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Methyl bromide and methyl chloride in the Southern Ocean

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[1] Air and water concentrations of methyl bromide (CH₃Br) and methyl chloride (CH₃Cl) were measured in the Southern Ocean (latitudes 45°–67°S, longitudes 144°–139°E) from late October through mid-December 2001. CH₃Br and CH₃Cl 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

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1. Introduction

[2] Methyl bromide (CH₃Br) and methyl chloride (CH₃Cl) are sources of inorganic halogen atoms that destroy stratospheric ozone (O₃). Both gases have natural sources and sinks, while CH₃Br also has substantial anthropogenic sources. The budgets for CH₃Cl and CH₃Br remain largely unbalanced with known sinks outweighing sources by ~ 20 – 25% for both trace gases [Montzka *et al.*, 2003].

[3] Supporting production as well as degradation, the oceans are both source and sink for these atmospheric gases. Net undersaturations of CH₃Br have been observed over much of the world's oceans [Lobert *et al.*, 1995a, 1996,

1997; 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].

[4] Assessing how the net oceanic fluxes of CH₃Br and CH₃Cl 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.

[5] Early attempts to parameterize oceanic production of CH₃Br relied on chlorophyll *a* as a proxy or on prescribing a fixed production rate. Such models suggested significant CH₃Br 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 CH₃Br in this region [Anbar *et al.*, 1996; Pilinis *et al.*, 1996]. During a previous Southern Ocean cruise, we observed large undersaturations ($-36 \pm 7\%$, 1σ , $n = 466$) for CH₃Br [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-

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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 CH₃Br and CH₃Cl 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 CH₃Br, CH₃Cl, trichlorofluoromethane (CCl₃F, 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 southbound transect. Twenty nine of these hydrocasts were sampled for methyl halides.

[7] Air was continuously pumped (~6 L min⁻¹) through 0.63-cm ID Dekabon tubing (Dekoron division of Furon, Aurora, Ohio) mounted on the mast at the bow of the ship. Samples from this air stream were collected and analyzed every 56 or 112 min, depending on the sequence of calibration samples, with a gas chromatograph-mass spectrometer (GC-MS) as described by Lobert *et al.* [1996] and with modifications summarized by King *et al.* [2000]. Prior to this cruise, the analytical column was changed from a DB-5 (0.25 mm ID, J&W) to a DB-VRX (0.25 mm ID, J&W). During this cruise, the precision (1σ) for a single CH₃Br, CH₃Cl, or CFC-11 air measurement was 2.3% (0.2 pmol mol⁻¹), 1.9% (10.0 pmol mol⁻¹), and 0.9% (2.3 pmol mol⁻¹), respectively.

[8] A GC-MS system with the same type of column and the same trapping design as described above, equipped with a custom-built automated purge system, was used to measure CH₃Br, CH₃Cl, and CFC-11 in discrete seawater samples. We automated the analysis of hydrocast samples by replacement of the typical single-calibrated volume (glass bulb) with a 32-port, 16-position loop selection valve (VICI Metronics, Texas). Sixteen bulbs were plumbed into the valve and housed in a temperature-controlled chamber. Water samples were collected from Niskin bottles into ground glass syringes and briefly stored in a bucket of cold seawater until they could be loaded into the calibrated glass bulbs. The computer-controlled valve stepped through the sequence of bulbs, and each sample, in turn, was pushed into the purge vessel. Blanks and calibration gas standards were included in the sequence to calibrate and monitor the system. The calibration gas standards for both GC-MS instruments were whole air working standards calibrated

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 CH₃Br, 2.7% (1.4 nmol m⁻³) for CH₃Cl, and 2.6% (0.08 nmol m⁻³) for CFC-11.

