Methyl chloride and methyl bromide degradation in the Southern Ocean

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[1] This study presents shipboard measurements of the loss rate constants of methyl bromide and methyl chloride in surface seawater in the Southern Ocean, using a \(^3\)C stable isotope incubation technique. The measurements were made during October–December, 2001, on a cruise track extending from Hobart, Tasmania to Buchanan Bay (Mertz Glacier) at the coast of Antarctica (46–67\(^{\circ}\)S, 138–145\(^{\circ}\)E). Significant loss rates were measured for both compounds, even in very cold waters where chemical loss rates were negligible. These observations are attributed to biological uptake, and they explain the tendency for high latitude waters to be undersaturated with respect to atmospheric methyl bromide and methyl chloride. These observations are the first open ocean measurements demonstrating the biological degradation of methyl chloride.


1. Introduction

[2] Methyl bromide (CH\(_3\)Br) and methyl chloride (CH\(_3\)Cl) are halocarbons with both anthropogenic and natural sources that contribute significantly to the stratospheric halogen burden \([\text{Kurylo and Rodriguez, 1999}].\) These gases have complex biogeochemical cycles, involving terrestrial and oceanic sources and sinks. Because the atmospheric budgets of these gases are influenced by variability in climate, biological systems, and human activities, the potential exists for various forcings/feedbacks between climate, the biosphere, and stratospheric ozone.

[3] Several studies have reported the uptake of methyl halides by bacteria isolated from marine waters \([\text{Goodwin et al., 1998, 2001; Hoeft et al., 2000}].\) During the past few years we have carried out coastal and shipboard incubation studies demonstrating that organisms (presumably bacteria) remove CH\(_3\)Br from seawater at rates that are environmentally significant \([\text{King and Saltzman, 1997}].\) This activity appears to occur throughout the oceans, having been detected in tropical, subtropical, temperate, and polar waters in the North Atlantic and North Pacific oceans \([\text{Tokarczyk and Saltzman, 2001; Tokarczyk et al., 2001}]\). In a recent study, CH\(_3\)Cl uptake was found in coastal waters of Nova Scotia at environmentally significant rates \([\text{Tokarczyk et al., 2003}]\).

[4] The high latitude oceans are of particular interest for methyl halides. \text{Moore et al. [1996]} reported undersaturations of CH\(_3\)Cl in surface waters of the Labrador Sea, and \text{Lobert et al. [1997]} reported undersaturations for CH\(_3\)Br in the Southern Ocean. In this study, we present the first shipboard measurements of CH\(_3\)Br and CH\(_3\)Cl degradation rates in the Southern Ocean. These measurements were carried out in conjunction with sea surface saturation state measurements, which are described elsewhere \([\text{S. A. Yvon-Lewis et al.}]\). Methyl bromide and methyl chloride in the Southern Ocean, submitted to Journal of Geophysical Research, 2003, hereinafter referred to as \text{Yvon-Lewis et al., submitted, 2003}]. The goal of this study is to examine the role of biological uptake in determining the saturation state of this region.

2. Methods

[5] The study was conducted during the CLIVAR SR3 cruise, in the Southern Ocean south of Tasmania, from October 30 to December 12, 2001, aboard the Australian icebreaker “Aurora Australis”. The cruise track extended south from Hobart, Tasmania, reaching Buchanan Bay (Mertz Glacier) at the coast of Antarctica on Nov 30, 2001. The cruise track ranged in latitude from 46\(^{\circ}\) to 67\(^{\circ}\)S and in longitude from 138\(^{\circ}\) to 145\(^{\circ}\)E (Figure 1). The cruise track is superimposed on the November average SEAWIFS chlorophyll image. The position of the ship relative to major water mass boundaries is described below.

[6] Samples were collected along the cruise track at random times as often as analytically feasible. Surface samples were routinely collected with a 20 l plastic bucket. Niskin bottles (10 l) were used to collect subsurface samples from within the mixed layer. The seawater sample was passed through 63-\(\mu\)m pore size mesh to remove large
particles and grazing organisms and transferred to 100 ml glass syringes. Occasional aliquots were passed through 0.2-μm pore size filter and used as controls to verify that handling did not introduce artifacts. The syringes were kept closed, with no headspace, submerged in a large volume of seawater in a temperature-controlled water bath at the temperature at which the samples were originally collected.

CH$_3$Br and CH$_3$Cl loss rate constants were measured using the stable isotope incubation technique [King and Saltzman, 1997; Tokarczyk et al., 2001]. Seawater samples in glass syringes were spiked immediately after collection with either $^{13}$CH$_3$Br or $^{13}$CH$_3$Cl to a concentration of 400 pM or 1 nM, respectively. The first order loss was followed over a course of 12–14 hours using gas chromatography with quadrupole mass spectrometric detection. Typically, 5–6 measurements were used to calculate the rate constant value, with an analytical uncertainty ranging from 0.005–0.025 d$^{-1}$. An isotopic fractionation factor of $^{13}$k/$^{12}$k = 1.074 was used to convert the measured $^{13}$C rate constants to the $^{12}$C rate constants reported here [King and Saltzman, 1997].

