

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

Technical Progress Report No. 1

OCCURRENCE OF HALOGENS IN ATMOSPHERIC AEROSOLS AND PRECIPITATION

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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

March 1968

The significance of the halogen contents of atmospheric aerosols and precipitation is several-fold. Natural halogens are injected from the sea surface into the atmosphere mainly as droplets from breaking bubbles and are carried inland by air movement. Halogens may be added to the atmosphere artificially by industrial processes, such as the combustion of iodine-rich organic fuels and of organic chlorine and bromine compounds present in automotive ethyl fluid. Both inorganic and organic compounds of the halogens may exist in the atmosphere, and both may undergo chemical reactions leading to partition of the halogens between gaseous and particulate forms and to redistribution of matter among particles of different size. Halogenated aerosols may serve as condensation or freezing nuclei or otherwise be scavenged from the atmosphere by precipitation. Halogen gases may be corrosive oxidizing agents and contribute to air pollution effects.

The present research project is directed to further documentation of the occurrence of halogens in aerosols and precipitation, building on the previous work of Duce, Winchester, and others at M.I.T. Because of the educational goals of research of this kind at The University of Michigan, smaller problems have been defined which are of appropriate size for student research and which relate to the overall aims of the project. During the first 9 months of this project the following specific areas have been investigated:

- (1) The halogen contents of rain water from hurricane Faith 1966.
- (2) The halogen contents of surface waters from Lake Superior and tributary streams.
- (3) The halogen contents of aerosols from rural Michigan and from the Niagara Falls vicinity.

Since work was initiated in the summer of 1967, a substantial amount of time has been invested in adapting the halogen analysis procedure to the neutron activation facilities at the Phoenix Memorial Laboratory at The University of Michigan and in training students in the Department of Meteorology and Oceanography in the radiochemical procedures required. It is now possible to report some preliminary analytical results in the areas listed above.

## 1. 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 analyses of 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.

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

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

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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  $Cl \sim 100 \mu\text{g/ml}$ ,  $Br/Cl \sim 0.0034$ , and  $I/Br \sim 0.01$ ) are:  $7 \mu\text{g Cl/ml}$ ,  $20 \text{ ng Br/ml}$ ,  $3 \text{ ng I/ml}$ ,  $Br/Cl = 0.0030$ , and  $I/Br = 0.14$ , and  $0.02 < I/Br < 1$ , a range typical of rain water from other locations.

## 2. THE HALOGEN CONTENTS OF SURFACE WATERS AND PRECIPITATION IN THE LAKE SUPERIOR AND LAKE MICHIGAN BASINS

A problem of hydrological interest is the material balance between chloride in precipitation and runoff in a watershed. Analyses of Cl and several other common trace elements in Great Lakes water may be found in the literature, but Br and I have apparently not been investigated. All three elements are particularly important in studies of natural waters because, at least in inorganic reactions, they remain in solution. Metallic elements, on the other hand, may be efficiently bound to sediments and potentially tell less about the history of a water mass because of their short residence time in it.

In an unpolluted lake the principal input of Cl, Br, and I is from the atmosphere. Since the halogens are not believed to be appreciably volatile from a large body of fresh water, evaporation will serve only to concentrate the solution. A steady state should be reached where the rate of halogen input from rainfall in the lake basin equals the rate of halogen removal by outflow in rivers draining the lake. If we had an accurate estimate of the average concentration of halogens in the rainfall input as well as an average value for the lake water composition, we could estimate the extent of evaporation relative to outflow. This result could be of considerable interest in hydrology. A. M. Beeton (*Limnol. & Oceanog.* 10, 240-254, 1965) has shown that Lake Superior, alone among the Great Lakes, has not shown significant increases in Cl and some other dissolved ions in the last 50 years. If this can be taken as an indication that this lake is still relatively pollution-free, a satisfactory material balance of this kind should be possible for Lake Superior. Furthermore, the analytical data for the three elements Cl, Br, and I should conform to the same model. Juang and Johnson (*J. Geophys. Res.* 72, 5641-5647, 1967) were not able to make a satisfactory balance of chloride in a New England watershed, but pollution sources were difficult to evaluate.

The 1965 study by Beeton (*op. cit.*), based on a review of previously published analytical data on waters of the Great Lakes, still seems to be the most thorough published study of the rise in dissolved salts in the Great Lakes during recent decades. Whether the rise is due to direct pollution input, to runoff of pollutants from land areas, or to increased erosion of natural soil components by the activities of man cannot be said unambiguously on the basis of this study. Furthermore, the extent of pollution by other substances, e.g., I and Br, which were not determined by the older analysis is unknown, for no samples of pre-1920 lake water are known to be available for analysis today.

