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BROMINATED ORGANIC SPECIES IN THE ARCTIC ATMOSPHERE

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Abstract. Measurements are reported of four gas-phase, brominated organic species found in the Arctic atmosphere during March and April 1983. Volume mixing ratios for CH_3Br , $\text{CH}_2\text{BrCH}_2\text{Br}$, CHBr_3 , and CH_2Br_2 were determined by GC/MS analysis from samples taken Arctic wide, including at the geographic North Pole and during a tropopause folding event over Baffin Bay near Thule, Greenland. Methyl bromide mixing ratios were reasonably constant at 11 ± 4 pptv while the other three brominated organics showed a high degree of variability. Bromoform (2 to 46 pptv) was found to be the dominant contributor to gaseous organic bromine to the Arctic troposphere at $38 \pm 10\%$ followed by CH_2Br_2 (3 to 60 pptv) at $29 \pm 6\%$. Both CH_3Br and $\text{CH}_2\text{BrCH}_2\text{Br}$ (1 to 37 pptv) reservoirs contained less than 20% of the organically bound bromine. Stratospheric samples, taken during a tropopause folding event, showed mixing ratios for all four species at levels high enough to support a stratospheric total volume mixing ratio of 249 pptv Br (888 ngBr/SCM).

Introduction

The atmospheric chemistry of bromine has received attention recently because of the role that bromine compounds may play in the stratosphere. Watson (1975) first recognized that bromine could perturb stratospheric ozone in an analogous manner to chlorine. Wofsy et al. (1975) suggested that bromine atoms could be more effective than chlorine atoms in the catalytic destruction of stratospheric ozone. Yung et al. (1980) showed that the reaction $\text{BrO} + \text{ClO} \rightarrow \text{Br} + \text{Cl} + \text{O}_2$ represents a synergistic effect between bromine and chlorine, leading to an efficient catalytic destruction of ozone in the lower stratosphere. At present a major uncertainty in stratospheric bromine chemistry is the absolute concentration of bromine in both the troposphere and the stratosphere. The only measurement reported to date of an individual stratospheric bromine species was of anthropogenic CBrF_3 at ≤ 1 pptv (Fabian et al., 1981).

In the background troposphere CH_3Br was identified by Singh et al. (1977) at mixing ratios in the 3 to 20 pptv range. Later, Singh et al. (1983a,b) found slightly higher concentrations. Two other brominated organic species ($\text{CH}_2\text{BrCH}_2\text{Br}$ and CBrF_3) have since been measured at mixing ratios less than 3 and 1 pptv, respectively (Singh et al., 1983a; Penkett et al., 1981; reviewed by Cicerone, 1981). In addition, Elias et al. (1976) measured CBr_2F_2 as a tracer of air motions. Singh et al. (1983b), using several years of predominantly mid-latitude CH_3Br data, concluded that this species is probably the major contributor to the organic gaseous bromine (Br_g) burden in the troposphere. Based on this conclusion background Br_g levels in the Northern Hemisphere should range between 10 and 30 pptv.

Recent data (Berg et al., 1983) have shown exceptionally high mixing ratios for particulate (Br_p) and gas phase (Br_g) bromine in the Arctic troposphere near Barrow, Alaska and Ny-Alesund, Spitsbergen (Norway). Concentrations averaged up to ten times higher than all previously reported measurements made in the natural troposphere. From four years (1976-80) of continuous sampling it was observed that the high

levels of Br_p occurred only during a three-month period beginning about 15 February each year. Mixing ratios for Br_g also appeared to exhibit this behavior with the Br_g maximum averaging 118 ± 14 pptv (422 ± 48 ngBr/SCM). Total atmospheric bromine loading during the peak period averaged 474 ± 49 ngBr/SCM. Conversely, during the other nine months of each year background mixing ratios for Br_g were similar to those reported by Singh and his co-workers for CH_3Br at lower latitudes.

The importance of the Arctic bromine maximum to both tropospheric and stratospheric chemistry remains unknown since the major Br_g compounds that contribute to the annual peak have not been identified. We report here measurements of four gas-phase, brominated organic species (CH_3Br , $\text{CH}_2\text{BrCH}_2\text{Br}$, CHBr_3 , and CH_2Br_2) during the March/April 1983 peak period across the Arctic from Anchorage, Alaska to Bodø, Norway, and for samples taken at the geographic North Pole and during a tropopause-folding event over Baffin Bay near Thule, Greenland.

