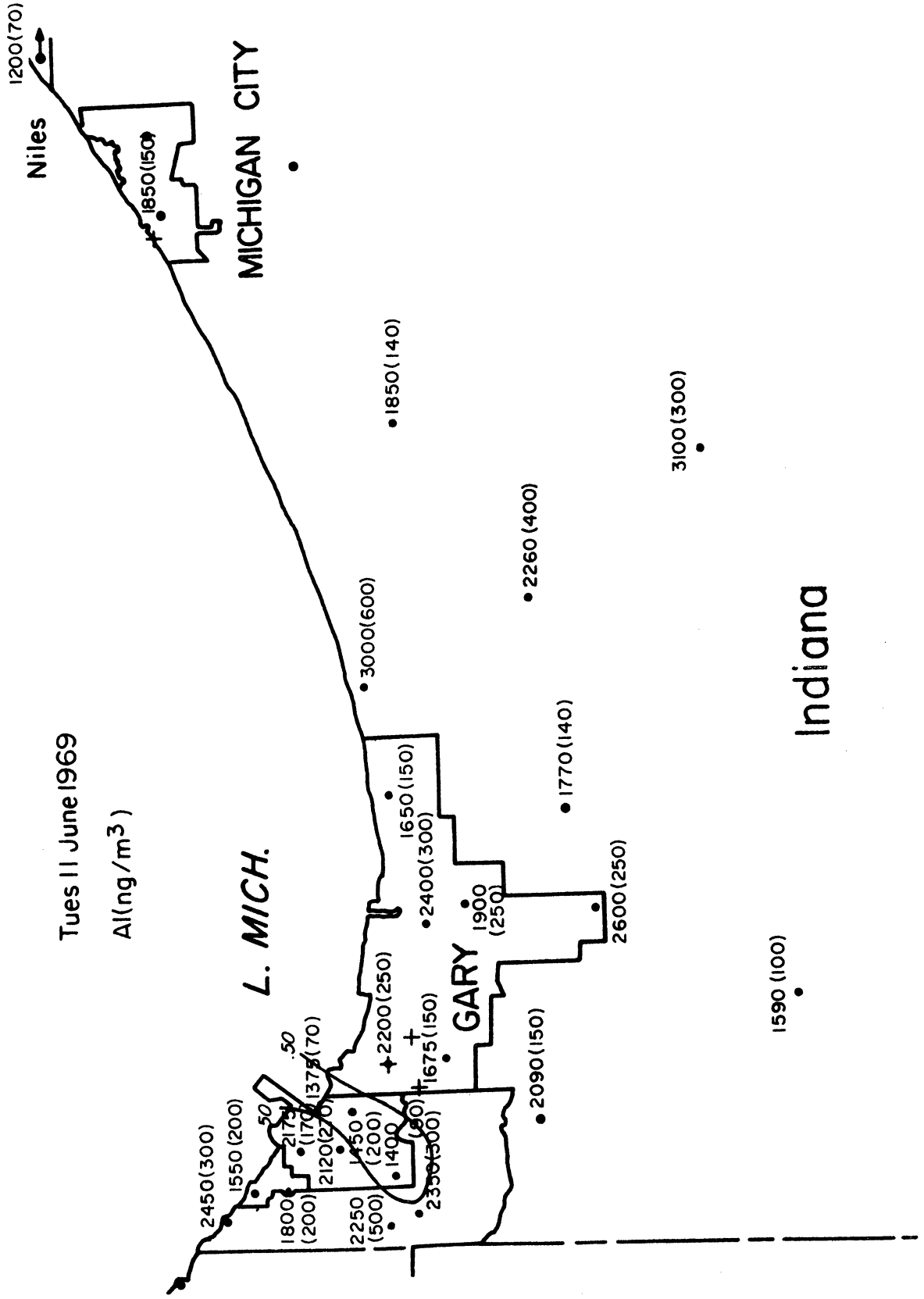
Indiana

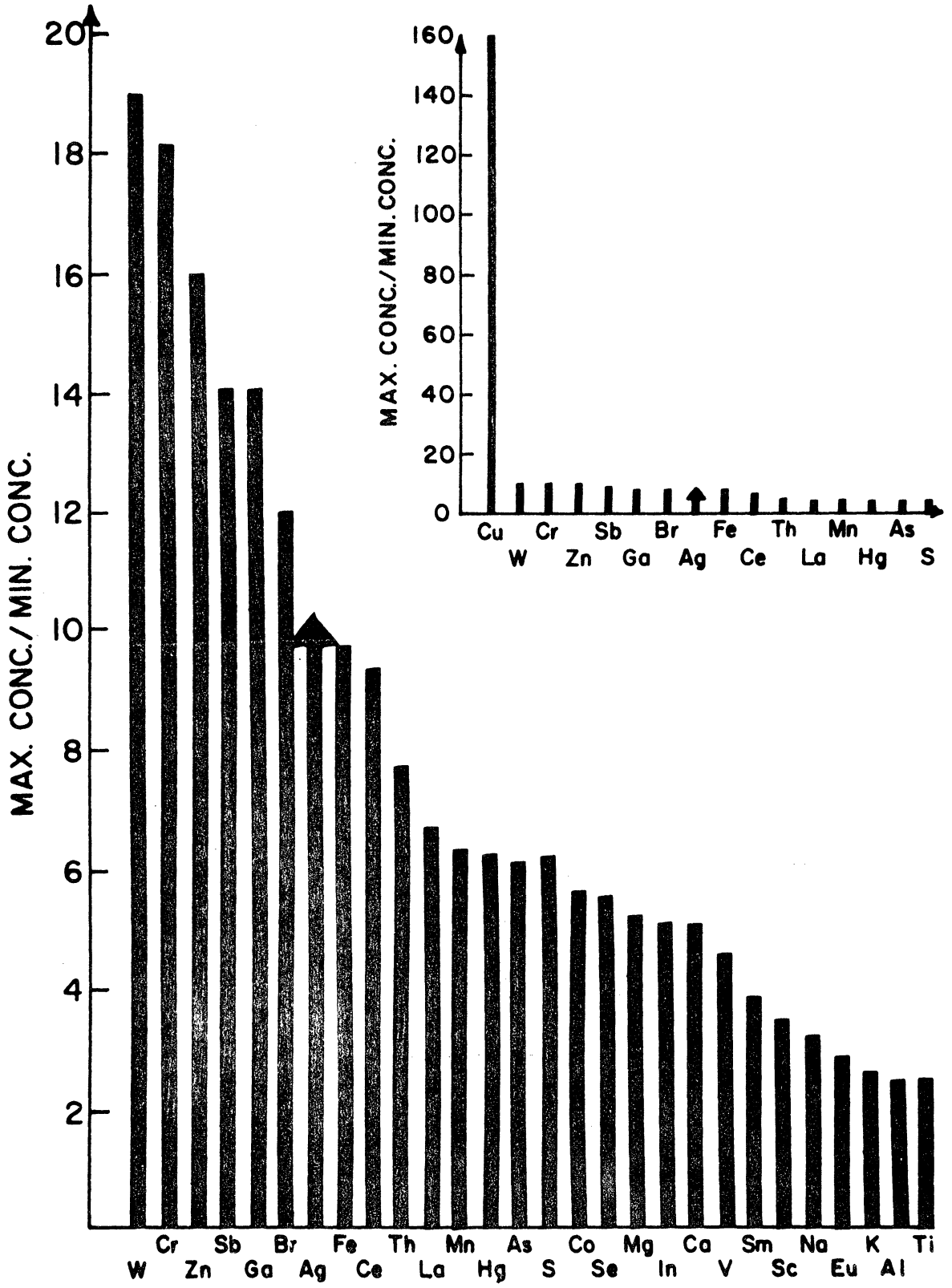




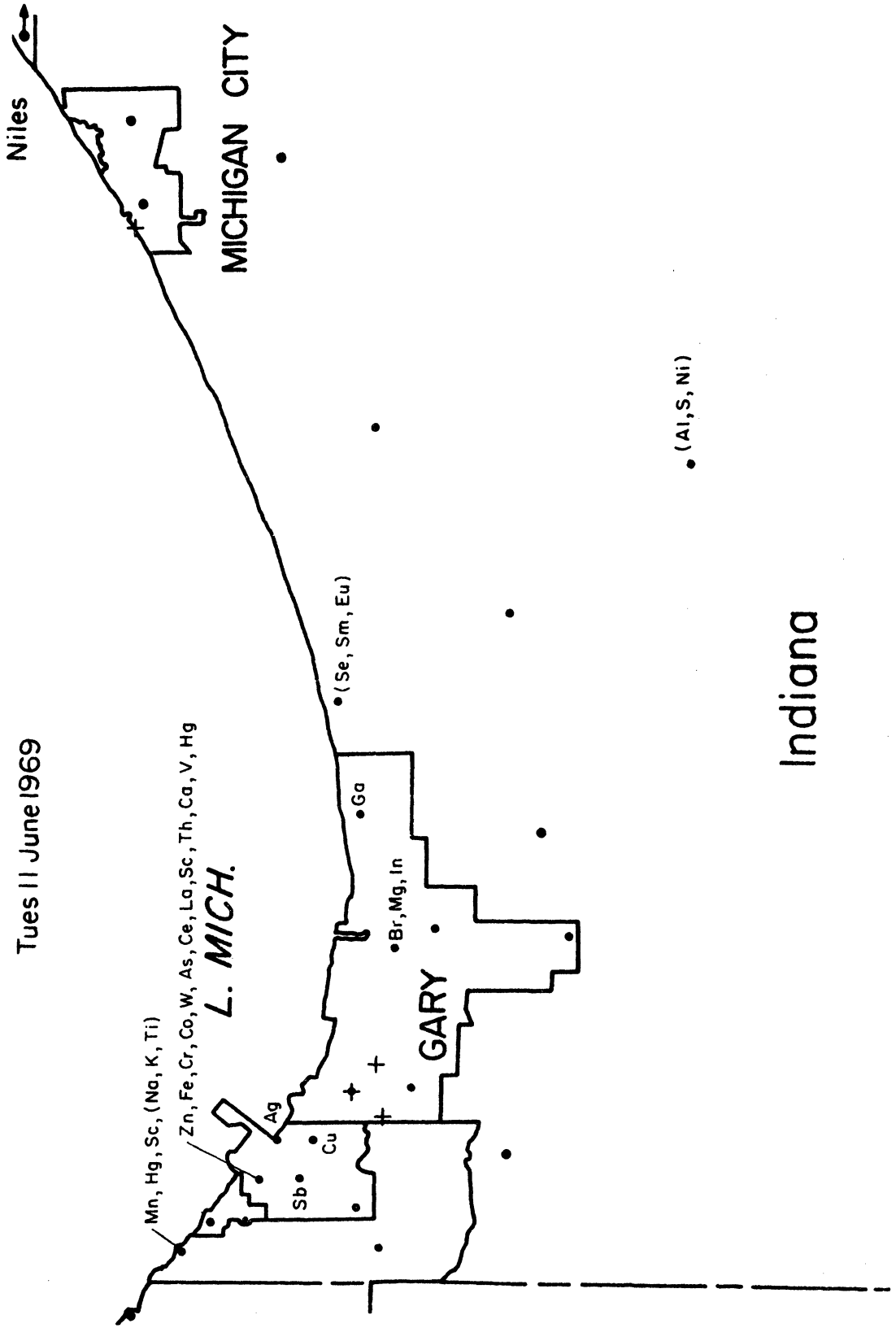
Tues 11 June 1969

Al (ng/m³)





Tues 11 June 1969



Diurnal Variations of Aerosol Trace Element Concentrations
as Determined by Nondestructive Neutron Activation Analysis

K. A. Rahn, R. Dams^a, J. A. Robbins, and J. W. Winchester^b

Dept. of Meteorology and Oceanography and Great Lakes Research Division
University of Michigan
Ann Arbor, Michigan 48104

a) Present address: Institute for Nuclear Sciences, University of Ghent,
Ghent, Belgium.

b) Present address: Dept. of Oceanography, Florida State University,
Tallahassee, Florida 32306.

ABSTRACT

Diurnal concentration variations of 20 trace elements have been studied over a 34-hour period in a rural area. 25 mm polystyrene filter samples were taken each 90 minutes and analyzed by nondestructive neutron activation analysis using Ge(Li) gamma-spectrometry and computer assisted data handling. Basic diurnal patterns are related to meteorological variables but variations from element to element are ascribed to differences in particle size distributions as determined by an Andersen Cascade Impactor. The behavior and particle size distribution of some elements suggested local sources.

A study of the diurnal concentration variations of atmospheric trace elements has recently been begun, as part of a larger study of their general atmospheric behavior. Previous investigations of daily patterns of pollution concentrations have been both theoretical (Hewson, 1960; HEW, 1965) and empirical (Commings, 1967; Munn, 1959; Summers, 1966; Weisman, 1969; USPHS, 1968) where in the latter cases soiling index, smoke, sulfur dioxide, nitrogen oxides and total particulate have served as indicators. To our knowledge, however, daily variations of individual trace elements have not yet been reported. Previous studies have all been in urban areas, whereas a rural setting was chosen for this investigation in an attempt to minimize the effects of source processes and urban micrometeorology relative to the mesometeorology.

This study was made possible by the recent development by the authors of a technique for nondestructive neutron activation analysis of aerosols collected on a high purity filter (Dams, 1970) in which up to 33 elements may be determined from 24 hour samples, many of which are recognized as being of pollution origin. Diurnal studies require sample lengths as short as possible, and the extreme sensitivity of this technique allows the determination of at least 15 elements in samples collected for as short a time as 90 minutes. In an effort to better correlate time variation patterns from element to element, particle size distributions were measured simultaneously.

Sampling

Sequential 90 minute filter samples were taken throughout the period, using a polystyrene material (Dams, 1970a) which combines good filtering performance with reasonably high purity. A high flow rate per unit surface area was achieved through the combination of a high vacuum pump (Gelman twin cylinder) and 25 mm diameter filter holders. Such a system produces flow rates through the polystyrene of $12 \text{ l-min}^{-1}\text{-cm}^{-2}$, as opposed to the figure of $4.5 \text{ l-min}^{-1}\text{-cm}^{-2}$ obtained with a high volume sampler (20x25 cm filter and low vacuum pump). Each sample consisted of aerosols from approximately 4m^3 of air.

Particle size distribution of the elements were determined by use of an Andersen Cascade Impactor, which separates aerosols into 7 fractions ranging from radii of roughly 8 μm down to 0.1 μm . Highly pure polyethylene sheets were used as impaction surfaces and analyzed in the same manner as the filters. A backup polystyrene filter (25 mm diameter) was used to catch the smaller particles. Because of the low flow rate of this instrument (28 l-min^{-1}) only one size distribution sample was taken throughout the experiment. All samples were taken in a ventilated instrument shelter 1.5 meters above ground, over short grass.

Sampling was performed in a rural area 3 miles west of Niles, Michigan and 15 km north of South Bend, Indiana. It is approximately 45 km east of Lake Michigan and 100 km northeast of the heavily industrialized Northwest Indiana area. Samples were taken during 34 hours on 21 and 22 August, 1969, when the entire north central and northeastern U.S. was under the influence of a broad Canadian high pressure area. Winds during this period varied from calm at night to 6.5 m/sec during the afternoon, and the extreme stability of the air mass prevented any clouds from forming. Light ground fog was observed during the early morning hours of the second day. Figures 1 and 2 give some of the meteorological conditions recorded at ESSA WBAS South Bend, Indiana. Figures 3 and 4 show surface weather conditions for 7 AM EST on both sampling days.

Analysis

The technique as described earlier (Dams, 1970) was applied. The complete filter (25 mm diameter) or the complete polyethylene sheet was irradiated twice with slow neutrons in the Ford Nuclear Reactor at the University of Michigan, first for 5 minutes, later for 4 hours. Each sample was counted 4 times, at 3 and 15 minutes after the first irradiation, and 20 hours and 20 days after the second irradiation. Counting was performed with a 30 cm^3 Ge(Li) high resolution gamma ray detector coupled to a 4096 channel pulse height analyzer. A digital computer program was used to integrate photopeaks of the sample, compare them with standard spectra, subtract

blank values, calculate concentrations of the elements in air and standard deviations on the obtained results.

Results

The results are summarized in Table 1. They reveal that 15 elements could be determined in nearly all of the samples, namely Al, V, Br, Na, K, Mn, Ti, Sm, Eu, La, Sc, Zn, Fe, Co, and Cr. A half dozen others (Sb, As, Ga, Mg, Cu, and Ce) could only be determined in some samples. Due to their incompleteness the results for the latter 6 elements are not very useful and are not given in Table 1. The behavior of a number of representative elements is shown in Figure 5. Particle size distributions of 18 elements are summarized in Table 2 and 9 of these are plotted in Figures 6 and 7. Standard deviations are given in parentheses. If high count rates were obtained these standard deviations may be as low as 10%. Because of the short sampling times the concentrations of several elements were at or near the limit of detection, and standard deviations of these results are much higher. On some stages of the Andersen impactor only an upper limit could be set for the concentration of several elements.

Discussion

It is obvious that very large variations occur in the concentrations of several elements during a 24 hour period. The behavior of aluminum, shown in Figure 5, is representative of a number of other elements such as Ti, Mg, Sc and the rare earths, Sm, Eu, and La. Concentration variations by a factor of up to 10 occur within a few hours. A number of other elements such as Na, K, Fe, Co, and Cr show less prominent variations, on the order of 2.5 rather than 10. The behavior of Mn seems to be in between these two extreme groups.

How can this consistent behavior pattern for a large number of elements be understood? Smoke, SO₂, NO, NO₂, CO, total oxidants, total hydrocarbons and visibility measurements have also shown consistent diurnal patterns, but with

average variations of at most a factor of three (Commins, 1967; Munn, 1959; Summers, 1966; Weisman, 1969; USPHS, 1968). Being urban measurements, these variations were mostly related to variations in local source processes and city ventilation. In the present case, one deals with a rural area, and measures primarily distant sources, and diurnal meteorological variations should thus be more important. The pattern found is indeed consistent with the predicted variations of ground-level concentrations from elevated sources (HEW, 1965).

With the previous considerations in mind the following tentative explanation is offered. Particulate pollutants released at stack height during the fair weather nocturnal temperature inversion conditions tend to remain at stack height until after sunrise. Daylight hours bring ground heating and generation of turbulent motions which build rapidly upwards until the pollutant layer is reached some one to three hours after sunrise. Eddy transport of these pollutants to the surface (Hewson fumigation type I) causes the steep morning peak. Continued increase of the maximum mixing level until the midafternoon further dilutes concentrations, after which the lowering mixing level and increasing thermal stability initiates the gradual concentration increase of late afternoon and early evening.

The concentration levels of evening, being effectively cut off from elevated sources by the temperature inversion, might be expected to decrease slightly during the night. Instead, they are in most cases observed to drop rapidly during the early morning hours, often reaching the lowest levels of the sampling period. Our hypothesis is that local ground fog at the sampling site was the primary agent responsible for this decrease, due to fog droplet nucleation, probably predominantly by the giant particle component of the aerosol population, followed by enhanced sedimentation and/or impaction of the enlarged droplets. Though fog was not recorded at the more urban South Bend Airport, the temperature there decreased to within 2 degrees of the dewpoint, and the relative humidity reached a maximum of 93% at the 4 AM and 8 AM observations (Fig. 1).

Confirmation of this idea comes from the observation that in general those elements showing the largest concentration variations share two characteristics, namely relatively deep morning minima and masses concentrated on larger particles. This relation can be verified from the plots of Al and V, and is also noted for Ti, Mg, Sc, La, Eu, and Sm. On the other hand, elements like Na, K, Cr, Co, and Mn, showing smaller diurnal variations, are more equally distributed over the 0.1-10 μm size range.

We then visualize the fog formation as involving the larger and more soluble aerosols (i.e. those ordinarily collected on the first stages of the impactor), rapidly growing to a quasi-equilibrium radius of some 5-10 μm . Because the droplet concentration in typical fogs (100-500 cm^{-3}) (Dingle, 1970) is large relative to the giant aerosol number density in continental aerosols (1 cm^{-3}) (Junge, 1963) but small relative to the large particle component of the same (1000 cm^{-3}), it is possible that a majority of the giant particles and a minority of the large particles served as nucleating agents. Removal of these droplets would preferentially decrease concentrations of those elements primarily in giant aerosols.

Certain of the observed elements show diurnal patterns suggestive of local sources. Br is the clearest example, the probable source being automotive exhaust from the road some 50 meters distant. Distinct traffic maxima are observed about 6-7 AM, 3-5 PM, and 11-12 PM, very nearly the times of Br maxima. Further evidence comes from the measured particle size distribution of Br, where 65% of its mass is found on the backup filter (Table 2). This is in agreement with the very small, condensation aerosol nature of auto exhausts, and indicates the fresh nature of most of the Br (Loucks, 1970).

The diurnal variation of Zn is not very consistent with the other elements, which may be partially due to the low quality of the analytical results for this element. It may however also be correlated with its predominant distribution on small particles, probably due to formation via a condensation process.

The steep morning peak makes the V pattern somewhat different from those of the other elements. The most important source of V is known to be fuel oils, but because of the August date this does not seem to provide a sufficient explanation. Heating of commercial establishments may be related to the steep morning peak, however. In addition, a considerable fraction (30%) of this element is found on the very small particles, pointing toward a condensation formation process and recent age for its Aitken component.

Conclusion

The obtained results demonstrate that nondestructive neutron activation analysis can very favorably be applied to the study of diurnal variations of trace elements in the atmosphere. The 15 elements which can be measured after sampling times as short as 90 minutes in a rural area show distinct variations in diurnal behavior and should be indicators enough for the behavior of most other trace elements. It seems that the application of this technique in studies of simultaneously measured total concentration variations and particle size distribution of airborne particulates should lead to significant advances in the understanding of source processes and identification of dilution and removal mechanisms. The observed size distribution patterns remote from the source may not only reflect differing source processes but may also result in a tendency toward different atmospheric behavior patterns. This specific investigation was however only of an exploratory nature and further experiments under different meteorological conditions are under way in order to expand upon the tentative conclusions reported here.