A study of I and Br may be a first step in reconstructing the past composition of polluted Great Lakes' waters. The Lake Superior study can serve as a test of the relation between rainfall input and river outflow of the halogens

in an unpolluted lake, and it may be a model for the natural state of any other of the Great Lakes. Since the halogens may be derived from different pollution sources with different halogen ratios, a polluted Great Lake may be experiencing different rates of increase for the different halogen elements, and its present halogen ratios, as well as halogen concentrations, may be altered by the pollution additions. By a comparison of halogen ratios and compositions of polluted and unpolluted lakes, a model for pollution inputs from different sources may be constructed.

The halogen elements are important in this study because they are relatively conservative properties of the water. Since they are closely related to each other in their chemical properties, variations in their abundance ratios may be more easily interpreted than variations in the abundances of quite unrelated chemical elements. Moreover, iodine and bromine may have additional significance.

In the oceans I is apparently concentrated strongly by marine organisms and ultimately by the sediments, in contrast to Br and Cl which remain in solution. Atmospheric I originates from sea spray and is strongly enriched in the atmosphere relative to other salts. The I content of rain water falling in the Great Lakes Basin is thus high relative to Cl, but its absolute concentration is 10 times less than in sea water. Without additional inputs the concentration of I in lake water cannot be greater than this, and if there are processes of concentration and removal of I in the lakes, the dissolved I available for organisms may be less. Weathering of glacial materials in the Midwest does not supply much iodine in the runoff, as may weathering of marine sediments, and dietary iodine deficiency is known. Marine fish, such as the alewife, which have adapted themselves to living in the fresh waters of the Great Lakes apparently suffer chronic thyroid malfunction owing to the low iodine concentration (Oceanology International, July-August 1967). Nothing is known of the effect of pollution-induced growth of phytoplankton in diminishing the availability of iodine for other organisms.

A major source of pollution bromine is the burning of automotive ethyl fluid (Winchester et al., *Atm. Environ.* 1, 105-119, 1967). The physiological importance of this to life in the lakes is not known, although increasing the ratio Br/Cl in man's diet produces a sedative effect. Both inorganic and organic compounds of Br may be present. The rate of natural Br addition from rainfall can be estimated by assuming a mean concentration of 10 ng Br/cm<sup>3</sup>, a value consistent with our current analytical work. For Lake Michigan, which discharges about 1% of its volume per year and loses perhaps an equal amount of water through evaporation, we may assume the annual rainfall input is 2% of the lake volume, i.e., 100 km<sup>3</sup>/yr, leading to a Br input of some 1000 tons/yr. A pollution input of 1000 tons Br/yr could also result from the burning of 3 million gallons of leaded gasoline per day, a not unreasonable number for the Lake Michigan basin. Thus the principal addition of Br to some of the Great Lakes at the present time could be from pollution sources.



A beginning has been made on a study of halogens in the Lake Superior and Lake Michigan basins. Before funding on the present AEC contract became available, The University of Michigan made a \$3000 grant from the Phoenix Memorial Fund to start sampling and analyses, and during the summer of 1967 about 50 surface water samples were taken from the Lake Superior shore and adjacent streams and lakes. Analyses of these and 12 additional deep water samples of Lake Michigan are being carried out now, although the data are not extensive enough for a report at this time. Rainfall or snowfall sampling has not yet begun in a systematic way, but this is a necessary part of the program. We are planning to coordinate some of this effort with Dr. E. W. Marshall of the U. S. Lake Survey in Detroit and take advantage of his field operation on Lake Superior.

### 3. THE HALOGEN CONTENTS OF AEROSOLS FROM RURAL MICHIGAN AND FROM THE NIAGARA FALLS VICINITY

Basic to understanding the chemical composition of aerosols is the distinction between heterogeneous gas-particle reactions in the atmosphere and chemical processes during aerosol formation, such as at the water surface during bubble bursting. Iodine and bromine are elements which may be involved in both types of processes. Iodine is enriched generally in the atmosphere relative to sea water, and the mechanism may be a combination of volatilization and of injection of iodine-rich organic matter. A number of investigators have pointed to the fact that a breaking air bubble at a water surface injects an aerosol droplet into the atmosphere which is enriched in surface-active organic matter that collects at the air-water interface before bubble rupture.

As part of his Ph.D. thesis research, Mr. Ronald Loucks is undertaking a study of environmental factors affecting the halogen composition of aerosols. The approach is primarily sampling and chemical analysis, and a combination of laboratory experimentation and environmental sampling is planned. Atmospheric sampling depends heavily on our 6-stage Scientific Advances Co. cascade impactor which collects particles with diameters greater than 0.5 micron and sorts them into groups with diameters differing by a factor of 2. We believe that the particle size distribution information will be extremely important in making it possible to interpret analyses of environmental samples in terms of chemical reaction mechanisms. The study has begun with sampling of the atmosphere in three locations.

