Iodine, bromine, and chlorine in winter aerosols and snow from Barrow, Alaska

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ABSTRACT

Iodine, bromine, and chlorine have been determined in atmospheric aerosols and in snow collected in Barrow, Alaska, during January, 1965, by means of neutron activation analysis. Aerosols collected using both an aircraft collector by impaction and a ground-based 1.0 μ Type EA Millipore filter collector show concentrations of Cl to be much more variable than either Br or I, and I/Br points cluster at 0.1–0.2 gI/gBr for the filter samples. Cl varies from < 0.02 to 4 μg Cl/m^{3}STP in the filter samples, and the aircraft concentrations agree with those taken by filter on the same days. Filter Br is 1–30 ngBr/m^{3}STP and I is 0.3–10 ngI/m^{3}STP, and the ratios I/Cl and Br/Cl increase sharply with decreasing Cl.

Snow samples from the ground have Br/Cl somewhat greater than in sea water, although all halogen concentrations decrease with increasing distance from the sea up to 10 km. Assuming a mixture of undifferentiated sea salt and a more permanent atmospheric component, we estimate for the atmospheric component in the snows I/Br$\approx$0.2. Sea water, sea ice, and related samples were analyzed, and I/Cl $= 4 \times 10^{-6}$ gI/gCl is normal for sea water, although Br/Cl $= 3.8 \times 10^{-3}$ gBr/gCl stands a little high.

Introduction

Recent investigations of the chemistry of iodine and chlorine in temperate marine atmospheres (KOMABAYASI, 1962; DUCE *et al.*, 1963; MIYAKE & TSUNOGAI, 1963; DEAN, 1963; DUCE *et al.*, 1965) have shown an enrichment of I with respect to Cl of two to three orders of magnitude over sea water. The various mechanisms suggested to explain this enrichment, such as photochemical oxidation of I^- in the sea and the presence of an I-rich organic film on the sea surface, require open water and either wave action or ultraviolet light. If one or both of these mechanisms are locally responsible for the observed effect, samples collected during winter in a polar marine environment, where little or no open water or ultraviolet light exist, should have markedly different I/Cl ratios. Such a location would also allow further investigation of some of the surprising results found in Hawaii concerning the atmospheric chemistry of bromine, especially the low Br/Cl ratios in aerosol particles collected over the open ocean from an aircraft, since a possible explanation of the low ratios was photochemical oxidation of Br^-.

The Arctic Research Laboratory at Barrow, Alaska, is an ideal location for these investigations, and the last two weeks of January, 1965, were spent there collecting aerosol, snow, sea ice, and sea water samples. Barrow is located on the Chukchi Sea of the Arctic Ocean and is the northernmost point in Alaska, 71°20′ N, 156°40′ W (Figure 1). From mid-November to late January the sun is below the horizon and the mean temperature is about −30°C, putting severe restrictions on the chemical reactions which can occur in the air. In addition, Barrow is far from any large source of air pollution, being separated from the populated part of Alaska by the Brooks Range, and the very persistent winds from the east (5–6 m/sec average) make it quite easy to select sampling locations that avoid the possibility of slight contamination from the ARL camp or the

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TABLE 1. *Chlorine, iodine, and sodium content of polar samples.*

Author	Location	Sample type	Concentrations Cl μg/ml	Na μg/ml	I ng/ml
Gorham (1958)	Nordaustlandet, Svalbard	Fresh snow	< 0.5	< 0.1	—
		Firn, 5 m deep	< 0.5	0.2	—
		1–14 m deep in crevasse	Av. 3.4	2.1	—
Junge (1960)	Greenland, 330 km from coast, 2300 m elev.	Ice cap, several depths	Av. 0.037	0.029	—
Georgii & Weber (1960)	Axel Heibergland, 2000 m elev.	Ice at various depths	Av. 0.07	0.05	—
Brocas & Delwiche (1963)	Antarctica	Snow, firn, and ice			
	Ocean		Av. 2.3	1.5	—
	Coast		Av. 2.1	1.9	—
	Continent		Av. 0.5	0.6	—
	Mountains		Av. 0.4	1.1	—
Bennington (1963)	Barrow. Alaska (?)	Fresh snow	78.	39.	—
		Top 4 cm of snow on level sea ice	3750.	2400.	—
Sugawara (1961 *a* + *b*)	Antarctica	Melt pools, Ongle I.	158.4	77.7	5.
		Snow	413.7	240.	10.5
		Snow	8.3	5.3	4.1
		Pack Ice	995.6	525.	8.0
		Pack Ice	3.4	1.5	1.4

Eskimo village of Barrow. In January the Arctic Ocean is frozen, the only open water being occasional leads which may comprise 0.1 % or more of the ocean's surface at any one time.

Samples of ice and snow from both arctic and antarctic regions have been analyzed for chlorine and sodium by previous investigators, and a summary is given in Table 1. The large differences in the concentrations found in these samples reflect the different sampling locations relative to the sea and the various times of the year for sampling and show that general comparison of polar samples is dangerous unless the exact sampling conditions are known.

