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Methyl bromide cycling in a warm-core eddy of the North Atlantic Ocean

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We conducted a detailed investigation of the evolution of methyl bromide concentrations, degradation rates, and ventilation rates for 26 days in a naturally contained, warm-core eddy of the North Atlantic Ocean. This is the first study of the oceanic cycling of methyl bromide in a natural, contained system with a complete suite of supporting measurements of physical and chemical variables. Methyl bromide concentrations in the mixed layer ranged from 2.3 to 4.2 nmol m\(^{-3}\), degradation rates ranged from 0.1 to 0.9 nmol m\(^{-3}\) d\(^{-1}\), net sea-to-air exchange rates ranged from 0 to 0.5 nmol m\(^{-3}\) d\(^{-1}\), and net loss rates through the thermocline were less than 0.1 nmol m\(^{-3}\) d\(^{-1}\). From a mass balance for methyl bromide in the mixed layer, we calculated production rates ranging from <0.1 to 1.3 nmol m\(^{-3}\) d\(^{-1}\). The median of this range, 0.48 nmol m\(^{-3}\) d\(^{-1}\), is higher than the ~0.15 nmol m\(^{-3}\) d\(^{-1}\) necessary to maintain the reported global oceanic emission of 56 Gg yr\(^{-1}\). This is reasonable, because our study area was supersaturated in methyl bromide, whereas the ocean as a whole is undersaturated.

INDEX TERMS: 0312 Atmospheric Composition and Structure: Air/sea constituent fluxes (3339, 4504); 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 4805 Oceanography: Biological and Chemical: Biogeochemical cycles (1615); KEYWORDS: methyl bromide, degradation, production, air/sea flux, vertical mixing


1. Introduction

Methyl bromide (CH\(_3\)Br) is an ozone-depleting trace gas that, unlike chlorofluorocarbons (CFCs) and some halogenated industrial solvents (e.g., methyl chloroform), has both natural and anthropogenic sources. At ~10 parts per trillion (ppt, 1 ppt = 1 pmol mol\(^{-1}\)) in the troposphere [Lobert et al., 1995], CH\(_3\)Br accounts for 55% of the total organic bromine transported from the troposphere into the stratosphere [Schauffler et al., 1993, 1998, 1999]. Once in the stratosphere, the organic bromine is converted to inorganic bromine, which depletes ozone (O\(_3\)) about 60 times more effectively than inorganic chlorine [Kurylo et al., 1999].

The oceans are both the largest known source and second largest known sink of atmospheric methyl bromide [Butler and Rodriguez, 1996; Yvon-Lewis and Butler, 1997]. Globally, the oceans are a net sink for atmospheric CH\(_3\)Br [Lobert et al., 1995, 1996, 1997; Groszko and Moore, 1998; King et al., 2000]. The response of the oceans to changes in anthropogenic emissions or to climate forcing cannot be determined without a better understanding of the oceanic sources and sinks and the factors that control them. The processes controlling the surface mixed layer CH\(_3\)Br concentration include production, degradation, vertical and horizontal mixing, and air/sea exchange.

In this paper, we present results from a process study of methyl bromide cycling in the North Atlantic surface ocean. This study was conducted as part of the 1998 Gas Exchange cruise (GasEx98) aboard the NOAA ship Ronald H. Brown. During Leg 2, the ship spent several weeks (May 28 through June 24, 1998) in a nearly stationary warm-core eddy northeast of the Azores, 45.9° to 46.3°N and 20.7° to 21.6°W (Figure 1). The eddy provided a natural contain-
ment area for a deliberate dual tracer experiment to study gas exchange coefficient parameterizations in a carbon dioxide (CO₂) sink region [Wanninkhof and McGillis, 1999; Feely et al., 2002] (Figure 2). The horizontal transport through the eddy’s walls was not measured. However, this exchange has to be relatively weak in order to maintain the water properties found inside the eddy. Assuming that this was the case, the data collected while the ship was in the eddy represent a four-week time series from what was essentially a coherent water mass and provide a unique opportunity to study the time-dependent behavior of methyl bromide in the surface ocean. From the measurements made during this study, the air/sea exchange, degradation, and vertical mixing components of the budget were estimated. Through comparison of these budget elements with the inventory of methyl bromide in the surface mixed layer, we examine the processes controlling the surface ocean concentration and estimate the in situ, presumably biological, production of methyl bromide.

