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Journal

Journal of Geophysical Research, 93(D4)

ISSN

0148-0227

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Publication Date

1988-04-20

DOI

10.1029/jd093id04p03745

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Measurements of Atmospheric Methyl Bromide and Bromoform

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We have measured gaseous methyl bromide (CH_3Br) and bromoform (CHBr_3) in air samples that were gathered approximately weekly from five ground-level sites: Point Barrow, Alaska; Mauna Loa Observatory and Cape Kumukahi, Hawaii; Matatula, Samoa; and Kaitorete Spit, New Zealand. Approximately 750 samples have been analyzed for CH_3Br between January 1985 and October 1987 and 990 samples have been analyzed for CHBr_3 between early 1984 and September 1987, all by gas chromatography/mass spectrometry. Methyl bromide concentrations are typically 10–11 parts per trillion (ppt) by volume; there are no clear indications of temporal increases. Bromoform concentrations are typically 2–3 ppt, but large seasonal variations are seen at Point Barrow.

INTRODUCTION

Atmospheric bromine measurements made in the 1960s and early 1970s characterized the amounts of Br as an element in atmospheric aerosol particles, precipitation, organic gases and inorganic gases (see, for example, *Moyers and Duce* [1972]; *Duce et al.* 1973] and some spatial variations in these amounts [*Rahn et al.*, 1976; *Cicerone*, 1981]. Later, several specific organic bromine gases (RBr) were detected and measured in tropospheric samples, including CH_3Br , $\text{C}_2\text{H}_4\text{Br}_2$, CF_3Br , and CF_2Br_2 [*Singh et al.*, 1983; *Cicerone*, 1981]. Recently, CHBr_3 and CH_2Br_2 have also been measured. To our knowledge, no inorganic gaseous species of bromine has yet been detected in the troposphere by species-specific methods; only measures of total inorganic bromine (BrX) are available. Few if any theoretical studies have been performed on the roles and behavior of bromine in the troposphere.

Stratospheric bromine has attracted more interest because of the potential role of BrX as an ozone-destroying catalyst [*Watson*, 1975; *Wofsy et al.*, 1975; *Yung et al.*, 1980]. Recent models continue to indicate that as little as 20 parts per trillion (ppt) by volume of BrX can affect ozone significantly [*Prather et al.*, 1984; *Rodriguez et al.*, 1986]. Very few data are available on stratospheric bromine amounts, but a few model calculations have attempted to estimate stratospheric bromine concentrations from known sources or from tropospheric concentrations of RBr species. RBr species measured in the stratosphere include CF_3Br [*Fabian et al.*, 1981], CBrClF_2 [*Lal et al.*, 1985], two samples for several RBr species by *Berg et al.* [1984] and our own Arctic and Antarctic profiles of CH_3Br and CHBr_3 , which will be included in a future publication.

To further our understanding of atmospheric bromine, both tropospheric and stratospheric, a much more detailed inventory is needed for the source gases, tropospheric RBr species: concentrations, spatial patterns, and temporal variability and trends. Recent exploratory studies [*Berg et al.*, 1984; *Penkett et al.*, 1985; *Class et al.*, 1986] have presented measurements of several bromomethanes and bromoethanes, including CHBr_3 and some mixed

bromochlorocarbons. Bromoform (CHBr_3) mixing ratios varied over more than 2 orders of magnitude in the data of these three groups of authors. *Berg et al.* were first to measure CHBr_3 ; they obtained about 35 individual data points from Arctic latitudes to altitudes of about 4 km and at various longitudes. *Penkett et al.* measured CHBr_3 in about 20 samples that were gathered through shipboard sampling from 50°N to 75°S . All of their CHBr_3 mixing ratios were less than 6 ppt and most were below 2 ppt. *Class et al.* measured several bromomethanes, bromochloromethanes, and iodomethanes in air, rain, and seawater samples that were collected between mid-1982 and late 1985. *Class et al.* analyzed about 45 air samples for CHBr_3 and found volume mixing ratios between 0.6 and 450 ppt, with most values near 2 ppt.