References

- B.T. Commins and R.E. Walter, (1967) Atmos. Environ. 1, 49.
- R. Dams, K.A. Rahn, and J.W. Winchester, (1970a) Environ. Sci. and Tech., submitted.
- R. Dams, J.A. Robbins, K.A. Rahn and J.W. Winchester, (1970) Anal. Chem., in press.
- A.N. Dingle, (1970) Dept. of Met. and Ocean., Univ. of Mich., private communication.
- E.W. Hewson, (1960) "Meteorological Measuring Techniques and Methods in Air Pollution Studies" in Industrial Hygiene and Toxicology, Vol. 3, L. Silverman (ed.) New York, Interscience.
- C.E. Junge (1963) Air Chemistry and Radioactivity, Academic Press, N.Y.
- R.H. Loucks and J.W. Winchester, (1970) J. Geophys. Res., in press.
- R.E. Munn and M. Katz, (1959) Int. J. Air. Poll. 2(1), 51.
- P.W. Summers, (1966) J. Air. Poll. Control Assoc. 16(4) 33.
- U.S. Department of Health, Education, and Welfare, (1965) "Meteorological Aspects of Air Pollution," course conducted by Air Pollution Training Program, Cincinnati, Ohio.
- U.S. Public Health Service, (1968) Air Quality Data from the National Air Sampling Networks and Contributing State and Local Networks, 1966 Edition, Durham, N.C.
- B. Weisman, D.M. Matheson and M. Hirt, (1969) Atmos. Environ. 3, 1.

Table 1. Diurnal Behavior of 15 Elements

Begin Sampling Time Total Sampling Time	ng/m ³ of element									
	8 h 10 80 min	9 h 30 90 min	11 h 00 90 min	12 h 30 90 min	14 h 00 90 min	15 h 30 90 min	17 h 00 90 min	18 h 30 90 min	20 h 00 90 min	
10 ⁻³ xAl	2.9(.3)	1.9(.2)	2.1(.2)	0.65(.07)	0.88(.09)	1.1(.1)	1.6(.2)	1.9(.2)	2.1(.2)	
V	11(1)	8.8(.9)	6.2(.7)	1.7(.3)	2.6(.3)	2.0(.4)	3.5(.4)	4.5(.5)	4.7(.5)	
Br	160(16)	105(11)	77(8)	48(5)	160(16)	125(12)	44(5)	122(12)	121(12)	
Na	540(50)	310(57)	580(50)	300(30)	300(60)	280(55)	290(30)	320(45)	405(40)	
K	-----	840(80)	1040(100)	460(50)	550(50)	650(60)	940(90)	560(60)	900(90)	
Mn	64(6)	31(3)	49(5)	20(2)	29(3)	27(3)	41(4)	51(5)	61(6)	
Ti	260(75)	185(60)	73(65)	67(45)	<47	39(50)	72(50)	155(50)	75(55)	
Sm	-----	0.30(.04)	0.30(.03)	0.055(.025)	0.15(.04)	0.22(.03)	0.25(.03)	0.17(.03)	0.33(.03)	
Eu	-----	0.045(.02)	0.07(.02)	<0.02	0.05(.02)	0.025(.015)	0.035(.015)	0.04(.015)	0.05(.02)	
La	-----	1.7(.4)	2.1(.4)	0.5(.35)	1.0(.3)	1.5(.35)	2.1(.35)	3.8(.4)	1.9(.3)	
Sc	-----	1.4(.3)	2.4(.4)	0.45(.20)	0.45(.20)	1.1(.3)	1.4(.3)	1.1(.3)	1.4(.3)	
Zn	-----	150(40)	50(50)	95(35)	65(30)	90(30)	<50	85(30)	130(30)	
10 ⁻³ xFe	-----	2.1(.6)	3.0(.6)	<0.9	1.6(.6)	1.1(.6)	1.3(.5)	1.7(.6)	1.0(.6)	
Co	-----	1(.8)	2(.81)	0.8(.8)	0.8(.8)	1.1(.8)	1.0(.8)	1.4(.8)	1.1(.8)	
Cr	-----	35(10)	25(10)	24(10)	12(10)	29(10)	25(10)	27(10)	29(8)	

Table 1 (cont.)

Begin Sampling Time Total Sampling Time	ng/m ³ of element									
	21 h 30 90 min	23 h 00 90 min	0 h 30 90 min	2 h 00 90 min	3 h 30 90 min	5 h 00 90 min	6 h 30 90 min	8 h 00 90 min		
10 ⁻³ xAl	1.2(.1)	1.6(.2)	1.2(.1)	0.56(.06)	0.39(.04)	0.51(.05)	1.3(.1)	1.8(.2)		
V	3.0(.5)	3.9(.6)	2.4(.5)	2.0(.4)	1.25(.4)	1.9(.4)	6.8(.7)	15.8(1.6)		
Br	89(9)	340(34)	231(23)	91(9)	61(6)	34(4)	970(90)	120(12)		
Na	230(50)	320(40)	345(35)	215(45)	150(50)	160(21)	230(55)	340(60)		
K	650(60)	690(70)	640(60)	430(40)	410(40)	330(30)	600(60)	860(80)		
Mn	51(5)	75(7)	46(5)	30(4)	28(4)	27(4)	32(3)	46(5)		
Ti	130(55)	140(65)	150(55)	<34	<42	<30	185(75)	145(60)		
Sm	0.33(.035)	0.16(.035)	0.27(.03)	0.12(.03)	0.12(.03)	0.16(.02)	0.33(.07)	0.39(.04)		
Eu	0.08(.015)	0.035(.015)	0.03(.015)	0.02(.01)	0.025(.015)	0.02(.01)	0.09(.02)	0.075(.02)		
La	1.2(.3)	1.6(.3)	0.8(.3)	1.2(.25)	0.3(.3)	0.7(.2)	1.1(.3)	1.7(.3)		
Sc	1.35(.3)	1.4(.3)	1.2(.3)	0.50(.20)	0.90(.20)	0.35(.20)	1.1(.3)	1.3(.3)		
Zn	220(30)	130(40)	60(40)	100(30)	150(30)	75(30)	100(30)	150(30)		
10 ⁻³ xFe	1.9(.6)	1.7(.6)	1.8(.6)	0.9(.6)	1.3(.7)	0.5(.5)	1.9(.7)	1.3(.7)		
Co	1.2(.8)	0.6(.8)	0.8(.8)	<0.7	0.8(.7)	0.5(1.0)	1.2(.8)	1.3(.8)		
Cr	15(10)	37(10)	18(8)	13(8)	30(10)	14(7)	21(10)	17(10)		

Table 1. (cont.)

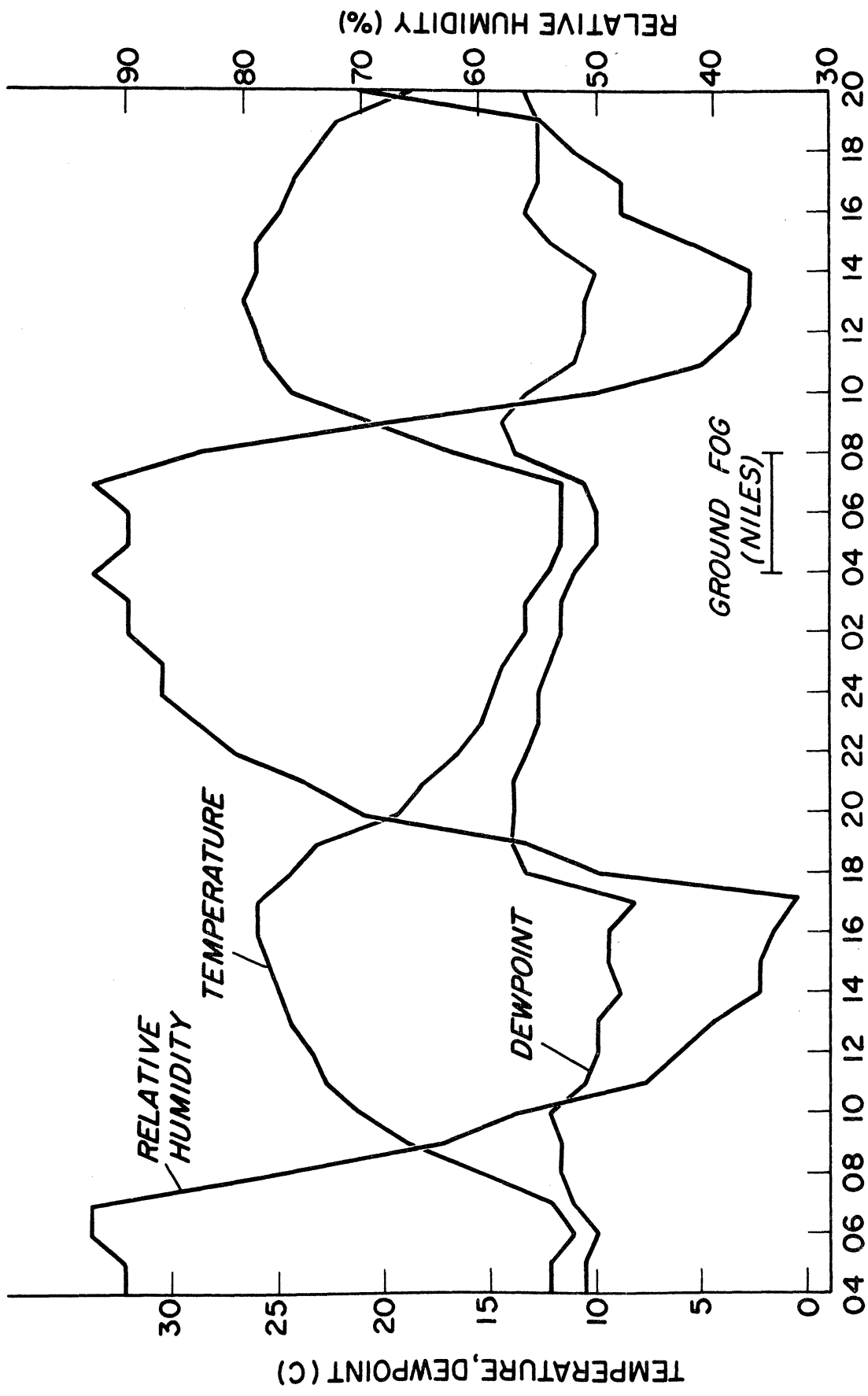
Begin Sampling Time Total Sampling Time	ng/m ³ of element							
	9 h 30 90 min	11 h 00 90 min	12 h 30 90 min	14 h 00 90 min	15 h 30 90 min	17 h 00 90 min	8 h 10 34h 20min	
10 ⁻³ xAl	1.3(.1)	0.93(.09)	1.4(.1)	1.4(.1)	1.5(.1)	2.6(.3)	1.6(.2)	
V	3.5(.4)	3.1(.5)	3.0(.5)	2.9(.5)	4.2(.6)	5.0(.7)	5.1(.5)	
Br	53(5)	36(7)	36(7)	47(6)	52(8)	59(9)	141(14)	
Na	190(21)	360(60)	330(50)	390(40)	360(70)	480(60)	330(35)	
K	370(40)	690(60)	670(60)	730(70)	740(70)	810(80)	630(60)	
Mn	40(5)	35(4)	38(40)	71(7)	106(11)	74(11)	53(5)	
Ti	78(38)	125(60)	<48	68(50)	82(68)	78(68)	240(35)	
Sm	0.21(.03)	0.16(.03)	0.10(.03)	0.22(.03)	0.39(.03)	0.20(.03)	0.165(.02)	
Eu	0.04(.01)	0.06(.015)	0.035(.015)	0.04(.015)	0.04(.015)	0.035(.015)	0.035(.015)	
La	0.8(.25)	0.5(.3)	0.3(.3)	0.8(.3)	3.0(.4)	1.1(.3)	1.25(.2)	
Sc	1.3(.3)	0.9(.25)	0.7(.25)	0.8(.25)	0.7(.25)	0.8(.25)	0.9(.25)	
Zn	55(25)	140(40)	<60	120(30)	80(30)	130(30)	120(30)	
10 ⁻³ xFe	0.9(.5)	0.9(.5)	<0.6	1.1(.5)	1.5(.5)	1.0(.5)	1.2(.4)	
Co	0.7(.8)	<0.8	<0.8	<0.9	<0.8	<0.8	0.7(.5)	
Cr	12(8)	24(8)	24(8)	20(7)	23(9)	25(9)	21(7)	

Table 2. Particle Size Distributions of 18 Elements - Concentrations in ng/m³.

Element	Backup Filter	Stage-Andersen							
		7	6	5	4	3	2	1	
Al	100(10)	25(2.5)	71(7)	106(10)	405(40)	532(55)	438(45)	417(42)	
V	0.75(.07)	0.11(.03)	0.077(.033)	0.16(.04)	0.38(.07)	0.39(.07)	0.44(.07)	0.58(.07)	
Br	63(6)	6.4(.6)	2.3(.5)	4.3(.6)	5.2(.6)	8.5(1.0)	3.7(.5)	2.1(.5)	
Cl	----	<11	<10	<10	14(4)	24(5)	28(5)	28(5)	
Na	46(5)	9.1(1.6)	14(2)	20(2.5)	18(2.5)	21(2.5)	30(4)	49(5)	
K	38(4)	22(2)	13(1.5)	24(2.5)	39(4)	99(10)	92(9)	154(15)	
Mg	<80	37(35)	35(33)	42(30)	120(40)	110(48)	190(50)	220(56)	
Mn	9.0(.9)	5.8(.6)	3.5(.3)	2.3(.2)	2.7(.3)	6.4(.6)	5.1(.5)	7.9(.8)	
Ti	14(7)	<3	<6	<8	6(6)	7(7)	18(7)	13(7)	
Sm	----	0.0015(.0015)	0.002(.001)	0.01(.002)	0.02(.002)	0.04(.004)	0.035(.003)	0.05(.005)	
Eu	----	0.001(.001)	0.0008(.0008)	0.0035(.001)	0.005(.001)	0.008(.001)	0.008(.001)	0.01(.0015)	
La	----	0.01(.01)	0.01(.01)	0.05(.03)	0.09(.02)	0.19(.02)	0.14(.03)	0.27(.03)	
Ce	<0.5	<0.5	<0.5	<0.5	0.75(.4)	0.5(.4)	0.6(.4)	1.1(.4)	
Sc	0.02(.01)	0.01(.01)	0.01(.01)	0.06(.02)	0.12(.02)	0.3(.04)	0.2(.04)	0.3(.04)	
Zn	26(5)	12(2)	10(2)	7.5(2)	3.5(2)	<2	<2	<2.6	
Co	0.08(.08)	0.06(.06)	0.06(.06)	<0.08	<0.08	0.08(.08)	0.16(.10)	<0.08	
Cr	2(1)	2.3(.8)	3.1(.8)	1.2(.6)	0.6(.6)	0.8(.8)	1.3(.8)	1.3(.8)	
Ga	----	0.08(.05)	0.04(.04)	0.05(.04)	0.10(.04)	0.12(.06)	0.13(.05)	0.16(.05)	

List of Figures

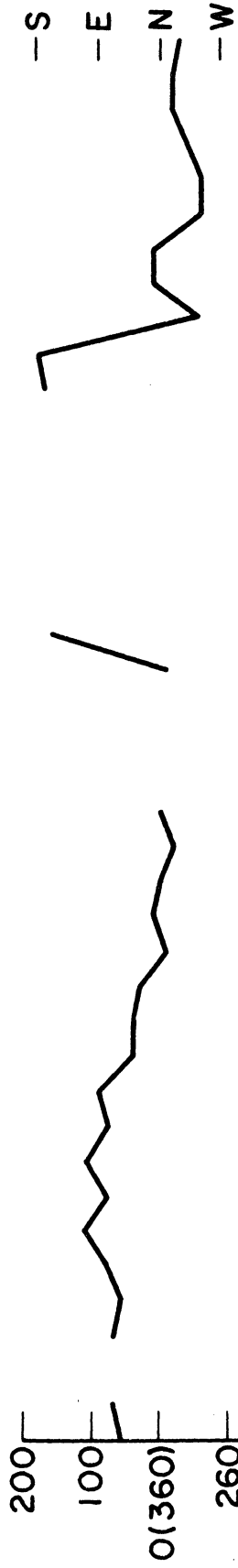
- Fig. 1 Relative humidity, temperature and dewpoint during sampling.
- Fig. 2 Wind speed and direction during sampling.
- Fig. 3 Surface weather map at 7:00 AM EST on August 21, 1969.
- Fig. 4 Surface weather map at 7:00 AM EST on August 22, 1969.
- Fig. 5 Concentration variations of 6 elements during sampling.
- Fig. 6 Particle size distribution of 4 elements as measured with an Andersen Impactor.
- Fig. 7 Particle size distribution of 5 elements as measured with an Andersen Impactor.



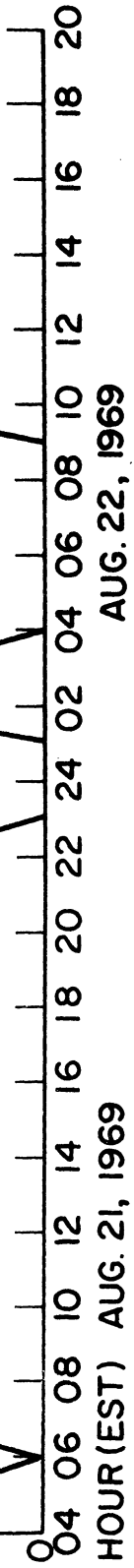
AUG. 22, 1969

HOUR (EST) AUG. 21, 1969

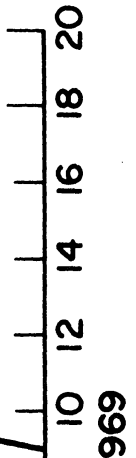
WIND DIRECTION (DEGREES)



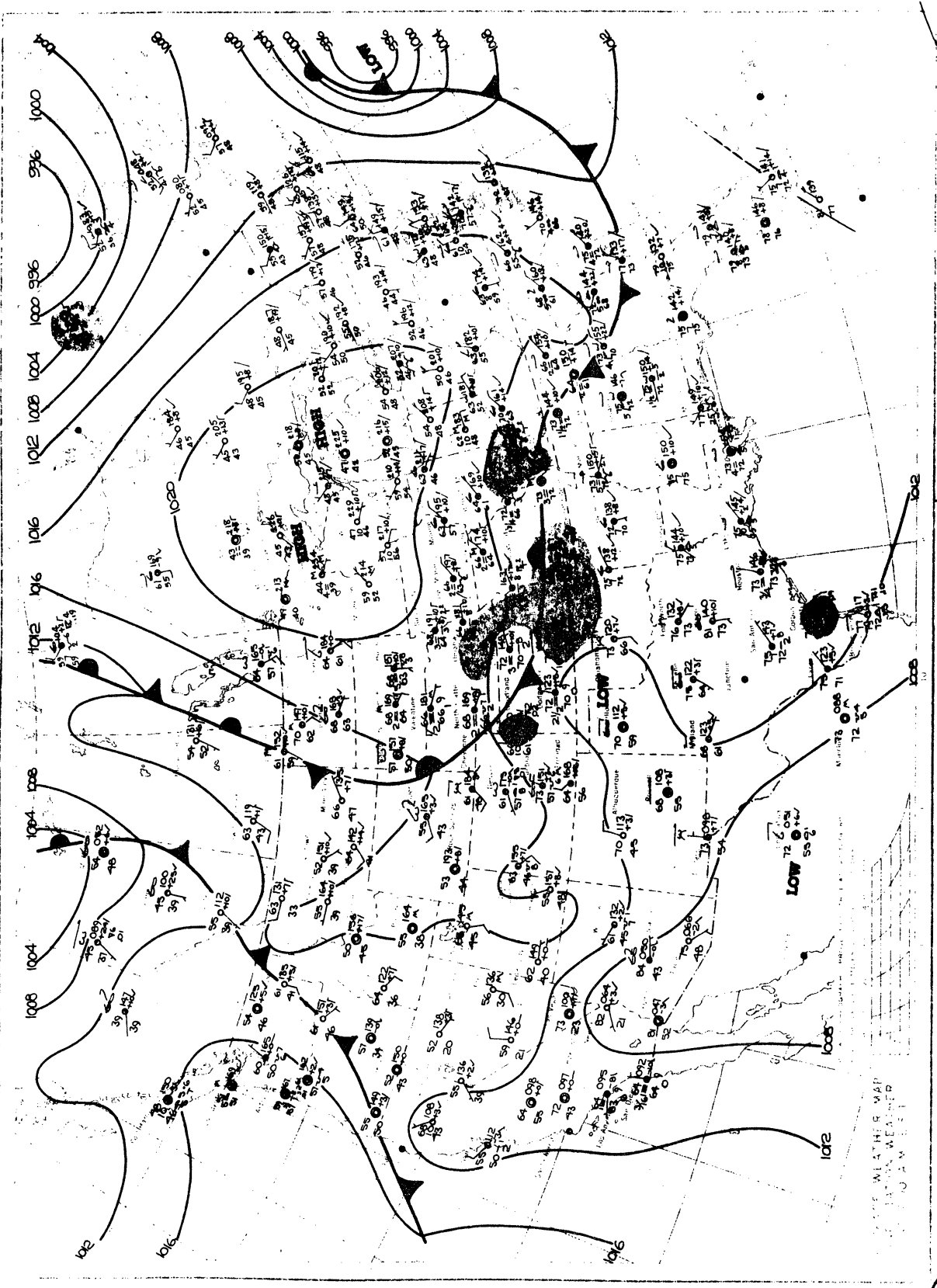
WIND SPEED (M-SEC⁻¹)