First, a series of cascade impactor samples is being taken in a rural location near Ann Arbor. These results will indicate the particle size distribution of halogens far from local sources, such as the oceans, fresh water aerosols, and pollution sources. Preliminary data show distinct particle size distributions for the halogens, but the maximum abundance may be on either intermediate or small particles. We are now trying to correlate this with humidity, wind direction, and other factors. In all future analyses lead will also be determined electrochemically as an indicator of pollution bromine and chlorine.

Second, an experimental test of iodine vapor uptake by aerosols is being conducted. Schaeffer (Science, December 1966) has drawn attention to the possibility that iodine vapor may activate pollution lead aerosols causing them to become freezing nuclei, but a direct chemical study of iodine and lead interaction in the atmosphere has not yet been made. Our initial plan is to draw urban air through the cascade impactor and analyze the fractions for halogens and lead. A series of comparisons are being made between air containing iodine vapor emanating from a nearby generator and air not containing added iodine. Since natural iodine is hundreds of times rarer than lead in

particles from urban air, efficient uptake of the added iodine by lead should be visible above background particulate iodine. If a positive effect is seen, additional experiments may be designed to learn more about the particle-vapor interaction involved.

Third, aerosol droplets from the Niagara Falls area have been sampled in an exploratory trip in October 1967, and additional sampling is planned during the warmer weather of 1968. Pollution-rich water from Lake Erie contains surface active material, and preliminary data indicate this to be iodine-rich. If these surfactants become airborne during the Falls action and bubble breaking, iodine may become enriched in the atmosphere by this process. By a judicious choice of sampling locations and times we may be able to determine if this mechanism of iodine enrichment in the atmosphere is operative. We will take advantage of the fact that the Falls are "turned off" at night by diverting substantial amounts of water through the hydroelectric plant, thus reducing the intensity of mist over the Falls. A correlation between iodine and organic matter in aerosols may provide a useful indicator for air pollution derived from water pollution sources.

Mr. Loucks' study will include a search for additional trace elements in atmospheric samples which can be determined by neutron activation and gamma-ray spectroscopy using a Ge(Li) detector. We also have the capability for high sensitivity determination of lead and other metals by anodic stripping voltammetry and for atomic absorption spectrophotometry and gas chromatography. Dr. Wayne Matson is offering supervision of critical importance in this work.

#### 4. ANALYTICAL NOTES

During the first several months of work under the present AEC contract, our halogen analysis procedure (Duce and Winchester, *Radiochim. Acta* 4, 100-104, 1965) has been adapted to The University of Michigan nuclear reactor. The pool design is different from that of the M.I.T. reactor, and the neutron flux distribution within the irradiation capsule has been found to exhibit a radial nonuniformity. Axially, however, the neutron flux is uniform to a few percent or better, and routinely two samples and a standard are now irradiated in an axial configuration. The neutron flux is a maximum of  $4 \times 10^{12}$  n/cm<sup>2</sup> sec in the pneumatic tube facility which is 2 to 10 times less than the M.I.T. reactor flux during the time halogen analyses were carried out there. Although this flux is quite adequate for the present investigation, and analytical blanks are still the main limitation on sensitivity in many of our samples, it is nevertheless important to use the time immediately following irradiation for counting the rather low sample activities, not neutron flux monitors. Accordingly, we now use an aqueous solution of chromate as a flux monitor, and we count its 27.8 day gamma of 0.32 MeV a few days after the day of irradiations using a well-type scintillation counter and a single-channel analyzer.

In carrying out halogen analyses it is necessary for a team of about four people to work together for maximum efficiency. Accordingly our group has set aside a full day, usually Saturday each week, for 10 irradiations of samples and standards giving analyses of 16 samples for the three halogens. We have used one or two undergraduate student technicians profitably as part of the team. Data plotting, calculations, and maintenance of supplies in the analytical laboratory are done at odd times during the week. Previous experience indicates that about two man-hours of time overall are required per sample analyzed, but we are still slower than that, partly because we do not yet use an automatic counter and because we have not yet computerized our calculations. During the summer of 1968 we expect both of these innovations to be made.

The halogen analysis program coordinates closely with other environmental chemical studies in our laboratory. Under NIH grant AP 00585-01, "Composition of Lead Halide Pollution Aerosols," we have begun a study of the relative Pb, Br, and Cl composition of aerosols formed by ethyl fluid combustion. Dr. Wayne Matson, who joined our group as a research associate in January 1968, has set up electrochemical apparatus for high sensitivity determination of lead by anodic stripping voltammetry with the capability of determining several other trace metals as well, and we plan to acquire a gas chromatograph under the same grant for determination of organic materials related to the inorganic. Fortunately, Dr. Matson wishes to divide his time between the lead halide study supported by the NIH grant and the general halogen investigation supported by the AEC; we consider his involvement in supervision of the chemical analysis

and sampling of the AEC sponsored work of our students in meteorology and oceanography vitally important for its success.

