Methyl bromide and methyl chloride in the Southern Ocean

Shari A. Yvon-Lewis, Daniel B. King, Ryszard Tokarczyk, Kelly D. Goodwin, Eric S. Saltzman, and James H. Butler (2004), Methyl bromide and methyl chloride in the Southern Ocean (latitudes 45°–67°S, longitudes 144°–139°E) from late October through mid-December 2001. CH$_3$Br and CH$_3$Cl were undersaturated with mean saturation anomalies of $-39 \pm 11\%$ and $-37 \pm 11\%$ between 45° and 65°S. The minimum degradation rate constants needed to maintain these saturation anomalies are consistent with the observed total degradation rate constants, suggesting that there is no significant production of these gases in this region. Near the Antarctic coast (south of 65°S) the saturation anomalies for both gases decreased to approximately $-80\%$, although CFC-11 measurements suggest these extreme anomalies are associated with enhanced vertical mixing rather than with degradation in the surface waters.

INDEX TERMS: 0312 Atmospheric Composition and Structure: Air/sea constituent fluxes (3339, 4504); 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 4805 Oceanography: Biological and Chemical: Biogeochemical cycles (1615); 4820 Oceanography: Biological and Chemical: Gases; KEYWORDS: methyl bromide, methyl chloride, air-sea flux

Citation: Yvon-Lewis, S. A., D. B. King, R. Tokarczyk, K. D. Goodwin, E. S. Saltzman, and J. H. Butler (2004), Methyl bromide and methyl chloride in the Southern Ocean, J. Geophys. Res., 109, C02008, doi:10.1029/2003JC001809.

1. Introduction

Methyl bromide (CH$_3$Br) and methyl chloride (CH$_3$Cl) are sources of inorganic halogen atoms that destroy stratospheric ozone ($O_3$). Both gases have natural sources and sinks, while CH$_3$Br also has substantial anthropogenic sources. The budgets for CH$_3$Cl and CH$_3$Br remain largely unbalanced with known sinks outweighing sources by $\sim 20$–$25\%$ for both trace gases [Montzka et al., 2003].

Supporting production as well as degradation, the oceans are both source and sink for these atmospheric gases. Net undersaturations of CH$_3$Br have been observed over much of the world’s oceans [Lobert et al., 1995a, 1996; Moore et al., 1996; Groszko and Moore, 1998; King et al., 2000, 2002], resulting in an estimated global, net sea-to-air flux ranging from $-10$ to $-18$ Gg yr$^{-1}$ [King et al., 2002]. Methyl chloride, on the other hand, is supersaturated over middle and low latitudes, but with undersaturations observed at high latitudes [Moore et al., 1996].

Assessing how the net oceanic fluxes of CH$_3$Br and CH$_3$Cl will respond to climate change or changes in anthropogenic emissions requires reliable modeling supported by reliable data. Although some recent modeling studies have used relationships between latitude or sea surface temperature (SST) and saturation anomaly to constrain the oceanic fluxes [e.g., Lee-Taylor et al., 1998; Khalil et al., 1999], these proxy relationships are not likely to remain valid in the future, unless SST is the sole driving force controlling the saturation anomaly. It is important to understand the processes underlying such relationships in terms of oceanic production and degradation and how they may change under changing climatic conditions.

Early attempts to parameterize oceanic production of CH$_3$Br relied on chlorophyll $a$ as a proxy or on prescribing a fixed production rate. Such models suggested significant CH$_3$Br production in the Southern Ocean and included only chemical degradation, which is very slow at the low temperatures in this region. This led to model predictions of large supersaturations of CH$_3$Br in this region [Anbar et al., 1996; Pilinis et al., 1996]. During a previous Southern Ocean cruise, we observed large undersaturations ($36 \pm 7\%, 1\sigma$, n = 466) for CH$_3$Br [Lobert et al., 1997], which demonstrated that the models overpredicted the saturation anomalies in that region. As there were no measurements of degradation rate constants or depth profiles to assess poten-
tially significant losses owing to vertical mixing, we could not estimate production rates for that expedition. During that cruise, production rates could have been high, but in order to maintain the observed saturation anomalies the corresponding degradation rates would have to have been much faster as well. In an attempt to determine actual production rates of these gases in polar and subpolar waters, we measured CH$_3$Br and CH$_3$Cl saturation anomalies, degradation rate constants [Tokarczyk et al., 2003], and depth profiles on a recent cruise in the Southern Ocean.

