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# Methyl bromide loss rate constants in the North Pacific Ocean

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**Abstract.** The degradation rate constant of  $\text{CH}_3\text{Br}$  in the North Pacific Ocean was measured in surface seawater between September and October 1999, using a stable isotope ( $^{13}\text{CH}_3\text{Br}$ ) incubation technique. Total degradation rate constants ranged from 0.02 to 0.43  $\text{d}^{-1}$ , decreasing in colder waters as a result of the temperature-dependence of chemical losses. Biological rate constants ranged from 0.01 to 0.20  $\text{d}^{-1}$ . 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  $\text{CH}_3\text{Br}$  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  $\text{CH}_3\text{Br}$  concentrations suggest that the  $\text{CH}_3\text{Br}$  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 ( $\text{CH}_3\text{Br}$ ) is currently the focus of research because of the importance of this compound as a source of stratospheric bromine [Kurylo & Rodriguez, 1999].  $\text{CH}_3\text{Br}$  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  $\text{CH}_3\text{Br}$  of 11–21 Gg/yr [King et al., 2000]. This net flux reflects a balance between the oceanic uptake of atmospheric  $\text{CH}_3\text{Br}$ , and the internal production and consumption of  $\text{CH}_3\text{Br}$  in the oceans. Laboratory production of  $\text{CH}_3\text{Br}$  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  $\text{CH}_3\text{Br}$  in seawater proceeds chemically via chloride substitution and hydrolysis [Elliott & Rowland, 1993; 1995, Jeffers & Wolfe, 1996] and by biological degradation [King & Saltzman, 1997; Goodwin et al., 1998]. The rates of  $\text{CH}_3\text{Br}$  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  $\text{CH}_3\text{Br}$  may change in response to future changes in anthropogenic emissions, terrestrial ecosystem fluxes, or ocean warming.

$\text{CH}_3\text{Br}$  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  $\text{d}^{-1}$ , with a biological contribution ranging from 0.00 to 0.28  $\text{d}^{-1}$  [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  $\text{CH}_3\text{Br}$  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.

$\text{CH}_3\text{Br}$  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- $\mu\text{m}$ ) to remove biological activity or passed through a 64- $\mu\text{m}$  sieve in order to remove large particles and grazing organisms. These samples were spiked with  $^{13}\text{CH}_3\text{Br}$  to a concentration of 400 pM 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.

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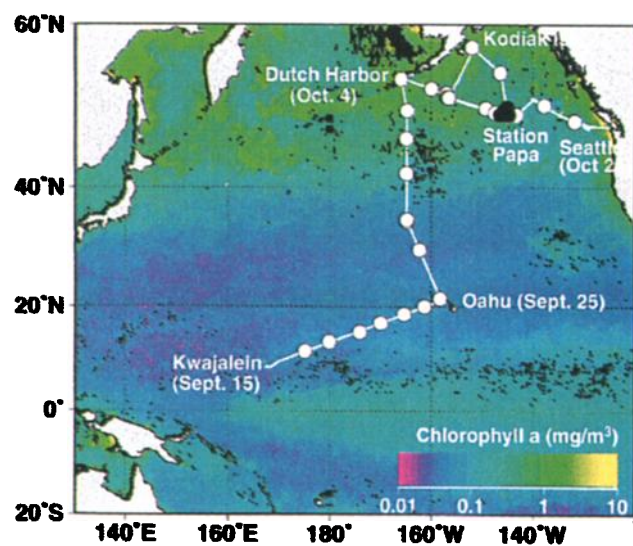


Figure 1. Cruise track, September-October, 1999, with September SEAWIFS chlorophyll-a image. Water sample locations are marked. Diel studies were carried out at Station Papa, as indicated by the black circles.

Incubations were carried out in the laboratory at a temperature close to that of the sample upon collection ( $\pm 1^\circ\text{C}$ ). Parallel dark (laboratory) and full light (deck) incubations of the same seawater yielded identical degradation rate constants.

The first-order loss of  $^{13}\text{CH}_3\text{Br}$  was followed over the course of 12-14 hours using gas chromatography with quadrupole mass spectrometric detection. Loss rate constants were measured in filtered and unfiltered aliquots of surface water samples. An isotopic fractionation factor of  $^{12}\text{k}/^{13}\text{k}=1.074$  was used to convert  $^{13}\text{CH}_3\text{Br}$  rate constants to  $^{12}\text{CH}_3\text{Br}$  rate constants reported here [King & Saltzman, 1997; Tokarczyk & Saltzman, 2001].

