

Undersaturation of CH₃Br in the Southern Ocean



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Abstract. Dry mole fractions of methyl bromide (CH₃Br) in marine boundary layer air and in air equilibrated with surface water were measured in the Southern Ocean. Saturation anomalies were consistently negative at $-36 \pm 7\%$. The observed undersaturations do not support recently published predictions of highly supersaturated Antarctic waters, but instead suggest a net uptake of atmospheric CH₃Br by cold, productive oceans. The observations do not appear to be supported by known chemical degradation rates and present strong evidence for an unidentified, oceanic sink mechanism such as biological breakdown. Our estimate for the global, net, oceanic sink for atmospheric methyl bromide remains negative at -21 (-11 to -32) Gg y⁻¹.

Introduction

Bromine released from atmospheric CH₃Br is highly effective in depleting stratospheric ozone. Recent budget estimates for CH₃Br suggest that sources exceed sinks by about 40 Gg y⁻¹, demonstrating a need for additional understanding of the behavior of this gas in nature [Butler and Rodriguez, 1996], particularly its air-sea flux. Lobert *et al.* [1995] reported that most of the East Pacific Ocean was undersaturated and probably a net sink for this gas. Those results were further supported by findings for the Atlantic Ocean, suggesting that the world's oceans could be a global, net sink for atmospheric CH₃Br [Lobert *et al.*, 1996].

Two recently published, numerical models suggested that the polar oceans might be a large, net source of atmospheric CH₃Br [Pilinis *et al.*, 1996; Anbar *et al.*, 1996]. The two models used production rates based on data published in Lobert *et al.* [1995], presuming them to be either constant over the entire ocean or a function of chlorophyll-a concentration. In the latter case, production was correlated with satellite ocean color data as a proxy for chlorophyll-a concentration and those correlations were extrapolated to polar regions. With chemical degradation being largely suppressed in cold, polar waters, and a very high biological productivity during the austral summer, the predicted saturation anomalies were positive and ranged up to 500%, indicating that this polar source could globally outweigh the sinks estimated in Lobert *et al.* [1995]. To resolve this discrepancy, our study was conducted to measure the actual saturation of CH₃Br in the Southern Ocean during a time of high biological productivity.

Experimental

The BLAST III cruise was conducted between 21 February and 07 April, 1996, starting in McMurdo, Antarctica (78°S) and ending in Punta Arenas, Chile (54°S; Figure 1).

The gas chromatograph / mass spectrometer (GC/MS) that was used to measure about 15 compounds, including CH₃Br, was virtually identical to the system used during the two previous cruises [Lobert *et al.*, 1995; 1996] with slight modifications in the trapping procedure. On this cruise we also measured CH₃Br with a custom-built GC equipped with an electron capture detector (GC/ECD) and different columns and ECDs in support of measurements by GC/MS. The sampling system and the equilibrator were identical to those used on previous cruises. Measurements by both GC/MS and GC/ECD were calibrated with the same whole-air standards, which were calibrated against gravimetrically prepared standards. Chlorophyll-a fluorescence was measured in surface waters with a continuous-flow fluorometer (Turner Designs, Model 10), which was calibrated with chlorophyll standards following the cruise.

Saturation anomalies, corrections for physical effects, and air-sea fluxes were derived following the approach of Butler *et al.* [1991] with the solubility, degradation rate, Schmidt number, and wind speed correction as described in Lobert *et al.* [1996].

Results and Discussion

Measured, dry mole fractions of CH₃Br in the atmosphere averaged 8.3 ± 0.3 ppt (GC/MS) and 8.5 ± 0.7 ppt (GC/ECD) over the entire cruise (Figure 2a) and are consistent with data from the BLAST I and BLAST II cruises. CH₃Br was undersaturated in the water, with a mean dry mole fraction in the equilibrated air of 5.5 ± 0.6 ppt (GC/MS) or 5.6 ± 0.8 ppt (GC/ECD). Mole fractions from MS and ECD systems agreed, on average, within 0.2 ppt, showed identical substructures everywhere, and were correlated at $>>99.9\%$ confidence. Most important, however, is that the ocean was consistently undersaturated in CH₃Br, with a mean saturation anomaly of $-36 \pm 7\%$, which becomes $-33 \pm 8\%$ after correcting for physical effects such as the seasonal warming of the surface ocean [Butler *et al.*, 1991]. Similarly large undersaturations were recently found by Moore and Webb [1996] for the Labrador Sea in the summer.

The calculated, chemical degradation rate for CH₃Br in these cold waters is $0.6\% \text{ d}^{-1}$ (D.B. King and E.S. Saltzman, Removal of methyl bromide in coastal seawater: Chemical and biological rates, submitted, *J. Geophys. Res.*, 1996). Maintaining a steady-state, 33% undersaturation of CH₃Br in the surface waters in the presence of air-sea exchange and with the absence of any *in situ* production requires an *in situ* degradation rate of about $5.8\% \text{ d}^{-1}$ at the given temperatures and wind speeds, which is a factor of 10 larger than that for chemical degradation alone. The most likely explanation of these findings is that dissolved CH₃Br is being degraded by an additional, significant mechanism other than reaction with H₂O and Cl⁻. In fact, current laboratory research suggests that biological removal of CH₃Br in subtropical waters is about as fast as the chemical sink (King and Saltzman, 1996).

