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**AN ESTIMATE OF THE GLOBAL AIR-SEA FLUX OF
METHYL CHLORIDE, METHYL BROMIDE,
AND METHYL IODIDE**

by

Wayne Groszko

**Submitted in partial fulfillment of the requirements
for the degree of Doctor of Philosophy**

at

**Dalhousie University
Halifax, Nova Scotia, Canada
January, 1999**

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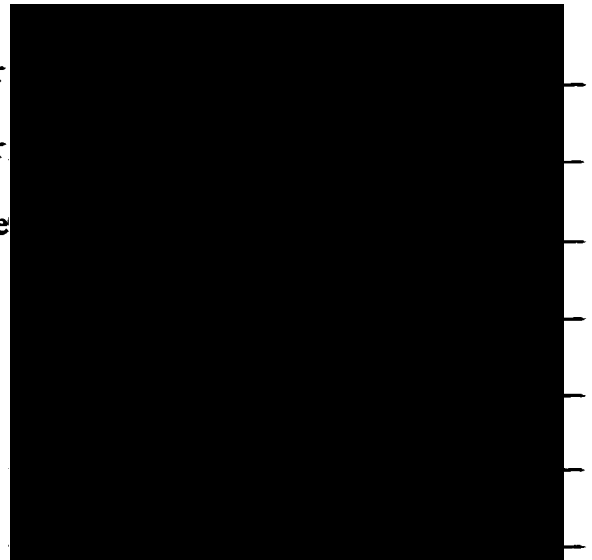
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by Wayne Groszko

in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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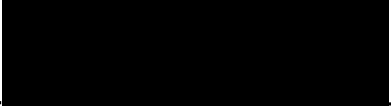
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to parents and angels

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Abstract

Methyl chloride (CH_3Cl), methyl bromide (CH_3Br), and methyl iodide (CH_3I) are trace gases of interest in atmospheric chemistry as carriers of halogen atoms. Chlorine, bromine, and iodine atoms are effective to varying degrees in catalyzing the destruction of stratospheric ozone. Knowledge of the sources and sinks of these compounds in the atmosphere can be used to improve the overall understanding of how halogens cycle between the atmospheric, terrestrial, and oceanic environments, and to determine the effects of anthropogenic activities on the natural cycle. In this work, the net annual air-sea flux of three methyl halide compounds (CH_3X) has been estimated based on field measurements made with an equilibrator and a mass selective detector over a wide range of latitudes and oceanic regions in several seasons. The global flux estimates have been calculated by using the monthly mean sea surface temperature as a proxy variable to predict the concentration anomalies of the methyl halides at each point on a $2^\circ \times 2^\circ$ map of the global ocean. The piston velocity at each grid point was calculated from climatological wind speeds. The primary conclusion of this thesis is that the global ocean represents a source of $\sim 0.55 \text{ Tg y}^{-1}$ (range 0.31 to 0.59 Tg y^{-1}) of methyl chloride and $\sim 0.32 \text{ Tg y}^{-1}$ (0.18 to 0.34 Tg y^{-1}) of methyl iodide to the atmosphere, and a sink of $\sim 7 \text{ Gg y}^{-1}$ (4 to 10 Gg y^{-1}) of methyl bromide from the atmosphere. When taken in the context of the tropospheric budgets of these three gases, the results suggest that the ocean is not the main source of methyl chloride to the atmosphere, but the ocean is apparently the main source of atmospheric methyl iodide. The atmospheric budgets of methyl chloride and methyl bromide remain significantly out of balance, with sinks exceeding sources, while the budget of methyl iodide may be balanced. Other significant sources of methyl chloride and methyl bromide to the atmosphere are predicted to exist, probably in the terrestrial environment. There is production of all three methyl halides in ocean surface waters, and the source of that production is not yet understood.

Abbreviations and Symbols

| | |
|--------------------|--|
| A | peak area (millions) |
| A_e | equilibrium peak area (millions) |
| a, b, c, d, e | constants |
| atm | atmosphere (pressure unit) |
| $^{\circ}\text{C}$ | degrees Celsius |
| CDOM | chromophoric dissolved organic matter |
| cm | centimetre |
| COADS | Combined Ocean-Atmosphere Data Set |
| CTD | conductivity/temperature/depth sensor |
| χ_a | dry gas mole fraction from an air sample |
| χ_w | dry gas mole fraction from an equilibrator sample |
| D | diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$) |
| d | day |
| DMS | dimethylsulfide |
| DMSP | dimethylsulfoniopropionate |
| Δ | depth difference between mixed layer and production layer |
| ΔC | concentration anomaly (pmol L^{-1}) |
| $\Delta\%$ | percent difference |
| ECD | electron capture detector |
| η_w | dynamic viscosity of pure water |
| F | flux from ocean to atmosphere |
| g | gram |
| GC | gas chromatography |
| Gg | Gigagram (10^9 grams) |
| Gmole | Gigamole (10^9 moles) |
| H | dimensionless solubility constant |
| H' | solubility of a gas in seawater ($\text{pmol L}^{-1} \text{atm}^{-1}$) |
| HO_x | active hydrogen species |
| " | inch |
| ITCZ | inter-tropical convergence zone |
| k | piston velocity (metres per day) |
| K | degrees Kelvin |
| k_{Cl^-} | rate constant of chloride ion substitution |
| kg | kilogram |
| L | litre |
| M | molar |
| M_w | molecular weight of water |
| mL | millilitre |
| m | metre |
| min | minute |
| MIMS | membrane introduction mass spectrometry |
| mm | millimetre |
| mol | mole |
| Mmol | Megamole (10^6 moles) |

| | |
|-------------------|--|
| molec | molecule |
| MSD | mass selective detector |
| µg | microgram |
| µL | microlitre |
| µm | micrometre |
| µmol | micromole |
| n | number of measurements |
| NH | northern hemisphere |
| nm | nautical mile |
| nmol | nanomole (10^9 moles) |
| NO _x | active nitrogen compounds NO and NO ₂ |
| P | barometric pressure (atmospheres) |
| p1, p2 | peak area from equilibrators 1, 2, respectively |
| patm | picoatmosphere |
| PH ₂ O | saturated vapour pressure over liquid water (atmospheres) |
| pmol | picomole |
| ppb | parts per billion (10^{-9} moles per mole) |
| ppt | parts per trillion (10^{-12} moles per mole) |
| q | association factor of water |
| PSC | polar stratospheric cloud |
| R ² | correlation coefficient |
| S | salinity |
| s | second |
| s | standard deviation |
| Sc | Schmidt number |
| SH | southern hemisphere |
| SST | sea surface temperature |
| σ _θ | potential density (kg m^{-3}) |
| t | time |
| t ₉₉ | time (seconds) to reach 99% of equilibrium peak area |
| t ₉₉₉₉ | time (seconds) to reach 99.99% of equilibrium peak area |
| T | temperature (degrees Celsius) |
| T _K | absolute temperature (degrees Kelvin) |
| Tg | Teragram (10^{12} grams) |
| τ | time constant (e-folding time) for a first-order process |
| u _{av} | climatological average wind speed (metres per second) |
| u _{clim} | monthly average climatological wind speed |
| u _{ship} | average wind speed from ship's anemometer |
| UHP | ultra-high purity |
| UV-A | ultraviolet A |
| UV-B | ultraviolet B |
| V _b | molar volume ($\text{cm}^3 \text{mol}^{-1}$) at normal boiling temperature |
| VOC | volatile organic compound |
| X | halogen atom (chlorine, bromine, or iodine) |
| y | year |
| Z | halogen atom (chlorine, bromine, or iodine) |

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Chapter 1: INTRODUCTION

Methyl chloride (CH_3Cl), methyl bromide (CH_3Br), and methyl iodide (CH_3I) are trace gases of interest in atmospheric chemistry as carriers of halogen atoms which are released upon photolysis in the troposphere or stratosphere. Chlorine, bromine, and iodine atoms are effective to varying degrees in catalyzing the destruction of stratospheric ozone [Penkett *et al.*, 1995; Solomon *et al.*, 1994]. Knowledge of the sources and sinks of these compounds in the atmosphere can be used to improve the overall understanding of how halogens cycle between the atmospheric, terrestrial, and oceanic environments, and to determine the effects of anthropogenic activities on the natural cycle.

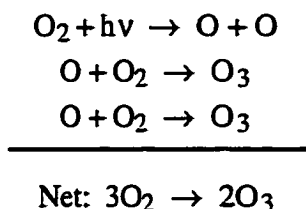
The focus of this study is on the exchange of methyl halides between the ocean and the atmosphere. Estimates of the net air-sea flux of each of these compounds have been made in the past, yet there remain substantial disparities between the various estimates (see text below for details). In this work, an extensive set of field measurements in surface ocean water and marine air, and a novel method of extrapolation to the global ocean, have been used to calculate new estimates of the global air-sea fluxes of the three gases.

The remainder of Chapter 1 provides a brief introduction to the stratospheric reactions involving halogen atoms which affect ozone, followed by a summary of the state of knowledge of the atmospheric sources and sinks of the methyl halides. Chapter 2 is a detailed description of the field campaigns and analytical methods used in the present study, and Chapter 3 concerns the invention and testing of equipment (equilibrators) of novel design. Chapter 4 is a report of the data collected in this study. The global flux estimates are calculated in Chapter 5, and the discussion of the results in the context of global atmospheric budgets follows in Chapter 6.

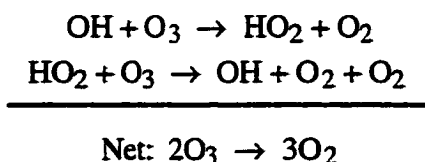
1.1 Ozone in the Stratosphere

Ozone (O_3) absorbs ultraviolet radiation in the stratosphere, thus preventing this harmful radiation from reaching the surface of the Earth. Radiation in the wavelength range 240-320 nanometres falls within the absorption spectrum of DNA [Cicerone, 1987], and is harmful to living organisms. Exposure to elevated levels of ultraviolet radiation in the wavelength range 280-320 nanometres (UV-B) can cause skin cancer [Setlow, 1974], and exposure to increased UV-B has been shown to reduce photosynthetic rates in Antarctic macroalgae [Post and Larkum, 1993]. The presence of ozone in the stratosphere is essential to the protection of living organisms from ultraviolet radiation.

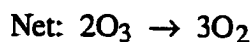
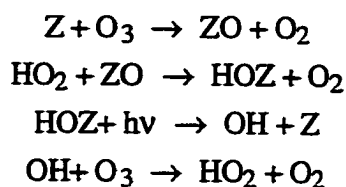
A theory of ozone production and removal in the stratosphere was originally outlined by *Chapman* [1930]. Ozone is produced in the stratosphere, primarily as a result of the photolysis of oxygen by sunlight at wavelengths <200 nanometres:



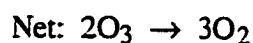
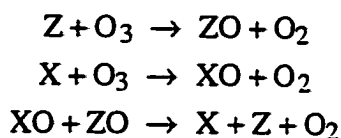
Numerous reaction cycles consume ozone in the stratosphere. The importance of the reactions of nitrogen oxides in stratospheric ozone chemistry was put forward by *Crutzen* [1970]. The proposal that reactions involving chlorine atoms from the anthropogenic chlorofluorocarbons could destroy ozone was made by *Molina and Rowland* [1974]. A sudden decrease in total ozone observed by *Farman et al.*, 1985 in the Antarctic springtime (commonly known as the "ozone hole") stimulated extensive observations of total column ozone around the globe. Decreases in total column ozone have since been observed over the Arctic, at mid-latitudes, and over the tropics [*Chipperfield*, 1991; *Brasseur*, 1991; *McCormick et al.*, 1992]. Considerable research work has been done to investigate the reaction cycles which affect ozone, and a recent summary of the relative contributions of various gas-phase reactions is given by *Wennberg et al.* [1994]. The reaction cycles are generally categorized into those involving the active nitrogen species NO and NO₂ (NO_x), the hydrogen radicals OH and HO₂ (HO_x), and the halogen radicals Z and ZO, where Z = Cl, Br, or I. *Wennberg et al.* [1994] estimated, based on measured concentrations of the various radicals and published reaction rates, that the following HO_x reaction cycle accounted for 30 to 50% of the total ozone loss rate in the lower stratosphere at mid-latitudes.



Wennberg et al. [1994] reported that catalytic cycles involving NO_x accounted for less than 20% of the photochemical loss rate of ozone in the area of their study, and that catalytic cycles involving chlorine and bromine were responsible for about one third of the ozone loss rate. The principal reactive-halogen cycle which destroys ozone is as follows:



Where Z = Cl, Br, or I. *Wennberg et al.* [1994] concluded that chlorine and bromine in this cycle could account for about 60% of the halogen-controlled ozone loss rate (about 20% of the total ozone loss rate). *Solomon et al.* [1994] predicted that iodine could also participate to a significant extent, but only in the lower stratosphere at mid-to-low latitudes. The interhalogen reactions are also predicted to contribute significantly to the ozone loss rate [*Wennberg et al.*, 1994; *Solomon et al.*, 1994]:



Where the combinations of halogens are: (Z = Cl, X = Br), (Z = Cl, X = I), and (Z = Br, X = I). The self-reaction of ClO (Z = Cl, X = Cl) is endothermic and limited by a relatively slow rate constant [*Solomon et al.*, 1994].

On a per-atom basis, bromine is more effective than chlorine at destroying stratospheric ozone [*Albritton and Watson*, 1992], and iodine is more effective than bromine [*Solomon et al.*, 1994]. The main reasons for this ranking are two-fold: First, in the stratosphere, the forms in which halogen atoms are found can be grouped into the reactive radical species (Z and ZO) and the relatively non-reactive reservoir species such as HZ and ZONO₂. At any given time, the ratio of the reactive to non-reactive species is determined by the rates of the chemical reactions which convert halogens between the two groups. The ratio of reactive species to the total halogen content determines the proportion of halogen atoms available for ozone destruction. According to model calculations, the ordering of this ratio is I > Br > Cl [*Solomon et al.*, 1994], so a greater proportion of total bromine is reactive than of total chlorine, and a still greater proportion of total iodine is reactive. Second, the fast rates of the interhalogen reactions BrO + ClO and IO + ClO allow for faster ozone removal rates than would be possible with ClO alone.

Although bromine and iodine are more effective at destroying ozone on a per-molecule basis, they are much less abundant than chlorine in air entering the stratosphere. The mole fractions of total organic chlorine and bromine in air near the tropical tropopause are reported to be ~3500 parts per trillion (ppt) and ~21 ppt, respectively [Schauffler *et al.*, 1993]. The tropical tropopause is the principal region of transport of tropospheric air into the stratosphere. Berg *et al.* [1980] reported an upper limit of 3 ppt for total iodine in the lower stratosphere. Wennberg *et al.* [1997] have reported measurements of the atmospheric column abundance of IO, and concluded that the contribution of iodine to lower stratospheric ozone depletion is not significant.

The discussion above has included only gas-phase reactions, but the observed ozone losses, particularly the springtime ozone depletion over the Antarctic, cannot be accounted for by gas-phase chemistry alone. Heterogeneous reactions at the surfaces of particles in polar stratospheric clouds (PSCs) are important in enhancing the loss rates of ozone [e.g. Molina *et al.*, 1987; Crutzen and Arnold, 1986]. PSCs are seeded by nitric acid trihydrate in the winter over the south pole (at temperatures below 195K). Reaction of the reservoir species chlorine nitrate (ClONO₂) with HCl adsorbed on the surface of PSC particles produces Cl₂ gas which can increase in concentration in the polar winter until sunlight returns and photolyses Cl₂ to release active chlorine. The conversion of a substantial part of the chlorine reservoir to active chlorine decreases the concentration of NO_x, so the conversion of active chlorine back to the ClONO₂ is limited by the lack of NO_x, and precipitous ozone losses are seen over a time scale of a few weeks due to enhanced rates of the ClO + ClO and ClO + BrO reaction cycles. Outside the polar regions, it has been proposed that heterogeneous reactions on sulfate aerosols can influence the ozone loss rate associated with reactive chlorine [Cadle *et al.*, 1975; Crutzen *et al.*, 1992].

1.2 Methyl Chloride

The first reported analysis of methyl chloride in atmospheric air was by Grimsrud and Rasmussen [1975] who found an average mole fraction of 530 ± 30 ppt in samples taken in a rural area in Washington State, USA. Nearly simultaneously, Lovelock [1975] reported a mean mole fraction of 1100 ppt in air at Bowerchalke, in southern England. Several other authors have reported atmospheric mean mole fractions between 600 and 700 ppt, based on samples taken at shoreline stations [Cox *et al.*, 1976; Singh *et al.*, 1977], from ships [Singh *et al.*, 1979; 1983] and from an aircraft sampling platform [Rasmussen *et al.*, 1980]. More recently, Kaye *et al.* [1994] reported a mean atmospheric

mole fraction of ~645 ppt, and *Koppmann et al.* [1993] reported average mole fractions of 532 ± 8 ppt for the northern hemisphere and 550 ± 12 ppt for the southern hemisphere.

Schauffler et al. [1993] measured the mole fractions of a suite of twelve chlorinated compounds, and found that methyl chloride represented ~15% of the total organic chlorine in air samples from near the tropical tropopause, which is the region of greatest transport of tropospheric air into the stratosphere. Methyl chloride is considered to be a naturally-occurring atmospheric constituent, because about 95% of the industrially produced methyl chloride is reportedly used as a chemical intermediate and therefore is not emitted to the atmosphere [*Lovelock, 1975; Singh et al., 1977*]. In the absence of the anthropogenic compounds such as chlorofluorocarbons which now dominate atmospheric chlorine content, methyl chloride would be the primary source of organic chlorine in the atmosphere [*Schauffler et al., 1993*]. Methyl chloride must have played an important role in the regulation of stratospheric ozone in the past through its contribution of chlorine atoms to the stratosphere before the emissions of chlorofluorocarbons began, and it continues to be a significant factor today.

In the afore-mentioned studies, the methyl chloride mole fraction in the atmosphere has generally been found to be rather uniform. However, various possible non-uniformities have been reported, including a 3% higher average mole fraction in the southern hemisphere than in the northern hemisphere [*Koppmann et al., 1993*]. By contrast, some studies have found no significant interhemispheric gradient [*Rasmussen et al., 1980; Singh et al., 1983*]. *Rasmussen et al.* [1980] also reported higher values (815 ± 25 ppt) in the planetary boundary layer (near the sea surface) over the Pacific ocean between the latitudes of 20°S and 20°N. Other studies have not found elevated mole fractions in air over equatorial regions of the Pacific [*Singh et al., 1983*] and Atlantic [*Koppmann et al., 1993*]. Several different authors report finding higher methyl chloride levels in air of marine rather than continental origin [*Lovelock, 1975; Grimsrud and Rasmussen, 1975; Singh et al., 1977*]. There are two reports of anomalously high atmospheric methyl chloride at shoreline stations in the U.K. (1100 ppt at Bowerchalke, England [*Lovelock, 1975*] and 1200 ppt at Adrigole, Ireland [*Rasmussen et al., 1980*]). Finally, two studies of urban air have found elevated levels of methyl chloride. *Singh et al.*, [1979] report mole fractions of 2200 ppt in Lisbon and 1500 ± 700 near Los Angeles, and in another study of seven U.S. cities, *Singh et al.* [1982] found average methyl chloride mole fractions of up to 960 ppt. It is important to note that analytical methods, including the procedure for calibration of the analyses, have varied from one study to another, and some of the differences found between studies may be due to biases in analytical methods.

The principal loss mechanism of methyl chloride in the atmosphere is by abstraction of a hydrogen atom by an OH radical to form CH_2Cl , which undergoes further reactions leading to the production of water-soluble HCl [Graedel, 1979]. The most recent published estimate of the lifetime of methyl chloride against reaction with OH is 1.26 years [Colman *et al.*, 1998], based on the recently revised average OH concentration (9.7×10^5 molecules cm^{-3}) [Prinn *et al.*, 1995], and the rate constant of 2.59×10^{-14} cm^3 molec^{-1} s^{-1} from the Jet Propulsion Laboratory review of kinetics [DeMore *et al.*, 1997] at the average tropospheric temperature of 277K chosen by Prather and Spivakovsky [1990]. With a total atmospheric burden of about 4 to 5 Tg (1 Tg = 10^{12} g) [Rasmussen *et al.*, 1980; Singh *et al.*, 1983; Koppmann *et al.*, 1993], the annual loss of methyl chloride to reaction with OH radicals would be about 3.2 to 4.0 Tg y^{-1} . Other reported estimates of the annual loss of methyl chloride include 3 Tg y^{-1} [Singh *et al.*, 1979], 2.5 to 5 Tg y^{-1} [Rasmussen *et al.*, 1980], and 3.5 Tg y^{-1} [Koppmann *et al.*, 1993]. A lower value of 1.9 Tg y^{-1} was calculated by Crutzen and Gidel [1983] using the latitudinal dependence of OH concentration derived from a two-dimensional photochemical model. Reports spanning 18 years, from Grimsrud and Rasmussen [1975] to Koppmann *et al.* [1993] have not shown any significant trend in atmospheric methyl chloride concentration over time, so the annual loss must be balanced by a total source of about 3.5 Tg y^{-1} . This estimate of the total supply rate accounts only for losses by hydroxyl radical attack.

Various potential sources of methyl chloride to the atmosphere have been studied, including direct industrial emissions, biomass burning, wood rot fungi, and emission from the surface of the ocean. Direct industrial emissions were estimated by Edwards *et al.* [1982] to total about 0.03 Tg y^{-1} , which is only 1% of the estimated total atmospheric source. Other reported sources are discussed below.

Elevated methyl chloride concentrations found in smoke from burning plant material [Crutzen *et al.*, 1979; Rasmussen *et al.*, 1980] have led to further studies of biomass burning as a source of methyl chloride. Biomass burning includes the burning of agricultural wastes, fires set intentionally in the process of clearing forested land, and wildfires, with the majority of present-day burning considered to be due to human activities [Crutzen *et al.*, 1979]. There is considerable variation in estimates of the global source of methyl chloride due to biomass burning. Crutzen *et al.* [1979] estimated a global source of 0.3 to 0.6 Tg y^{-1} , Rudolph *et al.* [1995] placed their estimate at 0.2 to 0.9 Tg y^{-1} , and Blake *et al.* [1996] gave several estimates from 0.4 to 1.0 Tg y^{-1} . Among the larger estimates, Lobert *et al.* [1991] calculated a global supply of 1.5 Tg y^{-1} , Andreae [1993] gave a global figure of 1.8 ± 0.9 Tg y^{-1} , and Andreae *et al.* [1996] estimated that savanna fires in Africa alone supply 0.42 Tg y^{-1} of their total estimated 1.1 to 1.5 Tg y^{-1}

global pyrogenic emissions. The most recent estimate is of about 1 Tg y^{-1} by *Lobert et al.* [1998], which would imply that about one third of the total emissions to the atmosphere may come from biomass burning. The potential source from combustion of other materials appears to have been the subject of little investigation, though there is a suggestion of a source of methyl chloride from combustion of polyvinyl chloride (PVC) plastic in building fires [*Palmer, 1976*].

Air in the vicinity of volcanic eruptions reportedly has elevated concentrations of methyl chloride [*Rasmussen et al., 1980*]. *Symonds et al.* [1988] used a model of homogeneous chemical equilibrium to calculate the distribution of chlorine among various chemical species under the conditions of a volcanic eruption, and concluded that the vast majority of the chlorine would be present as HCl, with no significant proportion of methyl chloride in the gases directly emitted by a volcanic eruption. Nevertheless, real observations have found significantly elevated methyl chloride concentrations in air at ground level near the 1979 Kilauea eruption [*Rasmussen et al., 1980*] and in the stratosphere in the plume of the 1980 eruption of Mount St. Helens [*Inn et al., 1981*]. Both *Rasmussen et al.* [1980] and *Symonds et al.* [1988] concluded that the observed high methyl chloride levels were due to burning of vegetation and the pyrolytic decomposition of organic matter buried under lava flows. There is no estimate of the potential magnitude of methyl chloride emissions from this source.

Wood rot fungi have been reported to produce methyl chloride [*Cowan et al., 1973; Harper, 1985; Harper et al., 1988*]. *Watling and Harper* [1998] reviewed the extensive literature on this subject and estimated that the global flux of methyl chloride from wood rot fungi is about 0.16 Tg y^{-1} , which could account for about 5% of the total atmospheric budget. Although this is apparently a small contribution to the total, at present it is the largest proposed source attributable to a single category of organism, and *Watling and Harper* [1998] consider their estimate of the fungal source to be conservative. Their estimate is based on the conversion rates of chloride ions in the growth medium to methyl chloride by fungal cultures grown in the laboratory. These conversion rates were extrapolated to a global estimate based on the relative abundances of methyl-chloride-producing fungi and the concentration of chloride ions in various types of wood. There are as yet no field data to demonstrate the magnitude of methyl chloride production by wood-rot fungi in the natural environment.

Emission of methyl chloride by higher plants has been reported by *Varns* [1982] who demonstrated that tubers of the potato (*Solanum tuberosum* L.) release methyl chloride for a short period after harvest. *Saini et al.* [1995] reported methyl halide release when leaf discs of herbaceous plants were floated in halide ion solutions. Although iodide ions

and sulphide ions were found to be more effective substrates than chloride ions by over three orders of magnitude, the relatively high concentrations of chloride ions in plant sap [Cram, 1976] make it conceivable that trace amounts of methyl chloride could be released by higher plants. A study of emissions from intact, live plants would be needed to address this question.

It has frequently been surmised that emission from the surface of the ocean is the predominant source of methyl chloride to the atmosphere [Penkett *et al.*, 1980; Singh *et al.*, 1983]. Singh *et al.* [1983] estimated that 5 Tg of methyl chloride is emitted annually by the oceans, based on measurements which showed surface concentrations greater than three times above atmospheric equilibrium in surface seawater in the eastern Pacific. This amount would more than account for the estimated total source of ~ 3 Tg y^{-1} . Tait *et al.* [1994] estimated a lower oceanic flux of 1.7 to 2.4 Tg y^{-1} , based on an extrapolation of northwest Atlantic measurements to the global ocean. There is a considerable disagreement between these two estimates, and each is based on measurements which are limited to one oceanic region.

Within the oceans, several different pathways for methyl chloride production have been proposed, but so far none has yielded a production rate which can account for any significant portion of the global atmospheric input. Zafirou [1975] pointed out that the reaction of methyl iodide with chloride ion in seawater may yield substantial amounts of methyl chloride, but no estimate of the total oceanic production by this reaction was given, and it has generally been thought that this source is not significant. This potential source may bear re-investigation.

Direct biological production of methyl chloride by marine organisms is also under study. Manley and Dastoor [1987] found that the giant kelp *Macrocystis pyrifera* releases methyl chloride, but if it is assumed that all macroalgae produce methyl chloride at the same rate as this giant kelp, the standing stock of macroalgae would be responsible for the production of only 0.003 Tg y^{-1} , which is an insignificant contribution to the total atmospheric flux. Microalgae grown in culture vessels have also been found to produce methyl chloride. Tait and Moore [1995] reported methyl chloride production in cultures of seven species of phytoplankton. It was not possible to be certain that the production was due to the phytoplankton alone, because bacteria were also present in these cultures. Similar experiments conducted by Scarratt and Moore [1996; 1998] demonstrated production in both xenic (bacterized) and axenic (bacteria-free) cultures of *Phaeodactylum tricornutum*, *Phaeocystis* sp., *Thalassiosira weissflogii*, *Chaetocerus calcitrans*, *Isochrysis* sp., *Synechococcus* sp., *Tetraselmis* sp., *Prorocentrum* sp., and *Emiliana huxleyi*. Observations during these experiments pointed to the possibility that

photosynthesis and cell reproduction may not be directly required for methyl chloride production. *Tait and Moore* [1995] reported that methyl chloride concentrations in the culture vessel continued to increase after the death of all the phytoplankton cells. *Scarratt and Moore* [1996; 1998] found higher methyl chloride production rates in the stationary phase of the cultures, after the logarithmic phase of rapid growth had ended. Also, both *Tait and Moore* [1995] and *Scarratt and Moore* [1996] noted that poisoning cultures with sodium azide or plunging them into prolonged darkness mid-way through an experiment did not change the methyl chloride production rate. They speculated that the algae may produce a precursor compound which then undergoes reactions in the culture medium to form methyl chloride. While these results provide clues to an eventual understanding of methyl chloride production mechanisms, the rates of production, when scaled to global concentrations of chlorophyll-a, could account for less than 0.5% [*Tait and Moore*, 1995] or 0.1 to 4% [*Scarratt and Moore*, 1996; 1998] of the total flux to the atmosphere.

1.3 Methyl Bromide

Despite the lower atmospheric concentration of organic bromine compared with organic chlorine [*Schauffler et al.*, 1993], organic bromine compounds are considered significant in atmospheric chemistry, particularly in relation to stratospheric ozone, because bromine is estimated to be 20-100 times more effective than chlorine at destroying stratospheric ozone [*Albritton and Watson*, 1992]. 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]. Much of the rest (39%) is from the halon compounds, which are used in fire extinguishers and are considered to be entirely anthropogenic in origin.

The first reported attempt to measure methyl bromide in the atmosphere was by *Grimsrud and Rasmussen* [1975], who stated that methyl bromide mole fractions were below the detection limit of their gas chromatography/mass spectrometry analytical system (<5 ppt). Analytical advances have since made it possible to measure methyl bromide in the atmosphere, and atmospheric mole fractions around 8-15 ppt have been found. The average atmospheric mole fractions found in three recent surveys [*Khalil et al.*, 1993; *Lobert et al.*, 1995; *Lobert et al.*, 1996] are summarized in Table 1.1. The studies included in the table all cover a significant range of latitude in both the northern and southern hemispheres. Note that in all the data sets the northern hemisphere is found to have a higher average mole fraction than the southern hemisphere, and the interhemispheric ratio has been calculated for each data set. The observation of higher

mole fractions in the northern hemisphere implies either that sources are stronger in the northern hemisphere, or that sinks are weaker in the northern hemisphere, or both.

Table 1.1. Atmospheric Methyl Bromide Measurements

| Study | Northern Hemisphere Mean (ppt) | Southern Hemisphere Mean (ppt) | Interhemispheric Ratio (NH/SH) |
|-----------------------------|--------------------------------|--------------------------------|--------------------------------|
| <i>Lobert et al.</i> , 1996 | 11.7 ± 1.2 | 9.4 ± 1.2 | 1.24 |
| <i>Lobert et al.</i> , 1995 | 11.1 ± 0.6 | 8.5 ± 0.6 | 1.31 ± 0.08 |
| <i>Khalil et al.</i> , 1993 | 10.7 | 8.0 | 1.34 |

Wingenter et al. [1998] have reported a seasonal trend in methyl bromide mole fractions in the northern hemisphere. They found that the temporal trend fits well to a sinusoid, with a maximum in February and a minimum in August. A major loss mechanism of atmospheric methyl bromide is the reaction with hydroxyl radicals (OH) [*Mellouki et al.*, 1992], and the observed seasonal trend in methyl bromide is consistent with the seasonal variation in OH concentration [*Wingenter et al.*, 1998]. That is to say, OH is produced through photochemical reactions, so OH concentrations are generally higher in the summer when light levels are higher. Higher concentrations of OH should result in lower methyl bromide concentrations, which is consistent with the minimum observed in the northern hemisphere in August. Although the southern hemisphere has a seasonal cycle in OH concentrations which is out of phase with that in the northern hemisphere, the authors reported that no seasonal cycle in methyl bromide was discernible in the southern hemisphere.

Based on air samples collected in canisters over a nine-year period from Alaska, Oregon, Hawaii, Samoa, and Tasmania, *Khalil et al.* [1993] reported a possible increasing trend of methyl bromide in the atmosphere. Over the period from 1988 to 1992, they estimated that the mole fraction of methyl bromide increased by 0.3 ± 0.1 ppt y^{-1} . However, over the period of a decade, they estimate an increase of 0.15 ± 0.1 ppt y^{-1} . This is a very small rate, with a substantial uncertainty, and it remains uncertain whether there is a consistent increase in methyl bromide concentrations over time.

Several processes act to remove methyl bromide from the atmosphere. Reaction with hydroxyl radicals is considered to be the primary removal process [*Penkett et al.*, 1995]. The lifetime of methyl bromide in the atmosphere with respect to the combined losses of photolysis and reaction with hydroxyl radicals was estimated by *Mellouki et al.* [1992] to be 1.7 years. Some other potential atmospheric sinks which have been investigated include uptake and degradation in soils [*Shorter et al.*, 1995], consumption by anaerobic

salt-marsh sediments [Oremland *et al.*, 1994], uptake by green plants [Jeffers and Wolfe, 1997], and uptake and subsequent chemical and biological destruction in the ocean [Yvon and Butler, 1996; Yvon-Lewis and Butler, 1997]. Available information on each of these sinks is examined in greater detail below.

Shorter *et al.* [1995] reported that degradation in soil is a significant sink of atmospheric methyl bromide. They estimated from soil uptake experiments that 42 ± 32 Gg ($1 \text{ Gg} = 10^9 \text{ g}$) of methyl bromide may be removed annually from the atmosphere by soils, through a process which they demonstrated to be mediated by bacteria. This work was extended by Hines *et al.* [1998], who demonstrated very rapid consumption of methyl bromide by soils in field and laboratory studies, even in experiments where the starting mole fractions of methyl bromide were between 5 and 15 ppt, which are very representative of actual atmospheric conditions. This consumption was found to take place very close to the surface of the soil, and several experiments with antibiotics demonstrated that essentially all (98%) of the removal was caused by bacteria. A separate set of field experiments on depositional fluxes to soils in four different ecosystems was conducted by Serça *et al.* [1998], who have estimated a larger global sink of $94 \pm 54 \text{ Gg y}^{-1}$ to soils.

Slurries of anaerobic sediments from a salt marsh were found by Oremland *et al.* [1994] to consume methyl bromide. Monitoring of the products revealed that this was mainly due to the nucleophilic substitution by sulfide (HS^-) to produce methanethiol and bromide ions, with some smaller contribution from the substitution reaction with chloride ions. The consumption proceeded even in autoclaved sediments, indicating that the mechanism is not directly biological, although the overall anaerobic conditions and high sulfide ion concentrations result from biological activity, so the reaction depends indirectly on biological processes. No estimate was made by Oremland *et al.* [1994] of the possible global significance of this methyl bromide sink. Degradation of methyl bromide in terrestrial green plants has also been reported [Jeffers and Wolfe, 1997], but the data are not extensive enough to permit an estimate of the magnitude of this potential sink.

It has been shown that methyl bromide is destroyed by chemical reactions in seawater, principally by nucleophilic substitution with chloride ions to form methyl chloride, but also by hydrolysis to form methanol [Elliot and Rowland, 1993]. The most recent experimental determination of the rate constants for these chemical loss processes is that of Jeffers and Wolfe [1996]. The loss rates increase strongly with temperature, and according to the more recent study, methyl bromide has a half-life of about 4 days against these two chemical reactions in typical surface seawater at a temperature of 22°C . The

half life is much longer at lower temperatures (16 days at 15°C). In addition to chemical losses in seawater, biological loss rates have been reported by *King and Saltzman* [1997]. Whole seawater samples showed faster loss rates of isotopically labelled methyl bromide than filtered or autoclaved samples, indicating that the rate of removal is enhanced by biological activity. The enhanced loss rate was associated with material in the size fraction between 0.2 µm and 1.2 µm, which suggests that bacteria are responsible for the biological portion of the loss rate.

Because methyl bromide is destroyed in seawater, any flux from the atmosphere to the ocean with subsequent destruction in seawater represents an atmospheric loss which decreases the atmospheric residence time of methyl bromide. It is important to note that this effect on the atmospheric lifetime is independent of the net ocean-atmosphere flux. Even if the ocean on the whole represented a net source of methyl bromide, the destruction of methyl bromide in the ocean would still affect the atmospheric lifetime. *Yvon-Lewis and Butler* [1997] re-evaluated the atmospheric lifetime of methyl bromide with respect to oceanic losses (both chemical and biological), and calculated a lifetime of 1.8 years (range 1.1 to 3.9 y). When other known atmospheric sinks were included, the overall atmospheric residence time of methyl bromide was calculated by *Yvon-Lewis and Butler* [1997] to be 0.7 y (0.6 to 0.9 y). The atmospheric lifetime with respect to oceanic loss and the overall lifetime had previously been estimated to be 2.7 y (2.4 to 6.5 y) and 0.8 y (0.6 to 1.4 y) respectively, without consideration of the biological removal rate in the oceans [*Yvon and Butler*, 1996].

Colman et al. [1998] have estimated the atmospheric lifetime of methyl bromide by a completely different method. They based their estimate on the Junge spatial variability relation, which is an expression of the intuitive idea that a chemical species which resides longer in the atmosphere will have more time to mix and will therefore be more uniform. With almost 4000 measurements from aircraft over the Pacific ocean, the authors estimated the spatial variability of methyl chloride, chloroform, tetrachloroethene, and ethane, and used these measured variabilities, along with published estimates of the lifetimes of these four compounds, to construct an empirical relationship between variability and lifetime. The variability of methyl bromide in the same data set was then converted to an equivalent lifetime through the empirical relationship. In this way, *Colman et al.* [1998] estimated that the atmospheric lifetime of methyl bromide is 0.8 ± 0.1 y, a figure which is in agreement with the most recent estimate of *Yvon-Lewis and Butler* [1997]. The method of *Colman et al.* [1998] is not subject to the uncertainties involved in trying to estimate all the sinks of methyl bromide from the atmosphere. On the other hand, it is dependent on the uncertainties in the lifetimes of the other compounds which

were used to "calibrate" the relationship between spatial variability and lifetime. In particular, it seems unsatisfactory to use lifetimes for the other compounds which account for only the loss due to reaction with OH, because the overall lifetimes of all the compounds, including methyl bromide, may be affected by other loss processes which are not randomly distributed in the atmosphere. Loss processes such as absorption by soils, uptake by plants, or destruction in the ocean take place only at the surface where the atmosphere comes into contact with these potential sinks. If the spatial distribution of the sinks is different for the various compounds used in the work of *Colman et al.* [1998], then using their variabilities and only their OH lifetimes in a relationship to estimate the lifetime of methyl bromide seems questionable.

Given the substantial sinks of methyl bromide which have been outlined above, and given the observations of its continuing, and possibly increasing presence in the atmosphere [*Khalil et al.* 1993], sources must exist to supply methyl bromide and at least balance all the sinks, which total 206 Gg y^{-1} if the ocean is considered to be both a source and a sink [*Yvon-Lewis and Butler*, 1997]. However, if the budget outlined by *Yvon-Lewis and Butler* [1997] is adjusted to include the ocean only as a net sink of methyl bromide, the total sink to be balanced by sources other than the ocean is 150 Gg y^{-1} . As with the other two methyl halides, in the earlier work the oceans were thought to represent a significant net source of methyl bromide [e.g. *Singh et al.*, 1983]. There are several other sources which have been under investigation in the intervening years, including biomass burning, anthropogenic emissions of industrially produced methyl bromide through its use as a pesticide, and exhaust from automobiles burning leaded gasoline. More details on each of these sources are given below.

Emissions from burning vegetation, including chaparral fires, boreal forest fires, and savanna fires all include elevated levels of methyl bromide [*Manø and Andreae*, 1994]. Based on the ratios of methyl bromide to carbon dioxide and to methyl chloride in the smoke from various kinds of fires, *Manø and Andreae* [1994] estimated that the total source of methyl bromide due to biomass burning is in the range of 10 to 50 Gg y^{-1} , with a best estimate of 30 Gg y^{-1} . A similar estimate of 20 to 30 Gg y^{-1} has been published by *Andreae et al.* [1996].

Exhaust from automobiles which burn leaded gasoline has been considered as a potential source of methyl bromide [*Baker et al.*, 1998]. Ethylene dibromide is an additive in leaded gasoline, and some of this compound is converted to methyl bromide, elevated levels of which can be detected in automobile exhaust [*Harsch and Rasmussen*, 1977; *Baumann and Heumann*, 1987; *Chakrabati and Bell*, 1993]. *Thomas et al.* [1997] have summarized the history of the use of lead and associated halogenated additives in

gasoline. The worldwide use of lead in gasoline peaked at about 400 Gg y⁻¹ in the early 1970s, and has declined since then because of the elimination of lead from use in gasoline in the United States and a few other countries. Although leaded gasoline is still available in many countries, the global consumption of lead in gasoline has declined to about 50 Gg y⁻¹ in 1995. Brominated compounds are ordinarily added to gasoline in proportion to the amount of lead, because the role of the bromine is to scavenge lead to prevent it from depositing in the engine. *Thomas et al.* [1997] estimated that the global average ratio of bromine to lead (by mass) in gasoline is 0.45±0.5, and therefore the annual global consumption of bromine in gasoline was ~170 Gg in 1970, and had declined to ~23 Gg in 1995. To calculate the methyl bromide emission rate from these figures, the fraction of total bromine released as methyl bromide in automobile exhaust must be known, but estimates of this value have ranged from 15-28% [*Baumann and Heumann*, 1987] to 0.12% [*Hao*, 1986]. Using the figures of *Baumann and Heumann* [1987], *Thomas et al.* [1997] estimated that 43 Gg of methyl bromide could have been emitted from leaded gasoline in 1970, which declined to about 6 Gg in 1995. The authors suggest that the decline of ~37 Gg y⁻¹ in emissions from leaded gasoline could have offset the increase in industrial emissions from fumigation over that time period (fumigation sources are discussed below). However, if *Hao's* [1986] much lower emission factor of 0.12% were used, then emissions from leaded gasoline would appear to be an insignificant contribution of less than 0.2 Gg y⁻¹ to the atmospheric budget.