Bromine analyses of polar atmospheric samples have not previously been reported and iodine has been reported only in samples of melt pool water, snow, and pack ice from Antarctica collected by the Japanese Antarctic Expedition during the summer of 1957 (SUGAWARA, 1961*a* and *b*; TAKAHASHI, 1960). The source of the pool water was apparently melted snow and rain, but probably part of the salt in the water had been transported as spray from the sea. It can be seen in Table 1 that the I/Cl ratio in these samples tends to be greater than in sea water, but is in general lower than in samples collected in more temperate latitudes. In comparing these results with the present investigation, it must be pointed out that the Antarctic samples were collected in the summer when there was open water nearby. This was not the case in the present Alaska sampling of the winter atmosphere.

Analytical

Iodine, bromine, and chlorine were determined by neutron activation analysis of aqueous solutions and Millipore filters using a straightforward radiochemical procedure (DUCE & WIN-

TABLE 2. *Filter aerosol sampling conditions.*

Sample No.[a]	Date Jan. 1965	Air vol. m³ STP	Wind[b] m/sec	Temp.[b] °C	Rel. hum[b] %	Met. cond.[b]
A	20	10.6	E10, G13	−21	69	Sctd St, BS
1 t	21	6.8	E7	−27	61	Brkn St
2 t, b	21	6.4, 8.2	E7	−27	77	Clr
3 b	21–22	28.6	ENE7–E11, G15	−27– −20	65–68	Clr, BS late in pd
4 t, b	22	9.4, 11.6	E11, G17	−20	68	Clr, BS
5 t, b	23–24	39.2, 48.8	E9–5	−22– −25	67–44	Clr, ocnl F & BS
6 t, b	24	15.0, 18.7	E5–NE3	−26– −22	51	Clr
7 t, b	24–25	23.9, 29.6	NNE–E6	−21– −31	60–49	Clr
8 t, b	25	18.2, 23.0	E4	−30	49	Clr to Ovc, St & S- late in pd
9 t, b	26	12.1, 15.0	ENE3	−24	72	Clr
10 t, b	26–27	41.7, 53.5	E4	−24	72–50	Brkn St bcmg Clr, late in pd, ocnl S-
11 t, b	27–28	36.9, 47.3	E6–E9, G11	−25– −21	68	Clr to Ovc, St late in pd, ocnl S-, IC, F
12 t, b	28–29	36.4, 43.9	ENE7	−23– −25	58–73	Clr, ocnl St, S- & IC

[a] Sampling heights of 15 m (t) and 5 m (b) above ground level ~2 km inland east of ARL camp, except sample A taken in the ARL camp area 2 m above ground level.

[b] Meteorological data calculated from U.S. Weather Bureau WBAN-10 record for Barrow, Alaska. Variation in wind, temperature and humidity during the sampling period were monotonic between the values indicated. Abbreviations for observed conditions: S- (light snow), BS (blowing snow), IC (ice crystals), F (fog); St (stratus), Ovc (overcast), Brkn (broken, 5/8–7/8 cloud cover), Sctd (scattered, 1/8–4/8 cloud cover), Clr (clear); pd (sampling period), bcmg (becoming), ocnl (occasional), G (gusts).

CHESTER, 1965) consisting of solvent extraction and beta counting of 25-min ^{128}I, 18-min + 4.5-hr $^{80+80m}$Br, and 37-min ^{38}Cl. (Filters were irradiated and leached with water before radiochemistry.) Using the M.I.T. Reactor, sensitivities attainable permit routine analysis of 5 ml of snow melt water and aerosols from several cubic meters of air for all three halogens, typically requiring one hour per sample. Analytical errors are S.D. ~5 % on concentrations of I, Br, and Cl unless a blank subtraction is required, such as the Millipore filters and the aircraft aerosol rinse water. Errors stated in the tables below include blank uncertainty.

Sampling

Filter aerosols. Millipore 47 mm Type EA 1.0 μ cellulose acetate filters were used to collect aerosol particles by impaction, probably down to a particle radius of ~0.1 μ. Table 2 presents data on sampling conditions. Two samples were collected simultaneously at two collection heights, 15 m and 5 m above ground level, by pumping the air at a rate of ~2 m³/hr with graphite-lubricated electrically-powered vacuum pumps (Gelman Instrument Co., Ann Arbor, Michigan, Model 25002). The sampling location (Figure 1) was about 2 km eastward from the sea coast and from the ARL camp and made use of an existing CO_2 sampling tower. Contamination of the samples by particles of blowing snow was guarded against by extending the 35 mm opening of the Millipore open-type filter holder with a cylindrical plastic baffle 13 cm long and 3.5 cm in diameter, and the opening hung vertically downward during collection. SHLYAKHOV (1964) has shown that in Antarctica there is a direct correlation between height of blowing snow and wind speed (Table 3), and we expect lower snow heights at Barrow, owing to the flatter terrain. Since most of the sampling was done with winds < 10 m/sec, we expect little contamination from this source, and com-