Post-cruise acridine orange direct counting (AODC) was used to determine bacterial concentrations. In the field, samples were frozen at −80°C with 4% gluteraldehyde. In this study, a subset of samples covering the range of degradation rate constants were counted (average cell density = 2.1 × 10$^5$ cells/ml, n = 16). Total and active bacterial concentrations were obtained for some samples using flow cytometry (Becton Dickinson FACscan) with SYTO 13 and 6CFDA stains, respectively. Subsamples of the same samples taken at the beginning and at the end of incubations show that the observed loss rate was not influenced by bacterial growth in syringes.

3. Results

3.1. Methyl Bromide

CH$_3$Br loss rate constants (Figure 2, upper panel) were measured over the course of the cruise in 98 unfiltered seawater samples. The rate constants ranged from 0.00 to 0.18 d$^{-1}$ (mean 0.04; sd. 0.04). The chemical component of the loss rate constant (attributable to hydrolysis and chloride substitution) was calculated for each seawater sample from its temperature and salinity using the rate expression given by King and Saltzman [1997]. The calculated chemical loss rate constants were low during the entire cruise, ranging from 0.00 to 0.02 d$^{-1}$. These low rates reflect the low seawater temperatures (−1.7 to 11.6°C) and small variations in seawater salinity (33.5 to 35.1). The chemical rates are shown in Figure 2 as the lower, dark bars. Biological loss rate constants were calculated as a difference between the measured loss rate constant and the chemical loss rate constant for each particular sample (upper gray bars in Figure 2). Biological loss of CH$_3$Br was detected in the majority of samples (62 of 98), and the biological loss rate constants ranged from 0.00 to 0.18 d$^{-1}$ (mean 0.03; sd. 0.04).

Biological uptake along the cruise track was patchy with two distinct regions of high biological rates. The highest biological degradation rate constants (0.10–0.18 d$^{-1}$) were observed between 54° and 59°S, in the area between the northern and southern branches of the Polar Front [Rintoul and Bullister, 1999; Rintoul and Sokolov, 2001], sometimes referred to as the Inter-Polar Front Zone [Trull et al., 2001]. The area was characterized by relatively low sea surface temperatures, 1.4–2.5°C, and a surface salinity of about 33.8. The high biological degradation rates were observed inside this zone both during passage from Tasmania to Antarctica and on the return leg, about 23 days later.

The second region of high biological uptake extended from 64° to 67°S. In these very cold waters, with sea surface temperatures of −1.2° to −1.7°C and salinities of 33.9 to

![Figure 1](Image) Cruise track of the R/V Aurora Australis, during the CLIVAR SR3 cruise. The track is superimposed on the November 2001 monthly average SEAWIFS chlorophyll image.

![Figure 2](Image) Upper-CH$_3$Br loss rate constants. The total height of the stacked bars represents total rate constants. Black and gray bars represent chemical and biological loss rate constants, respectively; closed circles represent sea surface temperature. Lower - CH$_3$Cl loss rate constants. The chemical loss rate constants for CH$_3$Cl are negligible. The vertical dotted lines indicate the positions of major oceanographic fronts: SAF = Subantarctic Front, PF-N = northern Polar Front, PF-S = southern Polar Front, SB = southern boundary of the Antarctic Circumpolar Current Frontal Zone.
were in the process of freezing and ice crystals were below 0.03 d⁻¹. The highest biological rate constant in this area (0.15 d⁻¹) was observed in Buchanan Bay (67.2°S, 144.8°E). These waters were in the process of freezing and ice crystals were suspended in the sample when it was collected.

[12] The rest of the study area was characterized by lower biological loss. Rate constants less than 0.05 d⁻¹ were observed north of the northern branch of the Polar Front in the waters of the Polar Frontal Zone and Subantarctic Zone (approx. 46–54°S, SST 5–11°C). Rate constants below 0.03 d⁻¹ were observed in the waters of the Southern Antarctic Zone between the southern branch of the Polar Front and the southern boundary of the Antarctic Circumpolar Current (59–64°S, SST −1° to 1°C) [Rintoul and Bullister, 1999, Trull et al., 2001].

[13] The majority of samples analyzed in this study (76 of 98) were collected at the surface. To address the issue of vertical variability of the degradation rates within the mixed layer, we collected three pairs of samples at the surface and at 5–10 m depth. In two of these cases biological loss was undetectable. In the third case, the loss rate constant at 5 m was identical to that at the surface. In addition, three vertical profiles to 75–100 meters were collected (5–7 samples each). Unfortunately, these depth profiles were obtained in regions with little biological uptake, and the range of variability observed was small compared to the analytical uncertainty. Such experiments should be repeated in areas of high biological uptake, where vertical variability may be larger.