2. Results and Discussion

2.1. Measurements

[5] The suite of measurements used in this study includes automated, discrete measurements (approximately every 40 min.) of the mixing ratio of methyl bromide in air alternating with air equilibrated with surface seawater, depth profiles of methyl bromide concentration, and daily measurements of the methyl bromide loss rate constant in surface

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Figure 1. Detailed map of the GasEx98 cruise track during Leg 2, including the locations of the CH₃Br depth profile measurements (red squares) and the degradation rate constant measurements (blue circles) with arrows indicating the ship’s heading before entering (DOY 148.4) and after exiting (DOY 174.5) the study area overlaid on sea surface height from a 10-day (June 9–19, 1998) average of TOPEX/ERS-2 data (CCAR, University of Colorado, www-ccar.Colorado.edu/~realtime/global-real-time_ssh). Only the data collected inside the oval are included in this analysis.

Figure 2. Schematic of the processes controlling trace gas concentration in the mixed layer of an eddy. Green arrows and text represent gross influx to mixed layer; red arrows and text represent gross outflux from mixed layer.
seawater from stable isotope incubations. Ancillary measurements include nutrients, dissolved inorganic carbon (DIC), continuous underway surface fugacity of carbon dioxide (fCO₂), chlorophyll a, sea-surface temperature (SST), salinity, and wind speed (Table 1). The CH₃Br depth profile samples, collected and analyzed according to the methodology described by Moore et al. [1996], show that CH₃Br was well mixed in the oceanic surface layer (Figure 3). The surface concentrations from the 5- and 10-m Niskin samples agree to within 3.5% (0.09 nmol m⁻³) of those determined from the discrete underway measurements (Figure 4a) [King et al., 2000].

CH₃Br concentrations in the surface waters of the eddy were about 3 nmol m⁻³ at the start of the experiment, decreased to about 2.5 nmol m⁻³ midway, and then increased to about 4 nmol m⁻³ at the end of the study. This variability can be examined by subdividing the data into six linear intervals (Figure 4a, Table 2). For each interval, we estimate the contributions to the mixed layer budget of CH₃Br from chemical and biological degradation [Tokarczyk and Saltzman, 2001], air-sea exchange, and net vertical diffusion, all of which were measured on this cruise.

2.2. Air/Sea Flux

The net sea-to-air fluxes of CH₃Br were calculated from the observed surface seawater concentrations and atmospheric mixing ratios [King et al., 2000]. Schmidt numbers from the De Bruyn and Saltzman [1997a] relationship, solubilities from the De Bruyn and Saltzman [1997b] relationship, wind speeds averaged over 24 hours prior to sampling (Figure 4b), and the air-sea exchange coefficient from the relationship of Wanninkhof [1992] (W-92). The CH₃Br saturation anomalies observed in the eddy were positive, ranging for the most part from <1% to 108% as a result of the increasing dissolved CH₃Br concentrations and yielding a mean net sea-to-air flux of 2.7 (±0.1, standard error) nmol m⁻² d⁻¹.

Division of the net sea-to-air flux by the depth of the oceanic mixed layer (Figure 4b), determined from the temperature and salinity depth profiles, yields the change in concentration expected solely from net sea-to-air exchange (Figure 4c). The decrease in this value during interval II (~yearday 151–156, Figure 4) reflects the declining wind speed, because the surface water concentrations, atmospheric mixing ratios, and mixed-layer depths remained nearly constant during this period. However, in interval III (~yearday 156–161) the contribution of sea-to-air exchange remained nearly constant despite increasing wind speeds. Here, escalating wind speeds lowered the surface concentrations primarily by deepening the mixed layer (Figures 3c, 3d, and 4b).

2.3. Chemical and Biological Degradation

Degradation rates were calculated as the product of the degradation rate constants measured during this cruise by Tokarczyk and Saltzman [2001] and the oceanic mixed

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Table 1. Species and Parameters Measured

<table>
<thead>
<tr>
<th>Species/Parameter Data/Methodology Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Underway CH₃Br (surface water and air)</td>
</tr>
<tr>
<td>CH₃Br degradation rate constants</td>
</tr>
<tr>
<td>CH₃Br depth profiles</td>
</tr>
<tr>
<td>Nutrients</td>
</tr>
<tr>
<td>Surface water fCO₂ and DIC</td>
</tr>
<tr>
<td>Thermocline diffusivity (Dz)</td>
</tr>
<tr>
<td>SST, salinity, wind speed, chlorophyll a</td>
</tr>
</tbody>
</table>

*These studies describe the methodologies used in this study but do not report the data presented in this study.

