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

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Received 7 March 2002; revised 7 May 2002; accepted 4 September 2002; published 26 December 2002.

[1] 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

Citation: Yvon-Lewis, S. A., J. H. Butler, E. S. Saltzman, P. A. Matrai, D. B. King, R. Tokarczyk, R. M. Moore, and J.-Z. Zhang, Methyl bromide cycling in a warm-core eddy of the North Atlantic Ocean, *Global Biogeochem. Cycles*, *16*(4), 1141, doi:10.1029/2002GB001898, 2002.

1. Introduction

[2] Methyl bromide (CH_3Br) 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_3Br 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].

[3] 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_3Br [*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_3Br concentration include production, degradation, vertical and horizontal mixing, and air/sea exchange.

[4] 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-

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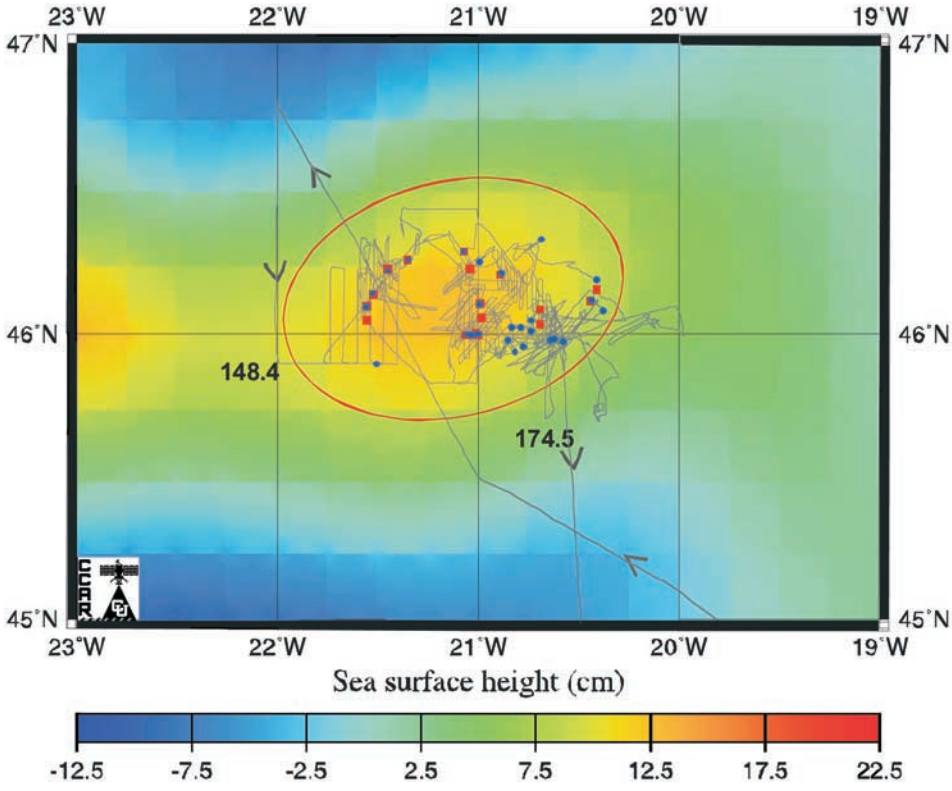

Figure 1. Detailed map of the GasEx98 cruise track during Leg 2, including the locations of the CH_3Br depth profile measurements (red squares) and the degradation rate constant measurements (blue circles) with arrows indicating the ship's heading before entering (DOY 148.4) and after exiting (DOY 174.5) 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.

ment area for a deliberate dual tracer experiment to study gas exchange coefficient parameterizations in a carbon dioxide (CO_2) 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