There is apparently a very large uncertainty in the emission factor of methyl bromide from leaded gasoline, and another research group has approached the estimate of methyl bromide emissions from automobile exhaust in a different way. Rather than measuring exhaust directly from the tailpipe of an automobile, *Baker et al.* [1998], analysed methyl bromide and carbon monoxide concentrations in air from roadsides in the UK. A correlation was found between carbon monoxide and methyl bromide, both of which are known to be present in exhaust gases, and the ratio of methyl bromide to carbon monoxide was used, along with published figures on carbon monoxide emissions, to estimate the total methyl bromide emissions from automobiles in the UK. This figure was then extrapolated to a global figure through multiplication by the ratio of the amount of leaded fuel used globally to that used in the UK, and adjusted for the variation in lead content (and presumably ethylene dibromide content) in fuel among different countries. The final estimate from this procedure was a global emission (for 1995) of 1.5 Gg. The authors also stated an upper limit of 3.0 Gg y⁻¹, based on the unrealistic assumption that all gasoline is leaded and contains ethylene dibromide in the molar ratio of 1:1 with lead.

Baker et al. [1998] concluded that global automobile exhaust emissions are insignificant in the context of the atmospheric budget of methyl bromide.

Methyl bromide is also produced industrially, and global production in 1992 was around 76 Gg [UNEP, 1994]. Methyl bromide is a toxic compound which is used as a broad-spectrum biocide in the fumigation of soil (73%), durable products such as grain, nuts, and timber (13%), perishable foods (8%), and structures and vehicles (3%), with the remaining 3% used as an intermediate in the synthesis of other chemicals [Butler and Rodriguez, 1996]. During and after fumigation applications, some fraction of the methyl bromide escapes to the atmosphere. The injection of methyl bromide into soils, which is its largest single use, is also the process from which the emissions are the most uncertain. Some of the methyl bromide is degraded in the soil, and the most recent estimates of the fraction escaping to the atmosphere were 34% and 87% (from two different fields) [Yagi et al., 1993]. Taking into account all the types of fumigation uses of methyl bromide, the total source to the atmosphere from fumigation is estimated to be between 29 and 65 Gg per year [Butler and Rodriguez, 1996]. These emissions are not likely to increase in the near future, as industrial production of methyl bromide has been frozen at 1991 levels in accordance with the Copenhagen amendments to the Montreal Protocol [UNEP, 1992].

The effect of the ocean on atmospheric methyl bromide levels has long been thought to be significant, but over time the estimates of the net flux between the ocean and the atmosphere have decreased dramatically. *Singh and Kanakidou* [1993] estimated that the ocean represents a net source of 40 to 80 Gg y⁻¹, based on their finding of supersaturation in surface waters in the eastern Pacific. *Khalil et al.* [1993] collected ambient air samples, and samples of air which had been equilibrated with surface seawater along various cruise tracks in the Pacific. Based on the analysis of these samples, and the application of the gas exchange model of *Liss and Slater* [1974], *Khalil et al.* [1993] estimated that the ocean represents a net source of 30 to 40 Gg y⁻¹ of methyl bromide to the atmosphere, which is significantly less than the estimate of *Singh and Kanakidou* [1993]. Two years later, a series of reports from one research group, based on extensive measurements across the Pacific [Lobert et al., 1995], Atlantic [Lobert et al., 1996], and Antarctic oceans [Lobert et al., 1997] all put forward the claim that the oceans are not a net source but a net sink of atmospheric methyl bromide. The magnitude of the net sink was estimated to be 6 to 18 Gg y⁻¹ [Lobert et al., 1995], and later revised to 11 to 32 Gg y⁻¹ [Lobert et al., 1997], based on inclusion of data collected in the southern ocean. Clearly, there are significant disagreements among the various estimates of the global flux of methyl bromide from the ocean to the atmosphere, which have ranged from a maximum

of +80 Gg y⁻¹ [Singh and Kanakidou, 1993] to a minimum of -32 Gg y⁻¹ [Lobert et al., 1997].

Even if the ocean represents a net sink of methyl bromide from the atmosphere, all data sets at mid- to low-latitudes have found some areas where methyl bromide was supersaturated in surface waters with respect to atmospheric equilibrium [e.g. Lobert et al., 1995]. This, coupled with the fact that methyl bromide degradation rates are quite high in warm waters [Jeffers and Wolfe, 1996; King and Saltzman, 1997], implies that methyl bromide is produced in seawater, at least in low- to mid-latitude temperate and warm waters. One estimate of the total global production rate of methyl bromide in seawater is ~150 Gg y⁻¹, based on the difference between the calculated *in-situ* loss rate and the atmospheric input [Lobert et al., 1995]. Several possible mechanisms for this oceanic production have been investigated, but so far none has been reported which adequately accounts for any significant fraction of the total. Production by the nucleophilic substitution reaction of methyl iodide with bromide ions is a possible chemical mechanism for methyl bromide production, but the relatively low ratio of bromide to chloride ions in seawater is likely to limit the rate of methyl bromide production by this mechanism [Zafiriou, 1975]. Possible photochemical production of methyl bromide appears not to have been investigated.

Biological production of methyl bromide has been demonstrated in cultures of macroalgae [Manley and Dastoor, 1987] and microalgae [Scarratt and Moore, 1996; 1998; Sæmundsdóttir and Matrai, 1998]. Manley and Dastoor [1987] reported methyl bromide production by whole blades of the giant kelp *Macrocystis pyrifera* grown in an aquarium. However, when the rates of production were scaled by the global macroalgal biomass, the global production of methyl bromide by macroalgae was estimated to be rather low (0.1 Gg y⁻¹). Methyl bromide production was reported in xenic (bacterized) cultures of all three phytoplankton species studied by Scarratt and Moore [1996] (*Phaeodactylum tricornutum*, *Phaeocystis* sp., *Thalassiosira weissflogii*). Production was also found in cultures of seven out of nine species grown in another study, including axenic cultures [Scarratt and Moore, 1998], thus demonstrating that bacteria are not essential to the production process. However, as for methyl chloride, the rates of production from these experiments, when scaled to the global biomass of phytoplankton, could not account for the estimated total production rate in seawater. Even when all phytoplankton biomass was assumed to produce methyl bromide at the same rate as *Phaeocystis* sp., which had the highest rate of any species tested, still the global production rate by phytoplankton biomass was about 43 Gg y⁻¹, or about 28% of the total oceanic production estimated by Lobert et al. [1995]. The other species tested by Scarratt

and Moore [1998] had production rates much lower than *Phaeocystis*, so a more realistic extrapolation based on known abundances of the various species would likely result in an estimate much lower than 43 Gg y⁻¹. *Sæmundsdóttir and Matrai* [1998] reported methyl bromide production in cultures of 13 out of 19 species studied. The cultures were axenic at the beginning of the experiment, but all except two had become bacterized by the end of the experiment. *Sæmundsdóttir and Matrai* [1998] found that species generally present in coastal waters had higher methyl bromide production rates than those which normally grow in open ocean waters. By scaling the production rates in cultures to observed open-ocean and coastal chlorophyll-a concentrations, they estimated that phytoplankton could produce 3 to 47 Gg of methyl bromide per year in the open ocean, and 4 to 78 Gg y⁻¹ in coastal areas. *Lobert et al.* [1995] estimated the production of methyl bromide in coastal waters to be 46 Gg y⁻¹, so the range of production rates estimated by *Sæmundsdóttir and Matrai* [1998] could possibly account for all of the production in coastal waters. *Sæmundsdóttir and Matrai* [1998] pointed to the need for studies of the *in-situ* production rate in seawater under conditions which more closely resemble those present in the ocean.

1.4 Methyl Iodide

It was *Lovelock et al.* [1973] who first proposed that methyl iodide is produced in the ocean and is an important carrier of gas phase iodine from the ocean to the atmosphere. The atmosphere in turn supplies iodine in precipitation to marine and terrestrial environments [*Miyake and Tsunogai*, 1963], a flux which is relevant to supplying the needs of living organisms for this essential element. In addition, *Solomon et al.* [1994] have proposed that iodine may play a role in controlling ozone concentrations in the lower stratosphere. However, *Wennberg et al.* [1997] have concluded, based on measurements of the atmospheric column abundance of IO, that the contribution of iodine to lower stratospheric ozone depletion is not significant.

Methyl iodide has been thought of as the principal organic iodine compound in the atmosphere [*Rasmussen et al.*, 1982; *Heumann et al.*, 1987], but several studies suggest that other iodinated compounds such as chloriodomethane, diiodomethane, iodopropanes, and iodobutanes may represent a significant fraction of atmospheric iodine [*Klick and Abrahamsson*, 1992; *Moore and Tokarczyk*, 1992]. There appears to be no report of a comprehensive study of iodinated compounds which would make it possible to quantify the relative contribution of methyl iodide to organic iodine in the atmosphere.

Typical atmospheric mole fractions of methyl iodide are from 1 to 2.5 ppt [*Rasmussen et al.*, 1982; *Reifenhäuser and Heumann*, 1992; *Oram and Penkett*, 1994]. *Yokouchi et al.*

[1997] reported mole fractions ranging from 0.05-5.0 ppt (average 0.87 ppt) over the western Pacific, and from 0.24-2.0 ppt (average 0.63 ppt) over the southeast Asian seas. Occasional anomalous values as high as 43 ppt have been reported in air from over the north Atlantic [*Oram and Penkett*, 1994], and up to 22 ppt in samples near coastal Iceland [*Rasmussen et al.*, 1982].

Methyl iodide differs from methyl chloride and methyl bromide in that the carbon-iodine bond is relatively weak [*Solomon et al.*, 1994], and can be broken by absorption of a photon in the solar spectrum. Methyl iodide therefore breaks down rapidly in sunlight, and the mean lifetime of methyl iodide against photolysis in the troposphere has been estimated to be about 4 to 8 days [*Zafiriou*, 1974]. This average lifetime is relatively short in comparison with average atmospheric vertical mixing rates, and it has generally been assumed that methyl iodide does not reach the stratosphere in significant quantities. However, deep convective storms in the tropics may transport chemical species from near the surface to the upper troposphere and even the lower stratosphere within a few hours [*Pickering et al.*, 1992]. According to *Solomon et al.* [1994], this rapid transport in the tropics can provide the means for short-lived iodinated compounds such as methyl iodide to supply iodine to the lower stratosphere and contribute to reduced ozone concentrations in that region.

The total loss rate of methyl iodide due to photolysis in the atmosphere was estimated by *Chameides and Davis* [1980] to be about 1.5 Tg y⁻¹. They arrived at this figure by using an average lifetime of eight days, and assuming average mole fractions of 10 ppt between 30°N and 30°S, and 5 ppt outside those latitudes. By a similar method, *Zafiriou* [1974] calculated an annual atmospheric loss rate of 1-2 Tg of methyl iodide. Regarding the loss rate calculation of *Chameides and Davis* [1980], it should be noted that recent reports [*Rasmussen et al.*, 1982; *Reifenhäuser and Heumann*, 1992; *Yokouchi et al.*, 1997] suggest that average atmospheric methyl iodide mole fractions are around 1-2 ppt, not in the range of 5-10 ppt. If the calculations of *Chameides and Davis* [1980] were repeated with mole fractions about one fifth of those originally used, in accordance with recent measurements, the calculated annual loss rate would be about one fifth as large, or roughly 0.3 Tg y⁻¹. The total loss rate is an important factor to consider in the global budget of methyl iodide, and it would bear a more comprehensive re-evaluation in the context of data that are now available. In particular, it should be possible to incorporate latitudinal dependencies of both the mole fraction and the incident solar radiation into the calculation.

When iodine compounds are broken down by photolysis, active iodine is released, most of which eventually forms water-soluble iodide ions, and as a result, about 0.5 Tg of

iodine per year washes down to the surface of the earth in rain, according to the estimates of *Miyake and Tsunogai* [1963], who measured the total iodine content of rainwater at 21 stations in Japan. If the adjusted global loss of methyl iodide due to photolysis mentioned above (0.3 Tg y^{-1}) is assumed to be correct, then methyl iodide loss in the atmosphere could supply a significant portion ($\sim 0.27 \text{ Tg y}^{-1}$) of the iodine which washes out in rain.

The sources of methyl iodide to the atmosphere must be similar in magnitude to the sinks in order that the observed methyl iodide levels are maintained. The anthropogenic source of methyl iodide to the atmosphere due to industrial production is thought to be negligible, but may increase in the future, as methyl iodide is under consideration as a replacement for methyl bromide in fumigation [*Ohr et al.*, 1996]. Several other potential terrestrial sources of methyl iodide have been studied, including biomass burning, wood rot fungi, and higher plants. Reports on these terrestrial sources are noted below.

Andreae et al., [1996] reported elevated concentrations of methyl iodide in smoke from savanna fires in Africa, along with fires in boreal forest and chaparral vegetation. They found methyl iodide emissions from biomass burning to be much lower than the emissions of methyl chloride and methyl bromide from the same fires. Based on the ratios of methyl iodide to carbon monoxide and carbon dioxide in the emissions from the fires, *Andreae et al.* [1996] estimated that savanna fires contribute 0.002 to 0.003 Tg of methyl iodide per year, and that globally the emission of methyl iodide from biomass burning is between 0.003 and 0.008 Tg y^{-1} , which is on the order of 2% of the adjusted total methyl iodide emissions of 0.3 Tg y^{-1} calculated above. Biomass burning appears to be a relatively insignificant source of methyl iodide to the atmosphere, at least based on the studies which have been published so far.

In the context of the extensive studies of halomethane production by wood fungi, as reviewed by *Watling and Harper* [1998], it has been found that wood rot fungi can produce several different halomethanes, including methyl iodide, if they are grown in a medium which is enriched in the appropriate halide ions [*Harper and Kennedy*, 1986]. However, *Watling and Harper* [1998] estimate that due to the relatively lower concentration of iodide ions in terrestrial plant matter, wood rot fungi in the wild are unlikely to produce globally significant amounts of methyl iodide.

There is a report of methyl iodide emissions from rice plants and oat plants grown in pots of soil to which radioactive iodide ($^{125}\text{I}^-$) had been added [*Muramatsu and Yoshida*, 1995]. This study was conducted partly to elucidate a transport pathway for a longer-lived radioactive isotope of iodide ($^{129}\text{I}^-$, half life 1.6×10^7 years) from soils contaminated by nuclear-fuels-reprocessing factories. Methyl iodide was emitted at a much faster rate by rice plants grown under flooded conditions than by the control, which was a pot of bare

soil kept flooded with water. The flooded pot of soil itself emitted methyl iodide at a faster rate than the oat plants, which were grown in unflooded soil. Although emission of methyl iodide was much lower from the oat plants than from the rice plants, the oat plants emitted methyl iodide more rapidly than their corresponding (bare, unflooded soil) controls. The authors speculated that the methylation of iodide ions was accomplished in the roots or by microbes associated with the roots, and that the methyl iodide travelled up the plants. The majority of the methyl iodide was found to emanate from the plant stem and leaves, rather than the soil surface. Based on estimates of the iodide content of Japanese rice paddy soils, and the global surface area involved in rice production, *Muramatsu and Yoshida* [1995] estimated that 0.02-0.03 Tg of (ordinary, non-radioactive) methyl iodide per year could be emitted from rice paddies. They cautioned that their estimate may be too high because Japanese rice paddies are thought to have higher than average iodide concentrations.

Since the first report by *Lovelock et al.* [1973] on atmospheric methyl iodide, the oceans have consistently been thought of as the primary source of methyl iodide to the atmosphere. Several authors have estimated the global air-sea flux of methyl iodide based on analyses of the concentration difference between ocean waters and the atmosphere. When *Liss and Slater* [1974] published their model of air-sea exchange of gases, they used the model to estimate the global flux of several gases, including methyl iodide, of which they estimated 0.27 Tg y⁻¹ to be emitted by the ocean to the atmosphere. *Singh et al.* [1983] estimated a similar flux of 0.27 to 0.45 Tg y⁻¹, based on measurements in the eastern Pacific. Another early estimate of the flux of methyl iodide from the ocean to the atmosphere was made by *Rasmussen et al.* [1982]. Their value of 1.3 Tg y⁻¹ was strongly influenced by their supposition that highly productive waters, accounting for 10% of the ocean area, would supply about 1.0 Tg y⁻¹, a value which was derived from *Lovelock's* [1975] measurements of relatively high concentrations for a region off SW Ireland - since they did not have measurements themselves for productive regions. *Reifenhäuser and Heumann* [1992] extrapolated their measurements of methyl iodide near Antarctica to the global ocean and estimated a flux of 0.8 Tg y⁻¹. It is clear from the reports in the literature that there are significant differences between the various flux estimates, and that no single estimate of the global methyl iodide flux has been based on data collected over a wide range of latitudes or oceanic regions. For example, no single data set in the above reports contains data from both warm and cold as well as both coastal and open ocean waters. Nevertheless, despite variation in the magnitude of the fluxes, all the reported flux estimates to date support the idea that the ocean is a major source of methyl iodide to the atmosphere.

Several means of methyl iodide production within the oceans have been proposed. Photochemical production of methyl iodide in filtered seawater has been demonstrated in laboratory experiments by *Moore and Zafiriou* [1994], who also outlined possible mechanisms for this production pathway based on the reaction of iodine atoms with photochemically-produced methyl radicals. The presence of oxygen inhibited photochemical production, and addition of iodide ions enhanced production in deoxygenated seawater. Coastal water had a higher rate of production than offshore water, and the authors speculated that this is due to higher concentrations of organic matter to absorb light and provide methyl radicals in coastal water. *Moore and Zafiriou* [1994] estimated that photochemical production rates of methyl iodide could be sufficient to account for a significant part of the air-sea flux. Support for the significance of photochemical production was put forward by *Happell and Wallace* [1996] based on their analysis of factors affecting methyl iodide saturation anomalies at high and low latitudes. They reported that the Greenland/Norwegian Sea area in November was undersaturated with respect to methyl iodide, and attributed this to low light levels. Of the factors they tested by analysis of variance, methyl iodide concentration was most strongly correlated with light intensity.

Methyl iodide is known to be produced by marine seaweeds [*Manley and Dastoor*, 1987; 1988]. *Manley and Dastoor* [1987] reported experiments in which methyl iodide concentrations increased in the water in an aquarium where whole blades of the giant kelp *Macrocystis pyrifera* were grown. They extended these experiments to show that kelp tissue grown in the absence of bacteria (an axenic culture) could also produce methyl iodide, and that populations of microbes associated with kelp could produce methyl iodide independently when grown on culture medium made from powdered kelp [*Manley and Dastoor*, 1988]. However, although kelp and associated microbes clearly produce methyl iodide, the production rates only amounted to about 0.0002 Tg of methyl iodide per year when extrapolated to the global standing stock of macroalgae [*Manley and Dastoor*, 1987].

The possible production of methyl iodide by phytoplankton has until recently been largely speculative. Both *Moore et al.* [1996] and *Manley and De La Cuesta* [1997] have found methyl iodide production in unialgal cultures of phytoplankton. Some of the species which were reported by *Manley and De La Cuesta* [1997] as producers of methyl iodide were grown in axenic cultures, thus demonstrating that bacteria are not essential for the production of methyl iodide. However, the production rates from phytoplankton cultures, when scaled to the global oceans based on phytoplankton biomass, could only account for a relatively small fraction of the estimated total source to the atmosphere.

Manley and De La Cuesta [1997] estimated that their culture experiments could only support a global production rate of about 0.004 Tg of methyl iodide per year by phytoplankton, which is about 1% of the estimated total emissions.

1.5 Variation in Oceanic Flux Estimates

It is clear from sections 1.1, 1.2, and 1.3 that for all three methyl halides substantial disagreements exist between various published estimates of the global net air-sea flux. What follows in this section is a brief outline of some of the plausible causes for these disagreements.

First, it is important to recognize the nature of the problem of estimating the annual global air-sea exchange of a trace gas such as methyl chloride, methyl bromide, or methyl iodide. These compounds are present at very low concentrations, and even simply measuring their concentrations accurately is fraught with difficulty. Inaccurate measurements can potentially be caused by sample contamination, interference from other compounds, inaccuracies in standards, or loss or accumulation of the compounds of interest in the sampling, storage, or analysis steps of the procedure. Then, even given accurate measurements, the calculation of the air-sea flux is also dependent on other data, such as the solubility and the exchange velocity. The accepted best values of these physical quantities have evolved over time, and various global air-sea flux estimates have been based on different solubilities and exchange velocities. Finally, given accurate fluxes for a particular data set, one is confronted with the uncertainties of making a global extrapolation. With measurements which are limited in spatial and seasonal coverage by practical constraints, it becomes necessary to predict what the most likely conditions are in other places and at other times of the year, in order to calculate a global annual flux. Since the production mechanisms of these compounds in oceanic surface waters are poorly understood, and the *in-situ* production rates are not yet directly known in various water types, there are substantial uncertainties in such a prediction.

On the subject of the analytical uncertainties, there are various differences among analytical methods which may have contributed to the variability in estimates of the oceanic saturation levels of these three compounds. Among various studies, the standards used to calibrate the response of the analytical instruments have differed in concentration, phase, and mode of preparation. Two other differences are the type of water sample taken (direct water sample or equilibrated air sample) and the type of detector used to quantify methyl halides in the sample. These two factors are discussed in more detail below.

Some estimates of the air-sea flux of methyl halides have been based on concentrations measured directly in seawater, typically by purging a sample of seawater to remove all the volatile compounds for analysis [e.g. *Singh et al.*, 1983]. This method is the most direct way to determine the absolute concentration of a volatile compound in seawater. However, the air-sea flux is considered to depend on the difference of the concentration in seawater from atmospheric equilibrium [*Liss and Slater*, 1974], so either the concentration in the water or the mole fraction in the air must be converted via the solubility in order to determine the sign and the magnitude of the concentration difference. If the solubility value is incorrect, it is possible to calculate a flux which is incorrect, not only in magnitude, but also potentially in direction, particularly if the true concentration difference is small. The alternative is to make both measurements in the same phase, typically the gas phase, which is accomplished by using an equilibrator to bring an air sample to equilibrium with surface seawater [e.g. *Khalil et al.*, 1993; *Lobert et al.*, 1995; 1996; 1997]. The equilibrated air can then be compared directly with ambient air to determine the sign and magnitude of the saturation anomaly. The magnitude of the flux eventually calculated from an equilibrator measurement still depends on the solubility value, but at least the direction of the calculated flux is not influenced by the uncertainty in solubility. The subject of equilibrator design is discussed more thoroughly in Chapter 3 of this thesis.

There are two different kinds of detectors which have been used in conjunction with gas chromatography to quantify methyl halides in air and water samples, namely the electron capture detector (ECD) and the mass selective detector (MSD). The majority of the published analytical work was performed with the ECD [*Lovelock et al.*, 1973; *Lovelock*, 1975; *Rasmussen et al.*, 1982; *Singh et al.*, 1983; *Reifenäuser and Heumann*, 1992; *Khalil et al.*, 1993; *Happell and Wallace*, 1996]. The ECD is sensitive to compounds containing halogen atoms, with the order of sensitivity being $I > Br > Cl > F$, and is more sensitive to polyhalogenated rather than monohalogenated compounds [*Clemons and Altshuller*, 1966]. The ECD is highly sensitive to compounds such as chlorofluorocarbons and sulfur hexafluoride, which have multiple halogen atoms, but its sensitivity to methyl halides is lower, and is particularly low for methyl chloride [*Grimsrud and Rasmussen*, 1975]. The sensitivity of an ECD to methyl halides can be enhanced by oxygen-doping of the chromatographic carrier gas [*Grimsrud and Miller*, 1978], and with this enhancement the ECD can quite adequately detect methyl halides in ambient air and water samples.

The use of an MSD in field measurements of methyl halides has been reported in at least four publications [*Grimsrud and Rasmussen*, 1975; *Lobert et al.*, 1995; 1996; 1997].

The MSD has approximately equal sensitivity to all compounds [Grimsrud and Rasmussen, 1975]. The principal advantage of an MSD is its higher selectivity, since the compounds eluting from the column are further selected on the basis of the mass-to-charge ratio of their ionization breakdown products. Each compound has a fairly consistent and characteristic pattern of ionization breakdown products. Seawater and air samples contain a complex mixture of volatile compounds, which are generally separated by gas chromatography. Under various chromatographic conditions, another compound may elute at the same time as the compound of interest and cause an interfering peak which, if not recognized and further separated, can render the analysis inaccurate. Interference of this kind is a problem of failed chromatographic separation, and not a fault of the detector itself. However, if a separation problem exists, the MSD is less likely to be affected by it. In order for a compound to interfere with an MSD analysis, it must not only elute at the same time as the compound of interest, but also have a significant peak (or peaks) in its mass spectrum matching the mass to charge ratio(s) being monitored for the compound of interest. This reduces, although does not entirely eliminate, the possibility of interferences. No published report of interference involving the ECD appears to exist, although an unsubstantiated claim of such interference has been mentioned [Lobert *et al.*, 1995]. From the literature, there appears to be no way to determine whether any of the widely varying results for methyl halide analyses have been due to chromatographic interferences.

1.6 Goal of the Present Study

The review of the literature confirms that the net air-sea fluxes of the methyl halides are still subject to substantial uncertainty. For methyl chloride and methyl iodide, no single estimate has been published in which a wide range of waters were sampled (both warm and cold, northern hemisphere and southern hemisphere, Atlantic and Pacific). In the case of methyl bromide, extensive sampling coverage of oceanic waters already exists [Lobert *et al.*, 1995; 1996; 1997], but the results of that extensive work are in disagreement with the results of the preceding studies [Singh *et al.*, 1993; Khalil *et al.*, 1993], and have yet to be independently confirmed by another research group.

The goal of the work presented in this thesis is to provide an estimate of the net annual air-sea flux of three methyl halide compounds (CH_3X), based on field measurements made with an equilibrator and a mass selective detector over a wide range of latitudes and oceanic regions in several seasons. Particular attention will be paid in this work to the method of extrapolation from a limited data set to a global flux estimate.

Chapter 2: DATA COLLECTION METHODS

The air-sea flux estimates in this work are based on mole fractions of methyl chloride, methyl bromide and methyl iodide measured in marine air and surface ocean water. These mole fractions were determined by equilibrator and air sampling with ship-board analysis during three voyages at sea. In order to be confident of the accuracy of a global flux estimate, it is important to sample as wide a variety of ocean regions as possible. In this work, the sampling coverage includes latitudes from 60° N to 35° S, and a range of water temperatures from 2 to 29°C. The oceanic regions sampled include the central Pacific, Tasman Sea, Labrador Sea, northwest Atlantic, Gulf Stream, Sargasso Sea, and coastal areas off Labrador, Greenland, Nova Scotia, Hawaii, New Zealand, Guyana, Venezuela, and Trinidad. The seasonal coverage includes summer and autumn in the northern hemisphere and spring in the southern hemisphere.

2.1 Cruise Tracks

2.1.1 Labrador Sea/North Atlantic

On the first voyage in July of 1995, the *CSS Hudson* departed from St. John's, Newfoundland, crossed the Labrador Sea to Greenland, then headed south to the Gulf Stream before turning west to go in to port at Halifax, Nova Scotia (Figure 2.1).

The cruise track passed through waters ranging in temperature from 2°C off Greenland to 25°C in the Gulf Stream. Chlorophyll *a* concentrations in surface waters along the cruise track also varied through a wide range, being below 0.5 µg L⁻¹ over much of the voyage, but rising to a peak of 4.25 µg L⁻¹ in the Labrador Sea. M. Webb determined chlorophyll *a* concentrations by fluorometry on acetone extracts [Holm-Hansen *et al.*, 1965].

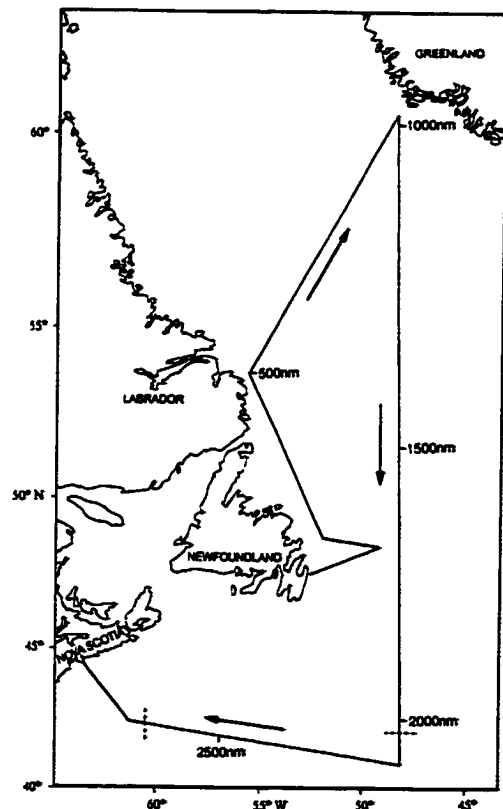


Figure 2.1. Labrador Sea/North Atlantic voyage, *CSS Hudson*, July 1995. Dashed lines indicate Gulf Stream boundaries. Distances are in nautical miles (nm).

2.1.2 Central Pacific

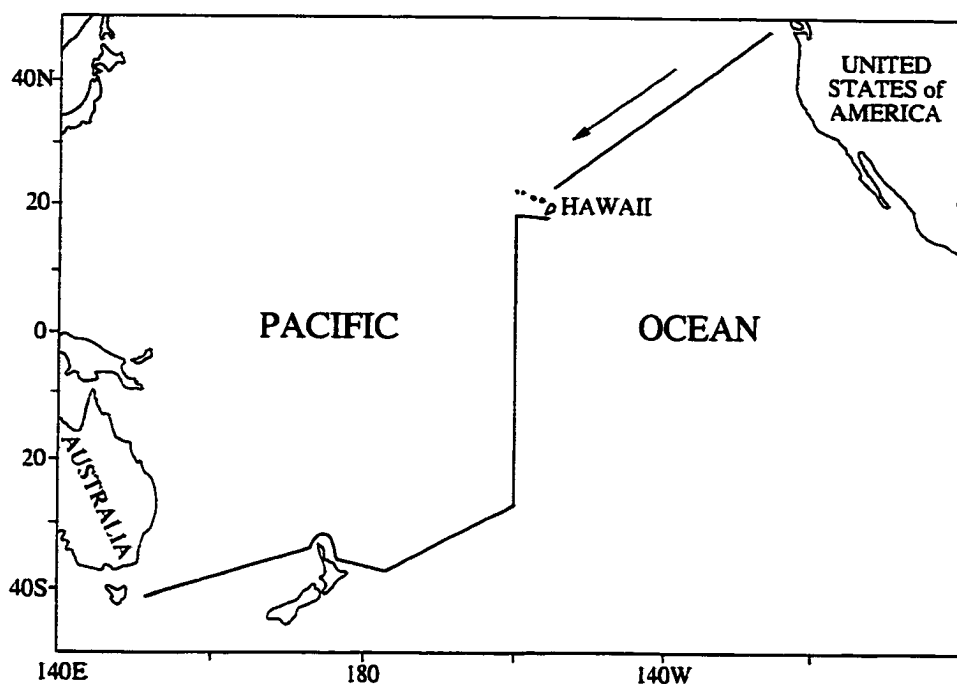


Figure 2.2. Track of the NOAA Ship Discoverer, October/November 1995.

The Pacific voyage took place in October and November of 1995 on the *NOAA Ship Discoverer*, which travelled from Seattle, USA to Hobart, Australia (Figure 2.2). The cruise track passed, for the most part, through open-ocean, oligotrophic waters at temperatures from 17 to 29°C. The track also crossed the Tasman Sea, the equatorial upwelling region, and coastal waters near Hawaii and New Zealand.

2.1.3 North Atlantic

The third voyage was in July and August of 1997, on the *R/V Knorr* in the North Atlantic, from Halifax to Trinidad, with a return leg to Woods Hole (Figure 2.3). The cruise track included open ocean, Sargasso Sea waters, as well as waters on the continental shelf near South America (Guyana and Venezuela) and along the northern coast of Trinidad. Early in the northbound leg of the *Knorr* cruise, equilibrator sampling was halted by an equipment breakdown. Therefore, on the northbound leg only air samples were taken, with the exception of seven stations at which depth profiles down to 200 metres were obtained using a purge-and-trap apparatus to analyze water sampled from Niskin bottles.

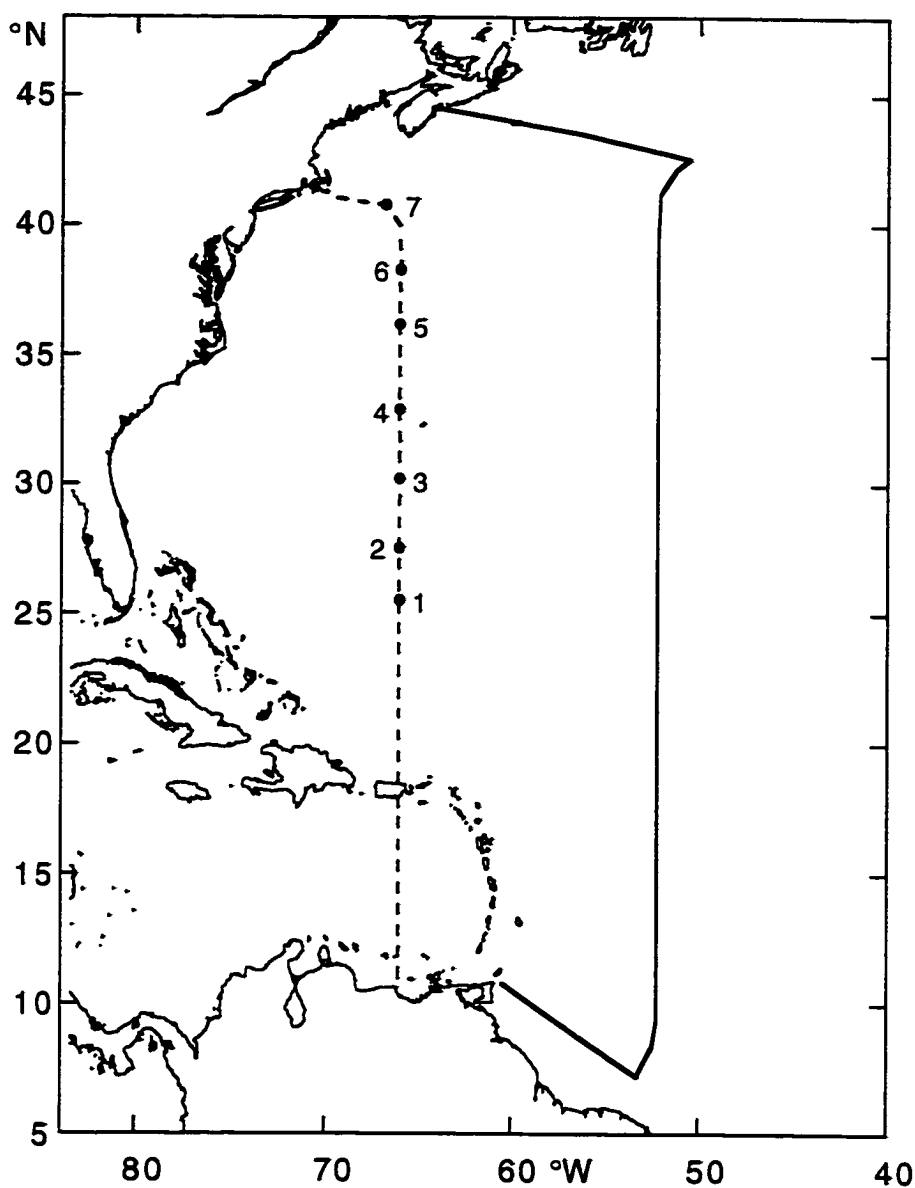


Figure 2.3. Track of the *R/V Knorr*, July/August 1997. The solid line indicates both equilibrator samples and air samples, the dashed line indicates air samples only, and the numbered dots mark the locations of depth profiles.

2.2 Sample Collection

On each voyage, ambient air samples and equilibrated air samples were collected at intervals along the cruise track and analysed on the ship. The hours of sampling and analysis were limited by the availability of the analytical instrument, which was in use for

other projects during the daytime hours, so that most of the samples reported in this thesis were taken at night. The possibility of diurnal cycles in the concentrations of these compounds in seawater and air could not be investigated under the constraints of the available sampling times. However, a significant diurnal cycle would probably have been revealed by nighttime trends in concentration from the beginning to the end of a watch (typically late evening to early morning). No consistent trends were observed through the night, and a small number of samples collected during daylight hours did not yield unusual results. The only exception to the pattern of nighttime sampling was that on the northbound leg of the Knorr cruise (Trinidad to Woods Hole, Figure 2.3), the analytical system was available all the time, and the air samples on that leg were taken in the daytime. As mentioned previously, there were no equilibrator samples on that leg. The analytical system used in this project required the attention of the operator for every sample and could not be left in automatic operation, so sampling times were also limited by the need for sleep.

More details of the sampling procedures are given in Sections 2.2.1 through 2.2.3, and the analytical procedure is described in Section 2.3. The equilibrators used in this work are mentioned in Section 2.2.2, but not in detail because Chapter 3 is devoted to the discussion of the equilibrators.

2.2.1 Air sampling

Samples of ambient air were taken using a portable steel diaphragm air sampling pump. Before each sample, care was taken to place the pump at the most upwind point of the ship to avoid contamination by exhaust and other emissions. When the ship was underway, this location was most often the bow or the most forward outside railing of a higher deck, though in some winds it was necessary to sample at the stern. Air was pumped into 900-mL, internally electropolished stainless steel canisters. For each sample, a canister was vented to the clean atmosphere and refilled four times to a gauge pressure of about three atmospheres, to flush out the previous sample. On the third voyage (*RV Knorr* in 1997), a vacuum pump was used to evacuate the previous sample from each canister before use.

Each canister was sealed with a Nupro bellows valve, then disconnected from the pump. Air samples were analyzed on the ship, as quickly as possible given the constraints of the analytical procedure, which in practice means within 30 minutes of sampling. Tests conducted to determine the precision of the analytical procedure involved repeated analyses of an air sample from the same canister (Section 2.4.6), and no trend in concentration within the canister was seen over a time period of 90 minutes. Therefore,

storage in the canister for up to 30 minutes before analysis did not affect the results. The analyses of air samples and equilibrator samples were both made in the same way, and the details of the analytical procedure are given in section 2.3.

2.2.2 Equilibrator Sampling

During all three voyages, samples were taken with equilibrators to determine the mole fraction of methyl halides in surface water. In the equilibrators, the methyl halides in a stream of ambient air were allowed to equilibrate with a flowing sample of seawater. The resulting equilibrated air was analyzed in the same way as an atmospheric sample, with the analytical procedure described in Section 2.3. Because equilibrator samples are in the gas phase and represent the mole fraction in the water, the results from their analysis can be used directly with their corresponding air samples to determine the degree of saturation of the compounds of interest in seawater.

Three different equilibrators were used during this work. Two equilibrators were used in parallel on the voyages in 1995 on the northwest Atlantic and the Pacific. The first of these will be referred to as equilibrator1 and was a conventional shower equilibrator based on the design of R. F. Weiss of the Scripps Institution of Oceanography [Butler *et al.*, 1988]. The second, equilibrator2, was a semipermeable membrane equilibrator developed during the course of the present work. Equilibrator3, a redesigned version of the semipermeable membrane equilibrator, was used alone on the 1997 voyage of *R/V Knorr* in the North Atlantic. Testing demonstrated that the semipermeable membrane design yielded results which were not significantly different from those of the more conventional equilibrators, and all equilibrator samples within the data set are considered to be equivalent. Further details on these equilibrators are given in Chapter 3, which is devoted to their design considerations, descriptions, and operational procedures.

On each ship, seawater was supplied to the equilibrators by a pump through an inlet in the bow at approximately 5 m depth. Between the pump and the equilibrators, the seawater flowed through plastic pipes over distances of up to ~80 m. This seawater delivery system has the potential to affect the sample quality in two ways. First, although the pipes are surrounded by thermal insulation, the temperature of the water may change during the journey from the inlet to the equilibrator. Secondly, parts of the system could alter the seawater sample through contamination or absorption.

At a given concentration, the equilibrium partial pressure of dissolved gases in seawater varies with temperature. Therefore, any temperature change in the seawater as it is travelling to the equilibrator will cause an inaccuracy in the measured mole fraction. To account for this potential problem, the water temperature at each equilibrator was

monitored and compared with the sea surface temperature (SST). During the first two voyages, this monitoring was conducted periodically, using a portable electronic thermometer to check each equilibrator, and the basis for comparison was the SST measured using either a shipboard CTD package or surface bucket samples, depending on availability. On the third voyage, SST and the equilibrator temperature were recorded for every sample by an underway logging system.