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Figure 3. Leg 2 depth profiles of CH₃Br grouped by yearday (YD) with position coordinates. Note deepening of profiles on yeardays (c)159 and (d) 162.
layer concentration (Figure 4c). The small temperature fluctuations observed in the eddy (Figure 4c) had a negligible effect on CH$_3$Br chemical degradation. Chemical degradation rate constants were nearly uniform at 0.039 ± 0.004 d$^{-1}$, while the observed biological degradation rate constants ranged from 0.00 d$^{-1}$ to 0.26 d$^{-1}$. Thus, most of the variability in CH$_3$Br degradation rates resulted from variability in the biological degradation rate constants (Figure 4c). During this study, degradation rates were similar in magnitude to the net sea-to-air exchange rates.

2.4. Vertical Mixing

[10] The observed CH$_3$Br depth profiles were used to determine the CH$_3$Br concentration gradient below the
mixed layer and the net loss rate of CH$_3$Br to the thermocline (Figure 3). This net loss rate out of the mixed layer was determined with the following equation:

$$\text{Net Loss Rate through Thermocline} = \left( \frac{D_z}{z} \right) \left( \frac{DC}{Dz} \right),$$

(1)

where $D_z$ is the thermocline diffusivity ($m^2 d^{-1}$), $z$ is the oceanic mixed layer depth (m), and $\Delta C/\Delta z$ is the concentration gradient below the mixed layer ($mol m^{-3} m^{-1}$). An average value for the thermocline diffusivity, $1.0 \pm 0.4 cm^2 s^{-1}$, was determined from depth profiles of the deliberate tracer SF$_6$ [Zhang et al., 2001; Feely et al., 2002]. The resulting net loss rates to the thermocline represent a small sink for CH$_3$Br in the oceanic mixed layer (Figure 4c).

### 2.5. Inferred Methyl Bromide Production Rates

Production of CH$_3$Br is calculated as the rate needed to balance the sum of the calculated mixed layer loss rates and the observed rate of change in concentration (dC/dt), as shown below (Figure 4d):

$$P = \frac{K_W}{\Delta t} \left( [CH_3Br]_{ML} - \frac{P_a}{H} \right) + \left( k_{chem} + k_{bio} \right) [CH_3Br]_{ML}$$

$$+ \left( \frac{D_z}{z} \right) \frac{DC}{Dz} + \frac{dC}{dt},$$

(2)

where $P$ is the production rate ($mol m^{-3} d^{-1}$), $K_W$ is the gas exchange coefficient ($m d^{-1}$), $[CH_3Br]_{ML}$ is the mixed layer CH$_3$Br concentration ($mol m^{-3}$), $P_a$ is the partial pressure of CH$_3$Br in the marine atmospheric boundary layer (atm), $H$ is the solubility ($m^3 atm mol^{-1}$), $k_{chem}$ and $k_{bio}$ are the chemical and biological degradation rate constants ($d^{-1}$), and all other terms are defined above. The calculated production rates are sensitive to the gas exchange coefficient formulation used. As mentioned above, the W-92 relationship is used here as our best estimate. The linear Smetheie et al. [1985] (S-85) relationship between gas exchange and wind speed generates higher production rates, while the quadratic Nightingale et al. [2000] (NI-00) relationship yields lower production rates (Figure 4d). The Wanninkhof and McGillis [1999] (WM-99) cubic relationship yields lower rates at low wind speeds and higher rates at elevated wind speeds. While this relationship has not gained widespread use, it was determined from the CO$_2$ covariance measurements made during this cruise [Wanninkhof and McGillis, 1999], and we include it here for comparison.

### Table 2. Linear Fit Results for the Six Intervals of Constant dC/dt

<table>
<thead>
<tr>
<th>Interval</th>
<th>Slope (dC/dt), nmol m$^{-3}$ d$^{-1}$</th>
<th>Standard Error, nmol m$^{-3}$ d$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>0.11</td>
<td>±0.12</td>
</tr>
<tr>
<td>II</td>
<td>0.00</td>
<td>±0.01</td>
</tr>
<tr>
<td>III</td>
<td>−0.20</td>
<td>±0.02</td>
</tr>
<tr>
<td>IV</td>
<td>0.19</td>
<td>±0.04</td>
</tr>
<tr>
<td>V</td>
<td>0.04</td>
<td>±0.01</td>
</tr>
<tr>
<td>VI</td>
<td>0.18</td>
<td>±0.03</td>
</tr>
</tbody>
</table>

