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An Investigation of the Oceanic Source of Methyl Chloride

by

Valerie K. Tait

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for the degree of Doctor of Philosophy

at

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To Shane and Liam,
who helped keep everything in perspective.

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Abstract

An analytical method involving purge-and-trap and gas chromatographic techniques was developed for the determination of methyl chloride in aqueous samples. Vertical profiles of methyl chloride in the North-west Atlantic during spring showed higher concentrations above the seasonal thermocline and a general decrease with depth. Near-surface maxima were a common feature and several broad, less intense maxima were observed within the main thermocline. No simple relationship existed between concentrations of chlorophyll-a and methyl chloride. The average surface saturation was 268% using an average atmospheric mixing ratio of 625 pptv.

The Henry's Law constant (H) for methyl chloride in seawater was measured at different temperatures by a dynamic stripping method and applied in the estimation of a sea-air flux of methyl chloride using the surface concentrations in the North-west Atlantic. The transfer velocity was corrected for temperature through the Schmidt Number. The calculated flux was 2.3×10^{12} g yr^{-1}, the lowest estimate to date.

Methyl chloride was measured in Bedford Basin, Nova Scotia, during February to June. Low concentrations in waters from below the sill depth required a loss rate greater than that predicted from its rate of chemical hydrolysis in distilled water. Microbial destruction of methyl chloride in waters containing low levels of oxygen was suggested. A moderate positive correlation ($r=0.65$) between methyl chloride and chlorophyll-a integrated over 0-20m depth could not be considered conclusive evidence of a phytoplankton source of methyl chloride due to the possibility of increasing emissions from macroalgae coincident with the bloom development.

Net production of methyl chloride was observed in xenic unialgal cultures of cold and warm water phytoplankton. Further increases in methyl chloride observed after the death of all the phytoplankton cells were evidence for the existence of chemical and/or bacterial mechanisms converting organic substrates released by the phytoplankton to methyl chloride. When scaled using levels of chlorophyll-a, the laboratory rates can account for <0.1% of the estimated oceanic source of methyl chloride.

BCF	buffer catalysis factor
ca.	circa
chl-a	chlorophyll-a
d	day
EC	Electron Capture
ECD	Electron Capture Detector
ft.	foot
g	gram
ng	nanogram (10^{-9} g)
μg	microgram (10^{-6} g)
pg	picogram (10^{-12} g)
GC	Gas Chromatograph
i.d.	inner diameter
in.	inch
(l)	liquid
[L]	dimensions of length
L	litre
mL	millilitre (10^{-3} L)
μL	microlitre (10^{-6} L)
m	metre

cm	centimetre
μm	micrometre
nm	nanometre
mCi	millicuries
min.	minute
[M]	dimensions of mass
M	molar
pM	picomolar = picomoles per litre (10^{-12} moles per litre)
μM	micromolar (10^{-6} M)
nM	nanomolar (10^{-9} M)
MS	Mass Spectrometric
n	number of samples or analyses
o.d.	outer diameter
PAR	Photosynthetically Active Radiation
PIN #	Product Identification Number
ppbv	parts per billion by volume
pptv	parts per trillion by volume
σ_{n-1}	sample standard deviation
σ_θ	potential density
R	ideal gas constant
r	sample correlation coefficient
s	second

S	salinity based on the Practical Salinity Scale (a ratio and therefore dimensionless)
S_c	Schmidt number
[θ]	dimensions of time
T	absolute temperature in Kelvin
U_{10}	wind speed at 10m above the sea surface
UV	ultra-violet
V	volume
z	depth in metres

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Chapter 1: Introduction and Review

1.0 *Introduction*

Methyl chloride (CH_3Cl) is the most abundant chlorocarbon in the troposphere. Despite increasing levels of anthropogenic organochlorine compounds, it is an important source of chlorine radicals to the stratosphere and plays a role in the regulation of stratospheric ozone. Although anthropogenic sources of methyl chloride do exist, natural emissions of methyl chloride are thought to dominate inputs to the troposphere. In pre-industrial times, methyl chloride must have been the major source of chlorine to the stratosphere. Even a small percentage change in the large tropospheric mixing ratio of methyl chloride could result in a significant increase in the amount of organic chlorine reaching the lower stratosphere (Prinn, 1988). Existing time series of tropospheric methyl chloride (Rasmussen *et al.*, 1980; Megie *et al.*, 1990) are of too short a duration to distinguish any long term global trend, natural or otherwise.

1.1 *Methyl chloride in the atmosphere*

1.1.1 The stratosphere

The 30% drop in total column ozone observed by Farman *et al.* during the

Antarctic spring of 1984 at Halley Bay (Farman *et al.*, 1985) motivated extensive ground and remote monitoring of atmospheric ozone distributions. Satellite measurements of total column ozone have shown that decreases are not restricted to the Antarctic vortex (Brasseur, 1991). Ozone losses have been observed at mid and high latitudes in both hemispheres (Anderson *et al.*, 1991; Brasseur, 1991; Chipperfield, 1991). Decreased ozone concentrations allow a greater flux of ultra-violet radiation (particularly within the wavelength range 240-320 nm) to reach the Earth's surface. Radiation of these wavelengths falls within the absorption spectrum of DNA (Cicerone, 1987). The increased flux of radiation may have harmful effects on biota. Exposure to elevated levels of UV-B radiation (280-320 nm) can cause skin cancer (Setlow, 1974). UV-B also causes erythrocyte lysis and conversion of deoxyhemoglobin to a form incapable of carrying oxygen (Kollias *et al.*, 1992). Post and Larkum (1993) report reduced intracellular chlorophyll levels and photosynthetic rates in Antarctic macroalgae subjected to increased UV-B. A link between declining populations of amphibians and increased fluxes of UV-B has also been suggested (Blaustein *et al.*, 1994).

It is now generally accepted that chlorine and bromine atoms released by photolysis of organohalogen compounds play a catalytic role in the regulation of ozone within the stratosphere. Theories to explain ozone depletion have evolved considerably since the original chlorine radical gas phase catalytic cycle proposed by Molina and Rowland (1974). Cycles involving ClO_x , BrO_x , and HO_x, and also methylperoxy radicals (CH_3O_2) (McElroy *et al.*, 1986; Molina and Molina, 1987; Anderson *et al.*, 1991; Crutzen *et al.*, 1992) have been suggested. Explaining observed decreases in

ozone, however, requires not only gas phase free radical chemistry, but also heterogeneous reactions and air mass transport. Polar stratospheric clouds (PSCs) are instrumental in causing ozone depletion (*e.g.* Crutzen and Arnold, 1986). Type I polar stratospheric clouds seeded by nitric acid trihydrate form at 195K, 50mb pressure. HCl adsorbs onto PSC surfaces. Chlorine nitrate ($ClONO_2$ (g)) reacts with HCl at the particle surface releasing Cl_2 gas and leaving HNO_3 within the ice matrix. In the presence of solar radiation, the chlorine gas is then photolysed to give active chlorine radicals. The net effects of PSCs are to release active chlorine from inactive reservoir compounds (HCl and $ClONO_2$) and to lower the ambient concentration of NO_x. The low concentration of NO_x suppresses the reconversion of active chlorine to chlorine nitrate ($ClONO_2$), leaving more active chlorine available to participate in ozone depleting catalytic cycles. A negative correlation has been observed between the time spent by an air parcel at temperatures low enough to allow the formation of PSCs and the ozone mixing ratio found within that air parcel (Hoffman and Deschler, 1991; Chipperfield, 1991). Heterogeneous chemistry involving stratospheric sulphuric acid aerosols is also important in determining ozone loss rates (Tolbert *et al.*, 1988; Rodriguez *et al.*, 1991; Brasseur *et al.*, 1991; Crutzen *et al.*, 1992).