Subsamples for bacterial counts were frozen with 4% glutaraldehyde 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  $6.1 \times 10^5$  cells/ml ( $n=42$ ), and bacterial growth in the syringes was not observed. Selected samples were incubated with antibiotics (20  $\mu\text{g}/\text{ml}$  streptomycin and penicillin, and 40  $\mu\text{g}/\text{ml}$  neomycin) or a eukaryotic inhibitor (200  $\mu\text{g}/\text{ml}$  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  $\text{CH}_3\text{Br}$  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

$\text{CH}_3\text{Br}$  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 good 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 ( $152^\circ\text{W}$ ,  $58^\circ\text{N}$ ) in which the loss rate constant in the filtered sample was  $0.08 \text{ d}^{-1}$ , compared to the expected value of  $0.01 \text{ d}^{-1}$ . The biological loss rate constant ( $0.16 \text{ d}^{-1}$ ) was 4-8 times greater than biological loss 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  $0.02$ - $0.43 \text{ d}^{-1}$  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  $0.01$ - $0.20 \text{ d}^{-1}$ , contributing 4-93% of the total loss rate constant in individual samples with a mean of  $44 \pm 29\%$ . These results are similar in magnitude to those obtained in the spring/early summertime North Atlantic,  $33 \pm 28\%$ , 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 ( $28^\circ\text{C}$ ), equatorial waters where biological loss

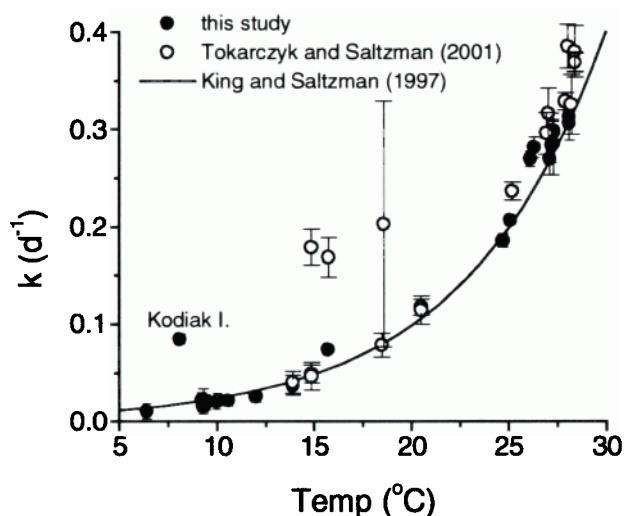
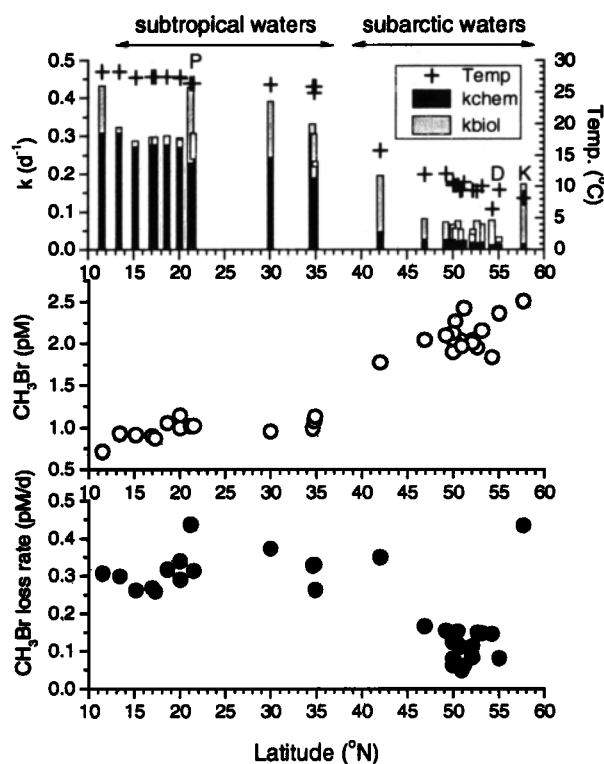


Figure 2.  $\text{CH}_3\text{Br}$  loss rate constants measured on filtered seawater samples from this study and previous measurements in the North Atlantic and eastern Pacific. The King and Saltzman [1997] rate expression is also shown.



**Figure 3.** Upper-  $\text{CH}_3\text{Br}$  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, and + symbols are sea surface temperature. Middle- surface ocean  $\text{CH}_3\text{Br}$  concentrations (King and Butler, in preparation). Lower-  $\text{CH}_3\text{Br}$  loss rate. P, D, and K represent Pearl Harbor, Dutch Harbor, and Kodiak Island coastal samples. Open ocean samples were collected between 06:00-08:30 local time.

was  $0.13 \text{ d}^{-1}$ , 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  $\text{CH}_3\text{Br}$  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  $0.07\text{--}0.15 \text{ d}^{-1}$ , and contributing up to 39% of the total loss rate. The biological rate constant for the Pearl Harbor sample was particularly high, at  $0.20 \text{ d}^{-1}$ , 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  $35^\circ\text{N}$ , 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  $\text{CH}_3\text{Br}$  loss. However, biological loss rates were relatively high in these transitional waters. At  $42^\circ\text{N}$ , duplicate incubations were carried out, yielding a mean biological degradation rate constant of  $0.15 \pm 0.01 \text{ d}^{-1}$ , or 77% of the total loss rate constant.

