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# Unexplained enhancements of $CH_3Br$ in the Arctic and sub-Arctic lower troposphere during TOPSE spring 2000

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[1] Elevated concentrations of methyl bromide ($CH_3Br$) were observed in the Arctic atmospheric boundary layer (BL) during periods of widespread BL ozone ($O_3$) depletion episodes (ODEs: $O_3$ mixing ratios $< 20 \times 10^{-9}$ or parts per billion by volume, ppbv) particularly during major ODEs (MODES: $O_3 < 4$ ppbv). No other organic gases measured during TOPSE (Tropospheric Ozone Production about the Spring Equinox) exhibited anti-correlations with $O_3$ during these ODEs. Methyl bromide has both natural and anthropogenic sources and contributes ~ half of the bromine (Br) to the stratosphere, where it can catalytically destroy $O_3$. Several known $CH_3Br$ sources are evaluated, but the current knowledge cannot explain the observed enhancements. If the mechanism is direct gas-phase photochemical production, a significant portion of the unknown $CH_3Br$ source may be found. *INDEX TERMS:* 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0317 Atmospheric Composition and Structure: Chemical kinetic and photochemical properties; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry. **Citation:** Wingenter, O. W., B. C. Sive, D. R. Blake, F. S. Rowland, and B. A. Ridley, Unexplained enhancements of $CH_3Br$ in the Arctic and sub-Arctic lower troposphere during TOPSE spring 2000, *Geophys. Res. Lett.*, *30*(22), 2160, doi:10.1029/2003GL018159, 2003.

## 1. Introduction

[2] Springtime Arctic ODEs have been the subject of several studies [e.g., *Barrie et al.*, 1988; *Bottenheim et al.*, 1990; *Jobson et al.*, 1994; *Hausmann and Platt*, 1994; *Ridley et al.*, 2003]. Background $O_3$ mixing ratios in the arctic BL are typically 30 to 50 ppbv. During ODEs, $O_3$ observations at surface sampling sites typically drop to 1 ppbv or less within a few hours. Observation of the rapid decay of nonmethane hydrocarbons and halocarbons, and direct observation of halogen oxides indicate that chlorine and bromine chemistry are responsible for the ODEs. The halogen atom sources are not fully understood. However, photolysis of halocarbons alone can not produce sufficient Br and Cl atoms needed for ODEs [*Yokouchi et al.*, 1994]. Recent studies suggest halogen atoms are generated on sea snow and ice [*Tang and McConnell*, 1996; *Adams et al.*, 2002], and recycled on sulfate aerosols [*Sander et al.*, 1997].

[3] Methyl bromide has both natural and anthropogenic sources with most of the latter emissions occurring in the northern hemisphere (NH). The concentration of $CH_3Br$ in the NH has a strong seasonal dependence, particularly at high latitudes [*Wingenter et al.*, 1998; *Yokouchi et al.*, 2002]. The seasonally averaged global tropospheric mixing ratio of $CH_3Br$ in 2000 was $9 \times 10^{-12}$ (parts per trillion by volume, pptv) [*Montzka et al.*, 2003] and has been declining in recent years [*Yokouchi et al.*, 2002; *Montzka et al.*, 2003] because of decreased anthropogenic usage mandated by international agreements. A comparison of the known sources with known loss processes indicates that sources of about 40% (~80 kt $y^{-1}$) of the atmospheric $CH_3Br$ burden are still unknown [*WMO*, 1999]. The observed interhemispheric ratio (N/S) of $CH_3Br$ suggests that a substantial fraction of the unknown sources must exist in each hemisphere [*Lee-Taylor et al.*, 1998; *Reeves*, 2003]. The estimated $CH_3Br$ lifetime is about 0.7–0.8 years [*WMO*, 1999], sufficiently long that a significant amount is transported to the stratosphere. Once there, $CH_3Br$ can release Br atoms, which can then catalytically destroy $O_3$ in cycles involving chlorine monoxide and hydrogen peroxy radicals [*WMO*, 1999]. Bromine atoms are about 50 times more reactive than Cl atoms in destroying ozone [*WMO*, 1999]. Therefore, small amounts of Br can have a significant impact on stratospheric $O_3$ levels.