AUG. 22, 1969

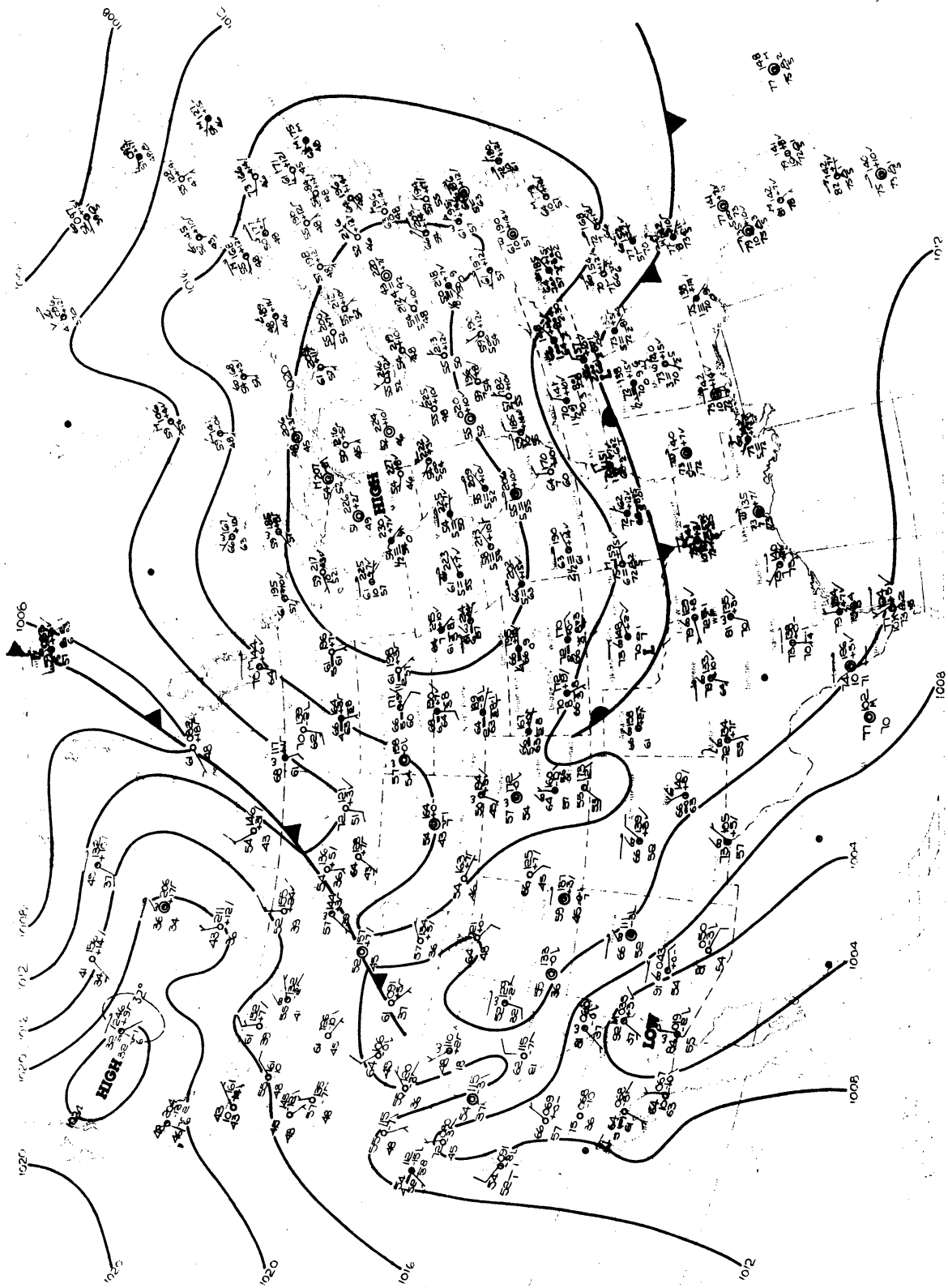


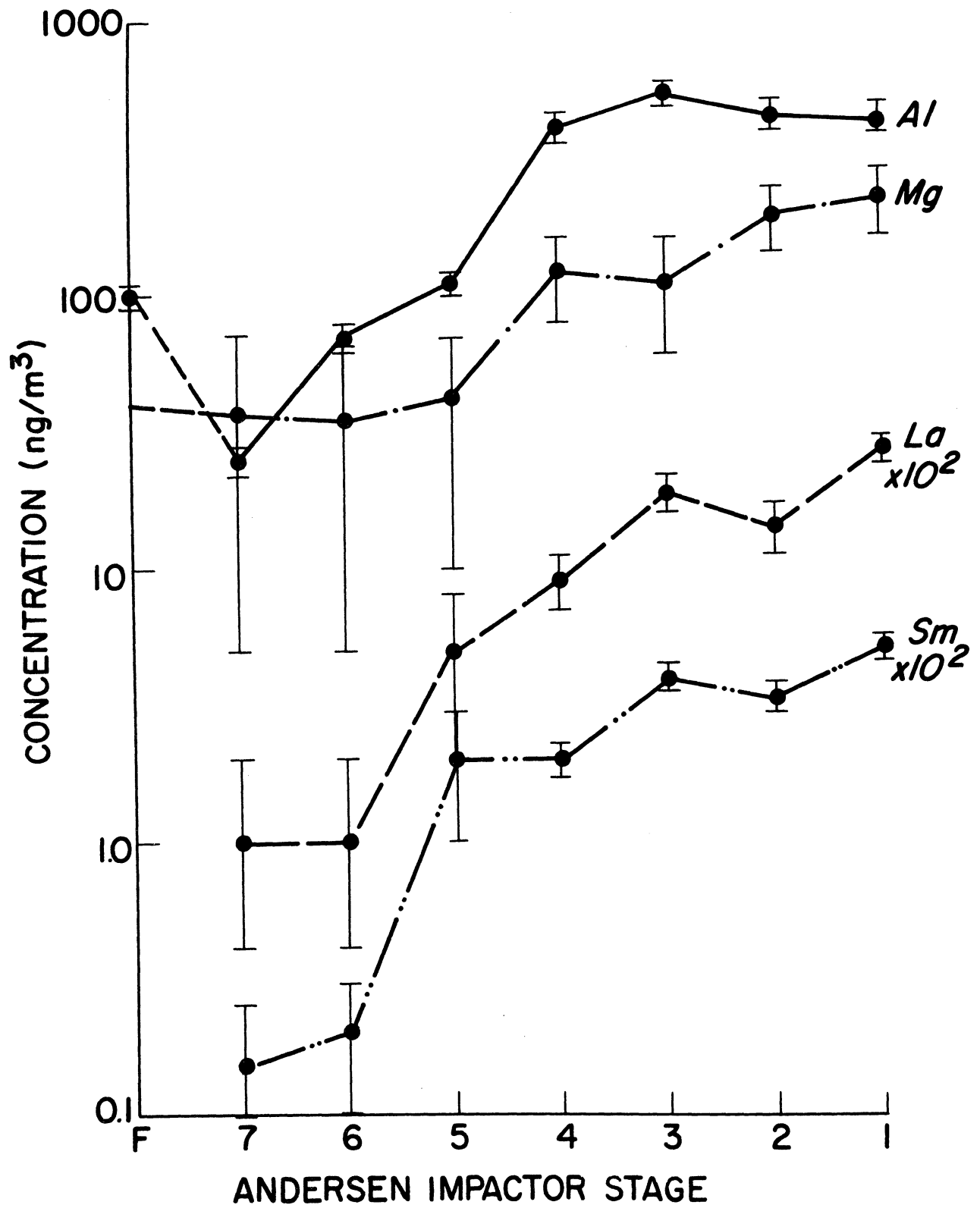
THURSDAY, AUGUST 21, 1969

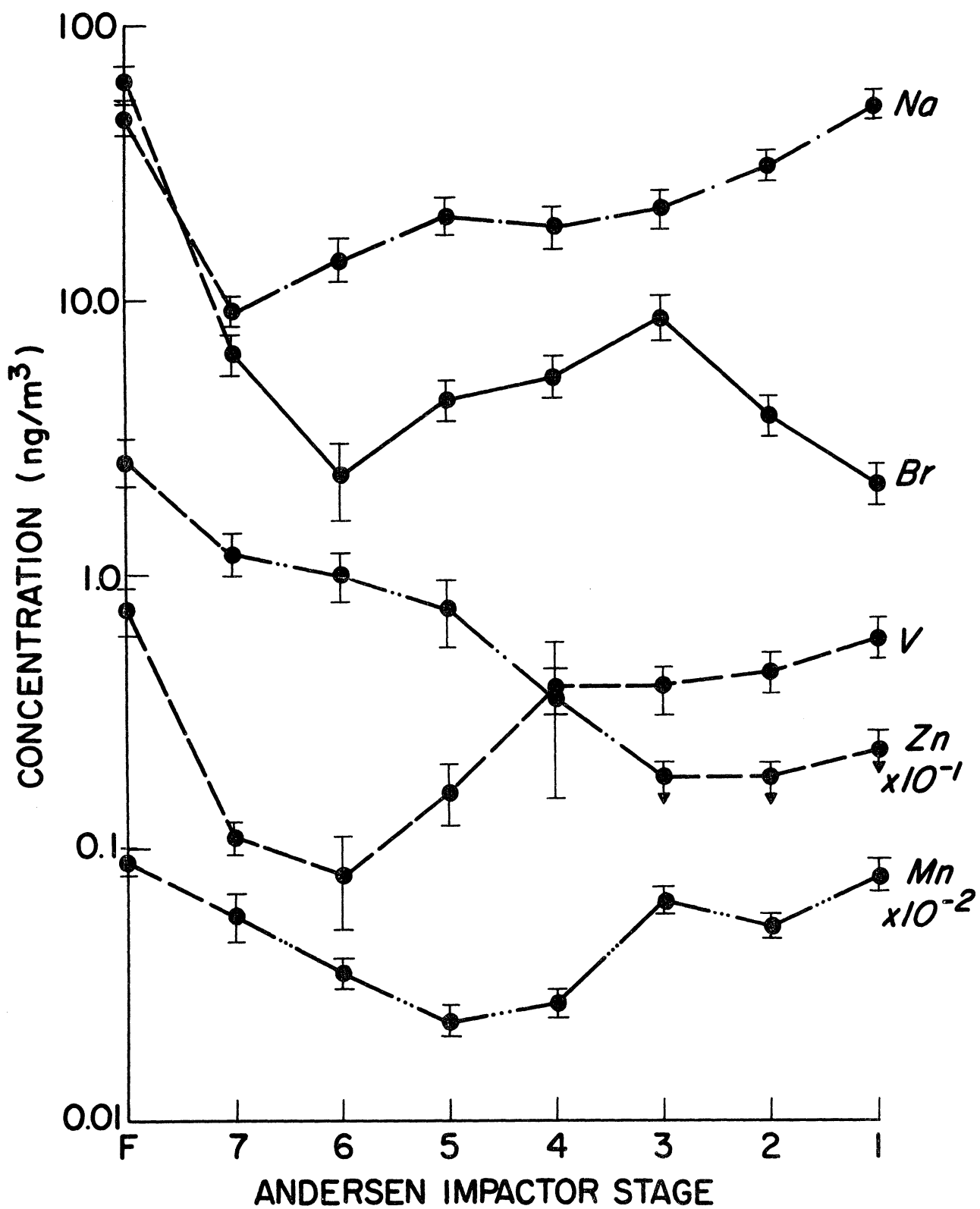


UNITED STATES WEATHER MAP
FOR THE REGION WEATHER
BUREAU OF METEOROLOGY
WASHINGTON, D.C.

FRIDAY, AUGUST 22, 1969







Paper to be presented at the THIRTEENTH CONFERENCE ON GREAT LAKES RESEARCH,
Buffalo, New York, 31 March - 3 April 1970.

CHEMICAL EQUILIBRIA OF IODINE IN GREAT LAKES WATERS*

John W. Winchester**

Dept. of Meteorology & Oceanography and Great Lakes Research Division,
The University of Michigan, Ann Arbor, Michigan 48104

Running Head: Iodine in the Great Lakes

Key words: WATER CHEMISTRY

2. Inorganic constituents
3. Ion distribution
4. Ion concentration
6. Nutrients

*This work was supported in part by the U.S. Atomic Energy Commission Contract No. AT (11-1)-1705. Contribution No. from the Dept. of Meteorology & Oceanography and No. from The Great Lakes Research Division, The University of Michigan.

**Now at: Dept. of Oceanography, Florida State University, Tallahassee, Florida 32306.

Abstract. Iodine in Great Lakes waters, 1-3 $\mu\text{g}/\text{l}$, is uniformly distributed and near the content of natural rainfall without evidence of strong additional pollution sources. These concentrations, 20-60 times lower than in sea water, may present an environmental stress to organisms where iodine is an essential element. In the sea iodine is utilized mainly as iodide by vertebrates and by brown and red algae. Although thermodynamically iodate is the most stable form in aerated water, about half the total iodine is believed to exist as iodide, and a biochemical recycling of iodide in the marine biosphere is suggested. In fresh water, blue-green and green algae are not known to require iodine and may not therefore aid in keeping iodine in the reduced form. Therefore, iodide available to vertebrates in lake water, and especially to anadromous fish which have become adapted to live in lake water, may be in much shorter supply than suggested by the low concentration of total iodine alone.

INTRODUCTION

It has been reported (Robertson and Chaney, 1953; Smith, 1968) that anadromous fish, including alewives, which have become adapted to permanent residence in fresh waters of the Great Lakes suffer widespread hypothyroid disability. Nevertheless a comprehensive study of the availability of iodine in the lake environment, possibly causally related to the disability, appears not to have been carried out. Although such a study is not unfeasible, certain analytical difficulties must be overcome in such a study, and specific chemical interactions dependent on chemical form of iodine must be studied separately and evaluated. Overall abundance of the element iodine is only one of possibly several factors which may be important, and it is the purpose of this note to outline some of these factors.

OCCURRENCE OF IODINE IN GREAT LAKES WATERS

Iodine occurs in the oceans at a rather uniform concentration of about 60 $\mu\text{g}/\text{l}$ (Goldberg, 1965) and is the large reservoir of the element in a cycle through the atmosphere, to the earth with precipitation, and back to the sea by land drainage. The iodine content of rainfall near the sea in Hawaii (Duce, Winchester and Van Nahl, 1965) is several $\mu\text{g}/\text{l}$, and in unpolluted regions far from the sea in Alaska and Antarctica (Winchester and Duce, 1966) values around 1 $\mu\text{g}/\text{l}$ are commonly found.

Iodine in the waters of the Great Lakes appears to average about 1 $\mu\text{g}/\text{l}$ (Tiffany et al., 1969) with little if any significant elevation in concentration due to pollution sources. Table 1 is a summary of concentrations found in each of the Great Lakes and in the streams flowing into Lake Superior. From the west to the east there appears to be at most a 3-fold increase in concentration, probably not greater than expected from natural concentration through evaporation. The

very close agreement in average concentrations for Lake Superior and its tributary streams, sampled in July 1967 and which serve as natural integrators of rainfall in that lake basin, support the view that the iodine is supplied mainly by rainfall without significant pollution contributions. These data indicate that, in the upper Great Lakes, the iodine concentration of 1 $\mu\text{g}/\text{l}$ is 60 times lower than the sea water value.

It was the view of Goldschmidt (1954) that endemic goiter areas, such as parts of the Great Lakes Basin, had suffered loss of iodine-rich soils from Pleistocene glaciation ending 10,000 to 15,000 years ago, and the slow recovery by supply of iodine from rainfall is still only partially complete. Consequently the supply of iodine to plants and hence to animals is low, and a dietary deficiency may develop. For creatures in the lakes, however, it is not the low soil iodine content but the composition of the rainfall which determines their iodine environment. Compared with the sea, fresh water iodine is scarce.

METABOLISM OF IODINE

The essential nature of iodine in vertebrates is well-known. Iodine has also been shown to be essential for some brown algae and red algae in the sea but apparently not for blue-green algae and green algae, the predominant fresh water forms (Bowen, 1966).

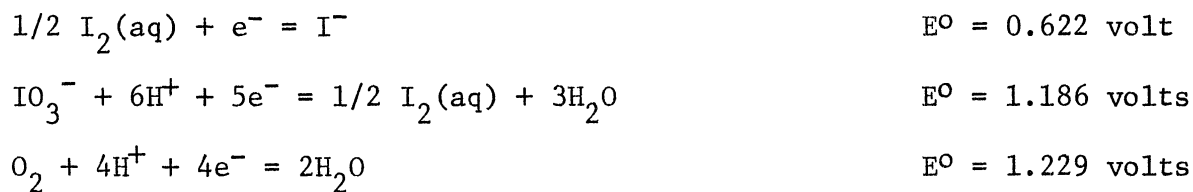
In vertebrate physiology iodine is utilized in the formation of thyroid secretions by the following steps (West and Todd, 1961):

1. Uptake of iodide, I^- , from the blood by the thyroid and storage as inorganic iodide.
2. Oxidation of I^- to iodine, I_2 , by an enzyme mechanism.
3. Conversion of the tyrosine portion of protein to monoiodo and diiodotyrosine by iodination reactions.

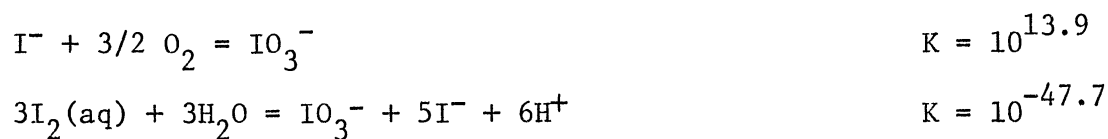
4. Coupling reactions to form thyroxine and triiodothyronine, and secretion into the blood following release of thyroid hormones.
 5. Ultimate deiodination in the liver and excretion of I^- ion in the urine.
- Marine algae which utilize iodine are able to convert I^- to I_2 enzymatically during the process of concentrating the element from sea water (Bowen, 1966). In both the vertebrate and the algae case it is important to note that the important oxidation-reduction cycle is between iodide, I^- , and molecular iodine, I_2 , but does not involve higher oxidation states.

THERMODYNAMIC STABILITY OF IODIDE, IODINE, AND IODATE

Although it is the reduced form iodide, I^- , which is required for vertebrates in fresh water, it can be shown that the thermodynamically stable form in oxygenated water is iodate, IO_3^- . Consider the following half cell potentials in aqueous solution at 25°C (Latimer, 1952; Sillén and Martell, 1964):



From these we calculate equilibrium constants for the reactions:



In water containing measurable oxygen we calculate the equilibrium activity ratio

$$\begin{array}{ll} a_{IO_3^-}/a_{I^-} = 10^{12.9} & \text{when } P_{O_2} = 0.21 \text{ atm} \\ = 10^{9.9} & \text{when } P_{O_2} = 0.0021 \text{ atm} \end{array}$$

Hence the overwhelmingly more abundant species at equilibrium in all but very reducing waters is iodate, IO_3^- .

According to the second reaction in dilute solution where the activity of

water $a_{\text{H}_2\text{O}} = 1$, the quantity

$$[a_{\text{IO}_3^-}^5 a_{\text{I}^-}^3 / a_{\text{I}_2(\text{aq})}^3] a_{\text{H}^+}^6 = 10^{-47.7}$$

In carbonate saturated waters where $\text{pH} \approx 8$ or $a_{\text{H}^+} \approx 10^{-8}$, the quantity in square brackets is of the order of unity. In natural waters where total iodine is about $1 \mu\text{g}/\text{l}$, i.e. about 10^{-8} M , $a_{\text{IO}_3^-} \approx 10^{-8}$, and we estimate, for the two oxygen conditions above of 100% saturation and 1% saturation,

$$a_{\text{I}^-} = 10^{-21} \text{ and } a_{\text{I}_2(\text{aq})} = 10^{-35} \text{ when } P_{\text{O}_2} = 0.21 \text{ atm}$$

$$a_{\text{I}^-} = 10^{-18} \text{ and } a_{\text{I}_2(\text{aq})} = 10^{-30} \text{ when } P_{\text{O}_2} = 0.0021 \text{ atm}$$

Only in distinctly acid solutions can I_2 exist in greater abundance than I^- when in equilibrium with dissolved oxygen, but neither species is more abundant than IO_3^- . All other species of inorganic iodine at equilibrium in natural waters are believed to be even lower in abundance.

NON-EQUILIBRIUM FACTORS

In two investigations (Winkler, 1916; Barkley and Thompson, 1960) it has been established that both high and low oxidation states of iodine in sea water coexist in about equal concentrations. Although the analytical chemistry is difficult, both investigators interpreted their findings as indicating the presence of I^- and IO_3^- , although because of analytical difficulties Sillén (1961) contests the exactness of this species identification. It has been regarded (Goldberg, 1963) that iodide is present because of recycling through biological material which utilize iodine and excrete it as the I^- form. We have seen that marine vertebrates and marine brown and red algae are possibly the principal agents for the recycling process in the sea. Since reaction rates of inorganic species of iodine are generally very slow at temperatures of natural waters, this explanation is quite plausible.

In fresh water no similar body of knowledge exists for the chemical state of dissolved iodine. It would appear that blue-green and green algae are not likely to play a role in recycling iodine through the biosphere, and in fresh water any such recycling may be performed by vertebrates without a symbiotic relationship with algae as possibly exists in the sea. In this event, the abundance of iodide which we suggest is biologically the most available form, may be very much lower relative to iodate than found in the sea, and the scarcity of available iodine in fresh water may therefore be far more severe than suggested by the 60-fold lower concentration of total iodine than in sea water. Presumably fresh water fish have adapted to this condition, but the adaptation may be much less successful for anadromous fish such as alewives which have come to live permanently in the Great Lakes.

Another source of reduced iodine of possible ecological significance is that released by the sediments either as inorganic iodide because of reducing conditions or as organically bound iodine which may be utilized in the food chain. Therefore, we should recognize a complex of interactions within aqueous solution and across the water-sediment and air-water boundaries in trying to understand the possibly important role iodine plays in the biological stability of the Great Lakes.