During the Labrador Sea cruise, when the *Hudson* was in cold waters, the water in the equilibrator was found to be consistently 0.3°C warmer than the measured SST. This was corrected for by adjusting the measured mole fractions to the actual SST, based on the solubilities measured by *Elliott and Rowland* [1993]. The effect of this adjustment was to decrease the mole fractions by between 0.4% and 1.1% of their raw values, amounts which are not significant to the conclusions of this work. On the *Discoverer* in the Pacific Ocean, no difference in temperature of the water between the sea surface and the equilibrators was detected, to the level of precision of the thermocouple (0.1°C), and therefore no temperature adjustment was made to the Pacific mole fractions. On the *Knorr* in the North Atlantic, temperatures at the equilibrator were found to be from 0.1 to 0.3°C warmer than the SST. Each data point was corrected for the temperature difference recorded by the logging system for that point.

2.2.3 Depth Profiles

For the purpose of estimating the air-sea flux, the surface samples which were taken with the equilibrators provided extensive coverage at one depth (3 to 5 metres, which is considered to represent the surface). This extensive data set was used in calculations to estimate the air-sea flux (Chapter 5). However, to understand the effects of production and loss in the water, along with mixing and stratification, it is beneficial to also collect data on methyl halide concentrations as a function of depth in the water column. The collection of depth profiles was not originally planned for this thesis work, but the opportunity to collect depth profiles was taken on the second leg of the *Knorr* cruise in the north Atlantic when an equipment failure had halted the collection of equilibrator samples.

During the northbound leg of the *Knorr* cruise, in the Sargasso Sea and on the continental slope off Cape Cod, seven near-surface depth profiles of methyl halide concentrations were taken. The locations of these depth profiles are indicated in Figure 2.3. Water for these profiles was collected using six 10-L Niskin bottles, triggered typically at 200, 150, 100, 50, 30, and 4 metres depth. One bucket sample was also taken with a galvanized steel bucket at each station. Samples were drawn into 100-mL glass

syringes, stored in a bucket of seawater in dim lab light and analyzed within 3 hours. Details of the analysis of these liquid samples are included with the other analytical information in section 2.3.

2.3 Analytical Methods

2.3.1 Trapping

All gas phase samples, including equilibrators samples and canisters of ambient air, were measured into a 207-mL stainless steel sample loop. This loop was housed in a box, the interior temperature of which was monitored with a thermistor. Both the loop temperature and atmospheric pressure were recorded for each sample, in order to correct the volume of sample in the loop to 25°C and one atmosphere pressure. The gas samples were not dried before being measured into the loop, to avoid potential wall losses associated with dry air on stainless steel surfaces. Results of air sampling are best reported as dry air mole fractions to eliminate the biases caused by variations in water vapour content. It therefore became necessary to estimate the amount of water vapour in the samples and adjust the results to find the dry gas mole fractions. The procedure for this adjustment had some subtle complexities which are explained in Section 2.4.

After the sample loop was filled, a four-port valve was turned to switch the loop into series with a 40 mL/min helium flow, which carried the sample through a tube of CO₂ absorbent (Ascarite II) and a magnesium perchlorate drying tube to a cold trap. Tests conducted using samples of calibration gas demonstrated that the CO₂ absorbent and the drying tube do not affect the concentration of methyl halides in the sample. The cold trap consisted of a coiled 30-cm-long piece of stainless steel tubing (ID 0.5 mm) held at -150°C over liquid nitrogen. After the gas sample was collected in the trap for ten minutes, the cold trap was isolated from the purge-gas flow and rapidly heated by an electric current to ~15°C. A helium carrier gas stream (5 mL/min) was then switched through the trap for 10 seconds to sweep the contents into a gas chromatography column for separation.

The analytical equipment used for liquid phase water samples was essentially the same as that used for air samples, with the addition of a glass pipet for measuring the samples, and a purge vessel. Volatiles were extracted from a 40-mL sample by a stream of helium (40 mL/min) separated into fine bubbles by a glass frit in the purge vessel. The sample was heated during the 12-min purge by a water jacket around the purge vessel maintained at 40°C by a circulating bath. Water vapour was removed from the purge flow in two steps; first, the moist helium passed through a short condenser jacketed with water at

~1°C and then through a drying tube containing magnesium perchlorate. No CO₂ absorbent was used for liquid phase samples, in order to maintain consistency with the analytical procedures in use for liquid samples analysed previously by other workers on the same system (R. M. Moore, personal communication). The helium flow carried the sample to the same trap as was used for air samples, and the procedure for injection into the gas chromatograph was the same.

2.3.2 Separation

For all samples, separation of the volatiles was achieved by gas chromatography in a Fisons 8030 gas chromatograph (GC). Two chromatographic columns were used in series, with the first column serving as a precolumn from which compounds eluting after dichloromethane were discarded by backflushing. The pre-column was 25 m long, and the main column was 75 m long. Backflushing was accomplished by automated switching of a Valco four-port valve six minutes after injection. The two columns (made by J&W Scientific) were of exactly the same type, namely megabore columns with an internal diameter of 0.53 mm and a DB-624 liquid phase with a film thickness of 3 µm. The carrier gas was helium at a flow rate of 4 mL min⁻¹. The temperature of the GC oven was held isothermal at 35°C for the first 8 minutes of each run, then increased at a rate of 10°C min⁻¹ up to 60°C, where it was held for a further two minutes. Under these conditions, the retention times of methyl chloride, methyl bromide, and methyl iodide were 5.6, 7.1, and 10.8 minutes, respectively.

2.3.3 Detection

Compounds were detected using a Fisons MD800 mass selective detector (MSD) fitted with a Varian 250 L s⁻¹ turbomolecular pump. The MSD was operated in single ion mode, and the ions monitored had mass-to-charge ratios of 50 and 52 for methyl chloride, 94 and 96 for methyl bromide, and 142 for methyl iodide. Other compounds routinely detected in the same samples included fluorotrichloromethane (CFC-11), dichlorodifluoromethane (CFC-12), carbon disulphide, and dichloromethane.

The detection limits of the analytical system, calculated as 3 times the standard deviation of the blank, were 3 ppt for methyl chloride, 0.7 ppt for methyl bromide, and 0.1 ppt for methyl iodide. The amount of methyl chloride in any sample was at least 100 times over the detection limit; for methyl bromide this ratio was at least 10 times. By contrast, methyl iodide mole fractions below 0.5 ppt in ambient air were not uncommon, so for air samples the amount of methyl iodide in a sample was closer to the detection limit than for the other two compounds. Despite these low mole fractions, it was never

difficult to detect and integrate the methyl iodide peak in an air sample. Methyl iodide mole fractions in equilibrator samples were always 10 to 400 times above the detection limit.

The stability of the detector was monitored by the addition of an internal standard with each sample. The internal standard consisted of a fixed volume (nominally 25 μL , but the actual volume is inconsequential since it is constant) of isotopically labelled (fully deuterated) methyl chloride, methyl bromide, and methyl iodide diluted in nitrogen. The temperature of the loop used for measuring this internal standard was held constant in a heated enclosure, and its contents were allowed to reach atmospheric pressure before being injected. Atmospheric pressure was monitored with the same Paroscientific or Setra barometer as was used for air samples, and the volume of internal standard was corrected to one atmosphere pressure. The mass-to-charge ratios monitored for the internal standard were 53 and 55 for methyl chloride, 97 and 99 for methyl bromide, and 145 for methyl iodide.

For data from the first two voyages (1995), the peak area in each sample was normalized to a constant value of the internal standard peak area. Adjustments of this kind were small and random, typically $\sim 5\%$. The use of an internal standard was begun because of testing in 1994 which demonstrated a gradual drift in the sensitivity of the instrument. By 1997, the problem of drift was eliminated by a change in the ion source, and it was determined by testing that the internal standard was no longer necessary. Therefore, on the third voyage, internal standard adjustment was not used, but an air reference (section 2.4.5) was analyzed more frequently to guard against the possibility of changes in sensitivity.

2.3.4 Calibration

Peak areas were calibrated by injection and analysis of a gravimetrically produced standard gas containing 1961.16 parts per billion (ppb) of methyl chloride, 98.85 ppb of methyl bromide, and 98.65 ppb of methyl iodide in nitrogen contained in an Aculife[®]-treated aluminium cylinder. This standard was made by Jim Happell at the Brookhaven National Laboratory, by breaking glass capillary tubes containing precisely known masses of the methyl halides in an enclosed stream of pure nitrogen which carried the halocarbons to the cylinder. The cylinder itself was evacuated and weighed before filling, then weighed again after filling to determine the total mass of gas. Daily calibration curves were established by finding the peak-area response of the analytical system to a series of known volumes of the standard gas between 10 and 200 μL . The standard gas was injected from a Hamilton syringe into the trapping system via a septum port. The

temperature of the syringe in its storage box and the atmospheric pressure at the time of injection were recorded and used to adjust the resulting peak areas to a constant temperature and pressure (25°C and one atmosphere). The calibration curves were linear.

Blanks were established several times per day by running the system without any air or water sample. The average blank value for each day was subtracted from all the peak areas of sample and calibration runs for that day. A typical blank peak area for methyl chloride was equivalent to ~14 ppt, or about 2% of the mole fraction of a typical 600-ppt air sample. For methyl bromide, a typical blank was equivalent to ~0.4 ppt, or about 3% of a 12-ppt air sample. For methyl iodide, a typical blank was equivalent to around 0.2 ppt. Because the mole fraction of methyl iodide in air is very low, this blank represents about 20% of the peak area of a typical 1-ppt air sample, but only about 1% of the area of a typical 20-ppt equilibrator sample.

2.3.5 Air Reference

As an additional reference point for the calibration of the analytical method, a 15-L, internally electropolished steel tank was filled to a pressure of 3 atmospheres with ambient marine air near the beginning of each cruise. On the first two voyages, samples of this air reference were analyzed once or twice per working shift, and the air reference peak area was used as a guide to check the calibration. Because the peak area of every sample was normalized to a constant value of the internal standard, it was possible to compare air reference values from one day to the next over the course of each of these two cruises. In this way it was determined that small random variations in the calibration slope appear to reflect variations in the injection volumes from Hamilton syringes rather than actual changes in sensitivity. Based on this observation, it was decided to compile together the normalized calibration curves and use the resulting calibration slope for all the samples within each cruise. This method of calibration was preferable to using each day's calibration separately because it resulted in lower variability in the analyses of the air reference.

On the third voyage, samples from the air reference tank were analysed more frequently, normally three times per working shift, in order to use the air reference peak area directly to calibrate the instrument on each day. Analyses of a range of volumes of the regular calibration standard were also performed each day, but they were compiled together into what is effectively a long-term calibration of the air reference itself. The average air reference peak area for each day was then used directly in the calculation of air and equilibrator sample mole fractions. This procedure was used to filter out the small random day-to-day variations in the calibration slope, in a similar way as for the first two

cruises, except that in this case each day required a separate calibration because the internal standard was not in use on this cruise. Another way to describe the difference in the calibration method on the third cruise is to say that the increased use of the air reference replaced the use of the internal standard. On the southbound leg of the *Knorr* cruise, the mean mole fractions in the air reference tank were found to be 532 ± 9 ppt for methyl chloride, 10.9 ± 0.1 ppt for methyl bromide, and 2.68 ± 0.07 ppt for methyl iodide (90% confidence intervals). There was no measurable drift in the mole fraction of methyl halides in the air reference over the duration of the voyage.

2.3.6 Reproducibility

Reproducibility testing was conducted by analyzing an air sample from the same canister three times, beginning immediately after collection and continuing for 90 min. In these tests, the instrumental precision of air measurements was found to be $\pm 1.4\%$ for methyl chloride, $\pm 2\%$ for methyl bromide, and $\pm 16\%$ for methyl iodide. The precision for each compound is reported as the 95% confidence interval of the mean. No trend in concentration in the canister was detected over the time scale of the measurements. Note that the much higher percentage (16%) for methyl iodide is in large part due to its very low atmospheric mole fraction. Expressed as an absolute mole fraction in ppt, the standard deviation of the methyl iodide samples in this test (0.08 ppt) was smaller than the standard deviation for methyl bromide (0.10 ppt) and methyl chloride (2.8 ppt).

A set of three analyses of equilibrator samples in succession, completed about 30 minutes apart, yielded variabilities of 4% for methyl chloride, 7% for methyl bromide, and 8% for methyl iodide (95% confidence intervals of the mean). This test with equilibrator samples does not truly reflect the instrumental precision, because the ship was moving during this time and the actual samples could not be expected to be identical. For this reason, the test conducted with repeat analyses from an air canister is more representative of the instrumental reproducibility.

2.4 Water Vapour Adjustments

The dry gas mole fraction was calculated by subtracting the partial pressure of water vapour from the barometric pressure to get the dry pressure, and then multiplying the wet gas mole fraction by the ratio of the barometric pressure to the dry pressure. To complete this calculation, the partial pressure of water vapour in the sample loop had to be estimated for each sample. For equilibrator samples, it was assumed that the gas stream leaving the equilibrator was saturated with water vapour at the temperature of the

seawater in the equilibrator. The partial pressure of water at equilibrium with seawater was calculated with the equation of *Weiss and Price*, 1980:

$$\ln p_{\text{H}_2\text{O}} = 24.4543 - 67.4509 (100/T_K) - 4.8489 \ln (T_K/100) - 0.000544 S \quad (2.1)$$

where $p_{\text{H}_2\text{O}}$ is the saturated vapour pressure of water (atm), T_K is the temperature (Kelvin), and S is the salinity.

A different procedure was used to estimate the partial pressure of water vapour in ambient air samples. Because air samples were compressed into canisters before being measured into the sample loop, water vapour must have condensed inside the canisters under nearly all meteorological conditions encountered in this work. The canisters were pumped to a total pressure of about 4 atmospheres, resulting in a partial pressure of water vapour in the canister about four times its initial value in ambient air. These canisters were then taken into the lab inside the ship and came to thermal equilibrium at the lab temperature (average 21°C for the *Hudson*, 22.6°C for the *Discoverer*, and 24.6°C for the *Knorr*). In cases where the air outside the ship was colder than the lab, the warming of the canister caused some of the condensed water inside the canister to evaporate. Nevertheless, assuming an outside relative humidity above 50%, it was calculated that all canisters filled at (outside) temperatures greater than 5°C would still have condensed water inside even after warming to the lab temperature. With condensation inside the canister, the water vapour pressure is equal to its saturation vapour pressure at the temperature of the canister. Samples were taken from the fully compressed canisters, and on expansion back to barometric pressure in the sample loop the partial pressure of water was then about one quarter what it was inside the canister.

For air samples, the vapour pressure of water in the sample loop was thus estimated simply to be equal to 25% of the saturation vapour pressure of water at the temperature of the lab. At 50% outside relative humidity, this approximation is valid if the outside temperature is higher than 5°C. Relative humidity data were available for the *Discoverer* and *Knorr* cruises, but not for the *Hudson* cruise. All samples taken on the *Discoverer* and *Knorr* cruises satisfied the conditions, with air temperatures all above 10°C and relative humidities all above 60%. For the *Hudson* cruise, it is likely that every sample condensed, but it is not possible to be certain, because of the lack of relative humidity data. However, only three samples were taken at temperatures below 5°C, and meteorological conditions did not seem unusually dry. Given the likelihood of condensation, the same adjustment was applied to all samples. There are five doubtful cases, but the error in dry gas mole fraction from this adjustment for those samples could not be more than about 0.6%.

Chapter 3: EQUILIBRATOR DESIGN

In general, an equilibrator can be defined as an apparatus designed to allow some property to come to equilibrium between two phases. In the context of this work, an equilibrator will be defined more specifically to mean an apparatus which allows a gas phase sample to come to equilibrium with a seawater sample in terms of the partial pressures of volatile compounds in the seawater.

The goal of using an equilibrator in this study is to obtain an equilibrated air sample in which the partial pressures of the methyl halides are equal to their partial pressures in ambient surface seawater. The partial pressure difference between the surface ocean and the atmosphere is found by direct subtraction of the two measured partial pressures. From the partial pressure difference, one can immediately determine whether the ocean surface is supersaturated or undersaturated, and therefore whether the water of that particular sample represents a source or a sink for the compounds of interest in the atmosphere. However, according to the thin-film model of air-sea gas exchange [*Liss and Slater, 1974*], the flux across the interface is proportional to the difference between the concentration in ambient water and the concentration in the water at atmospheric equilibrium (referred to in this thesis as the concentration anomaly). The concentration anomaly ΔC (pmol L^{-1}) can be calculated from the partial pressure difference if the solubility of the gas is known. The air-sea flux F can then be expressed as:

$$F = k\Delta C = kH'(p_w - p_a) \quad (3.1)$$

Where k (m d^{-1}) is the piston velocity (also referred to as the exchange velocity or transfer velocity), H' ($\text{pmol L}^{-1} \text{atm}^{-1}$) is the solubility of the gas, p_w and p_a are the partial pressures (patm) of the gas in the water and the air, respectively.

3.1 Performance Criteria

Several performance criteria are important in the design of an equilibrator. All the equilibrators in this work are flow-through equilibrators, in which both the air and seawater are flowing continuously, and the air leaving the outlet can be directed into a container to take a sample. One important consideration is that the process of equilibration with air should not significantly alter the partial pressures of the compounds of interest in the water, because the goal of the equilibration process is to produce a gas-phase sample which accurately represents the partial pressure at equilibrium with an unaltered seawater sample. This criterion drives a tendency toward designs in which a

relatively small volume (slow flow rate) of air is equilibrated with a large volume (fast flow rate) of water.

Two factors which indicate the performance of an equilibrator are the equilibration time and the response time. In this context, equilibration time is taken to mean the amount of time that a parcel of air must reside in the equilibrator in order to reach equilibrium with water having a constant concentration of methyl halides. By contrast, the response time is taken here to mean the amount of time required by the equilibrator to respond to a change in methyl halide concentrations in the water. This is related to the idea of "sample carryover", and the question of how well any given sample represents the actual concentration in the water at the time of sampling.

Because the solubility of a gas, and therefore the partial pressure at equilibrium, is dependent on temperature, it is important that the temperature of the water within the equilibrator remain constant, and it is preferable that the temperature of the water remain unchanged throughout the sampling system which brings water to the equilibrator. Designs including insulation and fast flow rates help to minimize temperature changes within the system. Nevertheless, in practice it is very difficult to prevent small temperature changes, and for this reason it is important to compare the sea surface temperature outside the ship with the water temperature in the equilibrator, in order to correct for any differences. The air pressure within the equilibrator is also important, and the equilibrators in this work are designed to remain as close as possible to atmospheric pressure. The atmospheric pressure at the time of sampling is monitored with a barometer in order to correct for pressure changes in the sample volume .

Three equilibrators were used in this work. The first, referred to as equilibrator1, is of a conventional design. The others, equilibrator2 and equilibrator3, are sequential versions of a semipermeable membrane equilibrator designed and built in our laboratory for this project. This chapter includes descriptions of the three equilibrators, along with the results of testing to determine the performance of the semipermeable membrane design in equilibrator2 and equilibrator3.

3.2 Conventional Equilibrator

Equilibrator1 (Figure 3.1) is a variation of a design by R. F. Weiss of Scripps Institution of Oceanography [*Butler et al.*, 1988]. Equilibrators of this general type may also be based on the "shower head" design, originally developed to measure the partial pressure of carbon dioxide in seawater [*Broecker and Takahashi*, 1966]. The general features of these equilibrators are a vertical acrylic housing, with a drip tray or "shower

head" in the top to distribute flowing seawater into a spray which falls through an air space to the bottom, where the water drains. Air is circulated through the space so that it comes in contact with the falling water. The compounds of interest exchange between the water and air until their partial pressures have equalized between the two phases.

Equilibrator1 was built in 1994 by M. Poliquin at Dalhousie University and first used for carbon dioxide measurements (O. Hertzman, personal communication). The housing is a cylinder of transparent acrylic, 25 cm in diameter and 62 cm tall. Equilibrator1 has a taller space in the water inlet than the Weiss design, and has only one equilibration stage, rather than two. (R. F. Weiss, personal communication).

During field work to measure partial pressure of methyl halides, the water flow rate through equilibrator1 was about 8 to 10 litres per minute. Fresh air was supplied to the equilibrator through stainless steel lines, and pumped by a clean stainless-steel-bellows air sampling pump. The air flow rate varied from 50 to 100 millilitres per minute, and the equilibrated air was sampled directly from the air outlet, without recirculation. The outlet of equilibrator1 was vented to barometric pressure.

Equilibrator1 was operated in parallel with equilibrator2 on the July 1995 voyage in the North Atlantic and the October/November 1995 transect of the Pacific. Details of the cruise tracks and analytical methods are given in chapter 2.

3.3 Semipermeable Membrane Equilibrator

3.3.1 Background

Several methods involving semipermeable membranes have been developed to analyze volatile organic compounds in seawater, one of which is membrane introduction mass spectrometry (MIMS) [Kotiaho *et al.*, 1991]. In MIMS, the analyte passes directly from the sample into a mass selective detector through a semipermeable membrane, often

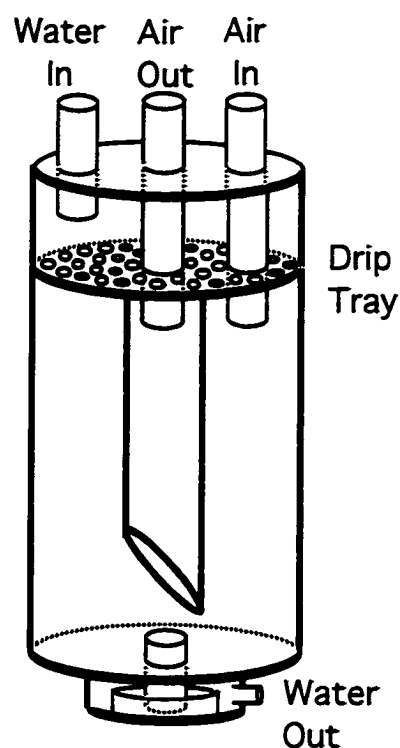


Figure 3.1. Schematic diagram of equilibrator1.

made of amorphous silicone rubber, which excludes the passage of liquid phase water. Preconcentration (e.g. purge-and-trap) and gas chromatography (GC) are not required, as the volatile compounds which pass through the membrane are separated on the basis of their mass spectra. Unfortunately, the detection limits reported for MIMS are not yet low enough for that technique to be used in the analysis of methyl halides in surface ocean waters. For example, there is a recent report of a MIMS detection limit of 300 parts per trillion by mass (pptm) for a similar compound, trichloromethane [Wong and Cooks, 1995], but ambient levels of methyl bromide in surface ocean waters are often less than 0.1 pptm [Lobert *et al.*, 1995] (converted to these units for comparison). At this point, there is no report of a MIMS system which can adequately detect methyl halides at levels ordinarily found in open ocean samples.

A similar method has been reported, in which a semipermeable hollow fiber membrane is used to separate volatile organic compounds (VOCs) from continuously flowing water, with the resulting gas stream preconcentrated in a microtrap for separation by GC. Using this method, the reported detection limit for dichloromethane is 280 pptm [Xu and Mitra, 1994], about three orders of magnitude too high to be used for ambient marine samples.

The use of a semipermeable membrane specifically to sample methyl bromide is demonstrated by the gas-liquid membrane equilibrators used by De Bruyn and Saltzman [1997b] to measure the solubility of methyl bromide in pure water, 35‰ sodium chloride and seawater. A microporous Teflon[®] tube was used as the membrane. The liquid phase concentrations sampled by the gas-liquid equilibrators in that work were $\sim 10^{-4}$ mol L⁻¹, around eight orders of magnitude higher than those found in oceanic samples. For solubility measurements it is advantageous to work with such high concentrations because smaller samples can be used, the higher signal increases analytical precision, and the possibility of contamination is decreased.

The work cited above demonstrates that semipermeable membranes can be used in analytical systems involving the exchange of methyl halides between a liquid phase and a gas phase, but that systems such as MIMS are not sensitive enough to be used to analyze ambient, uncontaminated seawater samples. Also, it is apparent that the Weiss equilibrator can be used to sample the partial pressures of methyl halides at the low levels present in ambient seawater [e.g. Lobert *et al.*, 1995]. Consideration of these two concepts together led to the idea that a coil of semipermeable membrane tubing immersed in a seawater sample could be an effective equilibrator. The problem of the detection limit could be solved simply by collecting an equilibrated air sample of sufficient volume from the outlet of the coil. Such an equilibrator was designed and built in this project. In

this equilibrators, semipermeable silicone tubing carries the gas phase through the liquid sample and allows the exchange of low molecular weight compounds across the tubing wall.

3.3.2. Benefits

There are several benefits and potential applications of using semipermeable membrane tubing in the equilibration process. One benefit is a reduction in the potential for contamination in the equilibrators, since the air stream is contained within the tubing and does not come into contact with any other surfaces. In addition, so long as the tubing is immersed in the sample, many constraints on the containment of the liquid phase are removed. For example, the equilibrators housing itself can be filled entirely with the flowing water sample, because no headspace is needed. This simplifies draining and pressure stabilization within the equilibrators.

Taking this a step further, with the gas phase contained in semipermeable tubing, the need to contain the liquid phase is eliminated. Instead, a "probe" with a semipermeable membrane could be immersed directly in the sample of interest, further reducing contamination from pumps and pipelines. This may be even more advantageous in measurements of compounds more widely used as solvents, such as dichloromethane and tetrachloroethene. Based on the experience of our research group, compounds which are widely used in commercial products often have significant contamination sources on ships which can make it impossible to accurately determine their ambient (outboard) concentrations from an on-board, pumped seawater supply. Comparison testing of bottle samples, bucket samples, and pumped samples revealed no such contamination problems for any of the methyl halides in the seawater supply systems used in this thesis work.

Equilibrator2 was built as a first step, to operate in essentially the same role as a conventional equilibrators, namely as an enclosed unit attached to a shipboard supply of flowing seawater. This was done in order to demonstrate that the principle works in practice, and to allow comparison with the conventional equilibrators. Equilibrator2 was operated in parallel with equilibrators1 on the July 1995 voyage in the North Atlantic and the October/November 1995 transect of the Pacific.

3.3.3. Equilibrator Description

Figure 3.2 is a schematic diagram of equilibrators2, the semipermeable membrane equilibrators. The housing is cylindrical, of 1/4" thick transparent acrylic, 10 cm in diameter and 52 cm long. Flowing seawater enters at the bottom right, fills the housing, and flows out at the upper left. Polyurethane foam insulation is wrapped around the

housing and the water inlet hose to minimize heat exchange between the water and the surroundings.

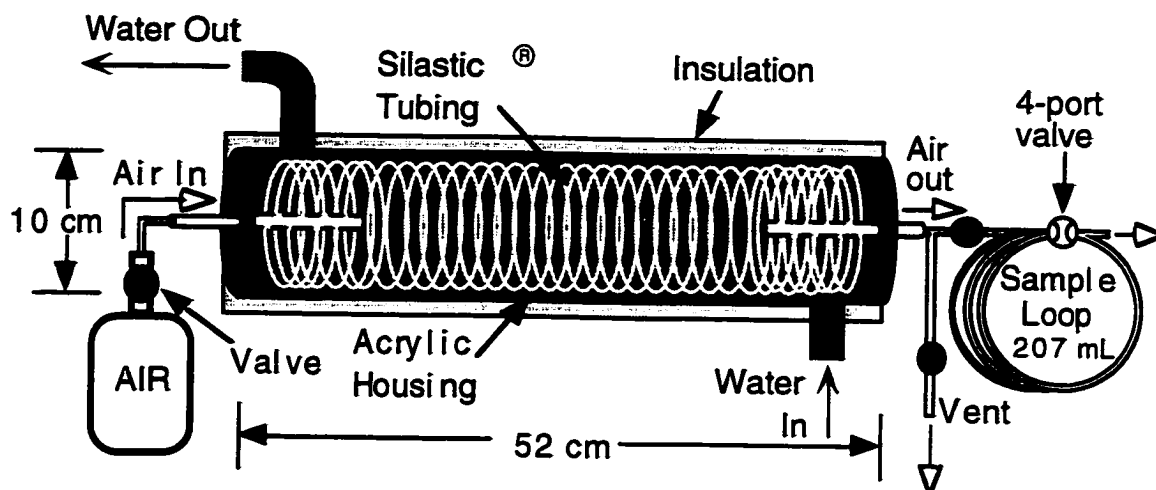


Figure 3.2. Schematic diagram of equilibrator2.

The air supply flows from a pressurized, internally electropolished steel canister. A metering valve controls the flow rate of the air, which is carried by stainless steel tubing to a 3/8" heavy walled glass tube that passes into the housing and distributes the flow into eight streams. Each stream passes through a 3.75 m length of Silastic® tubing (Dow Corning), which is completely immersed in the flowing seawater sample. The tubing is made of silicone rubber, with an outer diameter of 1.96 mm, wall thickness of 0.25 mm, and inner diameter of 1.47 mm. Silicone rubber was chosen based on its use in MIMS [Kotiaho *et al.*, 1991] and other membrane extraction techniques [Xu and Mitra, 1994], and because of its relatively high permeability to low molecular weight compounds [Pauly, 1989]. Including all eight parallel sections, a total of 30 m of tubing is coiled inside the housing. The tubing is held in its coiled position in the housing by a perforated acrylic frame (1/8" thick, not shown). The eight lengths of tubing come together at a 3/8" glass outlet. All connections between glass and silicone tubing are made by stretching the silicone tubing directly over glass. Outside the housing, the 3/8" glass outlet is connected via a Swagelok reducing union to 1/4" stainless steel tubing that carries the equilibrated sample to the sample loop.

3.3.4. Operating Procedure

During normal field operation, seawater is supplied at a rate of 4 to 5 L min⁻¹. The residence time of water in the equilibrator is 48 to 60 seconds.

An air canister is pressurized by detaching it from the equilibrator and using a portable air sampling pump to fill it with ambient air to a pressure of about 3 atmospheres. This reservoir can supply the equilibrator for about 5 hours. The air flow rate is 25 mL min^{-1} , equivalent to a residence time of 120 s in the silicone tubing. As in any gas-liquid equilibrator, it is essential that the gas phase can come to equilibrium without significantly changing the methyl halide concentrations in the sample. In equilibrator2, this requirement is met by the physical characteristics of the equilibrator and the relative residence times of the two phases. The volume ratio of water to air is high (80:1), and the residence time of air in the equilibrator housing is twice as long as that of the water. Under these conditions, the air comes to equilibrium with a maximum effect of 0.2% on the liquid phase concentrations, which is an insignificant change in the context of the other measurement uncertainties.

The equilibrator is vented to atmospheric pressure at the outlet end, but a pressure gradient must exist in the silicone tubing in order to drive the flow of gas. The magnitude of this pressure gradient is an important factor in the design of the equilibrator. An equation for the pressure drop in a pipe under conditions of laminar flow [Tietjens, 1934] was used to determine that the pressure difference between the inlet and outlet of the equilibrator is about 60 Pa, which is $\sim 0.06\%$ of atmospheric pressure. This pressure gradient was ignored because it is insignificant in the context of the other measurement uncertainties. The need for a suitably small pressure gradient led to the choice of eight parallel tubing sections rather than one long section.

After the outlet lines have been flushed with equilibrated air, a 207-mL sample loop is attached to the air outlet and filled. After ten minutes, the sample loop is capped by means of the four-port valve. The contents of the loop are then analysed as an air sample. The analytical system is described in section 2.4.

In the design and testing stages of the equilibrator, ultra-high-purity (UHP) nitrogen was used in the tubing as the gas phase instead of ambient air. The equilibrator can be operated well with UHP nitrogen as the gas phase. However, the canister of ambient air was chosen for field measurements, because ambient air has methyl halide concentrations which are closer to equilibrium, so it requires less equilibration time and represents a more realistic medium for comparison with air samples.

Depending on the biological productivity of the water, it is sometimes necessary to clean out the equilibrator every few days, as particles and zooplankton may collect on the bottom near the water outlet. Cleaning is accomplished by detaching the seawater supply and backflushing with distilled water or a 0.1 M aqueous solution of HCl.

3.3.5. Equilibration Time Test

Before construction of equilibrator₂, a test was conducted in the laboratory to determine the residence time required for equilibration of air in the silicone tubing. A 3 m section of Silastic® tubing was immersed in a reservoir of seawater at room temperature (22°C). A supply of UHP nitrogen flowed through a halocarbon trap (molecular sieve) to remove any residual halocarbons, then into the silicone tubing. The nitrogen flow was adjusted to various rates corresponding to nitrogen residence times between 1 and 16 seconds in the tubing. At each flow rate, an 80-mL sample was taken from the outlet and analyzed. It was expected that the peak areas of the halomethanes in each sample would increase with residence time until equilibrium was approached.

Figure 3.3 shows the peak areas of CH₃Cl, CH₃Br, and CH₃I as a function of residence time in the silicone tubing. The peak area data for each compound were fit by least squares to a function of the form:

$$A = A_e - (b)\exp(-ct) \quad (3.2)$$

where A is peak area in millions, A_e is the equilibrium peak area, b and c are constants, and t is the residence time in seconds. The resulting curves are shown in Figure 3.3.

From the fitted curves, the equilibration times t_{99} and t_{9999} were calculated, which are the residence times sufficiently long to allow the peak area of each compound to reach the values of $0.99(A_e)$ and $0.9999(A_e)$ respectively. These values were chosen to indicate the time required for the gas sample to come close enough to equilibrium for practical purposes, since the functional form used theoretically reaches equilibrium only at infinite residence time. The fitted constants A_e , b , and c , along with the correlation coefficients of the curve fits and the required residence times are summarized in Table 3.1.

Table 3.1. Equilibration time test results.

| Compound | A_e (millions) | b (millions) | c (s ⁻¹) | Correlation coefficient | t_{99} (s) | t_{9999} (s) |
|-----------------|---------------------|-------------------|---------------------------|----------------------------|-----------------|-------------------|
| methyl chloride | 11.16 | 10.64 | 0.187 | 0.9873 | 24 | 49 |
| methyl bromide | 1.283 | 1.409 | 0.334 | 0.9301 | 14 | 28 |
| methyl iodide | 0.4046 | 0.4404 | 0.346 | 0.9598 | 14 | 27 |

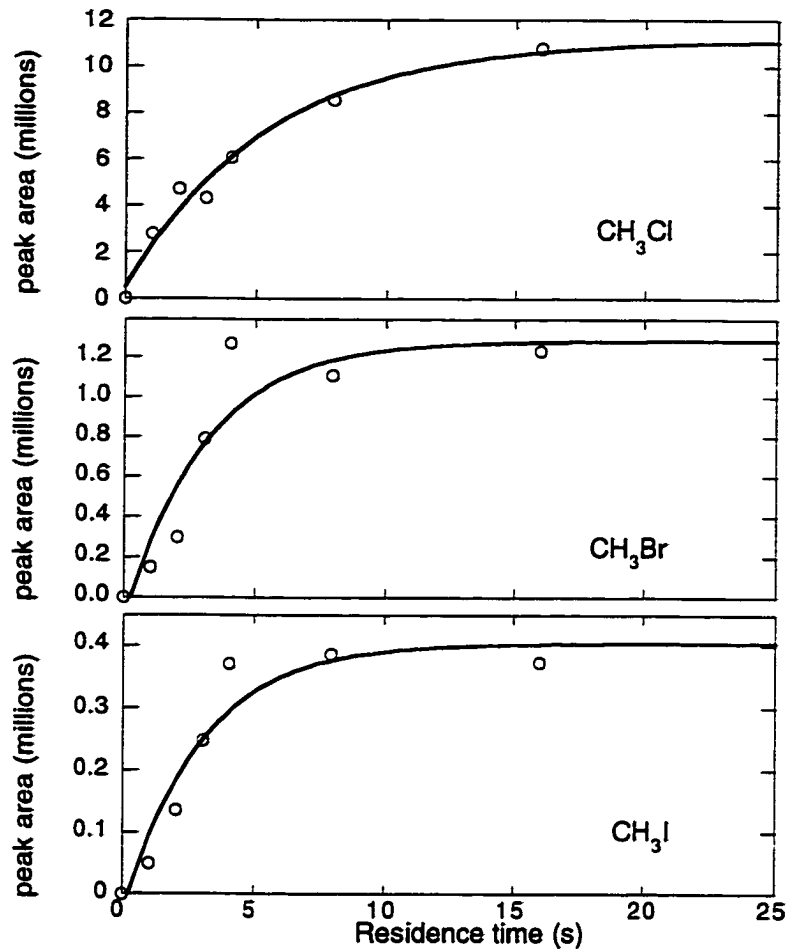


Figure 3.3. Peak areas of CH_3Cl , CH_3Br , and CH_3I in gas samples as a function of residence time in silicone rubber tubing.

The data for methyl chloride are less scattered than for the other two compounds, because of its relatively higher concentration. Methyl chloride peak areas in this experiment are on the order of 10 times larger than those of methyl bromide and 30 times larger than those of methyl iodide. Consequently, instrument noise has a larger effect on methyl bromide and methyl iodide peaks. Methyl bromide and methyl iodide also appear to rise faster than the exponential function in the first five seconds. Since the purpose here is to determine a residence time which will be sufficiently long for all three compounds, this faster equilibration of methyl bromide and methyl iodide is of no consequence, because they will remain at equilibrium while methyl chloride is still equilibrating.

Based on this test, a residence time of 50 seconds is sufficient to allow the equilibration of the three compounds tested. In field use, a residence time of 120 seconds was chosen as a safeguard. In addition, field measurements were made with ambient air

as the initial gas phase. Since ambient air starts with partial pressures of these compounds greater than zero, ambient air would generally require less time to approach equilibrium than UHP nitrogen required.

3.3.6 Comparison with Purge-and-trap

Equilibrator2 was connected to a supply of seawater from a tap in the laboratory. Six 40-mL aliquots of seawater from this tap were analyzed in succession, using the GC/MS and analytical system described in section 2.4, modified by the addition of a purge vessel to accept liquid samples. The purge vessel was then bypassed, and the flowing seawater was sampled five times with the equilibrator. Afterwards, the purge vessel was switched back in-line, and four more liquid phase (purge-and-trap) analyses were performed.

Analysis by purge-and-trap yields the liquid phase concentration in units such as pmol L⁻¹, but equilibrator analyses yield the partial pressure or mole fraction in the gas phase at equilibrium with the water. Since the two methods measure different yet related quantities, a comparison between them is not entirely satisfactory because the solubility must be used to convert from one to the other. The solubility itself is a measured quantity which may be inaccurate, and introduces uncertainty into the comparison, possibly causing apparent differences which may not be the fault of either analytical method.

The results are summarized in Table 3.2. Equilibrator concentrations have been calculated from the measured partial pressures, based on the cited solubility relationships. These solubility functions are given in Chapter 5 of this thesis (Equations 5.6 through 5.10).

Table 3.2. Comparison between purge-and-trap and equilibrator.

| Compound | Purge&Trap* (pmol L ⁻¹) | equilibrator* (pmol L ⁻¹) | % difference (equil-p&t) | solubility relationship used |
|-----------------|--|--|-----------------------------|--------------------------------------|
| Methyl chloride | 38 ± 1 | 39.7 ± 0.9 | 4 ± 5 | <i>Moore</i> [1998] [†] |
| Methyl bromide | 1.32 ± 0.05 | 1.45 ± 0.03 | 9 ± 6 | <i>De Bruyn and Saltzman</i> [1997b] |
| Methyl iodide | 5.15 ± 0.09 | 5.93 ± 0.08 | 13 ± 3 | <i>Moore et al.</i> [1995] |

*Mean over all trials, ±90% confidence intervals.

[†] R. M. Moore, submitted to *Chemosphere*, 1998.

For methyl chloride, solubility measurements made in our laboratory have been used to calculate the equilibrator concentrations [*R. M. Moore*, submitted to *Chemosphere*, 1998]. Using this solubility, the difference of 4% calculated between the equilibrator and purge-and-trap is found to be insignificant at the 90% confidence level. By contrast, if the solubility relationship of *Elliott and Rowland* [1993] had been used, the calculated

equilibrator concentration would have been $45.3 \pm 0.9 \text{ pmol L}^{-1}$, resulting in a significant difference of $16 \pm 4\%$ between the equilibrator and purge-and-trap values. A similar difference has been reported when using the solubility relationship of *Elliott and Rowland* [1993] with field data on methyl chloride [*Moore et al.*, 1996b].

For methyl bromide, the difference of 9% reported above with the solubility of *De Bruyn and Saltzman* [1997b] would have been 24% if the solubility relationship of *Elliott and Rowland* [1993] had been used. This gives an indication of the magnitude of differences between reported solubilities for methyl bromide.

In the case of methyl iodide, although there are actually significant differences of up to 25% between the solubilities reported by *Moore et al.* [1995] and *Elliott and Rowland* [1993] at higher and lower temperatures, it so happens that the two are relatively close to each other around the temperature of this test (15°C). Using the solubility relationship of *Elliott and Rowland* [1993] would result in a difference of 16% between the two methods, instead of the 13% reported above.

3.3.7 Test Under Field Conditions

Both equilibrator2 and equilibrator1 were used to equilibrate surface seawater samples during two voyages at sea. The first was in the northwest Atlantic on *CSS Hudson* in July, 1995 (Figure 2.1), and the second was a transect of the central Pacific Ocean on the *NOAA Ship Discoverer* in October/November, 1995 (Figure 2.2).