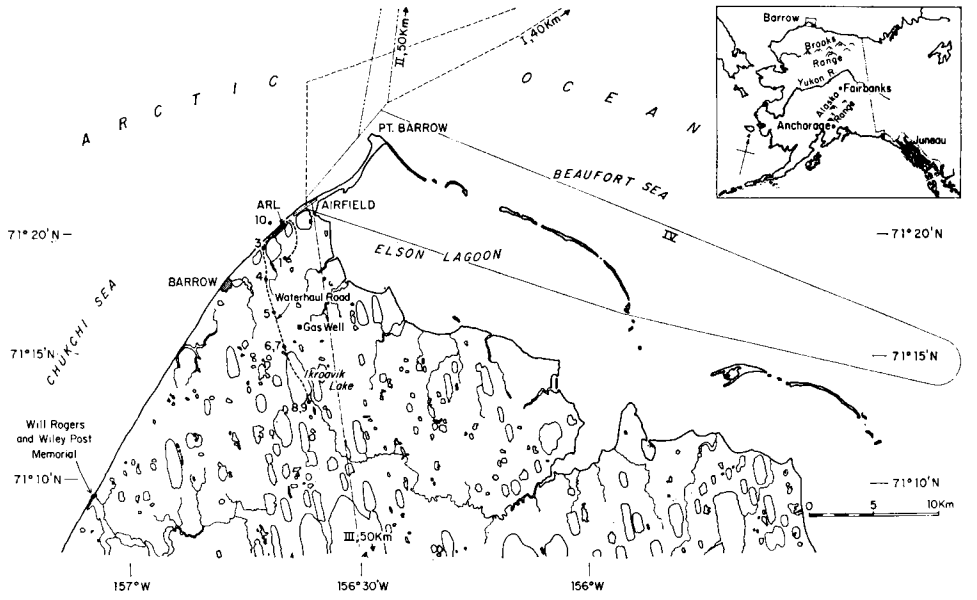

FIG. 1. Sampling locations in the region of Barrow, Alaska. Snow samples were collected at numbered sites between ARL and Ikroavik Lake. Filter aerosols were collected on Micromet tower at location "1". Aircraft flights were made along paths I through IV as shown. Sea ice and sea water were collected at location "10".

parison of the top and bottom members of each sample pair provides a check.

Aircraft aerosols. Four flights, each 40–50 min in duration, were made in a Cessna 180 aircraft with a strip-type impaction collector mounted on the left wing. Table 4 presents sampling conditions for these flights, and flight paths are shown in Figure 1. To minimize contamination from the ground, the collector was covered with plastic until a few seconds before take-off, and it was removed immediately after landing. Similar in design to that used in Hawaii (DUCE *et al.*, 1965), the Barrow collector contained 15 strips, each 0.051 cm wide, and 2 strips, each 0.16 cm wide, all strips being 10.5 cm long and made of type 316 stainless steel.

TABLE 3. *Height of blowing snow.*

Wind speed m/sec	Height of top of blowing snow, m
6–10	1–5
15–18	12–16
19–22	25–28
30 and gusty	~90

Flights averaged 55–60 m/sec at altitude (150–300 m), and ascent and descent times were each 1–2 min. Immediately after every flight, each strip was rinsed in ultrapure water and packaged for analysis. Sampling volumes were calculated from the air volumes swept out by strips of each size, but it is recognized that particle collection efficiencies may have been less than the 100 % sticking probability assumed by DUCE *et al.* (1965) for Hawaii owing to the low temperatures at Barrow.

Snow. Under conditions presented in Table 7, blowing snow (groups 1 and 2) and snow lying on the ground (groups 3 to 9) were sampled. Using a collector of 4 polyethylene bottles on a pole, blowing snow was collected at two times and locations, sample group 1 near the end of a severe wind storm, when considerable blowing snow was still in the air, and sample group 2 over the period of a week, including a period of extreme calm when the air was so clear that breath did not condense in the air before one's face (except in the ARL camp area or very near a running gasoline engine) and hoar frost collected thickly on buildings and poles.

In an attempt to collect snow which fell at

TABLE 4. *Aircraft aerosol sampling conditions.*

Sample No.	Date Jan. 1965	Local time	Location[a]	Altitude m	Air vol. m^3 STP
I L, S	28	1435–1515	60 km NE	150	39, 93
II L, S	29	1013–1052	60 km N	180	38, 92
III L, S	29	1105–1153	70 km S	150	47, 112
IV L, S	29	1309–1359	50 km E	300	50, 118

[a] Flights out and back in direction and maximum distance from ARL indicated, shown in Fig. 1. Each flight used 0.16 cm (L) and 0.051 cm (S) collector strips which sampled different particle size ranges. Flights I, II, IV over sea ice with much open water (I), some open water (II), and no open water (IV). Flight III over land. Meteorological conditions: I, surface wind NE5 m/sec, overcast, light snow (S-). II, III, IV, surface wind NE4 m/sec, clear, light haze.

different times during the winter, 6 depth profiles were taken at locations indicated in Figure 1. In most locations samples were taken from snow packed in small gullies between hummocks with the intent of sampling snow which fell at different times during the winter. It was expected that early snowfall would contain salts more strongly influenced by sea spray from open sea water than later snowfall when most of the sea was frozen over.

