

5.3. OCEAN PROJECTS

Observations

The oceans play an important role in the atmospheric budgets of halogenated, organic gases, both as sources and sinks. Natural halocarbons contribute a substantial amount of chlorine and bromine to the troposphere and, in some cases, the stratosphere. Methyl bromide (CH_3Br) and methyl chloride (CH_3Cl) together contribute about one quarter of the total equivalent chlorine to the atmosphere [Butler, 2000]. As the production and use of the anthropogenic, halogenated gases are phased out, methyl halides, which are primarily natural in origin, will play an increasingly important role in regulating stratospheric ozone.

Other halogenated compounds, such as dibromomethane (CH_2Br_2) and bromoform (CHBr_3), could be important sources of bromine to the stratosphere. While these compounds are generally present at low concentrations in the atmosphere and have short lifetimes, rapid vertical transport, particularly in the tropics, could provide a mechanism by which they could participate in stratospheric ozone depletion. An understanding of the sources and sinks of these compounds is needed to predict recovery of stratospheric ozone in the event of climate change.

The HATS group participated in two research cruises during 1998-1999 with the goal of quantifying the fluxes that constitute the oceanic cycle of CH_3Br . On both cruises, conducted aboard the NOAA ship *Ronald H. Brown*, the group made saturation measurements in conjunction with CH_3Br production and degradation measurements made by other groups. The first cruise, RB-98-02, Gas Exchange Experiment (GasEx 98), focused on the North Atlantic and coastal northeastern Pacific Oceans during May-July 1998 [King *et al.*, 2000]. The cruise departed from Miami, Florida, and ended in Newport, Oregon, with port stops in Lisbon, Portugal, Ponta Delgada, Azores, and Miami, Florida (Figure 5.28). The focal point of this cruise was a month-long air-sea exchange experiment in a cold-core eddy northeast of the Azores. The second cruise, RB-99-06, Bromine Air-Sea Cruise Pacific (BACPAC 99), was conducted in the North Pacific during September-October 1999, departing from Kwajalein, Marshall Islands, and ending in Seattle, Washington, with port stops in Oahu, Hawaii, and Dutch Harbor, Alaska (Figure 5.28).

During GasEx 98 CH_3Br was supersaturated in temperate waters and undersaturated in tropical and subtropical waters

(Table 5.10). Supersaturation implies a net flux from the ocean to the atmosphere, while undersaturation implies the reverse. These trends were particularly evident during the third leg of the cruise from the Azores to Miami, as the saturation anomaly became more pronounced with decreasing latitude (Figure 5.29). The CH_3Br supersaturations in the temperate northeastern Atlantic Ocean during GasEx 98 differed from previous observations [Lobert *et al.*, 1996; Groszko and Moore, 1998]. Direct comparison of springtime supersaturations ($23 \pm 8\%$, standard error of the mean, s.e., King *et al.* [2000]) and fall undersaturations ($-15 \pm 4\%$, s.e., Lobert *et al.* [1996]) in the same region of the North Atlantic ($37\text{-}45^\circ\text{N}$, $17\text{-}26^\circ\text{W}$) suggests that there may be a seasonal cycle in temperate North Atlantic waters. When seasonal cycling in temperate waters is incorporated into global flux calculations, estimates of the net, global, air-sea flux of CH_3Br range from -11 to -20 Gg yr^{-1} [King *et al.*, 2000]. This net CH_3Br sink is not as strong as previously reported [Lobert *et al.*, 1997], but the oceans are still estimated to provide an overall net sink for atmospheric methyl bromide.

Methyl bromide was undersaturated throughout most of the BACPAC 99 cruise with supersaturations observed primarily in coastal regions (Table 5.10, Figure 5.29c). In general CH_3Br was more undersaturated in the subtropics and closer to equilibrium in the temperate waters. The undersaturations in the temperate North Pacific during fall are consistent with the existence of a seasonal cycle in temperate waters as suggested by observations in the temperate North Atlantic. The data from BACPAC 99 showed less variability than that from GasEx 98. While the precision during BACPAC 99 was significantly better than during GasEx 98 (2.6% versus 5.8%, 1σ), this difference cannot completely explain the increased variability in the GasEx 98 data. It is likely that the remaining variability was a result of natural processes in the North Atlantic at that time of year.

Mean saturation anomalies for CH_3Cl , methyl iodide (CH_3I), CH_2Br_2 , and CHBr_3 are provided from both GasEx 98 and BACPAC 99 on a regional basis (Table 5.10). In contrast to CH_3Br , these trace gases were generally more supersaturated in the subtropics and tropics than in the temperate waters. Higher supersaturations of these compounds in the tropics are particularly important as tropical deep convection could transport these short-lived compounds to the upper troposphere and lower stratosphere, where they could participate in stratospheric ozone depletion.

