

## Measurements of methyl chloride in the northwest Atlantic

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**Abstract.** Methyl chloride was measured directly in seawater using a purge and trap system and gas chromatography with electron capture detection. The results indicate that surface waters of the northwest Atlantic are a source of methyl chloride to the atmosphere during late spring/early summer. The average surface concentration was 271 pM ( $\sigma = 68$  pM), supersaturated with respect to an assumed tropospheric boundary layer mixing ratio of 0.7 ppbv. Elevated concentrations were observed throughout the region in waters above the seasonal thermocline. Near-surface maxima of differing thickness and intensity were also seen within this upper layer. Broad maxima within the 200–800m depth range were associated with water masses more recently subducted from the surface than the surrounding main thermocline waters. Coastal inputs of methyl chloride appear not to be an important source in the area of study. Although there is some indication of elevated concentrations associated with higher phytoplankton activity in shelf edge regions, the picture concerning phytoplankton production of methyl chloride is still unclear. Further work is required to look at direct and indirect mechanisms by which phytoplankton may influence the distribution of methyl chloride in the oceans. The global ocean-to-atmosphere flux estimated from this data set,  $3.3 - 4.8 \times 10^{10}$  mol  $\text{CH}_3\text{Cl yr}^{-1}$  ( $1.7 - 2.4 \times 10^{12}$  g  $\text{CH}_3\text{Cl yr}^{-1}$ ) suggests that the oceans may contribute a smaller flux of methyl chloride to the atmosphere than previously thought.

### Introduction

#### Sources of Methyl Chloride to the Atmosphere

Unlike most other volatile chlorinated alkanes, methyl chloride ( $\text{CH}_3\text{Cl}$ ) appears to have a widespread natural source. A relatively uniform distribution has been observed in the free troposphere with a mixing ratio of 600–650 pptv ( $10^{-12}$  vol/vol) [Singh *et al.*, 1977; Singh *et al.*, 1979; Singh *et al.*, 1983; Rasmussen *et al.*, 1980; Khalil and Rasmussen, 1981]. Methyl chloride accounts for 20–28% of the 2–3 ppbv ( $10^{-9}$  vol/vol) organic chlorine in the troposphere [Singh *et al.*, 1977; Class, 1989]. Anthropogenic sources include biomass burning and other combustion processes. Minor emissions of methyl chloride may occur due to its use as a methylating agent in industry [Singh *et al.*, 1977; Crutzen *et al.*, 1979; Rasmussen *et al.*, 1980]. Elevated concentrations of methyl chloride have been found within the tropospheric boundary layer near major urban centers ( $>2$  ppbv near Lisbon, as high as 3.8 ppbv near Los Angeles [Singh *et al.*, 1979]). A seasonal cycle in methyl chloride has been observed at Point Barrow,

Alaska, where concentrations increased sharply during the winter months due to transport of polluted air masses from industrialized midlatitude regions [Khalil and Rasmussen, 1983]. A further increase in spring to early summer may be due to natural sources. Mixing ratios up to 2 ppbv have been observed in forest fire smoke [Rasmussen *et al.*, 1980].

Assuming that oxidation initiated by hydroxyl radical attack is the dominant removal mechanism for this compound, the tropospheric lifetime of methyl chloride is 1–2 years [Cicerone *et al.*, 1975; Graedel, 1979; Warneck, 1988]. So short a lifetime and the absence of interhemispheric gradient, observed by Rasmussen *et al.* [1980], are consistent with widespread sources not concentrated within the industrialized northern hemisphere. However, the lifetime is sufficient to allow transfer of some proportion of the surface flux to the stratosphere. Crutzen and Gidel [1983] calculate 5–10% using a two-dimensional photochemical model. Rapid vertical transport in vigorous updrafts associated with thunderstorms and tropical deep convection may transport elevated boundary layer concentrations to the middle and upper troposphere on timescales of only hours [Dickerson *et al.*, 1987]. A recent modeling study of chlorine in the present-day atmosphere [Weissenstein *et al.*, 1992] shows the pre-1950 dominance of methyl chloride as a chlorine source to the stratosphere and the progressive increase of anthropogenic chlorine species. Even today, however, only CFC-11, (chlorofluorocarbon

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11,  $\text{CFCl}_3$ ), with a free tropospheric mixing ratio of  $\sim 200$  pptv [Prinn, 1988], is thought to contribute a greater amount of chlorine than methyl chloride to the global stratosphere. Formerly representing more than 80% of the flux, methyl chloride now constitutes less than 25% overall.

Biomass burning is estimated to release  $5.3 \times 10^9$  to  $1.2 \times 10^{10}$  mol  $\text{CH}_3\text{Cl}$  ( $2.7 - 6 \times 10^{11}$  g  $\text{yr}^{-1}$ ), 7–30% of the calculated flux required to balance losses due to OH attack of  $\sim 5.9 \times 10^{10}$  mol  $\text{yr}^{-1}$  ( $3 \times 10^{12}$  g  $\text{yr}^{-1}$ ) [Crutzen *et al.*, 1979; Rasmussen *et al.*, 1980; Crutzen and Gidel, 1983; Warneck, 1988; Prinn *et al.*, 1992]. In 1975, industrial sources were less than 10% of the amount lost through OH attack in the troposphere. About  $4.75 \times 10^{10}$  mol  $\text{yr}^{-1}$  ( $2.4 \times 10^{12}$  g) remain to be explained through natural inputs. Continental natural sources include emissions due to volcanic activity (possibly combustion of vegetation in the lava flow [Rasmussen *et al.*, 1980; Symonds *et al.*, 1988]) and release by microorganisms [Cowan *et al.*, 1973; White, 1982a; Harper, 1985; Wuosmaa and Hager, 1990; Harper, 1993]. A methyl chloride transferase enzyme isolated by Wuosmaa and Hager [1990] in *Phellinus pomaceus*, a terrestrial white rot fungus, may be responsible for the methyl chloride production by this species reported by White [1982b]. Wuosmaa and Hager also discovered methyl chloride transferase activity in 50% of randomly sampled species of macroalgae in Monterey Bay, California.

The studies by Singh *et al.* [1983] and Rasmussen *et al.* [1980] conclude that higher tropospheric boundary layer mixing ratios of methyl chloride typify air masses of marine rather than continental origin, consistent with the idea of a widespread natural flux from the oceans. Lovelock [1975] was the first to suggest that the ocean was a likely source of methyl halides following analysis of seawater and air samples from a coastal site in the south of England. In the same year, Grimsrud and Rasmussen [1975] also detected methyl chloride in the atmosphere, although the levels reported were less (about 530 pptv compared with Lovelock's [1975] 1.14 ppbv).

### Sources of Methyl Chloride in Ocean Waters

The mechanisms by which methyl chloride is produced within the oceans are still uncertain. Elevated levels within some kelp beds [Lovelock, 1975] gave the first indication that biology might play some role. Manley and Dastoor [1987] looked at methyl chloride production in macroalgae more closely. Lab incubation experiments and profiles within *Macrocystis pyrifera* beds confirmed that this species, directly or indirectly, produced methyl chloride. Neither tissue wounding nor desiccation caused methyl chloride release. Wuosmaa and Hager's [1990] work supports the occurrence of methyl chloride as a by-product of active metabolism in some macroalgae. However, calculations based on measured emission rates and field studies of *M. pyrifera* and estimates of global macroalgal standing stock produce calculated global fluxes  $<0.1\%$  of the required oceanic source strength [Manley and Dastoor, 1987].