2. Experiment

[6] Air and water concentrations of CH$_3$Br, CH$_3$Cl, trichlorofluoromethane (CCL$_3$F, CFC-11), and a suite of other halogenated gases were measured in the Southern Ocean during the Australian National Antarctic Research Expedition (ANARE) 2001/2002 Voyage 3 (V3) aboard the research ice breaker Aurora Australis. The ship departed Hobart, Tasmania, on 29 October 2001, sailing southwest to 140°E longitude and then south to the coast of Antarctica, and returning via the same cruise track on 13 December 2001 (Figure 1). This cruise track is referred to as the Southern Ocean Repeat hydrographic section 3 (SR3) and was repeated 6 times during the World Ocean Circulation Experiment (WOCE) covering all seasons except the Austral Spring. One hundred thirty-four hydrocasts were conducted during this cruise, with 109 occurring during the cruise, the measurement uncertainties (1σ) were 9% (0.05 nmol m$^{-3}$) for CH$_3$Br, 2.7% (1.4 nmol m$^{-3}$) for CH$_3$Cl, and 2.6% (0.08 nmol m$^{-3}$) for CFC-11.

3. Results and Discussion

[16] Vertical sections of potential temperature and salinity are consistent with a late winter (late September through late October 1991) occupation of SR3 and the seasonal evolution of surface properties in this region (Figures 2a and 2b) [Rintoul and Bullister, 1999; Trull et al., 2001; Rosenberg et al., Aurora Australis marine science cruise AU0103: Oceanographic field measurements and analysis, manuscript in preparation, 2004, hereinafter referred to as Rosenberg et al., manuscript in preparation, 2004]. Rintoul and Bullister [1999] identified cold, fresh, CFC-enriched Antarctic Bottom Water forming off the Wilkes-Adelie coast of Antarctica. This feature is also present in the data collected south of 65°S during this cruise (Figures 2a–2c). Since CH$_3$Br and CH$_3$Cl are nonconservative trace gases undergoing both chemical and biological degradation in seawater, they are not enriched in the sinking waters along the Antarctic coast (Figures 2d and 2e).

[11] The characteristics of the fronts and zones of the Southern Ocean south of Australia, described by Rintoul and Bullister [1999], Trull et al. [2001], and Chaigneau and Morrow [2002], were used to identify the fronts and zones encountered during this occupation of SR3 (Figure 3). The assignment of all fronts and zones was based on the data from the densely sampled southbound transect. The Subtropical Front (STF) was located at ~46.5°S with the Subantarctic Zone (SAZ) extending from this front to the Subantarctic Front (SAF) located at ~49°S. The SAF was determined as the beginning of the steepest slope in SST and sea surface salinity (SSS) south of the STF. Subsurface features (Figures 2a and 2b) could place this front at ~51°S, however the data discussed below are for the surface mixed layer only. The Polar Frontal Zone (PFZ) extended from the SAF to ~54.5°S where the northernmost extent of the subsurface temperature minimum (Figure 2a), a constant 33.85‰ SSS, and an SST gradient (Figure 3) placed the northern Polar Front (PF-N). The Inter-Polar Frontal Zone (IPFZ) extended southward from the PF-N to the southern Polar Front (PF-S) located at ~58.5°S. South of the PF-S, the southern Antarctic Zone (AZ-S) extended to the Southern Antarctic Circumpolar Current (ACC) Front (SF) at ~63°S. The Southern Boundary (SB) of the ACC was located at ~64°S. As discussed above, the sinking waters of the Antarctic Slope Front (ASF) were located at ~65°S.

[12] Atmospheric CH$_3$Br, CH$_3$Cl, and CFC-11 mixing ratios averaged 6.8 ± 0.3 pmol mol$^{-1}$ (1σ, n = 613), 524 ± 21 pmol mol$^{-1}$ (1σ, n = 649), and 259 ± 4 pmol mol$^{-1}$ (1σ, n = 624) against gravimetric standards at the NOAA Climate Monitoring and Diagnostics Laboratory (CMDL).