In this paper we summarize the results of approximately 750 measurements of CH_3Br and 990 measurements of CHBr_3 .

SAMPLING AND ANALYSIS

In 1984 we began to collect and analyze air samples weekly from each of five surface sampling sites with the following latitudes, longitudes, and elevations above sea level: Point Barrow, Alaska (71.3°N , 156.6°W , 0 km), Mauna Loa Observatory, Hawaii (19.5°N , 155.6°W , 3.4 km), Cape Kumukahi, Hawaii (19.4°N , 154.8°W , 0 km), Cape Matatula, Samoa (14.3°S , 170.6°W , 0 km), and Kaitorete Spit, New Zealand (43.8°S , 172.6°E , 0 km). We collect whole-air samples in electropolished 2.5-L stainless steel canisters with bellows-sealed valves. All components are welded, to eliminate all polymers and lubricants which can absorb and adsorb trace gases. Following high-temperature bakeout, each of the canisters is filled with a moist air sample, allowed to equilibrate several hours, and then evacuated while being warmed to 80°C . This conditioning process is repeated at least 6 times before final storage at less than 10^{-6} torr until use. Further details of canister preparation and sample-handling techniques have been published earlier [*Heidt and Ehhalt*, 1972; *Heidt*, 1978].

All samples are analyzed with a Hewlett-Packard Model 5985 Gas chromatograph/mass spectrometer operated in the single-ion monitoring mode with electron-impact ionization. Masses monitored were CH_3Br (94, 96) and CHBr_3 (171, 173, 175). A fused silica column 30-m

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Paper number 8D0077.
0148-0227/88/008D-0077\$05.00

long x 0.255-mm OD (J. and W. Scientific) with a bonded, nonpolar silicone phase (1.0 μm) accomplishes the trace gas separations. The temperature profile for sample analysis is -25°C for 1 min, programmed temperature elevation at $15^\circ\text{C}/\text{min}$ up to 150°C , and maintenance of 150° for 20 min. Approximately 1000 mL of sample is 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 carryover of one sample to the next, the sample loops are heated during evacuation between sample runs. Initially, blank tests were run by purging with purified helium using the same preconcentration techniques employed for samples. However, since September 1984, we have used moist zero air, which better simulates a clean atmospheric sample and has proven to be more efficient in lowering the system background.

A standard mixture containing five organic bromine gases including CH_3Br and CHBr_3 (prepared by Scott Specialty Gases) has been used for sample quantification. The manufacturer allowed the mixture to equilibrate for approximately 1 month before analyzing and assigning absolute concentrations. Our own attempts to prepare absolute mixtures of CH_3Br have confirmed the necessity for an equilibration period. Aliquots of this mixture, stored in our sample containers, have been compared to the original mixture and each other to determine storage integrity. An additional gas mixture containing CH_3Br and chlorofluoromethanes (also prepared by Scott Specialty Gases) is used to corroborate the absolute concentration of CH_3Br in the original mixture and to monitor storage stability. Systematic comparisons of the two commercial mixtures from late 1984 through late 1987 have measured CH_3Br ratios of (1.00 ± 0.03) times the expected ratio, indicating no change in concentration in this 3-year period. The absolute value and stability of CHBr_3 in the original mixture are monitored through similar comparisons with mixtures prepared in our laboratory. The analytical error for sample analyses using these standards (a combination of known instrumental errors and precision based on repetitive measurements) is estimated to be 15% or less.

