The Global Distribution of Iodine, Bromine, and Chlorine in Marine Aerosols

John W. Winchester and Robert A. Duce*

Massachusetts Institue of Technology, Dept. of Geology
and Geophysics, Cambridge, Mass. 02139

Summary. Atmospheric samples have been analyzed for iodine, bromine, and chlorine by neutron activation analysis. Aerosols of marine origin, derived from sea spray, are found to contain the halogens in relative proportions different from sea water, and data from Hawaii and winter northern Alaska indicate fractionation of the elements both during transfer across the sea-air interface and by chemical reactions in the atmosphere. The ratio Br/Cl is usually severalfold greater in aerosols over land than in sea water (Br/Cl = 0.0034), but over open sea water it is less. In general, the ratio I/Br exhibits a greater degree of constancy (values cluster in the region I/Br $\sim$ 0.1—0.2) than does either I/Cl or Br/Cl, suggesting a long residence time and a coherence of I and Br in their movement as particulate material in the atmosphere. However, a singularly effective sea-air transfer mechanism for iodine is indicated by its generally high atmospheric concentration compared to sea water (I/Br = 0.001). Bromine of pollution origin and associated with lead has been observed in aerosols from Cambridge, Massachusetts. Chlorine and iodine concentrations are similar to the Hawaii values and provide a basis for resolving excess pollution bromine from the natural marine component. The ratio (excess Br)/Pb in aerosols appears to be correlated directly with the haziness of the air.

Introduction

The sea is the ultimate source of the salts in the air above the sea, but the sea-air transfer process is far from simple. One may think that aerosol particles derived from sea spray should be the same as evaporated sea water in their chemical composition, but this simple view is evidently not the case. It has often been assumed that observed differences in composition between "marine" aerosols and sea water are in fact evidence of mixing of aerosols of two sources, e. g. the sea and the land, but this cannot be the complete explanation. It is becoming increasingly apparent that sea spray droplets, which enter the air from bubbles breaking at the sea surface, may be chemically fractionated from sea water by the bubble breaking process. In addition, small particles of liquid or solid in the air present a large surface area compared to their volume for heterogeneous reactions involving the gas phase. For these reasons, the composition of marine aerosols need not be the same as sea water, and the aerosol composition may also vary in time and space.

The physical and chemical properties of aerosols have been completely reviewed by Junge [4]. Particles smaller than about 20 microns radius remain in a more or less stable suspension in air, their settling times in still air being so slow that normal atmospheric eddy currents are adequate to keep them aloft almost indefinitely. Particles smaller than about 0.1 micron radius are found to coagulate rapidly up to that size but not larger, and empirically the total mass of particulate material in the atmosphere per cubic meter of air is about the same in the range $0.1 < r < 1.0\,\mu$ ("large" particles) as it is in the range $1.0 < r < 10\,\mu$

("giant" particles). Particles in the "giant" range are more effective than "large" particles in raindrop nucleation, causing "giant" particles to be removed by precipitation more quickly. Two major sources for atmospheric aerosols are recognized: Sea spray aerosols are predominantly "giant" size, but the smaller of these may travel world-wide from their point of origin. Continental aerosols are predominantly "large" size or smaller and presumably live a long time and travel far before removal. Their composition is mainly $(NH_4)_2SO_4$, formed from gaseous reactions involving NH_3 and SO_2 or H_2S, but silicate or carbonate dust is also present.

The chemical properties of aerosol particles are closely related to a number of atmospheric phenomena, including the nucleation of raindrops and snowflakes, the removal of fallout radioactivity, and the behavior of air pollutants in cities. We have approached the study of these properties by measuring the closely related group of elements iodine, bromine, and chlorine in an effort to understand the variations in relative abundances in terms of more or less specific chemical processes. Our analytical method of choice has been neutron activation analysis, a method offering sensitivity sufficient to measure accurately iodine and bromine in the nanogram amounts of our typical samples. Details of the method employed are given by Duce and Winchester [2, 3a].

