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Methyl bromide loss rate constants in the North Pacific Ocean

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Abstract. The degradation rate constant of CH₃Br in the North Pacific Ocean was measured in surface seawater between September and October 1999, using a stable isotope (³CH₃Br) incubation technique. Total degradation rate constants ranged from 0.02 to 0.43 d⁻¹, decreasing in colder waters as a result of the temperature-dependence of chemical losses. Biological rate constants ranged from 0.01 to 0.20 d⁻¹. In subtropical waters (13-20°N), biological loss rate constants were small compared to chemical loss rate constants. North of Hawaii, biological processes played an increasingly significant role in CH₃Br degradation. In subpolar waters (40-58°N), biological losses dominated the removal of methyl bromide. Comparison of the measured loss rate constants with surface water CH₃Br concentrations suggest that the CH₃Br production rate is higher in warm, low latitude waters than in cold subpolar waters at this time of year. Diel studies revealed a midday maximum in biological degradation of methyl bromide.

1. Introduction

The tropospheric budget of methyl bromide (CH₃Br) is currently the focus of research because of the importance of this compound as a source of stratospheric bromine [Kurylo & Rodriguez, 1999]. CH₃Br has an active and complex biogeochemical cycle and has been used widely as an agricultural fumigant. Current estimates suggest that the oceans constitute a net sink for CH₃Br of 11–21 Gg/yr [King et al., 2000]. This net flux reflects a balance between the atmospheric uptake of CH₃Br, and the internal production and consumption of CH₃Br in the oceans. Laboratory production of CH₃Br by marine phytoplankton [Saemundsdottir & Matrai, 1998, Scarratt & Moore, 1998] and other algae [Manley & Dastoor, 1987; Sturges et al., 1993] has been observed, and evidence for algal production in the open ocean has been reported [Baker et al., 1999].

Destruction of CH₃Br in seawater proceeds chemically via chloride substitution and hydrolysis [Elliott & Rowland, 1993; Jeffers & Wolfe, 1996] and by biological degradation [King & Saltzman, 1997; Goodwin et al., 1998]. The rates of CH₃Br production and destruction in the ocean and the processes controlling this turnover are important parameters in terms of understanding how the ocean/atmospheric flux of CH₃Br may change in response to future changes in anthropogenic emissions, terrestrial ecosystem fluxes, or ocean warming.

CH₃Br lifetimes were recently measured in surface waters of the North Atlantic Ocean, Caribbean, and eastern Pacific shelf waters using a stable isotope incubation technique. Loss rate constants were found to be in the range of 0.03 to 0.40 d⁻¹, with a biological contribution ranging from 0.00 to 0.28 d⁻¹ [Tokarczyk & Saltzman, 2001]. In contrast to chemical rates, which are highly temperature dependent, biological removal exhibited no apparent relationship to seawater temperature and salinity. This paper presents measurements of the CH₃Br loss rate constant in surface subtropical, temperate, and subpolar waters of the North Pacific Ocean.

2. Methods

This study was conducted aboard the National Oceanographic and Atmospheric Administration (NOAA) ship Ronald H. Brown from Sept. 15-Oct. 21, 1999. The cruise track extended northeast from Kwajalein, Marshall Islands to Pearl Harbor, Hawaii, then northward to Dutch Harbor, Alaska (Unalaska), and eastward to Seattle, Washington. The cruise track ranged in latitude from 11-58°N and longitude from 168°E-125°W (Figure 1). The cruise track is superimposed on the September average SEAWIFS chlorophyll image, showing the position of the ship relative to the major oceanographic water mass boundaries. Subtropical waters have low chlorophyll content in comparison to the cooler waters further north. The cruise started a few degrees north of the equatorial divergence and crossed into subarctic waters between 35-40°N.

CH₃Br loss rate constants were measured using the stable isotope incubation technique of King & Saltzman [1997], with modifications for shipboard use as described by Tokarczyk & Saltzman [2001]. Seawater samples were either filtered (0.2-µm) to remove biological activity or passed through a 64-µm sieve in order to remove large particles and grazing organisms. These samples were spiked with [³CH₃Br] to a concentration of 400 µM and incubated in glass, matched barrel syringes with no headspace.

Seawater samples were collected just below the surface using a bucket. Most water samples (except for the diel studies) were collected at either 6:30 or 8:00 AM local time.
Incubations were carried out in the laboratory at a temperature close to that of the sample upon collection (±1°C). Parallel dark (laboratory) and full light (deck) incubations of the same seawater yielded identical degradation rate constants.

The first-order loss of $^{13}$CH$_3$Br was followed over the course of 12-14 hours using gas chromatography with quadruple mass spectrometer detection. Loss rate constants were measured in filtered and unfiltered aliquots of surface water samples. An isotopic fractionation factor of $^{12}$CH$_3$Br/CH$_3$Br = 1.074 was used to convert $^{13}$CH$_3$Br rate constants to $^{12}$CH$_3$Br rate constants reported here [King & Saltzman, 1997; Tokarczyk & Saltzman, 2000].