REFERENCES

- BARKLEY, R. A. and T. G. THOMPSON. 1960. The total iodine and iodate-iodine content of sea-water. *Deep Sea Res.*, 7: 24-34.
- BOWEN, H. J. M. 1966. *Trace Elements in Biochemistry*. Academic Press, New York.
- DUCE, R. A., J. W. WINCHESTER, and T. W. VAN NAHL. 1965. Iodine, bromine, and chlorine in the Hawaiian marine atmosphere. *J. Geophys. Res.*, 70: 1175-1799.
- GOLDBERG, E. D. 1965. Minor elements in sea water, pp. 163-196. *In*: J. P. Riley and G. Skirrow, eds., *Chemical Oceanography*, Vol. 1, Academic Press, New York.
- _____. 1963. The oceans as a chemical system, pp. 3-25. *In*: M. N. Hill, ed., *The Sea*, Vol. 2, Interscience, New York.
- GOLDSCHMIDT, V. M. 1954. *Geochemistry*, Clarendon Press, Oxford, England.
- LATIMER, W. M. 1952. *Oxidation Potentials*, 2nd ed., Prentice-Hall, Englewood Cliffs, N.J.
- ROBERTSON, O. H. and A. L. CHANEY. 1953. Thyroid hyperplasia and tissue iodine content in spawning rainbow trout: a comparative study of Lake Michigan and California sea-run trout. *Physiol. Zool.*, 26: 328.
- SILLEN, L. G. 1961. The physical chemistry of sea water, pp. 549-581. *In*: Mary Sears, ed., *Oceanography*, Am. Assn. Adv. Sci., Washington.
- SILLEN, L. G. and A. E. MARTELL. 1964. *Stability Constants of Metal-Iron Complexes*, Chemical Society, London.
- SMITH, S. H. 1968. The alewife. *Limnos*, 1: 12-20.
- TIFFANY, MARY A., J. W. WINCHESTER, and R. H. LOUCKS. 1969. Natural and pollution sources of iodine, bromine, and chlorine in the Great Lakes. *Jour. Water Pollution Control Federation*, 41(7): 1319-1329.

WEST, E. S. and TODD, W. R. 1961. Textbook of Biochemistry, Macmillan, New York.

WINCHESTER, J. W. and R. A. DUCE. 1966. Coherence of iodine and bromine in the atmosphere of Hawaii, northern Alaska, and Massachusetts. *Tellus*, 18: 287-292.

WINKLER, L. W. 1916. Der Jodid und Jodat Ionengehalt des Meerwassers. *Z. angew. Chem.*, 29: 205-207.

TABLE 1. Mean concentrations of iodine in the Great Lakes Basin, after Tiffany et al. (1969).

Location	No. of Samples	I, $\mu\text{g}/\text{l}$
Lake Superior	12	1.1
Lake Superior tributaries	25	1.2
Lake Michigan	15	0.9
Lake Huron	6	1.3
St. Clair River	2	2
Lake St. Clair	2	2
Detroit River	4	1.4
Lake Erie	14	1.7
Lake Ontario	8	2.9

Paper for presentation at 1970 Precipitation Scavenging Meeting,
Richland, Washington, June 2-4, 1970

A MODEL FOR VARIATIONS OF HALOGEN ION RATIOS IN MARINE AEROSOLS
WITH PARTICLE SIZE^a

John A. Robbins

Dept. of Meteorology and Oceanography

and Great Lakes Research Division

University of Michigan

Ann Arbor, Michigan 48104

^aWork supported in part by the U. S. Atomic Energy Commission under contract AT(11-1)-1705. Contribution No. from the Dept. of Meteorology and Oceanography and No. from the Great Lakes Research Division, University of Michigan.

ABSTRACT

A mathematical model has been formulated to account for published chemical analyses of marine aerosol size fractions for iodine, bromine, and chlorine. The model assumes that iodine vapor is gained and bromine vapor is lost by particles at rates determined by gaseous diffusion around the particle. Both iodine and bromine may saturate a particle surface layer, although the detailed mechanism of saturation is not crucial to the model. By nonlinear least squares fitting to observed data points the model satisfactorily accounts for a decrease in I/Cl with increasing radius as r^2 for larger unsaturated particles and as r for smaller saturated particles, and the former shows an inverse dependence on wind speed. The model accounts for the observed minimum in Br/Cl for intermediate size fractions and the inverse dependence of its depth on wind speed. The model requires that most of the aerosol mass sampled is derived from a fairly narrow band of particle ages in order to account for the observed composition variation with size fraction, and this assumption provides an explanation for dependence on wind speed. Among the specific questions raised in this mathematical study which may be tested experimentally are the band width of aerosol particle ages with wind speed and sampling location, the chemistry of iodine and bromine retention by particles, and the mechanism of bromine loss from particles.

INTRODUCTION

High sensitivity analytical techniques coupled with efficient particle size sorting by cascade impactors and other devices have recently been used for determining chemical composition as a function of particle size in aerosols of both natural and pollution origin. This information in principle can aid in formulating models for source processes and atmospheric transformations, although as yet little quantitative examination of such models for aerosol composition in the light of the chemical data appears in the literature. The halogen composition of marine aerosols is especially suitable for theoretical treatment because of the high quality of existing neutron activation analysis data (Duce⁽⁷⁾; Moyers⁽²¹⁾), and the relative simplicity of the processes by which they are formed. In this paper a model is set forth and tested by comparison with the data.

It is well-known that the ocean is a source of atmospheric trace gases and aerosols. Injection of sea-salt droplets into the atmosphere by the breaking of bubbles produced through wave action probably accounts for the ocean-derived sea-salt content of the air while gaseous evolution from the sea-surface or from sea water droplets may be another important production mechanism for the halogens. Consequently, ratios of I, Br, and Cl in sea-salt aerosols may undergo change throughout the lifetime of the aerosol in the atmosphere with particles acting either as sources or as sinks for the gas phase depending on conditions such as their pH, the sunlight intensity and gas concentrations.

Chloride appears to be a fairly conservative aerosol constituent. Samples of coastal rainwater, which presumably scavenges aerosols without acquiring

chlorine from the gas phase, often have Cl/Na ratios around 5-10% lower than the sea-water value of 1.80.⁽¹³⁾ Eriksson,⁽⁹⁾ however, obtained a value of 1.90 at a Hilo, Hawaii site. Seto et al.⁽²⁵⁾ observed that the Na/Cl ratio measured just under clouds at altitudes ranging from 200 to 2000 meters increased by less than 20% over this entire range. They concluded that previously observed altitude variations⁽⁶⁾ in the Br/Cl and I/Cl ratios could not be due to variations in the Cl content. The amount of Cl in the gas phase appears to be comparable to that in the aerosol phase ($\sim 2\mu\text{g}/\text{m}^3$),⁽⁶⁾ although it is not known if gaseous chlorine is evolved directly from the sea-surface. The ratio Cl/Na decreases markedly inland⁽¹³⁾ possibly due in part to the acidification of the aerosol by SO_3 or H_2SO_4 with subsequent release of Cl^- as HCl . Since SO_2 and presumably SO_3 are present over open ocean,⁽¹³⁾ in sufficiently old aerosols which have grown acidic, exchange between aerosol and gas may be significant.

It has long been known that iodine is markedly enriched in the marine atmosphere.⁽⁸⁾ The I/Cl ratio in rain water, in the gas phase and in aerosols is generally a factor of 100 to 1000 times higher than the sea-water value.⁽⁶⁾ Both iodine enrichment occurring directly at the sea-surface and an exchange occurring following gaseous evolution appear to be possibilities in light of existing work. Miyake and Tsunogai⁽²⁰⁾ have shown in laboratory experiments that gaseous I_2 may be liberated from the ocean surface by photochemical oxidation of I^- and suggest that since Cl_2 and Br_2 are not as readily liberated, the high I/Cl (and I/Br) ratios may result from diffusion of gaseous I_2 to aerosol surfaces. Chamberlain⁽³⁾ has shown that gaseous I_2 is readily absorbed on many surfaces and Blanchard⁽²⁾ has identified compressed surface-active films

on sea-salt particles which may facilitate I_2 retention through organic fixation. Alternatively iodine enrichment may occur directly at the sea-surface if the surface-active films possess a high I concentration at the time they became part of the aerosol. Apart from the possibility of organic I enrichment, purely electrostatic effects appear to account for some ionic enrichment effects. Komabayasi⁽¹⁴⁾ has developed a theory in which enrichment over sea-water increases monotonically with element atomic weight that appears to account for several element enrichment ratios including I but fails to correctly predict Br enrichment. Moreover the theory assumes that iodine is present only as I^- so its application to the halogens is uncertain.

Marine aerosols are somewhat depleted in Br relative to sea-water and may act as a source for Br_2 gas.⁽²¹⁾ Early measurements by Duce et al.⁽⁵⁾ suggested that the mode of transfer of Br into the atmosphere is the same as for Cl and no significant differences in the Br/Cl ratio in rain, sea spray or aerosols than in sea-water were found. However, later aircraft aerosol samples showed significantly lower values⁽⁶⁾ while there was some evidence that the ratio was higher than the sea-water ratio in the gas phase. It was suggested that the observed depletion of Br relative to Cl might be due to photochemical oxidation of aerosol Br^- to free Br_2 . De Brouckere⁽⁴⁾ found that in an acidic solution Br^- in the presence of oxygen can be converted to Br_2 by sunlight. In view of its high pH (~8.3) the sea-surface, however, does not appear to be a Br source through this mechanism. Hence observations tend to suggest that Br behaves like Cl in the formation of droplets but subsequently evolves from the aerosol more rapidly than Cl.

It can be seen that the dependence of halogen ratios on aerosol size may provide useful information on mechanisms by which these ratios differ from seawater values. MacIntyre⁽¹⁷⁾ has observed a particle size dependence in phosphate aerosol enrichment studies using various surface active agents. His results indicate that the particle size corresponding to maximum enrichment depends strongly on the nature of the surface active material. Laboratory observations of Blanchard⁽¹⁾ on aerosol production by breaking bubbles suggest that organic films are more likely to be on smaller aerosols generated by bubble film shattering processes than on larger members produced by the jet mechanism. If iodine is present in organic films and enrichment occurs primarily during bubble bursting, a particle size dependence with the I/Cl ratio decreasing with increasing particle size is expected although a quantitative dependence is difficult to predict. On the other hand if gaseous diffusion of I₂ is the primary enrichment route, it might reasonably be expected that the I₂ content should be proportional to aerosol surface area, while the Cl content should be proportional to aerosol volume thus giving an I/Cl ratio inversely proportional to aerosol size.

Only recently, careful observations of the size dependence of I/Cl and Br/Cl ratios have been made by Duce et al.^(6,7) The later work⁽⁷⁾ is especially important in this respect and forms the basis for the ad hoc model developed below. In their study aerosols were sampled using a six-stage cascade impactor mounted on a tower 14 meters above the windward shore near Hilo, Hawaii. Particles were collected in sizes varying from roughly ten microns radius or greater on the first stage to approximately 0.3 micron on the sixth stage, with adjacent stages differing by about a factor of two in mean collection radius. Care was

taken to sample during rain-free periods when the trade winds were transporting particles inland from the open sea. Thus land-derived contamination of the samples could be assumed to be minimal, as well as interferences from sea spray generated by the action of waves breaking on the lava headlands. The content of each stage, accumulated over about an eight hour sampling period, was analyzed for Cl, Br and I by neutron activation analysis. The results reported by the authors for eight independent runs exhibit several important and apparently reproducible features indicated in Fig. 1 which shows I/Cl and Br/Cl ratios averaged over the eight runs versus impactor stage. It will be seen that the I/Cl ratio is about 1000 times higher than the sea-water ratio ($\sim 3 \times 10^{-6}$) on the smallest particles collected and decreases with increasing particle size approximately inversely with radius squared. The Br/Cl ratio has nearly the sea-water value ($\sim 3.4 \times 10^{-3}$) at extreme ends of the observed size range with a minimum, lower by about a factor of 2, at intermediate sizes around 1μ .

MODEL FORMULATION

The observed I/Cl ratio decreases too rapidly with particle size to be accounted for in terms of the assumption of simple surface saturation mentioned above. The notion that gaseous diffusion determines enrichment need not be discarded in light of this result, however, for several explanations are possible. Perhaps the simplest is that the ability of the aerosol to retain I_2 molecules diffusing to its surface is dependent on aerosol size, being controlled by the amount of organic surface-active material present. This approach does not lead to a quantifiable treatment presently. A second possible explanation is that

saturation is not complete so that larger aerosols having shorter residence times on the average will have acquired less iodine through diffusion than older members. This possibility does not appear likely in view of Duce's calculation⁽⁶⁾ of I_2 gas-aerosol equilibrium times the order of a few hours. However, his result is based on the assumption of perfect I_2 retention. A third possibility is that the amount present is determined by the rate of diffusion as in the second case but that the aerosols have approximately the same age independent of their size and are comparatively young. Since the rate of diffusion is proportional to aerosol radius in the size range considered here, it can be seen that the I/Cl ratio will vary inversely with radius squared as observed. Clearly aerosols will not have a unique population age in general but the condition can be approximately met if there is a localized production site which accounts for the majority of detected aerosols. This can occur if surf-zone contributions predominate, which does not appear to be the circumstance of the measurements analyzed here, or if there is a band of wave action other than the surf-zone extending some distance out from the shoreline or if there is a short-range wind regime. Moreover, low altitude aerosol measurements should be weighted toward young aerosol components varying relatively less in age with size. This assumption of apparent source localization is adopted for the quantitative treatment developed and the implications are further explored below.

In accounting for the observed Br/Cl ratio dependence, it is assumed that Br^- evolves from the aerosol perhaps as Br_2 by means of a process in which evolution of Br per unit volume is greater on smaller particles. Such a process may involve a Br^- removal rate determined by the rate of diffusion of suitable oxidizing agents to the aerosol surface. The above authors⁽⁷⁾ speculate on such a

possibility. Here, the idea is added that in the course of Br^- evolution, some Br_2 is initially fixed in the surface layer with a surface density which is independent of aerosol size. This additional assumption is sufficient to account quantitatively for the observed Br/Cl ratios. It can be seen qualitatively to be a promising approach. A freshly generated aerosol is assumed to have a Br/Cl ratio independent of its size equal to the sea-water value. A sufficiently old aerosol, on the other hand, will possess only a surface bromine layer giving a Br/Cl ratio inversely proportional to radius. For intermediate ages the Br/Cl ratio will have reached some limiting value less than the sea-water value on small aerosols while for the largest members no significant Br evolution will have yet occurred. Hence for some aerosol size there is a minimum in the Br/Cl ratio. In the following section these ideas are developed in a mathematical form suitable for comparison with the data.

QUANTITATIVE TREATMENT OF CASCADE IMPACTOR DATA

Aerosols reaching the detector have an age-size distribution given by $n(r,t)$ where

$$d^2N = n(r,t)drdt \quad (1)$$

is the number of particles per unit volume of air with sizes between r and $r + dr$ and ages between t and $t + dt$. t is the total elapsed time between the formation of an aerosol particle and its collection. In general the size and age coordinates in Eq. (1) cannot be separated due to the complicated life history of each particle. Moreover their identity may be ill-defined because of the possibility of coagulation with Aitken nuclei or to a limited extent with other members of comparable size.

Here it is assumed that the measured aerosol population is sufficiently young that coagulation effects are not significant in the size range of interest (0.2-20 μ) and that its age, t , is well-defined in the sense that

$$n(r,t) = n(r) \delta(t-\tau) \quad (2)$$

where $\delta(t-\tau)$ is the usual delta function:

$$\delta(t-\tau) = 0 \text{ except at } t = \tau$$

and $\int \delta(t-\tau)dt = 1$. The aerosol size distribution is then

$$n(r)dr = \int_0^{\infty} \{n(r,t)dr\} dt \quad (3)$$

Aerosols are sampled by means of a cascade impactor (Scientific Advances Co.) in which each stage, k , collects unit density particles of radius r with an efficiency $\epsilon_k(r)$ shown in Fig. 2. The solid curves are smooth fits to data obtained by Mitchell and Pilcher⁽¹⁹⁾ for unit density polystyrene spheres and appear to correctly represent the operating stage efficiencies reported by Duce et al.⁽⁷⁾ The number of particles in the size range r to $r + dr$ deposited on the first stage is

$$dN_1 = V\epsilon_1(r)n(r)dr \quad (4)$$

where V is the volume of sampled air. When the stages are arranged in cascade fashion it will be readily seen that the number deposited on the k^{th} stage in this radius interval is

$$dN_k = Vf_k(r)n(r)dr \quad (5)$$

and the total number collected will be

$$N_k = V \int_0^{\infty} f_k(r)n(r)dr \quad (6)$$

where the apparent impaction efficiency $f_k(r)$ is given by

$$f_k(r) = \epsilon_k(r) \prod_{j=1}^{k-1} (1 - \epsilon_j(r)) \quad (7)$$

This function is discussed in detail by Sundelöf.⁽²⁶⁾ The broken curve shown in Fig. 2 gives the dependence of $f_k(r)$ on r where it differs from the value $\epsilon_k(r)$. The values $\epsilon_k(r)$ have not been corrected for side-impaction effects. Lundgren⁽¹⁶⁾ has shown that depending on impactor geometry, up to 30% of particles approximately 10 microns in radius may not be deposited on collection surfaces but impact elsewhere in the detector. Although the extent of this effect has not been determined for the Scientific Advances instrument, it may be classed with impactors of similar construction for which the correction is less than 10%.

Shown in Table 1 below for each stage k are values of the aerosol radius r_k for which $f_k(r)$ is a maximum. It can be seen that the cascade impactor is designed so that particles of unit density differing by a factor of about two in radius tend to be collected on adjacent stages.

TABLE 1
APPROXIMATE RADIUS FOR MAXIMUM COLLECTION
EFFICIENCY VERSUS IMPACTOR STAGE INDEX

Stage (k)	Radius (r_k) (Microns)
1	8 (50% cut-off value)
2	5
3	2.6
4	1.3
5	0.7
6	0.3

The equilibrium aerosol size and density are humidity dependent. Since sampling occurred under conditions of variable relative humidity ranging from 70 to 90%, on each stage the distribution of particle sizes referred to some standard humidity (90%) is broadened. Ranz and Wong⁽²⁴⁾ have shown that if $\epsilon_k(r)$ is known for unit density spheres, the efficiency for those of density, ρ , is approximately the function $\epsilon_k(\sqrt{\rho} r)$. On this basis Duce et al.⁽⁷⁾ estimate that particles collected at 70% R.H. on a given stage may be as much as 1.5 times larger referred to 90% R.H. than those actually collected at 90% R.H. However their result appears to be based on the properties of pure NaCl solutions and may be too large in view of recent measurements by Pueschel et al.,⁽²³⁾ on light scattering from NaCl solution and natural sea-water aerosols as a function of relative humidity. Natural aerosols appear to exhibit an anomalous deliquescence, changing in size markedly less with alterations in relative humidity, than their pure NaCl counterparts. An approximate size dependence, inferred from their reported light scattering coefficient variations, suggests that the shift in effective collection radius, r_k , is perhaps 10-20% rather than a factor of 1.5.

If $C^\beta(r, \tau)$ is the total weight of component β (e.g., $\beta = \text{Cl, Br or I}$) on an individual particle of radius r and age τ the amount of component β deposited on the k^{th} impactor stage is:

$$I_k^\beta = V \int_0^\infty C^\beta(r, \tau) f_k(r) n(r) dr \quad (8)$$

It is assumed here that during the sampling time interval a stationary state persists for which $n(r)$, the effective aerosol age τ , and the function $C^\beta(r, \tau)$ remain

unchanged. It is also presumed that during the interval between collection and analysis I_k^β does not change. That is, once an aerosol is deposited in the impactor there is no further alteration of its chemical content. This effect, of possible significance for halogens, is not readily assessed.

The ratio of two components β and β' is given by

$$R_k^{\beta, \beta'} \equiv I_k^\beta / I_k^{\beta'} \quad (9)$$

Since $f_k(r)$ is peaked around r_k , to a crude approximation it may be replaced by $\delta(r-r_k)$ for which it will be seen that

$$R_k^{\beta, \beta'} \sim C^\beta(r, \tau) / C^{\beta'}(r, \tau) \quad (10)$$

Eq. 10 merely expresses the fact that the ratio of component weights on a given stage of an impactor which accumulates particles of essentially only one size must be equal to the ratio of the amounts of the components in an individual particle of that size. The values for the halogen ratios versus impactor stage are not very sensitively dependent on the particle size distribution, $n(r)$.

By means of Eq. 8 a model for the dependence of component weight on aerosol size and age may be related to impactor data provided the size distribution, $n(r)$, is known. Conversely if I_k^β is known together with $C^\beta(r, \tau)$ for some component, $n(r)$ can be inferred.

In the present case $n(r)$ may be inferred from the chloride distribution data, I_k^{Cl} , with

$$C^{Cl}(r, \tau) = \frac{4}{3} \pi \rho^{Cl} r^3 \quad (11)$$

which is independent of τ . ρ^{Cl} is the density of Cl in the particle assuming

pure NaCl solution in equilibrium with the air at 80% relative humidity (R.H.), the unweighted mean R.H. of the range observed during sampling.

$\rho^{Cl} = 13.4 \times 10^{+4} \mu\text{g}/\text{cm}^3$ and is assumed to be independent of r . The observed Cl weight on the k^{th} stage is given by

$$I_k^{Cl} = \frac{4}{3} \pi \rho^{Cl} V \int_0^{\infty} r^3 f_k(r) n(r) dr \quad (12)$$

$$\sim \text{constant} \times r_k^3 \times n(r_k)$$

Inspection of the Cl data shown for run 11 (the authors⁽⁷⁾ designation) in Fig. 3 suggests that I_k^{Cl} versus r_k is approximately parabolic in form. It can be seen that this implies the following analytic form for $n(r)$

$$n(r) = e^{\alpha_1 + \alpha_2 \ln r + \alpha_3 (\ln r)^2} \quad (13)$$

A non-linear least squares computer program was written to find the parameter set $\alpha_i (i=1,2,3)$ which gives the best fit to the data using Eq. 12 minimizing the function

$$W(\alpha_i) = \sum_{k=1}^6 \left(I_k^{Cl} - \frac{4}{3} \pi \rho^{Cl} V \int_0^{\infty} r^3 f_k(r) n(r, \alpha_i) dr \right)^2 \quad (14)$$

(i.e., $\frac{\partial W}{\partial \alpha_i} = 0$ for all α_i). For each of seven of the eight reported runs, such a "best" fit was found. Data for run number 9 is too sparse for satisfactory treatment and has been excluded from this analysis. With the best fit functions in hand, I_k^{Cl} was calculated according to Eq. 12 for each stage k . The resulting fit for run 11 is also shown in Fig. 3 as a smooth curve. It should be understood that because of the discrete nature of the impactor stage designations, the smooth curve drawn between calculated values is merely an aid to visualization. The

results are excellent, as one would expect because of the choice of analytic representation for $n(r)$. Since the ratios $R_k^{I,Cl}$ and $R_k^{Br,Cl}$ calculated below are insensitive to the exact form of $n(r)$, this approximation is more than adequate. Fits for runs other than 11 are of comparable quality.