3. Results and Discussion

[10] 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 CH₃Br and CH₃Cl 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 CH₃Br, CH₃Cl, 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,

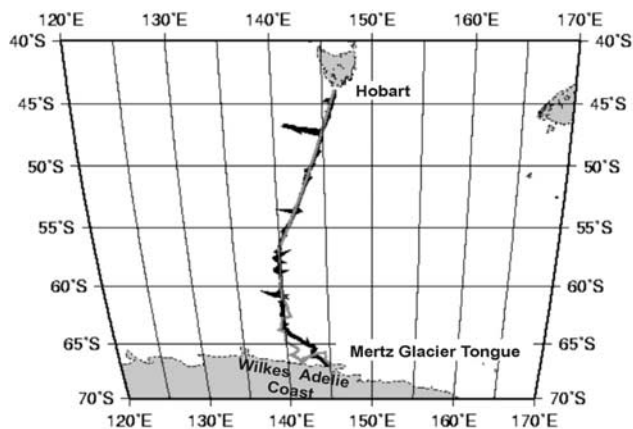


Figure 1. Cruise track, showing the southbound transect (black) and the northbound transect (shaded).

$n = 614$) 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] (CH₃Br), *Moore et al.* [1995] (CH₃Cl), 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 $2 \pm 1\%$ (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 CH₃Cl and CH₃Br did not exhibit such a strong anticorrelation between concentration and SST. These gases were substantially undersaturated with mean saturation anomalies of $-36 \pm 6\%$ (1σ , $n = 8$) for CH₃Br and $-34 \pm 7\%$ (1σ , $n = 8$) for CH₃Cl 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 CH₃Br and CH₃Cl 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 CH₃Br and CH₃Cl concentrations and saturation anomalies decreased rapidly from the SB past the ASF, with the lowest saturation anomalies reaching -80% for CH₃Cl and -82% for CH₃Br.

[14] Unlike CFC-11, CH₃Br and CH₃Cl were substantially undersaturated everywhere along the cruise track with saturation anomalies averaging $-39 \pm 11\%$ (1σ , $n = 19$) for CH₃Br and $-37 \pm 11\%$ (1σ , $n = 19$) for CH₃Cl north of the ASF (Figure 4d). The mean CH₃Br 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)), $-36 \pm 7\%$ (1σ , $n = 466$), [*Lobert et al.*, 1997]. These large undersaturations suggest that sinks are larger than sources for CH₃Br and CH₃Cl 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

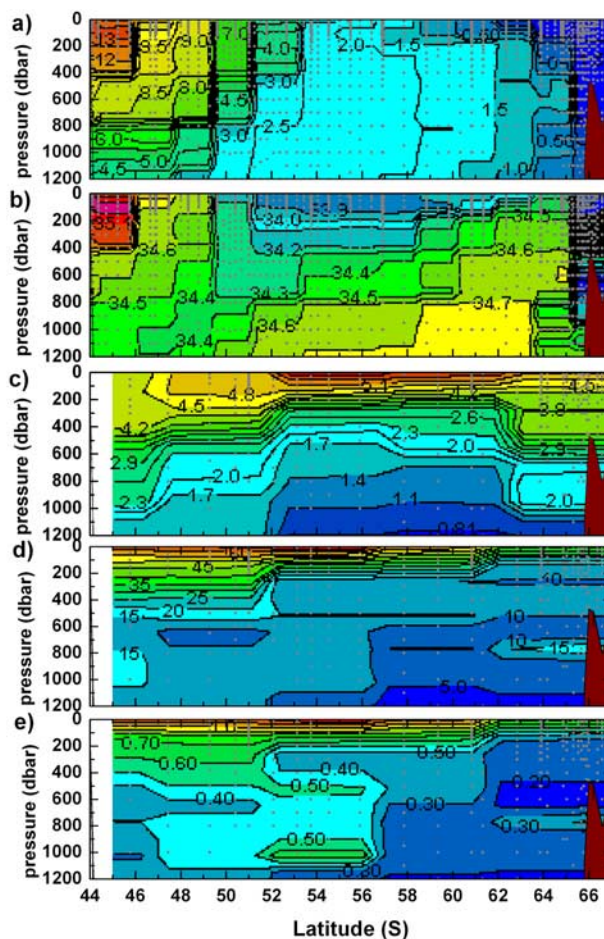


Figure 2. Vertical distributions of (a) potential temperature ($^{\circ}\text{C}$), (b) salinity (‰) (Rosenberg et al., manuscript in preparation, 2004), (c) CFC-11 (nmol m^{-3}), (d) CH₃Cl (nmol m^{-3}), and (e) CH₃Br (nmol m^{-3}) including data from both the densely sampled southbound and more sparsely sampled northbound transects. The CFC-11 enrichment in the sinking waters near the Antarctic coast, as recorded by *Rintoul and Bullister* [1999] along this cruise track in 1991, is clearly visible in Figure 2c.