Surveys of atmospheric methyl chloride carried out by Rasmussen *et al.* [1980] and Khalil and Rasmussen [1981] produced further evidence that the emission might be related to marine biological activity. Within  $15^\circ$  of the equator, methyl chloride mixing ratios in the tropospheric boundary layer were 20–30% higher than levels above the boundary layer. Equatorial upwelling of nutrient rich waters stimulates production at these latitudes. Measurements near a Pacific coral atoll showed a ratio of 2:1 between concentrations within and above the boundary layer. Outside this latitude band, elevated levels were observed only occasionally. The results reported by Khalil and Rasmussen [1981] show some indication of spring maxima in boundary layer mixing ratios at sites in both hemispheres. Again, there was evidence of a latitudinal gradient in the mixing ratios, with higher values at low latitudes. However, Singh *et al.* [1983] and Hoyt and Rasmussen [1985] found a more spatially uniform boundary layer distribution with no near-equator enhancement.

Indirect production of methyl chloride by reaction of biologically produced precursors is another possibility. The  $\text{S}_\text{N}2$  substitution of methyl iodide by chloride ion has been proposed by Zafirou [1975] and further considered by Zika *et al.* [1984]. Using rates determined in laboratory experiments with sodium chloride solution (chlorinity = 19 ppt), Zafirou estimated that an amount of methyl iodide similar to that which escapes to the atmosphere should be lost through conversion to methyl chloride. Current figures for methyl iodide fluxes sea-to-air range from 1 to  $9 \times 10^9$  mol  $\text{yr}^{-1}$  [Liss and Slater, 1974; Rasmussen *et al.*, 1982; Singh *et al.*, 1983; Nightingale, 1991], about 5–10% of the suggested transfer of methyl chloride from ocean to atmosphere.

Both Singh *et al.* [1983] and Manley and Dastoor [1987] question the importance of this mechanism. Manley and Dastoor [1987] reported 5 times greater methyl chloride production than methyl iodide from *Macrocystis pyrifera* in the first 3 days of incubation under conditions in which the half-life of the substitution reaction would have been 19 days using Zafirou's [1975] rate constants. Further, there was no correlation of methyl chloride and methyl iodide with depth throughout the kelp bed sampled. In the eastern Pacific, Singh *et al.* [1983] found high concentrations of methyl chloride where there was no corresponding elevation in methyl iodide concentrations, and vice versa. At steady state, methyl chloride and methyl iodide concentrations would be positively correlated, with levels being determined by their differing lifetimes in seawater. As noted by Zika *et al.* [1984], physical mixing, air-sea exchange, and biological processes occur on timescales comparable with the reaction rates and could destroy any correlation in the field. Considering the other extreme, a negative correlation would exist with distance from a localized, pulse source of methyl iodide. The surface layers of the ocean probably exist at some state between these two extremes, and a simple correlation between the two compounds would not be expected. Observations of open ocean methyl iodide concentrations suggest an average value of about 7 pM ( $1.0 \text{ ng L}^{-1}$ ) [Lovelock,

1975; Singh *et al.*, 1983]. This is 2 orders of magnitude less than methyl chloride (300–400 pM). It is unlikely that so small a pool of methyl iodide could support the much larger pool of methyl chloride.

White [1982a] proposed an alternative synthesis pathway for methyl chloride.  $\beta$ -dimethylsulphoniopropionate (DMSP), a compound common in many marine macroalgae and microalgae, can react with halide to produce methyl halides. A precursor of DMS (dimethylsulphide) in seawater, DMSP has an osmoregulatory function and may be preferred over nitrogen-containing compatible organic solutes such as proline and glycinebetaine in nutrient poor environments [Andreae, 1990]. Concentrations of dissolved DMSP range from 7 nM in open ocean surface waters to >200 nM in coastal regions. Intracellular levels show high species and site dependence [Turner *et al.*, 1989; Andreae, 1990]. Reaction of only a small fraction of the DMSP present could produce the observed levels of methyl chloride. No data are available concerning the rate of this reaction in seawater. The high abundance of both reactants suggests this pathway may be worth investigation.

To date there have been few measurements of methyl chloride in the oceans, all of which were made in the Pacific, and the picture of its distribution is far from complete. Methyl chloride is still the most abundant chlorocarbon in the troposphere despite today's increasing levels of anthropogenic organochlorines. With its predominantly natural source, it may be a useful index of an essentially unperturbed atmospheric organochlorine budget. However, insufficient data exist to determine whether anthropogenic emissions, particularly biomass burning, are increasing tropospheric mixing ratios. Measurements by Rasmussen *et al.* [1980] from 1977 to 1979 were over too short a time period to draw any conclusions on global trends. Very few studies of methyl chloride have been published since this time.

Attention throughout the mid-to-late 1980s has understandably been directed largely toward measurement of the anthropogenic chlorofluorocarbon compounds due to their role as carriers of chlorine to the stratosphere where it becomes involved in ozone destroying catalytic cycles [Farman *et al.*, 1985; Anderson *et al.*, 1991, and references therein]. However, due to the large mixing ratios of methyl chloride present in the troposphere, even a small percentage change could result in a considerable increase in the amount of organic chlorine reaching the lower stratosphere [Prinn, 1988]. Before any assessment of the effects of activities such as biomass burning can be made, an understanding of the natural variability within the system is required.

All studies of methyl chloride in aquatic samples to date used an equilibration step. This is a possible source of error due to the uncertainty in the values of Henry's constant for this low molecular weight halocarbon in seawater. The equation used by Singh *et al.* [1983] produces Henry's constants 20–40% greater than those measured by Gossett [1987] when both are multiplied by the same salting-out coefficient. The greatest differences occur at lower temperatures. The aims of this study were to obtain more information about the

distribution of methyl chloride in the oceans using a system capable of measuring methyl chloride directly in seawater and to look at the distribution in terms of suggested sources and sinks.

## Materials and Methods

### Sampling and Analysis

Methyl chloride was measured in the seawater samples using a purge and trap system interfaced with a gas chromatograph (GC) (HP 5890) with electron capture detector (ECD)(Ni-63 source). The purge and trap system was constructed in the laboratory, and the parameters were optimized for analysis of the most volatile organohalogen components in seawater.

The cruise track of the C.S.S. *Hudson* is shown on Figure 1. Samples were taken from the 8-L Niskin bottles (PVC) on the Rosette using glass syringes with Luer-Lok fittings. These were stored in a bucket of fresh seawater in the laboratory and analyzed as soon as possible. Storage of the samples over a 24-hour period caused no significant change in the methyl chloride levels found. Samples were analyzed within 12 hours of collection at all stations.

The sample was purged for 5 min with helium (40 mL min<sup>-1</sup>) onto a Porapak-Q trap (0°C). Following desorption (100°C), components were separated isothermally (70°C, helium carrier 7 mL min<sup>-1</sup> on a megabore PLOT column (GS-Q, J&W Scientific). Build up of the less volatile compounds on this column necessitated baking at 240–250°C every 50 or so samples.