In the cold waters of the Arctic convergence, north of  $40^\circ\text{N}$  and between  $165$  and  $150^\circ\text{W}$ , biological loss rates remained significant, ranging from  $0.03\text{--}0.07 \text{ d}^{-1}$ . These rate constants contributed 60–87% of the total loss rate constant in these

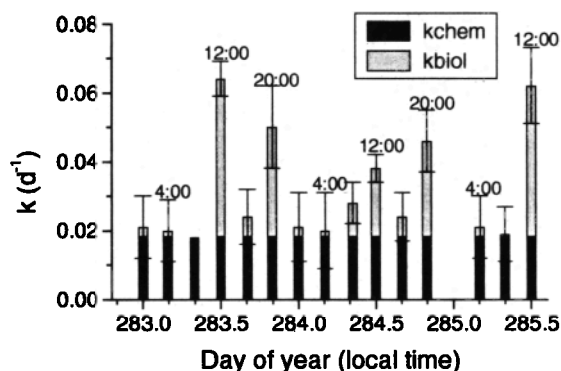
waters. The coastal Dutch Harbor (Unalaska) and Kodiak Island (Figure 3) samples (collected at 12:30 and noon) had even higher biological loss rate constants ( $0.07$  and  $0.16 \text{ d}^{-1}$ ) that comprised 87% and 93% of the total rate constants, respectively.

Surface water  $\text{CH}_3\text{Br}$  concentrations increased over the course of the cruise, from about  $1 \text{ pM}$  in equatorial and subtropical waters, to about  $2.5 \text{ pM}$  in polar waters (Figure 3; King and Butler, in preparation). The methyl bromide loss rate ( $\text{pM/day}$ ), calculated as the product of the  $\text{CH}_3\text{Br}$  concentration and the total loss rate constant, decreased approximately 5-fold between low and high latitudes, reflecting the fact that the latitudinal gradient in the  $\text{CH}_3\text{Br}$  loss rate constant was much steeper than that of the surface water  $\text{CH}_3\text{Br}$  concentration. Gas exchange calculations suggest that the air/sea flux of  $\text{CH}_3\text{Br}$  was a minor source for these waters (King and Butler, in preparation). Assuming that  $\text{CH}_3\text{Br}$  was approximately in steady state, these data indicate that the production rate of  $\text{CH}_3\text{Br}$  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  $\text{CH}_3\text{Br}$  loss rate constant and surface ocean  $\text{CH}_3\text{Br}$  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  $\text{CH}_3\text{Br}$  degradation rate constants was studied between October 10 and 12 in the subarctic NE Pacific, in the area of  $50^\circ\text{N}$ ,  $145^\circ\text{W}$  known as Ocean Station Papa. The region has high nutrient concentrations all year, consistently very low chlorophyll concentrations ( $< 0.5 \text{ mg m}^{-3}$ ) dominated by small cells ( $< 5 \mu\text{m}$ ), and low primary productivity ( $300\text{--}600 \text{ mg C m}^{-2} \text{ d}^{-1}$ ). 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  $10.3\text{--}10.8^\circ\text{C}$ , salinity from  $32.61\text{--}32.7$ ) and incubated at a constant temperature of  $10.1^\circ\text{C}$  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 4.** Diel variations in surface water  $\text{CH}_3\text{Br}$  loss rate constants at Ocean Station Papa ( $50^\circ\text{N}$ ,  $145^\circ\text{W}$ ). 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<sup>-1</sup>), 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 CH<sub>3</sub>Br may be related to some light-dependent process. The CH<sub>3</sub>Br-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 CH<sub>3</sub>Br or have CH<sub>3</sub>Br-degrading bacteria associated with them. Another possibility is variation in substrate availability for CH<sub>3</sub>Br-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 CH<sub>3</sub>Br is biologically removed from the oceans.

## 2. Summary

This study demonstrates that biological degradation of CH<sub>3</sub>Br occurs over large regions of the Pacific Ocean. Chemical processes are largely responsible for the oceanic loss of CH<sub>3</sub>Br in warmer waters, while biological losses predominate in cold, subpolar Arctic convergence waters. The observed variations in loss rate constants and surface ocean CH<sub>3</sub>Br 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 CH<sub>3</sub>Br in the oceans.

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