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Ocean-atmosphere exchange of methyl bromide: NW Atlantic and Pacific Ocean studies

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Abstract. Measurements of methyl bromide partial pressure and concentration in surface water and air samples in the NW Atlantic Ocean in July 1995 and the Pacific Ocean in October 1995 are presented. Mean atmospheric mixing ratios were found to be 11.4 ± 0.7 parts per trillion by volume (pptv) for the northern hemisphere and 10.0 ± 0.5 pptv for the southern hemisphere. Cold, high-latitude water in the Labrador Sea and warm water in the central Pacific were undersaturated in methyl bromide, and some supersaturated waters were found in the Gulf Stream in the Atlantic and around 35°S in the South Pacific. By a simple extrapolation, the global ocean is estimated to be a net sink of 10 (3 to 13) Gg of methyl bromide per year from the atmosphere, with the range including a factor of 2 uncertainty in the piston velocity.

1. Introduction

Methyl bromide is the most abundant carrier of organic bromine in the troposphere, accounting for about 54% of total organic bromine near the tropical tropopause [*Schauffler et al.*, 1993]. The potential effect of bromine on stratospheric ozone has prompted research on the atmospheric budget of methyl bromide, including the potential source or sink due to the global ocean. In the most recent reports, the ocean has been estimated to be a net sink for tropospheric methyl bromide, due to widespread undersaturation in surface seawater in the eastern Pacific, central Atlantic, and Southern Oceans [*Lobert et al.*, 1995, 1996, 1997].

In this work, measurements have been made of methyl bromide partial pressure and concentration in surface water in the Labrador Sea, the NW Atlantic Ocean, and on a transect of the central Pacific Ocean. An estimate of the net global air-sea flux of methyl bromide has been made based on these measurements, calculated exchange velocities, and an extrapolation to the global ocean.

2. Methods

Measurements of methyl bromide were made during two voyages: one in the Labrador Sea on *CSS Hudson*, July 1995 (Figure 1a), and the second across the central Pacific, between Seattle and Hobart (First Aerosol Characterization Experiment (ACE 1)), on the National Oceanic and Atmospheric Administration (NOAA) ship *Discoverer*, in October/November 1995 (Figure 1b).

For concentration measurements, seawater was collected in Niskin bottles, from which samples were taken with glass syringes. The concentration of methyl bromide in each sample was determined by a purge-and-trap method, with analysis by gas chromatography/mass spectrometry (GC/MS).

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The surface ocean partial pressure of methyl bromide was sampled with two equilibrators, one being similar in design to that of R. F. Weiss (Scripps Institution of Oceanography) [*Butler et al.*, 1988], and the other incorporating a semipermeable membrane [*Groszko and Moore*, 1998]. Air samples were pumped into electropolished steel canisters with a portable steel diaphragm sampling pump at the upwind rail of the ship and analyzed within 45 min. Both equilibrator samples and ambient air samples were analyzed by cold trapping and GC/MS, using the same equipment as for purge and trap samples, but with the purge vessel bypassed.

Peak areas for all the analyses were calibrated with a gravimetrically prepared standard gas containing 98.85 parts per billion by volume of methyl bromide in nitrogen. The standard gas was injected into the purge gas stream with a Hamilton gastight syringe in quantities from 5 to 100 μL. The response was linear. The same samples, analytical equipment, and procedure were used to study methyl chloride and are described in greater detail by *Moore et al.* [1996].

A reproducibility test was conducted by analyzing an air sample from the same canister three times in succession, beginning immediately after collection. In this test, the instrumental precision was found to be ±2% (95% confidence interval). Also, a comparison test over 29 pairs of methyl bromide measurements revealed no significant difference between the two equilibrators at the 90% confidence level [*Groszko and Moore*, 1998].

Fluxes were calculated using the exchange velocity relationship of *Wanninkhof* [1992], climatological winds from the Compiled Ocean Atmosphere Data Set (COADS) [*Woodruff et al.*, 1987], and solubilities according to the formula given by *De Bruyn and Saltzman* [1997].