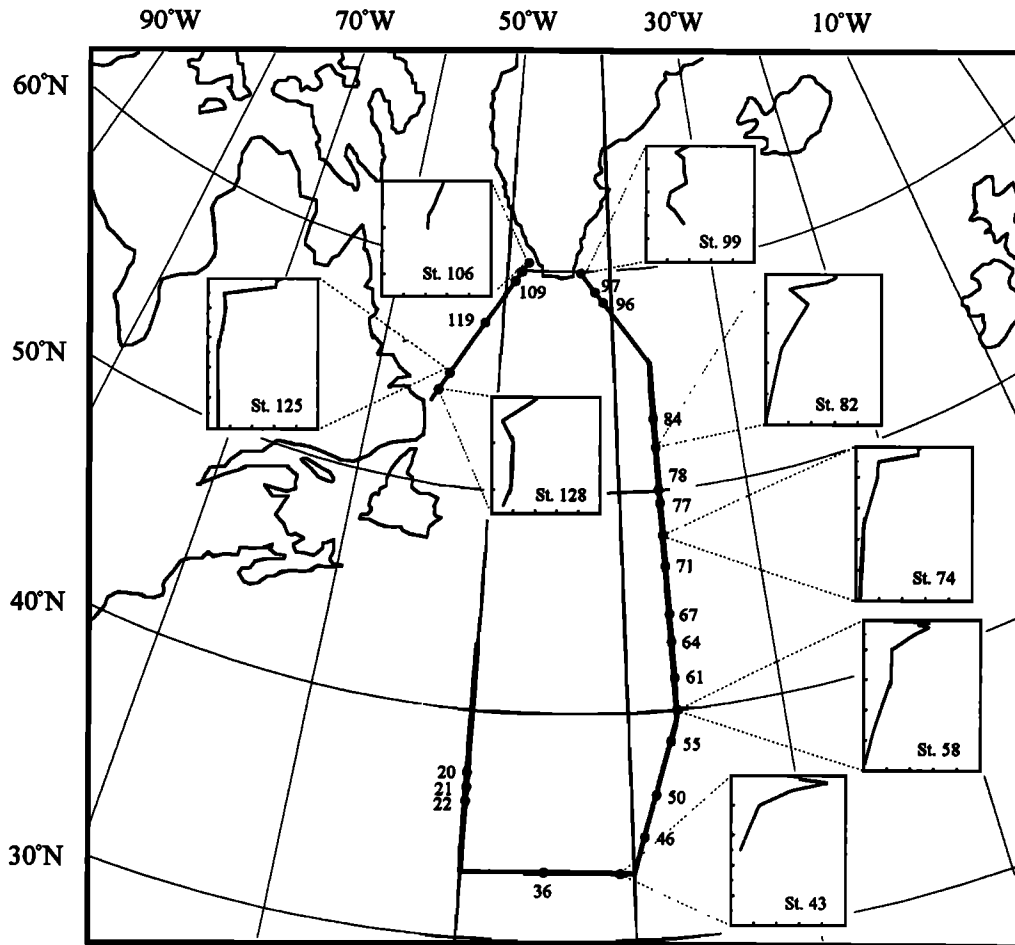
Sensitivity of the ECD to methyl chloride was enhanced by the use of oxygen doped (0.38%) nitrogen make-up gas [Grimsrud and Miller, 1978; Rasmussen *et al.*, 1980]. The detector temperature was held at 275°C. Overall precision was  $\pm 5\%$  (coefficient of variation) at the 200 pM level.

Methyl iodide and bromoform were measured also by purge-and-trap GC-ECD using a separate system (Tekmar purge-and-trap unit interfaced with a Varian 3400 gas chromatograph), the details of which have been published by Moore and Tokarczyk [1993].

Water samples for the determination of chlorophyll-*a* were collected independently at 10 m-depth intervals using a submersible pump, filtered onto Whatman GF/C filters, and stored at -20°C for subsequent extraction and fluorimetric analysis [Strickland, 1972].

### Standard Preparation

Five microliters of pure methyl chloride gas (Aldrich Chemical Company) was injected through a septum into a sampling bulb containing 500 mL of seawater collected from below 2000 m. The high ratio of liquid volume to that of the headspace ( $\sim 250$ ) and the value of the Henry's law constant (H) [Singh *et al.*, 1983; Gossett, 1987] make it reasonable to assume that all of the methyl chloride was contained in the liquid phase. The solution was shaken, mixing aided by the small gas headspace and also glass beads within the bulb. The standard solution was then used immediately by the



**Figure 1.** Cruise track and station positions. Also shown are a number of vertical profiles of methyl chloride. Depth axis is 0–1000 m for open ocean stations and 0–250 m for coastal. Methyl chloride on the x-axis is from 0 to 500 pM.

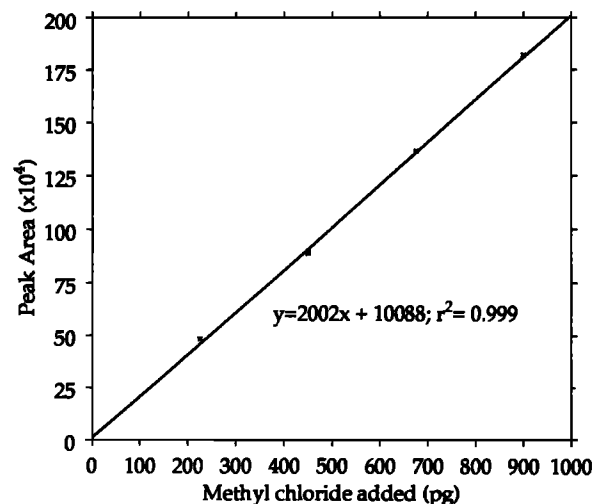
addition of microliter quantities to purged seawater in the purge vessel. A typical calibration curve is shown in Figure 2. The on-board solution standards and postcruise calibration using a system designed and built for the preparation of a dilute methyl chloride solution standard led us to estimate the accuracy of the results as  $\pm 15\%$ .

## Results and Discussion

### Lateral Distribution

Surface concentrations of methyl chloride are shown in Table 1. The average of 271 pM ( $\sigma = 68$  pM) is similar in magnitude to that observed by Singh *et al.* [1983] (228 pM ( $\sigma = 146$  pM)) but the variability is less. Most concentrations lie within the range 200–400 pM, except stations 36 and 58, where 455 pM and 69 pM, respectively, were measured. The temperature, salinity, and chlorophyll-*a* at these stations offer no insight into the reason for these outlying concentrations. In the absence of air measurements, percentage saturations were calculated assuming a boundary layer mixing

ratio of 0.7 ppbv [Lovelock, 1975; Singh *et al.*, 1977; Singh *et al.*, 1979; Singh *et al.*, 1983; Rasmussen *et al.*, 1980; Edwards *et al.*, 1982]. Values using both relationships between Henry's constant (H) and temperature