## 2. Experimental

[4] The National Science Foundation TOPSE experiment was conducted from early February through late May 2000 [*Atlas et al.*, 2003]. The National Center for Atmospheric Research C-130 aircraft payload consisted of a suite of chemical and photochemical instruments critical to the evaluation of the winter-spring transition in the northern mid-to-high latitude troposphere. We collected 1403 whole air samples north of 57°N latitude aboard the C-130 during 30 science flights that each lasted ~ eight hours. Of these samples, 241 were collected coincident with $O_3$ measurements at latitudes greater than 57°N and at

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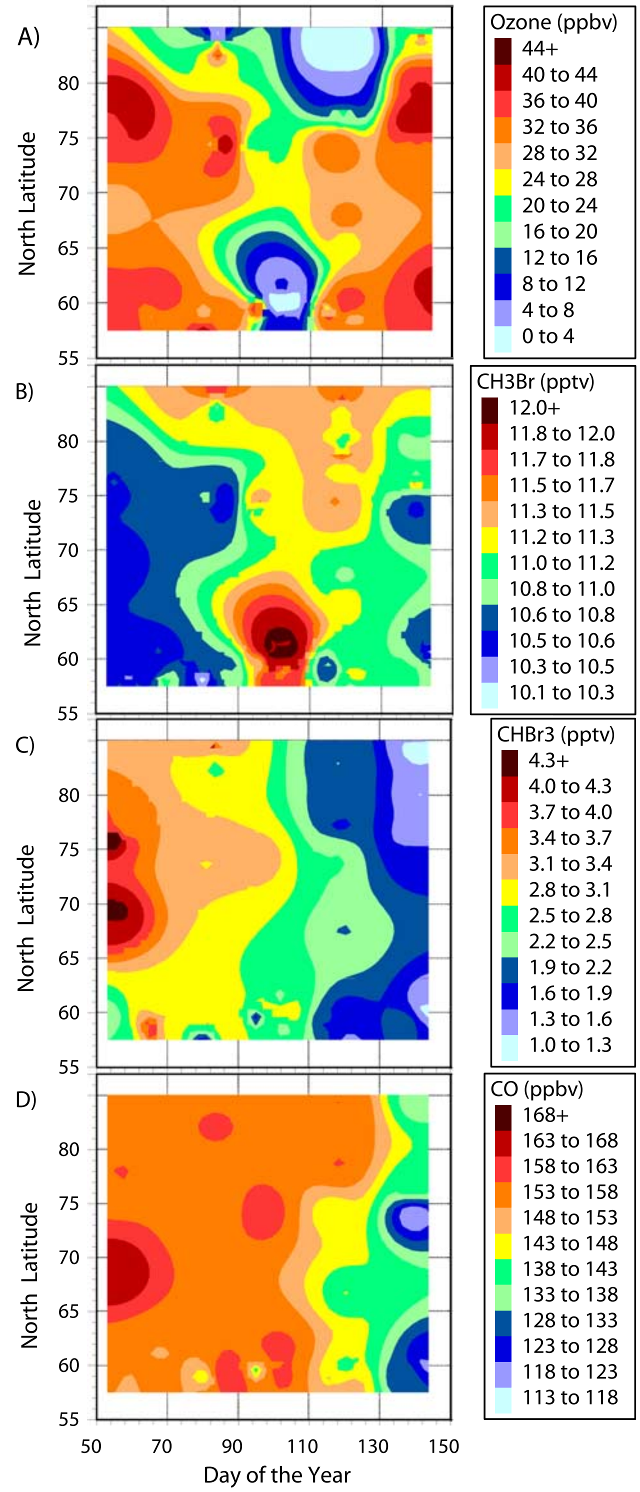

**Figure 1.** Color contour plots of A) $O_3$, B) $CH_3Br$, C) $CHBr_3$, and D) CO from measurements <300 m and north of 57°N.

altitudes less than 300 m. Air samples were collected throughout each flight into individual conditioned, evacuated 2-L stainless steel canisters. The average sampling duration lasted ~1 minute.