In a series of papers (I, [1]; II, [3a]; III, [5]; IV, [3b]; V, [7]) neutron activation analyses of atmospheric samples for iodine, bromine, and chlorine have been reported, and Winchester and Duce [paper V] have reviewed some of it. Sampling was carried out in the widely separated and climatically different localities of the island of Hawaii, Point Barrow in Alaska during January, and the city of Cambridge in Massachusetts, and additional samples from Antarctica and central Alaska have been studied. Rain and snow, aerosols gathered by different techniques, and gaseous halogens have been collected wherever possible. In this paper the data on aerosols in unpolluted and in polluted air from these areas will be discussed in order to show how comparative halogen analysis can help define some of the processes affecting aerosols in the atmosphere. Essential to this approach is the ability to measure accurately trace elements which are related chemically to more abundant elements. Neutron activation analysis makes this possible.

Unpolluted Air

The concentration of stably suspended particulate matter in air is extremely small, of the order of micrograms per cubic meter of air, and the trace elements iodine and bromine in that matter are rarer still. Consequently, precautions must be taken to

avoid local pollution of the air by these elements if the natural aerosol composition is to be studied. We chose the island of Hawaii, lying in the trade winds which blow persistently from the northeast, as the most likely of having aerosols of undisputed marine origin, and we sampled both over the land and over the sea to the east. Then we chose Point Barrow at the northern tip of Alaska as a second unpolluted area which, during January, lies hundreds of kilometers from appreciable open sea water, has little sunlight and a low temperature, and contrasts markedly from Hawaii in expected local atmospheric chemical reactions. In Hawaii, wave action and bubble breaking in the immediate vicinity may be the source of most of the sea salt aerosols observed, but along the northern Alaska coast during winter we expect only very low aerosol concentrations to result from local sources owing to the frozen condition of the sea surface. Mixing of air from more temperate latitudes is a more likely source of appreciable aerosol concentrations in winter arctic air.

In this work three methods were employed for collecting aerosol particles:

At ground-based stations in temperate air a cascade impactor was used. Air was passed by means of a pump through a train of four stages, each stage consisting of a small orifice and a glass collection plate. The largest particles strike the plate and stick, but the smaller sizes are aerodynamically deflected and pass to the next stage. Succeeding stages have smaller orifices, and a size fractionation is obtained.

Aircraft collection was carried out using a light plane and a wing-mounted impactor consisting of metal strips of different widths. Because of air flow patterns, the smaller strips gather particles down to a smaller radius than the larger strips do, giving a combined sample of large and small particles on the small strips.

Collection of aerosols from the cold winter air of Alaska was carried out mostly using Millipore filters of 1.0 micron diameter Type EA.

Some aircraft collection was carried out using a strip impactor, but the sticking probability of particles may have been less than quantitative owing to the low temperatures. All impactor samples were rinsed from the collectors with water, and analysis of the solutions and of the whole filters was carried out by pile neutron activation analysis. The radiochemical steps were straightforward and included irradiation of the sample and a comparator for 20 minutes in a neutron flux of 10^{13} neutrons/cm²sec, solvent extraction with CCl_4 to separate iodine and bromine, and beta counting of 25 min ^{128}I, 18 min $+4.5$ hr $^{80+80m}$Br, and 37 min ^{38}Cl in silver halide precipitated sources.

In the following we will pay particular attention to the total concentrations, per cubic meter of air, of the three halogens and to the relative concentrations of Br and Cl. Some of the other comparisons which could be made have already been pointed out (see especially paper V), and detailed sampling conditions have been described in papers I through IV.

Table 1 summarizes ground-based sampling of air on the island of Hawaii 1 km or more removed from the sea shore. Cl and Br occur mostly in particles with radius greater than 1 micron, and there is a suggestion of decreasing concentration with increasing altitude.