**Figure 2.** Calibration curve of solution standard.

**Table 1.** Surface Concentrations of Methyl Chloride

Station	Day	Latitude	Longitude	T, °C	CH <sub>3</sub> Cl, pM	Percent Saturation <sup>a</sup>		CH <sub>3</sub> I, pM	Water Depth, m
						Singh et al. [1983]	Gossett [1987]		
20	1.5	37°	50°15''	18.3	284	356	279	—	5530
21	1.5	36°30''	50°15''	18.2	257	321	251	—	5250
22	2.5	36°	50°15''	18.2	203	253	198	4.6	5380
36	6.5	33°	45°35''	20.3	455	613	492	4.9	4390
43	8.5	33°	40°55''	20.1	249	334	268	5.3	2900
46	8.5	34°	39°34''	19.6	280	368	293	4.0	3300
50	9.5	36°	38°43''	18.7	288	365	288	—	3280
55	11.5	38°30''	37°38''	17.9	294	363	283	0.5	4840
58	12.5	40°	37°	17.7	69	84	65	2.8	4750
61	13.5	41°30''	37°	17.0	244	292	225	4.0	4410
64	13.5	43°	37°	16.6	292	343	263	2.9	4000
67	14.5	44°30''	37°	15.5	294	332	251	3.1	4600
71	15.5	46°30''	37°	14.3	238	257	191	2.3	4680
74	16.5	48°	37°	13.5	282	296	218	2.4	4350
77	17.5	49°30''	37°	11.4	236	229	163	1.2	4015
78	17.5	50°	37°	10.4	258	241	169	4.6	4220
82	18.5	52°	37°	7.3	283	236	158	2.2	3610
84	18.5	53°	37°	5.7	270	212	138	0.8	3370
96	21.5	58°17''	41°9''	3.7	317	231	146	0.5	3200
97	21.5	58°42''	41°41''	3.5	338	245	153	5.8	2910
99	22.5	59°48''	43°5''	-1.6	194	116	66	2.8	170
106	26.5	60°32''	48°5''	0.0	363	231	136	5.7	105
108	26.5	60°23''	48°14''	1.2	246	164	99	6.6	150
109	26.5	60°19''	48°19''	2.9	262	186	115	7.6	970
125	31.5	55°23''	53°23''	2.2	332	229	140	0.0	2970
128	31.5	54°23''	54°23''	-1.3	216	131	75	0.0	240

<sup>a</sup>Calculated using H from Singh et al. [1983] and Gossett [1987], respectively.

[Singh et al., 1983; Gossett, 1987] are shown in Table 1. Considering uncertainty in H alone, the calculated saturations differ by about 50%. Singh et al. [1983] used an equation derived from a number of studies on the solubility of methyl chloride in distilled water collated in a comprehensive paper by Wilhelm et al. [1977]. Unlike these solubility measurements, Gossett worked with partial pressures of methyl chloride closer to environmental levels. However, for dichloromethane, vinyl chloride, and methyl chloride, three of the most volatile compounds investigated, Gossett found lower H values, and therefore greater solubility, than previously reported. It is possible that losses occurred during manipulation of concentrated stock solutions. Gossett also measured ionic strength effects on the solubility of some volatile C<sub>1</sub> and C<sub>2</sub> chlorocarbons. His results indicate that a change in salinity of 1 psu would cause a 0.5% change in H. The salting-out coefficient of 1.2 used by Singh et al. [1983] is reasonably consistent with this relationship. Until a more accurate assessment of the Henry's law constant of methyl chloride in seawater is made, percentage saturations or the flux between ocean and atmosphere cannot be calculated with uncertainty less than ±30–40%.

Even using the lower values of H, the average supersaturation (190%) suggests a driving force for a sea-to-air flux of methyl chloride, supporting the findings of earlier studies in the ocean and atmosphere [Lovell, 1975; Singh et al., 1977; Singh et al., 1979; Singh et al., 1983; Rasmussen et al., 1980; Khalil and Rasmussen, 1981; Hoyt and Rasmussen, 1985]. It is possible that some sites in coldest high-latitude waters may show undersaturation and local reversal of the flux direction.

In agreement with the eastern Pacific profiles of Singh et al. [1983], elevated concentrations of methyl chloride were found in the upper mixed layer; lower values were found within the main thermocline (Figure 3). From the methyl iodide values given in Table 1, it can be seen that methyl chloride is present at concentrations 2 orders of magnitude greater than methyl iodide. Some component of this difference is due to the longer lifetime of methyl chloride in both the atmosphere and ocean, allowing the build-up of higher background concentrations.

The average concentrations of the two compounds in the top 100 m were used to compare coastal stations with those in the open ocean (see Table 2, columns 4 and 5). During the May–June period of the study,

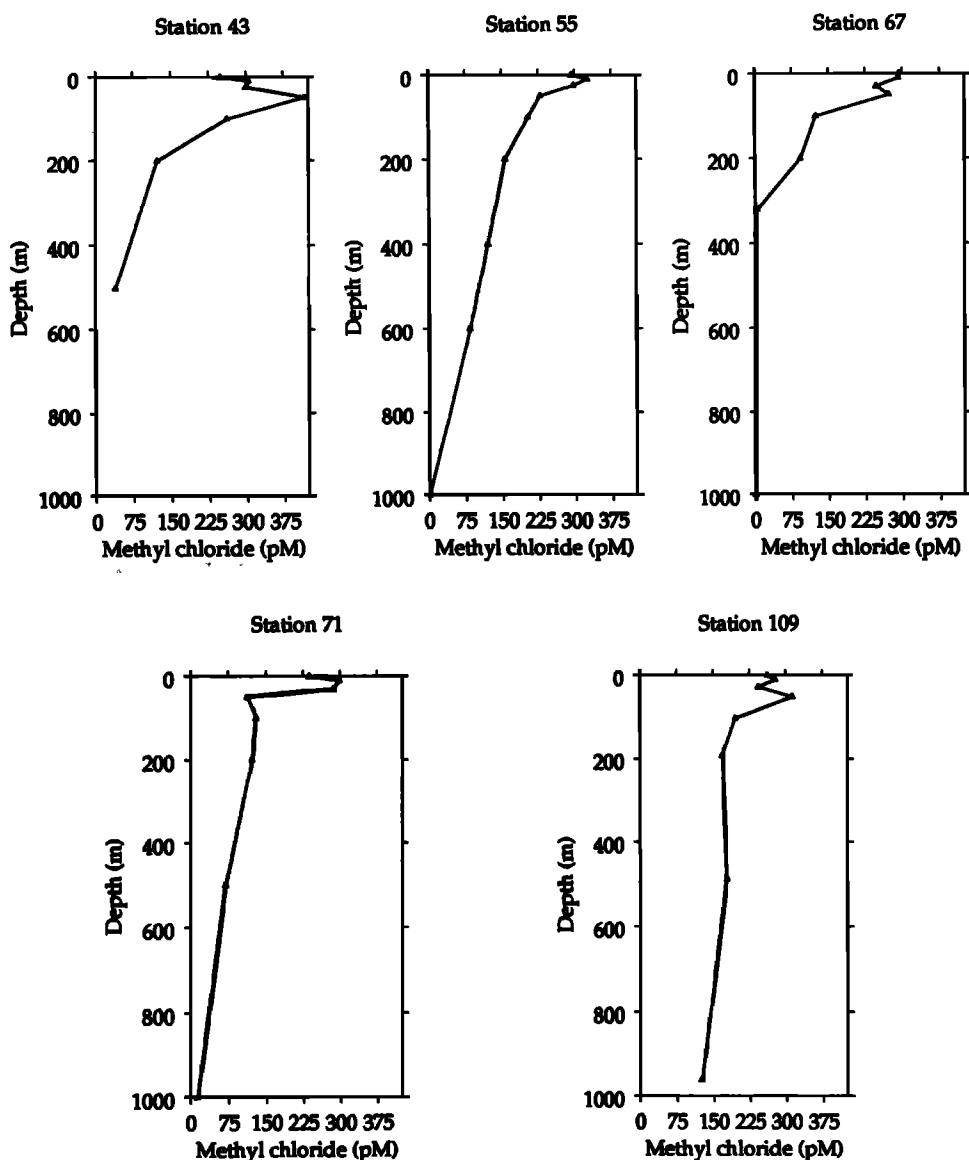


Figure 3. Elevated surface layer concentrations of methyl chloride.

any coastal inputs of methyl chloride are not sufficient to produce concentrations greater than those found in pelagic zones. In contrast, the higher concentrations of methyl iodide observed in southern Greenland coastal waters, relative to the open ocean, are consistent with a strong, local source. The lack of methyl iodide at station 28 approaching Labrador is not easily explained but may reflect the absence of a source in this region at this time of year [Moore and Tokarczyk, 1993].