Experimental Procedures

The present results are based on atmospheric bromine measurements from 37 whole-air (grab) samples taken from aircraft and ground sampling platforms in the Arctic. Sampling locations, dates, times, and altitudes are presented in Table 1. All of the samples taken above ground level were collected from the four engine NOAA WP-3D Orion aircraft during a ten-flight series in March and April 1983, part of the Arctic Gas and Aerosol Project (AGASP) investigation of Arctic haze. Two sea-level sampling locations were also operated near Anchorage and Barrow, Alaska.

Each of the 37 whole-air samples was collected in an electropolished 2.5 l stainless steel canister with a bellows-sealed valve. All components are welded to eliminate all polymers and lubricants which have been shown to arbitrarily absorb and desorb the halogenated trace gases. Following high-temperature bake-out, each of the canisters was filled with an air sample, allowed to equilibrate several hours, and then evacuated while being warmed to 80°C . This conditioning process was repeated 6 times before final storage at $< 10^{-6}$ torr until use. Further details of canister preparation and sample handling techniques have been published by Heidt and Ehhalt (1972) and Heidt (1978).

All samples were analyzed with a Hewlett-Packard Model 5985 gas chromatograph/mass spectrometer operated in the single-ion monitoring mode. Masses monitored were CH_3Br (94, 96), CH_2Br_2 (93, 174), $\text{CH}_2\text{BrCH}_2\text{Br}$ (107, 109), and CHBr_3 (171, 173). A fused silica column 30 m long x 0.255 mm OD (J. and W. Scientific) with a bonded, non-polar silicone phase (1.0 μm) accomplished the trace gas separations. The temperature profile for sample analysis was: 0°C for 2 min, programmed temperature elevation at $10^\circ\text{C}/\text{min}$ up to 150°C , and maintenance of 150° for 20 min. Approximately 1000 ml of sample was preconcentrated in the sample injection loops by pumping away the O_2 and N_2 while holding the glass-bead-packed stainless steel loops at -185.9°C (liquid Ar). To prevent hysteresis effects from carry-over of one sample to the next, the sample loops were heated during evacuation between sample runs. Additionally, backgrounds were run by purging with purified helium using the same preconcentration techniques employed for samples.

A mixed standard of all four gases, prepared by Scott Research, was

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TABLE 1. Measured Mixing Ratios of Four Brominated Organic Species Found in the Arctic Atmosphere during March and April 1983.