[5] After each flight, the filled canisters were transported back to the University of California, Irvine, and within 10 days of sample collection were analyzed for 60 hydrocarbons, halocarbons, alkyl nitrates, organic sulfur compounds, and carbon monoxide (CO). The mixing ratios of these organic gases were quantified using gas chromatography (GC) with flame ionization detection (FID), electron capture detection (ECD), and mass spectrometric detection (MSD) [*Colman et al.*, 2001]. Methyl bromide was always well above its limit of detection (LOD = 1 pptv) as were $CH_3I$ (0.03 pptv), $CH_3Cl$ (5 pptv), $CH_3ONO_2$ (0.01 pptv), $CH_2Cl_2$ (0.1 pptv) and CO (3 ppbv). Methyl bromide, $CH_3Cl$, $CH_2Cl_2$, and CO had measurement precisions of 2%. The precision for $CH_3I$ was 3% or 0.001 pptv (whichever is larger) and 5% or 0.005 pptv for $CH_3ONO_2$. Ozone measurements were made with a 1-sec response time aboard the aircraft by a chemiluminescence technique with a precision of 1% and estimated uncertainty of 5% [*Ridley et al.*, 1992]. The data are available at http://topse.acd.ucar.edu.

## 3. Results and Discussion

[6] For the purpose of making qualitative comparisons between the distributions of $O_3$ and $CH_3Br$, color contour plots were computed. (When viewing these plots, keep in mind that data for certain areas were interpolated and that maxima or minima should be compared.) Mixing ratios versus day of the year (DY) and latitude, for samples collected below 300 m, are presented for $O_3$ in Figure 1A and for $CH_3Br$ in Figure 1B. Severe $O_3$ loss was observed over widespread areas, particularly during DY 83, 101, and 118 (flights 21, 29, and 34). During these flights $CH_3Br$ was enhanced significantly relative to background levels. The

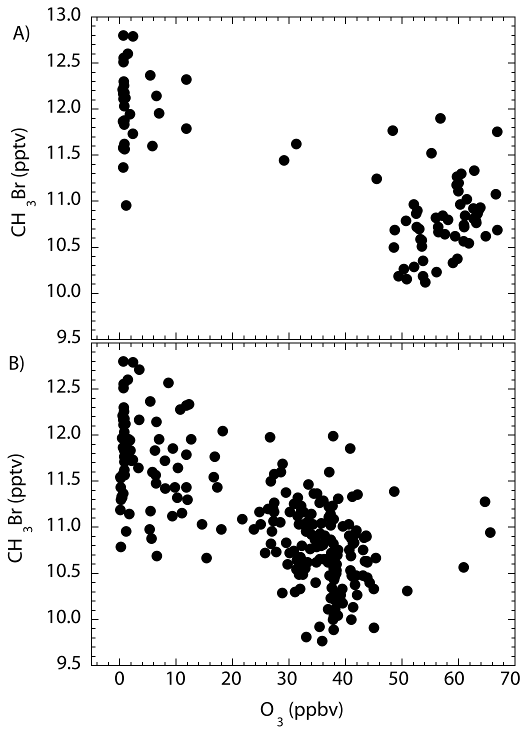

**Figure 2.** Correlation of $O_3$ and $CH_3Br$ A) all samples collected during flight 29 (altitudes ranging from about 30 m to 4600 m) B) from all on samples collected below 300 m and north of 57°N.

**Table 1.** Statistical data for $CH_3Br$ for all measurements made during flight 29 and all measurements made below 300 m during the TOPSE campaign, north of 57°N during low ($O_3 < 20$ ppbv) and high ($O_3 > 20$ ppbv) $O_3$ regimes.

| | Flight 29 | | All Data Below 300 m | |
|---|---|---|---|---|
| $CH_3Br$ (pptv) | low $O_3$ | high $O_3$ | low $O_3$ | high $O_3$ |
| No. of Measurements | 30 | 61 | 79 | 162 |
| Mean | 12.00 | 10.83 | 11.73 | 10.78 |
| Standard Deviation | 0.35 | 0.41 | 0.50 | 0.43 |
| Std Dev of Mean | 0.06 | 0.05 | 0.06 | 0.03 |

largest enhancements of $CH_3Br$ were observed during flight 29. This episode was observed on DY 101 near 60°N over Hudson Bay, Canada, and its extent was at least 600 km.