Assuming that oxidation initiated by hydroxyl radical attack is the dominant removal mechanism, the average tropospheric lifetime of methyl chloride is 1.6-1.7 years (Atkinson *et al.*, 1992; Weisenstein *et al.*, 1992; Koppmann *et al.*, 1993). This is sufficient to allow transfer of some proportion of the surface flux to the stratosphere; Crutzen and Gidel (1983) calculate 5-10% using a 2-D photochemical model. Based on

measurements of methyl chloride in the stratosphere during June 1978, Penkett *et al.* (1980) calculated that 27% of the stratospheric chlorine from organohalogens at that time was due to methyl chloride.

A recent study of chlorine in the atmosphere (Weisenstein *et al.*, 1992) addressed the time-dependent contributions of the major organochlorine source gases to stratospheric levels of active chlorine (Cl and ClO) using a two-dimensional model. The contribution of an organochlorine gas to the stratospheric load of active chlorine depends on its mixing ratio in the upper troposphere, the number of chlorine atoms per molecule, and its tropospheric and stratospheric lifetimes. Results for the 1985 atmosphere suggested that, at that time, methyl chloride contributed approximately 22% of the active chlorine found in the stratosphere. Only CFC-11, (Freon 11® (DuPont), chlorofluorocarbon-11, $CFCl_3$), with a free tropospheric mixing ratio of *ca.* 200 pptv (10^{-12} volume/volume) (Prinn, 1988), was found to contribute a greater amount of chlorine than methyl chloride to the global stratosphere. Schauffler *et al.* (1993) measured the concentrations of halogenated organic compounds near the tropical tropopause in 1991-1992. Only 15% of the 3.5 ppbv (10^{-9} volume/volume) total organic chlorine measured in this study was due to methyl chloride. CFC-11 ($CFCl_3$) and CFC-12 (CF_2Cl_2), with average mixing ratios of 264 pptv and 494 pptv respectively, accounted for 50% of the total organic chlorine load. The remainder was dominated by carbon tetrachloride (CCl_4), methyl chloroform (CH_3CCl_3) and CFC-113 (CCl_2FCClF_2). Prior to the increases in the atmospheric burdens of chlorine-containing solvents and long-lived chlorofluorocarbons, methyl chloride must have dominated the stratospheric chlorine budget and therefore must have been critical

in the control of ozone abundance. Methyl chloride now constitutes less than 20% overall. It remains, however, an important source of chlorine to the stratosphere.

1.1.2 The troposphere

The troposphere contains *ca.*3 ppbv (10^{-9} volume/volume) organically-bound chlorine (Rahn *et al.*, 1976; Schauffler *et al.*, 1993). Methyl chloride, the most abundant volatile chlorocarbon in the troposphere (Grimsrud and Rasmussen, 1975; Cronn *et al.*, 1977; Singh *et al.*, 1977), accounts for 15-30% of this reservoir (Cronn *et al.*, 1977; Singh *et al.*, 1977; Schauffler *et al.*, 1993). A range of tropospheric mixing ratios has been reported. Grimsrud and Rasmussen (1975), in the first published measurements of methyl chloride in air, reported mixing ratios of 530 ± 39 pptv at a continental rural sampling site. During 1974 and 1975 Lovelock (Lovelock, 1975) measured mixing ratios from 300 to >2000 pptv in air samples collected on the south coast of England. Air masses from over the ocean contained higher concentrations of methyl chloride than those from over continental Europe. Singh *et al.* (1977) reported a background northern hemisphere continental tropospheric mixing ratio of 713 pptv. They also observed a significant gradient between marine and continental air masses indicative of a marine source. Average levels in samples from two sites designated clean marine air were 780 and 1011 pptv. In a later study spanning latitudes from 90°S to 65°N (Singh *et al.*, 1979), the average northern and southern hemisphere mixing ratios of 615 ± 103 pptv and 611 ± 84 pptv respectively, suggested a relatively uniform distribution. The lack of

interhemispheric difference, despite the relatively short lifetime of methyl chloride in the troposphere (1.7 yr; Koppmann *et al.*, 1993; Atkinson *et al.*, 1992), is strong evidence for the existence of a widespread natural source.

Chemical and photochemical production of CH_3Cl within the troposphere is thought to be negligible (Graedel and Allara, 1976). Emissions from non-atmospheric sources are therefore required to explain existing levels.

Considering the vertical distributions of trace atmospheric compounds, the troposphere can be divided into two regions - the tropospheric boundary layer and the free troposphere. The tropospheric boundary layer may be defined dynamically as the lower region of the troposphere in which flow is affected by the presence of the Earth's surface. It is typically a few hundred metres to one kilometre in height. In the free troposphere between about 1 km and the tropopause (10-20km), flow can be approximated by the geostrophic balance of the Coriolis and pressure gradient forces. Characterisation of flow in the tropospheric boundary layer, however, requires consideration of friction and turbulence. Heating of the surface also affects the dynamics within this layer. For example, a temperature inversion can form due to radiative cooling of the near-surface air which acts as a barrier to vertical mixing and allows the accumulation of compounds released from the surface. From a chemical perspective, the tropospheric boundary layer is typified by relatively high temperatures, high concentrations of water vapour, particulates, and short-lived trace species with surface sources.

Pierotti *et al.* (1980) observed tropospheric boundary layer concentrations of

methyl chloride a factor of two higher than those within the free troposphere (740-1400 pptv compared with 400-900 pptv) over the North American continent and suggested a surface source for methyl chloride. Rasmussen *et al.* (1980), however, reported no discernible difference between methyl chloride concentrations in the boundary layer and those in the free troposphere over North America. These investigators observed elevated tropospheric boundary layer mixing ratios over the low latitude Pacific Ocean. At mid-latitudes, near-surface concentrations higher than those within the free troposphere were observed only occasionally (over a Pacific coral atoll, the Oregon coast, and the west coast of Ireland). Methyl chloride concentrations measured within the boundary layer outside the latitude band 30°N to 30°S ranged from 550 to 700 pptv.

Singh *et al.* (1983), Hoyt and Rasmussen (1985), and Koppmann *et al.* (1993) did not find elevated tropospheric boundary layer mixing ratios in tropical regions. The average mixing ratios reported in the former two studies were 633 pptv and 647 pptv respectively, in good agreement with those of Singh *et al.* (1979). In a recently published study (Koppmann *et al.*, 1993), an average of 530 pptv (range *ca.* 400-650 pptv) was reported for the boundary layer over the North and South Atlantic. Average free tropospheric mixing ratios of 643 ± 120 pptv and 640 ± 157 pptv for the northern and southern hemisphere, determined in a separate study (J. Rudolph, unpublished results) were also reported in this paper. A value of *ca.* 600 pptv is currently considered representative of the background tropospheric concentration (Prinn, 1988). Whether higher levels are observed within the tropospheric boundary layer (Singh *et al.*, 1977) may depend on proximity to a methyl chloride source and also the vertical structure of

the lower troposphere.