Subsamples for bacterial counts were frozen with 4% gluteraldehyde at the start of each incubation and at the end of selected incubations. In the laboratory, bacterial number was determined using DAPI stain [Porter and Feig, 1980]. The mean cell density was 6.1x10$^6$ cells/ml (n=42), and bacterial growth in the syringes was not observed. Selected samples were incubated with antibiotics (20 µg/ml streptomycin and penicillin, and 40 µg/ml neomycin) or a eukaryotic inhibitor (200 µg/ml cycloheximide) to determine if degradation rates or bacterial number were affected by inhibition of protein synthesis. The negative results of these experiments, along with the observed first-order kinetics of CH$_3$Br loss, suggest that the loss rate constants measured in syringes were not influenced by bacterial growth or induction of new enzyme.

2. Results and Discussion

2.1. Filtered Seawater Samples

CH$_3$Br loss rate constants measured in filtered seawater should reflect the chemical loss due to chloride substitution and hydrolysis [King & Saltzman, 1997]. Loss rate constants from the cruise were normalized to a salinity of 35. The results (Fig. 2) are in agreement with other recent field measurements from the North Atlantic and Eastern Pacific Oceans [Tokarczyk and Saltzman, 2001] and in most cases, lie within the experimental error of the rate expression of King and Saltzman [1997]. These results extend the experimental coverage to lower temperatures than previously measured.

Six of the 27 filtered samples had significantly greater loss rate constants than predicted from chemical processes alone. Four of these were collected in waters where biological loss rate constants were unusually high, suggesting that the filtration process did not entirely remove enzymatic activity from these samples. The most extreme case was the Oct. 16 sample collected near Kodiak Island (152°W, 58°N) in which the loss rate constant in the filtered sample was 0.08 d$^{-1}$, compared to the expected value of 0.01 d$^{-1}$. The biological loss rate constant (0.16 d$^{-1}$) was 4-8 times greater than biological rate constants measured offshore in the same region. While defects in filters cannot be ruled out, such observations could also indicate a contribution to methyl bromide loss from either ultramicrobacteria [Eguchi et al., 1996] or free enzymes present in solution, which pass through the filters.

2.2. Unfiltered Seawater Samples

Total loss rate constants measured in unfiltered seawater samples ranged from 0.02-0.43 d$^{-1}$ over the course of the cruise (Figure 3). Biological loss rate constants were obtained by subtracting the chemical loss rate constant (calculated using the King and Saltzman [1977] rate expression) from the total loss rate constant. Biological loss of methyl bromide was measurable in all water samples. Biological loss rate constants ranged from 0.01-0.20 d$^{-1}$, contributing 4-93% of the total loss rate constant in individual samples with a mean of 44±29%.

These results are similar in magnitude to those obtained in the spring/early summertime North Atlantic, 33±28%, in subtropical and mid-latitude waters [Tokarczyk and Saltzman, 2000].

The variability of the biological loss rate constants appears to be related to water mass type, but in a more complex way than the temperature-controlled variability of chemical losses. All samples were collected in open ocean waters, except for three coastal samples collected at Pearl Harbor, Dutch Harbor, and Kodiak Island (Figure 3). Samples were collected between 06:00 and 08:30, with exceptions as noted below. The cruise started in warm (28°C), equatorial waters where biological loss

**Figure 1.** Cruise track, September-October, 1999, with September SEAWIFS chlorophyll-a image. Water sample locations are marked. Diel studies were carried out at Station Papa, as indicated by the black circles.

**Figure 2.** CH$_3$Br loss rate constants measured on filtered seawater samples from this study and previous measurements in the North Atlantic and Eastern Pacific. The King and Saltzman [1997] rate expression is also shown.
was 0.13 d⁻¹, representing about 25% of the total loss. For the
next few days the ship passed through subtropical convergence
waters south of the Hawaiian Islands where biological CH₃Br
degradation rate constants were very low (<10% of total loss;
Figure 3). Biological loss rate constants were markedly higher
in the subtropical convergence waters north of Hawaii, ranging
from 0.07-0.15 d⁻¹, and contributing up to 39% of the total loss
rate. The biological rate constant for the Pearl Harbor sample
was particularly high, at 0.20 d⁻¹, making up 47% of the total
loss rate constant. This sample was collected under strong
coastal influence as showed by reduced salinity (33 as opposed
to 35 offshore). This sample and the subsequent one were
collected at 10:00 and 12:00, respectively, and could be
influenced by diel variations, as discussed below.

At about 35°N, the ship encountered decreasing temperature
and salinity that mark the transition between subtropical
convergence to the south and Arctic convergence waters to the
north. During passage through this transition zone, total loss
rate constants decreased rapidly. This reflects the strong
temperature dependence of chemical CH₃Br loss. However,
biological loss rates were relatively high in these transitional
waters. At 42°N, duplicate incubations were carried out,
yielding a mean biological degradation rate constant of 0.15
±0.01 d⁻¹, or 77% of the total loss rate constant.

