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Biological degradation of methyl chloride in coastal seawater

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Methyl chloride (CH\textsubscript{3}Cl) is the most abundant halocarbon in the atmosphere, and constitutes a significant fraction of the total atmospheric halogen burden. Chemical reactions of CH\textsubscript{3}Cl in seawater are slow, and it has been believed that the oceans are not an important sink for this compound. However, direct measurements of CH\textsubscript{3}Cl degradation rates in coastal seawater (Bedford Basin, Nova Scotia), using a stable isotope incubation technique, indicate rapid loss attributed to microbial activity. A series of weekly measurements from March 2000 to May 2001 yielded degradation rates ranging from 0–30% d\textsuperscript{-1}, with an annual mean of 7.4% d\textsuperscript{-1}. If biological uptake of CH\textsubscript{3}Cl occurs throughout the oceans at similar rates, the mean partial atmospheric lifetime of CH\textsubscript{3}Cl with respect to oceanic removal could be a few years, rather than several decades as previously thought. This rapid removal would make the oceans a major sink for CH\textsubscript{3}Cl and lower the overall atmospheric lifetime of CH\textsubscript{3}Cl from the current estimate of 1.3 to about 1.0 years. Measurements of the degradation rate of CH\textsubscript{3}Cl in open ocean waters are needed in order to quantify the oceanic uptake rate. 

INDEX TERMS: 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 1615 Global Change: Biogeochemical processes (4805); 4805 Oceanography: Biological and Chemical: Biogeochemical cycles (1615); KEYWORDS: methyl chloride, methyl halides, biogeochemistry of halocarbons


1. Introduction

Methyl chloride (CH\textsubscript{3}Cl) is a major source of atmospheric chlorine [Kurylo and Rodriguez, 1999], and a contributor to stratospheric ozone depletion. CH\textsubscript{3}Cl currently contributes about 12% of the total equivalent effective stratospheric chlorine. It is projected that this fraction will grow to as much as 30% later this century, as various solvents, CFCs, HCFCs, and other halogenated gases are purged from the atmosphere as a result of the Montreal Protocol [Madronich and Velders, 1999]. CH\textsubscript{3}Cl is largely natural in origin, with a complex biogeochemical cycle that is not well understood. The principal identified sources are terrestrial and include biomass burning and emission by wood-rotting fungi, and tropical plants [Lobert et al., 1999; Watling and Harper, 1998; Varner et al., 1999; Rhew et al., 2000; Yokouchi et al., 2000]. Oceanic emissions, which were previously thought to be the main source of atmospheric methyl chloride, have more recently been estimated to account for less than 12% of the global flux [Moore et al., 1996]. Oceanic measurements of methyl chloride show that the low latitude ocean is supersaturated with respect to the overlying atmosphere, while the high latitude ocean is undersaturated [Moore et al., 1996]. Since chemical reactions of methyl chloride in seawater are very slow [Elliott and Rowland, 1995], these observations suggest the existence of an additional, most likely biological, loss mechanism at high latitudes.

Biological degradation of methyl bromide in seawater and in marine bacterial cultures has been demonstrated [King and Saltzman, 1997; Goodwin et al., 1998; Hoefl et al., 2000; Goodwin et al., 2001; Schaefer et al., 2002]. One strain of facultative methylotroph cultured from seawater has shown the ability to metabolize CH\textsubscript{3}Br [Schaefer and Oremland, 1999], but no information is currently available about the rates of biological uptake in the oceans.

In this study, we utilize a stable isotope tracer technique to directly measure the loss rate of methyl chloride in Nova Scotia coastal waters between March 2000 and May 2001. These measurements reveal seasonally changing rates of methyl chloride degradation, with first order rate constants ranging from 0% per day in winter to 30% per day in summer. We attribute the observed CH\textsubscript{3}Cl degradation to microbial processes. These observations suggest that the loss rate for CH\textsubscript{3}Cl from the surface ocean due to biological uptake may be similar in magnitude to the loss by air-sea exchange, and can explain the methyl chloride undersaturation observed in high latitudes waters. These data indicate that oceans can be a significant global sink for atmospheric...
CH$_3$Cl, and that the lifetime of this gas in the atmosphere may be shorter than previously believed.