Table 2 also shows the maximum concentrations of methyl chloride, methyl iodide, and bromoform ( $\text{CHBr}_3$ ) for the three nearshore stations. Bromoform has strong coastal inputs [Moore and Tokarczyk, 1993]. However, unlike both monohalogenated methanes, it has higher concentrations at the two stations in the ice. This observation conforms with the findings of Nightingale [1991] that inputs of the monohalomethanes appear to be to some degree independent of the sources of bromoform

and possibly other bromine containing polyhalogenated species. Distributions of other volatile halocarbons measured during this cruise have been published by Moore and Tokarczyk [1993].

It is not known whether sediments contribute to the pool of  $\text{CH}_3\text{Cl}$ . Increasing concentrations of both methyl chloride and methyl iodide were observed approaching the bottom at coastal station 99 (Figure 4). The T-S plot for this station is also shown in Figure 4. Mixing of a water mass of lower temperature, salinity, and lower methyl chloride located around 100–125 m with warmer, more saline, higher methyl chloride water below is one possible explanation for the observed vertical distributions of temperature, salinity, and methyl chloride. Without knowledge of the origin of the near-bottom water, a sediment source cannot be ruled out.

Methyl chloride was found to be widespread throughout the biologically active surface layers. The number of

**Table 2.** Coastal Stations Compared With the Open Ocean

Site	Stn.	sea-surface	CH <sub>3</sub> Cl Mean <sup>a</sup>	CH <sub>3</sub> I Mean <sup>a</sup>	CH <sub>3</sub> Cl <sup>b</sup> pM	CH <sub>3</sub> I <sup>b</sup> pM	CHBr <sub>3</sub> <sup>b</sup> pM
Greenland east coast	99	30–40% ice	166	5.5	194	10.1	26.4
Greenland west coast	106	no ice	260	16.1	363	16.6	15.2
Labrador coast	128	40–45% ice	104	<0.2	216	<0.2	27.5
Open ocean <sup>c</sup>	–	open water	158–340 (248)	0.35–5.2 (2.4)	(271)	(3.2)	(5.1)

<sup>a</sup>Mean concentration (pM) 0–100 m.

<sup>b</sup>Concentrations given are maximum at station.

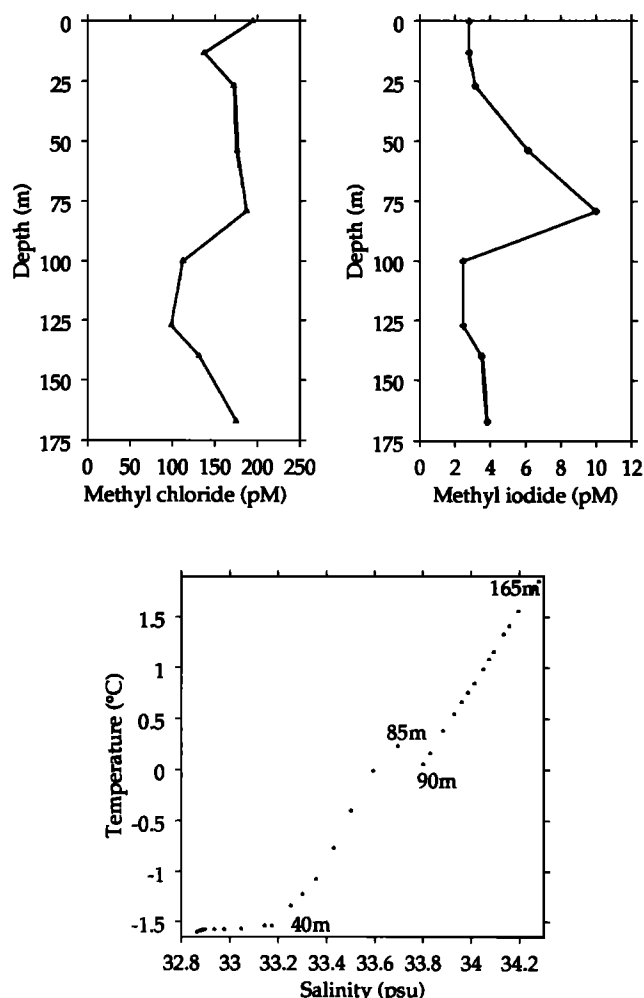
<sup>c</sup>Range with average value in parentheses.

stations at which both methyl chloride and chlorophyll-*a* were measured was limited (eight), and the samples were collected using different methods (see section 2) and are therefore not directly comparable. Although slightly higher concentrations were found near the shelf edges off Greenland and Labrador, regions often typified by more intense bioactivity, high chlorophyll-*a* was not consistently accompanied by high methyl chloride, and vice versa, suggesting no simple relationship between the two.

It should be mentioned that this observation does not exclude a phytoplankton role in methyl chloride production. Even if phytoplankton were a major source of the methyl chloride, a strong correlation may not be observed if the emission depended on species, growth stage, and/or environment. Alternatively, methyl chloride may be produced by reaction of chloride ion with a precursor released by some species of phytoplankton. Variable time lags introduced due to the temperature dependence of the chloride substitution reaction and other precursor decomposition pathways would smooth out any close relationship between methyl chloride concentrations and the biological processes, for example, active metabolism, grazing, stress response, which may cause the release of these compounds.

The distribution of a compound in seawater depends not only on its sources but also on its lifetime within the reservoir under the appropriate conditions. The most likely chemical sink for methyl chloride in seawater is hydrolysis. The temperature dependence of this reaction has been measured in distilled water [Moelwyn-Hughes, 1938], but no information is available on the rate at which it proceeds in seawater, and whether other factors, for example microbial processes, might catalyze the reaction. Within the range of surface layer water temperatures encountered throughout the cruise track, the lifetime of methyl chloride with respect to chemical hydrolytic destruction ranges from >130 years to about 5 years. To compete with losses due to efficient ventilation of the upper 50–100 m of the ocean, which occurs on timescales of only weeks to a month, the rate

constant for the hydrolysis would have to be 2 orders of magnitude larger. The supersaturation throughout much of the upper 100 m of the North Atlantic during late spring to summer implies that at this time of year,