On each ship, a pump located in the bow provided a continuous flow of surface seawater to the two equilibrators in parallel. The nominal depth of the intake was 5 metres, depending on sea conditions.

To compare the performance of the two equilibrators, 26 to 29 pairs of analyses were conducted, taking one sample from each equilibrator as the ship was under way. The time between each measurement within a pair was normally about 30 minutes, and not exceeding 60 minutes. Due to natural variability of these compounds in surface ocean water, there is no *a priori* reason to expect the two equilibrators to give equal results in each pair, since the ship travelled approximately 15 kilometres between measurements. However, the objective was to compare the performance of the equilibrators over the longer term, therefore the entire data set was tested for systematic differences.

For each of the n pairs of measurements of each compound, the percent difference of equilibrator2 from equilibrator1 ($\Delta\%$) was calculated:

$$\Delta\% = 100 \frac{(p2 - p1)}{p1} \quad (3.3)$$

where p_1 and p_2 are the peak areas obtained in a sample from equilibrators 1 and 2, respectively. The standard deviation (s), mean, and confidence intervals of $\Delta\%$ are shown in Table 3.3.

Table 3.3. Comparison of equilibrators 1 and 2.

| Compound | n | $\Delta\%$ | |
|-----------------|-----|------------|----------|
| | | s | mean* |
| methyl chloride | 29 | 4.6 | 0.61±1.5 |
| methyl bromide | 29 | 6.7 | 1.4±2.1 |
| methyl iodide | 26 | 28.2 | 7.1±9.5 |

*mean ± 90% confidence interval

At the 90% confidence interval, no significant difference is found between the two equilibrators for methyl chloride, methyl bromide, and methyl iodide. There is a larger range of uncertainty for methyl iodide than for the other compounds because of the greater natural variability of methyl iodide, which resulted in greater differences in methyl iodide peak area within each pair. Since this test was based on peak area alone, and each pair was completed within a short time scale over which the analytical instrument is known from past tests to be very stable, instrument calibration is not a factor in this test.

3.4 Equilibrator 3

Equilibrator 3 was built in 1997 as a second version of equilibrators 1 and 2. The design is essentially the same, but with a greater surface area of membrane and different materials chosen for the housing and support structures. In this design, a strong emphasis was placed on minimizing the use of plastics, to further reduce the possibility of contamination, particularly since equilibrator 3 was also intended for use in the analysis of compounds such as dichloromethane, trichloroethene and tetrachloroethene. In the experience of our group, compounds such as these, which are commonly used as solvents in manufacturing processes, often have significant sources of contamination in various plastics and glues. Equilibrator 3 was used on the July/August 1997 voyage on *R/V Knorr* from Halifax to Trinidad.

3.4.1 Equilibrator Description

The shape of equilibrator 3 (Figure 3.4) is like that of equilibrators 1 and 2. Its housing is a horizontal cylinder made from three sections of heavy-walled glass drain pipe. The diameter of the pipe is 10 cm, and the total length of the housing is 76 cm. The three

sections of pipe are held together by two clamps which are made of steel and rubber on the outside, with a Teflon gasket forming the seal. The inside face of the Teflon gasket, with a width of about 2 mm, is exposed to the seawater at each of the two joints between sections of glass pipe.

The water inlet end contains a stainless steel plug with three holes, one each for the water inlet, air inlet, and air outlet. Air is distributed into twelve sections of silicone tubing, and collected after equilibration, by a pair of manifolds made from 1/4" stainless steel tubes which have been gold-plated on the outside to reduce the corrosion effects of seawater. The silicone tubing sections are the same as those in equilibrator2 (Silastic® tubing, outer diameter 1.96 mm, inner diameter 1.47 mm, length 3.75 m). The silicone tubing is woven in loops around and through a hexagonal rack made from glass rods. Equilibrator3 has 50% more membrane surface area than equilibrator2 (twelve equivalent tubing lengths instead of eight).

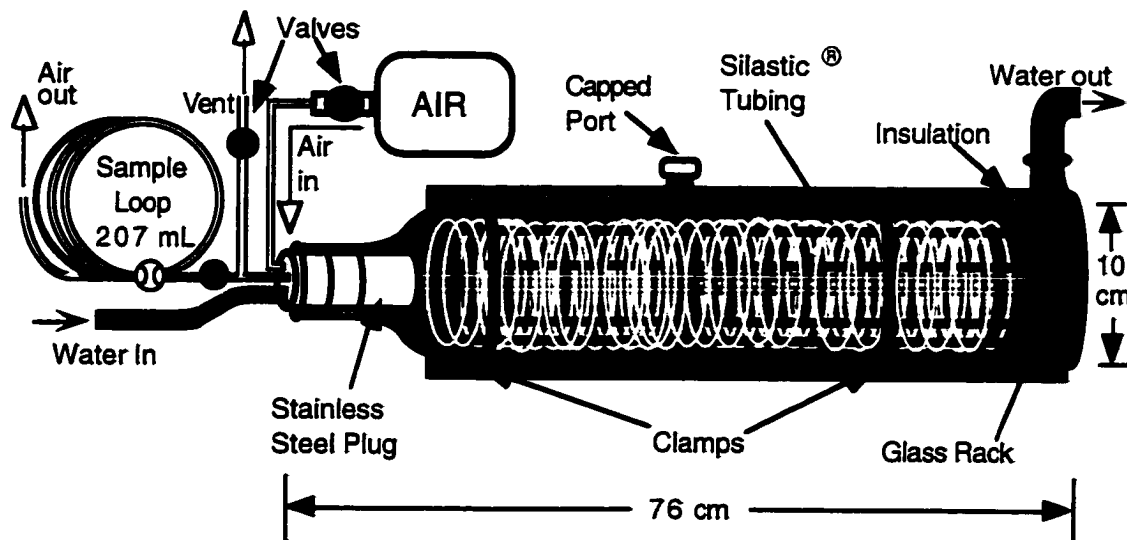


Figure 3.4. Schematic diagram of equilibrator3.

The operating procedure for equilibrator3 was the same as that of equilibrator2. Seawater flowed continuously through the housing at a rate of about 8 litres per minute. The air flow rate through the tubing was 50 mL/min. The air supply and collection systems were the same as for equilibrator2.

3.4.2 Response Time Test

As mentioned previously, the response time is the amount of time required for the equilibrator to respond to a change in methyl halide concentrations in the water. This is related to "sample carryover", which is the idea that the concentration of the previous

sample may affect the current sample. Since the equilibrators used here are flow-through systems, each sample represents an average partial pressure taken over the course of the equilibration, during which time at least 50 litres of seawater will have passed through the equilibrator and the ship itself may have moved about two nautical miles. It is not ordinarily expected that methyl halide concentrations in seawater would vary greatly over the time and space scale involved in equilibrating the sample. Nevertheless it is worthwhile to test the response of an equilibrator to changes in concentration in the water, in order to have some understanding of how well any given sample represents the actual concentration in the water at the time of the sample.

A convenient opportunity was found to test the response time of equilibrator³ to a large change in water phase concentrations. At the end of the Halifax-Trinidad transect of the North Atlantic on the *R/V Knorr*, the water flow was turned off, and coastal surface ocean water was left standing in the equilibrator during a two-day port stop, out of curiosity to see whether methyl halide concentrations would change in the stagnant water. During this time, the equilibrator was in the dark in a closed wooden box in the main lab of the ship. After two days, when the ship left port, the first sample was taken by equilibrating an air sample to the stagnant water in the equilibrator. Partial pressures of all three methyl halides were found to be highly elevated above ambient coastal levels (2.3 times for methyl chloride, 14.4 times for methyl bromide, and 14.5 times for methyl iodide). Immediately after this sample, the flow of "new" ambient seawater from the seawater intake was started, and two more samples were taken in succession, as quickly as the sample processing time allowed. As expected, over a short period of time the measured partial pressures fell as the equilibrator responded to the abrupt decrease in methyl halide concentrations in the water (Figure 3.5). This test was followed by three more samples to establish the average ambient partial pressure in seawater in that area.

The reason for the large increase in methyl halide concentrations in the stagnant water is unknown. This was a very simple experiment without any controls, so contamination from the air in the lab cannot be eliminated as a possibility. However, the equilibrator was effectively closed to exchange with the surrounding air. A more likely explanation is that the methyl halides were produced within the equilibrator during that port stop. A film of apparently biological material was observed on the inside walls of the equilibrator, and a distinct odour associated with rotting organic material could be easily detected by opening the capped port on the body of the equilibrator and sniffing. After the response time test, and before routine analyses were resumed, the equilibrator was cleaned by rinsing with 1 M hydrochloric acid in distilled water. No equipment or biological expertise was available on the ship to identify the organisms in the stagnant seawater. It is

significant to note that the box was opaque and closed, implying that the equilibrator was in darkness for two days during this experiment, so light is not essential to the process which resulted in anomalously high methyl halide concentrations. The high production rates implied by the large change in concentration over two days cannot be considered to represent the production rates in ambient seawater, because the conditions were not at all like those present in the ocean.

The dashed lines in Figure 3.4 show the 90% confidence interval of the mean for the samples taken after the test, to indicate the ambient levels of methyl halides. The partial pressures indicated by the equilibrator were already near these ambient levels by the time of the second sample, 30 minutes after the step change in concentration.

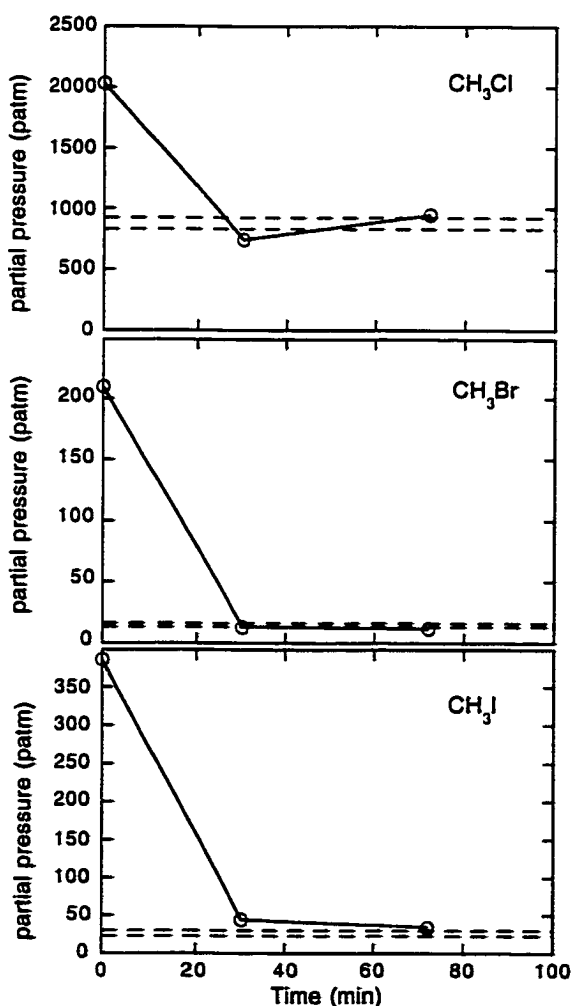


Figure 3.5. Response time test.

The measured partial pressures may have approached ambient values more quickly than is suggested by Figure 3.5, but it is not possible to determine this without another time point before 30 minutes.

This experiment indicates that the equilibrator can respond to extreme changes in concentration with a time lag of no more than 30 minutes, which translates to a distance of about 6 nautical miles as the ship moves.

Abrupt concentration changes of the magnitude used in this experiment are not ordinarily found in ambient seawater, so it is expected that the equilibrator can respond to the changes normally encountered on the time scale of taking the sample (~5 minutes).

It would be preferable to consider the response as a first-order process and calculate the e -folding time τ . However more data points are needed at the beginning, when concentrations are changing rapidly ($t < 20$ minutes), to find a reasonable fit and calculate τ .

3.4.3 Corrosion

The ends of the manifolds carrying the gas stream in equilibrator3 were subject to significant corrosion after 5 weeks of immersion in seawater. This was likely due to dissimilar metals used to solder caps on the ends of the manifolds. The gold plating on the manifolds was apparently not sufficient to prevent this corrosion. The unfortunate result was that after 5 weeks, seawater broke through into the manifolds, requiring that equilibrator3 be shut down during the second leg of the Knorr cruise (Trinidad-Woods Hole, Figure 2.3). Therefore, equilibrator data are not available for this second leg.

3.5. Summary

In the laboratory, some differences were observed between concentrations measured in seawater with a purge-and-trap system and those calculated from partial pressures in equilibrated air samples from the semipermeable membrane equilibrator2. The differences were in the vicinity of 4, 9, and 13% for methyl chloride, methyl bromide, and methyl iodide, respectively. The magnitude of the differences was found to vary significantly with various solubility expressions.

In testing at sea, equilibrator2 gave results which were very similar to those from a more conventional equilibrator. Mean differences between the two equilibrators over extensive field trials were less than 1.5% for methyl chloride and methyl bromide, and on the order of 7% for methyl iodide.

The semipermeable membrane equilibrator was found to have several advantages. It was simple to design and build, particularly since the flow-through design of the liquid phase requires no complicated plumbing or pieces. This made it very easy to clean out and backflush. Equilibrator2 is also relatively compact and does not require a large flow rate of water. Large flow rates of water through a shipboard pumping system are often required anyway to minimize temperature changes in the pipes, and the excess water flow is often split off to a drain. Therefore, the relatively low water requirement of equilibrator2 is only an advantage when the total demand for pumped seawater for all scientific activities is close to the capacity of the sampling pump. Equilibrator3 also worked well, but the use of soldered stainless steel parts in continual contact with seawater is inadvisable. Nonferrous metal alloys would give better performance, and other designs are possible which minimize the use of both plastics and metals by relying more heavily on glass.

A further consideration is that seawater sampling systems on ships can contribute significant contamination of some compounds. Testing by purge-and-trap analyses of

Niskin bottle, bucket, and shipboard supply samples demonstrated that there was no contamination of the monohalomethanes which are the focus of the present thesis. However, on the *Knorr* it was found that concentrations of dichloromethane and tetrachloroethene in the clean seawater supplying the equilibrators were about 10 times their ambient levels (measured by the purge-and-trap from Niskin bottle and bucket samples). That this contamination was not due to equilibrators themselves was proven by pouring bucket samples into the equilibrators to show that equilibration of seawater collected in a bucket yielded much more reasonable levels of these two chlorinated compounds. This experience points to the utility of the idea of an independent sampling probe to avoid shipboard seawater supply systems which may be unsuitable for some compounds.

This work indicates that semipermeable membrane tubing can be successfully used in equilibrators for methyl halides, opening the way to other possible applications, for example in incubation experiments or independent sampling probes. In other parts of this thesis, all equilibrators measurements are considered together as equivalent data points, without any distinction among the three equilibrators.

Chapter 4: DATA

This chapter contains data on methyl halides from all the air samples, equilibrator samples, and depth profiles collected in this study. The data are presented for each cruise separately, and the air sample data from all the cruises are also compiled together. The flux estimates in Chapter 5 are based on the equilibrator and air data shown in Chapter 4.

4.1 Labrador Sea/North Atlantic (1995)

Data from equilibrator and air samples from the Labrador Sea and North Atlantic, analyzed on *CSS Hudson* in July, 1995 are shown in Figure 4.1. For reference, the cruise track is shown in Figure 2.1 (page 25).

The data are displayed as a function of distance along the cruise track rather than as a function of latitude in Figure 4.1 to make it possible to distinguish the various regions through which the ship sailed. In this way, for example, data in region (iii) on the continental shelf off Nova Scotia are visually distinct from data in the open north Atlantic in region (ii), even though some of the samples in these two regions were taken near the same latitude. Data for the other two cruises will be plotted as a function of latitude because the other two cruise tracks cover wider latitude ranges and have simpler shapes.

A wide range of sea surface temperature was recorded on this voyage, from a low of 2°C near Greenland (600 nautical miles along the cruise track), to a high of 25°C in Sargasso Sea water (2500 nautical mile mark). A very sharp temperature gradient from ~10°C to ~24°C within a distance of about 45 nautical miles was observed upon entering the Gulf Stream (dashed line at 2100 nautical miles). The last two clusters of samples, at about 17°C, were taken on the continental shelf off Nova Scotia.

A wide range of biological productivity was also encountered. On the transect of the Labrador Sea (from 500 to 1000 nautical miles), surface chlorophyll-*a* concentrations were from 3 to 4 µg L⁻¹. By contrast, Gulf Stream and Sargasso Sea concentrations of chlorophyll-*a* were around 0.2 µg L⁻¹. M. Webb determined chlorophyll *a* concentrations by fluorometry on acetone extracts [Holm-Hansen *et al.*, 1965].

4.1.1 Data Summary

For the purpose of summarizing the data, the cruise track has been divided into three regions based on the surface water type: (i) the cold region (Labrador Sea/North Atlantic), (ii) the warm region (Gulf Stream/Sargasso Sea), and (iii) the shelf region (on the Nova Scotian continental shelf). There are 47 equilibrator samples in the cold region, 9 in the warm region, and 10 in the shelf region. As can be seen in Figure 4.1, all three

compounds show significant variation in surface water (equilibrator) partial pressure along the cruise track. The methyl chloride data in particular are distinctly different in these three regions.

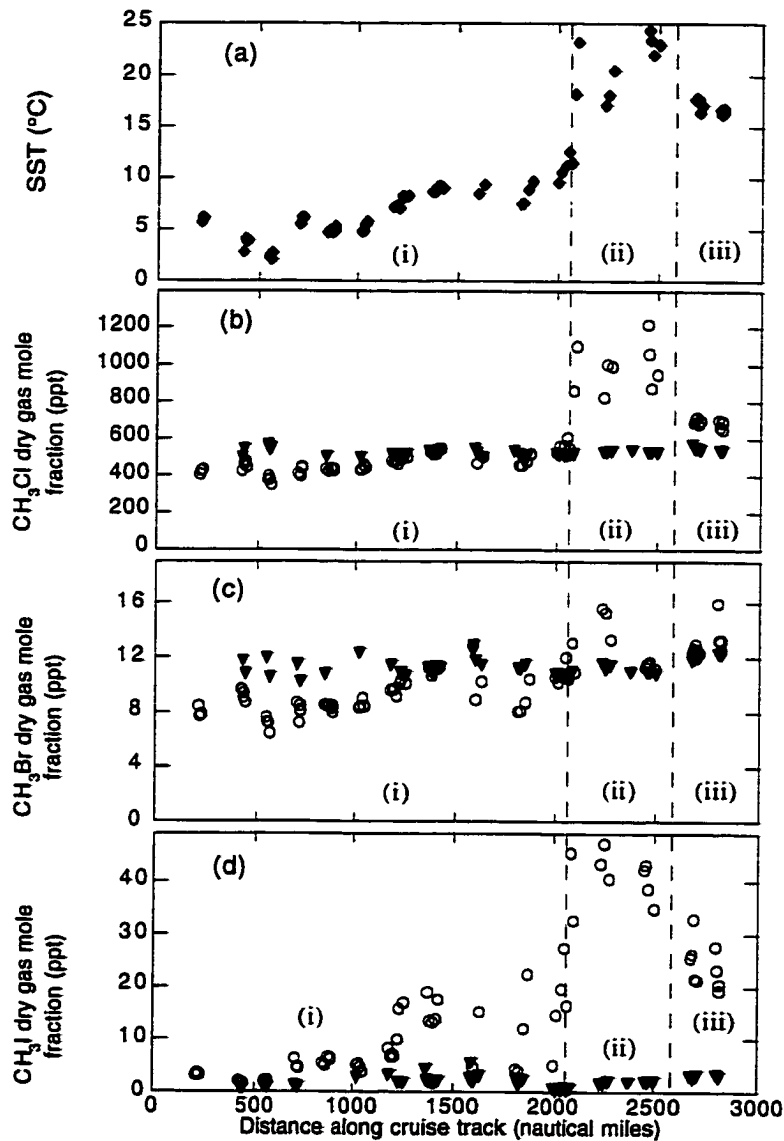


Figure 4.1: North Atlantic/Labrador Sea data (*CSS Hudson*, July 1995). (a) sea surface temperature; (b) methyl chloride; (c) methyl bromide; (d) methyl iodide. Solid triangles are air samples and open circles are equilibrator samples. Regions: (i) Labrador Sea/North Atlantic cold region; (ii) Gulf Stream/Sargasso Sea warm region; (iii) Nova Scotia continental shelf.

The average dry gas mole fractions (ppt) of the three compounds in each region are given as 95% confidence intervals of the mean in Table 4.1. In air measurements, no significant variation was found between different regions, so one mean atmospheric value

is given for each compound for the entire cruise track. The dry gas mole fractions have been calculated from wet equilibrator and air samples by factoring out the water vapour pressure, as described in Section 2.4. The maximum effect of this adjustment was 2.5%.

Table 4.1. Methyl halide average dry gas mole fractions (North Atlantic/Labrador Sea).

| | air | surface equilibrator samples (ppt) | | |
|-----------------|----------------|------------------------------------|------------------|--------------------|
| | (ppt) | (i) cold region | (ii) warm region | (iii) shelf region |
| Methyl chloride | 529 ± 5 | 460 ± 13 | 1011 ± 98 | 702 ± 14 |
| Methyl bromide | 11.4 ± 0.6 | 9.0 ± 0.3 | 13.0 ± 1.4 | 13.4 ± 0.8 |
| Methyl iodide | 1.7 ± 0.2 | 7.0 ± 1.5 | 42 ± 4 | 24 ± 3 |

Methyl chloride and methyl bromide were found to be undersaturated in surface seawater with respect to atmospheric equilibrium in the cold region (region i). Both these compounds were found to be supersaturated to varying degrees in warm Gulf Stream/Sargasso Sea waters (region ii) and on the continental shelf off Nova Scotia (region iii). Methyl bromide was not consistently supersaturated in region (ii). Some samples in that region showed about 7% undersaturation of methyl bromide. Methyl iodide was supersaturated in all samples, though the partial pressure in water varied greatly over the cruise track. For all three compounds, 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.

4.2 Pacific (1995)

Equilibrator and air sample data from the Pacific transect on *NOAA Ship Discoverer* in October/November of 1995 are shown in Figure 4.2. The ship track is shown in Figure 2.2 (page 26), and displayed again in Figure 4.3 below to show the region of supersaturation of methyl bromide (s).

4.2.1 Methyl Chloride

The atmospheric mole fraction of methyl chloride was generally higher in the southern hemisphere than in the northern hemisphere. The Pacific atmospheric data have been averaged separately for the northern hemisphere (NH) and southern hemisphere (SH) using a latitude of 9.5°-12.5°N as the position of the intertropical convergence zone, determined from radon and soot measurements (V. Kapustin, personal communication, 1996). The resulting average dry gas mole fractions are 547 ± 9 ppt (NH) and 565 ± 8 ppt (SH). The ranges given are 95% confidence intervals. In calculating these averages, each measurement has been weighted by the cosine of the latitude to account for the relative

atmospheric mass at that latitude. The logic behind weighting the samples in this way is as follows: If a given sample is considered to represent the latitude at which it was taken, then a sample taken at a lower latitude represents a larger portion of the atmosphere than one taken at a higher latitude. The mass of atmosphere in any narrow band of latitude ($d\phi$) is proportional to the cosine of the latitude (ϕ) at which $d\phi$ is centered. This weighting was used for the other two cruises and the compiled air data set (Section 4.4).

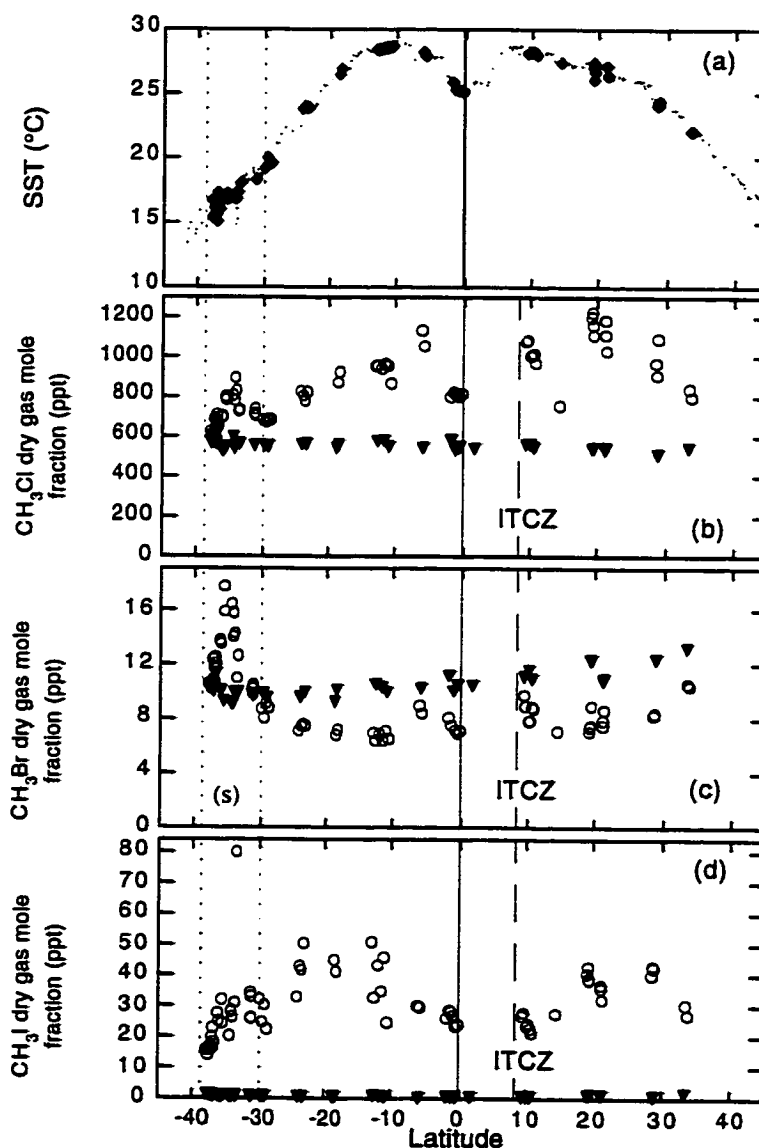


Figure 4.2: Pacific data (*NOAA Ship Discoverer*, October/November 1995). (a) sea surface temperature (solid diamonds at sample points; small dots are hourly data); (b) methyl chloride; (c) methyl bromide; (d) methyl iodide. Solid triangles are air samples and open circles are equilibrator samples. The Intertropical Convergence Zone (ITCZ) is marked by a dashed line, and (s) is the region in which supersaturation of methyl bromide was observed (see text and Figure 4.3).

These hemispheric averages can only be considered to represent conditions in October. Both the values and the interhemispheric ratios could be different in other seasons if there is a significant seasonal cycle.

Based on equilibrator samples, methyl chloride was supersaturated with respect to atmospheric equilibrium along the entire cruise track. Saturation anomalies ranged from +24% to +120%. 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.

4.2.2 Methyl Bromide

Atmospheric mole fractions of methyl bromide decreased as the ship moved south. For the October/November 1995 Pacific data set, latitudinally-weighted atmospheric average dry gas mole fractions for methyl bromide, calculated in the same way as for methyl chloride, were 11.8 ± 0.9 ppt for the northern hemisphere and 10.1 ± 0.5 ppt for the southern hemisphere.

On the basis of equilibrator measurements, methyl bromide in the central Pacific was found to be generally undersaturated, with partial pressures 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 4.3). In general, the finding of widespread undersaturation with some supersaturated areas agrees with the east Pacific study of *Lobert et al.* [1995], except that in the current study supersaturation was found in open ocean samples which are neither coastal nor upwelling zones, and the equatorial upwelling zone did not show supersaturation of methyl bromide. 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 supersaturated area east of New Zealand may be influenced by surface currents which pass near Australia and New Zealand. Such currents are reported, for example, in a general circulation model by *Semtner and Chervin* [1992]. If the observed supersaturation were due to currents which carry a coastal influence far out to sea, this would be consistent with the report by *Lobert et al.* [1995] of supersaturation in the Humboldt Current in the eastern Pacific.

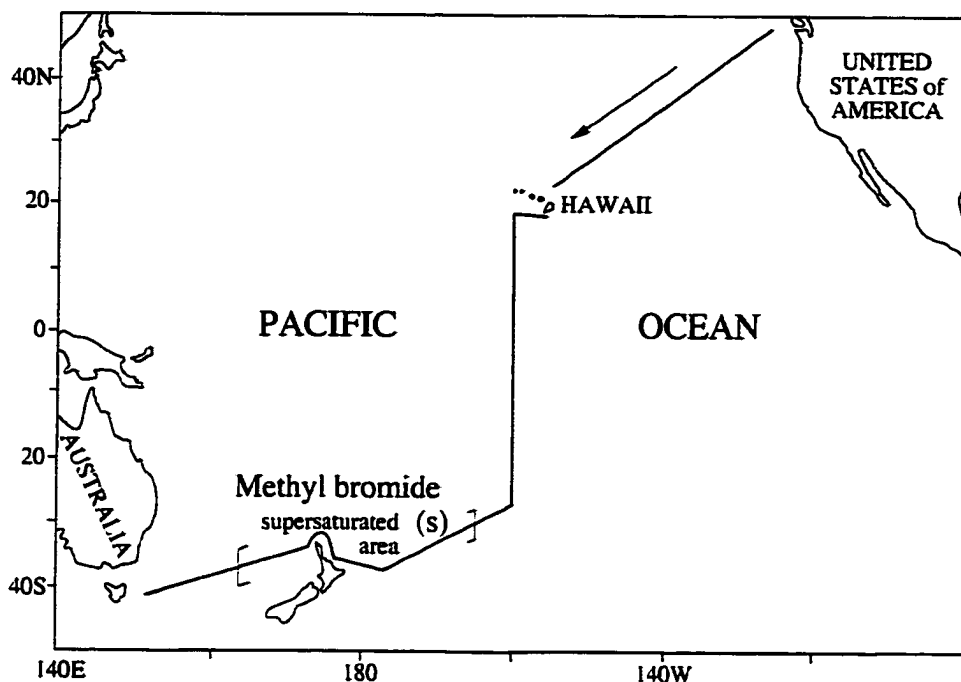


Figure 4.3. Region of methyl bromide supersaturation on the Pacific cruise track. (Region (s) in Figure 4.2c).

4.2.3 Methyl Iodide

The equilibrator analyses of surface water (Figure 3c) show ubiquitous supersaturation of methyl iodide, with mole fractions typically between 12 and 50 ppt. There is one unusually high value of 80 ppt. This sample was taken at 33 degrees south and 167 degrees west, about 500 nautical miles east of New Zealand. There was no indication of any sampling errors or any unusual concentrations of other compounds in this sample. The occurrence of three similarly anomalous data points in the *Knorr* cruise on the Atlantic (Figure 4.4d) adds weight to the idea that unusually high concentrations of methyl iodide may be found over relatively small spatial scales. The mean atmospheric mole fraction of methyl iodide over the entire Pacific cruise was 0.68 ± 0.09 ppt.

4.3 North Atlantic (1997)

Equilibrator and air sample data from the southbound leg (Halifax to Trinidad) of the *Knorr* cruise in July/August of 1997 are shown below (Figure 4.4). This leg is shown as a solid line in Figure 2.3 (page 27). The regions of the cruise are: (i) the Nova Scotia continental shelf (nearly the same location as region (iii) of the *Hudson* cruise (Figure 4.1)); (ii) the Sargasso Sea region, beginning at the Gulf Stream front; and (iii) the South American continental shelf region off Guyana and Venezuela.

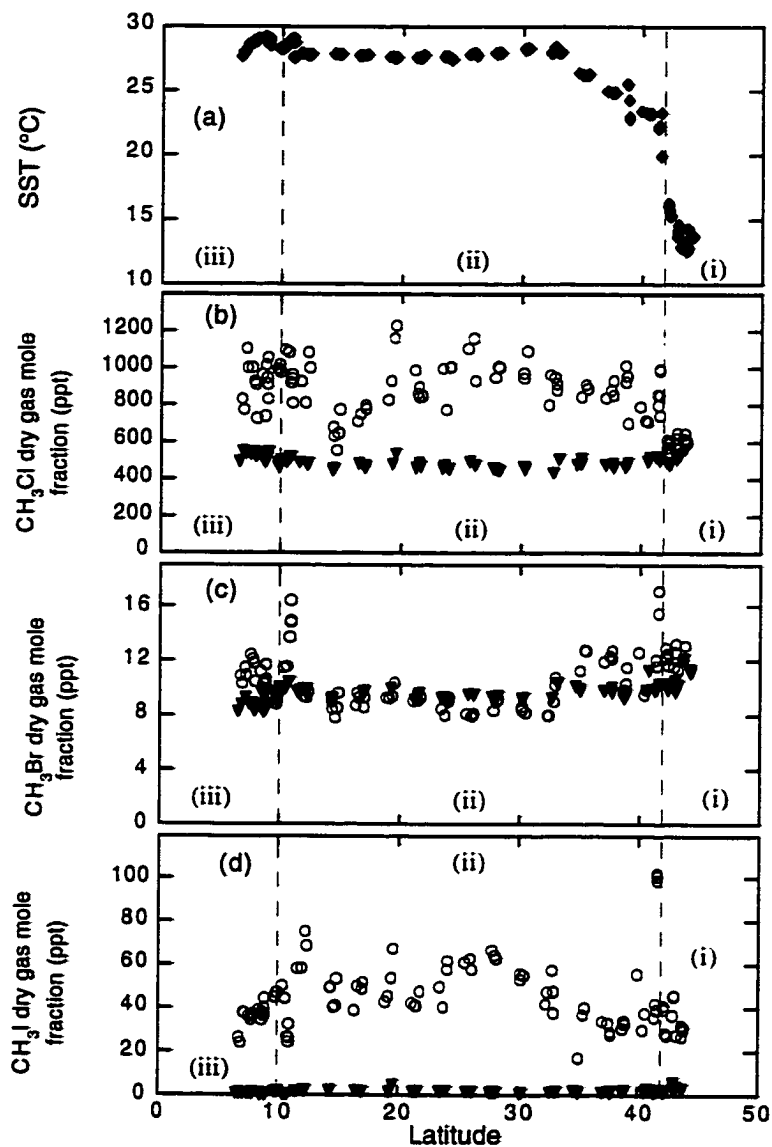


Figure 4.4: Atlantic data (*R/V Knorr*, July/Aug 1997). (a) sea surface temperature; (b) methyl chloride; (c) methyl bromide; (d) methyl iodide. Air samples (solid triangles) and equilibrator samples (open circles). Regions: (i) Nova Scotia continental shelf; (ii) Sargasso Sea; and (iii) Guyana/Venezuela continental shelf.

4.3.1 Methyl Chloride

A total of 87 atmospheric methyl chloride measurements in the northern hemisphere on the *Knorr* cruise yielded a latitudinally weighted average dry gas mole fraction of 496 ± 6 ppt. As the ship moved south of 10°N , the atmospheric mole fractions of at least four of the compounds changed significantly. Methyl chloride increased by $\sim 5\%$, and methyl bromide, methyl iodide, and dichloromethane decreased by 7% , 67% , and 40% ,

respectively. Dichloromethane was routinely measured in air samples, and the shift in dichloromethane is reported here as evidence that the chemical composition of the air samples south of 10°N was distinct from that of the samples taken north of 10°N. Atmospheric dichloromethane is reportedly lower in the southern hemisphere than in the northern hemisphere [Koppmann *et al.*, 1993], and the shifts in the three methyl halides are also consistent in direction with those seen between the northern and southern hemispheres on the *Discoverer* transect of the Pacific. Radon and soot measurements were not available on the *Knorr*, but the observed shifts in concentrations of halogenated trace gases are evidence that the *Knorr* entered the intertropical convergence zone around 10°N. Samples taken south of 10°N are associated with the meteorological southern hemisphere, and are not included in the northern hemisphere average. The average atmospheric methyl chloride mole fraction over the 13 samples taken south of 10°N was 521 ± 16 ppt, but this average cannot be expected to represent the southern hemisphere, because the latitude range is much too limited (6°N to 10°N).

The equilibrator data from the *Knorr* cruise are qualitatively consistent with the 1995 *Hudson* and *Discoverer* cruises. In all the areas where the sea surface temperature was above 12°C (in this case, nearly the entire cruise track) supersaturation of methyl chloride was found. The beginning of the *Knorr* cruise (Region (i) in Figure 4.4) corresponds approximately, both geographically and seasonally, with the end of the *Hudson* cruise of two years before, and the equilibrator data from both these cruises are in relatively good agreement at a mole fraction of 600 to 700 ppt of methyl chloride in that area.

4.3.2 Methyl Bromide

The latitudinally weighted average of all 85 atmospheric measurements of methyl bromide from north of 10°N on the *Knorr* cruise was 10.3 ± 0.2 ppt, and the average of the 13 samples taken south of 10°N was 9.0 ± 0.3 ppt. This latter number gives some indication of the southern hemisphere levels of methyl bromide, but cannot be considered as representative of the southern hemisphere because of the limited latitude range.

Supersaturation and undersaturation of methyl bromide are evident in the equilibrator data (Figure 4.4c). In Region (i), near the beginning of the voyage, methyl bromide was supersaturated, at mole fractions from 12 to 13 ppt, which is consistent with the data collected in the same region two years earlier on the *Hudson* cruise. Two samples with unusually high methyl bromide partial pressures (~16 ppt) were taken in the region of the sharp temperature gradient as the ship was entering the Gulf Stream (boundary between Regions (i) and (ii)). These samples also had exceptionally high methyl iodide levels (Figure 4.4d). As the *Knorr* continued south, at a latitude of about 32°N, methyl bromide

decreased to below atmospheric equilibrium, and remained undersaturated to about 11°N, where supersaturation was found on the South American continental shelf (Region (iii)). Equilibrator samples continued to indicate supersaturation of methyl bromide during the transit through continental shelf waters along the coast of Venezuela to Trinidad.

4.3.3 Methyl Iodide

On the *Knorr* cruise, the latitudinally-weighted average atmospheric dry gas mole fraction of methyl iodide for the northern hemisphere was 1.5 ± 0.2 ppt, based on the 85 samples which were taken north of 10°N. The average of air samples taken south of 10°N was 0.57 ± 0.06 ppt, which is quite consistent with air samples taken in the same latitude band over the Pacific Ocean in 1995.

In equilibrator samples, the methyl iodide mole fraction was nearly always within the range of 20 to 60 ppt, with the exception of three high samples (around 100 ppt) taken just inside the Gulf Stream boundary, between Regions (i) and (ii). Two of these high data points are from samples which also had elevated methyl bromide mole fractions (~16 ppt methyl bromide). The occurrence of relatively uniform methyl iodide mole fractions was also seen in the 1995 Pacific data set with the exception of one high value of ~80 ppt (Figure 4.2d).

4.4 Compiled Air Data

Air sample data from all the voyages are plotted together as a function of latitude (Figure 4.5). From the combined data sets, averages for the northern and southern hemispheres in July/August and October/November have been calculated (Table 4.2). The averages are given as 95% confidence intervals of the mean. However, atmospheric averages are frequently quoted with one standard deviation as the measure of natural variability, so to facilitate comparison with other work, the standard deviation is included in parentheses after each confidence interval.

Table 4.2. Atmospheric average partial pressures of the methyl halides.

| | Southern Hemisphere mean (ppt) | | Northern Hemisphere mean (ppt) | |
|-----------------|--------------------------------|--------------------------|--------------------------------|------------------|
| | October/November | July/August [†] | October/November | July/August |
| Methyl chloride | 565 ±8 (±21)* | 521 ±16 (±27) | 547 ±9 (±9) | 504 ±5 (±30) |
| Methyl bromide | 10.1 ±0.2 (±0.5) | 9.0 ±0.3 (±0.5) | 11.8 ±0.9 (±0.9) | 10.6 ±0.1 (±0.9) |
| Methyl iodide | 0.57 ±0.09 (±0.24) | 0.57 ±0.06 (±0.08) | 1.1 ±0.3 (±0.3) | 1.6 ±0.2 (±0.8) |

*Table entry format: average ±95% confidence interval (±one standard deviation)

[†]Latitude range too limited to be representative of the July/August southern hemisphere.