2. Methods

2.1. Sampling Location: Bedford Bay, Nova Scotia

We measured loss rates constants of $^{13}$CH$_3$Cl over an annual cycle, from March 2000 until May 2001, at Compass Buoy station (44°41'30"N, 63°38'30"W) in the Bedford Basin (Nova Scotia). The Bedford Basin is the inner component of the Halifax harbor (Figure 1), with a surface area of 17 km$^2$ and a volume of 5.6 x 10$^8$ m$^3$. It is connected to the open Atlantic Ocean by a channel, with a minimum width of 400 m and sill depth of 20 m. The residence time of water in the basin is approximately 260 hours. Surface water temperature changes gradually from about 1°C in winter to 20°C in summer. The average salinity remains around 30, however freshwater runoff can occasionally lower it to 25 near the surface. Inorganic nutrients decrease sharply in the spring and increase in the fall, with nitrate approaching the limits of analytical detection in summer. Primary production in the basin, as on the adjacent shelf, is dominated by phytoplankton without significant contribution from seaweed [Li, 1998]. Overall exchange of shelf and inshore waters is controlled by alongshore winds driving Ekman transport, which exerts strong control of the nutrients and chlorophyll in the basin [Mitchell, 1991]. Weekly averages of temperature, salinity and nutrient concentrations in the basin are usually similar to those on the shelf [Petri et al., 1999], but local events related to runoff do occasionally occur. It has been estimated from the water exchange at the inlet mouth, that such events normally exist for a maximum of 3–4 days [Lewis and Platt, 1982]. At longer timescales, external physical forces control the basin dynamics.

2.2. Experimental Techniques: Sampling and Analysis

Samples were collected between 0830–0900 (local time), just below the surface with a 20-L plastic bucket and immediately transferred to 100-mL glass syringes. One aliquot of each sample was kept unfiltered, but was passed through a 63 μm pore size mesh to remove large particles and grazing organisms. These unfiltered samples were considered “live.” A second aliquot of each sample was filtered through a 0.2-μm Millipore filter to remove organisms and reduce biological activity. These filtered samples were used as control samples to verify that sampling handling did not introduce artifacts and to confirm the rate of chemical loss of CH$_3$Cl in seawater. The syringes were kept closed, with no head space, submerged in a large volume of seawater, and transported to the laboratory. In the laboratory, they were placed in a temperature-controlled water bath at the temperature at which the samples were originally collected.

The methodology and instrumentation used in this study is essentially identical to that developed for methyl bromide loss rate studies [Tokarczyk and Saltzman, 2001; Tokarczyk et al., 2001]. Filtered and unfiltered seawater samples were spiked with $^{13}$CH$_3$Cl to a concentration of approximately 1 nM and incubated for 12–14 hours. Aliquots (15 ml) were withdrawn from each syringe for analysis at 2-hour intervals. The concentration of $^{13}$CH$_3$Cl was measured in the samples using purge and trap preconcentration, followed by gas chromatography with mass spectrometric detection. An isotope dilution method was used to improve the precision of the analysis, using a spike of CD$_3$Cl introduced at analysis time. During analysis, ions m/z 53 and 55 were monitored, for $^{13}$CH$_3$Cl and CD$_3$Cl, respectively.

First-order loss rate constants were determined from the slope of a least squares regression of ln($^{13}$CH$_3$Cl) versus time. Figure 2 shows the degradation rates measured on May 31, 2000. Data are plotted as natural log(C/C$_0$), where C is the measured concentration of $^{13}$CH$_3$Cl during the incubation, and C$_0$ is the initial concentration at the start of the incubation. The open and solid circles represent filtered and unfiltered aliquots of the same water sample, respectively. The slopes of the linear regression lines represent the degradation rate constants and the standard error of the slope for each line is given in brackets.
CH₃Cl<sub>initial</sub>) versus time (Figure 2). The overall precision of the rate constant measurements varied from 0.01–0.04 d<sup>-1</sup> (95% confidence level). No loss of <sup>13</sup>CH₃Cl was observed in filtered samples indicating that the chemical breakdown of CH₃Cl in seawater was undetectable over the applied incubation time and seawater temperature range, in agreement with laboratory rate constants [Elliott and Rowland, 1995]. Because rates were measured using <sup>13</sup>CH₃Cl, a minor correction due to isotopic fractionation should be applied in order to obtain rates for naturally occurring CH₃Cl, which consists primarily of <sup>12</sup>CH₃Cl. This fractionation factor has not been measured, and the rates in this study have not been corrected for this effect. Based on similar fractionation factors for chemical and microbial degradation of CH₃Br [Tokarczyk and Saltzman, 2001; Miller et al., 2001], this effect is expected to increase the rate constant by about 7.5% of the measured value, which is less than the experimental uncertainty of most of the measurements.