Natural sources of methyl chloride originating from continental areas include emissions associated with volcanic activity (possibly due to combustion of vegetation in the lava flow - Rasmussen *et al.*, 1980; Symonds *et al.*, 1988) and wildfires. Some terrestrial biota produce methyl chloride. Methyl chloride release has been observed in several species of wood-rot fungi (Cowan *et al.*, 1973; Harper, 1985; Harper, 1993a). This trait has been found to be widespread in the family Hymenochaetaceae (Harper, 1993a and b). In radiolabelling studies using *Phellinus pomaceus* (Harper, 1993b) it was shown that methyl chloride was derived from the amino acid methionine and that it acted as a methyl donor in the production of some methyl esters by this fungus. Harper (1993b) also noted that although no methyl chloride emission was detected in some other species of lignin-degrading fungi, it was utilised as a methyl donor in the biosynthesis of a component of a lignin-degrading complex. CH_3Cl emission from some higher plants has also been observed. Wuosmaa and Hager (1990) isolated a methyltransferase enzyme capable of methylating halide ions in a diverse range of biota. In addition to the white wood-rot fungus *Phellinus pomaceus*, the methyltransferase was found in *Mesembryanthemum crystallium*, a succulent found in saline environments, and *Endocladia muricata*, a marine rhodophyte. Methyl chloride may also be produced by the common mushroom, *Agaricus bisporus* (Turner *et al.*, 1975). Estimates of the magnitude of biological methyl chloride emission from terrestrial environments are not currently available.

Anthropogenic sources of methyl chloride do exist. Methyl chloride is used as

a methylating agent in the production of silicones, synthetic rubber, and also some herbicides and quaternary amines (Singh *et al.*, 1977, 1983; Crutzen *et al.*, 1979; Rasmussen *et al.*, 1980). Blowing of styrene foam and production of fluorinated refrigerants are other industrial processes involving methyl chloride (Edwards *et al.*, 1982, Ehman *et al.*, 1964). Apart from foam-blowing, emissions of methyl chloride from these applications are minimal, due only to leakage during transport, storage, and during production of the compound itself. An increase in concentrations during the winter months was observed at Point Barrow, Alaska, associated with polluted air masses transported from industrialised mid-latitude regions (Khalil and Rasmussen, 1983) while a further increase in spring to early summer may be due to natural sources. Elevated concentrations of methyl chloride were found within the tropospheric boundary layer near major urban centres by Singh *et al.* (1979) (>2ppbv near Lisbon, as high as 3.8 ppbv near Los Angeles). The reason for the high levels of methyl chloride has not been investigated, but possible sources include automobile exhaust and other combustion processes.

Convective activity such as thunderstorms can transport compounds in the tropospheric boundary layer to the middle and upper troposphere, and in some cases to the stratosphere, in hours instead of the weeks or months predicted by models based on eddy-diffusion. Dickerson *et al.* (1987) attributed high concentrations of ozone and carbon monoxide within a thunderstorm anvil to rapid upwards transport of lower tropospheric air within the convective updraught. Tropical regions are characterised by intense convective activity in the Inter-Tropical Convergence Zone (ITCZ). Troposphere

to stratosphere transport can be very rapid at these latitudes. The latitudinal distribution of surface inputs of methyl chloride is therefore of interest when considering the amount which will reach the stratosphere.

Assuming equilibrium gas/liquid partitioning, wet deposition of methyl chloride results in an insignificant loss of methyl chloride from the troposphere (Warneck, 1988). Based on the absorption cross section of methyl chloride (Robbins, 1976), photolytic destruction in the troposphere will also be negligible. The gas phase hydrogen abstraction reaction between hydroxyl radical (OH) and CH_3Cl is the dominant sink of methyl chloride in the troposphere. The following reaction scheme was proposed by Graedel (1979) yielding ultimately H_2O and HCl -

$$CH_3Cl + OH \rightarrow CH_2Cl + H_2O$$

$$CH_2Cl + O_2 \rightarrow CH_2ClO_2$$

$$CH_2ClO_2 + NO \rightarrow CH_2ClO + NO_2$$

$$CH_2ClO + O_2 \rightarrow CO + HCl + HO_2.$$

No heterogeneous pathways of methyl chloride destruction in the atmosphere have been reported. Prinn *et al.* (1992) calculated a global average tropospheric hydroxyl concentration of 8.7 ($\pm$1.0) x 10^5 molecules cm^{-3} based on the distribution of methylchloroform (CH_3CCCl_3). For an average tropospheric temperature of 253K, a recent evaluation of atmospheric chemical kinetic data (Atkinson *et al.*, 1992) recommends a rate constant of 2.19 x 10^{-14} cm^3 $molec^{-1}$ s^{-1} for the gas phase reaction

between OH and CH_3Cl (lifetime = 1.7 years). With a tropospheric load of 7.9 x 10^{10} - 1 x 10^{11} moles (4 - 5 x 10^{12} g) (Rasmussen *et al.*, 1980; Singh *et al.*, 1983; Koppmann *et al.*, 1993) the annual loss of methyl chloride due to reaction with hydroxyl radical is 4.2 - 6.6 x 10^{10} moles (2.1 - 3.4 x 10^{12} g). Crutzen and Gidel (1983) calculated a global loss of 3.8 x 10^{10} moles yr^{-1} (1.9 x 10^{12} g yr^{-1}) using a latitude dependent OH concentration derived from a two-dimensional photochemical model.

OH radicals are produced photochemically in the presence of ozone and water vapour -

$$O_3 + h\nu \rightarrow O(^1D) + O_2 \quad \lambda \leq 310 \text{ nm}$$

$$O(^1D) + H_2O \rightarrow 2OH$$

(e.g. Crutzen and Gidel, 1983).

The higher flux of solar radiation and high rates of evaporation in tropical regions lead to increased production of OH at these latitudes. At temperate latitudes the seasonal cycle in solar radiation will affect ambient OH concentrations. The rate constant for the reaction between OH and CH_3Cl is also temperature dependent, increasing as the temperature rises. Losses of methyl chloride due to reaction with OH radical are therefore greater at low latitude (Crutzen and Gidel, 1983). A seasonal cycle in methyl chloride mixing ratio was observed at Cape Grim, Tasmania (Megie *et al.*, 1990). The 10% lower mixing ratios observed during summer could be accounted for by seasonality in the magnitude of the OH initiated sink (Megie *et al.*, 1990).

Industrial emissions of methyl chloride are estimated to contribute only a small

fraction (<5%; Cox *et al.*, 1976; Edwards *et al.*, 1982) of the amount lost through OH attack in the troposphere. The magnitude of the urban source is not known.

It is well known that biomass burning releases methyl chloride (Palmer, 1976; Crutzen *et al.*, 1979; Rasmussen *et al.*, 1980). Mixing ratios up to 2 ppbv have been observed in forest fire smoke (Rasmussen *et al.*, 1980). Combustion of chlorine containing materials like PVC also releases methyl chloride (Palmer, 1976). Smouldering combustion favours methyl chloride release (Rasmussen *et al.*, 1980; Mano and Andreae, 1994). Crutzen *et al.* (1979) and Rasmussen *et al.* (1980) estimated that biomass burning emissions of methyl chloride amount to 5.3×10^9 - 1.2×10^{10} moles CH_3Cl ($2.7 - 6 \times 10^{11}$ g yr^{-1}). A recent estimate by Andreae (1993), however, suggests that biomass burning may contribute a greater amount of methyl chloride to the troposphere ($1.8 - 7.3 \times 10^{10}$ moles CH_3Cl yr^{-1} ($0.9 - 3.7 \times 10^{12}$ g yr^{-1})). The high end of the range of the more recent estimates of Andreae (1993) is comparable with estimates of the ocean source of methyl chloride.

1.2 *Methyl chloride in the oceans*

Measurements of methyl chloride in ocean waters (Singh *et al.*, 1983; Hoyt and Rasmussen, 1985) have shown the surface ocean to be significantly supersaturated. The percentage saturation can be calculated from the observed water and air concentrations using the Henry's Law constant (H; please see Chapter 4). Singh *et al.* (1983) found

surface concentrations from 125 to 820 pM with an average of 230 pM in the Eastern Pacific. Their average surface saturation was 375%. Saturations from 90 to 210% were reported by Hoyt and Rasmussen (1985), with an average of 143%.