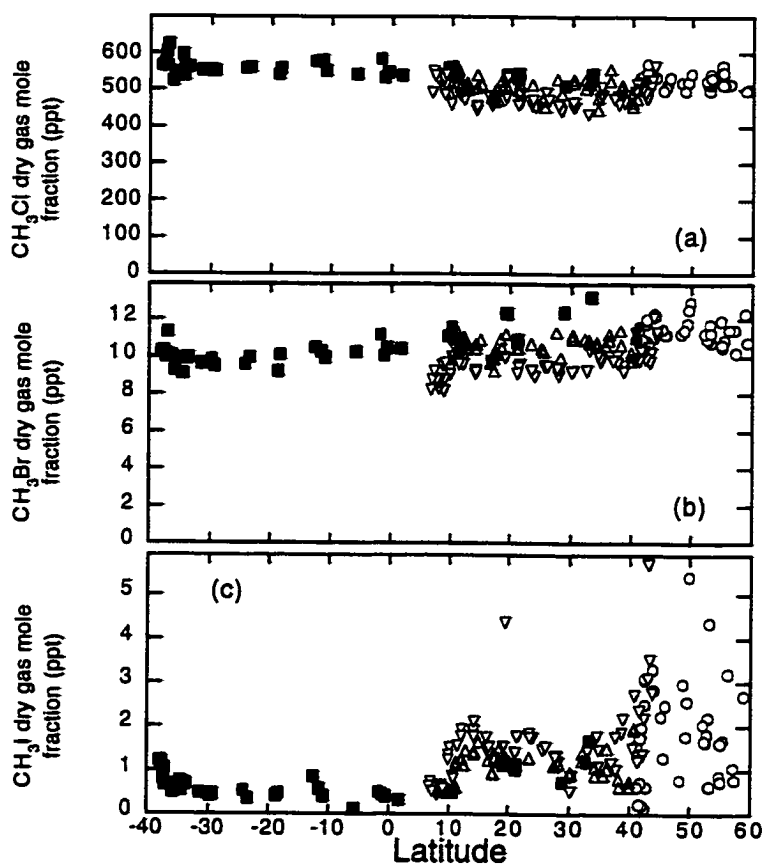


Figure 4.5: Mole fraction of methyl halides (ppt) in air samples from all cruises as a function of latitude. (a) methyl chloride; (b) methyl bromide; (c) methyl iodide. Solid squares are Pacific samples in October/November, 1995. Open symbols are Atlantic samples in July/August of 1995 (open circles) and 1997 (open triangles, point down for the southbound leg and up for the northbound leg).

It is important to note that the range of latitude covered, and consequently the reliability of the estimate, are different for each average. The best coverage is for the northern hemisphere in July/August (10°N to 59°N), followed by the southern hemisphere in October/November (10°N to 40°S). The northern hemisphere October average is calculated from seven samples ranging from 10°N to 35°N . The poorest coverage is for the (atmospheric) southern hemisphere in July/August, with samples ranging from 6°N to 10°N . This last category is only included to demonstrate that the data show the same qualitative interhemispheric trends in July as in October, namely higher methyl chloride, lower methyl bromide, and lower methyl iodide in the southern hemisphere than in the northern hemisphere.

4.4.1 Methyl Chloride

For methyl chloride, the interhemispheric ratio (NH/SH) calculated for October is 0.97 ± 0.03 . It so happens that the ratio calculated from the July data set is also 0.97, even though the July value for the southern hemisphere is based on insufficient data. These ratios apply only to the months for which they were determined (October and July), because they could vary seasonally. The atmospheric averages in the October data set of this study agree well with *Koppmann et al.* [1993], who reported 550 ± 12 and 532 ± 8 ppt for the southern and northern hemispheric partial pressures, respectively, which would yield an interhemispheric ratio of 0.97 ± 0.03 .

4.4.2 Methyl Bromide

For methyl bromide, the interhemispheric ratio for the October data set (northern hemisphere/southern hemisphere) is 1.17. The interhemispheric ratio calculated from the July data set of this study is 1.18, with the caveat that the July data set for the southern hemisphere is extremely limited in its latitudinal coverage. Methyl bromide has been the subject of considerable research attention, and Table 4.3 shows the averages calculated from the October data set of this study in comparison with three other published sets of averages.

Table 4.3. Comparison of Atmospheric Methyl Bromide Measurements

| Study | Northern Hemisphere Mean, ppt | Southern Hemisphere Mean, ppt | Interhemispheric Ratio (NH/SH) |
|-----------------------------|-------------------------------|-------------------------------|--------------------------------|
| This study (October) | $11.8 \pm 0.9^*$ | $10.1 \pm 0.5^*$ | 1.17 ± 0.08 |
| <i>Lobert et al.</i> , 1996 | 11.7 ± 1.2 | 9.4 ± 1.2 | 1.24 |
| <i>Lobert et al.</i> , 1995 | 11.1 ± 0.6 | 8.5 ± 0.6 | 1.31 ± 0.08 |
| <i>Khalil et al.</i> , 1993 | 10.7 | 8.0 | 1.34 |

* \pm one standard deviation.

The average 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]. The interhemispheric ratio found in this study is at the lower end of the other ratios reported in Table 4.3. *Wingenter et al.* [1998] have found a seasonal variation in tropospheric methyl bromide, and they report interhemispheric ratios of 1.10 ± 0.04 in September of 1994 and 1.28 ± 0.05 in December of 1994. The interhemispheric ratio found in the October/November data set of this study is in good agreement with the seasonal trend of *Wingenter et al.* [1998].

4.4.3 Methyl Iodide

The atmospheric data on methyl iodide (Figure 4.5c) have several noteworthy features. Most striking is the high variability at high latitudes in the northern hemisphere. For example, methyl iodide atmospheric mole fractions near 50°N range from <1 to >5 ppt. The scattered appearance and occurrence of relatively high values of atmospheric methyl iodide between 40°N and 60°N may be due to highly localized sources, or could result from variations in the photolytic loss rate. A feature in both the Pacific (1995) and Atlantic (1997) data sets is a steep decrease in methyl iodide partial pressure at latitudes from 12°N to 10°N. There appears to be a minimum in atmospheric methyl iodide between 10°N and 10°S. There may be an increasing trend from 30°S to 40°S, but the data set does not extend far enough to determine whether the high variability at northern high latitudes is mirrored in the southern hemisphere.

The measured atmospheric mole fractions of methyl iodide from the current study are consistent with those previously reported in the literature. *Reifenhäuser and Heumann* [1992] have tabulated data on atmospheric concentrations of methyl iodide from various sources, and show that typical mole fractions are 1-2.5 ppt, with the higher values being recorded in the Antarctic (their own measurements), Tasmania and Hawaii [*Rasmussen et al.*, 1982]. *Yokouchi et al.* [1997] found mole fractions ranging from 0.05-5.0 ppt (average 0.87 ppt) over the western Pacific, and from 0.24-2.0 ppt (average 0.63 ppt) over the southeast Asian seas.

4.5 Depth Profiles

The equilibrator data in this study provide extensive spatial coverage at the surface, but because the samples are all at the same depth (2 to 5 metres), they do not yield information about the variation of methyl halide concentration with depth in the water column. Concentration gradients of the methyl halides within the upper water column (roughly 0 to 100 metres) have the potential to affect air-sea fluxes, because the atmosphere interacts with the upper water column through mixing.

On the Trinidad-Woods Hole leg of the *Knorr* cruise in 1997, seven depth profiles of methyl halide concentrations were collected. The stations are marked on the cruise track (Figure 2.3, page 27). Calm weather and light winds prevailed during the nine days over which these depth profiles were obtained. Stations 1 through 5 were within the Sargasso Sea, with sea surface temperatures above 25°C, and the mixed layer depths were about 41 m, according to the density profiles (Figure 4.7) The profiles also showed a subsurface maximum in oxygen concentration at a depth of about 50 m (Figure 4.6). Chlorophyll profiles are not available for these stations. Station 6 was at the foot of the continental

slope, and station 7 was on the continental shelf east of Cape Cod. Water samples were taken at depths from the surface down to 200 metres. The depth profiles of the methyl halides are shown in Figures 4.8, 4.9 and 4.10.

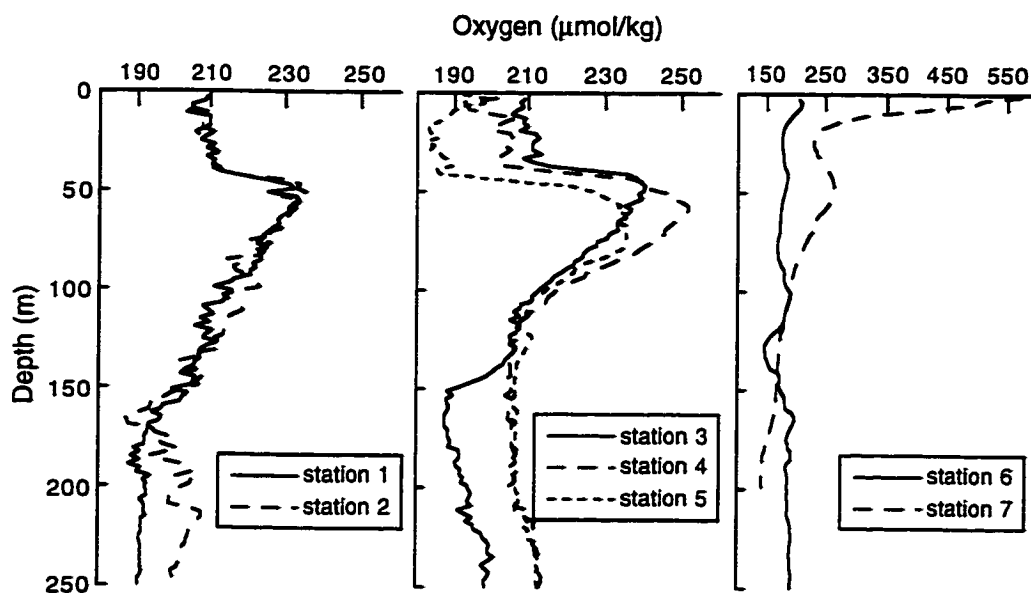


Figure 4.6. Depth profiles of oxygen concentration. (*R/V Knorr*, August 1997). Station numbers are marked on the cruise track (see Figure 2.3).

At stations 1 through 5, the most prominent feature of the methyl halide profiles is a subsurface maximum at a depth of approximately 50 metres. The exact depth and shape of this maximum are difficult to determine because of the limited number of depths sampled on each cast. The density profiles indicate that the observed maxima in methyl halide concentrations are located a few metres below the bottom of the mixed layer, in the pycnocline (Figure 4.6). Methyl chloride has the most pronounced subsurface maximum, with concentrations ~5 times higher at 50 metres than in the mixed layer. The subsurface maxima in methyl halide concentrations are absent or greatly reduced at stations 6 and 7.

The concentration at atmospheric equilibrium is marked with an asterisk (*) for all the methyl halide profiles (Figures 4.8, 4.9, and 4.10). For methyl bromide (Figure 4.9), there are two asterisks to mark the different equilibrium concentrations applicable to Station 6 (1.32 pmol L⁻¹), and Station 7 (1.5 pmol L⁻¹), because the temperatures and hence solubilities are significantly different for these two stations. This difference is not shown in the other figures because it is too small to be apparent on the scale of the axes. Methyl chloride and methyl iodide are supersaturated in the mixed layer, but methyl bromide is undersaturated at all the stations except 5 and 7.

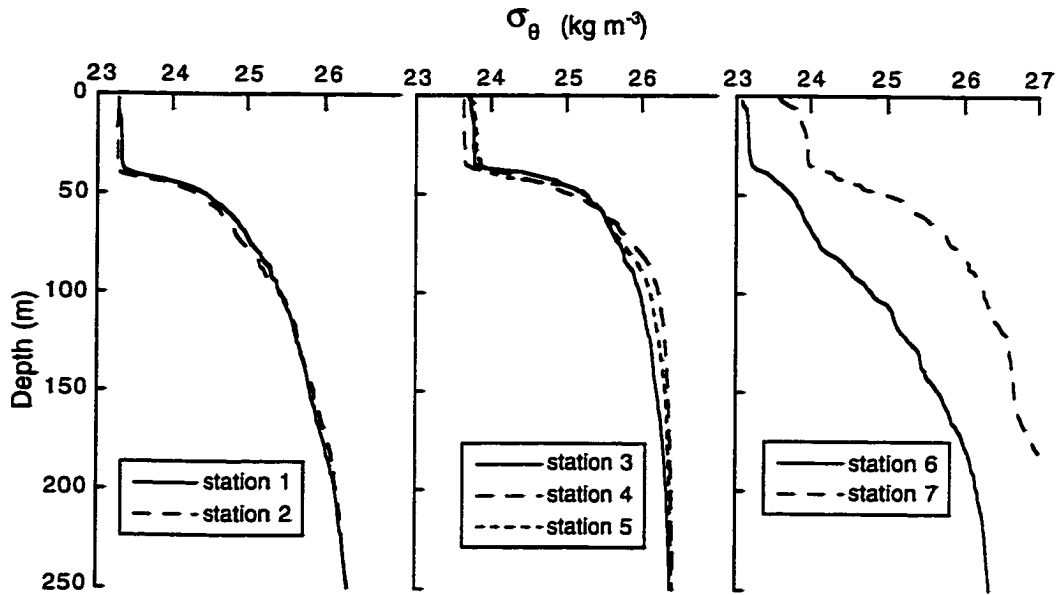


Figure 4.7. Depth profiles of potential density (σ_θ). (*R/V Knorr*, August 1997).

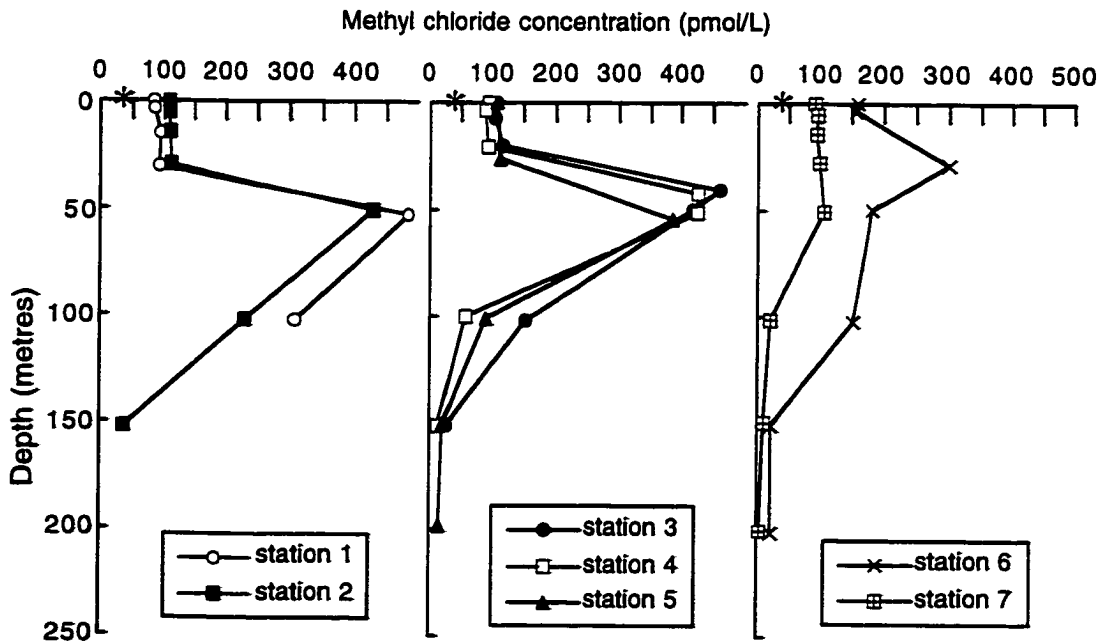


Figure 4.8. Methyl chloride depth profiles. Atmospheric equilibrium is marked by (*).

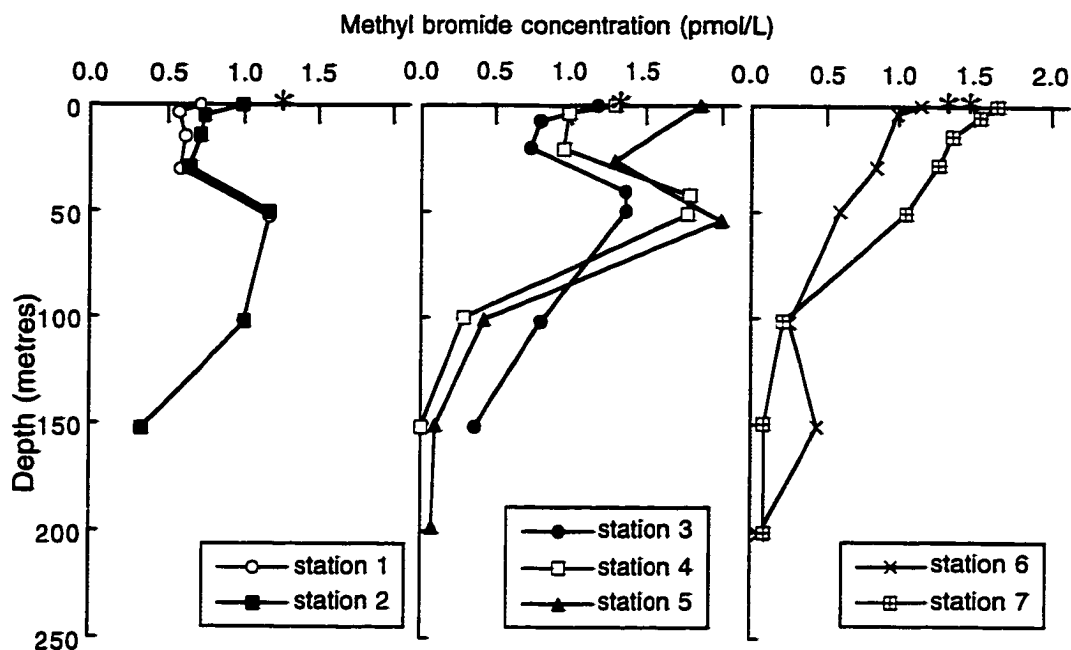


Figure 4.9. Methyl bromide depth profiles. Atmospheric equilibrium is marked by (*).

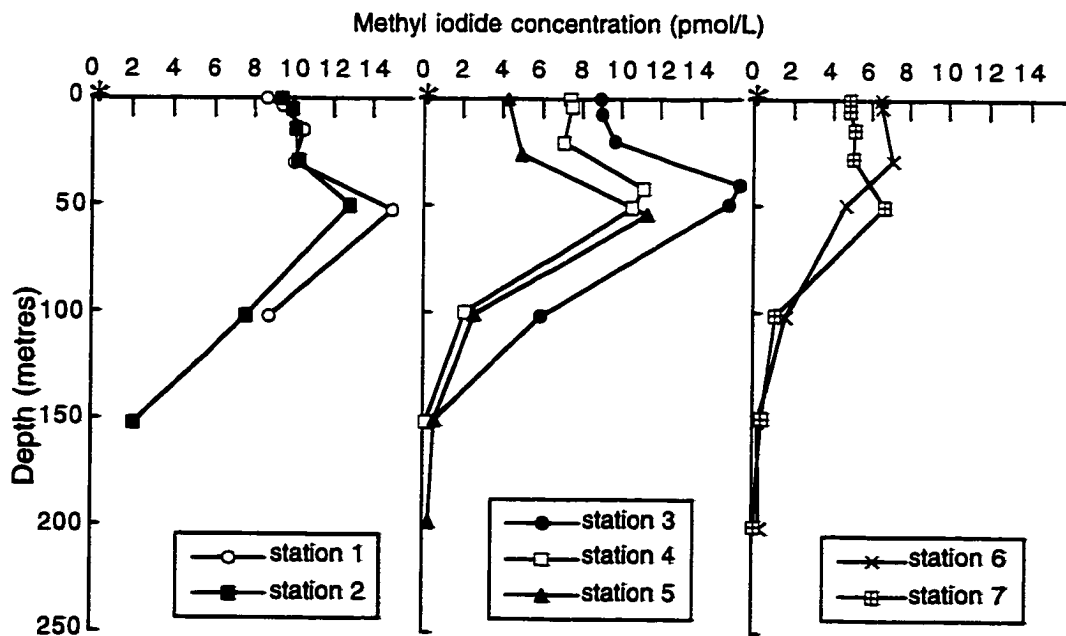


Figure 4.10. Methyl iodide depth profiles. Atmospheric equilibrium is marked by (*).

At each station, the uppermost concentration (at zero metres) was analyzed from a bucket sample collected at the same time as the shallowest Niskin bottle sample (at 3-7 metres). Any consistent and significant difference in methyl halide concentrations between zero and three metres depth could introduce an error in flux estimates made from equilibrator data, because the equilibrator intake is located about four metres below the surface, but atmospheric exchange usually occurs at the surface (in the absence of deep bubble injection). The average difference between the bucket sample (zero metres) and the shallowest Niskin sample (3 to 7 metres) was 0.66 ± 2.7 pmol L⁻¹ for methyl chloride, 0.22 ± 0.09 pmol L⁻¹ for methyl bromide, and -0.25 ± 0.27 pmol L⁻¹ for methyl iodide (90% confidence intervals). It can be concluded that, at the 90% confidence level, there is no significant difference in methyl chloride or methyl iodide concentration between a bucket sample and the shallowest Niskin bottle, but there is a difference for methyl bromide. This difference is visually apparent in Figure 4.9, where it can be seen that methyl bromide concentrations decrease in the depth range from zero to three metres at every station. The distinction between methyl bromide and the other two compounds in this regard can be made clear in another way. Even if the differences cited above were statistically significant for all three compounds, the mean difference represents only about 0.7% of a typical mixed layer concentration for methyl chloride, and about 3% for methyl iodide. However, for methyl bromide this difference is ~22% of a typical mixed layer concentration of 1 pmol L⁻¹.

The difference seen between zero and four metres depth may be due to the fact that the method of sample collection differs between the two depths. The amount of exposure to the atmosphere during sampling may differ between the bucket and the bottle. The bucket samples were pulled up onto the deck with a rope, and the bucket stayed on the deck, open to the ambient air for about one minute while sub-samples were drawn into glass syringes. The Niskin bottles were on the deck for about fifteen minutes with their air valves open while another research group took samples for chlorofluorocarbon analysis. However, if atmospheric exchange in the bucket were a significant factor in causing elevated methyl bromide concentrations, then a decrease of greater magnitude would be expected for methyl iodide, which is highly supersaturated in surface seawater. Therefore, the evidence is not consistent with the idea that bucket samples were significantly affected by atmospheric exchange during the sample time.

If methyl bromide concentrations are elevated in water within a few centimetres of the surface, then the question of the origin of these elevated concentrations becomes a puzzle requiring future investigation. Methyl bromide is generally undersaturated with respect to atmospheric equilibrium in these samples, so it appears plausible that concentrations at

the surface may be driven closer to atmospheric equilibrium, which is consistent with the observed trend. Once again, methyl iodide should be affected at least as much as methyl bromide by any such atmospheric forcing (though in the opposite direction), and the methyl iodide data do not support this scenario.

If the elevated surface concentrations seen in this small number of profiles were generally characteristic of methyl bromide, then flux estimates based on measurements from depths around 5 m could be in error by about 20%. However, this set of profiles does not have enough spatial or temporal coverage to support such a general conclusion. The flux estimate for methyl bromide in Chapter 5 of this thesis does not include any adjustment for elevated surface concentrations of methyl bromide.

Although this set of depth profiles is very limited in scope, several questions about methyl halide production mechanisms and air-sea fluxes are raised by these observations. Is a sub-surface maximum a widespread characteristic of methyl halide concentration, and what is the cause of the maximum? Also, what is the cause of elevated methyl bromide concentrations in surface samples? Finally, what effect could these variations with depth have on air-sea fluxes? Addressing any of these questions in a thorough way would require further research work beyond the scope of this thesis. Speculation on some of these topics is reserved for Chapter 6: Discussion.

Chapter 5: FLUX ESTIMATES

The flux of a gas between ocean and atmosphere is controlled by resistance in both water and gas phases [*Liss and Merlivat, 1986*]. However, the solubilities of the methyl halides are low enough that no significant error results from ignoring the gas phase resistance. The air-sea flux is therefore the product of a liquid phase piston velocity (k), and the concentration anomaly (ΔC), which is defined here as the difference between the concentration in surface seawater and the concentration at atmospheric equilibrium [*Liss and Slater, 1974*].

5.1 Piston Velocity

5.1.1 Wind Speed Dependence

The rate of gas exchange is reportedly influenced by several factors, including wind speed, fetch, surfactants, and bubbles [e.g. *Wanninkhof, 1992*]. However, wind speed is considered to be a major factor, and in the absence of more comprehensive predictive equations, a relationship based solely on wind speed has been used to calculate the piston velocities in this work.

A number of formulae exist for the calculation of piston velocities as a function of wind speed [*Liss and Merlivat, 1986; Wanninkhof, 1992; Erickson, 1993*], and there are substantial differences in the values of k that they yield. *Yvon and Butler [1996]* have discussed the choice of piston velocities and the influence on calculations of the ocean-atmosphere exchange of methyl bromide. The *Wanninkhof [1992]* approach addresses the nonlinearity of the relationship between exchange velocity and wind speed, is normalized to global measurements of $^{14}\text{CO}_2$, and is partially reconciled with global ^{222}Rn data [*Yvon and Butler, 1996*]. In this work, piston velocities have been calculated with the following relationship provided by *Wanninkhof [1992]*:

$$k = 0.39 (u_{av})^2 (Sc/660)^{-0.5} \quad (5.1)$$

where u_{av} is a climatological average wind speed, and Sc is the Schmidt number.

Equation 5.1 yields values of k in units of cm h^{-1} , which were then converted to the units used in the flux calculations in this thesis (m d^{-1}).

5.1.2 Schmidt Number

The Schmidt number is the ratio of the kinematic viscosity of seawater to the molecular diffusivity of the gas in seawater. The kinematic viscosity is the dynamic viscosity divided by the density. Direct measurements of the diffusivity of methyl bromide have been published, which form the basis of a formula for calculating Schmidt

numbers as a function of water temperature [De Bruyn and Saltzman, 1997a]. Most of the measurements of De Bruyn and Saltzman [1997a] were made in distilled water, and they reported no measurements in real seawater, but two experiments in 3.5% NaCl solution yielded the same diffusivity as in fresh water. This result is surprising because, due to the higher viscosity of salt water, the diffusivity of a gas might be expected to be lower in seawater than in pure water, as reported for helium and hydrogen by Jähne *et al.* [1987].

The diffusivities of methyl chloride and methyl iodide in seawater appear not to have been measured. For methyl chloride, Tait [1995] has estimated diffusion coefficients in pure water by the empirical correlation method of Wilke and Chang [1955]:

$$D = (7.4)(10^{-8})(qM_w)^{0.5}T_K / \eta_w V_b^{0.6} \quad (5.2)$$

Where D is the diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$), q is the association factor of water ($= 2.26$) [Hayduk and Laudie, 1974], M_w is the molecular weight of water (g), T_K is the absolute temperature (K), η_w is the dynamic viscosity of pure water, and V_b is the molar volume of methyl chloride at its normal boiling temperature ($50.6 \text{ cm}^3 \text{ mol}^{-1}$) [Reid *et al.*, 1987]. Tait [1995] used equation 5.2, and the kinematic viscosity of seawater from Wanninkhof [1992], to calculate Schmidt numbers for methyl chloride at 5°C intervals from 0 to 30°C . A third-order polynomial fit to the resulting values yielded the following formula for the Schmidt number of methyl chloride as a function of temperature ($^\circ\text{C}$) [Tait, 1995]:

$$Sc(\text{CH}_3\text{Cl}) = 2869.6 - 187.99 T + 5.8573 T^2 - 0.07292 T^3 \quad (5.3)$$

De Bruyn and Saltzman [1997a] found the experimentally determined diffusivity of methyl bromide to be $\sim 12\%$ higher than that estimated by the relationship of Wilke and Chang [1995]. Furthermore, the formula given by Tait [1995] (Equation 5.3), yields Schmidt numbers for methyl chloride which are higher (implying diffusion coefficients which are lower) than those reported for methyl bromide by De Bruyn and Saltzman [1997a]. Methyl chloride has both a smaller molecular weight and a smaller molar volume at the normal boiling point (V_b) than methyl bromide [Reid *et al.*, 1987]. Any of the empirical correlation methods [Wilke and Chang, 1955; Hayduk and Laudie, 1974] would predict that the diffusion coefficient should be higher for methyl chloride than for methyl bromide, not lower. To avoid this inconsistency, in the current work the Schmidt number for methyl chloride will be estimated from that of methyl bromide [De Bruyn and Saltzman, 1997a], because the formula for methyl bromide is based on experimentally determined diffusion coefficients. To estimate the Schmidt number for methyl chloride from that of methyl bromide, the ratio of the diffusion coefficients of the two compounds is assumed to equal the inverse ratio of their molar volumes at the normal boiling point (V_b) to the power 0.6, in accordance with the Wilke-Chang relationship.

$$D(\text{CH}_3\text{Cl}) / D(\text{CH}_3\text{Br}) = (V_b(\text{CH}_3\text{Br}) / V_b(\text{CH}_3\text{Cl}))^{0.6} \quad (5.4)$$

Therefore, since the Schmidt number is inversely proportional to D , the Schmidt number for methyl chloride is estimated as follows:

$$\text{Sc}(\text{CH}_3\text{Cl}) = \text{Sc}(\text{CH}_3\text{Br})(V_b(\text{CH}_3\text{Cl}) / V_b(\text{CH}_3\text{Br}))^{0.6} \quad (5.5)$$

Similarly, the methyl iodide Schmidt number is estimated from that of methyl bromide:

$$\text{Sc}(\text{CH}_3\text{I}) = \text{Sc}(\text{CH}_3\text{Br})(V_b(\text{CH}_3\text{I}) / V_b(\text{CH}_3\text{Br}))^{0.6} \quad (5.6)$$

The estimation of molar volumes (V_b) is outlined by *Reid et al.* [1987]. For methyl chloride, $V_b = 50.6 \text{ cm}^3 \text{ mol}^{-1}$. For methyl bromide and methyl iodide, V_b was estimated to be 52.9 and 62.9 $\text{cm}^3 \text{ mol}^{-1}$, respectively, by the additive method of *LeBas* [1915] as cited by *Reid et al.* [1987]. The equations used to calculate Schmidt numbers are shown below, and the resulting values are in Figure 5.1.

$$\text{Sc}(\text{CH}_3\text{Cl}) = (50.6 / 52.9)^{0.6} (\text{Sc}(\text{CH}_3\text{Br})) \quad (5.7)$$

$$\text{Sc}(\text{CH}_3\text{Br}) = 2004 - 93.5 T + 1.39 T^2 \quad \text{De Bruyn and Saltzman [1997b]} \quad (5.8)$$

$$\text{Sc}(\text{CH}_3\text{I}) = (62.9 / 52.9)^{0.6} (\text{Sc}(\text{CH}_3\text{Br})) \quad (5.9)$$

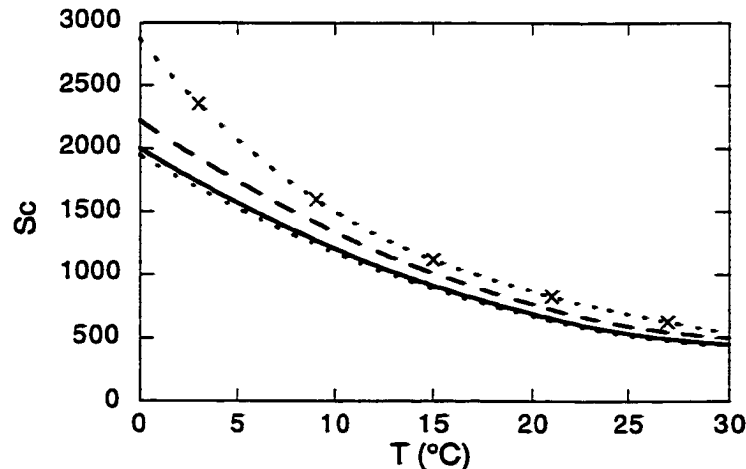


Figure 5.1. Schmidt number (Sc) as a function of temperature. Methyl chloride (dotted line) and methyl iodide (dashed line) are estimated from methyl bromide (solid line). The dotted line with (x) symbols is the Schmidt number of methyl chloride estimated by *Tait* [1995].

The values calculated by *Tait* [1995] for methyl chloride are also shown in Figure 5.1 for comparison. The method used in the current work (Equation 5.7 above) yields Schmidt numbers 32% lower at 0°C and 18% lower at 30°C, than that of *Tait* [1995].

5.2 Concentration Anomaly

The concentration anomaly ΔC was calculated by the following formula:

$$\Delta C = H'(\chi_w - \chi_a)(P - p_{H_2O}) \quad (5.10)$$

Where χ_w and χ_a are the dry gas mole fractions (ppt) from an equilibrator sample and the corresponding air sample, respectively, P is the barometric pressure (atm) and p_{H_2O} is the vapour pressure of water (atm) at the temperature of the sea surface where the equilibrator sample was taken. H' is the solubility of the gas in seawater, expressed as $\text{pmol L}^{-1} \text{ atm}^{-1}$. In this calculation, it is assumed that the air right at the sea surface is at 100% relative humidity and that the ideal gas law holds.

5.2.1 Solubilities

Solubilities were calculated for methyl chloride according to *Moore* (Submitted to *Chemosphere*, 1998), for methyl bromide according to *De Bruyn and Saltzman* [1997b], and for methyl iodide according to *Moore et al.* [1995]. The units in which the solubilities are reported differ from one report to another. The solubility relationship used in this thesis for methyl chloride is:

Methyl chloride:
$$H = \exp(8.8275 - 2865.68/T_K) \quad (5.11)$$

[*Moore*, submitted to *Chemosphere*, 1998]

Where H is the dimensionless solubility, expressed as the concentration in the gas phase (pmol L^{-1}) over the concentration in the liquid phase (pmol L^{-1}), at equilibrium at the absolute temperature of the water, T_K (degrees Kelvin). H as given by Equation 5.11 was converted to H' ($\text{pmol L}^{-1} \text{ atm}^{-1}$) for use in equation 5.10 by applying the ideal gas law. The assumption of ideality is an approximation with an error normally less than one percent at pressures around one atmosphere, but the exact magnitude of the error cannot be calculated without the cross-virial coefficients of the methyl halides in air. The equation for H' under the ideal assumption is:

$$H' = 12.188 / (T_K H) = 12.188 / T_K \exp(8.8257 - 2866/T_K) \quad (5.12)$$

The solubility for methyl bromide ($\text{pmol L}^{-1} \text{ atm}^{-1}$) used in this thesis is the following function of temperature and salinity [*De Bruyn and Saltzman*, 1997b]:

Methyl bromide:
$$H' = \exp[-171.2 + 254.3(100/T_K) + 77.04 \ln(T_K/100) + S\{0.2591 - 0.1828(T_K/100) + 0.03142(T_K/100)^2\}] \quad (5.13)$$

Where S is the salinity in parts per thousand (‰). The salinity dependence is not strong in the context of salinity variations normally seen in open-ocean waters. For example, over the range of salinities encountered on the *Discoverer* transect of the Pacific (~34 to 37‰), at a common temperature of 25°C, the value of H' calculated by Equation 5.13 ranges from 0.139 to 0.136 pmol L⁻¹ atm⁻¹, a range of about 2%. The solubility expressions for the other two compounds in seawater do not include a salinity dependence, but they were reported to be appropriate for ordinary open-ocean seawater with $S \approx 35$, which applies to the present work. Therefore, the effect of small variations in salinity has not been accounted for, but this approximation has no substantial effect on the conclusions of the present work.

The solubility function for methyl iodide in seawater used in the present study is based on that given by *Moore et al.* [1995]:

$$\text{Methyl iodide:} \quad H = \exp(13.32 - 4338/T_K) \quad (5.14)$$

$$H' = 12.188 / (T_K H) = 12.188 / T_K \exp(13.32 - 2866/T_K) \quad (5.15)$$

Where H is the dimensionless solubility defined as in 5.11 above, and H' is the solubility in pmol L⁻¹ patm⁻¹, calculated in analogous fashion as for methyl chloride.

5.2.2 Calculated Concentration Anomalies

Concentration anomalies were calculated for all three cruises (data from Figures 4.1, 4.2 and 4.4). The calculated concentration anomalies are shown together as a function of latitude (Figure 5.2). Positive concentration anomaly indicates supersaturation of surface water.

Several features of the concentration anomaly data are apparent from Figure 5.2. For all three compounds, the concentration anomaly is lowest at high latitudes in the northern hemisphere. For methyl iodide, with the exception of the low values at northern high latitudes and three very high values, the rest of the concentration anomalies are fairly uniform at about 5 pmol/L. In the methyl bromide data there are peaks above +1.0 pmol/L at about 40°N, 10°N, and 35°S. The peak at 40°N includes samples collected on the continental shelf and slope off Nova Scotia, and in the Gulf Stream, both in 1995 and 1997. The supersaturated samples around 10°N were taken in coastal waters off Guyana and Venezuela. The peak around 35°S is from Pacific samples, some of which were taken in coastal waters off New Zealand. However, the highest values in that region of supersaturation were taken approximately 1000 nautical miles away from New Zealand, in open ocean water, thus demonstrating that supersaturation of methyl bromide is not restricted to coastal waters.

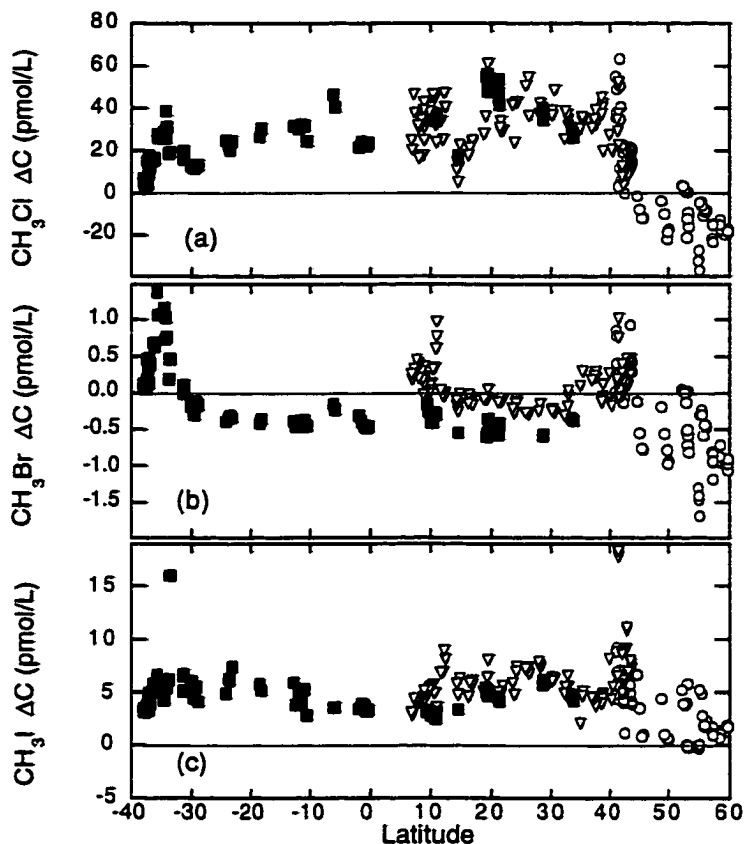


Figure 5.2. Concentration anomalies as a function of latitude. (a) methyl chloride; (b) methyl bromide; (c) methyl iodide. Pacific, October 1995 (squares); Atlantic, July 1995 (circles) and July/August 1997 (triangles).

5.3 Fluxes

The concentration anomalies shown in Figure 5.2 were used to calculate the air-sea fluxes shown in Figure 5.3. Fluxes from the ocean to the atmosphere are represented as positive numbers. Piston velocities were calculated as described in section 5.1, with monthly averaged climatological wind speeds for the appropriate months and locations obtained from the COADS data set [Woodruff *et al.*, 1987].

The regions of positive and negative flux in Figure 5.3 are the same as the regions of supersaturation and undersaturation, respectively, seen in the concentration anomaly data of Figure 5.2. The high latitude waters sampled in the northern hemisphere represent a sink of methyl chloride and methyl bromide from the atmosphere. The ocean is a source of methyl chloride to the atmosphere in all samples between 40°S and 40°N, and a source of methyl iodide in all regions. The source and sink regions of methyl bromide appear to be more complex and difficult to interpret. Most of the Pacific Ocean area that was

sampled in October, from about 35°N to 30°S represents a sink of methyl bromide from the atmosphere (solid squares in Figure 5.3b). The Sargasso Sea in July, from about 15°N to 35°N, also represents a sink of methyl bromide from the atmosphere (open triangles in Figure 5.3b). Of the three source regions (areas of positive methyl bromide flux) in Figure 5.3b, one is in coastal waters off South America at latitudes around 10°N. The other two source regions, around 35°S and 40°N, are at least partly in waters that are not coastal. In order to make a global flux estimate, and also to move toward understanding the processes which affect methyl bromide concentrations in seawater, it would be useful to determine what characteristics are common to these supersaturated regions. In both of the supersaturated regions found at higher latitudes (35°S and 40°N), the sea surface temperature (SST) is around 17°C. This observation, along with several other apparent temperature correlations in the data, led to an investigation of possible relationships between methyl halides and SST which will be discussed in greater detail in section 5.4.1.