[11] Calculated production decreased overall until year-day 158 (in interval III) and increased after yearday 160. The spikes in calculated production correspond to spikes in the biological degradation rate constant, but the overall trends are not attributable to any one term in the calculation. For example, if the biological features are removed by arbitrarily holding $k_{bio}$ at zero, the overall decreasing and increasing trends remain. In addition, these trends continue across intervals and are not the product of a single dC/dt value. The decreasing trend in calculated production spans the slight increase in concentration over interval I (positive dC/dt), the nearly constant concentrations in interval II (near zero dC/dt) and part of the decreasing concentrations of interval III (negative dC/dt).

[12] Interval III is characterized by a storm with high winds and a corresponding increase in surface seawater DIC, f$_{CO_2}$, chlorophyll, nitrate, and silicate (Figures 4b, 4e, and 4f). The nutrient pulses are indicators of increased entrainment of nutrient-rich waters from below the mixed layer [Zhang et al., 2001]. The increases in DIC and f$_{CO_2}$ are also functions of increased influx of water from below the mixed layer, and are influenced by biological uptake, respiration processes, and enhanced air-sea gas exchange [Feely et al., 2002]. The observed decrease in CH$_3$Br concentration began before the high wind event, and calculated production remained near zero, even during the storm when increased rates of vertical mixing and air-sea exchange caused mixed layer CH$_3$Br concentrations to decrease.

[13] An increasing trend in calculated production becomes noticeable after yearday 160, when the winds died down. Although the net sea-to-air exchange rate did reach zero briefly, the atmosphere never became a net source of CH$_3$Br to the mixed layer. It is possible that the influx of nutrients from below the mixed layer during the high wind event resulted in an increase in biological production of CH$_3$Br that exceeded its losses to the atmosphere and the thermocline. This vertical mixing did subsequently enhance phytoplankton production, as evidenced by the decrease in nitrate, DIC, and f$_{CO_2}$ over the first two days following the high wind event [Zhang et al., 2001; Feely et al., 2002].

[14] Calcuated CH$_3$Br production increased rapidly from yearday 160 to yearday 162, increased slowly from yearday 162 to yearday 172, and increased rapidly again near the end of the study. The nitrate concentrations decreased dramatically after yearday 162, while the elevated silicate concentrations remained nearly constant for the rest of the study. Two smaller storm events began on yearday 162 and 167 and are likely responsible for the smaller pulses of nitrate and DIC observed on yearday 164 and 168. These nitrate pulses may have sustained the continued increase in calculated CH$_3$Br production. The low variation in silicate during the latter part of the study suggests that diatoms were not largely involved in the production of CH$_3$Br. This observation is corroborated by counts of the >20 µm phytoplankton which were largely dominated by dinoflagellates, especially Ceratium sp. Culture studies performed by Saemundsdo´ttir and Matrai [1998] and Scarratt and Moore [1998] have shown that dinoflagellates produce CH$_3$Br; however, neither of the studies included the species we observed on this cruise. Picoplankton (e.g., Synedra-
coccus) were most likely dominant in these waters, and many such species are known CH₃Br producers [Saemundsdóttir and Matrai, 1998].

The production of methyl bromide calculated in this study ranged from <0.1 to 1.3 nmol m⁻³ d⁻¹. Not all CH₃Br produced in the water, however, is emitted to the ocean. Gross oceanic emission is the fraction or amount of a trace gas that is produced in the mixed layer that reaches the atmosphere and depends upon the degradation and transfer rates [Butler and Rodrigues, 1996]. The current best estimate for global oceanic emissions is 56 Gg yr⁻¹ [Kurylo et al., 1999], a rate that could be sustained with a constant global production of 0.15 nmol m⁻³ d⁻¹. While this production rate is within the range calculated for this study, it is below the median of 0.48 nmol m⁻³ d⁻¹. This is expected, since we were working in an area that was characterized by elevated seawater concentrations, as evidenced by the average 40% CH₃Br supersaturation, whereas the ocean as a whole is 10–20% undersaturated [King et al., 2000]. In addition, the constant global rate does not account for the distribution of production and its colocation with specific degradation rate constants, wind speeds, and other physical properties that affect emission. Further research is needed to determine the spatial and temporal variations in both production and degradation if we are to develop skillful predictive capabilities to assess the impact of climate forcing on the oceanic emission and uptake of this and other important trace gases.

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References

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