I does not show the decrease with altitude nor does it appear to be so consistently associated with the larger particles. From the data we calculate the ratio Br/Cl to average $11 \cdot 10^{-3}$ and to be up to 10 times the sea water value of $3.4 \cdot 10^{-3}$ in individual cases.

Table 1. *Hawaii aerosols over land by cascade impactor*

Altitude Meters	Impactor Stage*	Cl** µg/m³STP	Br** ng/m³STP	I** ng/m³STP	Br/Cl ×10³
0	BC	3.06	16.9	10.8	5.5
	D	0.74	5.1	13.8	6.9
		3.80	22.0	24.6	5.8
0	ABC	2.32	22.3	1.80	9.6
	D	0.64	2.2	0.09	3.4
		2.96	24.5	1.89	8.2
600	ABC	2.93	9.73	0.79	3.3
	D	1.16	2.25	1.02	1.9
		4.09	12.0	1.81	2.9
600	ABC	0.58	15.6	0.93	27.
	D	0.23	7.3	0.39	31.
		0.81	22.9	1.32	28.
1500	ABC	0.86	9.4	1.84	10.9
	D	0.36	4.0	0.46	11.2
		1.22	13.4	2.30	11.0
3400	ABC	0.55	5.61	1.66	10.2
	D	0.034	1.24	0.66	36.
		0.58	6.85	2.32	12.

* Stages A, B, and C combined collect particles of radius $\gtrsim 1\ \mu$. Stage D collects particles in the radius interval $0.5 \lesssim r \lesssim 1\ \mu$.
** Standard deviation of each measurement $\sim 7\%$.

Table 2. *Hawaii aerosols over the sea by aircraft impactor*

Date	Cl** µg/m³STP	Br** ng/m³STP	I** ng/m³STP	Br/Cl ×10³
May 1962 *				
19	1.5	3.7	0.40	2.5
21	8.8	18.	3.4	2.0
22	3.7	8.7	1.5	2.3
24	2.8	8.4	1.4	3.0
26	1.8	5.1	0.68	2.9
27	5.1	6.5	1.0	1.3
28	1.8	4.9	0.74	2.7
29	3.8	1.1	0.73	2.8
June 1963 *				
12 L	2.6	0.80	0.90	0.31
M	2.4	1.41	0.52	0.59
S	9.5	3.13	4.0	0.33
12 L	0.64	0.25	0.51	0.39
M	0.81	0.35	0.48	0.43
S	2.15	1.44	0.79	0.67
12 L	3.3	3.8	1.4	1.2
M	3.6	3.2	1.2	0.89
S	12.9	10.0	6.5	0.77
13 L	0.82	0.83	0.59	1.0
M	0.94	3.6	1.2	3.8
S	3.02	5.5	3.6	1.8

* May 1962 collection used 0.1 cm Ag strips and collected particles with radius $\gtrsim 1\ \mu$.
June 1963 collection used stainless steel strips L, 0.16 cm, $r \gtrsim 1\ \mu$; M, 0.051 cm, $r \gtrsim 0.5\ \mu$; S, 0.010 cm, $r \gtrsim 0.2\ \mu$.
** Standard deviation $\sim 10\%$.

Table 2 presents data for aerosols collected by an aircraft flying about 300 meters above open water (the second June 12, 1963, sample was at 1500 meters). The concentrations of Cl and I resemble those of Table 1, but Br is lower, particularly in the 1963 suite. The ratio Br/Cl is consistently *less* than the sea water value of $3.4 \cdot 10^{-3}$, and in the 1963 suite it is as low as 10% of that value. We believe the different aerosol collection techniques used for the samples in Tables 1 and 2 are not the cause of the different Br/Cl ratios found.