TABLE 1. Means and Standard Deviations of CH_3Br Measurements

Station	Time Period	<i>N</i>	Mean, ppt	s.d.
BRW	Jan. 1985 to Oct. 1987	212	11.14	2.50
	I	93	11.40	2.63
	II	119	10.93	2.38
MLO	Jan. 1985 to Oct. 1987	124	10.78	2.20
	I	75	10.92	2.30
	II	49	10.57	2.05
KUM	Jan. 1985 to Oct. 1987	139	11.35	2.59
	I	88	10.98	2.07
	II	51	12.00	3.22
SMO	Jan. 1985 to Oct. 1987	135	10.21	2.49
	I	78	10.03	2.12
	II	57	10.46	2.92
NZD	Jan. 1985 to Sept. 1987	139	9.58	2.14
	I	74	9.51	1.87
	II	65	9.66	2.41

The first 17 months, January 1985 to May 1986, are denoted as time period I, and the second period of 17 months, June 1986 to October 1987, is denoted as time period II; s.d., standard deviation; BRW, Pt. Barrow; MLO, Mauna Loa Observatory; KUM, Cape Kumukahi; SMO, Samoa; NZD, New Zealand.

TABLE 2. Monthly Averages of Methyl Bromide (CH_3Br) Mole Fractions Measured in Air at Five Sites, 1985–1987

Year	Month	BRW	MLO	KUM	SMO	NZD
1985	Jan.	10.6	13.0	12.3	12.3	8.5
	Feb.	11.3	13.3	10.5	12.0	8.5
	March	10.1	8.8	8.8	9.4	9.6
	April	12.0	9.4	10.5	9.5	8.4
	May	12.1	9.7	11.9	9.1	8.6
	June	8.5	10.1	10.5	8.3	8.0
	July	9.2	7.8	8.6	12.0	8.6
	Aug.	8.4	9.5	ND	ND	ND
	Sept.	10.6	11.1	11.9	9.2	8.9
	Oct.	10.1	11.0	11.8	10.3	10.0
	Nov.	10.5	10.6	10.2	10.2	8.9
	Dec.	10.5	9.9	9.4	9.0	ND
1986	Jan.	11.0	10.7	11.5	9.4	9.2
	Feb.	11.9	10.4	12.1	8.7	8.7
	March	13.8	11.5	10.9	11.2	9.1
	April	15.1	13.5	13.3	11.5	11.8
	May	13.0	11.2	10.9	9.8	10.9
	June	14.9	12.3	13.3	13.3	12.0
	July	11.2	10.3	16.3	11.9	12.0
	Aug.	10.3	10.6	12.5	8.5	8.1
	Sept.	9.9	12.2	12.0	10.9	11.5
	Oct.	11.6	11.6	13.0	10.2	10.3
	Nov.	10.8	13.8	13.4	14.4	10.3
	Dec.	12.4	11.8	12.6	11.6	10.6
1987	Jan.	12.2	10.5	12.6	11.7	13.7
	Feb.	11.7	11.2	11.2	10.8	9.4
	March	11.7	9.7	10.5	9.0	8.8
	April	12.1	9.0	9.8	9.7	7.9
	May	10.8	8.8	10.3	8.0	6.9
	June	8.5	9.0	7.5	7.9	6.9
	July	7.6	7.5	7.9	7.8	7.9
	Aug.	8.9	ND	ND	ND	9.0
	Sept.	9.8	ND	ND	ND	8.6
	Oct.	9.3	9.4	11.5	9.6	ND

BRW, Pt. Barrow; MLO, Mauna Loa Observatory; KUM, Cape Kumukahi; SMO, Samoa; NZD, New Zealand. Units are mole fractions in parts per trillion (10^{-12}). ND means no data available.

RESULTS AND DISCUSSION

Results of CH_3Br measurements are summarized in Tables 1 and 2. In Table 1 we show the number *N* of samples from each site and the mean value and standard deviation in parts per trillion by volume (pptv) for CH_3Br . For each of these quantities we present values for the entire measurement period (34 months for each station, except New Zealand's 33 months) and separate values for the first 17-month period (January 1985 to May 1986) and for the second 17-month period (June 1986 to October 1987). The two southern hemispheric sites have consistently lower CH_3Br concentrations, although their mean values are not separated from those of the northern hemisphere stations by a full standard deviation.