1.2.1 Sources of methyl chloride in ocean waters

1.2.1.1 Macroalgae

Halogen-containing metabolites are widespread in the marine environment. Over 150 have been identified in marine macroalgae (Fenical, 1975; Glombitza, 1979; McConnell and Fenical, 1979). These include several halogenated methanes. Fenical (1982) noted $CHBr_3$, $CHBr_2I$, $CHBr_2Cl$, $CHCl_3$, and CCl_4 release from *Asparagopsis taxiformis*, a marine red alga. $CHBr_3$ was released in the greatest amounts. Production of polyhalomethanes by green and brown temperate macroalgae has also been reported (Gschwend *et al.*, 1985; Gschwend and MacFarlane, 1986). Many halogenated organic compounds (particularly those containing bromine) exhibit anti-fungal and antibiotic activity (Fenical, 1975; McConnell and Fenical, 1977; Woodin *et al.*, 1987) and may be used in chemical defence. Polyhalomethanes are ubiquitous trace components in surface seawater with clear sources in coastal regions (Class and Ballschmiter, 1987, 1988; Fogelqvist, 1985; Moore and Tokarczyk, 1993). One route proposed to account for the production of polyhalomethanes by macroalgae involves the haloperoxidase-catalysed incorporation of bromide into organic compounds (Theiler *et al.*, 1978).

Bromoperoxidases containing a heme or vanadium prosthetic group have been isolated from several species of brown and red marine macroalgae (Manthey and Hager, 1981; Vilter, 1984; Wever *et al.*, 1987; Wever *et al.*, 1991). The halogenation step may occur via hypobromous acid (HOBr) as proposed by Wever *et al.*, (1991) and/or through an enzyme-bound halonium-ion intermediate (Geigert *et al.*, 1984). The brominated organic compounds which are formed then break down, either chemically or enzymatically, to give polybrominated methanes (Theiler *et al.*, 1978). *Ascophyllum nodosum*, a macroalga known to produce a variety of bromine-containing halomethanes (Gschwend *et al.*, 1985), contains two vanadium bromoperoxidases, one within and the other near the surface of the fruiting bodies (Wever, 1988). Wever *et al.* (1991) proposed that bromoperoxidase activity near the surface of the alga produces HOBr which, following its release to seawater, reacts with organic substrates to form unstable brominated compounds. These compounds then decompose to give bromoform. Bromoform production in this case would be an incidental by-product of HOBr formation by the seaweed.

Haloperoxidase activity may explain the occurrence of polyhalogenated methanes in the marine environment, but no production of methyl halides has been detected via this route (Wuosmaa and Hager, 1990). Despite this, some species of macroalgae are clearly capable of producing the methyl halides (Manley and Dastoor, 1987).

There is evidence for methyl iodide (CH_3I) release by a number of species of macroalgae (Lovelock, 1975; Gschwend *et al.*, 1985; Manley *et al.*, 1992). Manley and Dastoor (1987) looked at methyl halide production by macroalgae more closely using the giant kelp *Macrocystis pyrifera*. Both laboratory incubation experiments and profiles

within *Macrocystis pyrifera* beds confirmed that this species, directly or indirectly, produced methyl chloride, bromide, and iodide. Neither tissue wounding nor desiccation caused methyl halide release. It was suggested that the methyl halides were products of kelp metabolism. The hypothesis that methyl halides can be produced as direct by-products of metabolism in some macroalgae is supported by the work of Wuosmaa and Hager (1990). The methyltransferase enzyme isolated from *Endocladia muricata*, catalysed methylation of iodide, bromide, and chloride ions. Iodide was the favoured substrate in the presence of equal concentrations of the three ions. When whole cells or cell-free extracts of *E. muricata* were incubated in seawater, however, only methyl chloride production was observed due to the high concentration of chloride. In a survey of macroalgae collected randomly in Monterey Bay, California, 22 of 44 species were found to produce methyl chloride.

Although macroalgal production of polybrominated methanes is an important source of organobromine to the troposphere (Gschwend *et al.*, 1985; Manley *et al.*, 1992), the estimated macroalgal source of methyl chloride (Manley and Dastoor, 1987) contributes $<0.1\%$ of the sea-air flux calculated by Singh *et al.* (1983) (1×10^{11} moles CH_3Cl / 5×10^{12} g CH_3Cl yr^{-1}).

1.2.1.2 Microalgae

The widespread supersaturation of CH_3Cl (Singh *et al.*, 1983) and CH_3Br (Singh *et al.*, 1983; Khalil *et al.*, 1993) in open ocean surface water cannot be explained through

release by coastal macroalgae. Above average concentrations of CH_3I have been observed in seawater and air in regions of high bioactivity (Rasmussen *et al.*, 1982).

The first direct evidence of phytoplankton involvement in the natural production of some volatile organohalogens was $CHBr_3$ emission observed in laboratory incubations of microalgal communities collected from beneath Arctic annual ice (Sturges *et al.*, 1992). Release of CH_2Br_2, $CHBr_2Cl$, and $CHBrCl_2$ has also been detected in laboratory incubations of ice-algae from the Antarctic (Sturges *et al.*, 1993) and also *in situ* incubations in the Arctic (Moore *et al.*, 1994). The influence of bacteria and grazers present on halocarbon emission in these natural populations is not yet clear. Production of $CHBr_3$, $CHBr_2Cl$, $CHBrCl_2$, and CH_2ClI has been observed in unialgal laboratory cultures of two cold water phytoplankton species - *Porosira glacialis* and a *Nitzschia* sp. (Tokarczyk and Moore, 1994). Recently, the presence of bromoperoxidase in one species of microalgae (*Nitzschia* sp. CCMP 580) has been confirmed (Wever and Moore, pers. comm). Only circumstantial evidence has been published supporting a phytoplankton role in the production of monohalomethanes.

1.2.1.3 Indirect production of methyl chloride

Reactions of biologically-produced precursors with chloride ions ("indirect" production) offer other potential pathways of methyl chloride formation in seawater. S_N2 substitution of methyl iodide by chloride ion as a source of oceanic methyl chloride was proposed by Zafiriou (1975) and considered further by Zika *et al.* (1984). Using rates

determined in laboratory experiments with sodium chloride solution (chlorinity - 19 ppt), Zafiriou estimated that an amount of methyl iodide similar to that which escapes to the atmosphere could be lost through conversion to methyl chloride. Estimates of methyl iodide fluxes from sea-to-air range from 1-9 x 10^9 moles yr^{-1} (Liss and Slater, 1974; Rasmussen *et al.*, 1982; Singh *et al.*, 1983; Nightingale, 1991), about 2-14% of the suggested transfer of methyl chloride from ocean to atmosphere (Singh *et al.*, 1979, 1983). Other sources of methyl chloride are required.

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 (Zafiriou, 1975). Observations of open ocean methyl iodide concentrations suggest an average value of about 7 pM (1.0 ngL^{-1}) (Lovelock, 1975; Singh *et al.*, 1983). This is 2 orders of magnitude less than the average methyl chloride concentration reported by Singh *et al.* (1983) (230 pM). It is unlikely that so small a pool of methyl iodide could support the much larger pool of methyl chloride. In the Eastern Pacific, Singh *et al.* (1983) found high methyl chloride where there was no corresponding elevation in methyl iodide, and vice versa. This was considered evidence supporting the existence of other more important mechanisms of methyl chloride formation in the oceans. As noted by Zika *et al.* (1984), however, physical mixing, air-sea exchange, and biological processes occur on timescales comparable with the reaction rates, and could destroy any correlation between methyl chloride and methyl iodide in the field.

White (1982) proposed an alternative synthesis pathway for methyl chloride.