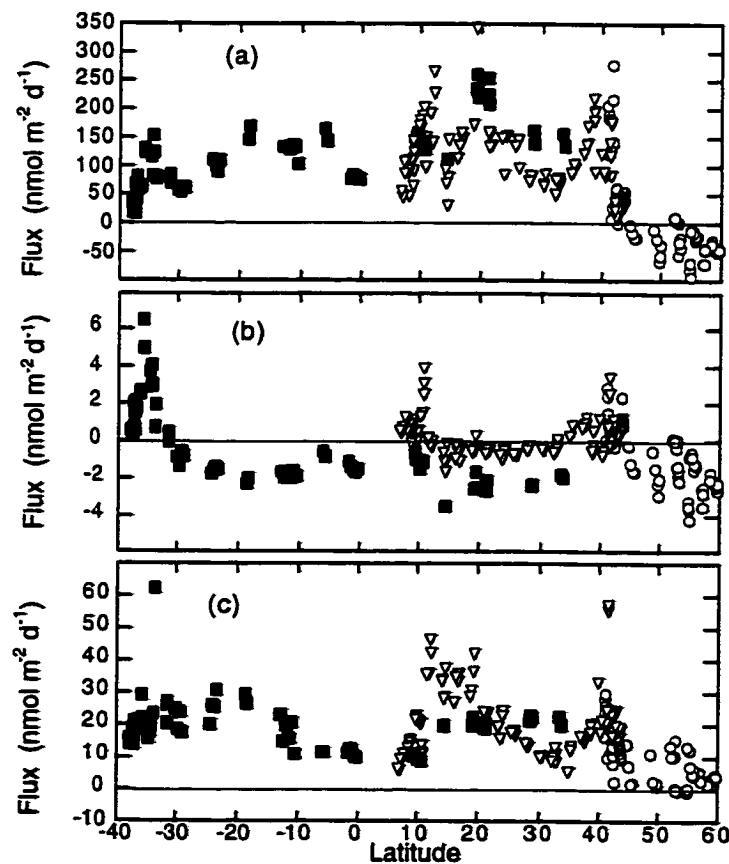


Figure 5.3. Air-sea flux as a function of latitude. (a) methyl chloride; (b) methyl bromide; (c) methyl iodide. Pacific, October 1995 (squares); Atlantic, July 1995 (circles) and July/August 1997 (triangles).

5.4 Global Flux Estimates

A truly comprehensive estimate of the air-sea flux of a gas would be based on data collected from all oceanic regions in all seasons, to take seasonal and spatial variation into account. However, due to practical constraints, it is not feasible to collect such a large data set. The usual procedure for making a global flux estimate under these constraints has been to calculate the flux at each point in a limited data set, such as in Figure 5.3, then partition the ocean into large regions, assume that the average flux per unit area in each region is equal to the average of all flux data points within that region, and multiply the average fluxes by the corresponding surface areas. For example, *Lobert et al.*, 1995, estimated the annual air-sea flux of methyl bromide by partitioning the ocean into three regions called "open ocean", "coastal", and "upwelling", which were assumed to account for 80%, 10%, and 10% of the total ocean surface area, respectively. This method is practical, and is likely to provide an acceptable estimate in the absence of other information, but it contains several unquantified uncertainties within its assumptions.

First, in the usual extrapolation method an assumption is made that the average flux for the entire region over the whole year is equal to the average flux of the data points within that region. There is the potential for significant unquantified errors in this assumption, because the data points typically represent only a small fraction of the places and seasons within that region. The procedure used in this study is unfortunately subject to a similar limitation.

A second problem, which will be corrected in this work, is due to the fact that the calculated flux is dependent on two factors, namely the piston velocity and the concentration anomaly. The piston velocity is considered to depend on the wind speed in a non-linear fashion, whether the formula of *Wanninkhof* [1992] or *Liss and Merlivat* [1986] is used. Because of this non-linear function, and because climatological wind speed and SST data exist for the global ocean, it is mathematically more correct to extrapolate based on average concentration anomaly than on average flux. Given the existing climatological data, it is possible (and preferable) to calculate the piston velocity for every grid point on a global ocean map, and then multiply this calculated piston velocity by an estimated concentration anomaly to obtain a flux estimate for each grid point. With this procedure one can take into account spatial and temporal variations in wind speed independently of variations in concentration anomaly, as was done by *Yvon and Butler* [1996] in their estimate of oceanic lifetime of atmospheric methyl bromide.

The method of extrapolation based on concentration anomaly depends on assigning a concentration anomaly value to each grid point. In this work, empirical relationships between concentration anomaly and SST will be used to predict concentration anomalies.

5.4.1 Relationship between Concentration Anomaly and SST

Figure 5.4 contains the concentration anomaly data from Figure 5.2 replotted as a function of SST. It is apparent that there exists an empirical relationship between concentration anomaly and SST. This observation was unexpected, because the production and loss rates of methyl halides in seawater could depend on many factors such as biological productivity, species composition, atmospheric exchange rate, light intensity, and the concentration of precursor compounds. Also, the concentration anomaly measured for a particular water parcel at a given time must depend on the wind speed history over the previous few days. The depth of the mixed layer should also influence the concentration anomaly, and further discussion of this relationship is included in Section 6.4. Given the number of factors which may affect the concentration anomaly, it is surprising that a relationship with temperature is observed. For the purpose of making flux estimates in this chapter, the observed relationships are accepted for their practical utility because they make it possible to use SST as a proxy for the concentration anomaly.

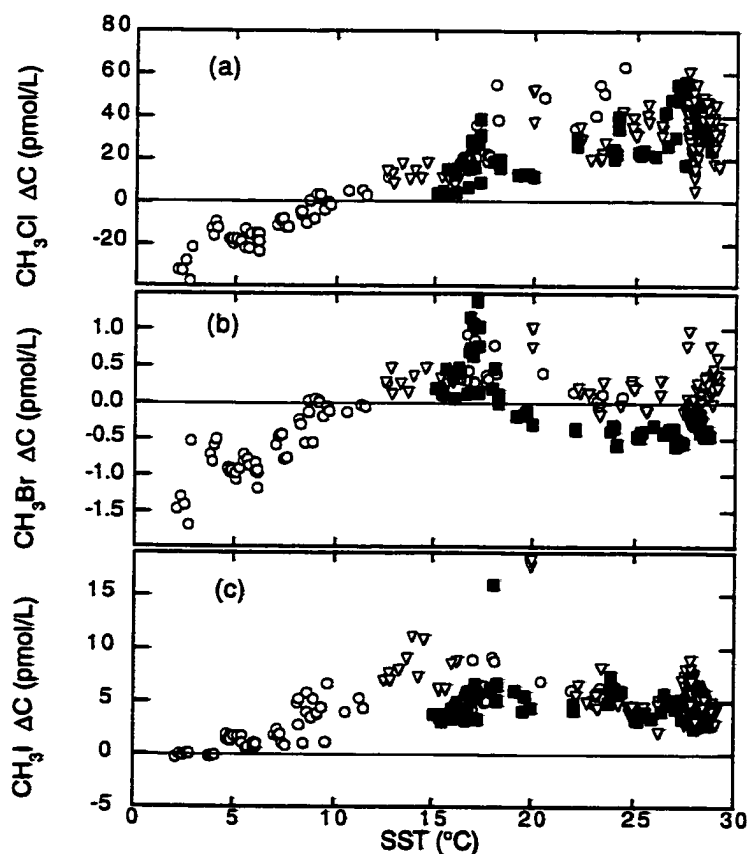


Figure 5.4. Methyl halide concentration anomaly ΔC as a function of sea surface temperature (SST). (a) methyl chloride; (b) methyl bromide; (c) methyl iodide. Pacific, October 1995 (squares); Atlantic, July 1995 (circles) and July/August 1997 (triangles).

For all three compounds, the concentration anomaly clearly increases with temperature below 15°C. Above 18°C, there is more scatter, but still the increasing trend can be seen for methyl chloride, while methyl bromide decreases and methyl iodide has no strong trend. All the data below 15°C were collected in the North Atlantic and Labrador Sea, and these show the clearest relationship between concentration anomaly and SST. Data from other cold areas such as the North Pacific and the Southern Ocean are needed to verify whether this relationship is generally valid. For methyl bromide this can be verified with data collected in the Southern Ocean by *Lobert et al.* [1997], and the agreement is found to be reasonably good, as will be seen in Section 6.2.2.

With the data shown in Figure 5.4, it is possible to predict the concentration anomaly to within a defined range of uncertainty, given the SST value. In order to make this prediction, empirical polynomial functions have been fit to the concentration anomaly data by least squares (Figure 5.5). The width of one standard deviation (the root mean square error) is shown by the dashed lines. The coastal data points have been plotted as distinct symbols (solid diamonds) in Figure 5.5, in order to show whether or not the coastal concentration anomalies differ from the open ocean values. Inspection of Figure 5.5 reveals that for methyl chloride and methyl iodide, the majority of the coastal data points lie within one standard deviation of the best fit curve, while for methyl bromide most of the coastal data are above the curve by more than one standard deviation. Based on this observation, the coastal data are included in the calculation of best fit curves for methyl chloride and methyl iodide, but not for methyl bromide.

The general form of the function used fit to the data is a fourth-order polynomial:

$$\Delta C = a + bT + cT^2 + dT^3 + eT^4 \quad (5.15)$$

where ΔC is the concentration anomaly (pmol L^{-1}), T is the sea surface temperature ($^{\circ}\text{C}$), and $a, b, c, d,$ and e are constants. For methyl chloride the constants 'd' and 'e' were set to zero, thus reducing Equation 5.15 to a quadratic function, because a quadratic resulted in a higher correlation coefficient for methyl chloride. The best-fit constants, correlation coefficients (R^2) and standard deviations (s) are given in Table 5.1.

Table 5.1. Best-fit constants for Equation 5.15.

| Compound | a | b | c | d | e | R^2 | $s < 15^*$ | $s > 15^*$ |
|-----------------|---------|----------|----------|-----------|----------|-------|------------|------------|
| Methyl chloride | -41.12 | 5.054 | -0.08199 | 0 | 0 | 0.80 | 4.43 | 10.95 |
| Methyl bromide | -1.303 | -0.03981 | 0.03456 | -2.231E-3 | 3.916E-5 | 0.80 | 0.222 | 0.334 |
| Methyl iodide | -0.8770 | 0.01114 | 0.09928 | -5.998E-3 | 9.638E-5 | 0.63 | 1.51 | 2.27 |

* s is the standard deviation of the curve fit in pmol L^{-1} , for $\text{SST} < 15^{\circ}\text{C}$ and $\text{SST} > 15^{\circ}\text{C}$.

The correlation coefficient for methyl iodide (Table 5.1) is considerably lower than for the other two compounds. In fact, only 63% of the variance in methyl iodide concentration anomaly is accounted for by the best-fit fourth-order function of temperature. In the temperature range above 15°C, a simple arithmetic average would yield about as good a prediction of the methyl iodide concentration anomaly as the best-fit curve. Nevertheless, the curve certainly does not give a worse prediction than the average would, and provides a single formula which can be used over the entire temperature range.

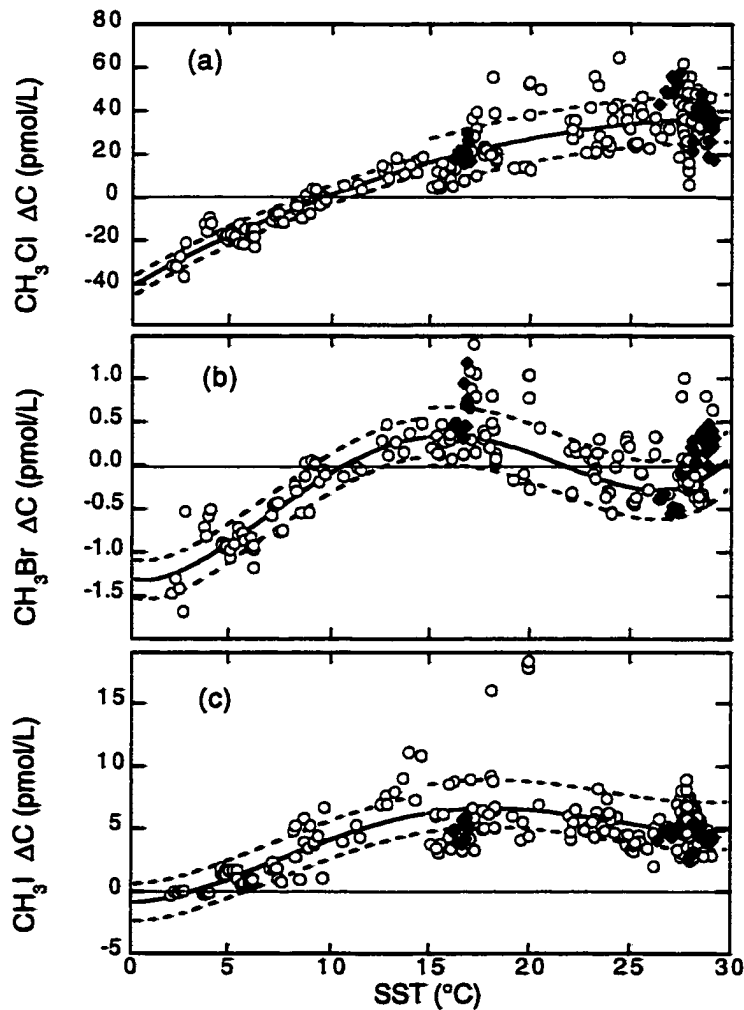


Figure 5.5. Methyl halide concentration anomaly ΔC as a function of SST, with empirical curve fit (solid line) and standard deviation (dashed lines). (a) methyl chloride; (b) methyl bromide; (c) methyl iodide. Circles are open ocean data; solid diamonds are coastal data.

5.4.2 Global Flux Calculation

Monthly averaged climatological wind speed and sea surface temperature data for the global ocean were obtained from the COADS data set on a 2° by 2° grid spacing [Woodruff *et al.*, 1987]. At each grid point, the piston velocity was calculated with equation 5.1, and the concentration anomaly was estimated from the SST with equation (5.15) and the appropriate set of constants. The flux per unit area was then calculated as the product of the piston velocity and the concentration anomaly, and this areal flux was multiplied by the area of the corresponding grid point. A flux estimate was thus obtained for each compound at each grid point and in each month of the year. The results were compiled by latitude and by month to enable latitudinal and seasonal trends to be distinguished, and the total annual global fluxes were obtained by adding all the grid points together for each month, then summing all twelve months.

The monthly global (area-weighted) average piston velocities and areal fluxes from the calculation procedure described above are shown in Table 5.2. Also, for all three cruise tracks, the fluxes calculated from SST along the track are plotted together with those calculated directly from the measured partial pressure difference (Figure 5.6). This is one way of verifying that the calculation procedure is internally consistent, and of visualizing the degree to which fluxes calculated with SST as a proxy variable represent the fluxes along the known cruise tracks. It can be seen in Figure 5.6 that the fluxes calculated from SST generally follow the same pattern as those based on measurements along the cruise track, but that in some regions the prediction based on SST does not fully reflect the variability seen along the cruise track, particularly for methyl bromide.

Table 5.2. Monthly global (area-weighted) average piston velocities and areal fluxes.

| Month | Piston velocity (k) (m day ⁻¹) | | | Areal flux (nmol m ⁻² d ⁻¹) | | |
|-------------|--|--------------------|-------------------|--|--------------------|-------------------|
| | CH ₃ Cl | CH ₃ Br | CH ₃ I | CH ₃ Cl | CH ₃ Br | CH ₃ I |
| January | 3.67 | 3.62 | 3.44 | 66.5 | -0.822 | 15.8 |
| February | 3.57 | 3.53 | 3.35 | 60.4 | -0.892 | 14.9 |
| March | 3.47 | 3.43 | 3.26 | 56.6 | -0.891 | 14.3 |
| April | 3.40 | 3.36 | 3.19 | 72.1 | -0.572 | 15.5 |
| May | 3.36 | 3.32 | 3.15 | 80.9 | -0.397 | 16.0 |
| June | 3.55 | 3.50 | 3.33 | 92.6 | -0.343 | 17.4 |
| July | 3.59 | 3.54 | 3.37 | 94.9 | -0.352 | 17.7 |
| August | 3.45 | 3.40 | 3.23 | 90.5 | -0.318 | 17.1 |
| September | 3.28 | 3.24 | 3.08 | 81.5 | -0.300 | 16.1 |
| October | 3.39 | 3.35 | 3.18 | 78.5 | -0.381 | 16.2 |
| November | 3.62 | 3.58 | 3.40 | 79.4 | -0.518 | 16.9 |
| December | 3.73 | 3.68 | 3.50 | 73.6 | -0.714 | 16.6 |
| Annual mean | 3.51 | 3.46 | 3.29 | 77.3 | -0.542 | 16.2 |

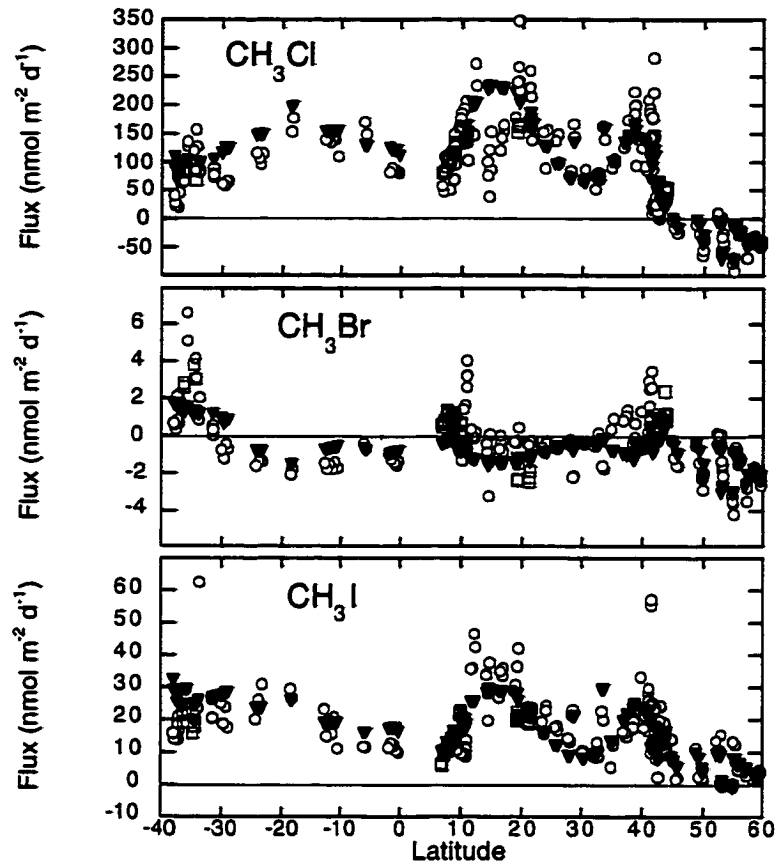


Figure 5.6. Air-sea fluxes from measurements and as calculated from SST. Open symbols are fluxes calculated from measured concentration anomalies (circles are open ocean data, squares are coastal data). Solid triangles are fluxes calculated with SST as a proxy variable (Equation 5.15).

5.4.3 Latitudinal and Monthly Distribution of Fluxes

The flux from a given latitudinal band of ocean depends on the average flux per unit area within that band and the total surface area of ocean at that latitude. The sea surface area for which wind speed and sea surface temperature data points exist in the COADS data set is given as a function of latitude in Figure 5.7. The global sea surface area used in these estimates is $3.35 \times 10^{14} \text{ m}^2$, which is 93% of the total sea surface area of $3.6 \times 10^{14} \text{ m}^2$ reported by *Levitus and Boyer* [1994]. The difference is likely to be due to variable coverage of high-latitude areas which are periodically ice-covered.

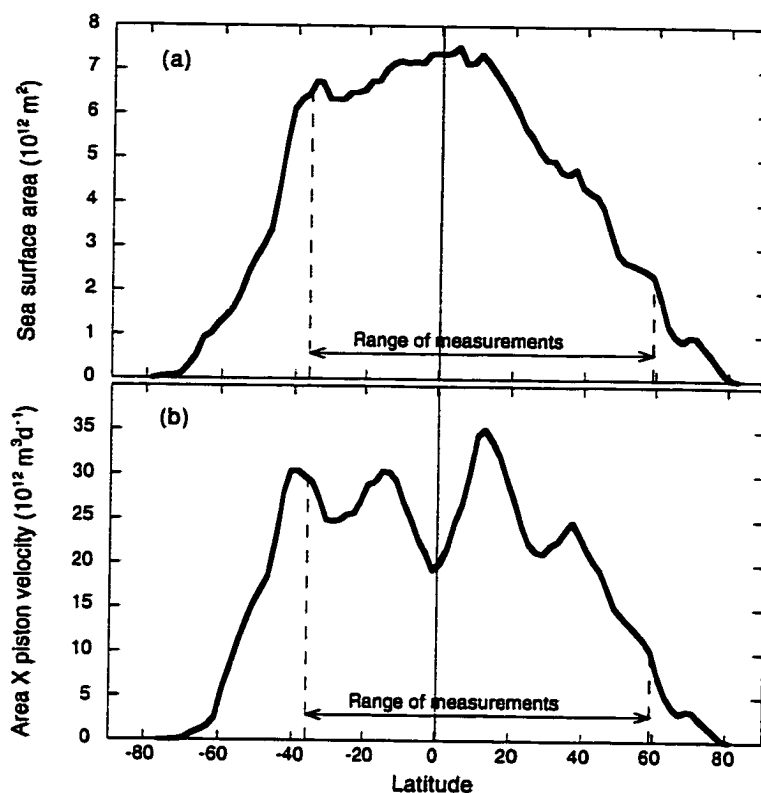


Figure 5.7. (a) Sea surface area as a function of latitude. (b) Sea surface area times average piston velocity of methyl bromide as a function of latitude. The range of latitudes sampled in the current study is also shown.

Total annual flux estimates in Mmoles (1 Mmole = 10^6 moles) for each 2° latitude band are shown in Figure 5.8. As would be expected, the form of the latitudinal dependence for each compound follows directly from the predictive equation used to estimate concentration anomaly, coupled with the relative sea surface areas as shown in Figure 5.7. For example, the largest emissions of methyl chloride to the atmosphere are predicted to occur at latitudes between 40°S and 40°N , while at higher latitudes the ocean is predicted to be a sink of methyl chloride. For methyl bromide, because the predictive equation for concentration anomaly has a peak in supersaturation at intermediate temperatures, in each hemisphere there is predicted to be a band of positive flux to the atmosphere at latitudes of 30 to 40 degrees, where SST is commonly between 13°C and 22°C . Regardless of the direction of the flux, the magnitude of the flux for all three compounds decreases in the vicinity of the equator because of lower wind speeds in that region. For methyl iodide, the extreme high-latitude ocean areas ($\sim 65^\circ\text{S}$ and $\sim 70^\circ\text{N}$) are predicted to represent a very small sink from the atmosphere. The origin of this prediction

can be seen in Figure 5.5, where the predictive equation for methyl iodide concentration anomaly descends into negative values below $+3^{\circ}\text{C}$. This part of the prediction is rather uncertain, as the data in Figure 5.5 really appear to go to atmospheric equilibrium at low temperatures, not to dip below. However, undersaturation of methyl iodide in high latitude waters has been observed [Happell and Wallace, 1996], and in any case this discrepancy is of little consequence to the global estimate because the amount of ocean area with SST below 3°C is a minute fraction of the total.

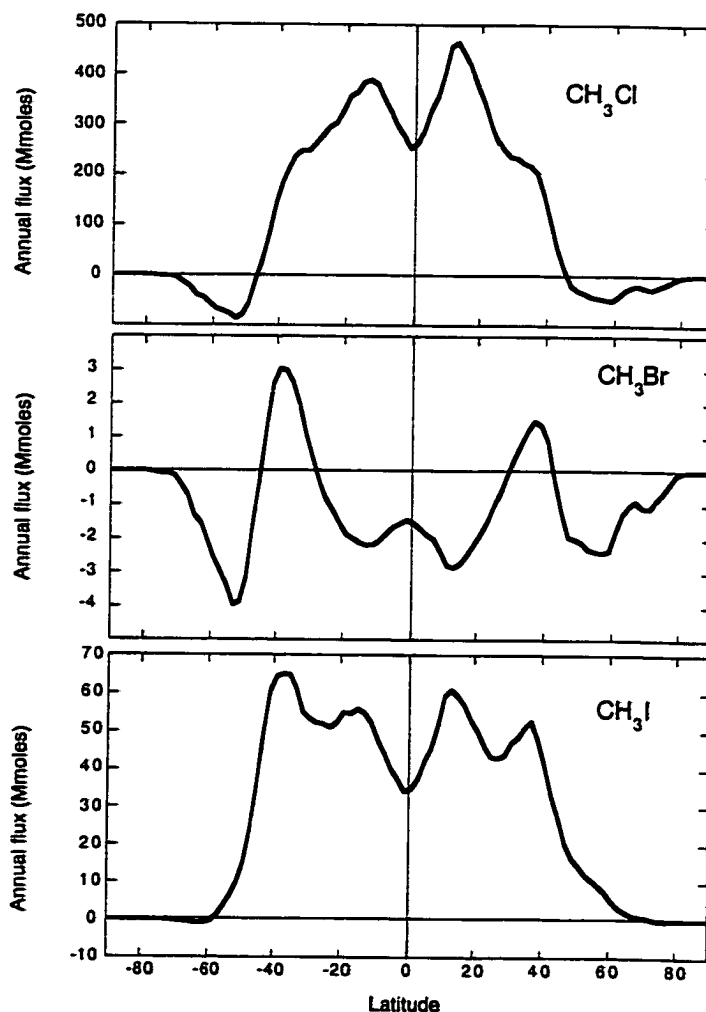


Figure 5.8. Annual ocean-atmosphere methyl halide flux as a function of latitude.

The results are also shown on a monthly basis (Figure 5.9), with the contribution from the northern and southern hemispheres also displayed for each month. It can be seen from Figure 5.9 that, according to the method of estimation in use here, there are considerable variations in monthly flux for methyl chloride and methyl bromide, while the global

methyl iodide flux is relatively constant throughout the year. The contributions from the two hemispheres also change during the year for all three compounds.

It should be noted that the variations in monthly fluxes are due only to changes in SST and wind speed. The same formula (Equation 5.15) was used to estimate concentration anomalies in every month. Therefore, in the algorithm used here, the only seasonal cycle of methyl halide concentrations in surface seawater is that due to seasonal changes in SST. In reality, the concentration in a particular region may vary independently of temperature, but the algorithm used for this estimate does not take this possibility into account. Since the principal goal of this study is to estimate the annual global flux for atmospheric budgeting purposes, the calculated latitudinal and monthly dependencies are shown simply as a matter of interest and will not be discussed further.

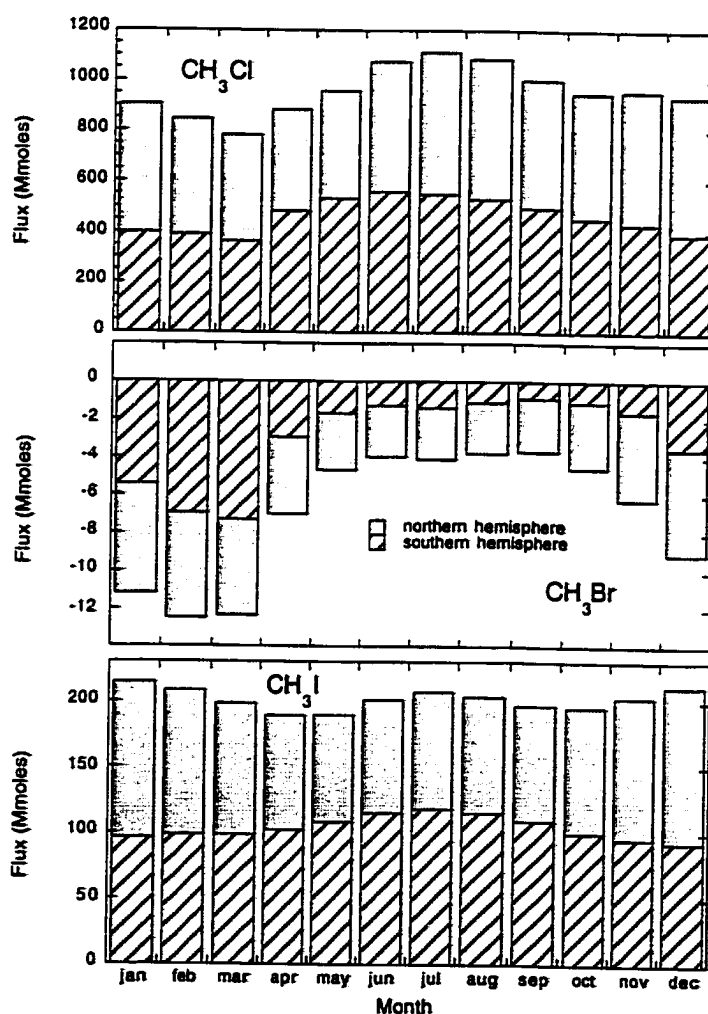


Figure 5.9. Monthly global flux of methyl halides from ocean to atmosphere. Columns: striped (southern hemisphere); and shaded (northern hemisphere).

5.4.4 Global Annual Fluxes

Addition of the monthly total fluxes yields the annual fluxes given in Table 5.3. Annual fluxes are shown for the southern and northern hemispheres, along with the global fluxes. The flux units are Gmoles y^{-1} (10^9 moles per year) and Gg y^{-1} (10^9 grams per year).

The uncertainty ranges given in Table 5.3 are 95% confidence intervals, based only on the uncertainties in the best-fit curves which were used to estimate the concentration anomalies. To calculate the ranges, the entire global calculation was repeated twice more for each month with the upper and lower limits of the 95% confidence interval of the concentration anomaly data about their best-fit equations. It is important to note that these intervals represent the very minimum range of uncertainty in the estimate, because they take into account only the statistical uncertainty in estimating concentration anomalies. As such, the ranges given can be taken to mean a hypothetical uncertainty under the set of assumptions made in this estimate (e.g.: the relationship assumed between wind speed and piston velocity, the assumption that this method of extrapolation based on temperature is valid, etc.). In reality, the flux estimates are subject to several uncertainties which are not accounted for in the ranges given in Table 5.3.

Table 5.3. Calculated annual fluxes from ocean to atmosphere.

| Compound | SH* flux (Gmoles y^{-1}) | NH* flux (Gmoles y^{-1}) | Global flux (Gmoles y^{-1}) [†] | Global flux (Gg y^{-1}) [†] |
|-----------------|--------------------------------|--------------------------------|--|--|
| Methyl chloride | 5.6±0.4 | 5.9±0.4 | 11.5±0.7 | 580±35 |
| Methyl bromide | -0.035±0.008 | -0.048±0.013 | -0.083±0.022 | -7.9±2.1 |
| Methyl iodide | 1.25±0.07 | 1.17±0.07 | 2.42±0.14 | 344±20 |

* SH = southern hemisphere, NH = northern hemisphere

[†]Uncertainties are 95% confidence intervals, based only on the uncertainty in the best-fit curves for concentration anomaly as a function of SST. Uncertainty in piston velocity is not included (see Table 5.4).

5.4.5 Uncertainty in Piston Velocity

The calculated piston velocity is very sensitive to wind speed, and various published formulae yield substantially different values. In their examination of the oceanic lifetime of atmospheric methyl bromide, *Yvon and Butler* [1996] summarized the differences that result from using the various published relationships between piston velocity and wind speed. They calculated that the area-weighted global mean exchange velocity derived from the *Liss and Merlivat* [1986] relationship was 44% of that derived from the

Wanninkhof [1992] or *Erickson* [1993] relationships. If the *Liss and Merlivat* [1986] relationship had been used instead of the relationship of *Wanninkhof* [1992], the global fluxes would have been about 307 Gg yr⁻¹ for methyl chloride, -4.2 Gg yr⁻¹ for methyl bromide, and 180 Gg yr⁻¹ for methyl iodide. *Liss et al.* [1993] report that the first results of the dual tracer technique for estimating exchange velocities described by *Watson et al.* [1991] provide support for the *Liss and Merlivat* [1986] predictions. Still other means of predicting gas transfer rates exist, such as scatterometer-derived winds [*Etcheto and Merlivat*, 1988] or direct relationships between radar backscatter and gas transfer [*Wanninkhof and Bliven*, 1991]. Until there is more general agreement on the best procedure for estimating the rate of gas transfer, the global air-sea flux of methyl halides will be subject to a significant degree of uncertainty from this factor alone.

5.4.6 Coastal Methyl Bromide Fluxes

Of the three compounds studied here, methyl bromide is the only one for which the coastal data appear to require special consideration. In the coastal waters studied in this data set, the majority of the samples have a concentration anomaly which is more than one standard deviation above the best-fit line which has been used to predict concentration anomaly from SST (Figure 5.5b). In particular, in data collected near the coast of South America (the highest temperature coastal data, at SST values greater than 28°C), supersaturation of methyl bromide is seen where slight undersaturation is predicted by the best-fit curve. For this reason, as explained in Section 5.4.2, the coastal data have been omitted from the calculation of the best-fit curve for methyl bromide. To the extent that these coastal data may be representative of coastal regions worldwide, the value which was given in Table 5.3 is likely to be an underestimate of the flux from ocean to atmosphere.

To determine approximately the magnitude of this error, for all the coastal data points the difference was found between the methyl bromide flux calculated directly from the equilibrator measurement (as in Figure 5.2) and the flux estimated from the best-fit of the concentration anomaly as shown in Figure 5.5. On average, over all the coastal data points the method of the best-fit curve was found to underestimate the methyl bromide flux by 0.57 nmol m⁻² d⁻¹. This average flux error was multiplied by the approximate coastal sea surface area, which is assigned here as 10% of the total ocean surface area. Oceanic regions with a water depth less than 200 metres are commonly defined as coastal waters, and the fraction of the ocean surface in this category was shown by *Menard and Smith* [1966] to be 7.5%. However, in the present work and in the report by *Lobert et al.* [1995], positive saturation anomaly of methyl bromide was found in areas with water

depths greater than 200 metres. In the absence of more information on the true extent of coastal supersaturation, the same figure (10%) as used by [Lobert *et al.*, 1995] was used in the present work. In this way, the error in annual methyl bromide flux is estimated to be $0.0075 \text{ Gmoles y}^{-1}$, which is equivalent to 0.7 Gg y^{-1} . Since the global ocean-to-atmosphere flux of methyl bromide given in Table 5.3 is negative (implying that the ocean represents a net sink for methyl bromide), this adjustment for coastal data reduces the magnitude of the global sink. The best estimate of the net global flux of methyl bromide from this work is therefore -6.9 Gg y^{-1} .

5.4.7 Final Flux Estimates

To give the final flux estimates of this work, the ranges of uncertainty have been expanded to include the uncertainty in the piston velocity relationship as calculated in section 5.4.5. The ranges given in Table 5.3 below have lower limits based on the piston velocity relationship of *Liss and Merlivat* [1986]. The upper limits are based on the piston velocity relationship of *Wanninkhof* [1992] and include the calculated uncertainty from Table 5.2. Within that range, the best estimate is considered to be the global flux based on the *Wanninkhof* [1992] piston velocities, and is the same as the best estimate from Table 5.2, with the exception of methyl bromide. In the case of methyl bromide, both the best estimate and the upper limit of the range have been adjusted to take into account coastal fluxes as per section 5.4.5.

Table 5.4. Annual ocean to atmosphere fluxes including uncertainty in piston velocity.*

| Compound | Best estimate (Gmoles y^{-1}) | Range (Gmoles y^{-1}) | Best estimate (Gg y^{-1}) | Range (Gg y^{-1}) |
|-----------------|--|------------------------------------|--|--------------------------------|
| Methyl chloride | 11.5 | 5.1 to 12.2 | 580 | 255 to 615 |
| Methyl bromide | -0.075 | -0.037 to -0.11 | -7 | -3 to -10 |
| Methyl iodide | 2.42 | 1.06 to 2.56 | 340 | 150 to 360 |

*Ranges include 50% uncertainty in piston velocity between *Wanninkhof* [1992] and *Liss and Merlivat* [1986] for all three compounds. Also, for methyl bromide, a correction for coastal fluxes has been included in the best estimate and range (see text Section 5.4.5).

5.4.7.1 Methyl Chloride

The magnitudes of the fluxes estimated in this work tend to be lower than the values reported in other studies. For methyl chloride, the ocean has previously been estimated by *Singh et al.* [1983] to be a net source of 5000 Gg y^{-1} to the atmosphere, which is about a factor of ten higher than the estimate made in this work. The estimate made by *Singh et*

al. [1983] was based on analyses of methyl chloride concentrations in the eastern tropical Pacific. There are several possible reasons for this considerable difference. The data set collected by *Singh et al.* [1983] showed average surface concentrations of methyl chloride in tropical Pacific waters about three times higher than those found in this study. This difference in concentrations may indicate high temporal or spatial variability of methyl chloride. However the data set collected in the current work covers several ocean regions in both the Atlantic and Pacific and at two different times of the year and yields no evidence of high variability of methyl chloride concentrations. There are also differences in the methods used in this work compared with *Singh et al.* [1983]. The specificity of the mass selective detector used in the present work allows for greater confidence that the measurements were not influenced by any interfering compounds.

Another previous estimate of the global flux of methyl chloride from the ocean to the atmosphere is that of *Tait et al.* [1994]. Based on measurements in the northwest Atlantic, they predicted a flux of 1700-2400 Gg y⁻¹. This is around six times higher than the estimate of 255 to 615 Gg y⁻¹ made in the present thesis. The measurements on which the estimate of *Tait et al.* [1994] was based were taken along a cruise track quite similar to the *Hudson* cruise track of the present work. In fact, the the leg across the Labrador Sea is a routinely-occupied transect which is identical in the two cruise tracks. However, in the present work this region was found to be undersaturated in methyl chloride, whereas in the data set of *Tait et al.* [1994] this area is supersaturated. The average concentration of methyl chloride reported by *Tait et al.* [1994] for this region is 271 pmol L⁻¹, but in the present study concentrations in the Labrador Sea are around 75 pmol L⁻¹. The only differences between the two studies which can possibly account for this significant disagreement are the analytical methods and the time of year. The measurements of *Tait et al.* [1994] were made in May (spring), and those of the present work were made in July (summer). It seems unlikely that methyl chloride concentrations would decrease so drastically from May to July. The differences are more likely to result from different analytical methods. The analyses of *Tait et al.* [1994] were made on seawater samples from Niskin bottles, with a purge-and-trap system, separation by GC, and detection by ECD. Their calibration standard was a liquid phase standard prepared on-board the ship by dilution of pure methyl chloride in seawater. Given the number of factors which differ between the two methods, it is not possible to determine the exact cause of the difference in results. Another cruise in 1994 in this same area, using a different purge-and-trap system and another ECD, revealed supersaturation of methyl chloride (R. M. Moore, unpublished data).

5.4.7.2 Methyl Bromide

For methyl bromide, the ocean has been reported to be a net source of 40 to 80 Gg y⁻¹ to the troposphere [*Singh and Kanakidou*, 1993], a net source of 30 to 40 Gg y⁻¹ [*Khalil et al.*, 1993], or more recently a net sink of 6 to 18 Gg y⁻¹ [*Lobert et al.*, 1995] or 11 to 32 Gg y⁻¹ [*Lobert et al.*, 1997] from the troposphere. The estimate made in the present work is a net sink of 3 to 10 Gg y⁻¹ of methyl bromide from the atmosphere to the ocean, which is closest in agreement to the estimate of *Lobert et al.* [1995]. It is also relatively close to the more recent estimate of *Lobert et al.* [1997], which is an extension of their previous estimate to include data they collected in the Southern Ocean. The three most recent investigations, including *Lobert et al.* [1995; 1997] and the current study all find the global ocean to be a net sink of methyl bromide from the atmosphere. Though some source areas were found in all these studies, they are outweighed by vast areas of undersaturated waters. The earlier studies characterize the global ocean as a significant net source of methyl bromide to the atmosphere. As with methyl chloride, the reason for this discrepancy is unknown, but it may be either due to real differences in the concentrations in the sampled areas or to differences between the methods used, particularly the previous use of electron capture detectors versus the more recent use of mass selective detectors. The reports of *Lobert et al.* [1995; 1997] and this study have in common both a wide range of coverage of latitudes and ocean areas, and the use of a mass selective detector to quantify methyl bromide concentrations.

5.4.7.3 Methyl Iodide

An early estimate of the flux of methyl iodide from ocean to atmosphere was made by *Rasmussen et al.* [1982]. Their value of 1300 Gg y⁻¹ is about 4 times higher than the estimate made in this study, and was strongly influenced by their supposition that highly productive waters, accounting for 10% of the ocean area, would supply 1000 Gg y⁻¹. This supposition was based on previous measurements made by *Lovelock* [1975], who reported methyl iodide concentrations of ~150 pmol L⁻¹ near Ireland. Two other early estimates agree much more closely with the current study. Both *Singh et al.* [1983] and *Liss and Slater* [1974] estimated the global oceanic source of methyl iodide to the atmosphere to be 300 Gg y⁻¹, which is well within the range of 150 to 360, and close to the best estimate of 340 Gg y⁻¹ from the current study. More recently, *Reifenhäuser and Heumann* [1992] estimated a global ocean source of methyl iodide to the atmosphere of 850 Gg y⁻¹ based on data collected in Antarctic waters. However, *Happell and Wallace* [1996] found the Greenland-Norwegian Sea to be undersaturated in methyl iodide in November, and suggested that this may be due to low light levels in that area. Low light

levels could contribute to undersaturation in two ways: low rates of photolysis in the atmosphere could allow higher atmospheric concentrations to be maintained, and possible photochemical production of methyl iodide in the seawater could be limited by the low light intensity. Methyl iodide concentrations seem to vary geographically and perhaps also seasonally, and future flux estimates may be able to take this into account.