3. Results and Discussion

The mean atmospheric mixing ratios were found to be 11.4 ± 0.7 parts per trillion by volume (pptv) for the northern hemisphere and 10.0 ± 0.5 pptv for the southern hemisphere (the natural variability is given as ±1 standard

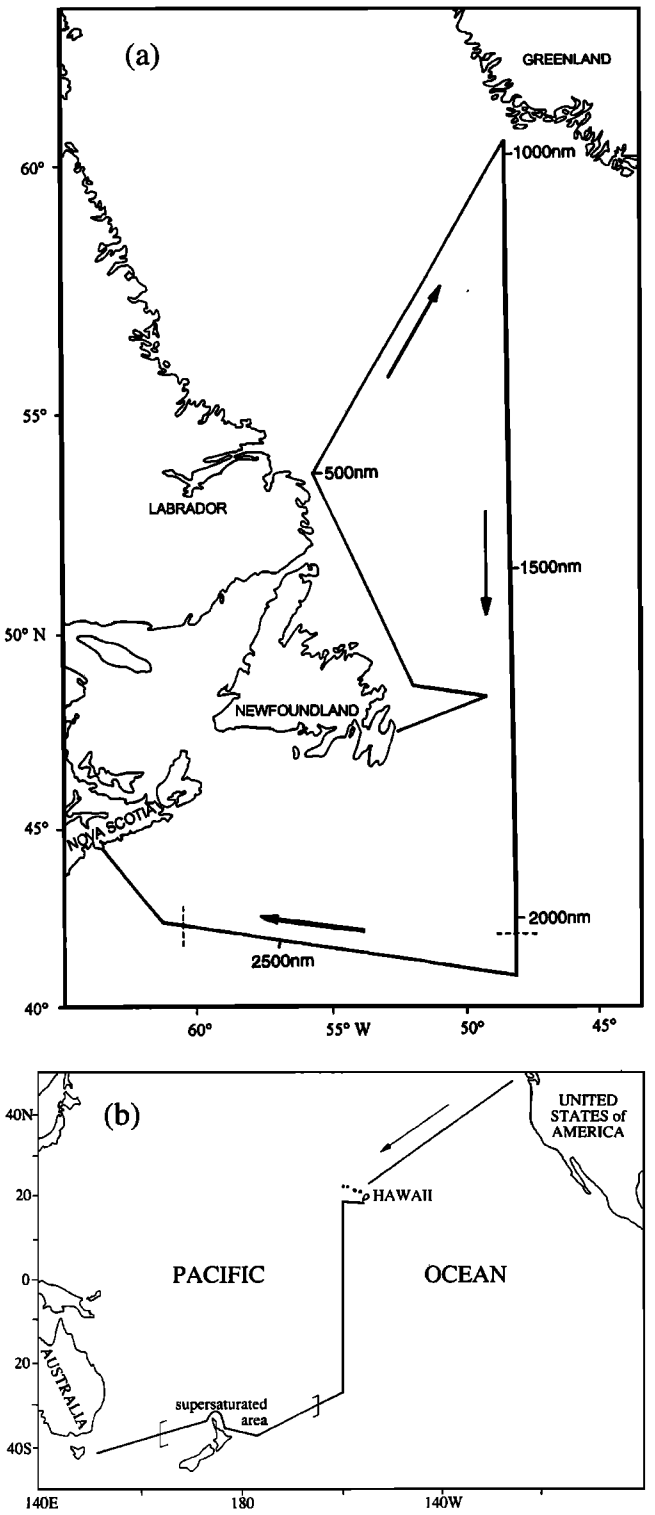

Figure 1. Cruise tracks: (a) *CSS Hudson* 1995; (b) NOAA ship *Discoverer* 1995. Distances in nautical miles. Position of boundary between Labrador Sea waters and Gulf Stream, (18°C contour) is marked as a dashed line in Figure 1a.. The area of the Pacific with observed methyl bromide supersaturation is bracketed in Figure 1b.

deviation). In the calculation of these means, both data sets have been included, and each data point has been weighted by the cosine of the latitude to account for the relative mass of the atmosphere at that latitude. The northern/southern interhemispheric ratio, using both data sets, was found to be in the range 1.10 to 1.18 (95% confidence interval). Table 1 shows a comparison of mean atmospheric mixing ratios between this study and three others. The values from this study agree very closely with the others in the northern hemisphere. The southern hemisphere mean found in this study appears to be somewhat higher than those of other studies, though it is within the variability reported by *Lobert et al.*, [1996].