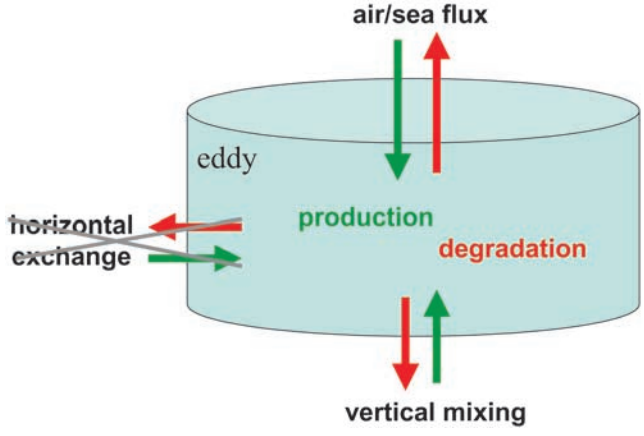

Figure 2. Schematic of the processes controlling trace gas concentration in the mixed layer of an eddy. Green arrows and text represent gross influx to mixed layer; red arrows and text represent gross outflux from mixed layer.

Table 1. Species and Parameters Measured

Species/Parameter	Data/Methodology Reference
Underway CH_3Br (surface water and air)	*King et al.* [2000]
CH_3Br degradation rate constants	*Tokarczyk and Saltzman* [2001]
CH_3Br depth profiles	*Moore et al.* [1996][a]
Nutrients	*Zhang* [2000][a], *Zhang and Berberian* [1997][a], *Zhang et al.* [2001]
Surface water f_{CO2} and DIC	*Feely et al.* [2002]
Thermocline diffusivity (D_z)	*Zhang et al.* [2001], *Feely et al.* [2002]
SST, salinity, wind speed, chlorophyll *a*	*Joint Global Ocean Flux Study* [1996][a] for chl *a*

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

seawater from stable isotope incubations. Ancillary measurements include nutrients, dissolved inorganic carbon (DIC), continuous underway surface water fugacity of carbon dioxide (f_{CO2}), chlorophyll *a*, sea-surface temperature (SST), salinity, and wind speed (Table 1). The CH_3Br depth profile samples, collected and analyzed according to the methodology described by *Moore et al.* [1996], show that CH_3Br 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].

[6] CH_3Br 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 CH_3Br 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

[7] The net sea-to-air fluxes of CH_3Br 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 CH_3Br saturation anomalies observed in the eddy were positive, ranging for the most part from <1% to 108% as a result of the increasing dissolved CH_3Br concentrations and yielding a mean net sea-to-air flux of 2.7 (±0.1, standard error) nmol m^{-2} d^{-1}.

[8] 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

[9] 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

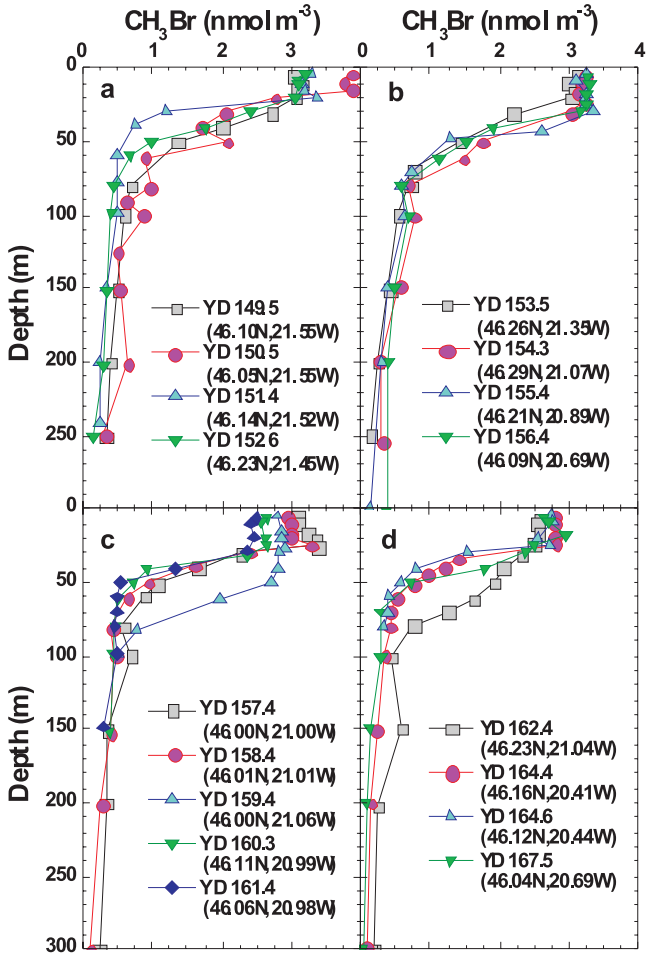

Figure 3. Leg 2 depth profiles of CH_3Br grouped by yearday (YD) with position coordinates. Note deepening of profiles on yeardays (c)159 and (d) 162.