### 2.3. Lifetime Calculations

A coupled surface ocean-atmosphere model was used to estimate the effect of oceanic loss rates on the atmospheric lifetime of methyl chloride [Yvon and Butler, 1996]. The model includes air/sea exchange, oceanic loss (via chemical or biological processes), and downward mixing across the thermocline. This model has recently been used to estimate the effect of oceanic uptake on the atmospheric lifetimes of a variety of gases, including CH₃Cl, based on chemical losses in the ocean [Yvon-Lewis and Butler, 2002]. These calculations were made assuming that the oceans and atmosphere are in steady state [Yvon and Butler, 1996], as follows:

\[
\frac{1}{\tau_{AO}} = \frac{r}{n_r} \frac{K_w A}{H} \left( \frac{k_d}{k_d + \frac{K_w}{z}} \right),
\]

where: \( k_d = k_s + \frac{\sqrt{D_z}}{z} \). The model parameters are defined as follows: \( \tau_{AO} \) is the partial atmospheric lifetime of CH₃Cl with respect to oceanic losses; \( r \) is the fraction of atmospheric CH₃Cl residing in troposphere; \( n_r \) is the number of moles of the troposphere; \( K_w \) is the air-sea gas transfer velocity; \( A \) is the surface area of the ocean; \( H \) is the solubility of CH₃Cl; \( z \) is the mixed layer depth; \( k_d \) is the oceanic degradation rate constant (corrected for vertical loss due to downward mixing from the mixed layer); \( k_s \) is the degradation rate constant at the mean thermocline temperature; \( D_z \) is the diffusivity through the thermocline. The two-box model calculation (described by equation (1)) was carried out for each cell of a 2° × 2° grid of monthly average sea surface temperature, 10 m wind speed, salinity [Woodruff et al., 1987], mixed layer depths, and thermocline diffusivities [Li et al., 1984].

### 3. Results

During the period between March 2000 and May 2001, 39 rate constant measurements were made, yielding values ranging from 0.00 to 0.30 d<sup>-1</sup> (Figure 3). Experimental data from an individual rate constant measurement are shown in
Figure 2, illustrating that the observed decays were first-order and that the degradation rate constant in unfiltered samples often far exceeded that in filtered samples. The annual mean degradation rate, as calculated from averaging the periods March 2000–February 2001 or June 2000–May 2001, is 0.07 ± 0.08 d⁻¹ (σ, n = 34 and 30, respectively).

The rate constants exhibit complex seasonality, with maxima at the beginning and end of the warm season. The largest rate constant occurred in June reaching 30% per day. A slightly smaller maximum occurred in October, equal to a loss of 17% per day, followed by a rapid decrease to below 10% per day during November and December. During January–February the CH₃Cl degradation rate constant approached the detection limit of the analytical method (0.00 ± 0.02 d⁻¹). During both years, the spring increase in the rate constant occurred just at the onset of spring warming in March.

The factors controlling the variability in CH₃Cl loss rate constants are not known. No consistent relationships were found between the observed degradation rate constants and ancillary parameters collected at this time series station, including nutrient concentrations, seawater salinity, chlorophyll contents or total bacterial abundance. The June maximum in the rate constant coincided with the maximum abundance of bacteria in coastal waters [Li and Dickie, 2001], while the October maximum coincided with the maximum abundance of microzooplankton. The latter suggests a possible link between abundance of these grazers and CH₃Cl-utilizing species (likely bacteria). However, it is also possible that there is an optimal temperature range, outside which the rate of biological degradation slows down significantly. It should also be noted that all of the samples in this study were collected during the morning. No measurements were made at other times of day, and if significant diel variability in degradation exists, it could systematically bias the results.

4. Discussion

The existence of an oceanic biological sink has significant implications for the CH₃Cl budget and lifetime, both in the ocean and atmosphere. For oceanic waters between 10° and 20°C, the rate constant for chemical loss of CH₃Cl varies between 0.07 and 0.33 yr⁻¹ [Elliott and Rowland, 1995], as compared with an annual average degradation rate constant of 27 ± 28 yr⁻¹ from this study. Using the coupled surface ocean-atmosphere model described above, a global mean area-weighted rate constant for chemical loss of CH₃Cl is calculated to be 0.54 yr⁻¹ [Yvon-Lewis and Butler, 2002]. Including vertical mixing in the water column brings the total aquatic loss rate constant to 0.80 yr⁻¹. This yields an oceanic lifetime of about 1.25 years and a partial atmospheric lifetime with respect to oceanic losses of about 70 years. These loss processes have a negligible effect on the overall tropospheric lifetime of CH₃Cl, with respect to the oceanic loss is reduced to 4.1 years. Considering both the OH loss and oceanic loss gives an overall atmospheric lifetime of CH₃Cl of 1.0 years.