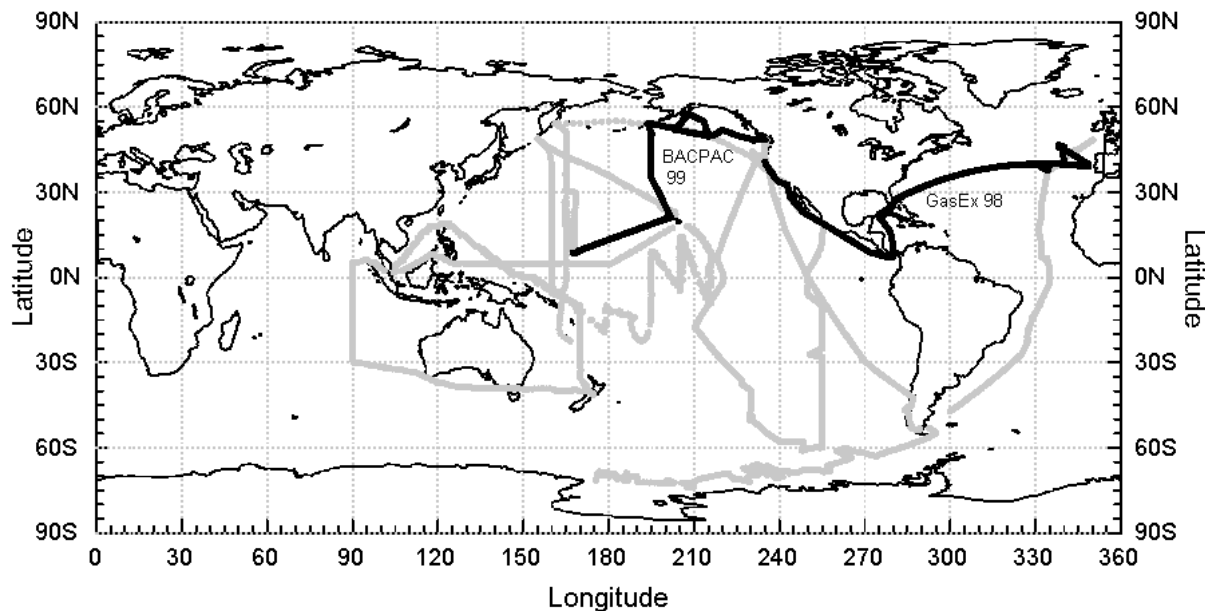


Fig. 5.28. Cruise tracks from RB-98-02 (GasEx 98) and RB-99-06 (BACPAC 99) and previous cruises (light gray) by the HATS group between 1987 and 1996.

TABLE 5.10. Average Measured Saturation Anomalies and Associated Standard Errors for Two Oceanic Regions From CMDL Cruises in 1998 (GasEx 98) and 1999 (BACPAC 99)

Compound	Saturation Anomaly (%) Spring/Summer 1998		Saturation Anomaly (%) Fall 1999	
	Subtropics/Tropics*	Temperate*	Subtropics/Tropics*	Temperate*
CH ₃ Br	-12 ± 2	37 ± 3	-35 ± 1	-19 ± 1
CH ₃ Cl	122 ± 3	37 ± 1	71 ± 3	2 ± 1
CH ₃ I	5067 ± 110	3351 ± 65	2603 ± 78	1113 ± 37
CH ₂ Br ₂	334 ± 75	76 ± 3	33 ± 3	37 ± 2
CHBr ₃	173 ± 11	69 ± 3	230 ± 17	69 ± 6

*Subtropics and tropics are defined as the region between 0° and 30°N, and temperate regions are defined to be between 30° and 60°N.

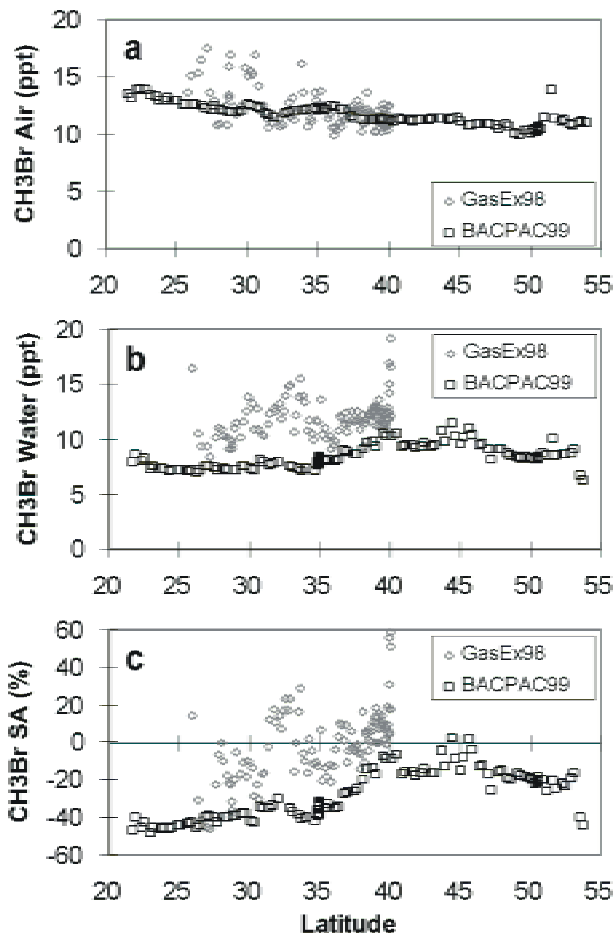


Fig. 5.29. Methyl bromide measurements in air (a) and air equilibrated with surface seawater (b). Saturation anomaly (c) is the percent difference between the partial pressure in water and air. Data from GasEx 98 are only shown from the third leg, between the Azores and Miami, Florida. Data from BACPAC 99 are only shown from the second leg, between Hawaii and Dutch Harbor, Alaska.