Sampling Date 1983	Time, Z	Altitude, meter	Arctic Location			Volume Mixing Ratio, pptv ^(b)				O ₃ ^(c) ppbv
			Location ^(a)	Lat.	Long.	CH ₃ Br	CHBr ₃	CH ₂ Br ₂	CH ₂ BrCH ₂ Br	
8/3	1825	SL ^(d)	Anchorage, AK	61.5°	149.5° W	18	32	32	23	NV ^(e)
9/3	1722	SL	Anchorage, AK	61.5	149.5	11	6	10	4	NV
11/3	2232	37	Barrow, AK	72.7	159.0	12	5	5	2	25
	2250	151	Barrow, AK	73.1	160.2	11	8	5	2	26
	2310	440	Barrow, AK	72.8	158.3	10	4	10	3	36
	2350	950	Barrow, AK	72.7	157.8	9	3	3	1	38
	0042	2100	Barrow, AK	72.3	155.4	11	2	3	NV	33
	0122	4100	Barrow, AK	72.8	158.5	19	46	21	19	32
	0220	7600	Barrow, AK	72.2	157.8	15	16	20	NV	46
13/3	2228	951	Barrow, AK	74.1	157.0	13	6	5	4	35
15/3	2320	40	Barrow, AK	72.5	156.9	9	5	3	DL ^(f)	11
16/3	0117	1800	Barrow, AK	73.7	149.9	10	7	8	DL	40
17/3	2326	158	Barrow, AK	72.6	156.8	11	41	26	23	34
21/3	1523	1515	Mould Bay	75.85	133.71	7	5	7	5	31
	1644	1502	Mould Bay	79.62	120.30	9	15	15	10	36
	1720	1500	Mould Bay	80.90	111.66	14	40	60	37	39
23/3	1635	7312	Thule, Greenland	66.56	53.48	22	41	33	2	49
	1713	8411	Thule, Greenland	68.11	54.33	15	16	30	19	201
	1841	8800	Thule, Greenland	69.94	55.47	7	34	38	32	260
28/3	1611	1498	North Pole	89.58	60.16	10	11	15	12	24
	1915	1521	Ny-Alesund, Norw ^(g)	81.09	24.90 E	11	3	5	4	27
	2045	8183	Bear Island, Norw	73.29	25.06	15	8	18	13	59
30/3	2252	SL	Barrow, AK, GMCC ^(h)	71.19	156.37 W	9	29	30	24	NV
31/3	1208	4253	Bear Island, Norw	74.40	24.71 E	10	4	9	5	48
	1320	3932	Ny-Alesund, Norw	79.03	23.31	18	4	6	4	41
	1635	3201	Bear Island, Norw	70.82	11.66	9	5	8	3	38
	1812	5570	Bodó, Norw	67.97	14.27	8	NV	3	NV	52
	2253	SL	Barrow, AK, GMCC	71.19	156.37 W	6	8	10	9	NV
1/4	1521	SL	Barrow, AK, GMCC	71.19	156.37	16	18	21	16	NV
4/4	0802	6734	Bodó, Norw	69.88	10.26 E	8	NV	6	NV	42
	0847	2136	Bodó, Norw	69.93	10.14	9	4	7	5	46
	0903	969	Bodó, Norw	70.08	9.85	10	11	12	12	36
	0910	198	Bodó, Norw	69.74	10.44	12	18	15	14	36
	0952	50	Bodó, Norw	70.19	10.33	10	5	4	2	36
	1410	90	Ny-Alesund, Norw	78.75	27.14	10	26	19	20	33
	1425	121	Ny-Alesund, Norw	78.44	27.24	8	NV	10	NV	39
5/4	1141	96	Bodó, Norw	71.06	1.56 W	12	14	13	11	35

(a) Nearest geographic landmark.

(b) Parts per trillion by volume, 1 pptv Br = 3.565 ngBr/SCM.

(c) Data furnished by AGASP project, from aircraft.

(d) SL — Sea Level, mean.

(e) NV — No Value, not measured

(f) DL — Detection Limit or less.

(g) Norw — Norway.

(h) GMCC — Geophysical Monitoring for Climatic Change, ground sampling site.

used for sample quantification. Experience has shown us that all bromine gas mixtures must be remixed before use by warming and/or rolling the cylinder. Storage integrity tests of both standards and randomly selected samples indicated no degradation over 60 days for any of the four brominated organic gases. All samples were analyzed within 26 days of collection. Analytical error (based on repetitive analyses of several standard concentrations) was 15% or less. "Background" air samples collected at our sampling sites near Boulder, Colorado have been routinely measured as an additional audit of canister stability as well as instrument performance. In contrast to the AGASP samples, CH₂BrCH₂Br levels are always below our detection limit in these samples while the concentration ranges for the other three gases are: 10-11 pptv for CH₃Br, 1-7 pptv for CH₂Br₂, and 1-4 pptv for CHBr₃. Data from aircraft cabin air samples and samples collected after exposing the sampling manifold to cabin air, together with sample

blanks carried throughout the expedition and surface samples collected at Pt. Barrow during the aircraft flights manifested our confidence that no contamination sources influenced our sample collections in the Arctic.

Results and Discussion

Four brominated organic species were identified in the Arctic atmosphere. Volume mixing ratios for CH₃Br, CHBr₃, CH₂Br₂, and CH₂BrCH₂Br are presented in Table 1 along with ozone mixing ratios. Plots of the halogen data vs. altitude above mean sea-level are presented in Fig. 1. Other brominated species were identified but are not reported here since we lack certified calibration standards for these compounds.