Sea ice and sea water.[1] Samples of sea ice and related materials, indicated in Table 8, were collected on 25 and 26 January 1965 roughly 0.5 km offshore from the ARL, for comparison with the atmospheric samples.

Core samples of sea ice were taken in 3 locations, and analyses of sections from one of these ice cores are reported here (Core 2-A, B,C,). The core was 7.5 cm in diameter and 114 cm long and was taken in the center of a very flat 200 m diameter area of ice believed to be less than 1 year old.

One sample was taken of ice core brine by shaving off the surface of core 2 with a knife and blotting up onto a Millipore filter the droplets of brine which appeared. Sea ice contains many brine tubes and pockets (KINGERY & GOODNOW, 1963) and these secrete brine onto the freshly cut surface shortly after the core is brought into contact with air colder than the ice. Such brine may be compositionally different from the sea ice as a whole.

One sample of fresh sea ice crystals was collected from a hole which had been dug in the ice and had been allowed to freeze overnight. The new ice was in the form of large needlelike crystals several mm long and in clumps 1–2 cm apart. In addition, one sample of snow lying on the surface of the ice was collected from a spot nearby.

Sea water was collected from two of the ice core holes from the water which filled the holes after removal of the cores. An additional sample of sea water was collected for us on 12 February 1965 from 5 m below the bottom of the ARL ice station Arlis II which at the time was near northeast Greenland, 79°31′ N, 8°7′ W. All three sea water samples may have been diluted by fragments of low-salinity ice, but it is the relative elemental composition of the dissolved salts which is of greatest interest in the work reported here.

Results

Filter aerosols. The analytical data given in Table 5 are plotted in Figures 2, 3, and 4. The trends of increasing I/Cl and Br/Cl with decreasing Cl concentration are reflections of the relatively constant I/Br ~ 0.2. The points for sample pairs lie close together in nearly every case and indicate that local blowing snow crystals are not a contaminant. The concentration of Cl varies widely, and the highest values are early in the sampling program when wind speeds were greatest. The lowest values (9, 10, and 11) coincide with a period of exceptionally calm and clear air, and, sensing the possibility

[1] We are indebted to Dr. K. O. Bennington and to Dr. N. Untersteiner, Dept. of Atmospheric Sciences, University of Washington, Seattle, for assistance in collecting these samples and for helpful discussions on the properties of sea ice.

TABLE 5. *Filter aerosol samples.*

Sample No.	Cl μg/m³ STP	Br ng/m³ STP	I ng/m³ STP	I/Cl × 10³	Br/Cl × 10³	I/Br
A	3.1 ±0.2	20.5 ±1.2	1.4 ±0.1	0.45 ±0.05	6.6 ±0.7	0.068 ±0.01
1 t	<0.2	8.3 ±1.0	1.4 ±0.1	>7	>40	0.17 ±0.03
2 b	<0.1	4.6 ±0.8	1.3 ±0.1	>13	>40	0.28 ±0.05
2 t	0.66 ±0.10	13. ±1.	2.0 ±0.1	3.0 ±0.5	20. ±4.	0.15 ±0.02
3 b	0.28 ±0.03	3.3 ±0.3	0.40 ±0.03	1.4 ±0.2	12. ±2.	0.12 ±0.02
4 b	3.6 ±0.2	7.9 ±0.7	0.79 ±0.05	0.22 ±0.02	2.2 ±0.3	0.10 ±0.02
4 t	3.0 ±0.2	5.2 ±0.6	0.85 ±0.06	0.28 ±0.03	1.7 ±0.2	0.16 ±0.02
5 b	0.49 ±0.03	1.56 ±0.14	0.42 ±0.03	0.86 ±0.08	3.2 ±0.4	0.27 ±0.03
5 t	0.36 ±0.03	1.6 ±0.2	0.48 ±0.03	1.3 ±0.2	4.4 ±0.7	0.30 ±0.04
6 b	0.28 ±0.04	7.0 ±0.4	0.33 ±0.03	1.2 ±0.2	25. ±4.	0.047 ±0.006
6 t	<0.07	11.1 ±0.7	9.4 ±0.5	>130.	>150.	0.85 ±0.07
7 b	0.49 ±0.03	4.0 ±0.3	0.69 ±0.04	1.4 ±0.2	8.2 ±0.8	0.17 ±0.02
7 t	0.41 ±0.04	3.6 ±0.3	0.59 ±0.03	1.4 ±0.2	8.8 ±1.1	0.16 ±0.02
8 b	0.54 ±0.04	10.1 ±0.6	0.86 ±0.05	1.6 ±0.2	19. ±2.	0.085 ±0.008
8 t	0.59 ±0.05	9.6 ±0.6	0.91 ±0.05	1.5 ±0.2	16. ±2.	0.095 ±0.009
9 b	<0.07	1.4 ±0.4	0.97 ±0.05	>14.	>15.	0.69 ±0.20
9 t	<0.08	1.4 ±0.4	1.25 ±0.07	>15.	>12.	0.9 ±0.3
10 b	<0.02	1.8 ±0.2	0.53 ±0.03	>25	>90.	0.30 ±0.04
10 t	<0.02	2.0 ±0.2	0.47 ±0.03	>20	>100	0.24 ±0.03
11 b	0.077 ±0.015	2.6 ±0.2	0.42 ±0.03	5.5 ±1.1	34. ±7.	0.16 ±0.02
11 t	<0.03	1.1 ±0.2	0.30 ±0.02	>10	>30	0.27 ±0.06
12 b	0.21 ±0.02	30. ±2.	7.8 ±0.4	37. ±4.	140. ±17.	0.26 ±0.03
12 t	0.77 ±0.05	10.8 ±0.6	0.89 ±0.05	1.2 ±0.1	14. ±2.	0.082 ±0.007