[9] Surface seawater CFC-11 concentrations measured with this instrument agreed well with those determined from a traditional purge-and-trap gas chromatograph with an electron capture detector that was also on this cruise (M. Warner, personal communication, 2002), suggesting that contamination during sampling and analysis was minimal. From replicate samples collected periodically during the cruise, the measurement uncertainties (1σ) were 9% (0.05 nmol m$^{-3}$) for CH$_3$Br, 2.7% (1.4 nmol m$^{-3}$) for CH$_3$Cl, and 2.6% (0.08 nmol m$^{-3}$) for CFC-11.
n = 614) and did not change significantly over the one to five weeks separating the southbound and northbound transects or latitude (Figures 4a–4c). Surface seawater concentrations reported here are the average of the concentrations of hydrocast samples collected from within the mixed layer or within the top 100 m, whichever is shallower (Figure 4d). Saturation anomalies (percent departure from equilibrium) for each trace gas were calculated from the surface water concentrations and 24-hour smoothed air concentrations, using the solubility functions from De Bruyn and Saltzman [1997] (CH$_3$Br), Moore et al. [1995] (CH$_3$Cl), and Warner and Weiss [1985] (CFC-11) (Figure 4e).

[13] As expected for a conservative tracer, north of the PF-N dissolved CFC-11 concentrations increased dramatically with decreasing SST while maintaining a nearly constant near-equilibrium saturation anomaly of 2 ± 1% (1σ, n = 9) between the STF and the PF-N (Figures 4d and 4e). At 51°S, the small shift in the CFC-11 mixed layer concentration and saturation anomaly between the southbound and the northbound transects is likely the result of the increase in SST that occurred between the two transects. The nonconservative trace gases CH$_3$Cl and CH$_3$Br did not exhibit such a strong anticorrelation between concentration and SST. These gases were substantially undersaturated with mean saturation anomalies of −36 ± 6% (1σ, n = 8) for CH$_3$Br and −34 ± 7% (1σ, n = 8) for CH$_3$Cl between the STF and PF-N. In the IPFZ, the mixed layer concentrations and saturation anomalies of all three gases decreased (Figure 4d). Both the mixed layer concentrations and the saturation anomalies for CH$_3$Br and CH$_3$Cl increased to values similar to those of the PFZ in the AZ-S. However, for CFC-11 only the concentration increased in the AZ-S. The CFC-11 saturation anomaly remained slightly undersaturated at approximately −7.5% in the AZ-S. From the SF to the ASF, the CFC-11 saturation anomaly decreased rapidly and remained at approximately −30% south of the ASF, which is consistent with a substantial input of upwelled CFC-free water. The CH$_3$Br and CH$_3$Cl concentrations and saturation anomalies decreased rapidly from the SB past the ASF, with the lowest saturation anomalies reaching −80% for CH$_3$Cl and −82% for CH$_3$Br.

[14] Unlike CFC-11, CH$_3$Br and CH$_3$Cl were substantially undersaturated everywhere along the cruise track with saturation anomalies averaging −39 ± 11% (1σ, n = 19) for CH$_3$Br and −37 ± 11% (1σ, n = 19) for CH$_3$Cl north of the ASF (Figure 4d). The mean CH$_3$Br saturation anomaly observed north of the ASF during this cruise agrees, within 95% confidence limits, with that observed during a late Austral Summer and early Fall (late February through early April) cruise from McMurdo, Antarctica, to Punta Arenas, Chile (Bromine Latitudinal Air/Sea Transect III (BLAST III)), −36 ± 7% (1σ, n = 466), [Lobert et al., 1997]. These large undersaturations suggest that sinks are larger than sources for CH$_3$Br and CH$_3$Cl in the surface waters of the Southern Ocean.