QUANTITATIVE MODEL FOR IODINE IN MARINE AEROSOLS

In obtaining an expression for $C^I(r, \tau)$ it is assumed that aerosols are formed with the sea-water iodine concentration, that they immediately adjust by evaporation of water to a size in equilibrium with air to 80% R.H. ⁽²⁷⁾ and remain at this size as they acquire I_2 through gaseous diffusion during their residence time in the atmosphere prior to collection. The instantaneous flux of gas molecules onto a sphere of radius r has the form ⁽¹⁵⁾:

$$\Phi(r, t) = 4\pi Dr F(r) \rho_I^*(t) \quad (15)$$

where $\rho_I^*(t)$ is the iodine vapor concentration at time t and D is the diffusion coefficient. The radius-dependent "correction" term $F(r)$ is given by

$$F(r) = \left\{ \frac{D}{\nu r} + \frac{r}{r+D} \right\}^{-1} \quad (16)$$

where $\nu = 3.9 \times 10^3$ cm/sec for I_2 at $T = 298^\circ K$, $\Delta =$ the mean free path of I_2 molecules in air = 0.14 micron, and $D = 0.08$ cm²/sec as found by Chamberlain et al., ⁽³⁾ from radio-iodine diffusion studies. With r expressed in microns

$$F(r) = \left\{ \frac{0.2}{r} + \frac{r}{r+.14} \right\}^{-1} \quad (17)$$

For $r \geq 0.3 \mu$, $F(r) \approx 1.0$, while for $r < 0.1 \mu$, $F(r) \approx r$. Thus for most aerosols in the size range of interest the diffusion rate is proportional to aerosol radius. If each incident iodine molecule is absorbed, then the amount of I present at aerosol age τ is found by integrating Eq. (15) over time:

$$\begin{aligned} C^I(r, \tau) &= 4\pi DrF(r) \int_0^\tau \rho_I^*(t) dt \\ &= 4\pi D\bar{\rho}\tau rF(r) \end{aligned} \quad (18)$$

If the mean concentration of iodine vapor, $\bar{\rho}$, experienced by each sampled aerosol is the same independent of its size as would be the case if they originate from a fairly localized source, the I/Cl ratio, $R_k^{I,Cl}$, by Eq. (11) and (18) will be approximately

$$R_k^{I,Cl} \sim \frac{C^I(r_k, \tau)}{C^{Cl}(r_k, \tau)} \sim 1/r_k^2 \quad (19)$$

The exact model expression is

$$R_k^{I,Cl} = \frac{3D\bar{\rho}\tau}{\rho^{Cl}} \times \frac{\int_0^\infty rF(r)f_k(r)n(r)dr}{\int_0^\infty r^3f_k(r)n(r)dr} \quad (20)$$

The fit to the data (Run 11) is shown in Fig. 4 as the dashed line labeled " $\tau \approx 0$ ". The agreement is satisfactory except in the case of stage 6 where Eq. 20 overestimates the ratio by a factor of five. This discrepancy is observed in every run. The normalization to the data giving a value for the product $\bar{\rho}\tau$ is discussed below.

The low values of $R_k^{I,Cl}$ observed on stage 6 suggests that sufficiently small aerosols have become surface-saturated while larger ones have not. If a surface

saturation density, ρ_s , exists which is independent of aerosol size, then the function $C^I(r, \tau)$ is given by

$$4\pi\rho_s r^2 \quad r \leq r_s \quad (21)$$

and

$$4\pi Dr F(r) \bar{\rho} \tau \quad r > r_s$$

where r_s is the radius of that aerosol of age τ which has acquired just enough iodine to be surface-saturated and is obtained from the requirement,

$$4\pi\rho_s r_s^2 = 4\pi Dr_s F(r_s) \bar{\rho} \tau \quad (22)$$

In this case the ratio is

$$R_k^{I, Cl} = \frac{3\rho_s \int_0^{r_s} r^2 f_k(r) n(r) dr + 3D\bar{\rho}\tau \int_{r_s}^{\infty} r F(r) f_k(r) n(r) dr}{\rho^{Cl} \int_0^{\infty} r^3 f_k(r) n(r) dr} \quad (23)$$

A two-parameter least-squares fit for ρ_s and the product $\bar{\rho}\tau$ produced the solid curve shown in Fig. 4. The curve labeled " $\tau \rightarrow \infty$ " is approached asymptotically as τ and $r_s \rightarrow \infty$ corresponding to surface saturation of aerosols of all sizes.

Curve $\tau \approx 0$ corresponds to the totally unsaturated case ($r_s \rightarrow 0$) of Eq. 20.

Resulting values for $\bar{\rho}\tau$ and r_s do not differ significantly from run to run. They are

$$\bar{\rho}\tau \sim 6000 \text{ ng-sec/m}^3$$

$$r_s \sim 0.5 \mu$$

giving a surface density of $\rho_s \sim 10 \text{ ng/cm}^2$ by Eq. (22) and (17). With the

exception of two high values, Duce et al. (6) report eleven sea level iodine

vapor concentrations in the Hawaiian marine atmosphere of less than 6 ng/m^3 measured at the same Hilo, Hawaii site. In later work by Moyers⁽²¹⁾ a mean value of 8 ng/m^3 was observed in marine air on the windward shore at Oahu, Hawaii. Assuming these values to be representative of concentrations experienced by aerosols in the present measurements,⁽⁷⁾ the effective age, τ , is the order of 15 minutes.

This rather small age may be a result from the assumption of perfectly efficient iodine uptake by the aerosol and represents an approximate lower limit, or it perhaps reflects the effects of dominant contributions from nearby sources. Although contributions from sea-spray have presumably been eliminated by elevation of the sampling unit, the region of ocean surface several hundred meters off-shore may contribute significantly more detected aerosols than the region further out. Consider a case in which a wind of speed, u , transports an aerosol through a distance, x , from its point of creation to the collector. If its atmospheric residence time is λ^{-1} , the probability it reaches the collector is $e^{-\lambda x/u}$ where x/u is the transit time. This obvious oversimplification elucidates several points. If contributions originate from a source of length l , measured out from the collector along the wind direction, the mean age of the measured aerosol population is,

$$\bar{\tau} = \frac{1}{\lambda} \left\{ \frac{1 - (1 + \alpha) e^{-\alpha}}{1 - e^{-\alpha}} \right\} \quad (24)$$

where $\alpha = \lambda l/u$. λ is strongly radius dependent, being the order of half a day for 10μ particles and 80 days for 1μ particles according to Toba.⁽²⁷⁾ As $l \rightarrow \infty$, $\bar{\tau} \rightarrow 1/\lambda$ while for lengths $l \ll u\lambda$ (as $\alpha \rightarrow 0$) the mean age approaches

$l/2u$, a result which is independent of particle size as has been assumed in this model. Wind speeds are not reported in the observations⁽⁷⁾ but a reasonable value around several meters/sec implies an effective production length, l , of about 1/2 km as a lower limit.

Pursuing the idea of a short effective production length somewhat further, the population of aerosol samples at the collector may be approximated by a superposition of line sources. The contribution to the distribution from a line source element at distance x corresponding to age $t = x/u$, is given by⁽²²⁾

$$n(r,t) \approx \frac{2Q}{\sqrt{2\pi}\sigma_z u} e^{-z^2/2\sigma_z^2} e^{-\lambda(r)t} \quad (25)$$

where z is the detector height, Q is the line-source aerosol production rate per unit length and σ_z is the vertical spread which increases with x . When σ_z is approximately equal to the mixing layer height, H , the contributions can be taken as uniformly mixed for which

$$n(r,t) \approx \frac{Q}{Hu} e^{-\lambda(r)t} \quad (26)$$

While the dependence of σ_z on x is complicated, a representation for $n(r,t)$ satisfactory for the present preliminary investigation can be obtained by assuming "neutral" stability conditions for which σ_z (meters) $\sim 0.07 x$ (meters) using the data of McElroy⁽¹⁸⁾ on the dispersion of stack plumes. The results of the calculation are shown in Fig. 5 for $\lambda^{-1} = 1$ day. It will be seen that for $z = 20$ meters, sources closer to the detector than about 80 meters do not contribute significantly to the sampled population. A maximum occurs around 300 meters and is about one order of magnitude above the long "tail." Thus it can be seen

that the aerosol contribution from the first 5 kilometers of ocean surface is comparable to the contribution from the next 50 or 100 kilometers depending upon mixing layer depth, but independent of particle radius in the range from 0.1-10 μ . Contributions from further out on the long tail are particle-size dependent and may indeed dominate the total aerosol population, but it is important to point out that removal processes (precipitation) occurring as far as 100 km off shore which cut off the long tail beyond, lead to a comparatively well-defined population age due to the dominance of the near-shore contributions even for a uniformly distributed source strength. This idea may receive further support from Toba's⁽²⁷⁾ analysis of the vertical distribution of giant sea-salt particles. He envisaged the possibility of relatively noninteracting "cells" of removal and production which would lead to averages of the sort observed in aircraft sampling covering large distances. If a stationary production cell of say 50 km in extent were responsible for observed on-shore aerosol populations, the assumption of a well-defined age especially near sea level measurements would be appropriate.

If there are predominant localized sources as envisaged above, it might reasonably be expected that the model age τ , derived from fits to the I/Cl data (and Br/Cl data) should show systematic variations from run to run depending on the mean wind speed during the sampling interval. While no wind speeds are reported⁽⁷⁾ for the eight runs, it was noted that Run 5 occurred during an especially windy day. As can be seen from the summary data, Table 4, the absolute Cl values for this run are higher by about a factor of 3 indicating a higher aerosol concentration due to increased production at higher wind speeds. Since on the average aerosols would have less time to acquire iodine during this run

than the others, the I/Cl ratio should be lower for Run 5 than for the average.

This can be seen to be the case from inspection of Table 2.

TABLE 2

MEAN I/Cl RATIO COMPARED TO THAT OF RUN 5 FOR EACH STAGE

Stage	I/Cl x 10 ⁴		Ratio (Run 5/Av.)
	Average	Run 5	
1	-	(.21)	-
2	.94	.51	.6
3	1.8	2.0	1.1
4	5.1	3.6	.7
5	20	18	.9
6	26	19	.7

The ratio is typically one standard deviation lower than the average value on each stage (~ 20% lower). The value of $\bar{\rho}\tau$ obtained from a fit to run 5 data is also somewhat lower than values for other runs but the errors in estimation of $\bar{\rho}\tau$ and r_s are too great in the case of the I/Cl data to make it a useful indicator of age. Further encouragement is to be found in the later work of Moyers⁽²¹⁾ in which wind speeds are reported for a number of cascade impactor measurements of aerosol Cl, Br and I. The iodine data have not yet been analyzed in terms of the above formalism, but the plot of the I/Cl ratio on Stage C versus wind speed, Fig. 6, indicates that the predicted inverse trend exists. It is especially satisfying to note that the ratio on Stage F is largely constant with speed as expected if saturation has occurred for smallest size aerosols but not for larger ones.

QUANTITATIVE MODEL FOR BROMINE IN MARINE AEROSOLS

The Br/Cl ratio should increase with increasing wind speed since there is less time for evolution of Br to occur as the aerosols travel toward the detector from the localized source region. It is interesting to observe that the Br/Cl ratio is inversely related to the I/Cl ratio. The data shown in Fig. 7 have a fair amount of scatter but indicate such a variation. This result suggests that aerosols were collected under conditions where alterations in their iodine and bromine content occur on comparable time scales.

In the foregoing treatment of iodine enrichment it has been necessary to assume that the aerosol surface plays a role in determining an upper limit to amount of iodine an individual particle can acquire. Similarly, it is assumed that the surface is important in retaining some amount of bromine as most of it evolves from the aerosol interior. At $\tau = 0$ the aerosol Br/Cl ratio is taken to be that of sea-water. With the onset of conversion of Br^- to Br_2 , the surface-retaining layer of thickness, δl , acquires converted bromine efficiently so that an equilibrium surface density is quickly established in relation to the half-life for Br removal from the aerosol volume, V_v . Under those conditions the desired model function is

$$c^{\text{Br}}(r, \tau) = \rho_s V_s + \rho_v V_v h(r, \tau) \equiv c_s + c_v \left. \begin{array}{l} \text{where} \\ V_v = \frac{4}{3} \pi (r - \delta l)^3 \sim \frac{4}{3} \pi r^3 \\ V_s = \frac{4}{3} \pi r^3 - V_v \sim 4 \pi r^2 \delta l \end{array} \right\} \quad (27)$$

and $h(r, 0) = 1$ while $\lim_{\tau \rightarrow \infty} h(r, \tau) \rightarrow 0$

The Br/Cl ratio is given by

$$R_k^{\text{Br,Cl}} = \frac{\int_0^\infty (4\pi r^2 \rho_s \delta l + \frac{4}{3} \pi r^3 \rho_v h(r, \tau)) f_k(r) n(r) dr}{\frac{4}{3} \pi \rho^{\text{Cl}} \int_0^\infty r^3 f_k(r) n(r) dr} \quad (28)$$

$$\approx \frac{3\rho_s \delta l}{\rho^{\text{Cl}} r_k} + \frac{\rho_v}{\rho^{\text{Cl}}} h(r_k, \tau)$$

$\rho_v / \rho^{\text{Cl}}$ should be the sea-water Br/Cl ratio, and ρ_s is taken to be independent of r . The form of the function, $h(r, \tau)$, depends on the mechanism limiting the evolution rate.

Br evolution from sea-salt crystals may be limited by the ability of Br^- to migrate to the aerosol surface where it is converted. The Br concentration half life, $\tau_{1/2}$, calculated treating the surface as a perfect Br sink, gives $\tau_{1/2} = 0.5$ hr, which is appropriately long using a diffusion coefficient, D , characteristic of ion migration in solids at room temperatures.⁽¹²⁾ For this limiting mechanism, a solution to the radial diffusion equation (Ingersol et al.⁽¹¹⁾) gives,

$$h(r, \tau) = \frac{6}{\pi^2} \sum_{j=1}^{\infty} \frac{1}{j^2} e^{-\gamma/r^2} \quad (29)$$

where $\gamma = \pi^2 D \tau$. Thus, $h(r, \tau)$ decreases most rapidly in time for smallest particles. The dependence of $R_k^{\text{Br,Cl}}$ on k for various assumed model age parameter values, γ , is shown in Fig. 8. The slight rise in $R_k^{\text{Br,Cl}}$ for small radii and $\gamma = 0$ occurs because the surface density is taken to have the equilibrium value even at $\tau = 0$ for purposes of simplification. It will be seen that the curves have the features expected on the basis of our earlier qualitative discussion.

For sufficiently small γ no minimum appears in the observed size range. As particles on stage 6 are fully depleted the minimum develops and shifts toward larger particle stages as γ increases. These results are not sensitive to the exact form of $h(r, \tau)$ provided it decreases with particle size at least as rapidly as $1/r$.

Aerosols with a predominantly crystalline form life-history appear unlikely in view of earlier arguments. However, a ten micron liquid aerosol droplet would lose 50% of its Br in about 0.001 sec if it is a perfect sink since the diffusion coefficient for Br in aqueous solutions is large, $D \sim 10^{-5}$ cm²/sec. (12) Alternatively the evolution rate may be determined by the rate of diffusion of suitable gaseous reactants such as O₃ toward the aerosol surface. In this case the rate is given by

$$\frac{dC}{dt} = K \Phi(r, t) \rho_s' \quad (30)$$

where $\Phi(r, t)$ is the instantaneous diffusion flux, ρ_s' is the surface density of Br⁻ available for reaction, and K is a suitable coupling constant. It is further assumed that

$$\rho_s' = K' \rho_v = K' C_v / \frac{4}{3} \pi r^3 \quad (31)$$

The diffusion coefficient D^* for O₃ is taken to be that of O₂, 0.2 cm²/sec, (12) while parameters in $F(r)$ analogous to those in Eq. (16) are $\nu = 4 \times 10^3$ cm/sec and $\Delta = 7 \times 10^{-6}$ cm (10) taking for O₃ values for N₂. The shape of the ratio

$R_k^{Br,Cl}$ is very insensitive to choices for these parameters. Combining Eq. 31 with 30 the solution for C_v is

$$C_v = C_v^0 e^{-\gamma F(r)/r^2} \quad (32)$$

where, of course,

$$C_v^0 = \frac{4}{3} \pi \rho^{Br} r^3$$

Thus

$$h(r,t) = e^{-\gamma F(r)/r^2} \quad (33)$$

where the model age parameter, γ , is given by

$$\gamma = 3KK'D* \int_0^\tau C(t)dt = 3KK'D*C*\tau \quad (34)$$

and C^* is the mean reactant concentration, e.g. O_3 , experienced by each aerosol member. While γ is proportional to the age, τ , the constant of proportionality is not as well determined as it is in the case of iodine diffusion. The Br/Cl ratio has the exact form

$$R_k^{Br,Cl} = \alpha \frac{\int_0^\infty \{ \beta r^2 + r^3 e^{-\gamma F(r)/r^2} \} f_k(r) n(r) dr}{\int_0^\infty r^3 f_k(r) n(r) dr} \quad (35)$$

where $\beta = \frac{3\rho_s \delta l}{\rho_v}$ and $\alpha = \rho_v / \rho^{Cl}$, the sea-water ratio. In a nonlinear least squares fit for each of the seven treated runs all three parameters (α, β, γ) were allowed to vary. The results are shown in Fig. 9 where the data have been ordered by the age parameter. Best fit parameter values are shown below:

TABLE 3

A THREE PARAMETER FIT TO THE Br/Cl DATA
Best Fit Parameters

Run Number	$\alpha \times 10^3$	$\beta(\mu)$	γ
4	3.3	0.33	7.3
5	4.3	0.28	1.6
6	5.4	0.28	3.0
7	14.5	0.10	31.0
8	4.1	0.24	3.9
10	5.3	0.22	6.0
11	4.4	0.31	3.5

It will be seen that the fit to the data is acceptable in most cases although α , the initial Br/Cl ratio at time $\tau = 0$, tends to be somewhat higher than the sea-water ratio. This effect might be attributable to a small Cl loss. In any event the model predicts that the ratio should be smaller on small particles than on the largest members as observed. This appears to be always the case both in the data of Duce et al., analyzed here and in later measurements by Moyers.⁽²¹⁾ The constancy of the surface density parameter, β , is possibly to be expected if variations in the aerosol surface characteristics associated with Br retention do not change markedly in time at a given sampling site. Taking the mean value of β as $\sim 0.3\mu$, the apparent Br surface density is $\rho_s \delta l \sim 10^{-5} \rho_v \sim 5 \text{ ng/cm}^2$, a result which is comparable to the inferred I surface saturation density of about 10 ng/cm^2 . Run 7 is "anomalous" due to the high Br/Cl ratio for Stage 1. Values for this stage are subject to greater systematic uncertainty because the first stage collects all airborne substances with sizes greater than about 10μ , and collection of a single large Br - rich particle will invalidate the results.

It is gratifying to note that Run 5 corresponds to the smallest age parameter γ as expected from the previous result with the I/Cl data. With age inversely related to wind speed and to absolute chloride concentration, the Br/Cl impactor spectrum should "flatten out" as the wind speed increases. The ratio of total Cl concentration in atmospheric particulates for Run 5 to total Cl for the other runs which is about 3 implies a ratio of wind speeds of about 3 based on the data of several authors on airborne sea-salt concentrations versus wind speed. (13) Thus, from the total chloride concentrations we obtain, $\tau_5/\tau_{\text{others}} \sim 1/3$, and the model age parameter ratio is also $\gamma_5/\gamma_{\text{others}} \sim 1/3$. It should be noted, however, that the run with the greatest aerosol age, 4 according to the model (excluding anomalous run 7), does not have a correspondingly low total Cl concentration.

Further evidence for this dependence is found in the data of Moyers. (21) While the data have not yet been treated fully, a preliminary inspection reveals that the Br/Cl ratios exhibit the predicted direct dependence on wind speed. It will be seen from Fig. 10 that ratios on Stages D and E show the strongest variation, as expected if full Br depletion has not yet occurred, while those on Stage B are essentially constant within the scatter of the data points. For 1μ particles (\sim Stage D) assuming a production length of 1 km, the rate of change of the Br/Cl ratio is $\sim 0.2 \times 10^{-4}$ /sec or about 1% per second, corresponding to the slope of the Stage D ratio versus wind speed. This high loss rate appears to be consistent with Moyers' thermodynamic calculation which indicates that after initial release into the atmosphere the aerosol should act as source for Br with a release rate which is fast when compared with the aerosol residence

time. Work is in progress to relate the model age parameter to wind speed from Moyers' data. One should observe $\gamma \sim u^{-1}$, and Fig. 11, the results of a preliminary calculation, indicate that this is approximately true.

Acknowledgements: The author is especially grateful to Professor J. W. Winchester for his sustained support and encouragement. Thanks are due Drs. R. Dams, R. Loucks and E. Monahan for their helpful comments and the author's wife, Renee, for her assistance in manuscript preparation.