ß-dimethylsulphoniopropionate (DMSP), a compound common in many marine macroalgae and microalgae, can react with halide to produce methyl halides. A precursor of DMS (dimethylsulphide, CH_3SCH_3) in seawater, DMSP has an osmoregulatory function, and may be preferred over the nitrogen-containing compatible organic solutes such as proline and glycine-betaine 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 (Andreae, 1990). Intracellular levels show high species and site dependence (Turner *et al.*, 1989; Andreae, 1990). White (1982) proposed that the elevated intracellular levels of iodide found in some algae might produce conditions favourable for the reaction of DMSP with iodide. Substitution of the methyl iodide formed with chloride or bromide either intracellularly or in the ambient seawater following release could produce the other methyl halides. Methyl bromide formation by this mechanism was catalysed by homogenates from *Ulva lactuca* (White, 1982). In the absence of additional experimental evidence, the importance of DMSP as a source of methyl chloride remains speculative.

1.2.1.4 Bacterial or fungal production of methyl chloride

Marine bacteria and cyanophyta also produce halogenated compounds (Fenical, 1982). Although the capacity to produce methyl chloride is widespread in the white wood-rotting fungi of the family Hymenochaetaceae (Harper, 1993b), whether any marine fungi are methyl chloride producers is not known. Epiphytic fungi on macrophytes have

been implicated in polyhalomethane production (Gschwend and MacFarlane, 1986). Manley and Dastoor (1987) observed an increase in methyl chloride, methyl bromide and methyl iodide approaching the bottom at a coastal site. Microbial production in the sediments was suggested as a possible explanation. Subsequent studies (Manley and Dastoor, 1988) demonstrated methyl iodide release from microbial cultures obtained from decaying *Macrocystis pyrifera*. Direct evidence of bacterial production of methyl chloride has not been reported.

1.2.2 Sinks of methyl chloride in ocean waters

The only chemical sink for methyl chloride in seawater which has been considered is hydrolysis. Hydrolysis in seawater may proceed via two mechanisms -

(a) neutral hydrolysis

$$CH_3Cl + H_2O \rightarrow CH_3OH + H^+ + Cl^-$$

and -

(b) basic hydrolysis.

$$CH_3Cl + OH^- \rightarrow CH_3OH + Cl^-$$

Acid hydrolysis will be negligible at seawater pH. The kinetics of basic and neutral hydrolysis of the methyl halides have been studied by Moelwyn-Hughes

(Moelwyn-Hughes, 1938, 1949, 1953). The rate constants measured by Moelwyn-Hughes (1949) suggest that basic hydrolysis is an insignificant pathway at seawater pH. Gentile *et al.* (1989), however, reported methyl bromide degradation rates 5-7 times those predicted for neutral hydrolysis alone at 18°C and pH = 8 (Moelwyn-Hughes, 1938, 1953; 1-1.5% per day). Gentile *et al.* (1989) also found that ultra-violet light enhanced the rate of CH_3Br degradation. A 0.2 M phosphate buffer was used by Gentile *et al.* (1989) in their determination of the rate of methyl bromide hydrolysis at pH=8. The mathematical model developed by Perdue and Wolfe (1983) can be used to predict the maximum contributions of commmonly used buffers to observed hydrolysis rate constants. The ratio of the observed pseudo-first order hydrolysis rate constant, k_{obs}, to that due to water and its ions alone, k_w, is related to the concentration of the buffer nucleophile, C_B (moles),

$$\frac{k_{obs}}{k_w} = 1 + (C_B [BCF]) \qquad (1)$$

- where BCF is a pH dependent buffer catalysis factor derived from the Bronsted equations for general acid-base catalysis. The predicted BCF for phosphate buffer at pH = 8.0 is 75. Thus, k_{obs}/k_w calculated using equation 1 is 16. As suggested by Elliott and Rowland (1993), it is likely that the high concentrations of buffer nucleophiles contributed to the high rates of methyl bromide degradation observed by Gentile *et al.* (1989). The rate of methyl bromide hydrolysis in distilled water measured by Elliott and Rowland (1993) was in reasonable agreement with that of Moelwyn-Hughes (1938).

Hydrolysis rates in seawater were not determined.

Hydrolysis rate constants determined in distilled water may not be directly applicable to seawater due to its greater ionic strength. Qualitatively, the presence of dissolved salts alters the rate of a substitution reaction in the same sense as an increase in solvent polarity (March, 1992). For reactions which proceed through an activated complex with greater charge density than the initial reactants, an increase in solvent polarity will increase the rate of reaction. This occurs due to the greater solvation, and therefore stabilisation, of the activated complex relative to the initial reactant(s) in a more polar solvent (Reichardt, 1988). The neutral hydrolysis of methyl chloride (reaction (a) above) involves a transition state in which positive and negative charges have been separated and is therefore of greater charge density than the initial uncharged reactants. In the basic hydrolysis mechanism, however, the charge in the transition state is dispersed relative to the reactants. Therefore, the rate of neutral hydrolysis of methyl chloride should be greater in seawater relative to distilled water while basic hydrolysis should be slower. Lifetimes calculated using the rate constants measured by Moelwyn-Hughes (1938, 1953) in distilled water may overestimate the persistence of methyl chloride in seawater. There have been no studies published that look at degradation rates of methyl chloride in natural waters.

Based on rate constants measured in distilled water, the lifetime of methyl chloride (e-folding time) is $>$ 50 years at 0 $^{\circ}$C and 0.5-1 years at 30 $^{\circ}$C (Table 1.1). To compete with losses due to ventilation of the upper 50-100m of the ocean, which occurs on timescales of 2-3 weeks, the rate of hydrolysis would have to be 10-100 times larger.

Table 1.1 Lifetimes (e-folding times in years) of the methyl halides with respect to chemical hydrolysis in distilled water

Temperature (°C)	0	10	20	30
CH_3Cl (1938)[a]	134	20.2	3.6	0.75
CH_3Cl (1953)[b]	53	10.4	2.2	0.53
CH_3Br (1938)	6.3	1.0	0.2	0.044
CH_3Br (1953)	3.0	0.6	0.14	0.036
CH_3I (1938)	42	6.2	1.1	0.21
CH_3I (1953)	18.4	3.5	0.7	0.17

[a] from Moelwyn-Hughes (1938)

[b] from Moelwyn-Hughes (1953)

Bacterial decomposition 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 favoured for the bacterial breakdown of chlorinated and brominated polyhalomethanes (Bouwer *et al.*, 1981; Bouwer and McCarty, 1983a) some degradation is also possible under denitrifying, and in the case of bromoform ($CHBr_3$), possibly

aerobic conditions (Bouwer and McCarty, 1983b; Cobb and Bouwer, 1991). The multi-component enzyme system (methane-monooxygenase) found in methane-oxidising bacteria is capable of oxidising methyl chloride and methyl bromide to formaldehyde along with methane (Stirling and Dalton, 1979, 1980). Species of methane-oxidising bacteria have recently been isolated from aerobic upper ocean waters (Sieburth *et al.*, 1993). Strains of *Nitrosomonas europaea*, an autotrophic ammonia oxidising bacterium, can be found in ocean waters (Austin, 1988). Ammonia mono-oxygenase, an enzyme system used by these bacteria, is also capable of performing co-oxidations of CH_3Cl and CH_3Br (Hyman and Wood, 1984). Rasche *et al.* (1990) found that *Nitrosoccocus oceanus*, a marine nitrifying bacterium, was capable of degrading methyl bromide. The amount of methyl bromide degradation depended on the availability of ammonium. Oremland *et al.* (1994) reported biologically mediated consumption of methyl bromide and methyl chloride in anaerobic saltmarsh sediments. Methyl bromide degradation occurred through the chemical attack of sulphide nucleophiles to produce methanethiol (CH_3SH). The methanethiol was then broken down by bacteria. Biologically controlled transformation of CH_3Cl to methanethiol by anaerobic bacteria was reported by Braus-Stromeyer *et al.* (1993). Methyl chloride can be used as both carbon and energy source by both certain anaerobic (Traunecker *et al.*, 1991) and aerobic (Hartmans *et al.*, 1986) bacteria found in sewage. Further studies of the distribution and physiology of bacteria from ocean waters are required to assess the importance of a bacterial sink of methyl chloride in different oceanic environments.