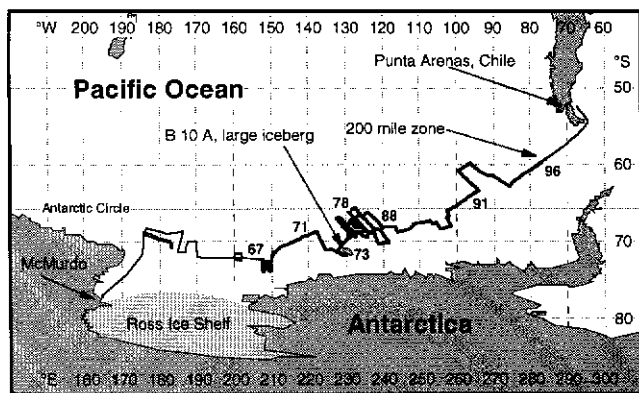


Figure 1. BLAST III cruise track from McMurdo, Antarctica, to Punta Arenas, Chile. Numbers along the cruise track indicate the Julian day of year 1996.

Thus, if there is any *in situ* production of CH₃Br in the Southern Ocean, then the degradation rate must be even higher than calculated in order to maintain the observed saturation anomaly. Our earlier estimates for aquatic production of CH₃Br were based upon the difference between net flux and chemical loss [Lobert *et al.*, 1995; 1996], but they did not include consideration of an additional sink. If this additional loss mechanism is significant and ubiquitous, then oceanic production of CH₃Br must be higher than previously estimated.

Our shipboard measurements show that the concentration of dissolved CH₃Br decreased along with chlorophyll-*a* concentra-

tion (between 0.8 and 14 μg chlorophyll-*a* l⁻¹) during the cruise. This contrasts with findings of Moore and Webb [1996], who showed that chlorophyll-*a* above 1 μg l⁻¹ correlated negatively with CH₃Br concentration in Labrador Sea and Northern Gulf Stream waters. Taken together, these results suggest that a simple, universal relationship between chlorophyll-*a* and dissolved CH₃Br does not exist. Because the large supersaturations suggested by models of Pilinis *et al.* [1996] and Anbar *et al.* [1996] are not supported by our observations, it becomes clear that the saturation or the net, air-sea flux of CH₃Br cannot be estimated directly from chlorophyll concentration or ocean color. Aquatic production could still be high and may even be correlated to chlorophyll, but it cannot be deduced from our measurements and must be balanced by equally high degradation.

Finally, from the corrected saturation anomaly of CH₃Br, we estimate a net air-to-sea flux of 8.0 Gg y⁻¹ for the polar oceans. This estimate includes assumptions that the undersaturation is independent of the season, that the investigated area represents polar oceans in general, and that polar oceans constitute 10% of the whole ocean. Under these conditions, our previously published estimates of the global, net air-sea flux of atmospheric CH₃Br [Lobert *et al.*, 1995; 1996] become more negative, with a best estimate of -21 (-11 to -32) Gg y⁻¹. The overall uncertainty of 50% is mostly due to uncertainties in the air-sea exchange calculation. The data presented here place considerable constraints upon CH₃Br emissions from polar waters, and provide further evidence for a global, net, oceanic sink for atmospheric CH₃Br.

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Data from this cruise are available for public use via world wide web at [ftp://ftp.cmdl.noaa.gov/noah/ocean/blast_iii/](http://ftp.cmdl.noaa.gov/noah/ocean/blast_iii/).

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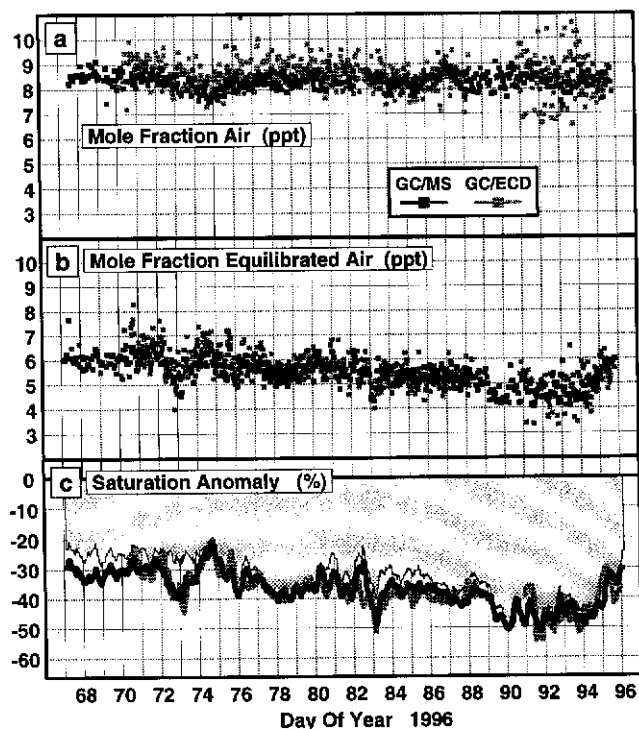


Figure 2. Measurements of methyl bromide in air (a), air equilibrated with surface water (b), and the resulting saturation anomaly (c) for both the GC/MS and the GC/ECD systems. The shaded area in panel (c) represents the saturation anomaly, corrected for physical effects, calculated from the GC/MS saturation anomaly (black line).

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