TABLE 4

A SUMMARY OF IMPACTOR DATA
(Duce et al., Tellus XIX (1967) 369-379)

Run	Stage	CI ($\mu\text{g}/\text{m}^3$)						I/CI $\times 10^4$						Br/CI $\times 10^3$					
		1	2	3	4	5	6	1	2	3	4	5	6	1	2	3	4	5	6
4	(.05)	.19	.80	1.0	.44	.08	<u>.35</u>	1.2	1.6	4	21	29	3.4	1.6	2.1	.82	1.1	2.7	
5	(.45)	1.6	2.9	2.7	1.1	.14	(.21)	.51	2.0	3.6	18	19	3.9	5.1	3.5	2.6	2.7	2.9	
6	.17	.45	.67	.58	.27	.05	(.1)	1.6	1.2	6	16	22	5.9	4.6	3.9	2.9	2.4	4.0	
7	.05	.13	1.0	1.2	.51	.05	(.1)	.8	2.7	7	28	37	7.9	2.8	1.5	.87	1.2	3.5	
8	.16	.51	.92	.86	.28	.06	(.6)	<u>.15</u>	1.4	5.7	18	28	3.8	3.9	2.8	1.4	1.1	2.6	
9	(.6)	(.8)	1.1	.8	.33	.05													
10	.05	.22	.76	.80	.23	.03	(.5)	1.6	2.1	3.9	16	30	4.9	4.0	2.7	1.2	.9	3.0	
11	.21	.77	1.2	.90	.24	.03	(.1)	.7	1.4	5.5	20	17	4.3	4.0	3.2	2.0	1.8	3.3	

() uncertain values

 upper limits

REFERENCES

1. Blanchard, D. C., The electrification of the atmosphere by particles from bubbles in the sea, Progress in Oceanography, Pergamon Press, v. 1 (1963), 171-202.
2. Blanchard, D. C., Sea-to-air transport of surface active material, Science, 146, (1964), 396-397.
3. Chamberlain, A. C. and R. D. Wiffen, Some observations on the behaviour of radioiodine vapour in the atmosphere, Geofisica Pura e Applicata, 42, (1959), 42-48.
4. de Brouckere, L., Sur l'adsorption des electrolytes par les surfaces cristallines, 3, J. Chim. Phys., 27 (1930) 543-565.
5. Duce, R. A., J. T. Wasson, J. W. Winchester, and F. Burns, Atmospheric iodine, bromine and chlorine, J. Geophys. Res., 68, (1963), 3943-3947.
6. Duce, R. A., J. W. Winchester and T. W. VanNahl, Iodine bromine and chlorine in the Hawaiian marine atmosphere, J. Geophys. Res., 70, (1965), 1775-1799.
7. Duce, R. A., A. H. Woodcock and J. L. Moyers, Variation of ion ratios with size among particles in tropical oceanic air, Tellus, XIX, (1967), 369-379.
8. Eriksson, E., Composition of atmospheric precipitation, 2, Sulfur, chloride, and iodine compounds, Tellus 4 (1952) 280-303.

9. Ericksson, E., The chemical composition of Hawaiian rainfall. Tellus 9 (1957) 509-520.
10. Handbook of Chemistry and Physics, 34th Edition, (1952) p. 2873.
11. Ingersol, L. R. and O. J. Zobel, Heat Conductivity, McGraw-Hill (1944), p. 162.
12. Jost, W., Diffusion in solids, liquids and gases, Academic Press, New York (1952).
13. Junge, C. E., Air Chemistry and Radioactivity, Academic Press, New York, (1963).
14. Komabayasi, M., Enrichment of inorganic ions with increasing atomic weight in aerosol, rain water, and snow in comparison with sea-water, J. Meteorol. Soc. Japan, 40, (1962), 25-38.
15. Lassen, L., and G. Rau, Die anlagerung radioaktiver atome an aerosole (Schwebestoffe), Z. Physik, 160 (1960), 504-519.
16. Lundgren, D. A., An aerosol sampler for determination of particle concentration as a function of size and time, J. Air Pollution Control Assn., 17, (1967), 225-228.
17. MacIntyre, F. and J. W. Winchester, Phosphate ion enrichment in drops from breaking bubbles, J. Phys. Chem., 73, (1969), 2163-2169.
18. McElroy, J., A comparative study of urban and rural dispersion, J. Appl. Meteorol. 8 (1969) 19-31.

19. Mitchell, R. I. and J. M. Pilcher, An improved cascade impactor for measuring aerosol particle sizes, Ind. and Eng. Chem., 51, (1959), 1039-1042.
20. Miyake, Y. and S. Tsunogai, Evaporation of iodine from the ocean, J. Geophys. Res., 68 (1963), 3989-3993.
21. Moyers, J. L., Studies of gaseous iodine and bromine in the marine atmosphere., Ph.D. Thesis, University of Hawaii, May 1970.
22. Pasquill, F., Atmospheric Diffusion, D. Van Nostrand Co. London, 1962.
23. Pueschel, R. F., R. J. Charlson and N. C. Ahlquist, On the anomalous deliquescence of sea-spray aerosols, J. Appl. Meteorol. 8, (1969), 995-998.
24. Ranz, W. E. and J. B. Wong, Jet impactors for determining the particle-size distributions of aerosols, Ind. Hyg. and Occupational Med., 5, (1952), 464-477.
25. Seto, Yuk-Bon, R. A. Duce and A. H. Woodcock, Sodium to chlorine ratio in Hawaiian rains as a function of distance inland and of elevation, J. Geophys. Res., 74, (1969), 1101-1103.
26. Sundelöf, L., On the Accurate Calculation of Particle-Size Distributions in Aerosols from Impaction Data, Staub-Reinhalt Luft, 27, (1967), 22-28.
27. Toba, Y., On the giant sea-salt particles in the atmosphere, Tellus XVII (1965), 131-145; 365-282.

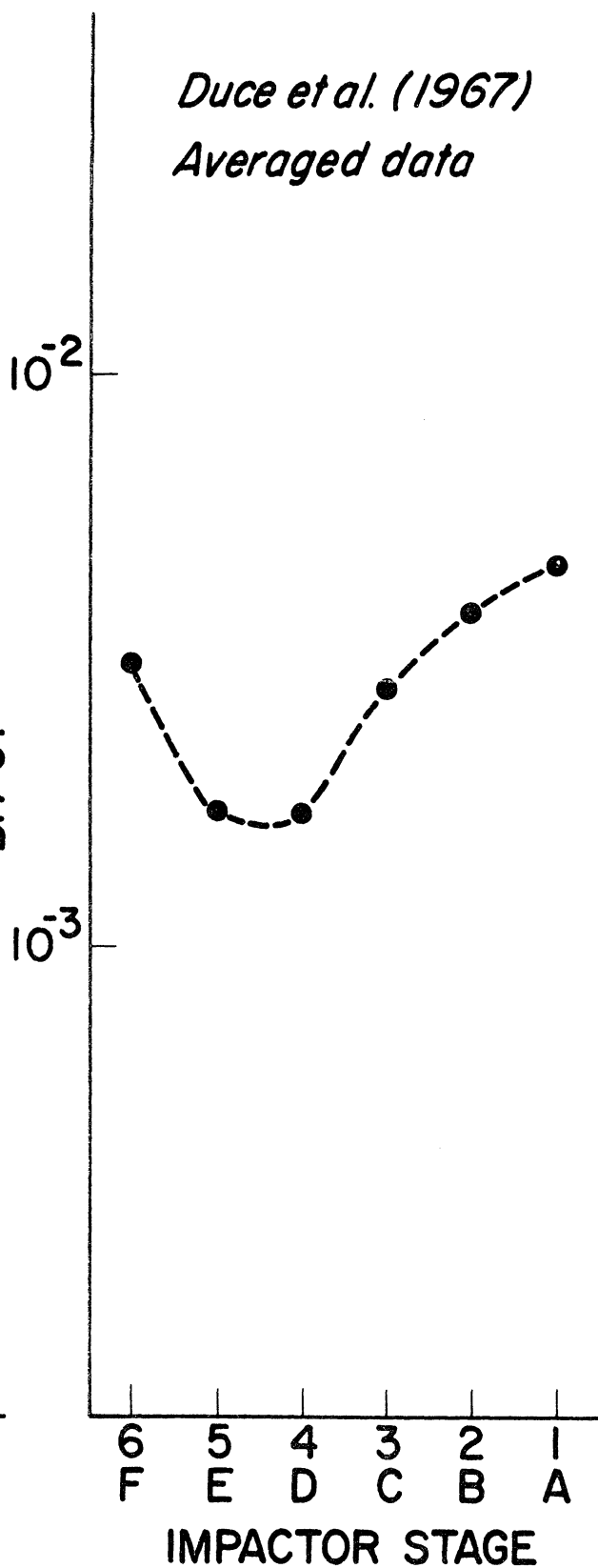
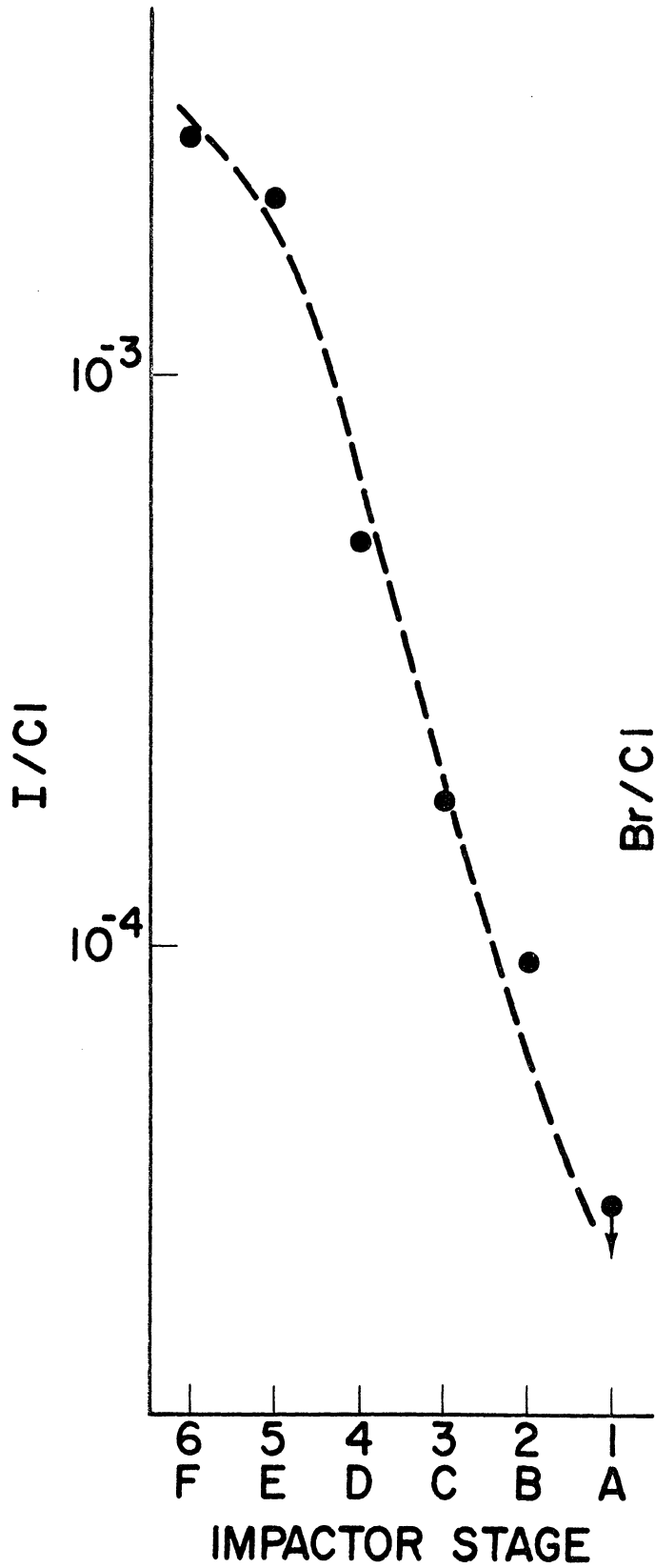
FIGURE CAPTIONS

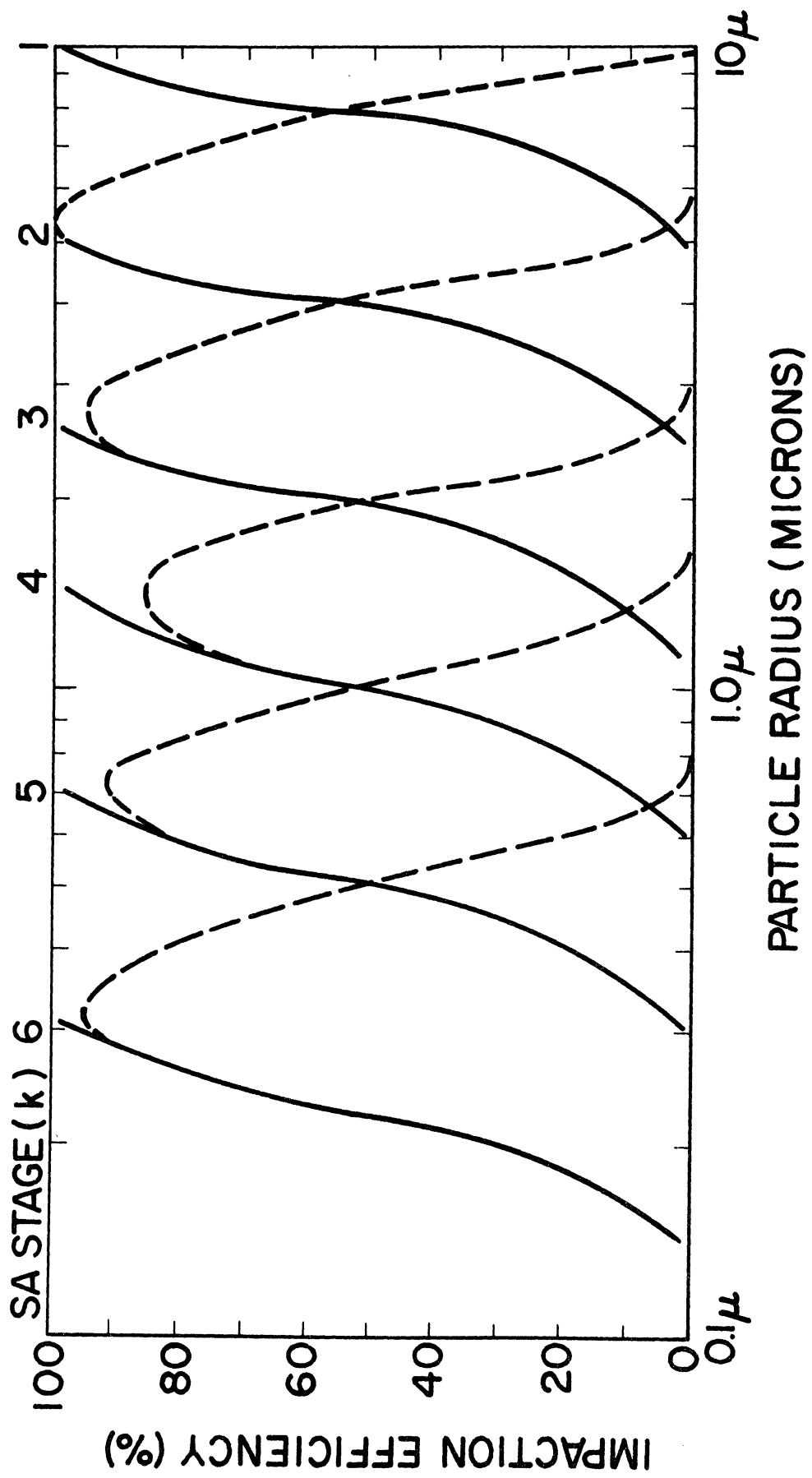
- Fig. 1. Average I/Cl and Br/Cl ratio values versus impactor stage. Data of Duce et al., (1967).
- Fig. 2. Stage efficiency curves $\epsilon_k(r)$ for the Scientific Advances impactor based on the data of Mitchell and Pilcher (1959). The dashed curve represents the apparent impactor efficiency $f_k(r)$ where it differs from $\epsilon_k(r)$.
- Fig. 3. Cl concentration, I_k^{Cl} , versus k for run 11, with a nonlinear least squares fit based on an analytic representation for the particle size distribution $n(r)$. A smooth curve is drawn through calculated points.
- Fig. 4. The I/Cl ratio versus k for run 11 showing the calculated variation for diffusion rate limited I absorption ($\tau \approx 0$), partial surface-saturation ($r_s \sim 0.5\mu$, solid curve) and complete surface-saturation ($\tau \rightarrow \infty$).
- Fig. 5. A representation of the aerosol age-size distribution, $n(r,t)$ resulting from a semi-infinite plane of line sources. The size dependence, determined by values of $\lambda(r)$, is not apparent for source distances less than about 50 km. ($H = 1\text{km}$, $Z = 20\text{m}$, $u = 5\mu/\text{sec}$ $\sigma_z = 0.07X$).
- Fig. 6. Variation of the I/Cl ratio with wind speed, u . An inverse relation is expected for stage 6 ($k = 3$) while the ratio should be constant on stage F ($k = 6$) if surface saturation has occurred. Data of Moyers (1970).
- Fig. 7. The I/Cl ratio versus the Br/Cl ratio on stages for which the greatest variation is expected. According to the model an inverse relation should be observed if the rate of Br evolution is comparable to the rate of I absorption.
- Fig. 8. Variation in the calculated Br/Cl ratio with model age parameter, γ , for internally limited Br evolution. Fresh aerosols ($\gamma \approx 0$) possess the sea-water Br/Cl ratio for all particle sizes while sufficiently old ones ($\gamma \rightarrow \infty$) have only a surface Br content leading to a $1/r$ dependence in the Br/Cl ratio.
- Fig. 9. The Br/Cl ratio versus k. The curves are obtained from a three parameter nonlinear least squares fit using an externally limited Br evolution model. The runs are ordered by the model age parameter γ .

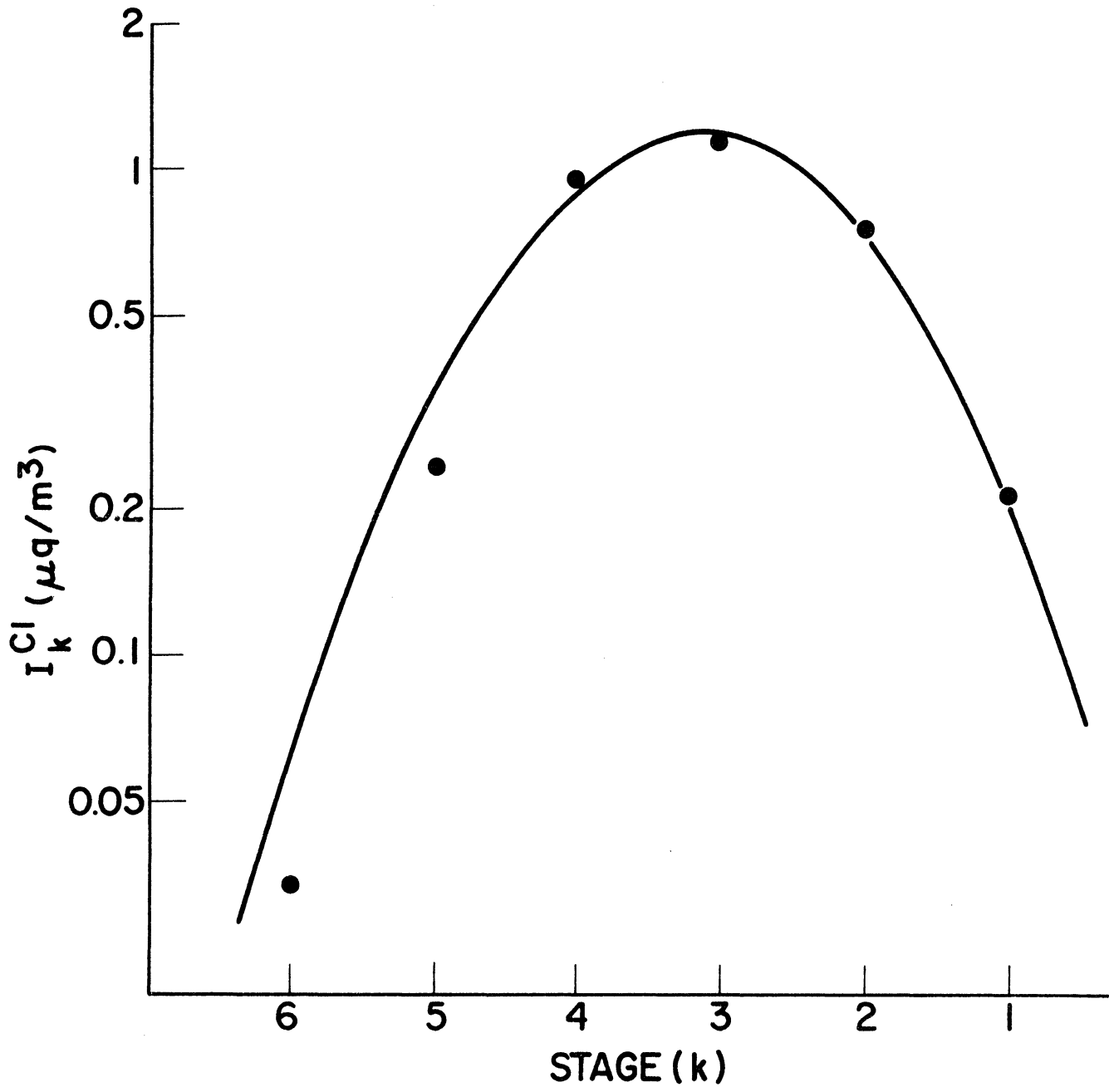
FIGURE CAPTIONS (Concluded)

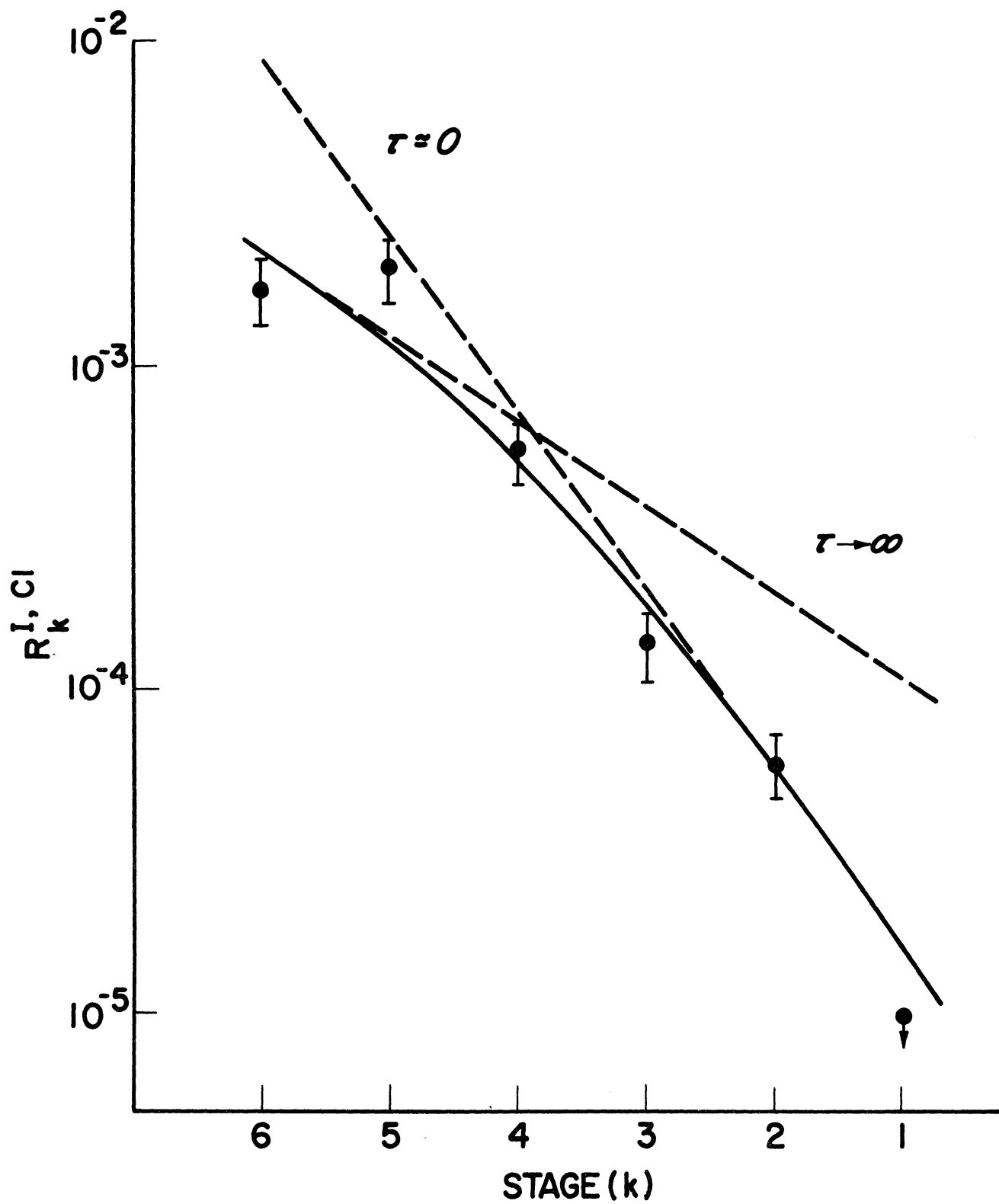
- Fig. 10. Variation of the Br/Cl ratio with wind speed, u . A direct relation is expected for stages D and E while the ratio should vary less on stage B. Data of Moyers (1970).
- Fig. 11. Dependence of the Br/Cl model age parameter on wind speed. The values for γ are obtained from a preliminary treatment of Moyers' impactor data. Points in parentheses result from analysis of limited data sets and are subject to greater uncertainty. An inverse dependence is expected.