1.3 *Summary*

Emissions from the surface ocean are reported to constitute a large part of the natural flux of methyl chloride (Singh *et al.*, 1979; Singh *et al.*, 1983). Mechanisms known to produce methyl chloride in the marine environment (chloride substitution of methyl iodide (Zafiriou, 1975) and macroalgal emissions (Manley and Dastoor, 1987), however, contribute only a fraction of the flux estimated to come from the oceans ($< 10\%$). Other as yet unidentified sources of methyl chloride are therefore required to explain oceanic concentrations of this compound. Temporal and spatial coverage of methyl chloride in surface ocean waters is still limited. Additional measurements of methyl chloride are required to improve sea-air flux estimates. Previous calculations of air-sea exchange can be further revised by the inclusion of more realistic, recently developed parameterisations of air-sea exchange (Wanninkhof, 1992).

Biomass burning, due to both human activities (*e.g.* slash-and-burn agricultural practices) and wildfires, also releases methyl chloride into the troposphere (Crutzen *et al.*, 1979; Rasmussen *et al.*, 1980). Andreae (1993), in a re-evaluation of the magnitude of biomass burning sources of methyl chloride, suggested that such emissions may be of greater magnitude than previously thought (Crutzen *et al.*, 1979, Rasmussen *et al.*, 1980), comparable to estimates of the oceanic source (Singh *et al.*, 1979, 1983).

To date there have been few measurements of methyl chloride in seawater, all of which were made in the Pacific (Singh *et al.*, 1979; Singh *et al.*, 1983; Hoyt and Rasmussen, 1985; Manley and Dastoor, 1987), and the knowledge of its distribution is

far from complete. The following chapters describe the development of an analytical method for the direct determination of methyl chloride in aqueous environmental samples and its application to investigate the nature and magnitude of the oceanic source of methyl chloride.

Chapter 2: Analytical Method Development

2.0 *Introduction*

With the health and environmental concerns associated with many halogenated organics, considerable effort has been directed towards the development of suitable methods for analysing trace levels of volatile halocarbons present in air and water samples. Gas Chromatography (GC) coupled with either Electron-Capture (EC) or Mass Spectrometric (MS) detection has been used extensively. This chapter describes the development, testing and use of a GC-EC system designed to measure methyl chloride in seawater both in the laboratory and in the field.

2.1 *System I: December 1990 - June 1991.*

A Hewlett-Packard 5890 gas chromatograph with a constant current ECD (Ni-63, 15 mCi) was used. Peaks were recorded and integrated on an HP 3390A integrator.

2.2 *Choice of chromatographic column*

Due to its high volatility, methyl chloride is one of the first components to elute

on most chromatographic columns. Both packed and capillary ($\leq$ 0.32mm inner diameter) columns have been used for its separation. Larger samples can be used with packed columns without risk of overloading. However, capillary columns offer far superior resolution. J&W Scientific introduced Megabore®(0.53mm i.d.) columns to bridge the gap between packed and capillary columns allowing larger samples and higher flow rates with less reduction in separating power. Specialty Megabore columns such as the DB-624 (J&W Scientific) are now specified in EPA methods for the analysis of a suite of volatile halocarbons in air and water samples.

The first method reported for the determination of CH_3Cl in air (Grimsrud and Rasmussen, 1975) used a 20ft. x 1/16in. packed column and although good resolution was observed, the operating temperatures were -60°C to 100°C. Ideally, above ambient temperatures are preferred to avoid the use of a cryogen such as $N_2(l)$ in the oven temperature control. A later study by Rasmussen *et al.* (1980) used two different 10ft. packed columns at 65°C to resolve the most volatile components in air - OV101 and SP2100 (dimethylpolysiloxanes) 10-20% on Chromosorb W and Porasil-B. In the analyses using the former, methyl chloride was not completely separated from CFC-12 (CCl_2F_2). Grimsrud and Miller (1978) report the co-elution of methyl chloride with an unidentified component using 10% SF-96 on Chromosorb-W. Hoyt and Rasmussen (1985) used a DB-1 (J&W Scientific) capillary column with a 1.0 μm film in their analyses of methyl chloride in and over the Pacific Ocean but methyl chloride was found to tail badly.

Separation of halocarbons, light hydrocarbons, and also carbon dioxide and water

at above ambient temperatures are possible using 30m of Megabore GS-Q column (J&W Scientific). It is a 0.53mm i.d. Porous Layer Open Tubular (PLOT) column which operates through gas-solid adsorption mechanisms using a layer of styrene-type copolymer as the adsorptive material. It was designed to give improved resolution and more rapid sample analysis than Porapak™-Q packed columns.

2.2.1 The retention time of methyl chloride on the GS-Q

To determine the retention time as a function of column temperature (Figure 2.1), nanogram quantities of CH_3Cl in 100 to 200 μL volumes of UHP (ultra-high purity) nitrogen were injected on-column through the septum injection port. The GS-Q was found to retain methyl chloride sufficiently to allow operation at above ambient temperatures.

2.3 *Detection*

2.3.1 The Electron Capture Detector (ECD)

The Electron Capture detector was developed throughout the 1960's by Lovelock and others (Lovelock and Lipsky, 1960; Lovelock, 1963; Wentworth *et al.*, 1966). It consists of a chamber containing a ß-emitter, usually Ni-63, an anode and a cathode.

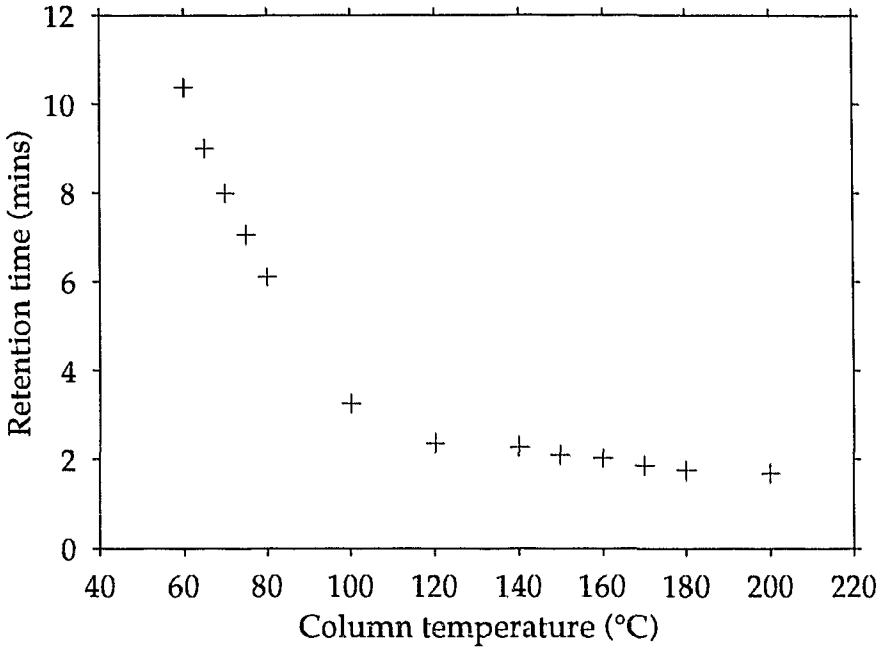


Figure 2.1 Methyl chloride retention time as a function of column temperature. Helium flow 6 mL/min, 30m GS-Q column.