For each of five sampling sites, the measured monthly averaged CH_3Br mole fraction is in Table 2, listed for each month from January 1985 through October 1987. These monthly averages were calculated from all available data points for each month, generally two to eight points for each site. A full listing of the individual data points is to be published elsewhere and will be available upon request. Where "ND" appears in Table 2, no data are available, either because no samples were gathered or because samples were demonstrably polluted (as evidenced

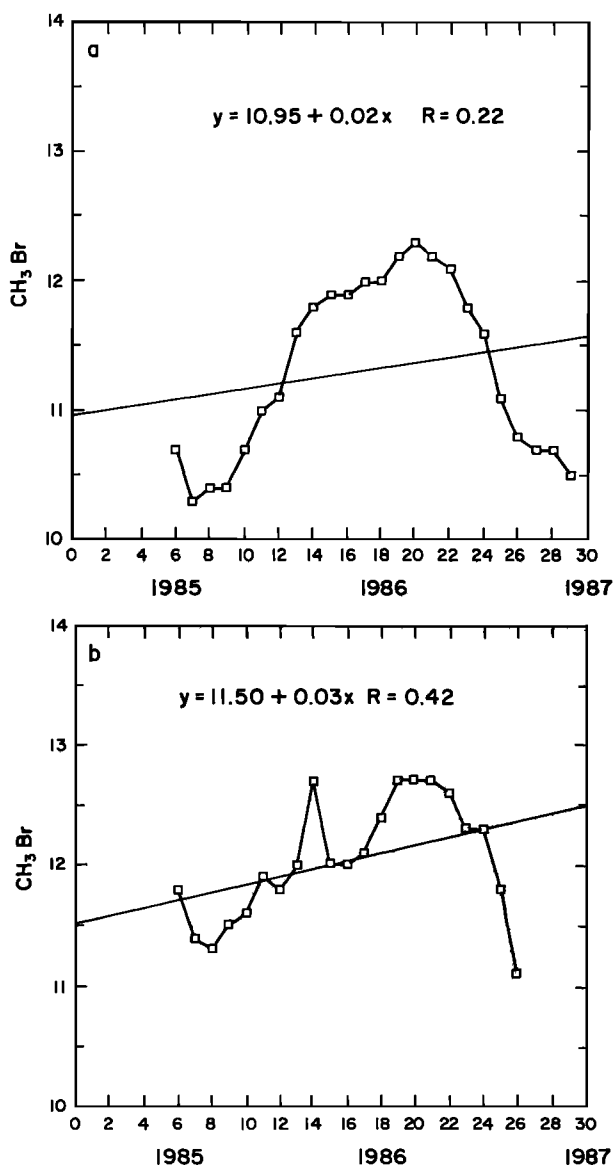


Fig. 1. Twelve-month running averages of CH_3Br mole fractions ($\text{ppt} = 10^{-12}$) measured at (a) Point Barrow, Alaska, and (b) Cape Kumukahi, Hawaii, during a 34-month period that began in January 1985. Equations for regression-line fits to the data are displayed in each panel; slopes are measured in ppt per month. R values are correlation coefficients.

by high concentrations of benzene, toluene, or methyl chloroform) or due to an identified problem in a particular analysis. During the summer of 1987, only Point Barrow and New Zealand sample analysis could be maintained because of other conflicting demands on our time.

Figures 1a and 1b display filtered CH_3Br data, i.e., 12-month running means of the data from Table 2. For each of two sites (Point Barrow and Cape Kumukahi) a regression line has been fit to the data; the lines shown are best fits in the sense of minimizing the squared differences of individual 12-month averages with the line.