[7] The correlation of $CH_3Br$ and $O_3$ for altitudes ranging from about 30 m to 4600 m during flight 29 clearly shows two separate distributions corresponding to background $O_3$ and $CH_3Br$ mixing ratios (Figure 2A) and times when $O_3$ was depleted and $CH_3Br$ was elevated. A similar correlation using all of the samples collected north of 57°N and below 300 m during the campaign also has two distinct distributions (Figure 2B). When the flight 29 $CH_3Br$ data are divided into two groups, one corresponding to high $O_3$ (>20 ppbv) and the other low $O_3$ (<20 ppbv), the two distributions have a 1.2 pptv difference (Table 1). Application of the Student's t test indicates that the two distributions during flight 29 are considered to be different (>99.9% confidence level). When the $CH_3Br$ data from all samples collected north of 57°N below 300 m are similarly divided into two groups corresponding to high and low $O_3$, the two means differ by 0.95 pptv and again are significantly different (>99.9%). Overall, the $CH_3Br$ mixing ratios are significantly higher in regions where surface $O_3$ was depleted than in regions where $O_3$ was at background levels.

[8] The source of the $CH_3Br$ enhancements during ODEs is unknown. Four possibilities are examined here. First, the $CH_3Br$ could be emitted from the ocean. Methyl bromide, methyl iodide ($CH_3I$), bromoform ($CHBr_3$) and other methyl halides are produced by marine micro and macroalgae [*Tokarczyk and Moore*, 1994; *Laturnus*, 1996]. Elevated amounts of $CHBr_3$ have been associated with air masses which have traveled over openings in the Arctic sea ice [*Sturges et al.*, 1993] and ODEs appear to occur only when air masses have recently spent time over the Arctic Ocean sea ice [*Anlauf et al.*, 1994; *Ridley et al.*, 2003]. At times, ODEs have coincided during periods of elevated $CHBr_3$ [*Bottenheim et al.*, 1990; *Sturges et al.*, 1993; *Yokouchi et al.*, 1994]. The mechanisms for ozone depletion in the Arctic BL and the marine emissions of methyl halides are quite dissimilar and any link may be a result of air masses having contact with both source regions. However, during the TOPSE flights where enhancements of $CH_3Br$ were observed, no other trace gas with a marine origin, such as $CHBr_3$, $CH_3I$, and $CH_3Cl$, was elevated (Figures 1C, 1SA[1] and 1SB[1]). Furthermore, during the MODEs observed on flights 21, 29, and 34, which coincided with elevated $CH_3Br$, no open ocean areas were observed [*Ridley et al*, 2003; Figure 2S[1]].

[9] Another possibility is the production of $CH_3Br$ in the Arctic surface snow or on aerosols. Recent experiments in the surface snow in Greenland show that $CH_3Br$ is produced in snow, but not exclusively, and that $CH_3I$ (Figure 1SA[1]) and $CH_3ONO_2$ (Figure 1SC[1]) have similar or greater production rates [*Swanson et al.*, 2002]. In our study, the lack of enhancement of the concentrations of these gases relative to $CH_3Br$ enhancements indicate that production in surface snow is unlikely to be the source of the elevated $CH_3Br$ during ODEs. However, the composition of the snow and ice in the Canadian Arctic is likely different from that at Summit, Greenland. Production of $CH_3Br$ on aerosols has yet to be reported.