[15] From the observed saturation anomalies, we calculated the minimum degradation rate constant needed to sustain the observed surface water concentrations in the presence of air-sea exchange. This calculation assumes...
steady state; however, a portion of the air-sea flux is likely the result of changes in certain physical properties (e.g., seasonal warming or cooling of the sea surface) and not the result of the in situ production and degradation [Kester, 1975]. In order to correct for these physical effects, the observed saturation anomaly for the conservative tracer CFC-11 (\(\text{CFC-11}^{\text{sat}}\)) was subtracted from the saturation anomaly of the trace gas of interest (\(\text{trace gas}^{\text{sat}}\)). The minimum degradation rate constant (\(k_{\text{min}}\)) was determined from the following equation:

\[
k_{\text{min}} = \frac{K_W}{z} \left( \frac{-\Delta s - \Delta \text{sat}}{100 + \Delta s} \right),
\]

where \(K_W\) is the gas exchange coefficient (m d\(^{-1}\)) from Wanninkhof [1992] and the full range in uncertainty estimated with Nightingale et al. [2000] and Smethie et al. [1985], \(z\) is the observed mixed layer depth (m), and all other terms are defined above. This equation is derived from a balance of in situ degradation and air-sea exchange and assumes vertical mixing is negligible [Butler et al., 1991; Lobert et al., 1995b]. As discussed above, vertical mixing was enhanced south of the ASF, therefore this equation was not applied to the data collected south of 65°S. For this cruise, the mean \(k_{\text{min}}\) for CH\(_3\)Br and CH\(_3\)Cl north of the ASF were \(0.039 \pm 0.029\) d\(^{-1}\) (1\(\sigma\), \(n = 19\)) and \(0.036 \pm 0.025\) d\(^{-1}\) (1\(\sigma\), \(n = 19\)) (Figure 5), whereas for BLAST III the mean \(k_{\text{min}}\) for CH\(_3\)Br was \(0.062 \pm 0.051\) d\(^{-1}\).

Figure 3. Surface water properties (a) temperature and (b) salinity during southbound (black) and northbound transects (shaded). The vertical lines indicate the positions of the fronts (STF, Subtropical Front; SAF, Subantarctic Front; PF-N, northern Polar Front; PF-S, southern Polar Front; SF, southern ACC Front; SB, southern boundary of the ACC; and ASF, Antarctic Slope Front). The zones between the front are indicated by SAZ, Subantarctic Zone; PFZ, Polar Frontal Zone; IPFZ, Inter-Polar Frontal Zone; and AZ-S, southern Antarctic Zone.

Figure 4. Measurements of (a)–(c) air concentrations (pmol mol\(^{-1}\)) for CH\(_3\)Cl (triangles), CFC-11 (squares), and CH\(_3\)Br (circles), (d) surface water concentrations (nmol m\(^{-3}\)) with 1\(\sigma\) error bars, CH\(_3\)Cl/10, and (e) saturation anomalies (%) including uncertainties in air, water, and solubilities. Data shown are from both the southbound (solid symbols) and northbound (open symbols) transects. The shaded lines in Figures 4a–4c represent the 24-hour running mean. Vertical shaded lines in Figures 4d and 4e indicate fronts, as described in Figure 3.
occurred during BLAST III. It also is possible that during the Austral Fall, when BLAST III took place, both degradation and production were faster. These results along with the negative saturations observed ubiquitously in high-latitude waters further suggest that there is no significant production of CH$_3$Br and CH$_3$Cl in polar and subpolar waters.

**Figures**

**Figure 5.** Mixed layer loss rate constants (d$^{-1}$) for (a) CH$_3$Br and (b) CH$_3$Cl with $k_{min}$ (circles) and the observed $k_{total}$ (squares). Observed $k_{total}$ values are from Tokarczyk et al. [2003]. Data shown are from both the southbound (solid symbols) and northbound (open symbols) transects. Vertical shaded lines indicate fronts, as described in Figure 3.

(1σ, n = 466), corrected from the 0.058 d$^{-1}$ given by Lobert et al. [1997].