5.4.8 Summary

For all three of the compounds studied here, global flux estimates have yielded a wide range of results. The estimates made in the current study show the ocean source of methyl chloride to be significantly smaller than that reported by other researchers. For methyl chloride, past estimates of the global source have been six to ten times higher than the current study. For methyl bromide, the finding of a net oceanic sink in the current study agrees most closely (to within about 5 Gg y^{-1}) with the estimate of *Lobert et al.* [1995]. For methyl iodide, the global oceanic source estimated in the current work is in agreement with the lowest previous estimates [*Liss and Slater*, 1974; *Singh et al.*, 1983].

The current study provides an estimate which is based on data covering a relatively large and varied sample of ocean areas over parts of three seasons. The analyses were performed with a very selective detector to minimize the risk of interference from other compounds, and the calculation of the estimate was done in a novel way. Some possible directions for future work are included in Chapter 6: Discussion.

Chapter 6: DISCUSSION

The primary conclusion to be drawn from this thesis is that, according to analyses of air and equilibrator samples on three voyages, with an extrapolation based on climatological wind speed and sea surface temperature, the global ocean represents a source of $\sim 0.58 \text{ Tg y}^{-1}$ (range 0.26 to 0.62 Tg y^{-1}) of methyl chloride and $\sim 0.34 \text{ Tg y}^{-1}$ (0.15 to 0.36 Tg y^{-1}) of methyl iodide to the atmosphere, and a sink of $\sim 7 \text{ Gg y}^{-1}$ (3 to 10 Gg y^{-1}) of methyl bromide from the atmosphere. In this chapter, figures will be quoted in Tg (10^{12} g) for methyl chloride and methyl iodide, and in Gg (10^9 g) for methyl bromide, to be consistent with the figures quoted in the introduction.

In this chapter, the flux estimates will be placed in the context of the atmospheric budgets of these three compounds. This will be followed by discussion of some of the remaining uncertainties in the estimates, speculation about missing sources, and discussion of oceanic production in light of the observed methyl halide distributions. Finally, some possible directions for future work will be outlined.

6.1 Atmospheric Budgets

The atmospheric budgets of the three methyl halides are summarized in Tables 6.1, 6.2, and 6.3. These budgets include the net ocean-atmosphere fluxes calculated in Chapter Five, along with other sources and sinks from the literature which were presented in Chapter One.

6.1.1 Methyl Chloride

For methyl chloride (Table 6.1), the best estimate of the total sink exceeds that of the total source by 1.4 Tg y^{-1} . There are, however, substantial uncertainties in several of the budget terms. Biomass burning is the largest source term and has a considerable uncertainty, which is based on the range of various published estimates. It should be noted that each published estimate is subject to its own uncertainty, which is often quoted to be on the order of a factor of 2 or 3 [e.g. *Andreae et al.*, 1996]. The flux estimates for biomass burning are primarily based on field and laboratory measurements of pyrogenic emissions, in which correlations have been found between methyl chloride and CO , CO_2 , and CH_4 [*Blake et al.*, 1996]. An estimate of the global emission of one of the reference compounds is then multiplied by the ratio of methyl chloride emissions to those of the reference compound. Large uncertainties in the global emission estimate result from two factors, namely that the global pyrogenic emissions of CO and CO_2 are only known to

within about $\pm 50\%$ [Andreae *et al.*, 1996], and the emission ratios vary from one fire to another, so the representative emission ratio is uncertain. Biomass burning is also a significant term in the methyl bromide budget (Table 6.2), and further discussion of biomass burning will follow in section 6.1.4.

Table 6.1. Budget for methyl chloride in the atmosphere

| Source Type | Emission rate (Tg y ⁻¹) | Sink Type | Loss rate (Tg y ⁻¹) |
|----------------------|--|------------------|------------------------------------|
| Biomass burning | 1.0* (0.5 [†] -1.8 [‡]) | Reaction with OH | 3.2 (2.9-3.4) ^{††} |
| Oceans (this work) | 0.58 (0.26-0.62) | | |
| Wood rot fungi | 0.16 [§] | | |
| Industrial emissions | 0.03 ^{‡‡} | | |
| TOTAL | 1.8 (1.0-2.6) | TOTAL | 3.2 (2.9-3.4) |

^{††}Tropospheric burden 4 Tg, [OH] of Prinn *et al.* [1995], rate constant 2.59×10^{-14} cm³ molec⁻¹ s⁻¹

*Lobert *et al.* [1998]

[†]Rudolph *et al.* [1995]

[‡]Andreae [1993]

[§]Watling and Harper [1998]

^{‡‡}Edwards *et al.* [1982]

The results of the present work suggest that the importance of the oceanic source of methyl chloride has been overestimated in the past. In two previous reports, the oceanic source has been estimated to be 5 Tg y⁻¹ [Singh *et al.*, 1983], and 1.7 to 2.4 Tg y⁻¹ [Tait *et al.*, 1994]. The oceanic source strength estimated in the present work is only ~ 0.58 Tg y⁻¹, which is on the order of one fifth to one tenth as large as the two previous estimates. This puts the oceanic source of methyl chloride in the same order of magnitude as the fungal source of 0.16 Tg y⁻¹ estimated by Watling and Harper [1998].

Regarding the source of methyl chloride from wood-rot fungi, it is important to bear in mind that the source estimate of 0.16 Tg y⁻¹ is based on methyl chloride release rates from culture experiments in the laboratory, with an extrapolation based on the amount of wood available to be rotted each year, the chloride content in various kinds of wood, and the relative abundance of methyl-chloride-producing species of fungi [Watling and Harper, 1998]. There are no field studies to determine the rates of methyl chloride production by fungi in the wild. Field studies are essential to verify the production seen in laboratory cultures, particularly since production rates could depend on various environmental factors which may not be accounted for in laboratory studies. Field studies may reveal larger or smaller production rates which could influence the relative importance of the fungal source.

The uncertainty in the total sink term for methyl chloride is likely to be larger than the range of 2.9 to 3.4 Tg y⁻¹ given in Table 6.1. That range is based on the uncertainty in the average concentration of OH radicals [Prinn *et al.*, 1995] and the rather small uncertainty in the average atmospheric mole fractions of methyl chloride found in the present thesis (± 10 ppt). It does not take into account the uncertainty in the reaction rate constant, nor does it account for the range of average methyl chloride mole fractions seen in other studies. Furthermore, the sink term given in Table 6.1 is based on a very simplistic calculation in which only the average temperature, rate constant, and OH concentration are used. A sink as low as 1.9 Tg y⁻¹ (which could be balanced in the present budget) was reported by Crutzen and Gidel [1983] from a two-dimensional model of the OH distribution, but rate constants which have been updated since that time may yield a different result. A comprehensive re-evaluation of the lifetime of methyl chloride against reaction with OH, with particular attention to the uncertainty range, would be desirable, but would not likely change the conclusion that the methyl chloride budget is significantly out of balance. Finally, the sink due to reaction with OH can only be considered as the lower limit of the total, since other potential sinks exist, such as destruction in soils and consumption by bacteria. An additional sink of ~ 0.2 Tg y⁻¹ is implied if about 5% of the methyl chloride in the troposphere is transported to the stratosphere each year.

6.1.2 Methyl Bromide

For methyl bromide, it can be seen from Table 6.2 that the sum of the reported total sinks exceeds that of the sources by ~ 59 Gg y⁻¹. The sources from fumigation and biomass burning, as well as the sink due to soil uptake, all have very large uncertainties, and the upper limit of the total emissions can balance the lower limit of the total losses. Nevertheless, it would be unwise to conclude that the budget of methyl bromide can really be balanced by taking the extreme ends of all the estimates, because it is unlikely that all the best estimates err in the same direction. To take the other extreme, using the lowest estimated source and the highest estimated sink results in a budget with the sinks exceeding the sources by ~ 131 Gg y⁻¹, which is also rather unlikely. The most probable conclusion is that the atmospheric budget of methyl bromide is unbalanced by about 60 Gg y⁻¹. Despite the considerable uncertainties in the known sources and sinks, it is likely that other significant sources exist which have not yet been discovered.

The industrial source of methyl bromide through emissions from fumigation appears to account for a significant fraction (22-48%) of the loss rate. This percentage is based on a total net sink of 136 Gg y⁻¹ from the atmosphere (Table 6.2). Some other authors [Yvon

and Butler, 1996; Yvon-Lewis and Butler, 1997] have constructed methyl bromide budgets in which the ocean appears as both a source and a sink, in order to emphasize the effect of oceanic degradation of methyl bromide on the atmospheric lifetime. However, when considered strictly from the point of view of the atmosphere, the ocean is a net sink as in Table 6.2. Approximately 76 Gg of methyl bromide is used in fumigation per year [Butler and Rodriguez, 1996], and the large uncertainty in the emission from fumigation is based primarily on the uncertainty in the emission factor, which is the fraction escaping to the atmosphere when methyl bromide is applied, primarily by injection into soils.

Table 6.2. Budget for methyl bromide in the atmosphere

| Source Type | Emission rate (Gg y ⁻¹) | Sink Type | Loss rate (Gg y ⁻¹) |
|-----------------|--|------------------------------------|------------------------------------|
| Fumigation | 45* (30-65) | Reaction with OH and photolysis | 86†† |
| Biomass burning | 30† (10-50) | Soil | 42‡‡ (10-74) |
| Automobiles | 1.5‡ (1.5-6.0§) | Oceans (this work) | 7 (3-10) |
| | | Atmospheric increase | 1 (0-3) |
| TOTAL | 77 (42-121) | TOTAL | 136 (99-173) |

*Butler and Rodriguez [1996]

†Manø and Andreae [1994]

§Thomas et al. [1997] (estimate for 1995)

††Yvon-Lewis and Butler [1997], based on Penkett et al. [1995] and Prinn et al. [1995]

‡‡Shorter et al. [1995]

‡Baker et al. [1998]

Based on the report by Manø and Andreae [1994], the biomass burning source of methyl bromide is significant and has a large uncertainty. The wide uncertainty range they reported is mostly due to the difference between two methods of estimating the global emissions. The correlation between methyl bromide and carbon dioxide emitted by the fires yielded an estimate of 9 to 37 Gg y⁻¹, while that between methyl bromide and methyl chloride yielded 22 to 50 Gg y⁻¹. Andreae et al. [1996] reported a smaller range of 20 to 30 Gg y⁻¹, based on the correlation between methyl bromide and CO in pyrogenic emissions. Blake et al. [1996] reported various estimates of the global emission of methyl bromide from biomass burning, all in the range from 10 to 24 Gg y⁻¹. With these various studies intersecting at around 24 Gg y⁻¹, the upper limit of 50 Gg y⁻¹ from Manø and Andreae [1994] seems increasingly unlikely. Further discussion of biomass burning is included in section 6.1.4 below.

The source from combustion of leaded gasoline in automobiles appears to be a very small part of the total. Even if relatively high emission factors are used in the estimate,

the global consumption rate of leaded gasoline has decreased over time so that by 1995, global emissions of methyl bromide from this source have an upper limit of 6 Gg y⁻¹ [Thomas *et al.*, 1997].

There is a very large range of 10 to 74 Gg y⁻¹ reported for the soil sink of methyl bromide [Shorter *et al.*, 1995]. An even larger sink of 94 Gg y⁻¹ with a greater uncertainty (± 54 Gg y⁻¹) was estimated by Serça *et al.* [1998]. The larger estimate would imply an even greater disparity between sources and sinks of methyl bromide in the atmosphere. A further consideration is that field studies on soil alone should be extended to include terrestrial plants, to determine whether terrestrial soil/plant systems constitute net sources or net sinks of all the methyl halides. Uptake of methyl bromide by the foliage of some plants has been reported [Jeffers and Wolfe, 1997], but initial studies of terrestrial ecosystem biomes in the Biosphere2 research facility suggest that terrestrial soil/plant systems can be both sources and sinks for methyl bromide [Rhew *et al.*, 1997].

There are apparently two main problems which need to be resolved in the atmospheric budget of methyl bromide. First, the budget appears to be out of balance. The reported sinks exceed the reported sources, which suggests that other sources exist that have not yet been included in the budget, such as emissions from the terrestrial environment, or production in the marine atmosphere. Discussion of some potential sources which could be investigated follows in Section 6.3. Second, the uncertainties in many of the budget terms are large, which creates a difficulty in drawing conclusions about the relative contributions of various sources and sinks, and even casts some doubt on the magnitude of the budget imbalance.

6.1.3 Methyl Iodide

For methyl iodide, the annual oceanic source of -0.34 Tg y⁻¹ calculated in this work is in agreement with the low end of the previous estimates of -0.30 Tg y⁻¹ [Liss and Slater, 1974; Singh *et al.*, 1983], and the ocean still appears to be the largest known source of methyl iodide to the atmosphere. When considering the oceanic source in the context of the global budget, it is important to note that the total loss rate of methyl iodide given in the budget in Table 6.3 (0.30 Tg y⁻¹) is an estimate based on a simple scaling of the calculation of Chameides and Davis [1980] to more realistic atmospheric mole fractions of methyl iodide in light of recent measurements (see Section 1.3, page 18). A comprehensive re-calculation of the photolysis loss rate, based on light levels, the current figure for the absorption cross-spectrum of methyl iodide, and recently measured atmospheric mole fractions as a function of latitude, may yield a different global loss rate. Therefore, the total sink of 0.30 Tg y⁻¹ given in Table 6.3 can only be considered as very

approximate. Losses other than photolysis appear not to have been quantified and are therefore not included. Under these conditions, it appears that the sources of methyl iodide can balance the estimated total sink from photolysis.

Table 6.3. Budget for methyl iodide in the atmosphere

| Source Type | Emission rate (Tg y ⁻¹) | Sink Type | Loss rate (Tg y ⁻¹) |
|--------------------|--|--------------|------------------------------------|
| Oceans (this work) | 0.34 (0.15-0.36) | Photolysis | -0.30 [‡] |
| Rice paddies | 0.025* (0.02-0.03) | | |
| Biomass burning | 0.005 [†] (0.003-0.008) | | |
| TOTAL | 0.37 (0.17-0.40) | TOTAL | -0.30 |

*Muramatsu and Yoshida [1995]

[†]Andreae et al. [1996]

[‡]Chameides and Davis [1980], adjusted as per section 1.3 (page 18) of this thesis.

The latitudinal and seasonal dependence of the atmospheric loss rate should also be significant for a compound like methyl iodide, for which the principal loss mechanism is photolysis. Some of the observed variations in methyl iodide mole fractions in the atmosphere may have an explanation in the variation of photolysis rates due to variable light intensities. Methyl iodide is considered to be a short-lived compound in the troposphere, with an average lifetime around 4 to 8 days [Zafiriou, 1974]. However, the local lifetime must be considerably above average in regions of reduced light levels, such as at high latitudes, particularly in winter and also in areas which are subject to heavy fog. For example, during the *Hudson* cruise, from latitudes of 50-60°N on the Labrador Sea in July, calm winds and dense fog prevailed for many days. Many of the air samples taken in this area had atmospheric mole fractions which were higher than those taken at lower latitudes (up to 5 ppt, see Figure 4.4c). Low loss rates and a longer lifetime may have allowed methyl iodide to accumulate in the atmosphere to levels which were observed to be almost at equilibrium with the surface of the ocean (see section (i) of Figure 4.1d, around a distance of 500 nautical miles along the cruise track, where methyl iodide partial pressures in the water and air are practically equal).

Although many potential terrestrial sources of methyl iodide remain uninvestigated (e.g. production by plants other than rice), the ocean seems likely to remain the largest source of methyl iodide to the atmosphere, based on the relatively small contribution from biomass burning. The apparent dominance of oceanic over terrestrial sources of methyl iodide may reflect the relative abundances of iodine in the marine and terrestrial environments, if the biological and chemical rates of methylation of iodide are similar in

these different ecosystems. The main priority in improving the methyl iodide budget would be to make a more reliable estimate of the total sink, in order to determine whether the budget is really balanced.

6.1.4 Biomass Burning

Since biomass burning is a significant source term in the budgets of methyl chloride and methyl bromide (Tables 6.1 and 6.2), it is worthwhile to consider its emission factors, temporal trends, and geographical and seasonal distribution. *Andreae* [1991] reviewed the history and distribution of biomass burning. In present times, biomass burning must be considered primarily as an anthropogenic source of emissions to the atmosphere, because the vast majority of fires are intentionally set by humans, and over half the wildfires are also caused unintentionally by human activities. However, fire is a natural and frequent part of some ecosystems, so in the absence of human intervention (both in fire ignition and fire suppression), there would naturally be a significant amount of biomass burning, though its rate would likely be lower and its geographical distribution quite different from what it is today. Tropical rainforests, for example, are naturally too wet to be subject to significant natural fire cycles, yet in present times they are being burned extensively.

If biomass burning is a significant source of methyl chloride and methyl bromide to the atmosphere, then the geographical and seasonal distributions of the burning are important because they may influence the latitudinal and seasonal variations seen in the atmospheric concentrations of these compounds. The majority of biomass burning occurs in the tropics [e.g. *Hao and Liu*, 1994; *Mack et al.*, 1996]. Of the total amount of carbon emitted to the atmosphere by biomass burning, it has been estimated that 87% is emitted in the tropics [*Andreae*, 1991]. About 65% of biomass burning emissions are estimated to occur in the northern hemisphere [*Lobert et al.*, 1998]. Although burning continues to some extent year-round, in any given area the time of peak burning is simply determined by the time of the dry season. In general, the peak months were bimodal according to latitude, being around March/April north of 5°N and around October/November south of the equator, with an ambiguous combination of these two seasons in the zone from 0°N to 5°N [*Hao and Liu*, 1994]. The line between these two seasonal modes lies consistently north of the equator, principally because the intertropical convergence zone (ITCZ) lies, on average, north of the equator throughout the year in most places [*Griffiths*, 1985]. The ITCZ is the latitudinal band where the northern and southern trade winds converge, and represents the heat equator of the earth (the zone of warmest sea or land temperature).

One characteristic which is often cited for the methyl halides is the ratio of average atmospheric concentrations between the northern and southern hemispheres. In the

compiled data set of this thesis (Section 4.4, page 62), the north-south ratio is -0.97 for methyl chloride and ~ 1.17 for methyl bromide. These observations of slightly higher methyl chloride in the southern hemisphere and higher methyl bromide in the northern hemisphere are consistent with other reports [e.g. *Koppmann et al.*, 1993; *Wingenter et al.*, 1998]. However, since seasonal cycles in atmospheric concentration exist for both these compounds, and since these cycles are likely to be out of phase in the two hemispheres, the interhemispheric ratio is likely to vary throughout the year. The ratios calculated in this thesis apply only to October. There is a pronounced seasonal cycle for methyl bromide in the northern hemisphere, which may be explained by seasonal variations in the loss rate due to reaction with OH [*Wingenter et al.*, 1998], but the corresponding (out-of-phase) seasonal cycle was not seen in the southern hemisphere. In the northern hemisphere, a seasonal cycle in fumigation rates could also contribute to the observed cycle in methyl bromide mole fractions.

In the limited data set of the present thesis, methyl chloride levels were higher in October/November than in July (both hemispheres) (Table 4.2). However, the figure for the southern hemisphere in July is based on data collected from 6°N to 10°N . The intertropical convergence zone appeared to be at 10°N (as explained in Section 4.3.1, page 59), so these samples are not representative of the northern hemisphere, but it would be unwise to place confidence in how well they represent the southern hemisphere. Therefore, no firm conclusion about the existence or magnitude of a seasonal cycle in atmospheric methyl chloride can be drawn from the present work. One long-term study of atmospheric methyl chloride (R. F. Weiss, unpublished data, 1999) demonstrates that there are significant seasonal cycles in both hemispheres, and suggests that, on an annual average, methyl chloride is slightly higher in the northern hemisphere than in the southern hemisphere. The finding in the present thesis of slightly higher methyl chloride in the southern hemisphere may simply be due to the season in which these measurements were made.

Any balanced atmospheric budget would have to account not only for the total global source strength, but also for the interhemispheric and seasonal patterns. *Lobert et al.* [1998] have estimated the ratio of emissions in each hemisphere. However, the equator is not necessarily the most appropriate line to divide the biomass burning emissions between the northern and southern hemispheres. Due to the position of the ITCZ, which is biased toward the northern hemisphere, particularly over South America and Africa [*Griffiths*, 1985], the emissions from biomass burning which occur in very low latitudes of the northern hemisphere are likely to have more effect on the southern hemisphere than the northern hemisphere. This is consistent with the fact that the timing of the burning

season in many areas slightly north of the equator matches the southern hemisphere burning season, particularly in South America [*Hao and Liu*, 1994]. With the ITCZ as the dividing line (at 5°N), *Lobert et al.* [1998] estimated that 59% and 41% of biomass burning emissions are in the northern and southern hemispheres, respectively.

What are the implications of this distribution of biomass burning for the hemispheric and seasonal budgets of methyl chloride and methyl bromide? Biomass burning emissions seem to be somewhat larger in the northern hemisphere, but the most significant aspect of their distribution is the importance of tropical regions. If biomass burning is the primary source of methyl chloride, elevated mole fractions might be expected in the tropics, but this could be counteracted by the relatively higher OH concentrations and consequent higher loss rates of methyl chloride in the tropics. The data set in this thesis does not indicate any elevation of methyl chloride in the tropics. However, the much larger atmospheric data set of *Colman et al.* [1998], which was collected over the Pacific in September of 1996 (at the beginning of the southern hemisphere burning season), does have a number of relatively high methyl chloride values in the region between 5°N and 10°S. A thorough analysis of the concentrations as a function of latitude in this large data set would be in order.

The elevated levels of methyl bromide in the northern hemisphere cannot be explained by emissions from biomass burning. The fumigation source of methyl bromide is predominantly in the northern hemisphere, and may contribute significantly to this trend. If plans to phase out the use of methyl bromide in fumigation are implemented, future measurements of methyl bromide as a function of latitude will provide an excellent opportunity to determine in hindsight the actual and past contributions of fumigation to the methyl bromide budget, and thereby help determine the distribution of the missing sources. In terms of seasonal variations, there are several observations which can be made. In the southern hemisphere, where the fumigation sources are lower and the biomass burning source may be more dominant, methyl bromide mole fractions do not follow the cycle which would be expected based on the seasonality of OH concentrations alone [*Wingenter et al.*, 1998]. In particular, lower-than-average methyl bromide concentrations would be expected in January/February in the southern hemisphere, when OH concentrations are greatest, but this is not the case. Elevated emissions during the burning season in the southern hemisphere (September to December) may contribute to maintaining methyl bromide concentrations in that season. In the northern hemisphere, the peak biomass burning season in March coincides with relatively high observed methyl bromide mole fractions [*Wingenter et al.*, 1998]. It should be noted, however, that biomass burning cannot contribute to a higher amplitude seasonal cycle at high latitudes

than at low latitudes, because most of the biomass burning occurs at low latitudes. The seasonal cycle in OH concentrations, which influences the loss rate of methyl chloride and methyl bromide, does have a higher amplitude at high latitudes because of the greater seasonal cycle in sunlight intensity.

Given the imbalances in the total budget of methyl bromide and the lack of knowledge on the distribution of potential unknown sources, it cannot be said with certainty that biomass burning is a significant factor in controlling seasonal variations. However, the seasonality of the biomass burning source of methyl bromide does not conflict with observed seasonal patterns in methyl bromide concentration in either hemisphere. For methyl chloride, more data are needed on the seasonal variation in its atmospheric mole fraction in the southern hemisphere. If biomass burning is a significant source term for both methyl chloride and methyl bromide, then in October in the southern hemisphere they should both have higher mole fractions than would be expected from the variation in OH concentration alone. In the southern hemisphere, October/November is springtime, and OH concentrations have not yet reached their summer peak, and it is also the peak burning season, so methyl chloride emissions may be unusually high. In July there is relatively little biomass burning in either hemisphere, and the northern hemisphere concentrations would be expected to be relatively low because of high summertime OH concentrations. In the present study, higher atmospheric methyl chloride is seen in October/November than in July in both hemispheres, but this cannot be considered as strong evidence of the biomass burning source, because of the limited latitude range covered in July.

Overall, it seems that latitudinal and seasonal variations in biomass burning emissions are not inconsistent with the observed patterns in methyl chloride and methyl bromide concentrations in the atmosphere. However, the current data set does not provide enough information on seasonal variations of methyl chloride to be certain whether or not those variations are consistent with the idea that biomass burning is the primary source of both methyl chloride and methyl bromide.

6.2 Uncertainties in the Oceanic Flux Estimates

There are many different sources of uncertainty and potential error in the global oceanic fluxes which have been estimated in this work, and some of these uncertainties are more difficult to quantify than others. A large uncertainty in the fluxes is due to the variations between estimates of the piston velocity. This source of uncertainty has been discussed in Section 5.4.4, and the ranges of the oceanic fluxes given in Table 5.3 and the

budget tables (Tables 6.1, 6.2, and 6.3) take into account the different piston velocity formulae of *Wanninkhof* [1992] and *Liss and Merlivat* [1986]. Two uncertainties which are more difficult to quantify are the possible seasonal variations in oceanic emissions, and the uncertainty associated with the use of SST as a proxy variable. These two uncertainties are the subjects of further discussion in sections 6.2.1 and 6.2.2 below.

6.2.1 Seasonality in Oceanic Emissions

There is no strong evidence for a seasonal cycle in the concentrations of any of the methyl halides in the data set which was collected for this thesis. However, in this data set, no samples were taken in the winter and early spring in the northern hemisphere, nor in summer, autumn, or winter in the southern hemisphere, and these limitations make it impossible to eliminate the possibility that a seasonal cycle in oceanic emissions may exist. One small piece of circumstantial evidence which could be interpreted as indicative of a seasonal signal is the observation of supersaturation of methyl bromide during springtime around 35°S in the Pacific in late October and early November of 1995. However, without a time series over several months it would be pure speculation to propose that the supersaturation seen in that area was associated only with the spring season. This observed supersaturation is also consistent with the relationship based on temperature which has been observed in this work, and might be independent of season in that location. Without a better understanding of the production mechanism(s) of methyl bromide in seawater, it would be unreasonable to conclude the existence of any seasonal trend from the data set in this work.

Nevertheless, several of the production mechanisms for methyl halides which have been observed in laboratory studies might suggest the likelihood of a seasonal cycle in seawater concentrations. Production of methyl bromide by microalgae [*Scarratt and Moore*, 1996; 1998, *Sæmundsdóttir and Matrai*, 1998], and photochemical production of methyl iodide [*Moore and Zafiriou*, 1994], both would likely imply seasonal cycles at mid-to-high latitudes. A report from other researchers indicates a seasonal cycle in methyl bromide saturation anomalies in the North Sea [*Baker et al.*, 1998b]. In that work, methyl bromide at a coastal site in the North Sea was found to remain undersaturated from February to May, then to increase rapidly to 100% supersaturation by July before beginning to fall again. The observed increase in methyl bromide concentrations was positively correlated with a bloom of *Phaeocystis*. To date, this appears to be the clearest available evidence of a seasonal cycle of methyl bromide production in seawater.

Several factors impose limitations on the magnitude of the effect which seasonal production cycles could have on the global net fluxes of the methyl halides. First, there

are large areas of the ocean at latitudes within and near the tropics which are not subject to substantial seasonal variations in temperature or light levels. A strong seasonal cycle of methyl halide production in these areas is unlikely. Second, the duration of any event involving elevated emission rates of methyl halides is likely to be short, if the evidence for methyl bromide is considered representative. The extensive data sets on methyl bromide from the present work and those of *Lobert et al.* [1995; 1996; 1997] have found no particular season to be characterized by unusually high methyl bromide levels in water. Any mild seasonal variation which may be present in those data sets must to some degree be already accounted for in a statistical sense, and still the ocean appears to be a net sink of methyl bromide. In addition, the preliminary report by *Baker et al.* [1998b] is of a state of supersaturation of methyl bromide which lasted less than two months. To suggest a rough example, it is apparent that a seasonal cycle which could affect perhaps one third of the ocean for less than one sixth of the year would have to be quite intense in order to change the broad conclusions about the oceanic source of the methyl halides. Finally, *Wingenter et al.* [1998] reported that atmospheric methyl bromide ratios in the northern hemisphere begin to decrease in March, and continue to decrease until well into summer, which is at odds with the idea of a large oceanic emission of methyl bromide to the atmosphere in the spring. Very little evidence exists to assess the possibility of seasonal cycles for methyl chloride and methyl iodide. Studies of the seasonal dependence of all three compounds in ocean waters would improve the flux estimates and provide clues to help deduce the sources of methyl halides within the oceans.

6.2.2 SST as a Proxy Variable

The global fluxes calculated in this study are dependent on the assumption that the observed relationship between sea surface temperature and concentration anomaly is valid globally and in all seasons. This assumption introduces an uncertainty in the estimates which is practically impossible to quantify. Data from other regions and at other times of year are needed to test this assumption and test the uncertainty.

The concentration anomaly of methyl chloride has been observed to increase with SST in this work (Figure 5.4a), and this observation has been used to estimate the concentration anomaly for each grid point in the global flux estimate. There is, however, another implication of the observed trend, which is that absolute methyl chloride concentrations in surface waters are quite uniform in this data set. Because the solubility varies as a function of temperature, if the absolute concentration of methyl chloride in surface waters were constant, the concentration anomaly would be higher in warmer waters than in cold, simply because of the change in solubility. Figure 6.1 is adapted from

Figure 5.4, with concentration anomalies shown as a function of SST, but instead of best-fit curves, contour lines of constant concentration have been added to Figure 6.1. The contour lines are based on average atmospheric mole fractions of 530 ppt, 10.3 ppt, and 0.96 ppt, along with the solubility relationships of *Moore* (submitted to *Chemosphere*, 1998), *DeBruyn and Saltzman* [1997b], and *Moore et al.* [1995] for methyl chloride, methyl bromide, and methyl iodide, respectively.

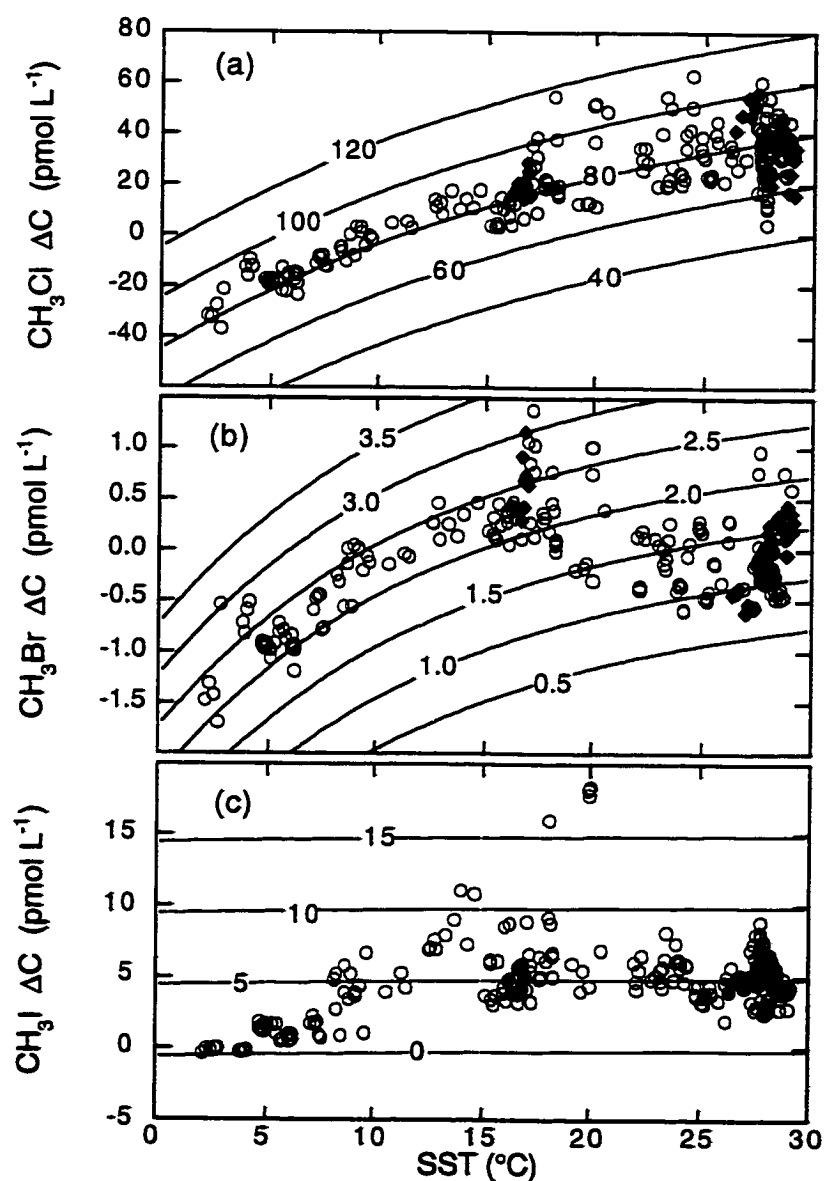


Figure 6.1. Concentration anomaly as a function of SST, with contour lines of absolute concentration shown in pmol L^{-1} . Open ocean data (open circles) and coastal data (solid symbols), for (a) methyl chloride; (b) methyl bromide; (c) methyl iodide.

Nearly all the methyl chloride data points lie between 60 and 100 pmol L⁻¹ (Figure 6.1a), and the majority are clustered between 75 and 90 pmol L⁻¹. Another way to look at this is to note that if the global flux estimate had been based simply on the assumption that methyl chloride concentrations everywhere in the surface ocean are uniform at 85 pmol L⁻¹, the result would not have been greatly different from that based on the quadratic best-fit curve which was used in Chapter 5. There is no apparent *a priori* reason why methyl chloride concentrations should be so uniform. For the other two compounds, this uniformity does not extend over the entire domain. In the temperature range from 0°C to 15°C, most of the methyl bromide data points have quite consistent absolute concentrations between 2.0 and 2.5 pmol L⁻¹. Above 17°C, the concentrations of methyl bromide decrease, and in the high temperature range between 24°C and 28°C, most of the methyl bromide data points are at concentrations between 1.0 and 1.5 pmol L⁻¹.

The contour lines of constant concentration look very different for methyl iodide than for methyl chloride and methyl bromide, and in fact the concentration anomalies of methyl iodide are essentially equal to the absolute concentrations, because the atmospheric concentration is very low. Methyl iodide concentrations appear to rise with temperature from 0 to 15°C, but above 15°C they are clustered around 5 pmol L⁻¹. Given that nearly 75% of the ocean surface area has a temperature greater than 15°C [*Levitus and Boyer, 1994*], an estimate based simply on a constant concentration of 5 pmol L⁻¹ of methyl iodide in seawater and a global average piston velocity of 3.29 m d⁻¹ (Table 5.2) would yield an estimated global flux of 0.29 Tg y⁻¹, which is not greatly different from the estimate of 0.34 Tg y⁻¹ made in Chapter 5.

Of the three compounds, methyl bromide is the most likely to be affected by the uncertainty in using SST as a proxy variable, because its fluxes are the smallest in magnitude, and its concentration is relatively close to atmospheric equilibrium in much of the data set. For example, it is apparent from the methyl bromide concentration anomaly data in Figure 5.4b that both supersaturated and undersaturated samples exist in the temperature range from 20°C to 30°C. Throughout this temperature range, the best-fit curve may predict that a given grid point is a source when it is really a sink, and vice-versa. An important feature of this discrepancy is that, for the temperature range from 20°C to 30°C, the methyl bromide concentration anomalies measured in the Atlantic in July appear to be consistently higher than those measured in the Pacific in October. This is clearly visible in Figure 5.3b, where the Pacific samples in that temperature range are all undersaturated (solid squares), while many of the Atlantic samples are supersaturated (open circles and open triangles). There is no such clear distinction for methyl chloride or methyl iodide. In the future, it may be worthwhile to refine the estimate for methyl

bromide by considering the Atlantic and Pacific separately, perhaps with other divisions for other oceanic regions and several seasons if more data are available.

Methyl bromide is also the only one of the three compounds for which there is evidence in this data set that coastal waters should be considered separately. An adjustment for higher coastal fluxes has been made in this work. However, one issue remains which may affect the global flux estimate for methyl bromide. Based on the observations of supersaturation in water at intermediate temperatures (from 12°C to 22°C), in this study all oceanic areas in this temperature range have been considered to be sources of methyl bromide to the atmosphere. As a result, the ocean area between 30 and 40 degrees of latitude in both hemispheres is predicted to be a source of methyl bromide to the atmosphere, because many of the oceanic grid points between those latitudes have SSTs between 12 and 22°C. However, it so happens that many of the samples in that temperature range were taken either in or near coastal areas, or in regions which could plausibly be affected by currents which interact closely with land masses. Specifically, supersaturated samples in this temperature range were found in the Atlantic in the region between the Gulf Stream and Nova Scotia (both *Hudson* and *Knorr* cruises) and in the Pacific in a region from 1000 nautical miles east of New Zealand, all the way west to the central Tasman Sea on the *Discoverer* cruise. Not all these areas can be considered coastal, and they are also not upwelling zones. In addition, one upwelling zone which was sampled (the equatorial upwelling), did not show any enhancement in methyl bromide concentrations. This demonstrates that the association between coastal or upwelling waters and methyl bromide supersaturation, as proposed by *Lobert et al.* [1995] may not always be true. On the other hand, an extensive database of samples in the intermediate temperature range (12-22°C) from areas which could not plausibly be affected by coastal influences, is lacking in the present work. The possibility cannot be ruled out that open ocean areas in the intermediate temperature range may not all represent sources to the atmosphere, in which case the calculated net sink of methyl bromide from the atmosphere would be larger by as much as 7 Gg y⁻¹, and would agree more closely with the estimate of *Lobert et al.* [1997]. This uncertainty could be resolved by further sampling in open-ocean areas at intermediate temperature.

One step in the evaluation of the empirical relationship between concentration anomaly and SST is to determine whether this relationship is seen in other data sets. The extensive data on methyl bromide partial pressures collected by *Lobert et al.* [1995; 1996; 1997] are publically available, and were obtained with the assistance of J. H. Butler. The merged data sets are shown in Figure 6.2. The set of data collected by *Lobert et al.* [1995; 1996; 1997], hereinafter referred to as the Lobert data set, includes samples from

BLAST'94 (a transect of the eastern Pacific from 45°N to 50°S), BLAST2 (a transect covering a similar latitude range on the Atlantic), and BLAST III (a voyage on the southern ocean from McMurdo Station, Antarctica, to Punta Arenas, Chile). The data set from the present work, which was shown in Chapters 4 and 5 of this thesis, will be referred to as the Groszko data set. All of the data in the Lobert data set are shown in Figure 6.2a, along with the best fit line which was calculated for the Groszko data set in Chapter 5 (Figure 5.4), in order to show that the Lobert data set is not inconsistent with the general form of the relationship between ΔC and SST which has been used in the flux estimate.

Figure 6.2b includes all the data from both the Lobert and Groszko data sets, and a new fourth order polynomial curve which is fit to all the data. The Groszko data set is represented by (+) symbols. Visual inspection of Figure 6.2b reveals that the data sets are quite similar in their general pattern, but there are some differences. There are points from the Lobert data set in the region between 7 and 10°C which are supersaturated ($\Delta C > 0$), where the Groszko data set shows undersaturation. Also, in the temperature range from 17 to 25°C, the Lobert data set generally has lower saturation anomalies than the Groszko data set. This is perhaps more visible in Figure 6.2a, where the points in the Lobert data set between 17 and 25°C appear to be in greater number below the (Groszko) curve fit than above.

Figure 6.2c shows three different fourth-order polynomials which are the best-fit lines to the Groszko data set (dotted line), the Lobert data set (dashed line), and combined set of all the data (solid line). The differences outlined above are apparent in Figure 6.2c, especially the lower concentration anomaly predicted by the Lobert data set between 20 and 28°C. One other apparent difference is that the best-fit curves of the Lobert data set and the combined data set both predict supersaturation at very high temperatures (28 to 30°C). It is important to note that for this comparison the Lobert data set and the combined data set have been taken whole, without filtering out any coastal samples. Considering the increase in methyl bromide loss rate with temperature [Jeffers and Wolfe, 1996], the prediction of supersaturation at very high temperature seems unlikely to be generally true for the open ocean. The shape of the curves in this high-temperature range may be unduly influenced by coastal data points. In addition, the Lobert data were collected at a much higher frequency of sampling, so there are many more data points in the Lobert data set, although the ocean areas represented by the two data sets are similar in size. If the data were weighted in some way, such as by length of cruise track, the influence of the Groszko data set would be more significant. However, in this simple treatment it suffices to treat all the data points with the same weight. The functional form

of the curves is given by Equation 5.6. The best-fit constants of methyl bromide for the Groszko, Lobert, and combined data sets are given in Table 6.2.