Conventional electron-capture theory explains ECD operation as follows. Inert gas flowing through the chamber (nitrogen or argon/methane) is bombarded with electrons. After many inelastic collisions, these electrons reach temperature equilibrium with the gas and are collected at the anode producing a steady background current. When molecules with sufficient electron affinities enter the chamber, some electrons are captured forming negative ions. The negative ions drift much more slowly in an applied electric field and react more readily with positive ions than do the electrons causing a reduction in the background current.

In the constant current mode of operation, voltage is applied to the electrodes in narrow rectangular pulses. The pulse frequency is constantly adjusted to maintain a constant current. As the pulse frequency is inversely proportional to the electron density, it gives a measure of the concentration of electron absorbing analytes within the detector.

The ECD is highly sensitive to molecules containing halogen atoms due to their high electron affinities. On entering the ECD most halogen-containing compounds react according to the following reaction -

$$e^- + RX \rightarrow RX^- \rightarrow R^\cdot + X^-$$

- to release the halogen atom (X) as a halide ion. The sensitivity of the ECD to halogens follows the order -

$$I > Br > Cl > F.$$

In general, a greater response is observed the more highly halogenated the molecule (Clemons and Altshuller, 1966). Prediction of absolute response factors, however, even to an order of magnitude, is not possible due to lack of knowledge about the kinetics of reactions, and indeed the reactions themselves, taking place inside the ECD. Moreover, the absolute response of the ECD to a compound depends critically on the presence of any trace contaminants in the carrier gases.

2.3.2 The ECD for the detection of methyl chloride

There are two documented problems with the detection of methyl chloride with the ECD. First, as methyl chloride contains only a single chlorine atom, the ECD's sensitivity to it is at the low end of the scale. Second, non-linear calibration curves have been observed for methyl chloride and also other monochloroalkanes (Grimsrud and Miller, 1980). One factor affecting the probability of electron absorption by a compound is its absorption cross-section. Halogenated molecules have absorption cross-sections which vary significantly with electron energy (Lovelock and Lipsky, 1960). Grimsrud and Miller (1980) speculate that electrons produced in the ECD may have small but significant differences in energy. Therefore, only some proportion of the electrons present result in electron absorption on collision with the analyte. As the concentration of analyte in the detector increases, the response will approach an asymptotic value dependent on the number of electrons present with energies suitable for electron absorption by the analyte. This effect would be most pronounced for weakly absorbing

molecules such as methyl chloride.

Grimsrud and Miller (1978) and Rasmussen *et al.*(1980) independently observed that trace amounts of oxygen (0.1-0.4%) flowing through the detector caused an appreciable and reproducible enhancement in the response of the ECD to some halogenated methanes. A mechanism explaining this had been previously discussed by Van de Wiel and Tommassen (1972) in their study of the effect of electronegative contaminants in the ECD -

$$M + O_2 + e^- \rightarrow M + O_2^- \qquad (1)$$

$$M + O_2^- \rightarrow M + O_2 + e^- \qquad (2)$$

$$O_2^- + RX \rightarrow R^\cdot + X^- + O_2 \qquad (3)$$

$$RX + e^- \rightarrow R^\cdot + X^- \qquad (4)$$

Karasek and Kane (1973) used plasma chromatography to show that the O_2^- was in fact $(H_2O)_nO_2^-$, but the explanation remains essentially the same. The presence of oxygen in the ECD cell leads to an overall decrease in the electron concentration due to reaction (1). Dissociation reaction (2) occurs only when the captured electron is of relatively high energy. When a halogenated compound is also present it can be dissociated by the superoxide anion-water complexes as well as the electrons (reactions

(3) and (4)). The effect of oxygen on the response of the ECD to a particular halogenated methane depends on the relative rates of reactions (3) and (4). For weakly electron-absorbing halogenated methanes, reaction (3) is faster and the superoxide catalytic cycle (reactions (1) and (3)) acts to consume electrons at a more rapid rate and therefore produce a signal enhancement. However, for highly halogenated molecules such as carbon tetrachloride which already have rapid rates of electron capture, the superoxide capture of electrons acts in competition resulting in little or no increase in response (Grimsrud and Stebbins, 1978). Such signal enhancement occurs with either nitrogen or argon/methane as the make-up gas (Van de Wiel and Tommassen, 1972). Reaction (1) is exothermic and therefore the response modification due to the presence of oxygen is highly temperature dependent. Grimsrud and Miller (1978) suggest that detector temperatures of 300-350 $^{\circ}$C optimise the signal-to-noise ratio for methyl chloride analysis. However, Rasmussen *et al.* (1980) found that lower temperatures 250-275 $^{\circ}$C gave the best response in their system and they attributed a reduction in response of the detector to methyl chloride at temperatures above 300 $^{\circ}$C to thermal lability. In the absence of air and water, methyl chloride is stable to thermal degradation at temperatures approaching 400 $^{\circ}$C (Ehman *et al.*, 1964). Trace amounts of oxygen in the detector may result in an increased rate due to oxidative degradation. In the present study, a decrease in response by a factor of 3-4 was found at a detector temperature of 315 $^{\circ}$C relative to that at 275 $^{\circ}$C. A detector temperature of 275 $^{\circ}$C was used in this work.

In previous analyses of methyl chloride using oxygen doping (Grimsrud and Miller, 1978; Rasmussen *et al.*, 1980), oxygen was added to the carrier flow. Even trace

amounts of oxygen flowing through a chromatographic column can decrease its operating lifetime due to oxidative degradation of the stationary phase. Grimsrud *et al.* (1980) in a study of oxygen doped electron capture detection of PAH's (polynuclear aromatic hydrocarbons) found that the signal enhancement was independent of whether the oxygen was introduced to the carrier or the make-up gas flows. To protect the chromatographic column, it was decided to introduce oxygen to the detector via the nitrogen make-up gas flow.

Figure 2.2 shows the HP 5890 ECD response as a function of oxygen concentration at 275 °C for 840 pg direct injections of methyl chloride in UHP nitrogen (prepared by the two step gas dilution method described in the standardisation section). The oxygen concentration was varied by merging a rotameter controlled flow of 0.5% O_2 in N_2 (unanalysed) with the UHP N_2 make-up gas. The baseline frequency allowed continuous monitoring of the oxygen concentration passing through the detector (Grimsrud and Miller, 1978). A concentration of *ca.* 0.38% oxygen produces a signal enhancement of 65 under these conditions.

Hoyt and Rasmussen (1985) measured CH_3Cl in marine air and seawater samples using both ECD and MS detection. They reported no interferences in EC detection of CH_3Cl in seawater. Rasmussen *et al.* (1980) compared oxygen-doped EC with MS detection for methyl chloride in air samples and found good agreement.