Table 3 presents concentrations observed using a groundbased Millipore filter collector during January 1965 at Point Barrow, Alaska. The generally good agreement between upper and lower collector values indicates little local interference due to blowing snow, and the aerosols must be more or less "permanent". Br and I concentrations are remarkably similar to

Table 3. *Barrow, Alaska, winter aerosols by filter collector*

Date, 1965 January*	Cl** μg/m³STP	Br** ng/m³STP	I** ng/m³STP	Br/Cl ×10³
21	< 0.2	8.3	1.4	> 40.
21	< 0.1	4.6	1.3	> 40.
,,	0.66	13.	2.0	20. ± 4.
21—22	0.28	3.3	0.40	12. ± 2.
22	3.6	7.9	0.79	2.2 ± 0.3
,,	3.0	5.2	0.85	1.7 ± 0.2
23—24	0.49	1.6	0.42	3.2 ± 0.4
23—24	0.36	1.6	0.48	4.4 ± 0.7
24	0.28	7.0	0.33	25. ± 4.
,,	< 0.07	11.1	9.4	> 150.
24—25	0.49	4.0	0.69	8.2 ± 0.8
,,	0.41	3.6	0.59	8.8 ± 1.1
25	0.54	10.1	0.86	19. ± 2.
,,	0.59	9.6	0.91	16. ± 2.
26	<0.07	1.4	0.97	> 15.
,,	< 0.08	1.4	1.25	> 12.
26—27	< 0.02	1.8	0.53	> 90.
,,	< 0.02	2.0	0.47	> 100.
27—28	0.077	2.6	0.42	34. ± 7.
,,	< 0.03	1.1	0.30	> 30.
28—29	0.21	30.	7.8	140. ± 17.
,,	0.77	10.8	0.89	14. ± 2.

* Most samples were taken in pairs with collector heights 5 m and 15 m above the snow surface. The ditto mark indicates the upper member of each pair.
** Standard deviation of each measurement is usually 5—15 %.

Table 4. *Barrow, Alaska, winter aerosols by aircraft impactor*

Sample No.*	Cl** μg/m³STP	Br ng/m³STP	Br/Cl ×10³
I L	0.056	< 0.4	< 6
S	0.049	< 0.2	< 3
II L	0.116	0.8 ± 0.4	7.0 ± 3.5
S	0.113	1.9 ± 0.2	17. ± 2
III L	0.187	0.9 ± 0.3	4.7 ± 1.5
S	0.140	1.6 ± 0.1	11.5 ± 0.7
IV L	0.216	< 0.3	< 1.3
S	0.30	0.6 ± 0.1	2.0 ± 0.3

* Approximate particle radii collected by L-strip (0.16 cm), $r \gtrsim 1$ μ; by S-strip (0.051 cm), $r \gtrsim 0.5$ μ. Flights on 28—29 January 1965.
** Standard deviation ~6%.

those found in Hawaii, but the Cl concentrations are usually lower, particularly on January 26—28. This was a period of extreme calm and one's breath did not condense in the air but instead on clothing, presumably because of a deficiency of nucleating aerosols. The ratio Br/Cl is variable and much greater than in sea water, but the ratio I/Br is usually not far from 0.1—0.2.

Table 4 presents the results of four flights using an aircraft impactor. The absolute concentrations should be interpreted cautiously because of the uncertain sticking probability at below-freezing temperatures, but the Br/Cl ratio is of interest. In the three flights where large and small-plus-large particles may be compared, appreciable Br, but not appreciable Cl, is found in the small size range. It would be of interest to sample this air with a cascade impactor and obtain small particles uncomplicated by larger ones, but the data show an unambiguous association of Br with a

smaller size range of particles than Cl. Because of an analytical blank and small sample size, I could not be determined.