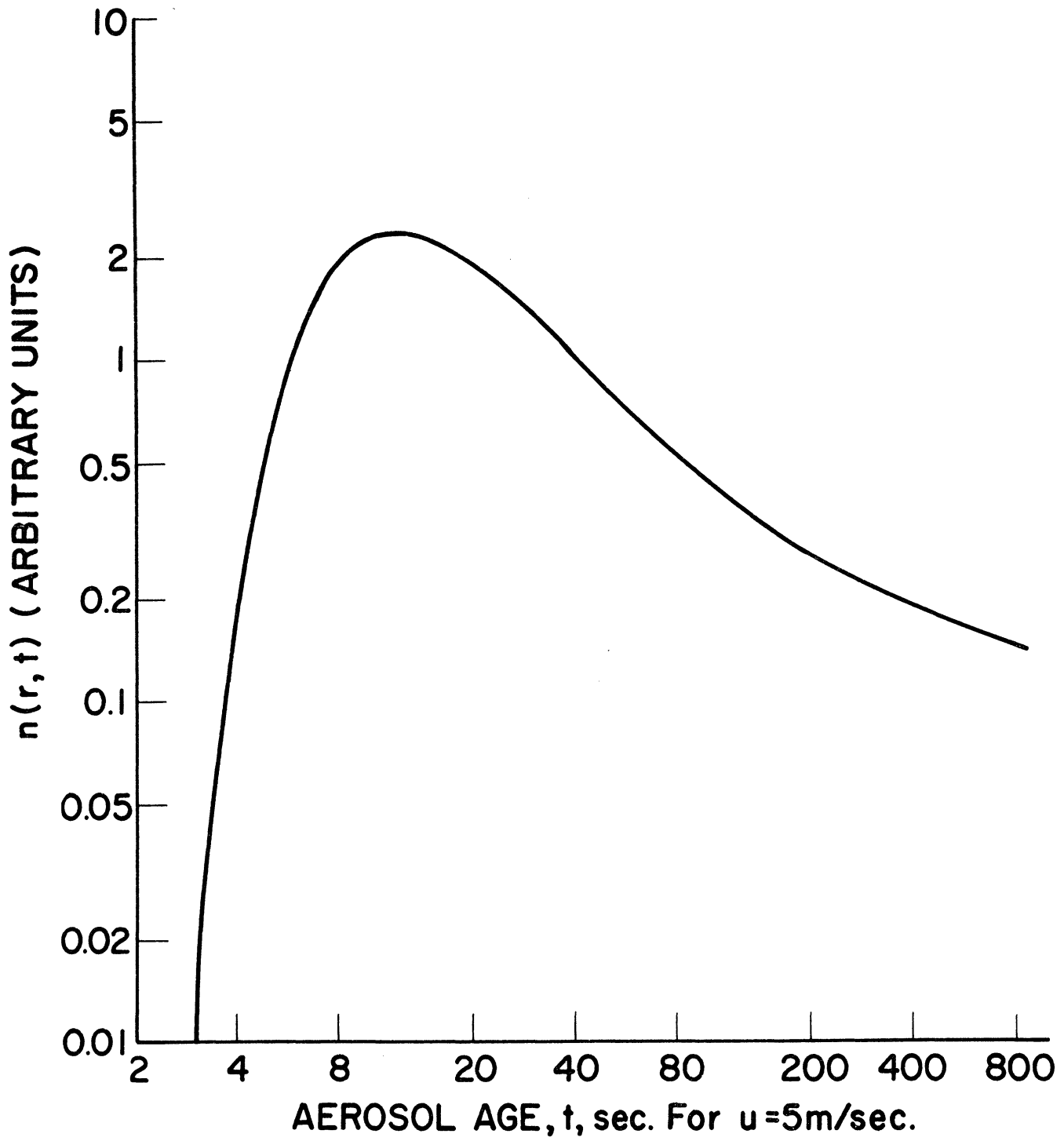
Duce et al. (1967)
Averaged data

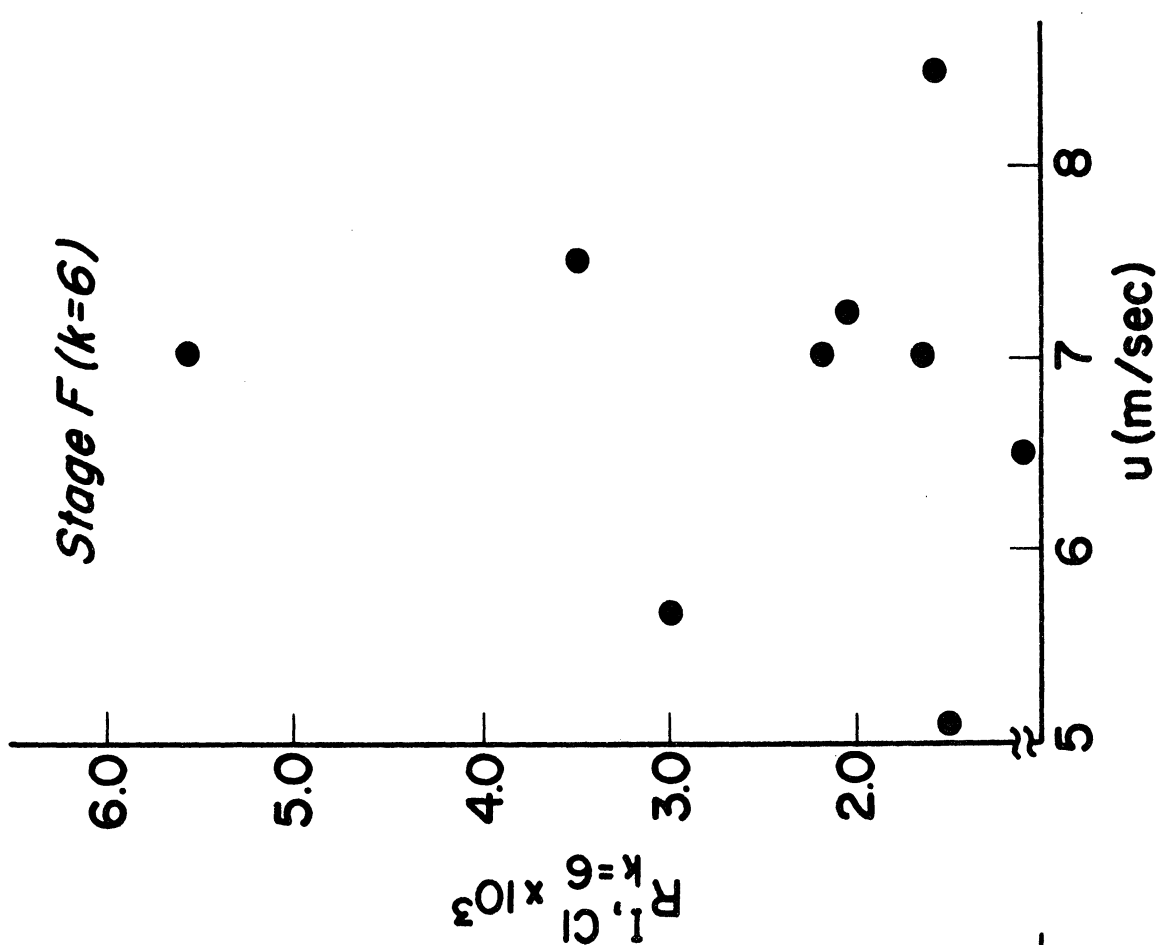
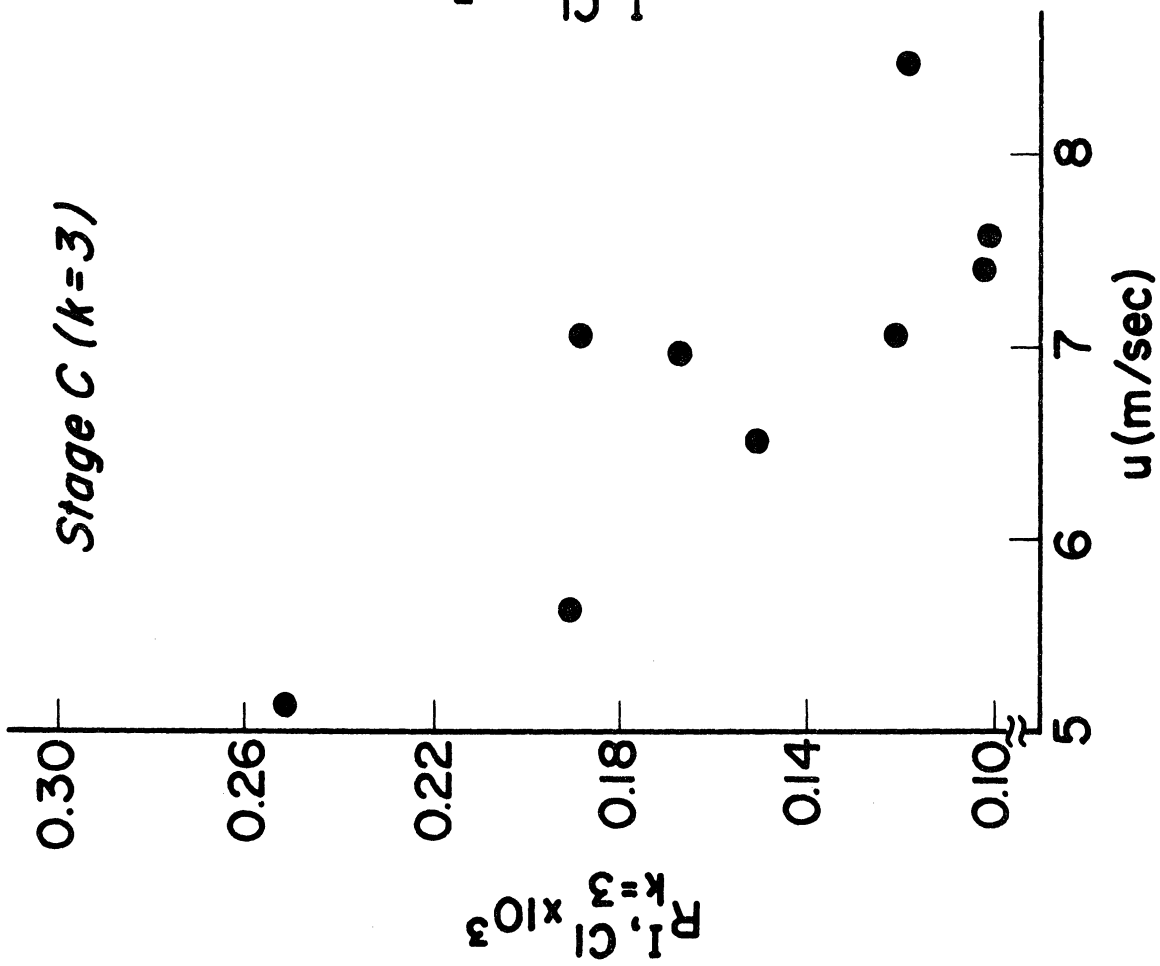