of this result, we lengthened air sampling times. Br shows a smaller minimum in concentration among these samples, but I shows no minimum.

Aircraft aerosols. The data of Table 6 are plotted in Figure 5. Flight I occurred during light snowfall on the day previous to flights II, III, and IV, and its Cl concentration is appreciably less than the other three. All Cl concentrations are generally less than those determined by Millipore filtering, and this is consistent with the higher altitude of collection by aircraft and with the possibility that the aircraft aerosol impactor collection efficiency is less than quantitative. However, if appreciable Cl exists in smaller size particles than the impactor would collect, the filter may still collect it and give

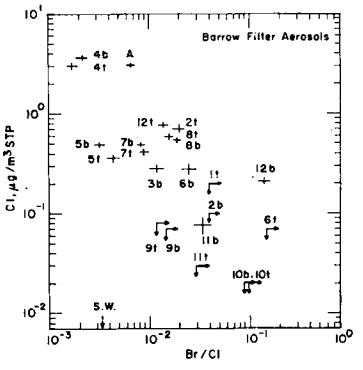

Fig. 2

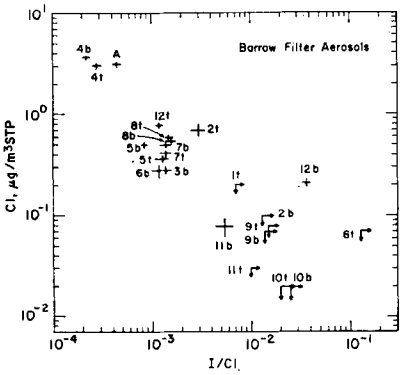

Fig. 3

FIG. 2. Results for filter aerosols collected at location "1" in Fig. 1. S.W. denotes sea water ratio Br/Cl.

FIG. 3. See caption to Fig. 2.

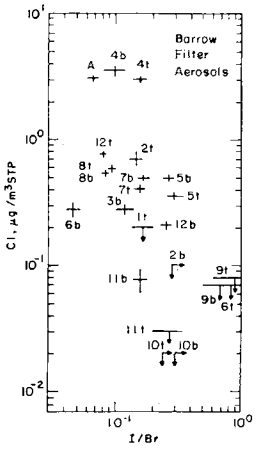

FIG. 4. See caption to Fig. 2.

an apparent higher Cl concentration in the air sampled. DUCE *et al.* (1965), after WOODCOCK & GIFFORD (1949), give the following collection efficiencies for the aircraft metal strip impactor used in Hawaii:

Particle raadius, μ:	0.1	0.5	1	5	10
L-strip (0.16 cm) efficiency, %:	< 1	10	55	95	95
S- strip (0.051 cm) efficiency, %:	< 1	60	85	100	100

These figures apply to particles of 1 g/ml density and 40 m/sec collector speed and assume 100 % sticking probability. If the mass of Cl in the smaller particles is significant, concentrations by L-strip should be less than by S-strip. If the Millipore Type EA 1.0 μ filter actually collected particles down to ~0.1 μ, we may expect L-strip concentrations to be especially less than Millipore concentrations. The close agreement between L and S Cl concentrations

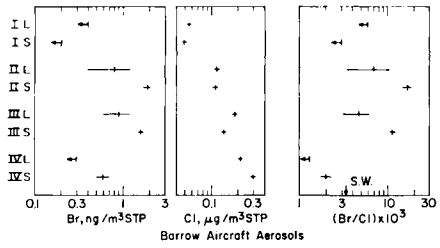

FIG. 5. Results of four flights, each with large (L) and small (S) collector strips. Br shows smaller average particle size than Cl.

for flights I and II (both over the sea with open water present) and the only slight differences for flights III (over land) and IV (over sea ice, no open water) indicate not much small particle Cl.