**Figure 4.** Station 99, methyl chloride, methyl iodide, and T-S plot.

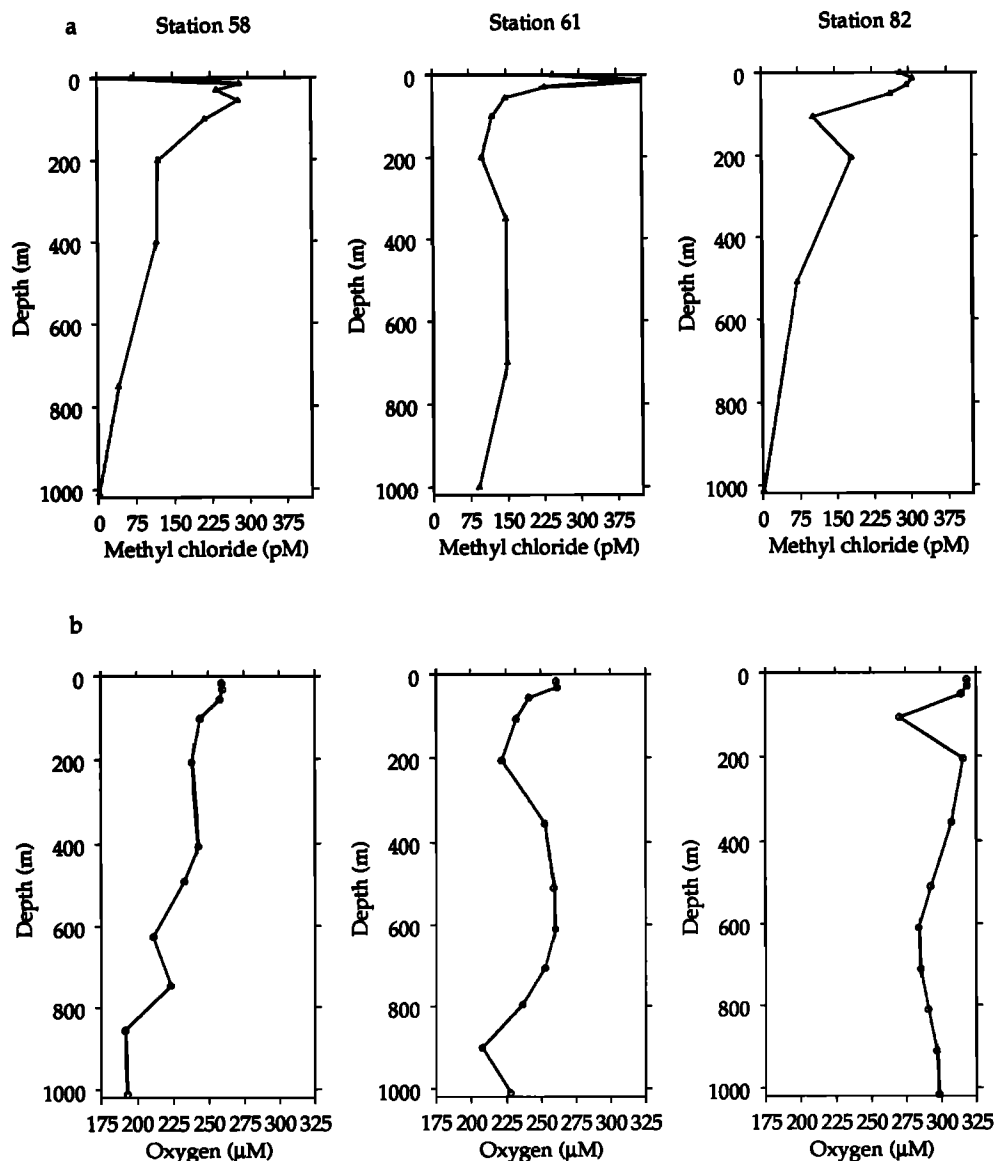
the rate of methyl chloride production exceeds both sea-to-air transfer and losses within the surface layer.

Bacterial and microbial roles in the release and destruction of methyl chloride within and below the euphotic zone cannot be ruled out. Studies in waste water treatment have shown that although anaerobic conditions are favored for the bacterial breakdown of chlorinated and brominated polyhalomethanes [Bower *et al.*, 1981; Bower and McCarty, 1983a] some degradation is also possible under denitrifying, and, in the case of bromoform ( $\text{CHBr}_3$ ), possibly aerobic conditions [Bower and McCarty, 1983b; Cobb and Bower, 1991]. Methyl chloride and methyl bromide are broken down to formaldehyde by mono-oxygenase enzymes produced by some methanotrophic [Stirling and Dalton, 1980; Patel, 1984] and ammonia-oxidizing bacteria [Hyman and Wood, 1984] in oxygen-limited chemostats and batch cultures. Bacterial catalysis of this hydrolytic con-

version was found to cease when anaerobic conditions developed. To our knowledge, no studies have been done to address the possibility of bacterially mediated degradation of methyl chloride under the aerobic conditions encountered throughout the surface water and much of the intermediate and deep waters of the oceans.

### Vertical Distribution

Higher concentrations of methyl chloride were found above the main thermocline in all the deep water profiles (see Figure 3). However, the depth, intensity, and width of near-surface maxima varied between stations. This may have had some relation to the rates of production of methyl chloride, but the hydrographic structure of the water column had an observable effect. The shallow, sharp maximum at station 61 (Figure 5a) was due to a shallow seasonal thermocline and conditions of low wind mixing.



**Figure 5.** Mid-depth maxima of (a) methyl chloride, (b) oxygen, and (c) stations 58, 61, and 82 gradients of potential density.



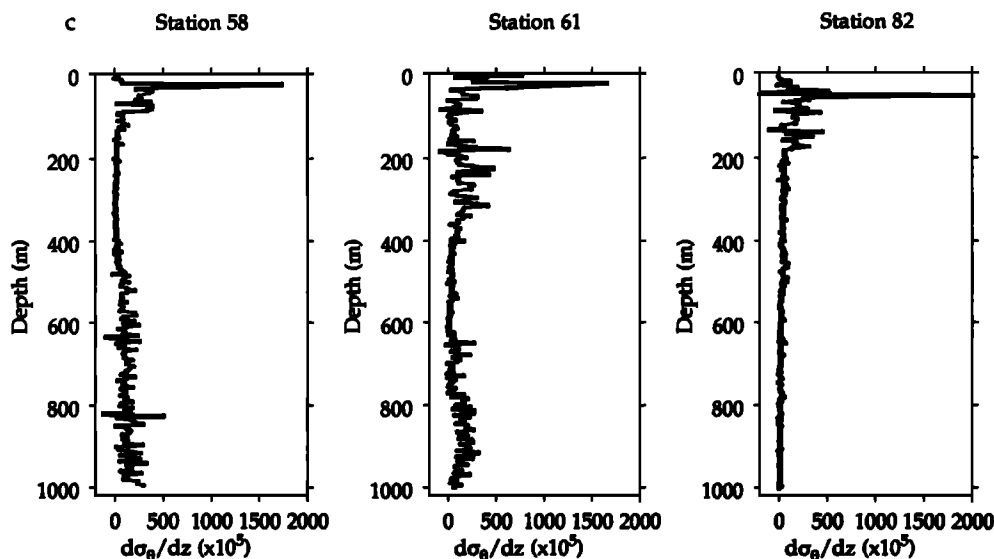


Figure 5. (continued).