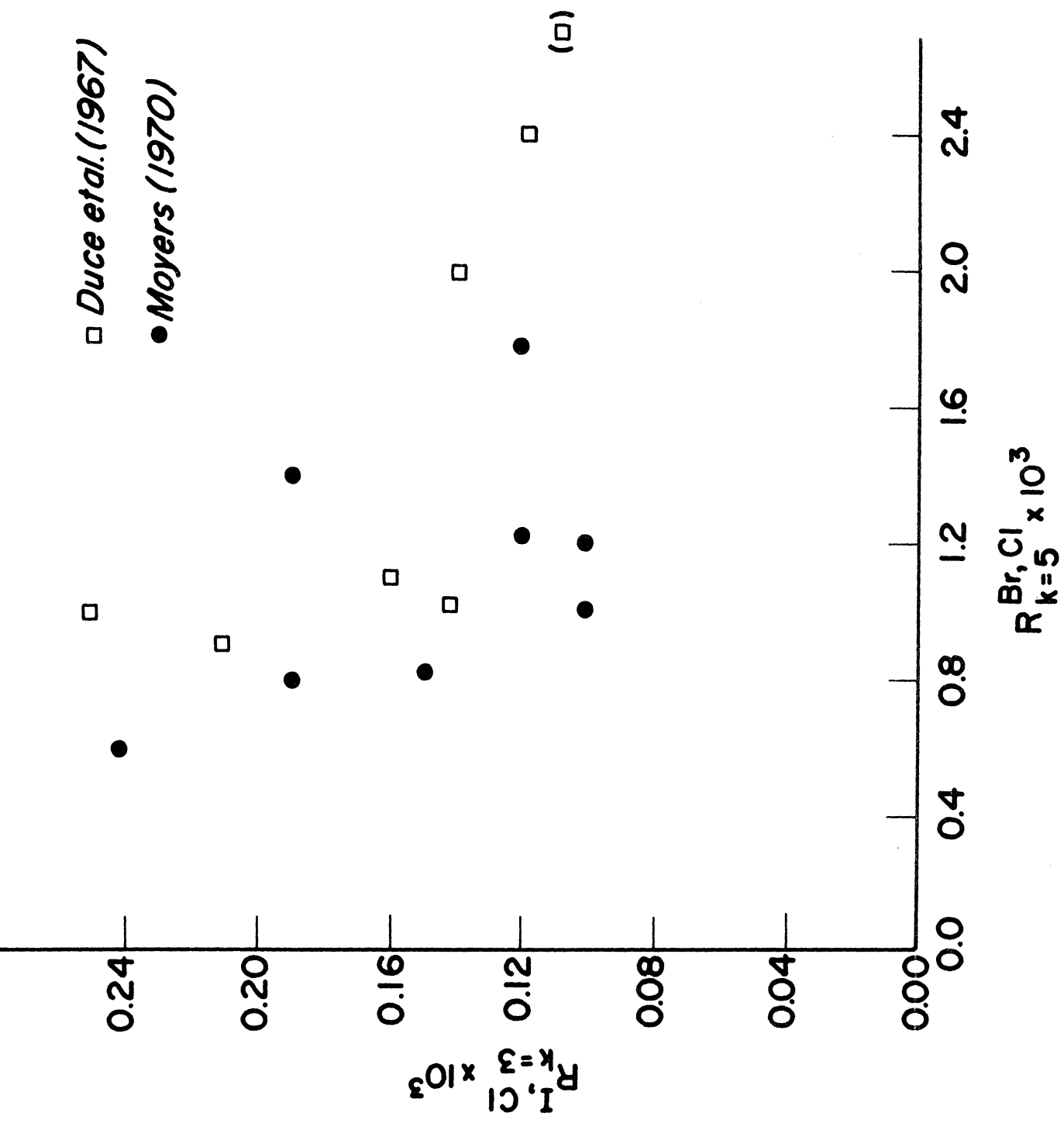


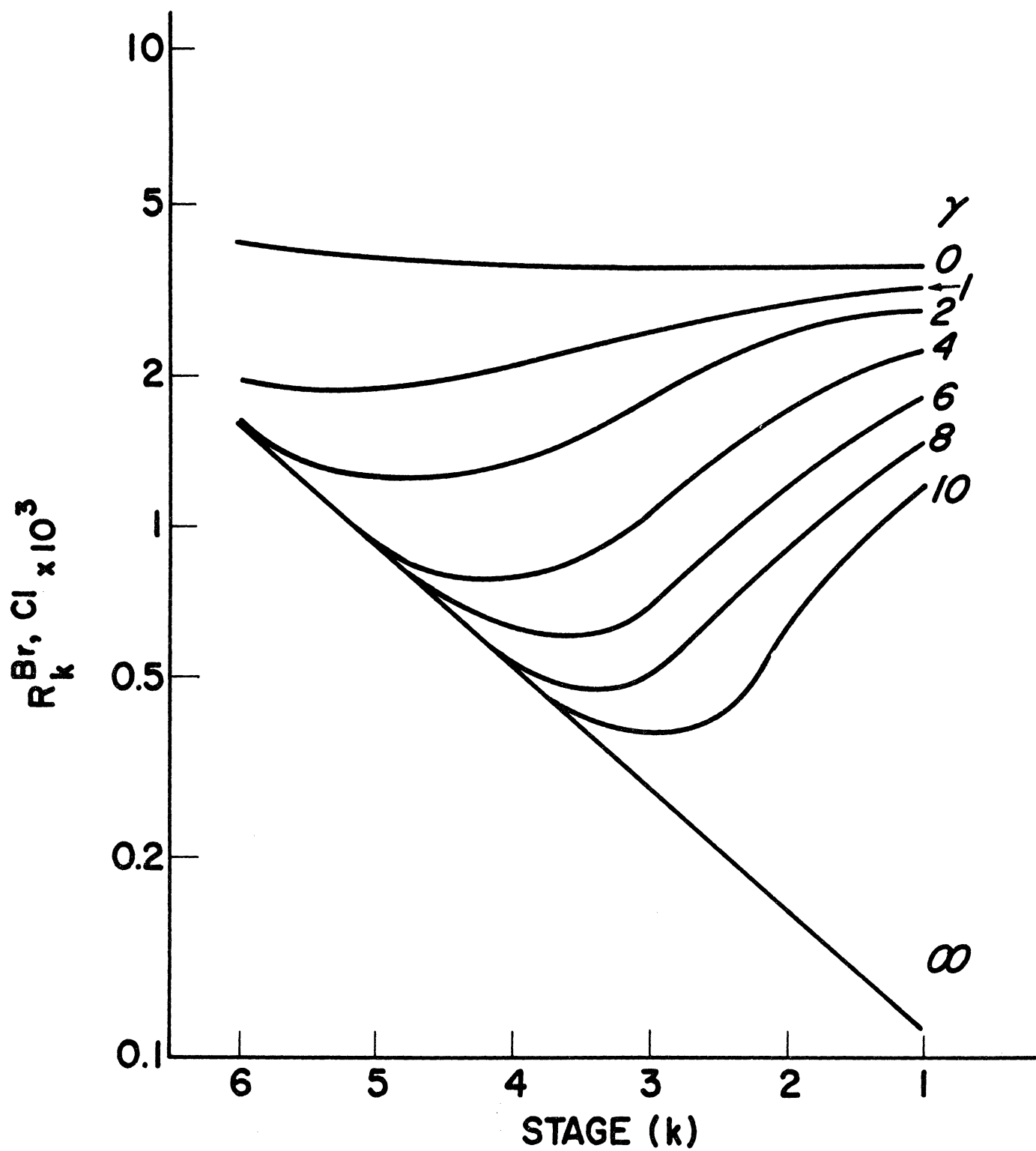


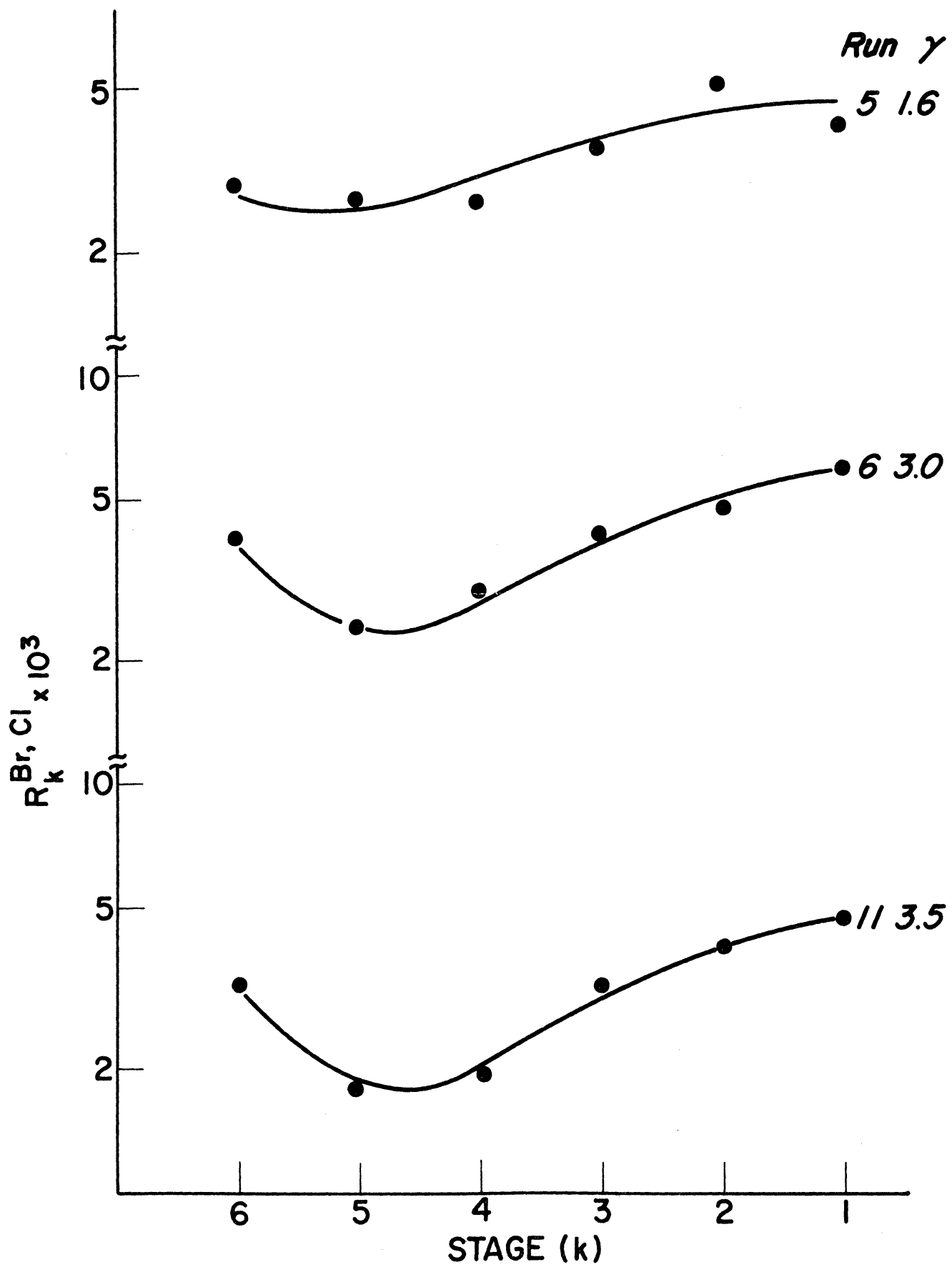


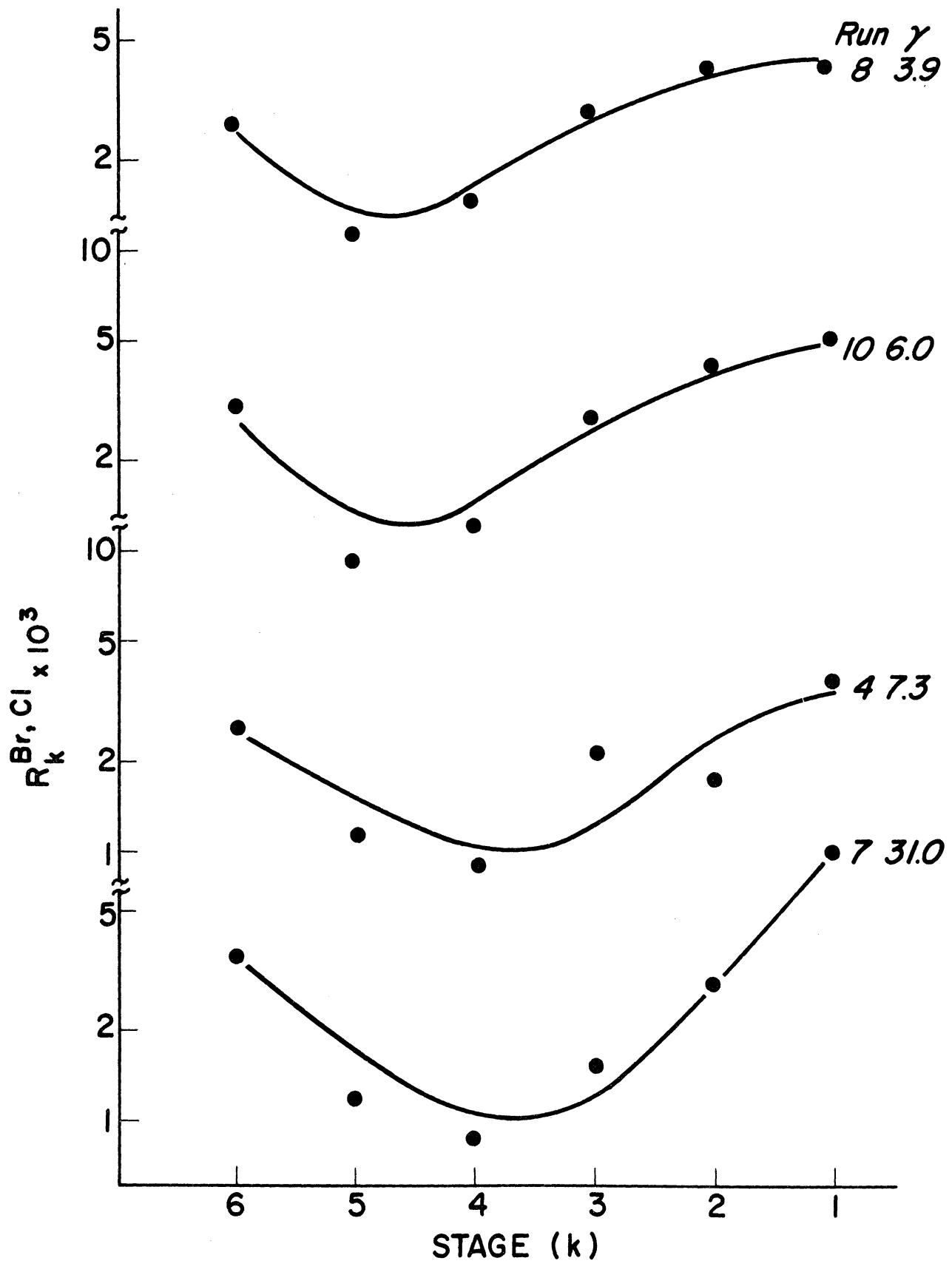


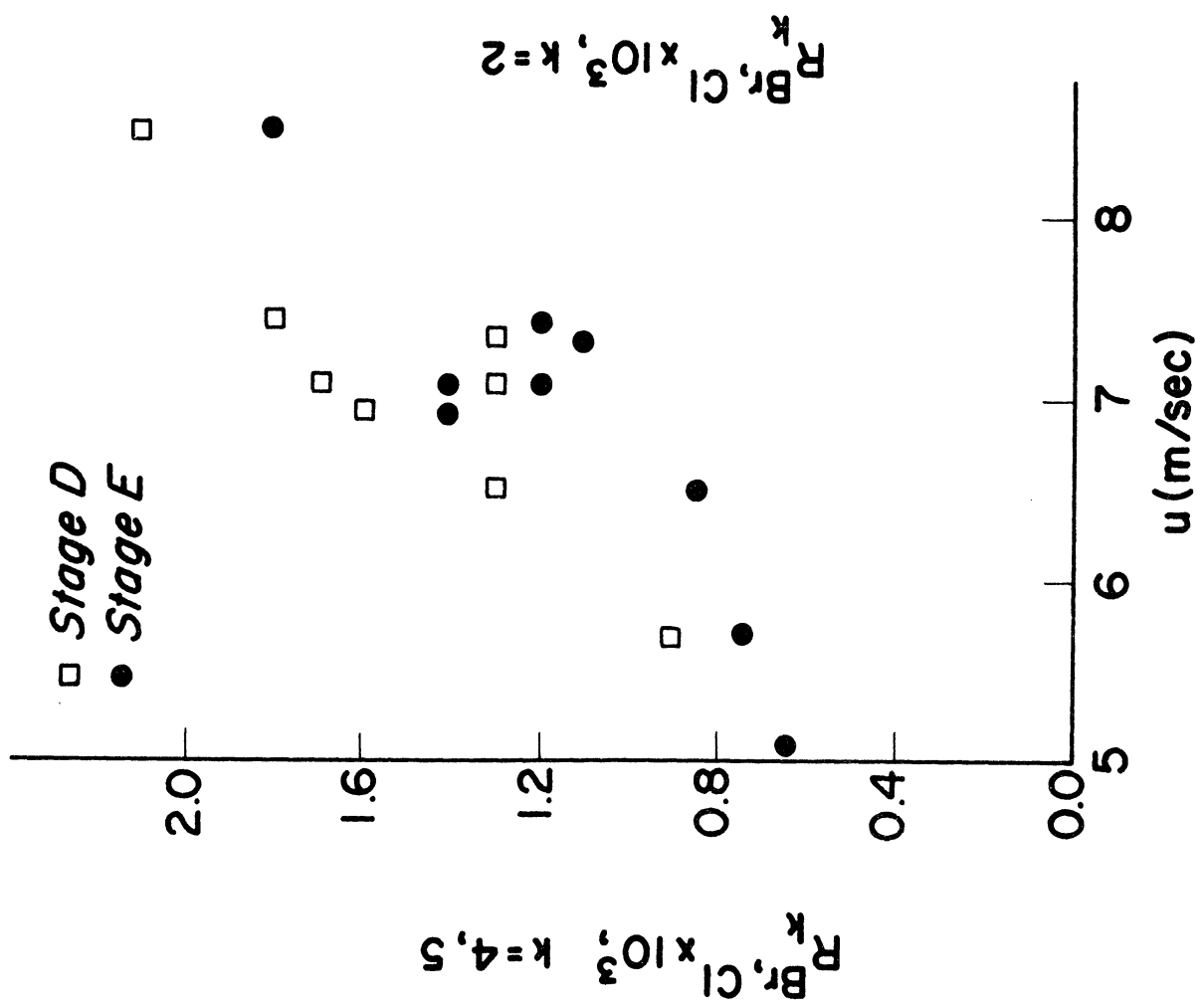
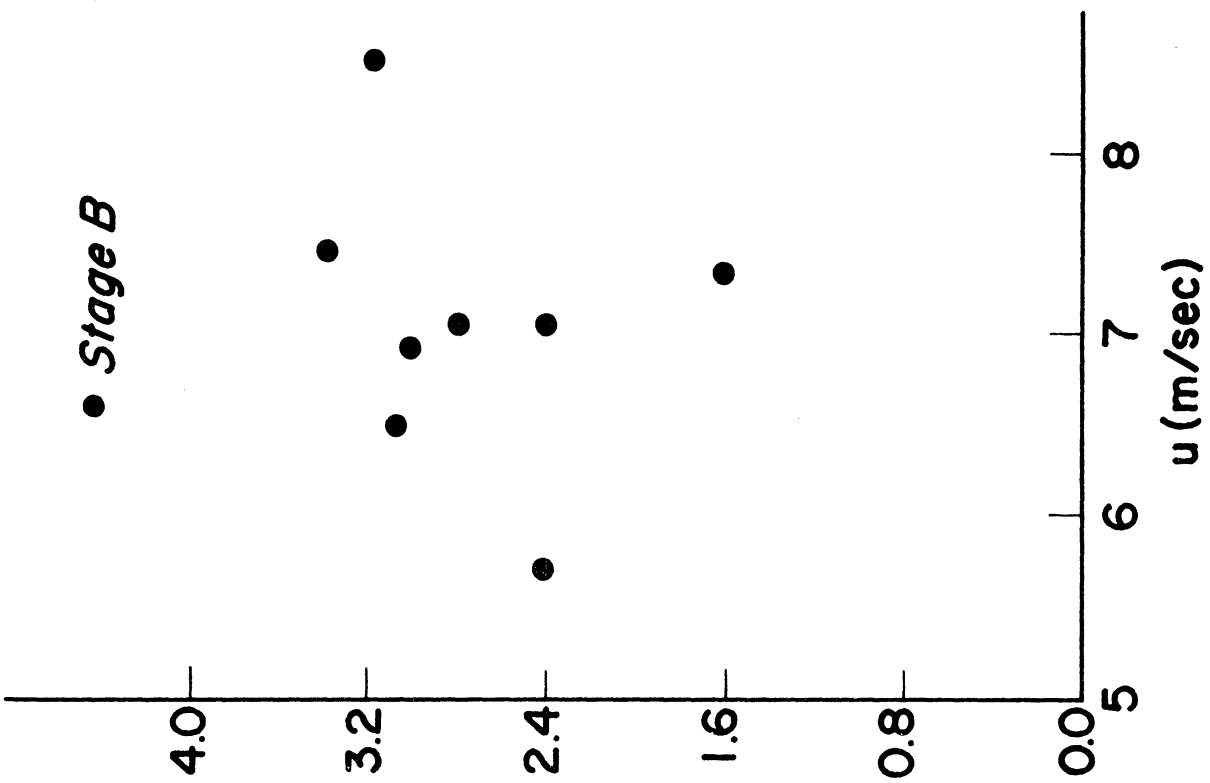


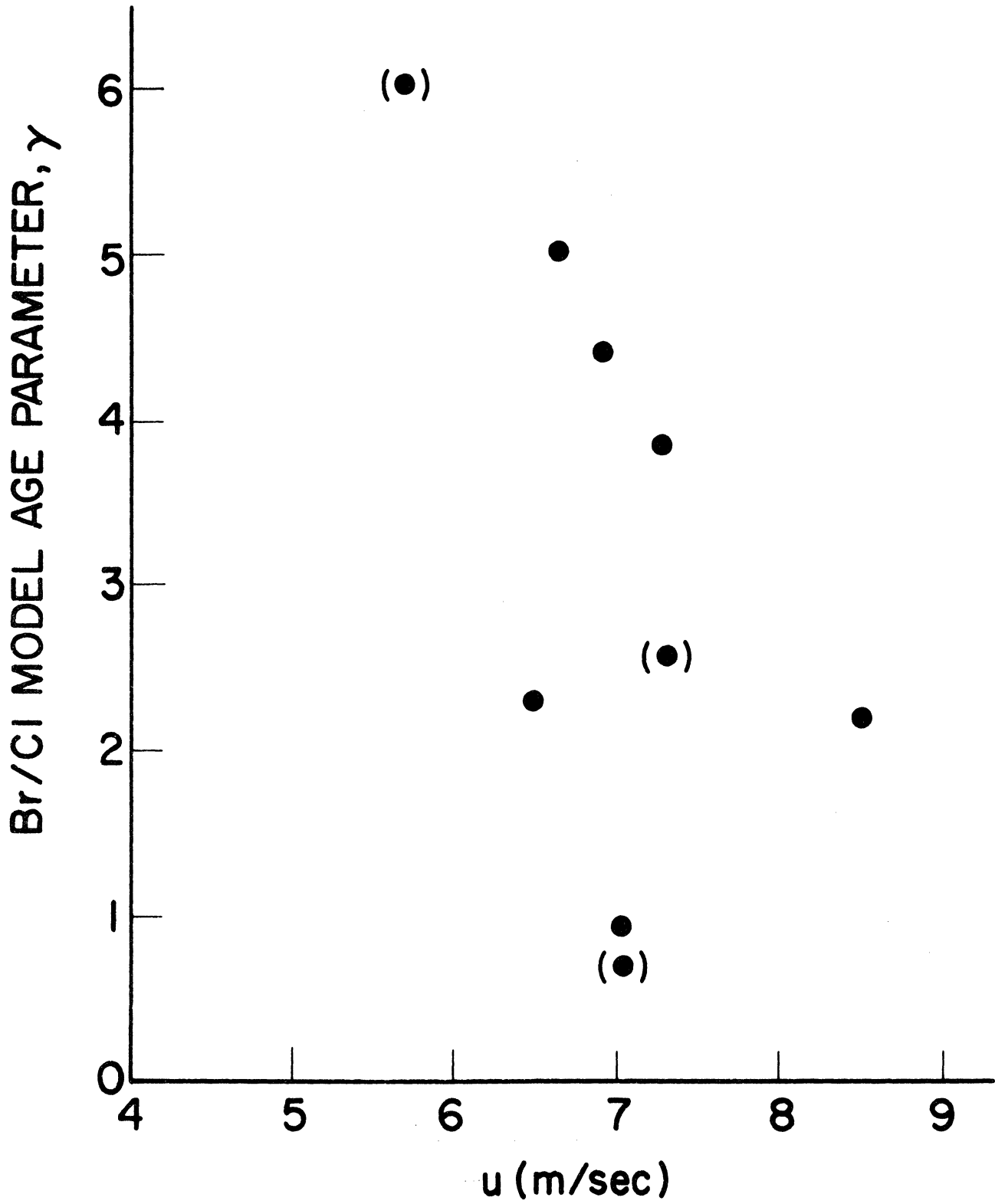












Excerpted from John W. Winchester, "Occurrence of Halogens in Atmospheric Aerosols and Precipitation", Technical Progress Report No. 1, COO-1705-1, March 1968.

THE HALOGEN CONTENTS OF HURRICANE RAIN WATER

The mixing of sea water with condensed water vapor in the atmosphere is a subject of interest in the study of hurricanes. Recently Östlund has been successful in using the tritium content of hurricane rain water as an indicator of the fraction of water originating in the sea surface, and his studies have revealed a pattern of tritium contents which corresponds to the radial variation of physical features of the hurricane. If the water was largely the result of evaporation from the sea surface, such that the sea salts are added to the atmosphere without unusually great efficiency, then the sea salt content of the rain water should not be greater than is typical of marine rains. Marine rains are very much less salty than sea water, e.g., the chloride content of Hawaiian orographic showers is usually 10^{-4} or less of the sea water value. Therefore, as little as 0.1% of sea water admixture with rain water should make a significant increase in the halogen content, and the halogens can serve as a tracer for the liquid sea water component of rain water.

A valuable suite of 98 rain water samples collected by aircraft from hurricane Faith 1966 has been obtained from Prof. H. Göte Östlund of the University of Miami. These samples have been given the highest priority in the analytical program of the AEC project, and 36 samples have been analyzed. Analysis of a set of 62 additional samples recently received is planned for the summer of 1968. All samples were collected in the rain cloud under controlled conditions with documentation on aircraft altitude and location with respect to storm center by radar. Determinations of tritium and of stable isotopes of hydrogen and oxygen are being made on the same samples by Östlund and by Ehhalt at NCAR, Boulder. Tables 1 and 2 are a summary of the 36 hurricane analyses and a comparison with Hawaiian orographic rain water previously published. A striking resemblance in the modal concentrations and in the log normal pattern of the distributions is apparent.

The following is an abstract of a paper to be presented at the April 1968 meeting of the American Geophysical Union in Washington.

Note added May 1970: This study was suspended in order to develop more precise analytical methods for Br/Cl ratio determinations. These methods are now developed, and this line of inquiry is now ready for further pursuit. With the understanding of marine aerosol composition gained by the Robbins model for halogen composition further research on marine aerosols may be especially profitable both in understanding the atmospheric chemistry of the marine environment and in understanding the properties of natural and pollution aerosols of the continental regions.

Invited paper for presentation at the Symposium on Climate Modification and Air Chemistry, Section of Meteorology, American Geophysical Union, Washington, April 1968.

SEA SALT HALOGENS AS NATURAL ATMOSPHERIC TRACERS IN HURRICANE STUDIES

John W. Winchester, Dept. of Meteorology and Oceanography, The University of Michigan, Ann Arbor, Michigan
Douglas R. Sendelbach, (same as above)
H. Göte Östlund, Institute of Marine Science, University of Miami, Miami, Florida

ABSTRACT

The feasibility of using halogens in rain water as a natural atmospheric tracer for sea salt has been tested by neutron activation analysis. Samples of rain water from hurricane Faith, collected by aircraft over a 500 km diameter on 1 September 1966, have been analyzed for chlorine, bromine, and iodine in 1 ml volumes. Concentration mean values and variations of 25 analyses are close to those previously found for orographic showers over Hawaii and do not show general evidence for strong admixture of bulk sea water with rain water. Significant individual sample variations frequently occur on a time and distance scale shorter than the sampling intervals; no conclusive pattern of radial dependence is apparent. Unlike rains over Hawaii Island but similar to aerosols collected over the open Pacific, hurricane Br/Cl is frequently much less than the sea water ratio $Br/Cl = 0.0034$ and may be accounted for by oxidation and volatility loss of bromine from aerosol spray droplets. Mean values for 23 hurricane samples (excluding two samples with $Cl \sim 100$ $\mu g/ml$, $Br/Cl \sim 0.0034$, and $I/Br \sim 0.01$) are: 7 μg Cl/ml, 20 ng Br/ml, 3 ng I/ml, $Br/Cl = 0.0030$, and $I/Br = 0.14$, and $0.02 < I/Br < 1$, a range typical of rain water from other locations.

TABLE 1

COMPARISON OF HALOGEN CONTENTS OF RAIN WATER FROM HURRICANE FAITH 1966
AND FROM HAWAIIAN OROGRAPHIC SHOWERS*

(Figures Represent Numbers of Samples in Each Concentration Range)

Cl, $\mu\text{g/ml}$	Hurricane	Hawaii	Br, ng/ml	Hurricane	Hawaii	I, ng/ml	Hurricane	Hawaii
0.125-0.25	1	1						
0.25-0.5	7	9				<0.5	5	0
0.5-1	4	17				0.5-1	9	0
1-2	5	23	<2	1	0	1-2	9	9
2-4	5	16	2-4	7	2	2-4	8	34
4-8	4	13	4-8	7	28	4-8	3	32
8-16	6	6	8-16	8	35	8-16	0	10
16-32	1	0	16-32	5	14	>16	2	0
32-64	1	0	32-64	6	6			
64-128	2	0	>64	2	0			
Total	36	85		36	85		36	85

*R. A. Duce, J. W. Winchester, and T. Van Nahl, J. Geophys. Res. 70, 1775-1799 (1965).

TABLE 2

MODES OF HALOGEN CONCENTRATION DISTRIBUTIONS IN RAIN WATER
FROM HURRICANE FAITH 1966 AND FROM HAWAII

	Hurricane	Hawaii
Cl, $\mu\text{g}/\text{ml}$	2	1.5
Br, ng/ml	10	10
I, ng/ml	1.5	4