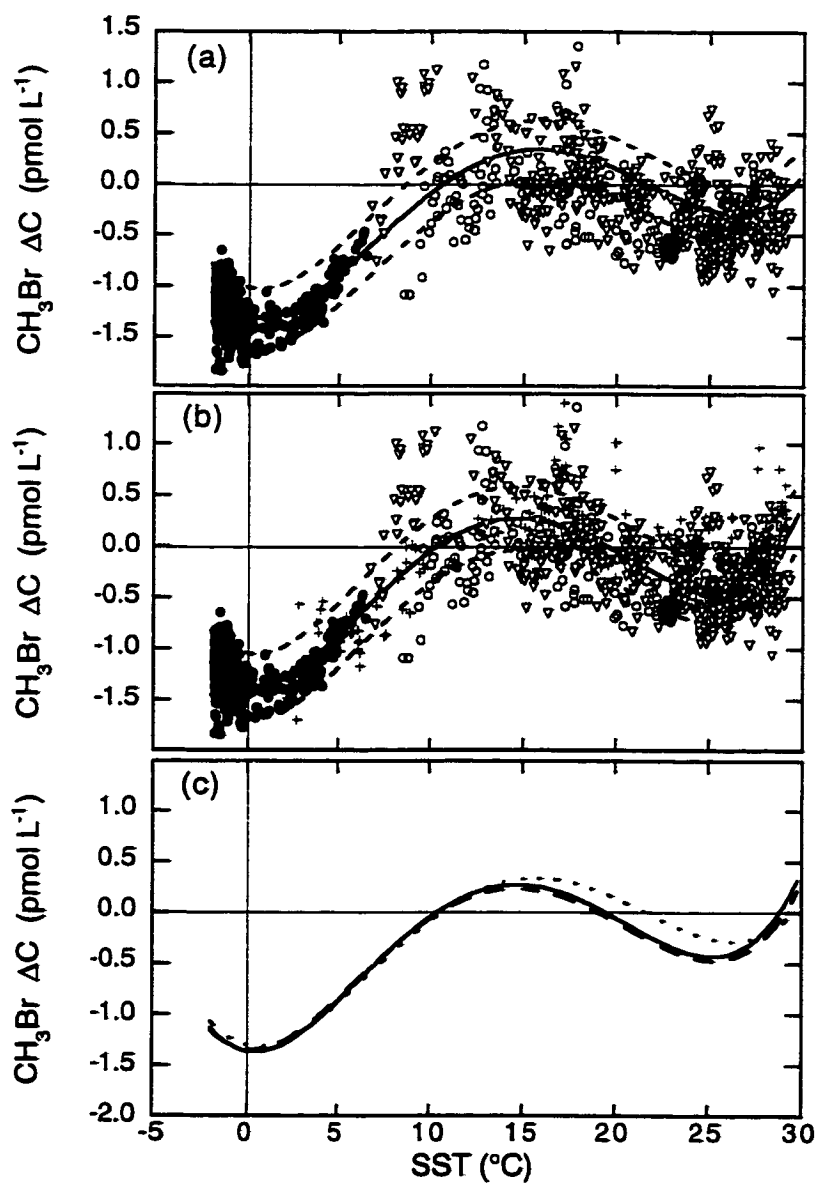


Figure 6.2. Concentration anomalies of methyl bromide as a function of SST, for (a) data of Lobert *et al.* [1995; 1996; 1997], from the Pacific (open circles), Antarctic (solid dots), and Atlantic (open triangles), with curve fit and standard deviation from Figure 5.4b of this thesis for comparison; (b) same as (a) with the addition of the data from this thesis (+ symbols) and a new curve fit to all the data; (c) curve fits to the data of this thesis (dotted line), Lobert *et al.* [1995; 1996; 1997] (dashed line), and all data combined (solid line).

$$\Delta C = a + bT + cT^2 + dT^3 + eT^4 \quad (5.6)$$

Table 6.4. Best-fit constants (Equation 5.6) for methyl bromide.

| Data set | a | b | c | d | e | R ² | s* |
|------------------|--------|---------|---------|-----------|----------|----------------|-------|
| Groszko | -1.303 | -0.0398 | 0.03456 | -2.231E-3 | 3.916E-5 | 0.80 | 0.287 |
| Lobert | -1.343 | -0.0171 | 0.03394 | -2.388E-3 | 4.453E-5 | 0.76 | 0.308 |
| all of the above | -1.358 | -0.0287 | 0.03666 | -2.543E-3 | 4.728E-5 | 0.76 | 0.313 |

* s is the standard deviation of the curve fit in pmol L⁻¹

The global air-sea flux calculation for methyl bromide, as described in Section 5.4.2, was repeated with the best-fit curve for all the data in the combined data set, using piston velocities calculated by the formula of *Wanninkhof* [1992]. The result was a net sink of about 10 Gg y⁻¹ from the atmosphere, with a range of 7 to 13 Gg y⁻¹ based on the 95% confidence interval of the curve fit. The equivalent calculation, based on the Groszko data set alone, resulted in a similar net sink of about 8 (6 to 10) Gg y⁻¹ (Table 5.3).

The calculation of the net air-sea flux of methyl bromide could be refined by taking the existing combined data sets and using a more sophisticated algorithm for estimating the concentration anomaly at each oceanic grid point. An appropriate method would be to sort the entire combined data set into categories such as coastal waters, upwelling zones, open ocean gyres, and different seasons where possible. Each grid point in the ocean would then be assigned to a category, and the concentration anomaly in each category would be predicted based on the available data for that category. For example, the open ocean gyres and cold, high-latitude waters have a substantial data set associated with them, and a predictive equation based on temperature, such as Equation 5.6, could be used to estimate concentration anomalies for grid points within those categories. Once the estimated concentration anomalies were established, the piston velocity calculated from the climatological wind speed would be used to determine the flux associated with each grid point. The global flux estimate would then proceed as in section 5.4.2. This would be the most comprehensive and thorough means to estimate the net global air-sea flux of methyl bromide, and would result in the best possible estimate from the existing data. However, the result would very likely be quite similar to the estimates already put forward in this work and by *Lobert et al.* [1995; 1997], namely a net sink somewhere between 7 and 30 Gg y⁻¹. Sorting the concentration anomaly data into categories, and sorting the oceanic grid points into the same set of categories, would require a

considerable investment of time, and may not be worth the effort, especially considering that a large part of the uncertainty comes from the piston velocity and cannot be reduced by this method.

It should be noted that, while the reliance on observed relationships between SST and concentration anomaly does introduce some unquantified uncertainties into the flux estimates, these uncertainties are not worse than those introduced by other methods of extrapolation, such as averaging fluxes or averaging concentrations.

6.3 Where Are the Missing Sources of Methyl Halides to the Atmosphere?

For methyl chloride and methyl bromide, the current budget estimates are significantly unbalanced, with sinks exceeding sources. Unless the magnitudes of the known sources are considerably underestimated (and/or the sinks are considerably over-estimated), it seems there must be other sources to the atmosphere which are not in the mixed layer of the ocean. One obvious place to look for other sources is in the terrestrial environment. Other possibilities exist, including the marine atmosphere and the surface microlayer at the interface between the atmosphere and the ocean. These possibilities are discussed below.

6.3.1 Sources from the Terrestrial Environment

Sources from the terrestrial environment appear to be lacking in the budgets shown in Tables 6.1 and 6.2. Given the report of methyl iodide production by rice plants [Muramatsu and Yoshida, 1995], it is worthwhile to investigate potential terrestrial sources of methyl chloride and methyl bromide, such as emission by higher plants. Preliminary work has been reported by Rhew *et al.* [1997], in which air measurements were made within the desert, savanna, and tropical rain forest biomes of the Biosphere 2 research facility. The Biosphere 2 facility is enclosed in glass, which absorbs ultraviolet radiation and consequently prevents the production of OH radicals in the air inside the enclosure, thus reducing the atmospheric loss rates of methyl chloride and methyl bromide. This, coupled with the low ratio of air volume to land area, magnifies the effect of any production or consumption by the terrestrial ecosystems in Biosphere 2. Rhew *et al.* [1997] found significant and rapid changes in methyl chloride and methyl bromide concentrations within the enclosures of Biosphere 2. For methyl bromide, the positive and negative fluxes implied by these changes were comparable in magnitude to the soil consumption estimates of Shorter *et al.* [1995], and could indicate significant terrestrial sources and sinks. The results from different biomes varied widely, with dry

environments favouring production of methyl chloride and methyl bromide, and wet environments favoring consumption. In flux chamber studies, desert vegetation was found to be a net source of methyl bromide, while desert soils were a net sink. Flux chamber studies conducted in the natural environment outside the Biosphere 2 facility also revealed production of methyl bromide by plants. Global extrapolations of the net desert sources from the enclosure studies did not balance the global budget of methyl bromide, but the sources and sinks were significant, and further field studies are required to determine the magnitudes and variabilities of fluxes in the terrestrial environment.

The finding by *Rhew et al.* [1997] that terrestrial plants can be significant producers of methyl bromide has an interesting implication for the anthropogenic source of methyl bromide from soil fumigation. When methyl bromide is injected into soil, a significant (and variable) fraction escapes to the atmosphere on the time scale of a few days, and the rest is degraded in the soil [*Yagi et al.*, 1995]. The degraded fraction is thought to eventually produce bromide ions, and by measuring the increase in bromide ions in soil after fumigation, *Yagi et al.* [1995] obtained a reasonably good mass balance between the total bromine injected as methyl bromide and the sum of the bromine lost to the atmosphere in methyl bromide plus the increase in bromide ions in the soil. Fumigation of soil with methyl bromide could thus be considered a bromide-enhancement experiment, and in fact soil bromide concentrations were observed to be three to five times higher in soils after fumigation than before [*Yagi et al.*, 1995]. Crops are grown in such soils after fumigation, and several common crop plants of the *Brassicaceae* family (cabbage, broccoli, rapeseed, etc.) reportedly emit methyl bromide [*Gan et al.*, 1998]. The rate of methyl bromide emission by growing *Brassica* plants was found to increase with increasing soil bromide concentration [*Gan et al.*, 1998]. The clear implication is that the loss of anthropogenic methyl bromide in fumigated soils may not be so much a loss as a delay in emissions to the atmosphere. As crop plants grow in soils which have elevated bromide ion concentrations because of previous soil fumigation, it is logical to expect that their methyl bromide emissions will be higher than if the soil had not been fumigated. Of course, it is rather unlikely that all the excess bromide resulting from fumigation will be methylated and emitted to the atmosphere, since it can also be transported in the soil to depths below the root systems of crop plants, and it may become incorporated into molecules other than methyl bromide. Nevertheless, methylation by plants has the potential to increase the anthropogenic source term for methyl bromide. Simple field and laboratory experiments could be designed to determine the magnitude of this source. Controlled laboratory experiments, such as those of *Gan et al.* [1998], where more varieties of crop plants are grown in soil enhanced in bromide ions would reveal the

potential for methyl bromide production and its dependence on the bromide ion concentration. Flux chamber studies in the field could focus on measuring relative emissions from crops grown in fumigated and unfumigated soils, or simply in soils with varying bromide ion concentrations.

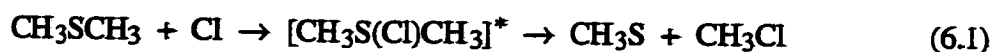
There is an obvious upper limit for the anthropogenic portion of any emissions from crops. In the current estimate, about half of the methyl bromide used in soil fumigation is assumed to escape to the atmosphere. If the other half were methylated by plants and emitted to the atmosphere as methyl bromide in the course of one growing season, the anthropogenic source estimate would increase by about 28 Gg y⁻¹. This is an extreme upper limit, is unlikely to be reached in reality, and still would not result in a balanced budget for methyl bromide. The total source would be 105 Gg y⁻¹, compared with a sink of 136 Gg y⁻¹.

A proposed source of methyl chloride in the terrestrial environment is that from wood-rot fungi, which were estimated to contribute 0.16 Tg y⁻¹ [Watling and Harper, 1998]. As noted before, there are no field studies to verify this source, and the authors consider their estimate to be conservative. Field studies of emissions from rotting wood in the terrestrial environment are needed to substantiate and further quantify this source. In general, more field studies of net emissions from terrestrial ecosystems are needed to determine the effect of the terrestrial biosphere on the atmospheric budgets of methyl chloride and methyl bromide.

6.3.2 Sources in the Marine Atmosphere

Several possible mechanisms for *in situ* atmospheric chemical and photochemical production of halocarbons were considered by Graedel and Allara [1976], who concluded that significant *in situ* production of any of the halocarbon species by atmospheric reactions is unlikely. The main production mechanisms they considered center around reactions of chlorine atoms (Cl) with methyl radicals (CH₃) and various hydrocarbons. More information on the concentrations of various radical species is currently available, and possible atmospheric production mechanisms for methyl chloride are again under investigation.

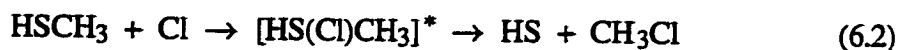
The reaction of Cl with dimethyl sulfide (DMS) has been demonstrated to produce methyl chloride [Langer *et al.*, 1996]. The same authors reported the most likely mechanism to be:



The experimental yield of methyl chloride from the reaction of DMS with Cl was found to be $0.134 \pm 0.007\%$. DMS is emitted to the atmosphere by the oceans, and total emissions of DMS to the atmosphere may contribute as much as 35 Tg of sulfur to the atmosphere per year [Andreae, 1990]. The amount of methyl chloride which could be produced globally by reaction 6.1 was estimated by Langer *et al.* [1996] from the experimental yield, the upper limit of the DMS source strength, and the relative rates of DMS reactions with Cl and its other principal reactants, OH and NO₃. This analysis suggested that only 0.01 to 0.07 Tg of methyl chloride could be produced annually by this reaction, which is only 2% or less of the global atmospheric methyl chloride sink.

A recent report of unexpectedly high marine atmospheric concentrations of molecular chlorine (Cl₂) (which photolyses to Cl in the daytime), adds weight to the idea that chlorine atoms are an important reactive species in the marine troposphere [Spicer *et al.*, 1998]. An apparently unrecognized source produces up to 330 ppt of Cl₂ per day in marine air. Photochemical production of Cl₂ in the presence of ozone and aqueous sea-salt particles has been demonstrated [Oum *et al.*, 1998], but a photochemical mechanism cannot account for the fact that Cl₂ concentrations in marine air have been observed to increase at night [Spicer *et al.*, 1998]. These recent reports do not change the conclusion that production of methyl chloride from DMS is insignificant, because the daytime Cl concentrations implied by the report of Spicer *et al.* [1998] are included in the range of possible Cl concentrations considered by Langer *et al.* [1996] in their global methyl chloride production estimate.

The chlorine atom reacts rapidly with many atmospheric molecules including hydrocarbons [Spicer *et al.*, 1998]. There are several reactions which could produce methyl chloride, but it is difficult to propose a mechanism which is likely to produce globally significant amounts under normal atmospheric conditions. A few examples of reactions which seem unlikely to be significant are shown below. The first of these is analogous to the DMS reaction studied by Langer *et al.* [1996], but with methanethiol:



Methanethiol (HSCH₃) is produced in seawater from dimethylsulfoniopropionate (DMSP) [Kiene, 1996]. Its source strength from the ocean to the atmosphere is much smaller than that of DMS, because it is rapidly destroyed in seawater [Kiene, 1996]. Regardless of the availability of methanethiol, reaction 6.2 appears unlikely to occur to any significant extent, because the S-H bond in methanethiol seems more likely to be the site of attack by Cl, resulting in the following reaction and no methyl chloride production:



Methyl radicals (CH_3) react quickly with either Cl [Graedel and Allara, 1976], I [Moore and Zafiriou, 1994], or I_2 [Ree et al., 1997], to form methyl chloride or methyl iodide, and presumably would react quite quickly with Cl_2 or Br_2 to form methyl chloride or methyl bromide as well. The key problem with reaction mechanisms involving CH_3 is that reactions with oxygen dominate its removal in the O_2 -rich environment of the atmosphere, thus limiting its participation in other reactions, as was pointed out by Graedel and Allara [1976].

None of the gas-phase reactions found in a preliminary overview seems likely to result in globally significant production of methyl chloride, and it is beyond the scope of this thesis to undertake a comprehensive analysis of all the potential reactions. Nevertheless, gas phase or heterogeneous reaction mechanisms may exist which could produce methyl chloride and methyl bromide in the atmosphere, and this may be a fruitful area of future research. On the other hand, it should be noted that the observations of elevated reactive chlorine in marine air [Spicer et al., 1998] imply that the total sinks of methyl halides may be higher and their lifetimes shorter, as Cl reacts quickly with methyl halides to produce HCl and CH_2X .

6.3.3 Sources in the Surface Microlayer of the Ocean

Brief mention will be made here of the possibility that, if a large production rate of methyl halides were located in the top few molecular layers at the surface of the ocean, it seems plausible that the methyl halides produced there would be preferentially emitted to the atmosphere rather than diffusing through the surface microlayer in the liquid phase to be mixed into the water column. The implication is that an enhanced production rate right at the very surface of the ocean could create a flux to the atmosphere which would not be accounted for in measurements of the bulk concentration in the water column. No guesses will be ventured here as to a mechanism which could cause production specifically at the ocean surface, but the surface is apparently different from the bulk seawater in several ways. The surface is directly affected by atmospheric oxidants such as ozone, and also accumulates surface-active species.

It should be noted that, because methyl chloride is a surface active compound which adsorbs at the surface of water [Chiang and Toor, 1960], an excess surface concentration can exist in the top molecular layer of water even when concentrations in the two bulk phases are at equilibrium. Chiang and Toor [1960] used measurements involving methyl chloride and pure water, along with mass-transfer models, to show that the flux is adequately determined by the bulk concentration difference and the exchange coefficient, and the excess surface concentration due to adsorption at the surface can be ignored for

the purpose of flux calculations. These considerations can likely be assumed to extend to seawater and to the other two methyl halides.

6.3.4 Urban Sources

There have been at least two reports of elevated levels of methyl chloride in urban air [Singh *et al.*, 1979; 1982], but no estimates of the potential global source implied by those levels. There appear to be no recent studies of methyl halide concentrations in urban air. For methyl chloride, any emission from cities would have to be a relatively small term in the global budget, because emissions in urban air would be weighted towards the northern hemisphere. On average, over the course of a year, methyl chloride may be slightly higher in the northern hemisphere than in the southern hemisphere (R. F. Weiss, unpublished data), but not to the extent that one would expect if emissions were primarily anthropogenic, so it is unlikely that emissions are predominantly in the northern hemisphere. However, for methyl bromide a significant source in cities (besides combustion of leaded gasoline) would at least not conflict with the observed hemispheric distribution.

An apparently little-known potential source reaction for methyl bromide is the reaction of methyl radicals with Halon 1301:



This reaction does not occur at room temperature, but Halon 1301 is used as a fire suppressant, and elevated concentrations of methyl radicals and high temperatures increase the rate of reaction 6.5 under the conditions of a fire [Berry and Marshall, 1998]. There are no reports of methyl bromide emissions from fires in buildings with Halon fire suppression systems, and the overall impact of this reaction is likely to be insignificant on the global scale, particularly since most Halons have been released to the atmosphere through periodic testing of firefighting systems, not during fires.. The example is included to give an idea of the variety of possible sources which remain unexplored.

6.3.5 Summary

Overall, there are several possibilities for unidentified sources which could help balance the atmospheric budgets of methyl chloride and methyl bromide. Of the possibilities discussed above, the terrestrial biosphere seems to be the most likely candidate. In the case of methyl chloride, it should also be emphasized that measurements in the Southern Ocean are lacking in this study. It is possible that the Southern Ocean represents a large source of methyl chloride. However, in the absence of evidence to the

contrary, cold waters are assumed to be undersaturated in methyl chloride in both hemispheres.

6.4 Methyl Halide Production in the Ocean

Methyl halides have been shown to be produced in several different ways, as outlined in Chapter One. Photochemical production of methyl iodide has been demonstrated in laboratory experiments [Moore and Zafiriou, 1994], and seaweeds and marine phytoplankton have been shown to produce all three methyl halides in culture [Manley and Dastoor, 1987; 1988, Manley and de la Cuesta, 1997; Scarratt and Moore, 1996; 1998, Sæmundsdóttir and Matrai, 1998]. The rates of production by macroalgae and microalgae which have been observed in culture, when scaled to the global ocean on the basis of biomass or chlorophyll, have not been sufficient to account for the global production implied by the combined *in situ* loss rates and atmospheric fluxes. The work of this thesis is focused on air-sea fluxes, not production rates and mechanisms in the ocean. Nevertheless, the data collected in this work provide evidence from which some comments can be made on the production of methyl halides in surface ocean waters.

6.4.1 Depth Profiles

The small number of depth profiles collected during the course of the present work demonstrate the existence of subsurface maxima in methyl halide concentrations just below the mixed layer in the Sargasso Sea. These maxima are located just below the mixed layer, at depths coinciding with a subsurface maximum in oxygen concentration (see Figures 4.6 through 4.10).

One very likely explanation for the subsurface maximum of methyl chloride is simply the relationship between the depth of the zone of production and the depth of the mixed layer. Methyl chloride will be discussed here as an example because it has the most pronounced subsurface maxima, and therefore any consequences of these observations apply most strongly to methyl chloride. The layer of the water column in which methyl chloride production occurs will be referred to as the production layer, and the mixed layer will be defined as usual to mean the upper layer of the water column in which density is uniform. The profiles collected in the Sargasso Sea in this work showed a sharply defined mixed layer with a depth of about 41 m. For simplicity, the production layer will be assumed to extend from the surface to some depth. Methyl chloride production could vary throughout this depth, but it is clear that there is some depth below which no significant production occurs, because the concentrations fall towards zero. Little is

known, generally, about the maximum depth of production or any variation in the production rate with depth in the production layer. In the profiles collected in the present study, production seems to occur at least down to depths of 50 m, and perhaps as deep as 75 m.

Several of the possible production mechanisms for methyl chloride may be consistent with the observation of production down to depths on the order of 75 m in oligotrophic Sargasso Sea waters. If the process is due to phytoplankton, either directly or through reactions on algal exudates, the zone of production may extend to the depth of the euphotic zone, which could reasonably be 75 m deep in the Sargasso Sea in August. Unfortunately, no measurements of light intensity, chlorophyll, or primary production are available to go along with the depth profiles, but the subsurface maximum in oxygen is suggestive of photosynthetic activity down to 60-75 m depth. Alternatively, if methyl chloride production is a photochemical process involving reaction of radicals produced through UV absorption by chromophoric dissolved organic matter (CDOM), then the depth of production could depend primarily on the attenuation coefficient of the water at the maximum wavelength of the action spectrum. The variation of the absorbance of CDOM and the availability of the reactants with depth would also be important. If the wavelengths important to the reaction are in the UV-A region, it seems feasible that photochemical production could extend to 75 m depth in clear, oligotrophic waters in the open-ocean gyres.

The mixed layer is caused by mixing of the water due to wind and waves, so the mixed layer depth depends on the history of wind stress at the surface over a time scale of weeks, as well as the heat flux at the surface, which can drive stratification or mixing. The mixed layer is generally deeper in seasons when there are higher winds, more storms, and lower air temperatures. Three possible scenarios for the relationship between the depths of the mixed layer and the production layer are shown in Figure 6.3:

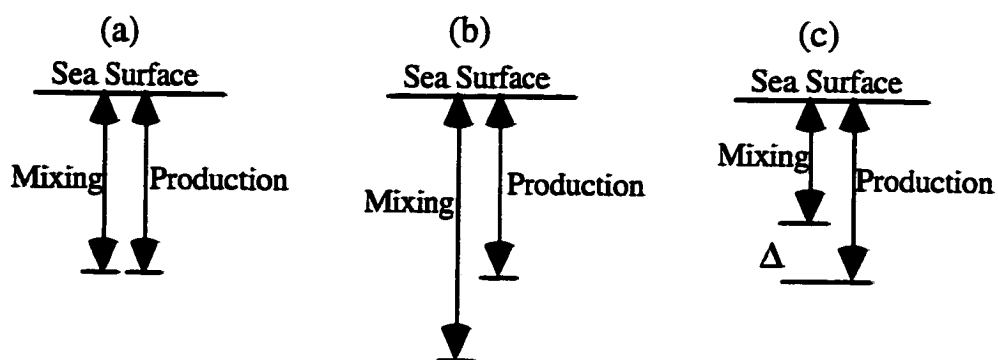


Figure 6.3. Relative depths of mixing and methyl halide production.

In scenario (a) (Figure 6.3a), where the depths of mixing and production are equal, at steady state the total production will equal the sum of the fluxes to the atmosphere and to deeper water. It is assumed here that *in situ* loss of methyl chloride is slow, since the lifetime of methyl chloride against hydrolysis is on the order of one year or more in seawater [Tait, 1995]. It is also assumed that methyl chloride is supersaturated with respect to atmospheric equilibrium, which is true of all the warm-water samples taken in the Sargasso Sea. In order to isolate the effect of the mixed layer depth, in this argument the total production rate is assumed to be equal in the three scenarios (Figure 6.3 a, b, and c). In scenario (b) the mixed layer extends deeper than the production layer. It might appear that this could result in lower concentrations in the mixed layer and consequent lower fluxes, but at steady state the total production would still match the same total losses. On the reasonable assumption that the diffusion coefficient through the bottom of the mixed layer is still the same in scenario (b), the steady state concentration and atmospheric flux are the same in (b) as in (a).

There is, however, a difference in scenario (c), with the mixed layer shallower than the production layer. In (c), some of the production is "trapped" below the mixed layer because transport through the mixed layer boundary (the pycnocline) is slow on account of the steep density gradient. Coefficients for diffusion processes carrying methyl chloride out of the region Δ (below the mixed layer but within the production layer) are slower than those for transport in the mixed layer. The concentration will build in the region Δ until the concentration gradients are sufficient to cause transport which can equal the production. This is a plausible explanation for an observed sub-surface maximum in the pycnocline, which does not require elevated production rates in that area. If this explanation is true for the depth profiles recorded in the current study, then clearly the Sargasso Sea stations are represented by scenario (c). It is potentially important, then, to note that scenario (c) implies a smaller flux to the atmosphere than either (a) or (b). This is because the diffusion coefficient for downward mixing must increase with depth below the pycnocline, which is clear from the density profile. The simplest way to see the effect of this is to ignore concentration gradients within the production layer and consider the production layer as one box, with losses due to fluxes out the top and bottom. At steady state, the total loss rate is equal in all three scenarios because it is equal to the total production rate. The diffusion coefficient for loss out the bottom of the box is larger in scenario (c) than for the other two, so the probability of downward escape is larger in scenario (c), and the atmospheric flux is smaller.

A quantitative treatment of the magnitude of this difference would be difficult to construct without accurate data on eddy diffusion coefficients at various depths. In addition, the constructed model of Figure 6.3 is exceedingly simplistic, since real production rates could vary with depth. In addition, fluctuations of the mixed layer depth can be episodic due to mixing caused by storms which occur on timescales too short to allow the steady state to be established. In a qualitative sense, it is clear that general conditions where the mixed layer is deeper than the production layer would tend to result in higher fluxes to the atmosphere if the production rate is constant. This means, for example, that in areas where there is a broad seasonal cycle in the depth of the mixed layer, samples taken only in the season of shallowest mixed layers could yield an underestimate of the flux of a supersaturated compound such as methyl chloride to the atmosphere. It should be noted that this simplistic treatment ignores changes in the *in situ* loss rates which may be caused by temperature changes due to mixing.

It may also be important to consider that deepening of the mixed layer could change the production rate. In nutrient-limited situations common to mid-ocean gyres, deepening of the mixed layer due to a storm will entrain a fresh supply of nutrients and increase the rate of biological activity in the upper water column. If methyl halide production is positively related to biological activity, the production rate would increase under these circumstances. Simultaneously, any subsurface maximum which had developed over the time preceding the storm would be mixed into the surface layer and the surface concentration would be increased. That, coupled with high wind speeds, could result in very high fluxes over the short term, supplied from reserves which might otherwise have been lost to deeper waters. On the other hand, the existence of an extremely deep mixed layer could reduce overall biological activity by keeping phytoplankton below the euphotic zone for longer periods. It is clear in these considerations that the mass balance must be maintained - over the annual time scale no more methyl chloride can be transported out of the ocean than is produced there. However, any event which tips the balance of fluxes towards the atmosphere at the expense of irretrievable losses to deep waters will enhance the annual flux.

6.4.2 Production of Methyl Chloride from Methyl Bromide and Methyl Iodide

Both methyl bromide and methyl iodide react with chloride ions in seawater to produce methyl chloride, and the rates of these two substitution reactions increase strongly with temperature [Elliott and Rowland, 1993]. It is therefore worthwhile to investigate the potential importance of these sources of methyl chloride in the ocean. The integrated production rate of methyl chloride from these sources in the water column can

be estimated based on the depth profiles of methyl bromide and methyl iodide. As an example, the depth profiles at Station 1 in the Sargasso Sea at 25°N latitude and 66°W longitude will be considered as a case study. SST at this station is 29.2 °C, the mixed layer depth is about 41 m, and the layer of production of methyl chloride will be taken to extend to about 60 m, to include the maximum concentration seen at 50 m. For the purpose of this example, consider the production of methyl chloride in a column of water 60 metres deep, with a surface area of one square metre. The average temperature in the layer from zero to 60 m is 28.3°C. From the total amounts of methyl bromide and methyl iodide in the production layer and their respective chloride substitution rate constants [King and Saltzman, 1997; Elliott and Rowland, 1993], the total production of methyl chloride in the 60 m water column has been calculated and included in Table 6.5.

For reference, the air-sea fluxes have also been calculated for the three methyl halides, based on the concentration difference from atmospheric equilibrium at the surface and the piston velocity calculated from two different available wind speeds, with the formula of Wanninkhof [1992]. The two wind speeds used were u_{clim} , which is the monthly averaged climatological wind speed for that location August from the COADS data set [Woodruff *et al.*, 1987], and u_{ship} , which is the arithmetic mean of 1440 spot measurements of wind speed from the ship's anemometer, taken at one minute intervals throughout the day on which the profiles were sampled. The values of these two different average wind speeds are different, and the non-linear dependence of the piston velocity on wind speed contributes to a marked difference in the calculated flux. These were the only two types of mean wind speed available to apply to this calculation, and unfortunately neither is the most appropriate wind speed. The depth profiles are like a snapshot of the results of processes which act on the water column over a time scale of about ten days, so the most correct wind speed would be the average (and ideally the distribution) over that parcel of water in, say, the past ten days. However, since this is unavailable, the average wind speed on the day of sampling is probably more representative than the climatological wind speed. There is, however, a potential technical problem with the wind speeds from the ship's anemometer, which is that it is not apparent in the data set whether they were measured at (or corrected to) a height of 10 m above the sea surface, which is the standard height of wind speeds for use in flux calculations. Since wind speed generally increases with height, the fluxes based on u_{ship} may be an overestimate. However, the purpose of this exercise is simply to estimate whether the production of methyl chloride from the other two methyl halides could be a significant source to help maintain the atmospheric flux of methyl chloride. For this purpose, a fairly approximate flux will suffice. The air-sea fluxes of all three methyl halides are shown in Table 6.5, with fluxes

into the atmosphere defined as positive. The fluxes and production rates are given in nmol d^{-1} , and apply to a unit area of one square metre of sea surface.

Table 6.5. Fluxes of methyl halides and production rates by chloride ion substitution.

| | ΔC (nmol m^{-3}) | k (m d^{-1}) | | Atmospheric flux (nmol d^{-1}) | | Column amount (nmol) | k_{Cl^-} (d^{-1}) | CH_3Cl production (nmol d^{-1}) |
|--------------------|--|----------------------------|-------|--|-------|---------------------------------------|--|--|
| | | clim* | ship† | clim* | ship† | | | |
| Methyl chloride | 49 | 2.94 | 5.03 | 144 | 246 | 11300 | - | - |
| Methyl bromide | -1.2 | 2.90 | 4.96 | -3.5 | -6.0 | 45 | 0.260 | 12 |
| Methyl iodide | 8.0 | 2.75 | 4.71 | 27 | 38 | 675 | 0.122 | 83 |

ΔC = concentration difference from atmospheric equilibrium at the surface (nmol m^{-3})

k = piston velocity (m d^{-1})

*clim = based on climatological wind speeds (see text)

†ship = based on arithmetic mean of wind speeds measured by the ship's anemometer

Column amount = total number of nmoles of the compound in 60 m column $\times 1 \text{ m}^2$

k_{Cl^-} = rate constant of chloride ion substitution at $[\text{Cl}^-] = 0.546 \text{ mol L}^{-1}$

The key point to note is that the total methyl chloride production from the two substitution reactions is 95 nmol d^{-1} , which is 39 to 66% of the atmospheric flux of methyl chloride (144 to 246 nmol d^{-1}). This indicates that chloride ion substitution on methyl iodide and methyl bromide were significant sources of methyl chloride at this station. However, the calculation made here is an overestimate of the contribution of these reactions to the atmospheric flux of methyl chloride, because that part of methyl chloride produced below the mixed layer has a lower probability of reaching the atmosphere. Also, the temperature of the mixed layer at this station was very high (29°C), which results in above-average loss rates of methyl iodide and methyl bromide. Another calculation of the average production rate of methyl chloride from methyl iodide at a set of stations in the central Pacific was much lower ($15 \text{ nmol m}^{-2} \text{ d}^{-1}$) [Moore and Groszko, 1999], so the case-study in the present thesis is apparently unrepresentative of general conditions, but could apply to the warmest areas of the Sargasso Sea. The substitution reaction rates decrease at lower temperatures, so these reactions become insignificant in cold, high-latitude waters. Even at the high temperature of station I from this case study, there are clearly other sources of methyl chloride in addition to these reactions. The remainder of the atmospheric flux of methyl chloride, along with downward mixing and

the loss to hydrolysis, still need to be supplied. In addition, the production of methyl chloride from the other two methyl halides cannot be said to be fully explained, because the origins of methyl bromide and methyl iodide themselves are still poorly understood.

Some of the observations of methyl halide distributions in this work are qualitatively consistent with the idea that significant source terms are temperature-dependent. For example, the observation that methyl chloride concentrations are fairly constant over a wide range of temperatures (Figure 6.1a) is consistent with the idea that two temperature-dependent processes are acting against each other. The air-sea flux (a significant loss term from the ocean pool) tends to increase with increasing temperature, due to changes in both the solubility and the Schmidt number. If a significant source term (such as the reaction of methyl iodide with chloride ions) also increases with increasing temperature, then it is plausible that the concentration could be fairly constant over a range of temperatures. For methyl bromide, the concentration drops off at high temperatures, which could simply be interpreted as due to the great increase in the rate of the chemical loss reactions.

The distribution of methyl iodide in surface seawater in the present study is at least qualitatively consistent with the idea of photochemical production of methyl iodide. Methyl iodide concentrations in surface waters were significantly lower at high latitudes than at mid-to-low latitudes, which could be attributed to lower light intensities. *Happell and Wallace* [1996] reported undersaturation of methyl iodide at high latitudes, which was not seen in the current work. However, all the measurements at high latitude in this work are in the summer, when light levels are at their seasonal peak, whereas *Happell and Wallace* [1996] made their measurements in the dark of winter on the Greenland/Norwegian Sea. Overall, there is nothing in this data set which conflicts with the possibility that photochemical production of methyl iodide is a significant process.

6.5 Directions for Future Work

There are several ways in which the global air-sea flux estimates of the methyl halides could be improved. With the data sets that already exist, it would be beneficial to make flux estimates based on combining data sets from other researchers with the data collected for this thesis. One shortcoming of the present work is a lack of data from the southern ocean. For methyl iodide, this could be addressed by a combined estimate which includes the data of *Reifenhäuser and Heumann* [1992] to represent the Southern Ocean. The methyl iodide data collected by *Happell and Wallace* [1996] could also supplement the data set. For methyl chloride, no extensive data set appears to have been published for

the Southern Ocean, although methyl chloride was sampled by *Lobert et al.* [1997] along with methyl bromide (J. M. Lobert, personal communication). For methyl bromide, considering only the data of *Lobert et al.* [1995; 1996; 1997] and the data in the present work, a combined data set of over 1400 points exists, which could be used to make a more refined flux estimate, as outlined in Section 6.3.1 above. However, a flux estimate from the combined data set is not likely to yield a substantially different result from those already given in this work and the work of *Lobert et al.* [1995; 1996; 1997].

If any more data on surface partial pressures are to be collected, they should focus on the southern ocean for methyl chloride and methyl iodide. For methyl bromide, the question of whether waters of intermediate temperature in the open ocean are a source or a sink remains unresolved. In order to resolve this issue, it would be best to measure methyl bromide in open ocean areas at temperatures between 12°C and 22°C, far from the influences of upwelling and land masses. Two appropriate candidate areas could be in 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. For all three compounds, temporal studies of seasonal trends of surface concentration are lacking. A study of a coastal and an open ocean site over a period of two years would be useful in establishing the seasonal cycle of methyl halide concentrations in surface waters.

The observation of subsurface maxima in methyl halide concentrations in the water column, and the arguments in Section 6.1.4 on the relevance of the depth of the mixed layer, suggest that more focus should be placed on the distribution of methyl halides with depth. A surface data point alone does not tell the whole story. In light of the argument that the depth of the mixed layer can influence the concentration anomaly and the flux, regions with a seasonal deep mixed layer or overturn should be sampled in the seasons of deep mixing and shallow mixing. There already exist significant collections of methyl halide profiles, some of which are published [*Moore and Groszko*, 1999]. Profiles which have already been collected could be used to try to understand in a more comprehensive way the distribution of methyl halides with depth in the water column and the effect of that distribution on the air-sea flux.

A useful field study would be to choose an oceanic area at mid-latitudes, which is subject to frequent mixing events, and collect data there in a time series over at least one month. Simultaneous measurements of *in situ* production rates, loss rates, depth profiles, surface partial pressures, and mole fractions in air, for all three methyl halides, would allow a mass balance to be constructed. The effects of mixed layer variations, and the high wind speeds associated with storms, could be measured and compared with models of the production in the mixed layer. Simultaneous observation of biological and physical

parameters such as species composition of phytoplankton, chlorophyll concentration, light intensity, and water-column density profiles would allow greater insight into the processes affecting methyl halides in the surface waters of the ocean.

One of the most significant uncertainties in the flux estimates for all three compounds is that due to the relationship between piston velocity and wind speed. The piston velocity is thought to be most directly dependent on the surface turbulence, not the wind speed itself [Wanninkhof, 1992]. This implies that measurable surface properties which are more related to surface turbulence, such as scatterometer-derived winds [Etcheto and Merlivat, 1988], or the radar back-scatter itself [Wanninkhof and Bliven, 1991], which can be measured by satellites, provide a more promising avenue to estimating piston velocities. Algorithms for estimating piston velocities will likely be improved in the next few years, and global flux estimates should be adjusted accordingly. The development of a different method of measuring the air-sea flux, such as eddy accumulation, would allow for an independent comparison with the air-sea exchange models now in use. Eddy accumulation is a method involving sampling the air above the sea surface in such a way that parcels of air with positive vertical velocity are collected and analysed separately from those with negative vertical velocity. The flux can be calculated from the statistical difference between the up and down samples (J. Smith, personal communication). Such a method would be difficult to apply to the methyl halides, because the differences between the up and down parcels of air are likely to be smaller than the analytical uncertainty in their measured partial pressures. If some way could be found to make this work for methyl halides, it could provide an alternative method for estimating air-sea fluxes.

Although the work of this thesis implies that the oceanic source of methyl chloride to the atmosphere is lower than previously thought, and confirms that the ocean represents a net sink for methyl bromide, still there is implied production of all three compounds in seawater, the sources for which remain largely unexplained. Future work in this area should focus on measuring actual *in situ* net production rates along with loss rates under oceanic conditions in order to directly determine the real production rates in surface seawater. Investigation of the dependence of the production rate on various factors such as primary productivity, bacterial activity, species composition, water temperature, and light levels may reveal insights into the production mechanism. As stated in the Introduction, culture experiments have demonstrated methyl halide production by microalgae [e.g. Scarratt and Moore, 1996; 1998; Manley and de la Cuesta, 1997] and macroalgae [Manley and Dastoor, 1987], but the production rates, when scaled to the biomass concentrations in the ocean, have not accounted for the amounts produced in the ocean. Also, some of the results from the experiments have suggested that the production

in cultures can occur after photosynthesis has stopped, so it would seem appropriate to investigate processes that do not require photosynthesis. This is consistent with the observation in the current study that methyl halide concentrations became elevated to many times their ambient levels in seawater which was left inside an equilibrator in a dark box during a port stop. The distinct smell of rotting plant matter from that seawater is suggestive of the idea that methyl halides could be generated during the decomposition of plant cell materials and other organic matter. Experiments could be designed to investigate this possibility under controlled conditions.

Finally, from the point of view of atmospheric budgets, the results presented in this thesis imply that the ocean contributes substantially less methyl chloride to the atmosphere than has previously been believed, and confirm that the ocean is a net sink for methyl bromide. This leaves the atmospheric budgets of methyl chloride and methyl bromide with a substantial imbalance which is unlikely to be countered by undiscovered oceanic sources. The most obvious priority is to seek non-oceanic sources of these compounds. Flux-chamber studies should be undertaken to determine the net fluxes from various terrestrial ecosystems.

6.6 Conclusions

The principal conclusions of this work are (1) that the ocean source is not the main source of methyl chloride to the atmosphere, (2) that the ocean represents a net sink for methyl bromide, and (3) that the ocean is apparently the main source of methyl iodide to the atmosphere. The atmospheric budgets of methyl chloride and methyl bromide remain significantly out of balance, with sinks exceeding sources, while the budget of methyl iodide may be balanced. Other significant sources of methyl chloride and methyl bromide to the atmosphere are predicted to exist, probably in the terrestrial environment. There is production of all three methyl halides in ocean surface waters, and the source of that production is not yet understood.

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