As well as peaks within the upper 100 m, some profiles exhibited broader and less intense mid-depth maxima (see Figure 5a). Maxima were also seen in the oxygen distribution (Figure 5b) suggesting a surface source for the water masses. Ventilation of the thermocline by sea surface outcropping of isopycnals is now a widely accepted phenomenon [McCartney, 1982; McCartney and Talley, 1982; Luyten *et al.*, 1983]. McCartney and Talley [1982] discuss the formation of “mode” waters by winter deep convection. Development of seasonal density structure in the upper ocean isolates these water masses from the atmosphere. They are transported downwards and laterally along isopycnals. The high oxygen values (Figure 5b) occurring within well-mixed layers at mid-depth (Figure 5c) are characteristic of pycnostads formed by winter deep convection. Such pycnostads are a common feature in the 200–800 m depth range of the North Atlantic. The temperature and salinity characteristics of the pycnostad 200–400 m at station 58 (temperature of 15.9–16.2, salinity of 36.21–36.26,  $\sigma_\theta = 26.7 \text{ kg m}^{-3}$ ) are intermediate between warmer subtropical mode water and colder subpolar modes [McCartney and Talley, 1982, 1984] and suggest it was formed within or at the edge of the Gulf Stream between 38 and 40°N. The denser pycnostad at station 61 ( $\sigma_\theta = 27.1 \text{ kg m}^{-3}$ ), 400–600 m, likely originated farther north on the eastern boundary of the North Atlantic Current. Vertical profiles of methyl chloride in the top 1000 m of the mid-North Atlantic show in situ signals within the upper mixed layer and also inputs deeper in the water column advected from sources nearer the western boundary.

Jenkins [1980, 1982] determined a relationship between oxygen utilization rate (OUR) and density in the Sargasso Sea based on transient tracer measurements. Assuming this relationship holds at station 58 northeast of the Sargasso Sea, the OUR in the pycnostad between

200 and 400 m is approximately  $0.112 \text{ mL L}^{-1} \text{ yr}^{-1}$  ( $\sigma_\theta = 26.7 \text{ kg m}^{-3}$ ). The observed apparent oxygen utilisation (AOU) of  $0.1 \text{ mL L}^{-1}$  suggests that the water mass has been isolated from the surface for less than a year. A possible explanation for the profile of methyl chloride observed in the upper water column at station 58 is the presence of a seasonal thermocline overlying the remnants of a deep convective layer developed the previous winter. Supersaturation within the upper layers must result from methyl chloride produced since the development of this thermocline.

For reasons unclear as yet, apparently convective water masses originating in the Labrador Sea contain low levels of methyl chloride. Methyl iodide is below the detection limit of  $0.2 \text{ pM}$  ( $0.03 \text{ ngL}^{-1}$ ) [Moore and Tokarczyk, 1993]. Station 125 in the Labrador Sea (Figure 6a) shows strong gradients of methyl chloride and methyl iodide within the intense pycnocline between the spring–summer stratified upper water column and the cold, dense, well-mixed waters below. This station is within a region of higher phytoplankton biomass, indicated by an increase of chlorophyll-*a* nearing the ice-edge.

#### Relationship Between Methyl Iodide and Methyl Chloride

There are common features in the distributions of methyl iodide and methyl chloride, suggesting that their sources may be related to some degree. Production appears to be restricted to the surface 75–100 m, and concentrations decrease in water masses isolated from the biologically active upper ocean. Coastal station 106 on the west coast of Greenland has higher concentrations of both compounds compared with station 99 on the east coast. However, at some stations high methyl chloride concentrations exist in the absence of higher methyl iodide, and vice versa at others. Low surface

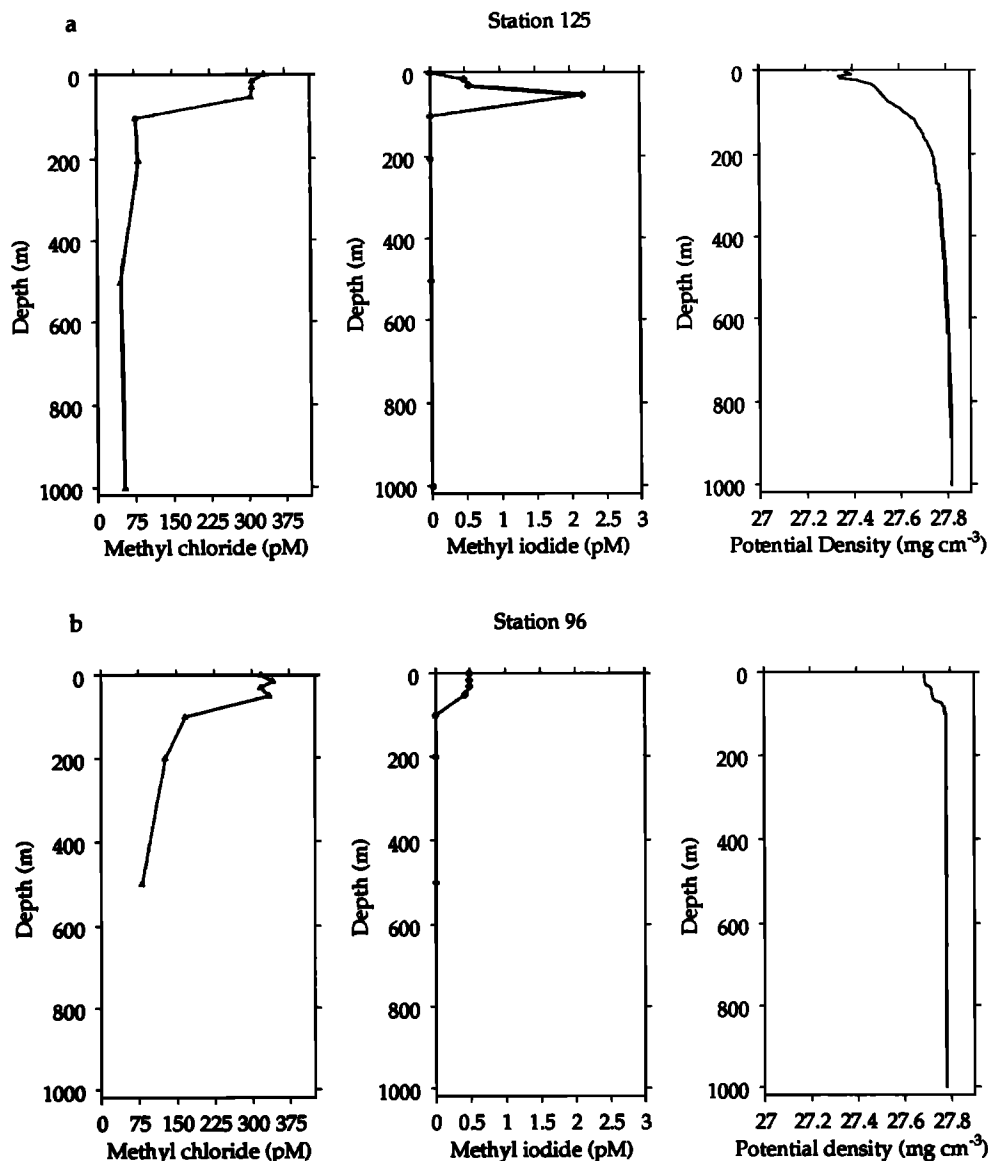


Figure 6. (a) Methyl chloride and (b) methyl iodide in Labrador Sea Water.

layer concentrations of methyl iodide were observed at station 96 near the shelf edge off the east coast of Greenland (average  $0.35 \text{ pM}$  over 0–100 m compared with a 0–100 m mean of  $2.4 \text{ pM}$  for all open ocean stations) accompanied by higher than average methyl chloride concentrations ( $289$  and  $248 \text{ pM}$ , station 96 and open ocean stations average, respectively). At this station the water column 100–1000 m is dominated by Labrador Sea Water ( $\sigma_\theta = 27.78 \text{ kg m}^{-3}$  (Figure 6b)) in which methyl iodide could not be detected. Methyl iodide is plotted against methyl chloride in Figure 7 (labels refer to station numbers). The disproportionately high methyl iodide relative to methyl chloride at coastal station 106 is clearly shown.