The credibility of the present data is supported by three observations. First, as seen in Fig. 1a, all of our CH₃Br data fall within the limits

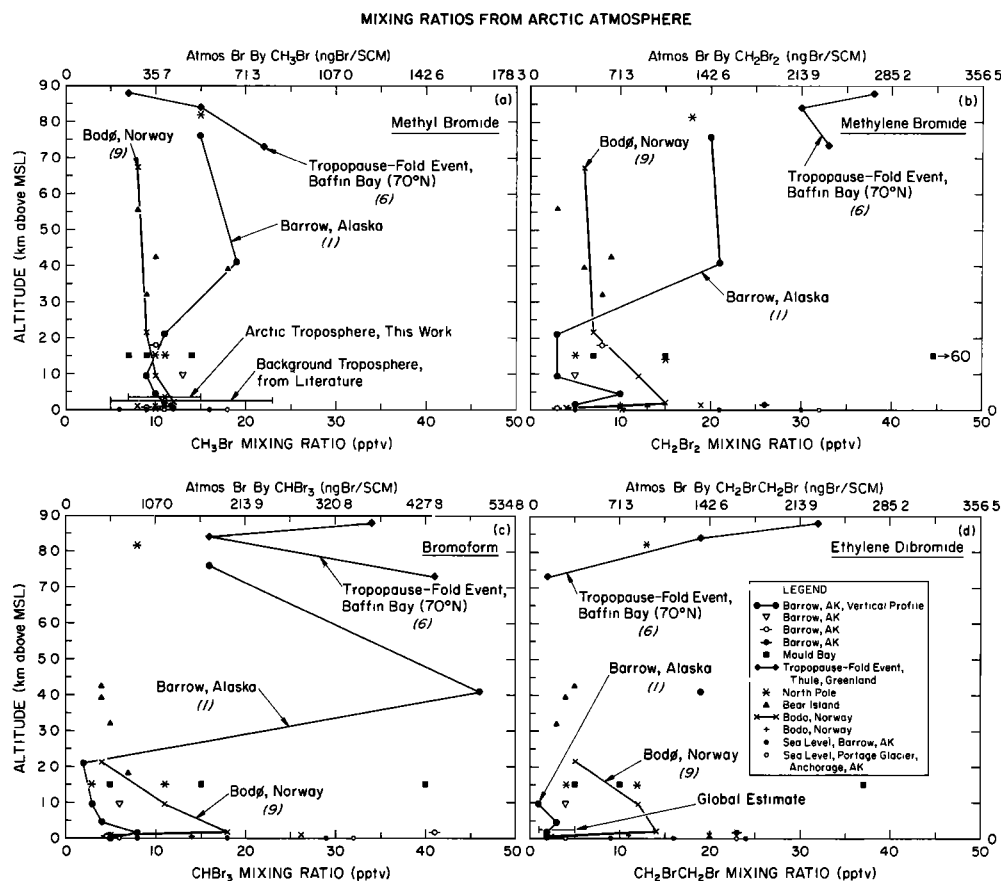


Fig. 1. Volume mixing ratios vs. altitude for CH_3Br , CHBr_3 , CH_2Br_2 , and $\text{CH}_2\text{BrCH}_2\text{Br}$. The italicized numbers for each of the vertical profiles are flight mission numbers. The two x-axis are related as follows: 1 pptv Br = 3.565 ngBr/SCM. The top x-axis for each plot is the atmospheric elemental bromine contribution made to the Arctic atmosphere by a particular brominated organic compound. MSL = Mean Sea Level.

(5 to 23 pptv) set by measurements made by other investigators at lower latitudes (e.g., Singh et al., 1983a,b). A mean ratio for CH_3Br in the Arctic troposphere was found to be 11 ± 4 pptv, with a range of 7 to 22 pptv. Similar comparisons could not be made, however, for the other three species since we could find no comparable data sets in the literature. Second, contamination did not appear to be the source of the high levels of bromine found in most of the aircraft samples. As seen in Table 1 and Fig. 1, all of the data taken in the boundary layer and in the free troposphere are comparable. This observation, coupled with the fact that the free troposphere samples were all taken by different personnel (on different dates) employing a different sampling geometry not associated with the aircraft, supports the contention that cabin-air contamination of the flight samples was unlikely. Blank canister runs further support this conclusion. And third, sample degradation during the time lag after collection and before analysis was not a factor as evidenced by storage tests reported above.