Under NSF Grant GA-811, "Laboratory Equipment for Air and Water Chemistry," we have purchased components for a first rate nuclear measurements laboratory for activation analysis. The system consists of a 4096 Nuclear Data Model 2200 multichannel analyzer, a Nuclear-Chicago automatic sample changer with interchangeable beta proportional and NaI(Tl) detectors, and a coupling of the two units for automatic gamma-ray spectrum recording. Readout of the analyzer contents will be made by computer compatible magnetic tape (partly acquired by AEC funds), and the sample changer also has Teletype readout with computer compatible punched paper tape. For tests of high resolution gamma spectroscopy in activation analysis we have purchased a small 2 cm<sup>3</sup> Ge(Li) detector; if this proves useful we hope to acquire a larger detector with higher sensitivity.

It is important in our program that we are building a laboratory with several analytical capabilities. Besides the nuclear techniques we plan gas chromatographic studies of organic materials, electrochemical studies of trace metals, and determination of trace elements using atomic absorption spectrophotometry. Finally, research is beginning in our laboratory on the measurement of natural radioactivity by a study of C-14 in urban CO<sub>2</sub> using sampling and benzene synthesis equipment acquired through our Air Pollution Traineeship program and a liquid scintillation counter at the Phoenix Memorial Laboratory.

5. RELATION TO OTHER AEC-SPONSORED RESEARCH IN THE  
DEPARTMENT OF METEOROLOGY AND OCEANOGRAPHY

Under sponsorship of Contract AT(11-1)-1407 "Rain Scavenging Studies," Prof. A. Nelson Dingle and Prof. Winchester have collaborated in developing a technique for using indium in particulate tracer material applied to studies of convective storms. Professor Dingle directed the meteorological aspects of the work while Prof. Winchester directed the chemical and radiochemical aspects, and most of the experimental work was performed by Dr. Donald F. Gatz and three student technicians. The experiment consisted of the injection of fine particles of  $\text{InCl}_3$  from flares on an aircraft flying under convective storm clouds in Oklahoma during May 1967. Rain was then collected at ground level for indium analysis. Neutron activation analysis was employed for detecting the indium at a sensitivity much better than the few nanograms per liter of natural background indium found in untagged rains. Significant signals of indium due to the injected tracer were detected in the pilot experiment, and a final report on these results is now being prepared. A preliminary report was given orally at the 48th Annual Meeting of the American Meteorological Society, San Francisco, January 29, 1968. The following two abstracts were published in the Bulletin of the American Meteorological Society, 48, No. 11, 835, 1967:

"Detection of indium as an atmospheric tracer by neutron activation,"  
by Donald F. Gatz and John W. Winchester.

"A pilot experiment using indium as tracer in a convective storm," by  
A. Nelson Dingle.

6. PERSONNEL DURING THE FIRST CONTRACT YEAR (1 JUNE 1967-31 MAY 1968)

(1) Principal investigator, John W. Winchester, associate professor, full-time 2 months summer 1967, quarter time 9 months academic year 1967-68.

(2) Wayne R. Matson, post-doctoral research associate, half-time 4 months, February-May 1968.

(3) Ronald H. Loucks, graduate student, full-time 2 months summer 1967, half-time 10 months academic year 1967-68. Note: Mr. Loucks is an employee of the Bedford Institute of Oceanography, Nova Scotia, Canada, on leave of absence for graduate study. He receives partial salary support from the B.I.O. and his work on the project is without salary cost to the AEC.

(4) Douglas R. Sendelbach, graduate student research assistant, half-time 6 months September 1967-February 1968.

(5) Mary Ann Tiffany, graduate student technical assistant, half-time 5 months January-May 1968.

(6) Lawrence Timte, undergraduate technical assistant, quarter-time 5 months January-May 1968.

(7) Richard Heaton, undergraduate technical assistant, quarter-time 5 months January-May 1968.

(8) Nelson Frew, undergraduate technical assistant, quarter-time 1 month November-December 1967.

## 7. PUBLICATIONS

- (1) "Detection of indium as an atmospheric tracer by neutron activation," Donald F. Gatz and John W. Winchester, Bull. Am. Meteorol. Soc. 48, 835, 1967 (abstract).
- (2) "Sea salt halogens as natural atmospheric tracers in hurricane studies," John W. Winchester, Douglas R. Sendelbach, and H. Göte Östlund, Trans. Am. Geophys. Un., in press, 1968 (abstract).