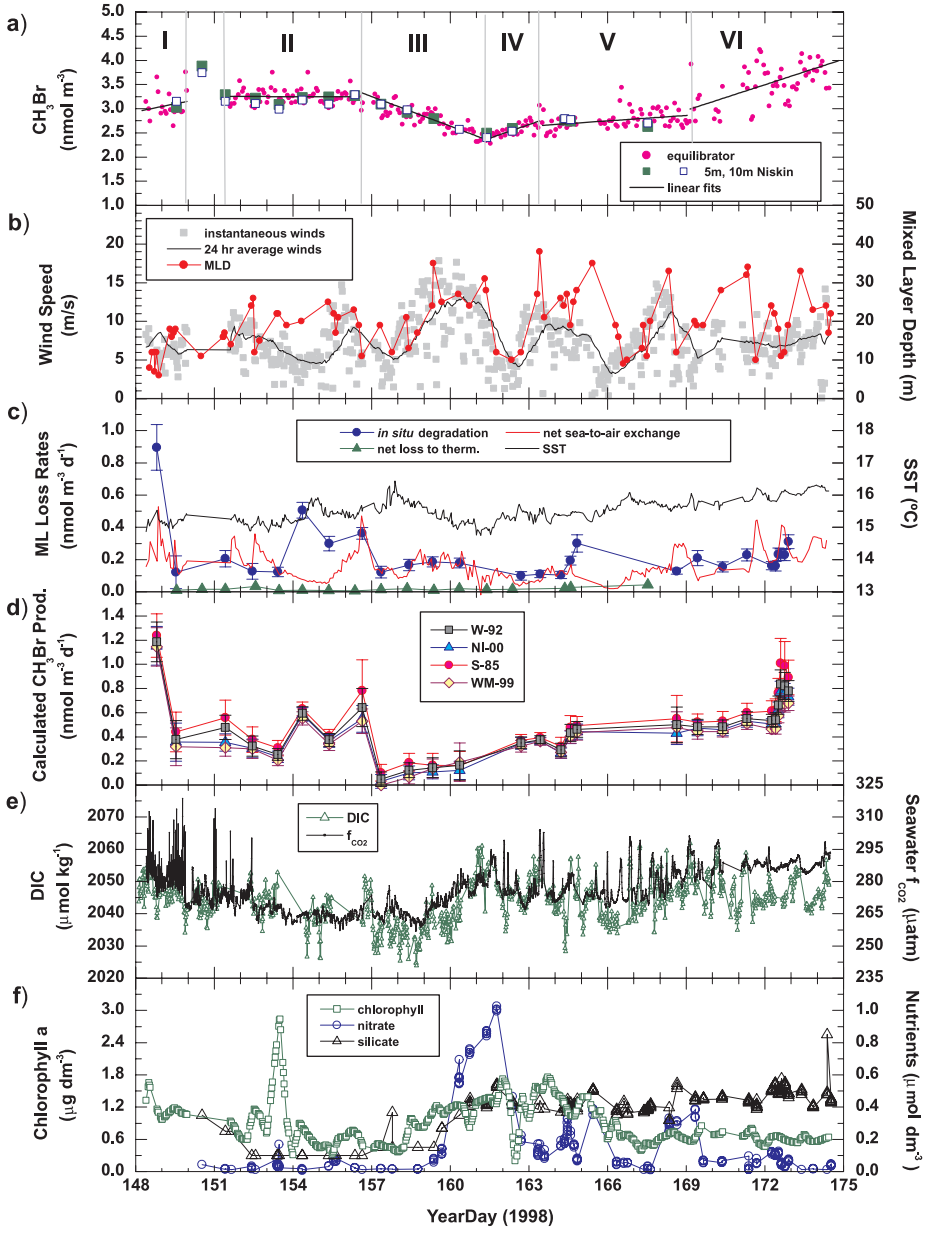

Figure 4. (a) Leg 2 methyl bromide surface seawater concentrations from the underway measurements of *King et al.* [2000] and discrete 5-m and 10-m Niskin samples, with the intervals of constant slope indicated and their linear fits plotted against time; (b) instantaneous and 24-hour average wind speeds shown with mixed layer depths; (c) SST and mixed layer loss rates including degradation, net sea-to-air exchange, and net loss to the thermocline; (d) calculated methyl bromide production rates using the W-92, NI-00, S-85, and WM-99 gas exchange wind speed relationships; (e) observed DIC and f_{CO2} from *Feely et al.* [2002]; (f) chlorophyll *a* and nitrate from *Zhang et al.* [2001] and silicate. The degradation rate error bars represent the uncertainties in the degradation rate constants and concentrations, while the production rate error bars include those uncertainties as well as uncertainties in thermocline diffusivity and mixed layer depths.

layer concentration (Figure 4c). The small temperature fluctuations observed in the eddy (Figure 4c) had a negligible effect on CH_3Br 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_3Br 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_3Br depth profiles were used to determine the CH_3Br concentration gradient below the

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

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

mixed layer and the net loss rate of CH_3Br to the thermocline (Figure 3). This net loss rate out of the mixed layer was determined with the following equation:

$$\text{Net Loss Rate through Thermocline} = (D_z/z)(DC/Dz) \quad \left(\text{mol m}^{-3}\text{d}^{-1}\right), \tag{1}$$

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 ± 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_3Br in the oceanic mixed layer (Figure 4c).

2.5. Inferred Methyl Bromide Production Rates

[11] Production of CH_3Br 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):

$$P = \frac{K_W}{z}\left([CH_3Br]_{ML} - \frac{p_a}{H}\right) + (k_{chem} + k_{bio})[CH_3Br]_{ML} + \left(\frac{D_z}{z}\right)\frac{\Delta C}{\Delta z} + \frac{dC}{dt} \tag{2}$$

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_3Br concentration (mol m^{-3}), p_a is the partial pressure of CH_3Br 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 *Smethie 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.