Along the cruise track, surface water temperatures ranged from  $< 0$  to  $> 20^\circ\text{C}$ , with corresponding methyl iodide half-lives  $> 300$  days to 2 weeks with respect

to chloride substitution (rate constants from Zafriou [1975]). Rate constants for the hydrolytic destruction of methyl iodide are 1–2 orders of magnitude less than those for the nucleophilic attack of chloride and hence do not change these estimates by very much. Hydrolytic decomposition is, however, the only known chemical sink for methyl chloride in seawater.

With an observed average methyl iodide concentration of  $2.9 \text{ pM}$  over 0–100 m depth, and average temperature of  $15^\circ\text{C}$ , about  $1.6 \times 10^9 \text{ mol CH}_3\text{Cl yr}^{-1}$  ( $7.9 \times 10^{10} \text{ g}$ ) can be produced by chloride substitution, 2 orders of magnitude less than the ocean-to-atmosphere flux of  $5.8\text{--}9.7 \times 10^{10} \text{ mol CH}_3\text{Cl yr}^{-1}$  ( $2.9\text{--}4.9 \times 10^{12} \text{ g yr}^{-1}$ ) calculated by Singh *et al.* [1979, 1983]. If methyl chloride supersaturation above the seasonal thermocline results from chloride substitution of methyl iodide, the rate at which the reaction proceeds must exceed the

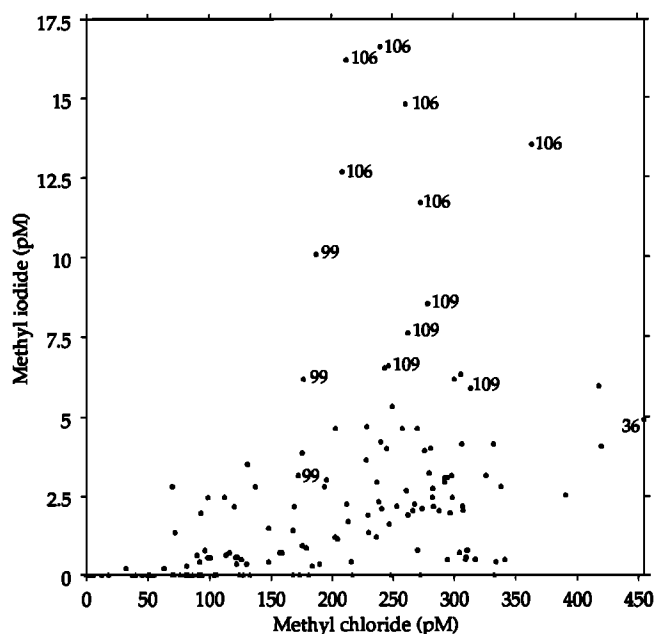


Figure 7. Methyl chloride and methyl iodide.

rate of air-sea exchange. The rate constant of *Zafirou* [1975], albeit not determined under environmental conditions, and the low levels of methyl iodide observed in the open ocean do not support this supposition. Additional sources of methyl chloride are indicated. It is also possible that the chloride substitution of methyl iodide and the hydrolysis of methyl chloride proceed via alternative reaction pathways in ocean waters. The influence of microbial activity and light require consideration.

#### Flux of Methyl Chloride Between Ocean and Atmosphere

*Singh et al.* [1983] calculated an ocean to atmosphere flux of methyl chloride based on actual measurements in surface seawaters and the atmosphere. Using the double film model of *Liss and Slater* [1974] and the Henry's law constant ( $H$ ) derived from *Wilhelm et al.* [1977], they proposed that  $9.7 \times 10^{10}$  mol  $\text{CH}_3\text{Cl}$  ( $4.9 \times 10^{12}$  g) are released from the oceans each year. Wind speed has a strong effect on the magnitude of the exchange coefficient [*Liss and Merlivat*, 1986; *Watson*, 1991], and hence on the transfer of low molecular weight halocarbons across the ocean surface [*Nightingale*, 1991].

Assuming an average wind speed of  $6\text{--}7 \text{ ms}^{-1}$ , the exchange coefficient used by *Singh et al.* [1983], and therefore the calculated flux, is reduced by almost 50%. A further reduction of about 10% occurs when the Henry's constants measured by *Gossett* [1987] are used.

The absence of air measurements concurrent with the analyses of sea surface concentrations creates difficulties in the calculation of a sea-to-air flux. Values in the literature for marine air range from about 550 to 1200 pptv [*Singh et al.*, 1977; *Singh et al.*, 1979; *Rasmussen et al.*, 1980; *Khalil and Rasmussen*, 1983; *Singh et al.*,

1983; *Hoyt and Rasmussen*, 1985]. A marine boundary layer mixing ratio of 0.7 ppbv was assumed in order to calculate a flux from ocean to atmosphere using the spring/summer surface concentrations measured on this cruise. Assuming the data set is representative of mid to high-latitude ocean areas ( $30\text{--}90^\circ$ ), an estimated  $2.3 \times 10^{10}$  mol  $\text{CH}_3\text{Cl}$  ( $1.2 \times 10^{12}$  g) are released from these regions per year using the Henry's constants of *Singh et al.* [1983]. This decreases to  $1.6 \times 10^{10}$  mol ( $7.9 \times 10^{11}$  g)  $\text{CH}_3\text{Cl}$  using *Gossett's* data for  $H$ . Extrapolating to the entire ocean, the estimated fluxes are  $3.3\text{--}4.8 \times 10^{10}$  mol  $\text{CH}_3\text{Cl}$  ( $1.7\text{--}2.4 \times 10^{12}$  g)  $\text{yr}^{-1}$ , 30–50% of that calculated by *Singh et al.* [1983]. There are several other sources of uncertainty, in addition to the Henry's constant, in these extrapolated fluxes. These include the assumed boundary layer mixing ratio, possible seasonality in methyl chloride production and its release from the surface oceans, and the absence of samples from equatorial and tropical regions. Greater temporal and spatial coverage of surface waters of different ocean areas is required to better estimate the magnitude of the ocean-to-atmosphere flux of methyl chloride.

These calculations do, however, suggest that the oceanic source of methyl chloride may have been overestimated, and if so, the input from biomass burning and anthropogenic sources could represent a greater fraction of the total  $\text{CH}_3\text{Cl}$  entering the troposphere.

#### Conclusions

Measurements of methyl chloride in surface waters of the northwest Atlantic during spring/summer suggest that in agreement with previous studies, the ocean is an important natural source of this compound to the atmosphere. However, the magnitude of the flux from ocean to atmosphere may have been previously overestimated. Further study into the magnitude and temperature dependence of the Henry's law constant for methyl chloride in seawater is needed. Production of methyl chloride appears restricted to depths above the seasonal thermocline. The depth and intensity of subsurface maxima differed between stations (due to varying histories of air-sea exchange and possibly also different rates of production). Strong coastal inputs of methyl chloride were not observed. Broad, middepth methyl chloride maxima observed within the main thermocline are indicative of water masses more recently at the surface than the surrounding waters. Formed by winter deep convection, these pycnostads originate within or on the edge of currents along the western boundary of the North Atlantic.

There is some indication that elevated concentrations of methyl chloride are associated with higher phytoplankton activity in shelf edge regions. However, a clear picture of the phytoplankton role in methyl chloride could not be ascertained from this data set. The possibilities of microbial pathways of methyl chloride production and release also need to be investigated.

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