In the atmospheric results reported above, the northern hemisphere mean is calculated from a compilation of data from both cruises. However, the two cruises were in different months of the year, and *Wingenter et al.* [1998] have reported a seasonal variation in tropospheric methyl bromide. Therefore, to remove possible seasonal effects on the calculation of the interhemispheric ratio, the northern hemisphere tropospheric means have also been calculated separately for the two data sets. These means are 11.3 ± 0.6 (July 1995 on the North Atlantic) and 11.7 ± 0.9 (October 1995 on the North Pacific). The interhemispheric ratio is 1.17 ± 0.08 for October, calculated with only Pacific data. This is at the lower end of the other ratios reported in Table 1, but since it is consistent with interhemispheric ratios reported by *Wingenter et al.* [1998] for September of 1994, our relatively low value is likely to be due to the season in which our measurements were made.

The measured concentrations and partial pressures in surface seawater are shown for the NW Atlantic (Figures 2b and 2c) and the Pacific (Figures 3b and 3c). On the basis of equilibrator measurements, the central Pacific was found to be generally undersaturated, with partial pressures of methyl bromide in surface water from 20 to 40% below atmospheric equilibrium. Some supersaturation (up to +64% saturation anomaly) was found in Pacific waters around 35°S, in a zone extending from ~1000 nautical miles east of New Zealand, westward to the Tasman Sea (Figure 1b). Saturation anomaly is defined here as the percent difference of the surface water partial pressure from equilibrium with the atmosphere, with positive saturation anomaly implying supersaturation. In general, the finding of widespread undersaturation with some supersaturated areas agrees with the east Pacific study of *Lobert et al.* [1995], except that we have found supersaturation in open ocean samples which are neither coastal nor upwelling zones. This provides evidence that coastal influences or upwelling may not be necessary conditions for supersaturation of methyl bromide. However, an alternate possibility is that the area in which we found supersaturation may be influenced by surface currents traveling eastward from Australia and New Zealand. Such currents are reported, for example, in a general circulation model by *Semtner and Chervin* [1992]. If this current-carried influence were the explanation for the observed supersaturation, it would be consistent with the report by *Lobert et al.* [1995] of supersaturation while passing through the Humboldt Current in the eastern Pacific. In the absence of more evidence, it is beyond the scope of this work to entirely resolve this issue.

The cold, high-latitude regions of the Labrador Sea were generally undersaturated, with a mean saturation anomaly of -20±3%, which is similar to the high-latitude value of -36±3% reported by *Lobert et al.* [1997] for the Southern Ocean. The Labrador Sea in July is a highly productive

Table 1. Comparison of Atmospheric Measurements

Study	Northern Hemisphere Mean, pptv	Southern Hemisphere Mean, pptv	Interhemispheric Ratio (NH/SH)
This study	11.4 ± 0.7*	10.0 ± 0.5*	1.14 ± 0.04†
Lobert et al., 1996	11.7 ± 1.2	9.4 ± 1.2	1.24
Lobert et al., 1995	11.1 ± 0.6	8.5 ± 0.6	1.31 ± 0.08
Khalil et al., 1993	10.7	8.0	1.34

* ± one standard deviation.
† ± 95% confidence interval.

area in terms of phytoplankton biomass, and the question of whether or not methyl bromide production rates in this area are related to chlorophyll *a* concentrations has been discussed by *Moore and Webb* [1996].

Some supersaturation was found in the Gulf Stream (average +30% saturation anomaly) and in continental shelf waters off Nova Scotia (average +9% saturation anomaly). Gulf Stream and Sargasso Sea waters were not consistently supersaturated, with different samples having saturation anomalies varying from -7% to +38%. Equilibrator samples taken as the ship was crossing the boundary into the Gulf Stream did not indicate any unusually high supersaturation at the front, compared with the waters inside the Gulf Stream.