[12] Calculated production decreased overall until yearday 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).

[13] Interval III is characterized by a storm with high winds and a corresponding increase in surface seawater DIC, f_{CO2}, 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_{CO2} 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_3Br 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_3Br concentrations to decrease.

[14] 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_3Br 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_3Br 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_{CO2} over the first two days following the high wind event [*Zhang et al.*, 2001; *Feely et al.*, 2002].

[15] Calculated CH_3Br 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_3Br 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_3Br. This observation is corroborated by counts of the >20 μm-phytoplankton which were largely dominated by dinoflagellates, especially *Ceratium* sp. Culture studies performed by *Saemundsdóttir and Matrai* [1998] and *Scarratt and Moore* [1998] have shown that dinoflagellates produce CH_3Br; however, neither of the studies included the species we observed on this cruise. Picoplankton (e.g., *Synecho-*

coccus) were most likely dominant in these waters, and many such species are known CH_3Br producers [*Saemundsdóttir and Matrai*, 1998].

[16] The production of methyl bromide calculated in this study ranged from <0.1 to 1.3 nmol m^{-3} d^{-1}. Not all CH_3Br 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 Rodriguez*, 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% CH_3Br 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.

[17] **Acknowledgments.** The authors thank the crew of the NOAA ship *Ronald H. Brown*. This work was funded in part by the NASA Ocean Biology/Biogeochemistry Program, the NASA Upper Atmosphere Research Project, the Atmospheric Chemistry and Global Carbon Cycle Projects of the NOAA Climate and Global Change Program, and the NSF Chemical Oceanography Program. Data from Figures 3 and 4 are available by ftp at ftp.aoml.noaa.gov/ocd/pub/syvon/GasEx98.

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