With this kind of smoothing of the data, best fit regression lines yield correlation coefficients of only 0.22 and 0.42, respectively. Similar graphs of 12-month running means for CH_3Br at Mauna Loa, Samoa, and New Zealand

all display similar positive-slope regression lines; slopes are 0.05, 0.08 and 0.05 ppt per month, respectively, with higher correlation coefficients of 0.55, 0.79 and 0.50. It should be noted that all five stations display more convincing positive trends if the data had stopped in June or earlier in 1987. This is because rather low CH_3Br mixing ratios were measured at all five stations in the most recent months; see Table 2. When we analyze data only through May of 1987, the 12-month running mean graphs give slopes of +0.08 to +0.14 ppt per month, with correlation coefficients between 0.78 and 0.94.

A second way to look for possible CH_3Br trends is to examine the deviations from the overall mean over the measurement period. In Figure 2 we plot the differences of 3-month averages (i.e., January, February, and March; April, May, and June; July, August, and September; October, November, and December) of CH_3Br from the 34-month means at each location. In general, these deviations are negative at each station during 1985, they are significantly positive in 1986, and they are negative in 1987. Thus if one looks only at the 1985 and 1986 data, for example, one concludes that CH_3Br concentrations grew significantly. The decreases in 1987 change this conclusion.

The similarities in the temporal behavior of the CH_3Br deviations from the means at each station lead one to ask if perhaps time-dependent drifts in our system calibration for CH_3Br could be involved. Such hypothetical drifts would have had to change signs at least twice during the 34-month period. To confront this possibility, we consider two types of tests: (1) ratios of measured CH_3Br amounts in two differently prepared and stored commercial standards, and (2) comparison of raw mass spectrogram peak areas from gas chromatograph/mass spectrometer (GC/MS) analyses of our calibration tanks, with results from our analysis of environmental CH_3Br samples as a function of time in the 34-month period. As to test 1, we stated earlier that analyses of the separate standards have yielded ratios within 3% of the expected stable ratios in our tests. Under test 2, we have examined the GC/MS peak areas for analyses of calibration mixtures and the results of sample analyses that were performed using the instrument-sensitivity factors deduced from the peak areas for standards. We found no apparent correlation between excursions in CH_3Br sample concentrations and the GC/MS response factors; in this search we compared several hundred analysis runs for various stations from sample dates in 1985, 1986 and 1987. On the basis of tests 1 and 2, we conclude that the temporal changes in the CH_3Br deviations in Figure 2 are real, i.e., that CH_3Br concentrations generally increased in 1986 and decreased in early and mid-1987. The maintenance of stable calibration standards is nontrivial and ppt analysis is always difficult, but our evidence shows that our CH_3Br results cannot be explained by calibration or analysis drifts. Further, no such questions have arisen in our CHBr_3 work.

Considering the present data, what can be said about CH_3Br temporal trends? While regression lines that are fit to 12-month running means of CH_3Br give slight indications of increases from January 1985 through October 1987, two other indicators show no sustained increase. Table 1 shows that when we divided the data into the first half of the 34-month period and the second half, the differences between the means for the two subperiods were