Concentrations found in liquid samples by the purge and trap system have been converted to equivalent partial pressures and included in Figures 2c and 3c for comparison with equilibrator measurements. Results from the two types of analysis show the same qualitative pattern, but the purge-and-trap analyses generally yield partial pressures from 9 to 15% lower than the equilibrator analyses. To further investigate this difference, a comparison test was conducted while the *Discoverer* was on station. From the pumped seawater supply, four equilibrator samples were analyzed, followed by six purge-and-trap samples. The mean concentration measured by the purge-and-trap in this test was 12% lower than that calculated from equilibrator samples.

There is no evidence which would lead with certainty to the cause of this difference. One factor which could be involved is the solubility which is used to convert from concentration to partial pressure; however, we have used the most recent available solubility relationship [*De Bruyn and Saltzman*, 1997]. In the comparison test, if the solubility equation of *Elliott and Rowland* [1993] had been used instead, the purge-and-trap result would have been 24% lower than the equilibrator. The difference is not due to the calibration, since the same standard and calibration procedure were used for each method. The most probable source of the difference is in the subtraction of the instrument blank. The peak areas measured in purge-and-trap blanks are higher than those measured in blanks with the purge vessel bypassed, which is the configuration for equilibrator samples. If the concentrations in the comparison test are recalculated without subtracting either blank, the purge-and-trap results are only 4% below those from the equilibrator. This serves to illustrate the magnitude of the potential effect of variations in blanks.

Partial pressures measured by the equilibrators have been used in all the flux calculations which follow. This choice was made based on the higher signal-to-noise ratio of equilibrator samples, compared with purge-and-trap samples.

The air-sea flux is the product of the concentration difference across the interface (Δc) and a piston velocity (k). Values for the piston velocity we have calculated based on the formula of *Wanninkhof* [1992]. In the following discussion, we will refer to the concentration difference Δc as the "concentration anomaly." A negative concentration anomaly implies that the water is undersaturated and represents a sink from the atmosphere.

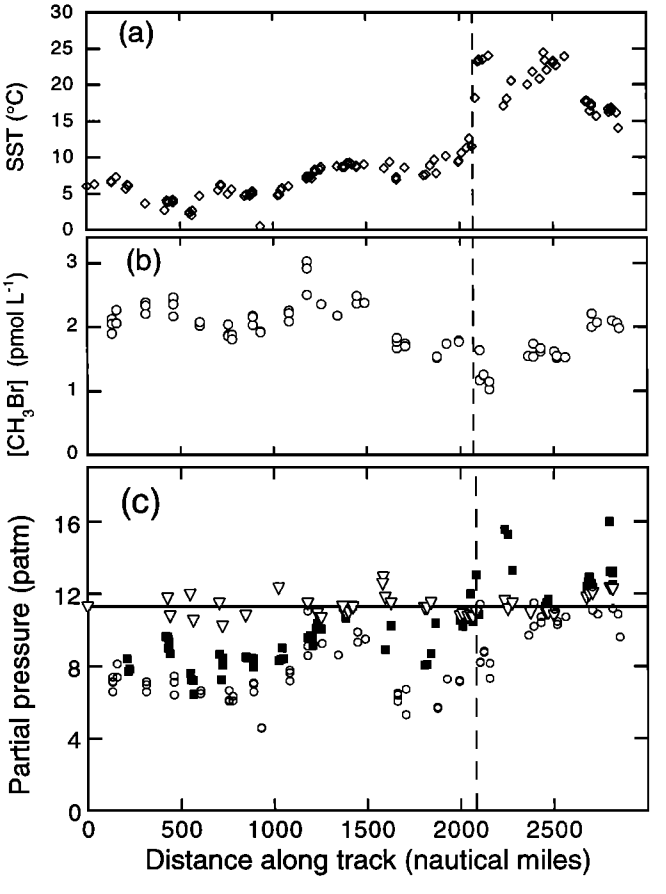

Figure 2. Data from *CSS Hudson* 1995, as a function of distance along the cruise track: (a) sea surface temperature (SST); (b) methyl bromide concentration in surface waters; (c) methyl bromide partial pressure from equilibrator measurements (solid squares), derived from water analyses (open circles), and measured in atmosphere (open triangles).