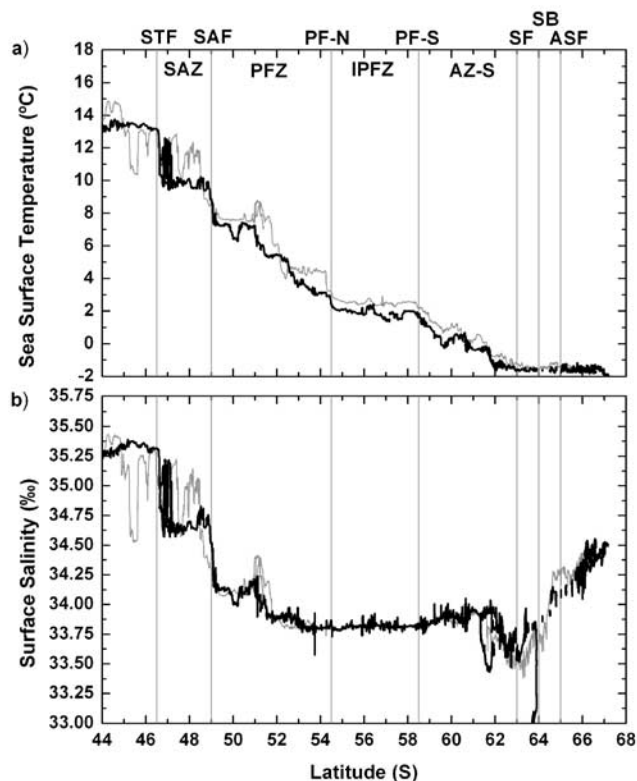


Figure 3. Surface water properties (a) temperature and (b) salinity during southbound (black) and northbound transects (shaded). The vertical lines indicate the positions of the fronts (STF, Subtropical Front; SAF, Subantarctic Front; PF-N, northern Polar Front; PF-S, southern Polar Front; SF, southern 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

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 (Δ_{f11}) was subtracted from the saturation anomaly of the trace gas of interest (Δ_g). The minimum degradation rate constant (k_{min}) was determined from the following equation:

$$k_{min} = \frac{K_W}{z} \left(\frac{-(\Delta_g - \Delta_{f11})}{100 + \Delta_g} \right), \quad (1)$$

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_{min} for CH₃Br and CH₃Cl north of the ASF were $0.039 \pm 0.029 d^{-1}$ (1σ , $n = 19$) and $0.036 \pm 0.025 d^{-1}$ (1σ , $n = 19$) (Figure 5), whereas for BLAST III the mean k_{min} for CH₃Br was $0.062 \pm 0.051 d^{-1}$