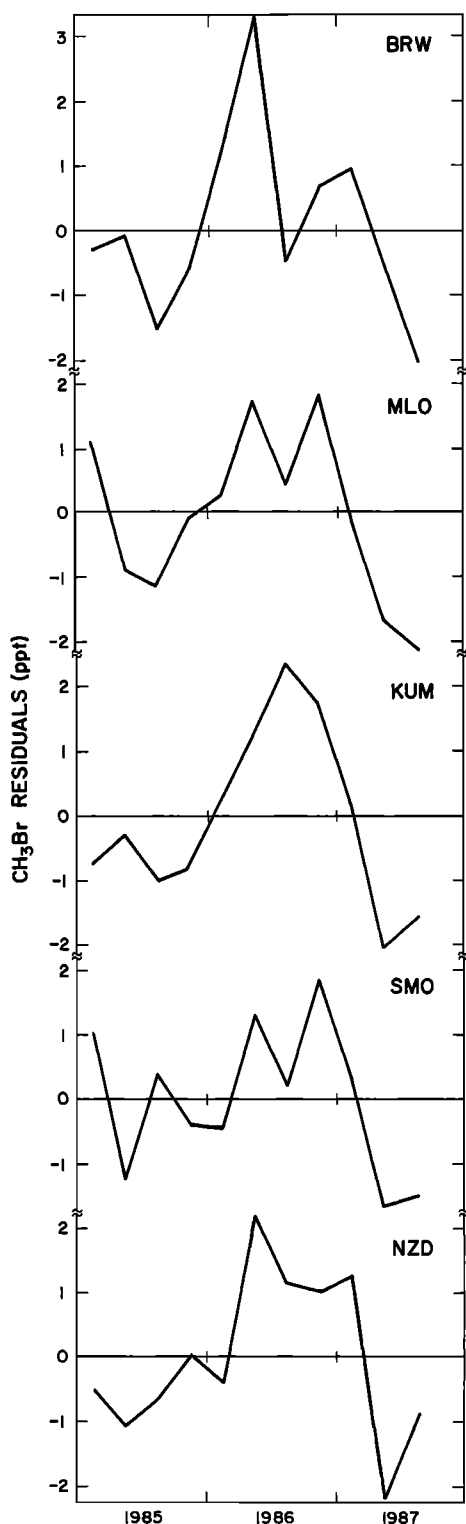


Fig. 2. CH_3Br residuals (differences of 3-month averages minus the 34-month mean) plotted for each quarter of the years 1985 and 1986 and for the first three quarters of 1987, for the five measurement locations defined in Table 2.

insignificant. Also, the analysis of residuals in Figure 2 shows no sustained trend, only interannual variability. In the coming months we shall see if late 1987 and early 1988 CH_3Br concentrations remain low or increase. A longer data record and the application of a variety of trend-detection schemes are needed.

Previous data on atmospheric CH_3Br include those of Singh *et al.* [1983] by electron-capture gas chromatographic analysis and the analysis of elemental bromine in (1) samples of total gaseous bromine [Moyers and Duce, 1972; Duce *et al.*, 1973] and in (2) samples of organic gases [Rahn *et al.*, 1976]. Singh *et al.* reported almost 50 data points, for which the average concentration of CH_3Br was 23 ppt, about twice our average values. Rahn *et al.* found values of 14 to 68 ngBr/m^3 STP in 16 samples; if this Br was entirely in CH_3Br (reasonable for 1974) this range translates to 4–19 ppt CH_3Br . Their mean concentration was 8 ppt. Rahn *et al.* also showed that the amount of organic gaseous Br was typically 5 times the amount of inorganic gaseous Br. With this ratio we can infer that the total gaseous bromine data of Moyers and Duce [1972] could have been due to about 13 ppt CH_3Br in Hawaii and 2 ppt in Antarctica [from Duce *et al.*, 1973].