In the cold waters of the Arctic convergence, north of 40°N
and between 165 and 150°W, biological loss rates remained
significant, ranging from 0.03-0.07 d⁻¹. These rate constants
contributed 60-87% of the total loss rate constant in these
waters. The coastal Dutch Harbor (Unalaska) and Kodiak
Island (Figure 3) samples (collected at 12:30 and noon) had
even higher biological loss rate constants (0.07 and 0.16 d⁻¹)
that comprised 87% and 93% of the total rate constants,
respectively.

Surface water CH₃Br concentrations increased over the
course of the cruise, from about 1 pM in equatorial and
subtropical waters, to about 2.5 pM in polar waters (Figure 3;
King and Butler, in preparation). The methyl bromide loss rate
(pM/day), calculated as the product of the CH₃Br
correlation and the total loss rate constant, decreased
approximately 5-fold between low and high latitudes,
reflecting the fact that the latitudinal gradient in the CH₃Br
loss rate constant was much steeper than that of the surface
water CH₃Br concentration. Gas exchange calculations suggest
that the air/sea flux of CH₃Br was a minor source for these
waters (King and Butler, in preparation). Assuming that CH₃Br
was approximately in steady state, these data indicate that the
production rate of CH₃Br must have been greater in the
warmer, low latitude waters than in the cold, high latitude
waters in the North Pacific at this time of year. A similar
negative correlation between CH₃Br loss rate constant and
surface ocean CH₃Br concentration was also observed in the
springtime North Atlantic ocean [Tokarczyk and Saltzman,
2001] suggesting that this may be a general feature of the
oceans.

### 2.3. Diel Variability

Diel variability of the CH₃Br degradation rate constants was
studied between October 10 and 12 in the subarctic NE
Pacific, in the area of 50°N, 145°W known as Ocean Station
Papa. The region has high nutrient concentrations all year,
consistently very low chlorophyll concentrations (< 0.5 mg m⁻³)
dominated by small cells (< 5 μm), and low primary
productivity (300-600 mg C m⁻² d⁻¹). It is one of the three
major high nitrate, low chlorophyll regions of the world, which
are estimated to cover 20-30% of the world's oceans [Harrison
et al., 1999].

Surface water samples were collected for 2.5 days at
approximately 4-hour intervals (during this period SST varied
from 10.3-10.8°C, salinity from 32.61-32.7) and incubated at a
constant temperature of 10.1°C for 12-14 hours. While
chemical loss rate constants did not vary between samples
collected at different times of day, biological rate constants
varied significantly revealing a consistent diel pattern. The
measurements show biological loss rate constants near zero in

![Figure 3](image_url)

**Figure 3.** Upper- CH₃Br 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, and + symbols are sea surface temperature.

**Middle-** surface ocean CH₃Br concentrations (King and Butler,
Pearl Harbor, Dutch Harbor, and Kodiak Island coastal samples. Open ocean samples were collected between 06:00-
08:30 local time.

![Figure 4](image_url)

**Figure 4.** Diel variations in surface water CH₃Br loss rate
constants at Ocean Station Papa (50°N, 145°W). Sample
collection times are indicated.
samples collected during the late night/early morning hours (0:00 to 4:00 local time), and larger loss rate constants during samples collected during daylight and evening hours (Figure 4).

Although the range of the biological loss rate constant was small (0.00 to 0.04 d⁻¹), the trend is significant at the 95% confidence level. These results confirm a trend previously observed with more limited data in the North Atlantic ocean [Tokarczyk and Saltzman, 2001]. This suggests that biological loss of CH₃Br may be related to some light-dependent process. The CH₃Br-degrading organisms are not believed to be phototrophic, as the measured loss rate constants are not sensitive to the light levels that the samples are exposed to during incubation. The diel changes were observed in samples collected at the sea surface (0 to 30 cm) and could reflect a migratory pattern of organisms that either degrade CH₃Br or have CH₃Br-degrading bacteria associated with them. Another possibility is variation in substrate availability for CH₃Br-degrading organisms as a result of diel changes in phytoplankton activity. This interesting phenomenon requires further investigation.

The observation of diel variability could have implications for the interpretation of the biological loss rate constants obtained from the daily samples during the cruise (Figure 3). Those samples were collected between 06:00 and 08:30, when the diel study suggests biological loss rate constants are at their lowest levels. During the diel study, the mean biological loss rate constant for all data was approximately 3.5-fold greater than the average of the three samples collected near 08:00. If the diel variations observed at Ocean Station Papa occur at all depths in the water column, and in all regions of the Pacific, then the results of this study should be considered a lower limit on the rate at which CH₃Br is biologically removed from the oceans.

2. Summary

This study demonstrates that biological degradation of CH₃Br occurs over large regions of the Pacific Ocean. Chemical processes are largely responsible for the oceanic loss of CH₃Br in warmer waters, while biological losses predominate in cold, subpolar Arctic convergence waters. The observed variations in loss rate constants and surface ocean CH₃Br concentration suggest higher production in warmer regions of the oceans. Diel changes in the loss rate constant were observed, suggesting that photosensitive organisms play some role (either directly or indirectly) in the rate of degradation of CH₃Br in the oceans.

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