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THE HALOGEN COMPOSITION OF AEROSOL PARTICLES

OVER LAKE MICHIGAN

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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

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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 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

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

^a For locations see Figure 1 and text.

Table 2. Iodine concentrations.

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

observed compare favorably with those observed in Hawaii and in polluted as well as unpolluted 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 direc-

Table 3. Bromine concentrations.

Run	Total concentration ng/m ³	Percent of total with radius <0.25 μ m	Percent of total with radius <0.5 μ m
1	24 $\pm$ 3	91	94
2	11 $\pm$ 1	50	75
3	1380 $\pm$ 90	61	77
4	407 $\pm$ 20	29	64
5	22 $\pm$ 2	50	89
6	13 $\pm$ 2	80	80
7	27 $\pm$ 2	56	78
8	42 $\pm$ 2	45	68
9	31 $\pm$ 2	46	79
10	22 $\pm$ 1	51	74
Mean of runs 3 and 4:	900		
Mean of the other runs:	24 $\pm$ 4		
Fairbanks background:	35 $\pm$ 3 ^a		
Fairbanks pollution:	500 $\pm$ 50 ^a		
Hawaii background:	>11 ^a		

^a See notes to Table 2.

tion, 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.

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

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:		$>3.6^a$		

^aSee notes to Table 2.

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.

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.

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Addendum:

In Table #4, the percentage of total chlorine with radius less than 0.25 microns is probably too low in all runs except #3 and #4 . Experiments we have carried out subsequent to the preparation of this paper indicate that in the very smallest particles collected by the impactor back-filter the chlorine concentration may be substantial.

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