When $k_{min}$ equals the sum of the chemical and biological degradation rate constants ($k_{total}$), no production is needed to maintain the observed saturation anomaly. If $k_{total}$ is greater than $k_{min}$, the trace gas must be produced at a rate sufficient to balance that additional degradation (Production = ($k_{total} - k_{min}$) $C_W$, where $C_W$ is the surface water concentration). Values for $k_{min}$ that are higher than $k_{total}$ suggest additional losses (e.g., mixing) are occurring. During this cruise, Tokarczyk et al. [2003] measured chemical and biological degradation rates and determined mean $k_{total}$ values of 0.035 ± 0.044 d$^{-1}$ (1σ, n = 70) for CH$_3$Br and 0.07 ± 0.08 d$^{-1}$ (1σ, n = 36) for CH$_3$Cl (Figure 5). The magnitude of and trends in the observed CH$_3$Br $k_{total}$ correlate well with the calculated $k_{min}$ for CH$_3$Br, suggesting that the observed loss rate constants are sufficient to balance the net air-sea flux and maintain the observed saturation anomaly for CH$_3$Br with no mixed layer production. South of the ASF, additional losses are indicated and consistent with the enhanced mixing previously discussed for this region. The same is true for CH$_3$Cl south of the PF-N. North of the PF-N, the observed CH$_3$Cl $k_{total}$ are larger than the calculated $k_{min}$ suggesting that some mixed layer production of CH$_3$Cl is needed to balance the observed degradation and net air-sea flux while maintaining the observed saturation anomaly for CH$_3$Cl.

[18] Acknowledgments. We thank the master, crew, and support staff of the Aurora Australis and the Australian Antarctic Division’s Australian National Antarctic Research Expedition (ANARE). We are grateful to S. Montzka for helpful discussions during the preparation of this manuscript. This work was funded in part by NASA’s Upper Atmosphere Research Program, NOAA’s Atmospheric Chemistry Program, and a NOAA Assistant Administrator’s Fund Award to S. A. Yvon-Lewis. Data are available by ftp at ftp.aoml.noaa.gov/ocd/pub/syvon-clivar_sr3_2001.

**References**

Anbar, A. D., Y. L. Yung, and F. P. Chavez (1996), Methyl bromide: Ocean sources, ocean sinks, and climate sensitivity, Global Biogeochem. Cycles, 10, 175 –190.

Butler, J. H., J. W. Elkins, T. M. Thompson, B. D. Hall, T. H. Swanson, and V. Koropalov (1991), Oceanic consumption of CH$_3$Cl: Implication for tropospheric OH, J. Geophys. Res., 96, 22,347 –22,355.

Chaigneau, A., and R. Morrow (2002), Surface temperature and salinity variations between Tasmania and Antarctica, 1993–1999, J. Geophys. Res., 107, 8020, doi:10.1029/2001JC000808.

De Bruyn, W., J. H., and E. S. Saltzman (1997), The solubility of methyl bromide in pure water, 35% sodium chloride and seawater, Mar. Chem., 56, 51 –57.

Groszko, W., and R. M. Moore (1998), Ocean-atmosphere exchange of methyl bromide: NW Atlantic and Pacific Ocean studies, J. Geophys. Res., 103, 16,737–16,741.

Kester, D. R. (1975), Dissolved gases other than CO$_2$, in Chemical Oceanography, vol. 1, edited by J. P. Riley and G. Skirrow, pp. 497–556, Academic, San Diego, Calif.

Khalil, M. A. K., R. M. Moore, D. B. Harper, J. M. Lobert, D. J. Erickson, V. Koropalov, W. T. Sturges, and W. C. Keene (1999), Natural emissions of chlorine-containing gases: Reactive chlorine emissions inventory, J. Geophys. Res., 104, 8333–8346.

King, D. B., J. H. Butler, S. A. Montzka, S. A. Yvon-Lewis, and J. W. Elkins (2000), Implications of methyl bromide supersaturations in the temperate North Atlantic Ocean, J. Geophys. Res., 105, 19,763–19,769.

King, D. B., J. H. Butler, S. A. Yvon-Lewis, and S. A. Cotton (2002), Predicting oceanic methyl bromide saturation from SST, Geophys. Res. Lett., 29, 2199, doi:10.1029/2002GL016091.

Lee-Taylor, J. M., S. C. Doney, G. P. Brasseur, and J.-F. Muller (1998), A global three-dimensional atmosphere-ocean model of methyl bromide distributions, J. Geophys. Res., 103, 16,039–16,059.

Lobert, J. M., J. H. Butler, S. A. Montzka, L. S. Geller, R. C. Myers, and J. W. Elkins (1995a), A net sink for atmospheric CH$_3$Br in the East Pacific Ocean, Science, 267, 1002–1005.