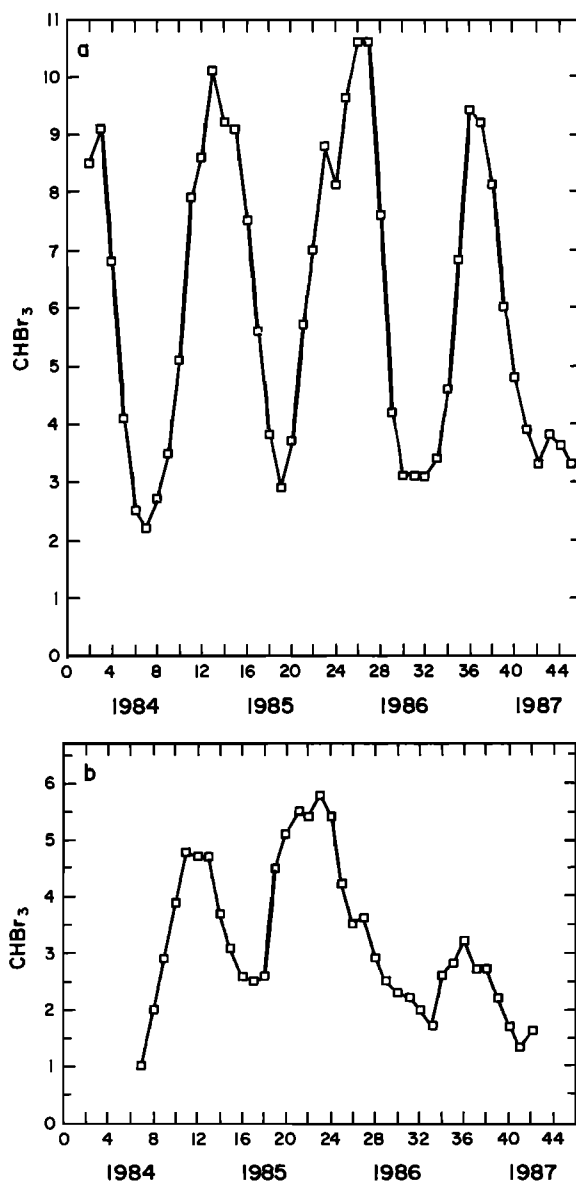


Fig. 3. Bromoform (CHBr_3) mole fractions (in ppt) measured at (a) Point Barrow, Alaska, and (b) Cape Kumukahi, Hawaii, from early 1984 through September 1987. The points shown are 3-month running averages.

Bromoform (CHBr_3) data are displayed in Figures 3a and 3b for two locations. Data from 1984 are included here along with 1985 through September 1987. Strong seasonal cycles are apparent in these graphs (3-month running averages). Bromoform concentrations are maximum in December, January and February each year and are least in June, July, and August. This is clearer for Point Barrow than for Cape Kumukahi. The average CHBr_3 concentration is about 6.3 ppt at Point Barrow and 3.1 ppt at Cape Kumukahi. Aside from the seasonal cycle, no temporal trend is apparent.

The cause or causes of these seasonal variations in CHBr_3 concentrations are not clear. Wintertime maxima in sources of bromoform or summertime maxima in bromoform sinks (OH radical concentrations and solar UV irradiance) are obvious candidates. To the extent that the observed CHBr_3 decrease after the December–January–February peak at Point Barrow each year is due to photochemical decomposition of CHBr_3 , this source of gaseous Br atoms and BrO radicals should be investigated. Gaseous inorganic bromine could serve as an important tropospheric oxidant, and it could be involved in ozone photochemistry. Photochemical data indicates a several-week photochemical lifetime for CHBr_3 in the troposphere, but its photoabsorption cross section is presently uncertain at wavelengths longer than 305 nm.

In future publications, we will report the results more fully for each of the five sampling sites as well as data for CH_2Br_2 , $\text{C}_2\text{H}_5\text{Br}$, and $\text{C}_2\text{H}_4\text{Br}_2$. We also intend to continue this bromine-monitoring investigation.

Acknowledgments. We thank the personnel of the Geophysical Monitoring for Climate Change program of the National Oceanic and Atmospheric Administration for collecting samples for us at BRW, KUM, MLO, and SMO. Marcel Verstraete of NCAR and Sharyn Latchford of the New Zealand Meteorological Service have collected our NZD samples. Richard Lueb developed the analytical systems used; Bruce Henry and Curt Gilliland provided competent computer programming and data processing. S. C. Wofsy provided helpful discussion. The National Center for Atmospheric Research is sponsored by the National Science Foundation.

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(Received October 30, 1987;
revised January 20, 1988;
accepted January 20, 1988.)