[10] A third possibility is that the enhanced $CH_3Br$ encountered during TOPSE could be of urban origin [*WMO*, 1999]. However, contours of the urban tracers CO (Figure 1D) and dichloromethane ($CH_2Cl_2$) (Figure 1SD[1]) illustrate that their mixing ratios were not enhanced during the ODEs. Data for all quantified urban tracers indicate that recent urban emissions were not the source of $CH_3Br$ enhancements observed during the low $O_3$ events of TOPSE. Moreover, back trajectories for flights 21, 29 and 34 (Figure 3S[1]) indicate that within the last 10 days the sampled air masses had not passed over any urban areas and that the air masses had spent the last ten days either over Greenland, the Arctic, or Hudson Bay. Furthermore, observation of $CH_3Br$ between 300 and 1000 m supports the conclusion that advection is not the source of the $CH_3Br$ enhancements below 300 m in the TOPSE study area (Figure 4S[1]).

[11] A fourth possible source is the gas-phase production of $CH_3Br$ from the reaction of methyl peroxy radical ($CH_3O_2$) with bromine monoxide (BrO) or Br.

$$\text{(R1)} \qquad CH_3O_2 + BrO \rightarrow CH_3Br + O_3$$

$$\text{(R2)} \qquad CH_3O_2 + Br \rightarrow CH_3Br + O_2$$

High levels of atomic Cl, Br and BrO have been reported at the surface during Arctic sunrise [e.g., *Jobson et al.*, 1994; *Hausmann and Platt*, 1994]. Atomic Cl is the dominant oxidizing agent of methane during these periods, which leads to the production of $CH_3O_2$. The formation of $CH_3Br$ by R1 is thermodynamically favorable by 7.5 ± 1.4 kcal $mol^{-1}$, and R2 by 37.9 ± 1.3 kcal $mol^{-1}$ [*Sander et al.*, 2003].

[12] The overall rate constants for the reactions of $CH_3O_2$ with BrO ($k1_{total} = 5.7 \times 10^{-12}$ $cm^3$ $molecule^{-1}$ $s^{-1}$) and Br ($k2_{total} = 4.4 \times 10^{-13}$ $cm^3$ $molecule^{-1}$ $s^{-1}$) at 298 K have been measured [*Aranda et al.*, 1997, 1998]. In these studies $CH_3Br$ was not reported as a product. However, only small branching ratios are needed to produce the observed $CH_3Br$ enhancement via the $CH_3O_2$ and BrO and Br reactions. These branching ratios are estimated to be on the order of 1 in 1000 to 1 in 20, respectively for R1 and R2, based on results employing a photostationary state point model, which includes halogen chemistry [*Davis et al.*, 1996].

[13] Recent comparisons of balloonborne Differential Optical Absorption Spectroscopy measurements with those

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[1] Auxiliary material is available at ftp://ftp.agu.org/apend/gl/2003GL018159.

made aboard the Global Ozone Monitoring Experiment satellite indicate that a substantial portion of the vertical column of BrO must reside in the free troposphere. This suggests that BrO is ubiquitous throughout the global sunlit troposphere, with approximate mixing ratios of 1–2 pptv [*Fitzenberger et al.*, 2000]. If we assume an average tropospheric mixing ratio of BrO of 1.5 pptv, estimate a concentration of $1 \times 10^7$ $CH_3O_2$ $cm^{-3}$ from *Logan et al.* [1981], and use a 1/1000 branching ratio ($5.7 \times 10^{-15}$ $cm^3$ $molecule^{-1}$ $s^{-1}$), we arrive at a yearly global tropospheric production on the order of 40 kt of $CH_3Br$ produced annually via R1.

[14] At this time the source of the $CH_3Br$ enhancements observed in the Arctic and subarctic are unknown. If photochemical production of $CH_3Br$ is the source of the enhancements over the Arctic during the springtime, this mechanism could be a significant tropospheric global source of $CH_3Br$ with fairly equal production in the northern and southern hemispheres. Further laboratory studies, which look specifically for $CH_3Br$ as a product in reactions R1 and R2, are suggested. Chemical tracer model simulations employing these reaction rates, if merited, will yield a more accurate production estimate of photochemically-produced $CH_3Br$.

[15] **Acknowledgments.** Dedicated to our friend and colleague Murray McEachern. We thank each member of the NMIMT, UCI, and NCAR teams for their outstanding contributions.

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