Lobert, J. M., T. J. Baring, J. H. Butler, S. A. Montzka, R. C. Myers, and J. W. Elkins (1995b), OAXTC 92: Ocean atmosphere exchange of trace compounds 1992, NOAA Tech. Memo., ERL CMDL-9, 43 pp.

Lobert, J. M., J. H. Butler, L. S. Geller, S. A. Yvon, S. A. Montzka, R. C. Myers, A. D. Clarke, and J. W. Elkins (1996), BLAST94: Bromine latitudinal air-sea transect 1994, Report on oceanic measurements of methyl bromide and other compounds, NOAA Tech. Memo. ERL CMDL-10, 39 pp.

Lobert, J. M., S. A. Yvon-Lewis, J. H. Butler, S. A. Montzka, and R. C. Myers (1997), Undersaturation of CH$_3$Br in the Southern Ocean, Geo- phys. Res. Lett., 24, 171–172.

Montzka, S. A., et al. (2003), Controlled substances and other source gases, in Scientific Assessment of Ozone Depletion: 2002, Global Ozone Research and Monitoring Project, vol. 47, chap. 1, pp. 1.1–1.83, World Meteorol. Org., Geneva.

Moore, R. M., C. E. Geen, and V. K. Tait (1995), Determination of Henry’s Law constants for a suite of naturally occurring halogenated methanes in seawater, Chemosphere, 30, 1183–1191.

Moore, R. M., W. Groszko, and S. J. Niven (1996), Ocean-atmosphere exchange of methyl chloride: Results from NW Atlantic and Pacific Ocean studies, J. Geophys. Res., 101, 28,529–28,538.

Nightingale, P. D., G. Malin, C. S. Law, A. J. Watson, P. S. Liss, M. I. Liddicoat, J. Boutin, and R. C. Upstill-Goddard (2000), In situ evaluation of air-sea gas exchange parameterizations using novel conservative and volatile tracers, Global Biogeochem. Cycles, 14, 373–387.
Pilinis, C., D. B. King, and E. S. Saltzman (1996), The oceans: A source or a sink of methyl bromide?, *Geophys. Res. Lett.*, 23, 817–820.

Rintoul, S. R., and J. L. Bullister (1999), A late winter hydrographic section from Tasmania to Antarctica, *Deep Sea Res., Part I*, 46, 1417–1454.

Smethie, W. M., T. Takahashi, D. W. Chipman, and J. R. Ledwell (1985), Gas exchange and CO₂ flux in the tropical Atlantic Ocean determined from ²²²Rn and pCO₂ measurements, *J. Geophys. Res.*, 90, 7005–7022.

Tokarzyczk, R., K. D. Goodwin, and E. S. Saltzman (2003), Methyl bromide and methyl chloride degradation in the Southern Ocean, *Geophys. Res. Lett.*, 30(15), 1808, doi:10.1029/2003GL017459.

Trull, T., S. R. Rintoul, M. Hadfield, and E. R. Abraham (2001), Circulation and seasonal evolution of polar waters south of Australia: Implications for iron fertilization of the Southern Ocean, *Deep Sea Res., Part II*, 48, 2439–2466.

Wanninkhof, R. (1992), Relationship between wind speed and gas exchange over the ocean, *J. Geophys. Res.*, 97, 7373–7382.

Warner, M. J., and R. F. Weiss (1985), Solubilities of chlorofluorocarbons 11 and 12 in water and seawater, *Deep Sea Res., Part A*, 32, 1485–1497.

---

J. H. Butler, Climate Monitoring and Diagnostics Laboratory, National Oceanic and Atmospheric Administration, 325 Broadway, Boulder, CO 80305, USA.

K. D. Goodwin and S. A. Yvon-Lewis, Atlantic Oceanographic and Meteorological Laboratory, National Oceanic and Atmospheric Administration, 4301 Rickenbacker Cswy., Miami, FL 33149, USA. (shari.yvon-lewis@noaa.gov)

D. B. King, Chemistry Department, Drexel University, Philadelphia, PA 19104-2875, USA.

E. S. Saltzman, Earth System Science, University of California at Irvine, 220 Rowland Hall Irvine, CA 92697-3100, USA.

R. Tokarzyczk, Department of Oceanography, Dalhousie University, Halifax, Nova Scotia, Canada B3H 4J1.

---

6 of 6