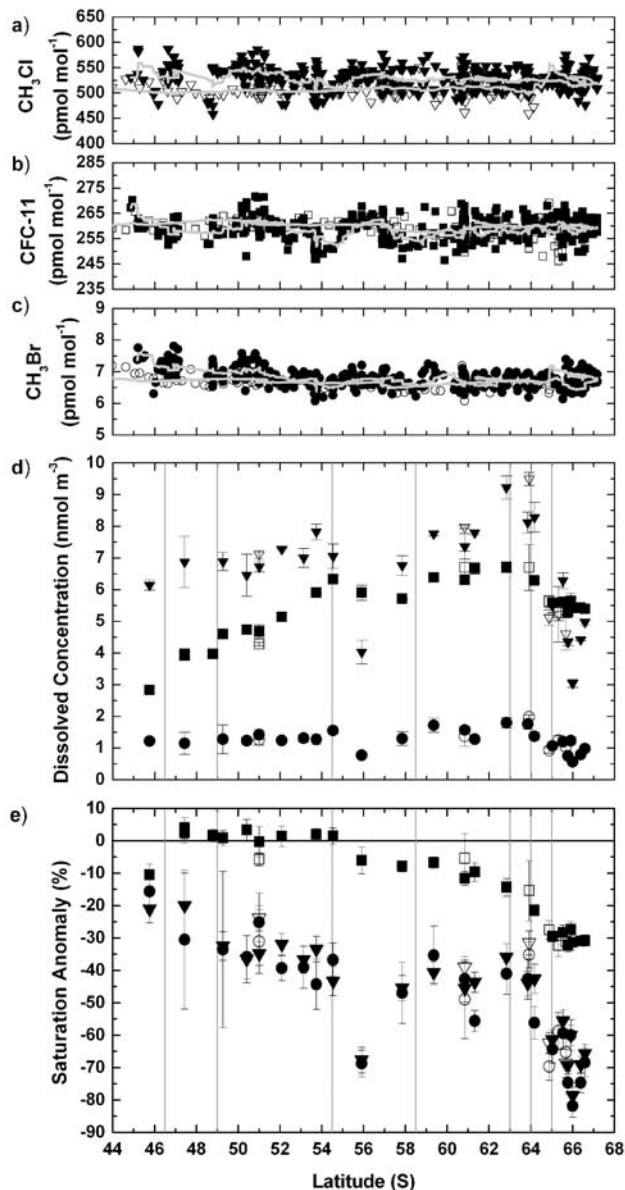


Figure 4. Measurements of (a)–(c) air concentrations ($pmol mol^{-1}$) for CH₃Cl (triangles), CFC-11 (squares), and CH₃Br (circles), (d) surface water concentrations ($nmol m^{-3}$) with 1σ error bars, CH₃Cl/10, and (e) saturation anomalies (%) including uncertainties in air, water, and solubilities. 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.

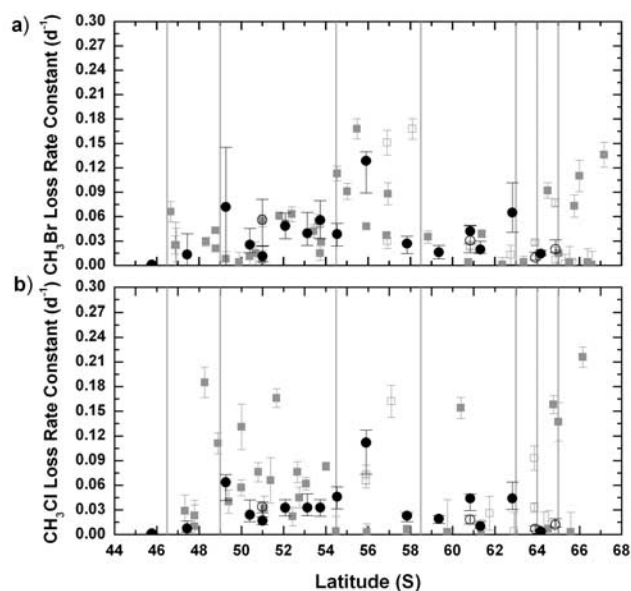


Figure 5. Mixed layer loss rate constants (d^{-1}) for (a) CH_3Br and (b) CH_3Cl with k_{\min} (circles) and the observed k_{total} (squares). Observed k_{total} values are from Tokarczyk *et al.* [2003]. Data shown are from both the southbound (solid symbols) and northbound (open symbols) transects. 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].

[16] 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 ($\text{Production} = (k_{\text{total}} - k_{\min}) C_W$, 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 $0.035 \pm 0.044 \text{ d}^{-1}$ (1σ , $n = 70$) for CH_3Br and $0.07 \pm 0.08 \text{ d}^{-1}$ (1σ , $n = 36$) for CH_3Cl (Figure 5). The magnitude of and trends in the observed CH_3Br k_{total} correlate well with the calculated k_{\min} for CH_3Br , suggesting that the observed loss rate constants are sufficient to balance the net air-sea flux and maintain the observed saturation anomaly for CH_3Br 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_3Cl south of the PF-N. North of the PF-N, the observed CH_3Cl k_{total} are larger than the calculated k_{\min} , suggesting that some mixed layer production of CH_3Cl is needed to balance the observed degradation and net air-sea flux while maintaining the observed saturation anomaly for CH_3Cl .

[17] Thus the data from this cruise suggest that there is no production of CH_3Br in these waters and perhaps a small source of CH_3Cl north of the PF-N. The BLAST III mean k_{\min} value is higher than the mean k_{total} observed by Tokarczyk *et al.* [2003] for this cruise, suggesting that k_{total} may have been larger or additional losses may have

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_3Br and CH_3Cl in polar and subpolar waters.

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