The marine aerosols from unpolluted air indicate behavior more complicated than simple evaporation of sea water droplets. First of all, iodine is strongly enriched in all samples compared to sea water where I/Cl $\sim 3 \cdot 10^{-6}$ and I/Br $\sim 10^{-3}$. The bromine data from Hawaii indicate that sea spray, once in the air, suffers a selective loss of Br relative to Cl, perhaps by photochemical oxidation to Br_2. Then, as the particles are carried inland by the trade winds, we may suggest that interchange between the gaseous and condensed particulate phase and some removal of particles by fallout leads to a net increase in Br/Cl with time, altitude, and distance from open water. In the long run, I and Br tend to become associated with each other and migrate further than Cl. In the winter air above Barrow, Alaska, we must presume the Br and I are present in long residence time aerosols whose origin is in open water hundreds of kilometers to the south. Here the different behavior of these elements and Cl is pronounced, including the association of Br (and presumably I) with the small particles easily kept aloft for extended periods.

Polluted Air

Chlorine, bromine, and iodine may all be important air pollutants under certain circumstances. Inorganic and organic chlorine compounds may be added to the air from industrial sources. Iodine has been known to emanate from seaweed processing plants. Bromine and chlorine are emitted as lead halide particles from vehicles burning leaded gasoline. In Cambridge, Massachusetts, we expect the latter pollution to be the most easily detected, and of that the bromine should be the most prominent owing to the proximity to the sea and large natural concentrations of chlorine.

Because natural aerosols show a history of chemical reactions and behavior dependent on particle size, we may ask if the same is true of pollution aerosols. In our investigation, we have directed our attention to lead bromide particles from motor fuel exhaust. In ethyl fluid the weight ratio Br/Pb = 0.4, and, if we can resolve the atmospheric bromine into pollution and natural marine components, we may test the coherence of pollution bromine with lead in atmospheric particles.

Samples of Cambridge air were collected using a cascade impactor similar to that used in Hawaii, and analysis was carried out by neutron activation for the halogens and electrochemically for lead using anodic stripping voltammetry [6]. Two sampling locations were chosen, the roof of the 90 meter high Green Center for Earth Sciences, on the M. I. T. campus 200 meters from the street, and the curb along Memorial Drive 12 meters from traffic. The sampling, during November 1964, included both clear and hazy air conditions.

Table 5 summarizes the concentrations of halogens and lead found in Cambridge aerosols. The Cl values resemble those in Hawaii, Table 1, both in total amount and in the preference for large particle sizes. The I values likewise are not very different from those of Hawaii, including the lack of the clear-cut preference

Table 5. *Cambridge, Mass., aerosols by cascade impactor*

Location, Date, 1964	Impactor Stage*	Cl** μg/m³ STP	Br** ng/m³ STP	I** ng/m³ STP	Pb** μg/m³ STP
Roof	ABC	1.87	53.	2.2	
Oct. 31, AM	D	0.06	17.	2.8	
		1.93	70.	5.0	
Roof	ABC	0.52	44.	2.8	0.31
Nov. 3, PM	D	3.0	40.	3.0	0.91
		3.5	84.	5.8	1.22
Roof	ABC	3.2	46.	0.4	0.24
Nov. 4, PM	D	1.1	60.	1.4	0.17
		4.3	106.	1.8	0.41
Roof	ABC	0.56	12.5	2.0	0.05
Nov. 6, PM	D	0.48	9.5	1.8	0.96
		1.04	22.	3.8	1.01
Roof	ABC	5.5	46.	3.0	0.24
Nov. 11, AM	D	0.2	16.	2.6	0.07
		5.7	62.	5.6	1.31
Curb	ABC	1.7	500.	3.0	0.66
Nov. 12, AM	D	1.3	295.	6.2	0.77
		3.0	795.	9.2	1.43
Curb	ABC	1.7	370.	1.3	1.01
Nov. 12, PM	D	1.2	305.	5.8	1.22
		2.9	675.	7.1	2.23
Curb	ABC	0.7	62.	1.1	0.27
Nov. 13, AM	D	0.7	42.	2.0	0.16
		1.4	104.	3.1	0.43
Curb	ABC	0.51	22.	0.8	0.06
Nov. 14, AM	D	0.29	14.	1.3	0.02
		0.80	36.	2.1	0.08
Curb	ABC	1.8	18.	0.5	0.09
Nov. 14, PM	D	0.09	14.	2.5	0.03
		1.9	32.	3.0	0.12