Temperature Dependence

Groszko and Moore [1998] suggested that there is a relationship between methyl bromide concentrations in the surface water and sea surface temperature. CH_3Br saturation anomalies were used from five CMDL research cruises to test this relationship for a wider range of waters (Figure 5.30a). The correlation observed from the CMDL data is similar to that reported by Groszko and Moore [1998] with CH_3Br supersaturated in ocean waters between 11° and 21°C. Based on this relationship, sea surface temperature can account for 40-70% of the variability in CH_3Br saturation anomaly on a global basis. However, only a small fraction of the observed seasonal cycle in temperate waters can be accounted for by the change in sea surface temperature [King et al., 2000].

A global oceanic net flux of methyl bromide of -14 Gg yr^{-1} can be calculated with the temperature relationship shown in Figure 5.30a and a global map of sea surface temperature, wind speed, solubility from De Bruyn and Saltzman [1997], and a gas exchange coefficient based on the equation from Wanninkhof [1992]. This estimate falls within the range predicted by other methods [Lobert et al., 1997; King et al., 2000]. However, it does not accurately describe the temporal and spatial distribution of dissolved CH_3Br , especially in

temperate waters, where widespread supersaturations are predicted year-round. Predicted supersaturations in temperate waters are not supported by data obtained from several field campaigns [Lobert et al., 1995, 1996; Groszko and Moore, 1998], which indicates temperature is not the only variable controlling the concentration of CH_3Br in surface waters.

Methyl chloride and methyl iodide have a different relationship to sea surface temperature than that of methyl bromide (Figures 5.30b and 5.30c). For both of these compounds, this relationship is best described with a linear regression. About three-quarters of the variability in the saturation anomaly of CH_3Cl can be explained by the variability in sea surface temperature. For CH_3I , only about one-half of the variability in the saturation anomaly can be explained by the variability in sea surface temperature. Global maps of both CH_3Cl and CH_3I will be created in the near future to estimate global air-sea fluxes for these compounds.

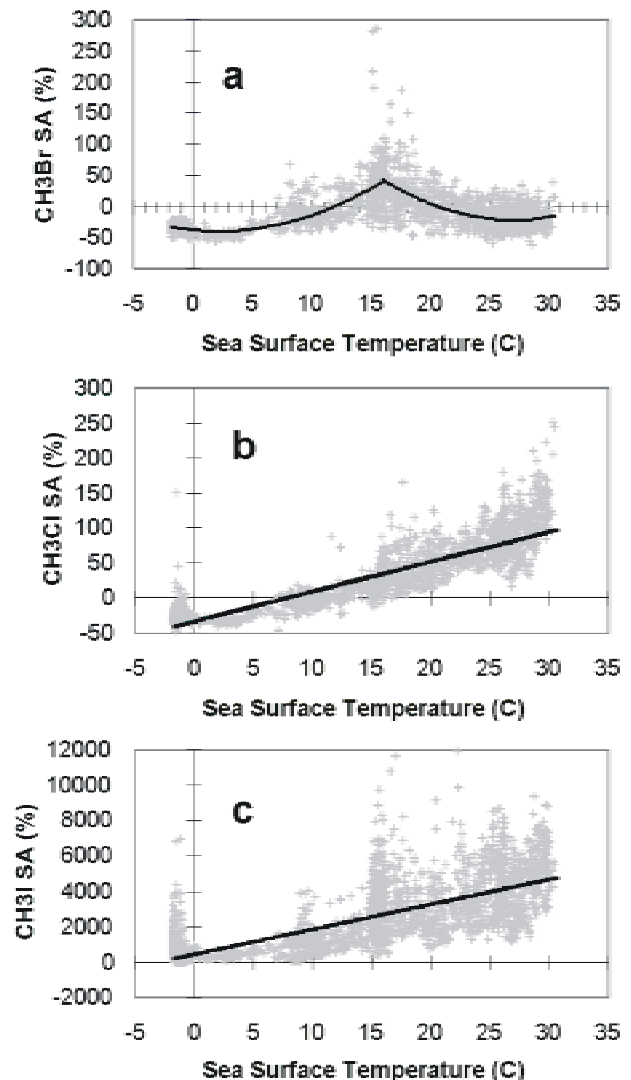


Fig. 5.30. Correlations between the saturation anomalies of the methyl halides (methyl bromide (a), methyl chloride (b), and methyl iodide (c)) and sea surface temperature based on data from five CMDL research cruises between 1994 and 1999.