The Br concentrations were significantly above blank levels in five of eight samples but I was detected in only one sample. The S-strip Br concentrations are consistently greater than L-strip concentrations, agreeing with the Millipore filter Br concentrations measured at about the same time (except ≠ 12 b and t), and we may crudely estimate that half of the Br exists in sub-micron particles. The Br/Cl ratios are greater for the S-strip collector than for the L-strip, and two pairs are greater than and one pair is less than the sea water value. The single I/Br ratio lies in the middle of the range of filter aerosol values, but the upper limits set for other I/Br and the I/Cl ratios generally are less than similar ratios for the filter aerosols.

Snow. Snow analyses are given in Table 7 and plotted in Figures 6 and 7. The horizontal axis is the approximate perpendicular distance from the sampling location to the west (Chukchi

TABLE 6. *Aircraft aerosols.*

Sample No.	Cl μg/m³ STP	Br ng/m³ STP	I ng/m³ STP	I/Cl × 10³	Br/Cl × 10³	I/Br
I L	0.056 ± 0.003	< 0.4	< 0.09	< 2	< 6	—
S	0.049 ± 0.003	< 0.2	< 0.04	< 0.8	< 3	—
II L	0.116 ± 0.006	0.8 ± 0.4	< 0.10	< 0.8	7.0 ± 3.5	< 0.1
S	0.113 ± 0.006	1.9 ± 0.2	< 0.04	< 0.3	17 ± 2	< 0.02
III L	0.187 ± 0.009	0.9 ± 0.3	< 0.07	< 0.3	4.7 ± 1.5	< 0.1
S	0.140 ± 0.009	1.6 ± 0.1	< 0.03	< 0.3	11.5 ± 0.7	< 0.02
IV L	0.216 ± 0.011	< 0.3	< 0.06	< 0.3	< 1.3	—
S	0.30 ± 0.02	0.6 ± 0.1	0.11 ± 0.02	0.4 ± 0.1	2.0 ± 0.3	0.18 ± 0.05

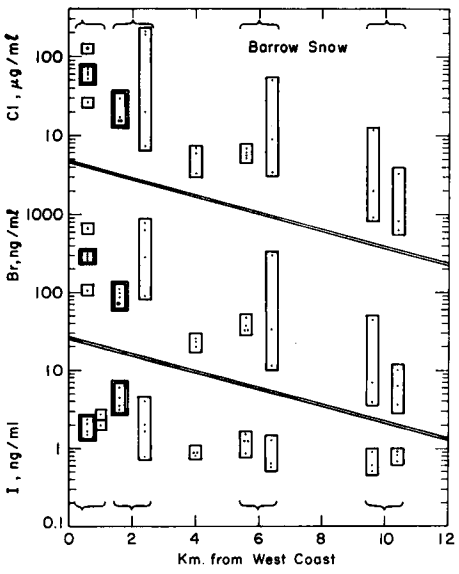

Fig. 6

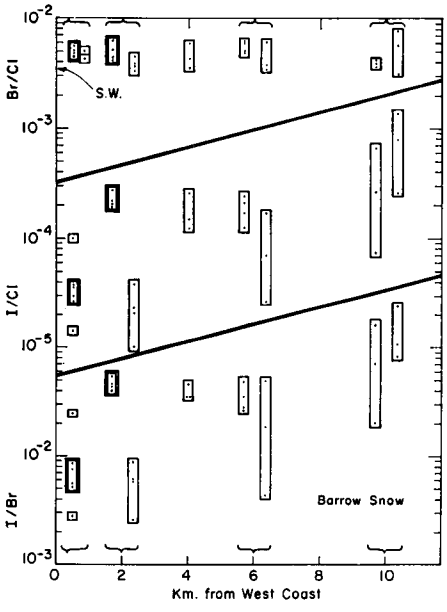

Fig. 7

FIG. 6. Ground lying snow (single boxes) and blowing snow (double boxes) plotted against distance from west coast. Wind direction during autumn storms over open sea water was mainly from the west.

FIG. 7. See caption to Fig. 6. S.W. denotes sea water ratio Br/Cl.

Sea) coast. Although the prevailing winds are from the east to southeast, larger amounts of sea salt may be blown in during brief autumn storm periods by winds from the west over open water.

The blowing snow shows somewhat higher Cl and Br, but lower I, concentrations in group 1 (high wind speed) than in group 2 (low wind speed) and the I/Br ratio is greater in group 2 than in group 1 by a factor of 7. We may infer that a sea salt component, with low I/Br, is mixed with an I-enriched salt component, and the mixing ratio depends on wind speed, proximity to the sea, and air mass. Both groups show slightly greater Cl values at higher levels above the snow surface. If the 2-meter altitude variation is significant, the somewhat higher Cl concentrations in the upper collector bottles may be attributed to salt occurring preferentially in smaller size snow particles.