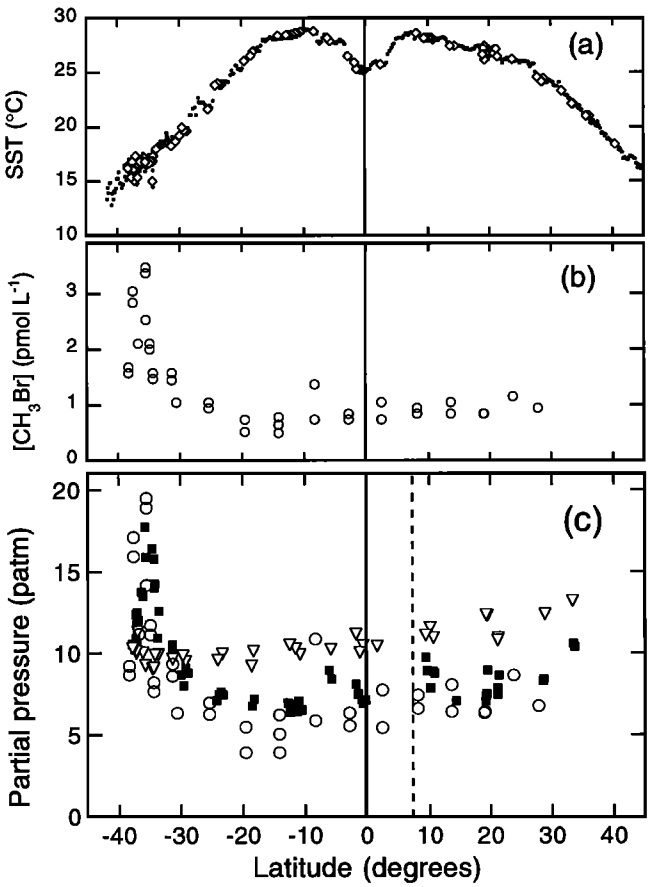

Figure 3. Data from NOAA ship *Discoverer* 1995, as a function of latitude: (a) sea surface temperature; solid points are the hourly log; temperatures at sampling locations are open diamonds; (b) methyl bromide concentration in surface waters; (c) methyl bromide partial pressure from equilibrator measurements (solid squares); derived from water analyses (open circles); and measured in atmosphere (open triangles). Dashed line indicates intertropical convergence zone.

The measured partial pressures from equilibrator samples from the Atlantic and Pacific data sets were converted to concentration anomalies, which were then plotted as a function of sea surface temperature (SST) (Figure 4). This revealed an unexpected pattern of increasing concentration anomaly at low temperatures, up to 17°C and decreasing values above that temperature. Qualitatively, both the Atlantic and Pacific samples display the same pattern, though there is an offset between them at temperatures above 18°C. There was no a priori reason to expect this relationship because the methyl bromide concentration in surface seawater could depend on many other factors such as biological productivity, species composition, atmospheric exchange rate (wind velocity), and the concentration of potential precursor compounds. Nevertheless, the observed relationship has a utility because it can be used to partition the ocean into source and sink regions to estimate the net global air-sea flux.

To make this partition, a bimodal function of SST, linear up to 17°C and quadratic at higher temperatures, was fit to the concentration anomaly data by least squares. The resulting empirical curve, and the root mean square (RMS) error of 0.24 pmol L^{-1} are shown in Figure 4. The curve fit passes through zero concentration anomaly at 12°C and 20°C, so these temperatures were chosen as the boundaries between source and sink regions. Cold water (<12°C) and warm water (>24°C) are predicted to be sinks of methyl bromide from the atmosphere, while intermediate temperature water between 12°C and 20°C is predicted to be a source.