Table 1 suggests that, in most cases, bromoform is the dominant contributor of bromine to the Arctic atmosphere within the four species group. Of the mass of organically bound bromine in the Arctic atmosphere during this period (based on the four measured bromine compounds), $38 \pm 10\%$ is bound in CHBr_3 with $29 \pm 6\%$ in CH_2Br_2 . Both the CH_3Br and $\text{CH}_2\text{BrCH}_2\text{Br}$ reservoirs each contain less than 20% of the organically bound bromine. Mean concentrations (pptv) \pm one standard deviation for data of Table 1 are: CH_3Br (11 ± 4), CHBr_3 (15 ± 13), CH_2Br_2 (15 ± 12), $\text{CH}_2\text{BrCH}_2\text{Br}$ (11 ± 10).

The source or sources for the Arctic bromine are not known at present. Candidates include: (1) long-range anthropogenic pollution from the Eurasian continent, as part of the Arctic haze phenomenon; (2) biogenic emissions on a large scale by marine organisms such as red

benthic algae (a major producer of CHBr_3), molluscs, and sponges; (3) surface or sub-surface volcanic and sea-floor vent emissions, as probably occurred on Bennett Island during February 1983; (4) bromine-containing emissions from fires which have smoldered for perhaps thousands of years (e.g., the Smoking Hills of Franklin Bay along the southeast edge of Beaufort Sea); (5) stratospheric intrusions; and (6) oil field emissions from areas such as Prudhoe Bay. Of these possibilities the first two are most likely, with biogenic surface emissions probably representing the largest single source. For example, red benthic alga production of bromoform in the Arctic has been suggested by Dyrssen and Fogelqvist (1981) who measured CHBr_3 levels at up to 300 ng CHBr_3/l in the surface seawater, over a distance of more than 1000 km between Greenland and Franz Josef Land.

It is clear from our data and those of Berg et al. (1983) that brominated compounds accumulate in the Arctic atmosphere during certain times of the year. A possible explanation may lie in the distinctive character of Arctic atmospheric chemistry and meteorology. During most of the year typical low-latitude chemical processes probably occur in the Arctic atmosphere. For the three months near the end of the Arctic winter, however, the situation changes significantly. Sluggish meteorological systems in the Arctic Basin together with strong radiative temperature inversions create stagnation almost Arctic-wide. Rainout, washout, and other normal atmospheric cleansing processes are greatly reduced due to the lack of low-level cloud formation and the near absence of precipitation events (low available water vapor due to the nearly complete ice cover and the low air temperatures). Also, there is little energy input from solar radiation during the dark Arctic winter. As a result, the production of hydroxyl radicals, which is initiated by the photolysis of ozone at wavelengths shorter than 315 nm in the clean

background troposphere, is effectively shut down. This situation, compounded by the lack of water, inhibits the final step in the tropospheric production of hydroxyl radicals by $O(^1D) + H_2O \rightarrow 2OH$. Similarly, production of OH from H_2O_2 , HNO_2 and CH_2O is very limited in the background troposphere. With tropospheric OH sharply reduced to levels less than $1 \times 10^5 \text{ cm}^{-3}$, the normal removal process, OH attack on the brominated organic species, is also shut down in the Arctic atmosphere. Additionally, any photolytic destruction of these compounds is inhibited during the dark Arctic winter. The overall effect of these Arctic processes most likely is a sharp elevation in particulate and gas-phase bromine throughout the Arctic provided sources exist to actively feed the region. However, if the Arctic troposphere contains high levels of NO_x and hydrocarbons, as in a polluted environment, several other potential OH sources may exist (e.g., oxidation of aldehydes by NO_x , a process that requires no photons (Stockwell and Calvert, 1983)).

Stratospheric mixing ratios for several brominated organic compounds were also determined. During the 23 March mission a stratosphere-troposphere exchange event over Baffin Bay was penetrated by the aircraft and whole-air samples were taken at three altitudes. The samples at 8.8 km were taken from stratospheric air (ozone levels averaging 260 ppbv and other supporting chemical and meteorological data corroborate the stratospheric nature of this sample). For this sample $CHBr_3$ and CH_2Br_2 are the major carriers of bromine, with very little organic bromine as CH_3Br . If all the $CHBr_3$, CH_2Br_2 , CH_3Br and CH_2BrCH_2Br in our stratospheric sample were converted to monobrominated inorganic gas its concentration would be 249 pptv (888 ngBr/SCM). The sample taken at slightly lower altitude (8411 m), which was predominantly stratospheric air, also showed these high bromine mixing ratios.

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