In the snow profiles 4–10 km from the coast (groups 5–9) Cl and Br concentrations are variable but are several times smaller than nearer the coast. I concentrations are much less variable, and I/Br is similar to blowing snow group 2 and several times greater than nearer the coast. There is no uniform pattern of variation of salt composition with depth, although in the surface samples 7-1, 8-1, and 9-1 there is evidence of extra large amounts of low-I/Br salt. Snows 3 and 4, collected nearer the sea, show higher Cl and lower I-Br, characteristic of a strong admixture of less differentiated sea salt, presumably blown inland early in the winter before freeze-up. In all snow samples I/Br lies between the sea water value (0.001) and Hawaii rain samples (mostly 0.2–0.6) found by DUCE *et al.* (1965).

Sea ice and sea water. Analytical data are presented in Table 8 and Figure 8. The sea water Cl concentrations are lower than typical, 19 mg/ml, probably owing to sinking of saltier and denser water or to admixture of melt water in the samples, and the ratios Br/Cl seem to exceed the typical value of 3.4×10^{-3} by 10–15 %. The ratios I/Br fall within the range found for normal sea water.

The ice cores show halogen concentrations much less than normal for sea water, as expected, and the halogen ratios agree well with the

TABLE 7. *Snow samples.*[a]

Sample No.	Position[b] cm	Cl μg/ml	Br ng/ml	I ng/ml	I/Cl × 10³[c]	Br/Cl × 10³[c]	I/Br[c]
1–1	210	66	310	1.71	0.026	4.7	0.0055
1–2	150	61	270	2.3	0.038	4.4	0.0086
1–3	90	58	280	2.1	0.036	4.9	0.0074
1–4	30	52	290	1.50	0.029	5.6	0.0051
2–1	210	29	114	6.2	0.21	4.0	0.054
2–2	150	17	86	3.5	0.20	5.1	0.040
2–3	90	16	97	4.3	0.28	6.2	0.045
2–4	30	16	69	3.0	0.19	4.3	0.044
3	1–25, av.	132	660	1.88	0.014	5.0	0.0028
4–1	1	21	90	0.79	0.038	4.4	0.0087
4–2	25	210	790	2.0	0.0095	3.7	0.0026
4–3	50	195	630	3.9	0.020	3.3	0.0062
4–4	75	74	280	1.68	0.023	3.8	0.0060
5–1	1	6.8	24	0.83	0.123	3.5	0.035
5–2	25	3.4	20	0.89	0.26	5.9	0.045
5–3	50	5.9	25	0.88	0.150	4.3	0.035
6–1	1	6.9	33	0.85	0.123	4.8	0.026
6–2	30	6.3	37	1.32	0.21	5.9	0.035
6–3	60	6.6	33	1.57	0.24	5.0	0.048
6–4	90	7.8	48	1.32	0.169	6.1	0.028
7–1	1	51	306.	1.34	0.026	6.0	0.0044
7–2	25	3.5	12.2	0.60	0.169	3.4	0.049
7–3	50	9.1	34.	0.64	0.070	3.8	0.0185
8–1	1	12.3	45	0.90	0.073	3.7	0.020
8–2	20	1.87	7.1	0.51	0.27	3.8	0.072
8–3	40	0.92	3.8	0.61	0.66	4.1	0.161
9–1	1	3.3	10.5	0.86	0.26	3.2	0.082
9–2	15	0.84	6.4	0.68	0.80	7.6	0.106
9–3	30	0.65	3.7	0.88	1.36	5.7	0.24
ARL-1	1	27	106	2.8	0.103	3.9	0.026
ARL-2	1	26	112	2.5	0.097	4.3	0.023

[a] Sample groups 1 and 2 of blowing snow; groups 3 to 9 and ARL of snow on ground. Sampling dates (January 1965): 1, 20–21; 2, 24–31; 3–9, 30. Extra samples ARL, 22 December 1964. Analytical errors are 5 % on concentrations and 7 % on ratios.

[b] Groups 1 and 2, heights of collectors above snow surface. Groups 3 to 9, approximate depths below snow surface. Ground level 5–10 cm below deepest sample. Sampling locations (distances from west coast): 1 (ARL camp) & 3, <0.5 km; 2 (Micromet tower), ~ 2 km; 4, ~ 2 km; 5, ~ 4 km; 6 & 7, ~ 6 km; 8 & 9, ~ 10 km; ARL, <0.5 km, collected by ARL staff.

[c] Weight ratios calculated from unrounded values.

TABLE 8. *Sea ice and sea water samples.*

Samples	Depth cm	Cl mg/ml	Br μg/ml	I ng/ml	I/Cl × 10⁶	Br/Cl × 10³	I/Br
Core 2-A	20	3.25	12.0	13.9	4.2	3.7	0.0012
Core 2-B	60	2.87	11.3	11.0	3.8	3.9	0.00097
Core 2-C	100	1.50	6.18	6.18	4.1	4.1	0.0010
Brine 2	73–97	—	—	—	18. ±9	0.9 ± 0.4	0.02 ± 0.01
Crystals	0	38.	160.	200.	5.3	4.2	0.00125
Snow	0	4.68	23.6	114.	24.	5.0	0.0048
Sea Water							
ARL-1	—	12.4	47.8	47.8	3.9	3.9	0.0010
ARL-2	—	7.59	28.8	28.8	3.8	3.8	0.0010
Arlis	500	12.1	47.4	40.8	3.4	3.9	0.00086

sea water values. The single ice core brine sample, however, shows an uncertain, but unusually low Br/Cl ratio and high I/Cl. The freshly formed ice crystals are quite concentrated in halogens, compared to sea water, and the small ratio differences are perhaps significant. The snow from the ice surface appears to contain a mixture of sea salt and halogens of usual snow composition, as evidenced by the high I/Cl and I/Br ratios.