3.2. Methyl Chloride

[14] CH₃Cl loss rate constants (Figure 2 lower panel) were measured over the course of the cruise in 39 unfiltered seawater samples. Biological uptake was detected in most of these (30 of 39). The loss rate constants ranged from 0.00 to 0.22 d⁻¹ (mean 0.07, sd 0.08). The loss rate constant was also measured in filtered samples representing each of the major surface water regimes encountered during the cruise. In all cases, the loss rate constant in filtered samples remained at 0.00 d⁻¹. The observed stability of CH₃Cl in filtered seawater samples is consistent with earlier measurements of the CH₃Cl hydrolysis rate in seawater [Elliott and Rowland, 1995]. We therefore assume that the loss rate constants observed in unfiltered seawater samples were due to biological uptake.

[15] CH₃Cl degradation was observed throughout the regions of the Southern Ocean sampled on this cruise. In contrast to CH₃Br, there was no clear water mass-related spatial variability of the CH₃Cl degradation rate constants. As was the case for CH₃Br, there was no clear dependence of the CH₃Cl degradation rate constants on sea surface temperature. The highest degradation rate constant (0.23 d⁻¹) was observed in the waters of Buchanan Bay (67.2°S, 144.8°E; SST −1.7°C), and the next highest rate constant (0.20 d⁻¹) was observed in relatively warm waters (SST = 5°C) north of the northern branch of Polar Front at 49°S.

[16] These CH₃Cl degradation rate constant measurements are the first to be made in any region of the open oceans. The only previous measurements were a two-year time series of weekly measurements in the coastal waters of Bedford Bay, Nova Scotia [Tokareczk et al., 2003]. Those measurements exhibited strong seasonal variability, with summertime values slightly higher than those observed in this study. Wintertime degradation rate constants in those coastal waters were below detection, although the sea surface temperatures approached those in the Southern Ocean. This suggests that while seasonality may be an important source of variability of CH₃Cl degradation, water temperature per se is not the controlling parameter.

4. Discussion

[17] Early models of the oceanic cycling of methyl bromide suggested that the Southern Ocean could be a large net source of methyl bromide [Pilinis et al., 1996; Anbar et al., 1996]. Those models assumed that the degradation of methyl bromide occurred via hydrolysis and chloride substitution only. These chemical losses are highly temperature-dependent, and are negligible in very cold polar waters. A striking consequence of that assumption was the incorrect prediction that the high latitude oceans would be highly supersaturated with respect to the overlying atmosphere. Shipboard measurements by Lobert et al. [1997] demonstrated that the Southern Ocean is, in fact, significantly undersaturated. The undersaturations observed by Lobert et al. [1997] required an additional degradation rate constant of at least 0.05 d⁻¹ above the chemical loss rate constant to maintain the observed saturation anomaly in the presence of air-sea exchange.

[18] The results of this study provide direct confirmation that biological degradation of methyl bromide occurs in cold Southern Ocean waters, at rates sufficient to account for the observed undersaturation. For example, between 45–63°S, the mean CH₃Br saturation anomaly on this cruise was −39 ± 11% [Yvon-Lewis et al., submitted, 2003], and the gas exchange coefficient was estimated as 4.8 ± 2.3 m d⁻¹. To remain in steady state, these waters require a CH₃Br degradation rate constant of about 0.04 d⁻¹. The observed mean degradation rate constant from our surface shipboard measurements in this region was 0.04 d⁻¹ ± 0.004 se. For CH₃Cl, the saturation anomaly in this region was −37 ± 11%, and the gas exchange coefficient was 4.4 ± 2.1 md⁻¹. These conditions require a degradation rate of 0.02 d⁻¹. The observed mean CH₃Cl degradation rate in this region was about 0.07 d⁻¹ ± 0.01 se. One caveat on this comparison is that our measurements are surface values, while the ocean saturation state reflects processes averaged over the whole wind-mixed layer. Another potential complication is that negative saturation anomalies can also be produced by physical processes in areas of strong vertical mixing. This is not the case in the region of between 45–63°S during this study, as evidenced by measurements of CFC-11 in the mixed layer, but was the case south of 65°S [Yvon-Lewis et al., submitted, 2003].

[19] An interesting aspect of this data is that the patterns of geographic/temporal variability in CH₃Br and CH₃Cl degradation rates are different. This raises the possibility that the organisms involved may be different. Although many of the known methyl halide degrading enzymes can dehalogenate both compounds [McDonald et al., 2002; Dalton and Stirling, 1982], soil studies indicate that CH₃Br and CH₃Cl degrading populations may be distinct [McDonald, personal communication].
[20] Biological degradation of CH$_3$Br has now been observed to occur at environmentally significant rates in the North Atlantic, North Pacific, and Southern Oceans. Biological degradation of CH$_3$Cl has been observed in North Atlantic coastal waters and in the Southern Oceans. No correlation between the total bacterial cell number and the degradation rate constants has been observed during this cruise or during a previous Pacific expedition [Tokarczyk et al., 2001]. Most likely the abundance of specific bacterial strains responsible for the degradation process is not related to the overall bacterial abundance in seawater. Although the specific biochemical pathway(s) responsible for methyl halide uptake in oceanic waters are not known, the activity is probably widespread, and occurs under a wide range of temperatures and oceanographic conditions. It appears likely that this process is largely responsible for the undersaturation of the high latitude oceans, and hence, may play a major role in maintaining the current saturation state of the oceans with respect to the atmosphere.

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References

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