The partial atmospheric lifetime of a gas with respect to oceanic loss is highly sensitive to oceanic degradation at low loss rate constants [Butler, 1994]. At very high loss rate constants, air/sea transfer rather than in situ loss limits the gas flux into the ocean, and the atmospheric lifetime approaches a constant limiting value. For CH₃Cl, assuming instantaneous loss in the ocean yields a minimum partial atmospheric lifetime with respect to oceanic loss of approximately 2.0 years, corresponding to a total atmospheric lifetime of 0.8 years. This calculation places a strong upper limit on the rate at which the ocean can remove atmospheric CH₃Cl.

The observed degradation rates can explain the reported undersaturation of cold North Atlantic waters with respect to atmospheric concentrations of CH₃Cl. The minimum degradation rate constant (kₑ) needed to support an observed saturation anomaly is estimated from the expression

$$kₑ = \frac{Kₑ}{z} \left(\frac{-\Delta g}{100 + \Delta g}\right).$$

where Kₑ ranges from 2000 to 3000 m yr⁻¹ (10° to 0°C) and Δg is the gas saturation anomaly. Δg is defined as 100(pₑw − pₑga)/pₑga, where pₑw and pₑga are the partial pressures of the gas in seawater and air. A positive saturation anomaly indicates that the seawater is oversaturated with respect to the overlying atmosphere.

Saturation anomalies as low as −24% have been observed in cold Labrador Sea surface waters [Moore et al., 1996], which cannot be explained by chemical losses and vertical mixing alone. A loss rate constant of approximately 7 yr⁻¹ is needed to support this level of undersaturation. This far exceeds the rate constant for the known chemical loss of CH₃Cl in the seawater, but falls well within the range of the degradation rate constants observed in this study. The actual degradation rate required to explain the Labrador Sea undersaturation could be larger, if there were in situ production of CH₃Cl in those waters. The annual average degradation rate constant observed in this study can support a saturation anomaly of −40%, in the absence of in situ production.

The only known in situ oceanic source of CH₃Cl is the chloride substitution of CH₃Br and CH₃I. It is estimated that this source can account for 40–75% of the net flux of CH₃Cl emitted from the oceans to the atmosphere [Moore et al., 1996; Moore, 2000]. The annual average rate constant for biological degradation (27.0 yr⁻¹) obtained from this study is similar to the global mean time constant for air-sea exchange (Kₑ/z = 23.5 yr⁻¹). Since the oceanic production of CH₃Cl must balance both the air/seawater flux and in situ degradation, there must be a significant additional in situ oceanic source of CH₃Cl. This source is estimated to be approximately 0.3 to 0.7 Tg yr⁻¹, and is presumed to be biological. Laboratory culture studies have demonstrated production of CH₃Cl by some species of marine macro and micro-algae [Manley and Dastoor, 1987; Tait and Moore, 1995]. However, extrapolation of the production rates observed in the laboratory is not sufficient to explain the required oceanic production rate. There are many possible
reasons for this, including the fact that laboratory cultures are very different from natural phytoplankton in terms of species and growing conditions. Furthermore, these experiments yield net production rates of methyl chloride that mask any possible biological consumption processes.

5. Conclusions

[19] This study presents the first observations of degradation of CH₃Cl in ocean waters. These results provide a preliminary estimate of the potential strength of the biological sink for CH₃Cl in the ocean and its effect on the overall atmospheric lifetime of this compound. These estimates are based on the extrapolation of Bedford Basin results to the entire ocean, and should therefore be viewed with caution. Open ocean and coastal measurements are needed in a variety of environments on a seasonal basis in order to provide a firm basis for regional or global extrapolations. However, it has recently been demonstrated that biological loss of CH₃Br occurs at measurable rates across wide regions of the North Atlantic and Pacific Oceans [King and Saltzman, 1997; Tokarczyk and Saltzman, 2001; Tokarczyk et al., 2001]. Therefore it is reasonable to suspect that biological degradation of CH₃Cl in ocean waters is a widespread phenomenon that has a significant impact on the global CH₃Cl budget. Measurements of the degradation rate of CH₃Cl in the open ocean are clearly needed in order to better constrain the atmospheric lifetime of CH₃Cl and the role of the oceans in the biogeochemical cycle of this compound.

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