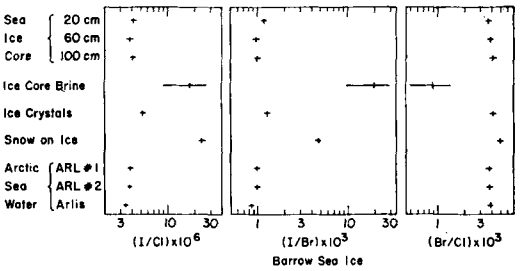

FIG. 8. Sea water and sea ice results.

Discussion

A full understanding of the halogen data from the winter Barrow atmosphere can be gained only in the context of halogen data from other climatic regions, as discussed by WINCHESTER and DUCE (1966). However, a comparison of the Barrow samples of different types leads to some generalizations.

Ground-lying snows become notably less salty with just a few km increasing distance from the *west* coast, even though wind directions are more common from the east. Apparently occasional autumn storm winds from the west over open water carry most of the sea salt inland, and this drops out rather quickly with distance. In a number of samples Br/Cl exceeds the sea water value, and I/Cl and I/Br increase markedly with increasing distance from the sea. In the snows a mixture of an "atmospheric" component, containing nearly all of the I, some of the Br, and very little of the Cl, and "sea salt", containing nearly all of the Cl, some of the Br, and very little of the I, is implied. According to this crude approximation, the composition of the atmospheric component is

$$\left(\frac{I}{Br}\right)_{atm} \approx \frac{(I/Cl)}{(Br/Cl) - (Br/Cl)_{sea}},$$

where we may take $(Br/Cl)_{sea} \approx 3.8 \times 10^{-3}$ from this work. It is probably not worthwhile examining the snow data of Table 7 in detail using this simple model, but if we compute grand averages of the individual ratios, we find

$$\left(\frac{I}{Br}\right)_{atm} \approx \frac{0.20}{4.7 - 3.8} = 0.2$$

as an order of magnitude estimate for the atmospheric component of the snow in the two component model. (The value 0.1 would be obtained from ratios of the concentration averages.)

Aerosols collected by Millipore filter exhibit a clustering of ratios I/Br near 0.1–0.2, in rough agreement with the snow atmospheric component. The Br/Cl ratios, largely owing to a variable Cl concentration, range up to 30 times the sea water ratio, and the Br can be attributed largely to the atmospheric rather than to the sea salt component. In the aircraft aerosols Br seems to be consistently somewhat preferentially associated with smaller sized particles, whereas Cl shows no such tendency. All of these observations point to a Br existence distinct from Cl and similar to I. It would be of interest to sample gaseous halogens in arctic winter air and compare with the temperate climate of Hawaii where atmospheric chemical reactions may be more prominent.

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СОДЕРЖАНИЕ ИОДА, БРОМА И ХЛОРА В ЗИМНИХ АЭРОЗОЛЯХ И СНЕГЕ В БАРОУ (Barrow) АЛЯСКА

В течении января 1965 г. с помощью радиоактивирования нейтронами определялось содержание иода, брома и хлора в атмосферах, аэрозолях и снеге, собранных в Бароу (Аляска).

Аэрозоли собирались ударным колектором установленным на самолете и 100 μ фильтром типа E. A. Millipore на поверхности земли. Анализы показали, что концентрация Cl более переменна чем концентрация Br или I, причем отношение массовых концентраций I/Br имеет порядок 0,1–0,2 для наземных проб. Концентрация хлора менялась от 0,02 до 4 μgm^{-3} в наземных пробах, что согласовывалось с результатами самолетных измерений в те же дни. Концентрации полученные с помощью фильтра равняются для Br 1–30 μgm^{-3} и для I 0,3–10 μgm^{-3}. Отношение концентраций Br/Cl и I/Cl резко увеличивается с уменьшением концентрации Cl.

В пробах снега с поверхности земли отношение Br/Cl несколько больше чем в морской воде, хотя содержание всех галогенов уменьшается с увеличением расстояния от моря вверх до 10 км. Рассматривая смесь невидоизменившейся морской соли и более постоянной атмосферной компоненты авторы устоновили для атмосферной компоненты в снеге $I/Br \approx 0{,}2$. Из анализа морской воды, соли и родственных проб было найдено, что отношение $I/Cl = 4 \cdot 10^{-6}$ нормально для морской воды, хотя Br/Cl $3{,}8 \cdot 10^{-3}$ является немного выше нормы.