Annual average SST data from the World Ocean Atlas [*Levitus et al.*, 1994] were used to determine the fraction of the ocean surface area in each temperature category. The areas of intermediate SST, assigned here as source regions of methyl bromide to the atmosphere, lie mostly in two midlatitude bands from 30° to 45°, south and north. For each area, the mean flux calculated from equilibrator measurements was multiplied by the area fraction and the total ocean surface area of 3.6×10^8 km^2 [*Broecker and Peng*, 1982] to determine the flux. This is summarized in Table 2.

By this method, we estimate that the global ocean represents a net sink of 7 to 13 Gg yr^{-1} of methyl bromide from the atmosphere. The range is based on the uncertainty in the flux per unit area attributed to each region. However, if the exchange velocity formula of *Liss and Merlivat* [1986] had been used instead of that of *Wanninkhof* [1992], all fluxes would have had smaller magnitudes [*Yvon and Butler*, 1996], and the result would have been a net sink of 3 to 7 Gg yr^{-1} from the atmosphere to the ocean. Therefore the overall estimate, accounting for this uncertainty in exchange velocities, is a net sink of 10 (3 to 13) Gg yr^{-1} from the atmosphere. By comparison, *Lobert et al.* [1997] estimate the ocean to be a net sink of 21 (11 to 32) Gg yr^{-1}.

Several other unquantified uncertainties affect this estimate, including the uncertainty in the area fractions, and the assumption that this relationship with temperature is globally applicable. In particular, *Lobert et al.* [1995] concluded that coastal and upwelling regions are sources of methyl bromide to the atmosphere, independent of SST, a possibility which is not accounted for in this estimate.

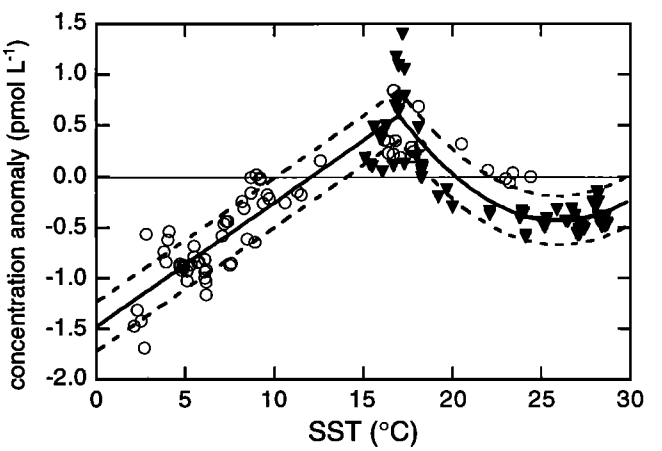

Figure 4. Concentration anomaly as a function of sea surface temperature (SST): Atlantic data (open circles), Pacific data (solid triangles) empirical curve fit (solid line), and RMS error (dashed line).

Table 2. Global Flux Estimate

SST Range	Area Fraction, %	Mean Flux, nmol m^{-2} d^{-1}	Total Annual Flux, Gg yr^{-1}
< 12°C	25%	-1.1 ± 0.2	-3.5 ± 0.6
12 to 20°C	18%	+1.3 ± 0.5	+3 ± 1
> 20°C	57%	-1.4 ± 0.3	-10 ± 2
Net total			-10 ± 3

Negative fluxes are from air to sea. Uncertainties are 95% confidence intervals of the mean.

However, due to the relatively vast areas of warm, undersaturated waters found in the Pacific, these uncertainties are unlikely to change the conclusion that the ocean represents a net sink for methyl bromide.

An unresolved issue is the question of whether methyl bromide supersaturation exists only in coastal, coastally influenced, and upwelling areas, or also in remote, open ocean areas at intermediate SST (around 17°C), a scenario for which there is evidence in this work. If future data collection is to resolve this issue, it would focus on measuring saturation anomalies in areas which are both at intermediate SST and as far as possible from any land masses or currents which may carry a coastal influence. Two examples of such areas are the southeastern Pacific, between the latitudes 30°S to 50°S and longitudes 100°W to 150°W, and the northeastern Pacific, from 30°N to 50°N and 140°W to 170°W.

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