* Stages A, B, and C combined collect particles of radius $r \gtrsim 1 \mu$. Stage D collects particles in the radius interval $0.3 \gtrsim r \gtrsim 1 \mu$.
** Standard deviation of each measurement usually 5—10% for Cl, Br, I and 0.02 μg/m³STP for Pb.

for large particle sizes exhibited by Cl. The Br values, however, are usually very much greater in Cambridge than in Hawaii. The lead concentrations, around 1 μg/m³, should imply some four hundred ng/m³ of Br in particulate form if motor fuel pollution is the cause.

A more precise measure of the correlation of the high Br values with Pb can be obtained in the following

Table 6. *Correlation between excess Br and Pb in Cambridge, Mass., aerosols*

Date, 1964	Location	Visibility, miles	Excess Br* ng/m³STP	Excess Br/Pb	Excess Br/Pb, weighted mean
Oct. 31, AM	Roof	≧15	54 ± 9		
Nov. 4, PM	Roof	≧15	6 ± 8	0.006 ± 0.008	
Nov. 14, AM	Curb	≧15	20 ± 9	0.25 ± 0.12	0.04
Nov. 14, PM	Curb	≧15	16 ± 8	0.13 ± 0.07	
Nov. 3, PM	Roof	10	68 ± 9	0.056 ± 0.007	
Nov. 4, PM	Roof	10	90 ± 9	0.22 ± 0.03	0.1
Nov. 11, AM	Roof	10	46 ± 9	0.15 ± 0.03	
Nov. 13, AM	Curb	3—5	88 ± 9	0.20 ± 0.02	0.2
Nov. 12, AM	Curb	¾—1¾	779 ± 30	0.54 ± 0.02	0.4
Nov. 12, PM	Curb	⅛—1¾	659 ± 26	0.30 ± 0.012	

* Assumed natural background of 16 ± 8 ngBr/m³STP has been subtracted from each total Br.

way: Noting that Cl and I values are similar in Cambridge and Hawaii, we assume the marine component of Br is also the same in the two locations. Let us take 16 ± 8 ng Br/m³STP as this natural concentration from Table 1. Subtracting this from the total Cambridge particulate Br, we obtain the "excess Br" values given in Table 6. Of the several meteorological observations made during sample collection, the visibility in miles as a measure of haze density is rather clearly correlated with the magnitude of excess Br, and Table 6 is arranged in order of decreasing visibility for clarity. The ratio (excess Br)/Pb is also given, and weighted means of this ratio are given for the samples taken at the same visibilities.

Interestingly, (excess Br)/Pb ranges from about the ethyl fluid value on the haziest day downward to a small fraction of that on clearest days. Although these few data are not sufficient to say with certainty why this is so, it is apparent that lead halide particles formed initially in the motor fuel exhaust suffer a loss of Br to the vapor phase (strictly speaking, to a form not collected by the cascade impactor, where the minimum particle radius collected is $\sim 0.2 \mu$). During hazy conditions this process seems to be inhibited.

Conclusions

Neutron activation analysis provides the sensitivity and analytical accuracy necessary to study the related group of elements I, Br, and Cl in aerosols. Sampling in Hawaii, northern Alaska during winter, and Cambridge, Massachusetts indicates that the composition of marine aerosols is different from sea water in the enrichment of I and the variability of Br/Cl. In the atmosphere I and Br are more closely associated with each other than is either with Cl, and they may circulate world-wide before removal from the atmosphere by fallout or precipitation. Knowledge of the natural halogen aerosol composition enables one to distinguish pollution Br and to test its correlation with Pb in city air. Apparently lead halide particles formed from ethyl fluid combustion lose bromine, although under hazy conditions the loss is inhibited.

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