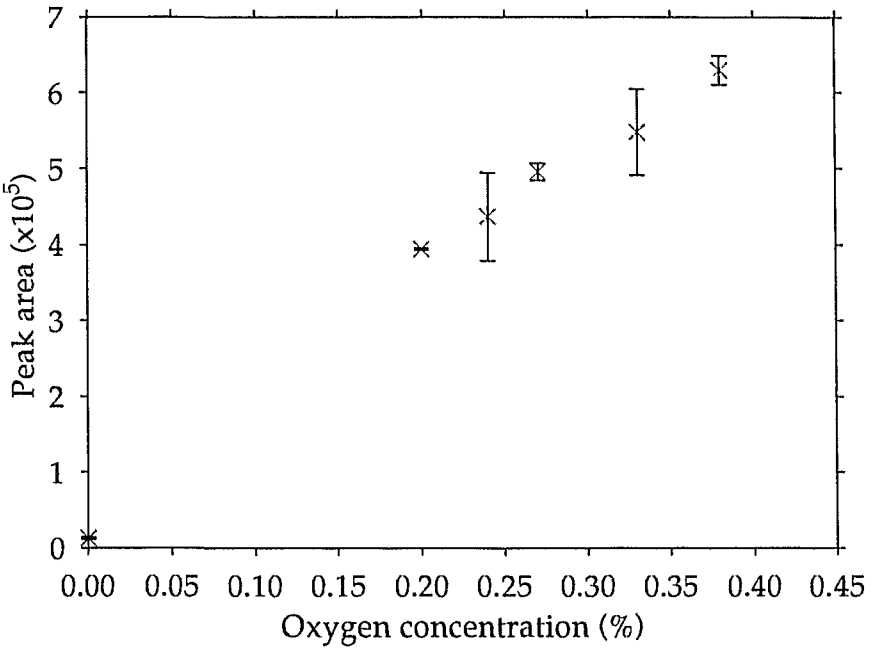


Figure 2.2 Response of the detector to methyl chloride as a function of oxygen concentration. Detector temperature 275°C, range = 5, 840 pg direct injections from 3 separate gas standards. Error bars show range of peak areas observed.

2.4 *Preconcentration from seawater*

Two methods have been used previously for the extraction of trace organohalogens from seawater - liquid-liquid extraction into pre-purified pentane (e.g. Klick and Abrahamsson, 1992) and 'purge-and-trap' (e.g. Class and Ballschmiter, 1988). The former method has been used only for the less volatile halomethanes such as $CHBr_3$, CCl_4, CH_3CCl_3, and CH_2I_2 and is unlikely to be as precise for a compound as volatile as methyl chloride. 'Purge-and-trap' methods involve no manual handling of samples, thereby reducing the possibility of contamination and/or losses. A sample of seawater is purged with a reproducible volume of inert gas onto a trapping material. The analyte is thermally desorbed from the trap into a gas chromatograph for separation and analysis.

2.4.1 Choice of trapping material

Different trapping materials were tested using a 10-port Valco™ (Valco Instruments Co.) valve to switch the trap into the helium carrier flow. Methyl chloride diluted in UHP N_2 was injected onto the cooled trap using a gas-tight syringe. The valve was then switched to pass helium through the cooled trap for a given time before desorption.

As the retention time of methyl chloride on the GS-Q increases steeply at temperatures less than 80°C (Figure 2.1), a short length of GS-Q was tested as a possible trap. Quantitative trapping of methyl chloride at close to room temperature or 0°C is desirable to avoid the use of a cryogen such as $N_2(l)$ or $CO_2(s)$.

A sixty centimetre length of GS-Q was attached with glass butt connectors to short pieces of deactivated fused silica coming from the valve. The volume of gas above which methyl chloride was lost from this trap was determined as a function of temperature (Figure 2.3). Trap temperatures below 0.5°C were obtained using a saline ice/water bath. Higher trap temperatures were achieved by fixing the trap to a copper pipe through which water at a controlled temperature could be pumped. Even at 0°C breakthrough occurred when less than 50 mL of helium have passed through the trap. To attain a breakthrough volume greater than 250mL required a Dri-ice/Ethanol bath (T = -70°C). Sixty centimetre lengths of DB-5 and DB-624 column did not trap methyl chloride even at -70°C. Moreover, immersion in an ice/water mixture for trapping and then in boiling water for desorption was impractical due to the fragility of the fused silica tubing and glass butt joins.

Attention was turned to the possibility of using a stainless steel packed trap. A packing material was required which would efficiently trap methyl chloride at 0°C or above, but allow complete and rapid desorption at 90-100°C or below. Porapak-N (Waters Limited) is capable of trapping the most volatile components such as methyl chloride and CFC-11 ($CFCl_3$) and CFC-12 (CF_2Cl_2) at room temperature, however desorption requires temperatures greater than 100°C. Porapak-Q, the porous polymer equivalent of the stationary phase of the GS-Q column, is less retentive. A 1mL volume Porapak-Q trap was constructed (1/8" stainless steel tubing, wall thickness 0.020", *ca.* length 27.3 cm) and conditioned.

The trap was completely immersed in ice/water (0°C) during trapping. The

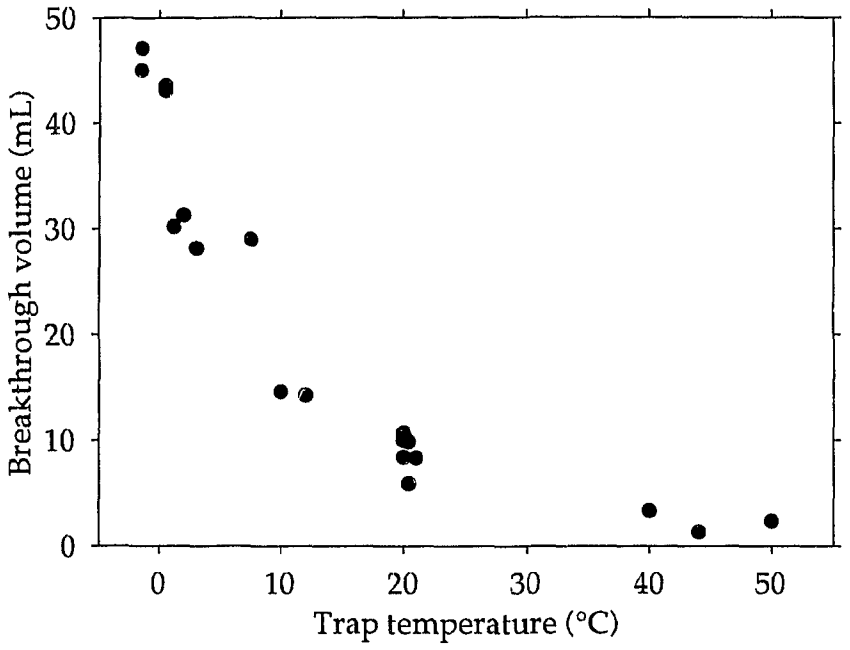


Figure 2.3 Breakthrough volume of 60cm GS-Q trap as a function of temperature. Range = 5, 840 pg direct injections

breakthrough volume was greater than 300mL. However, the desorbed peak was very wide (>2 minutes) compared with direct injection. Removal of an in-line filter after the trap reduced the peak width by 50%, suggesting that its dead volume contributed to the peak broadening. Further reduction in peak width was obtained using a smaller volume trap (0.2 mL). The breakthrough volume of the smaller trap was *ca.* 250 mL. Peak width was 0.8 minutes.

2.5 *Construction of the purge-and-trap system*

Figure 2.4 is a diagram of the first purge-and-trap system. Components were mounted on a framework of bars and clamps. The system could be isolated from the GC using the toggle valve, A. Helium purge flow was controlled using pressure regulator, P, and checked using a bubble flow meter at valve D. The sample was injected from an all-glass Luer-Lok syringe through the Hamilton distribution valve, B, into the purge vessel (maximum volume 25 mL). Draining of the sample was also through the distribution valve driven by the pressure in the system. The vessel was flushed once or twice with sample, depending on the volume available, and then the system was flushed with purge gas and the trap heated and vented to the atmosphere for 7 minutes before injection of the sample volume itself. After leaving the purge vessel, the purge gas flowed through a Nafion drier and magnesium perchlorate drying tube (1/4" o.d., 1/6" i.d. glass) to the trap (0.2mL; Porapak-Q in 1/8" stainless steel tubing). Trapped

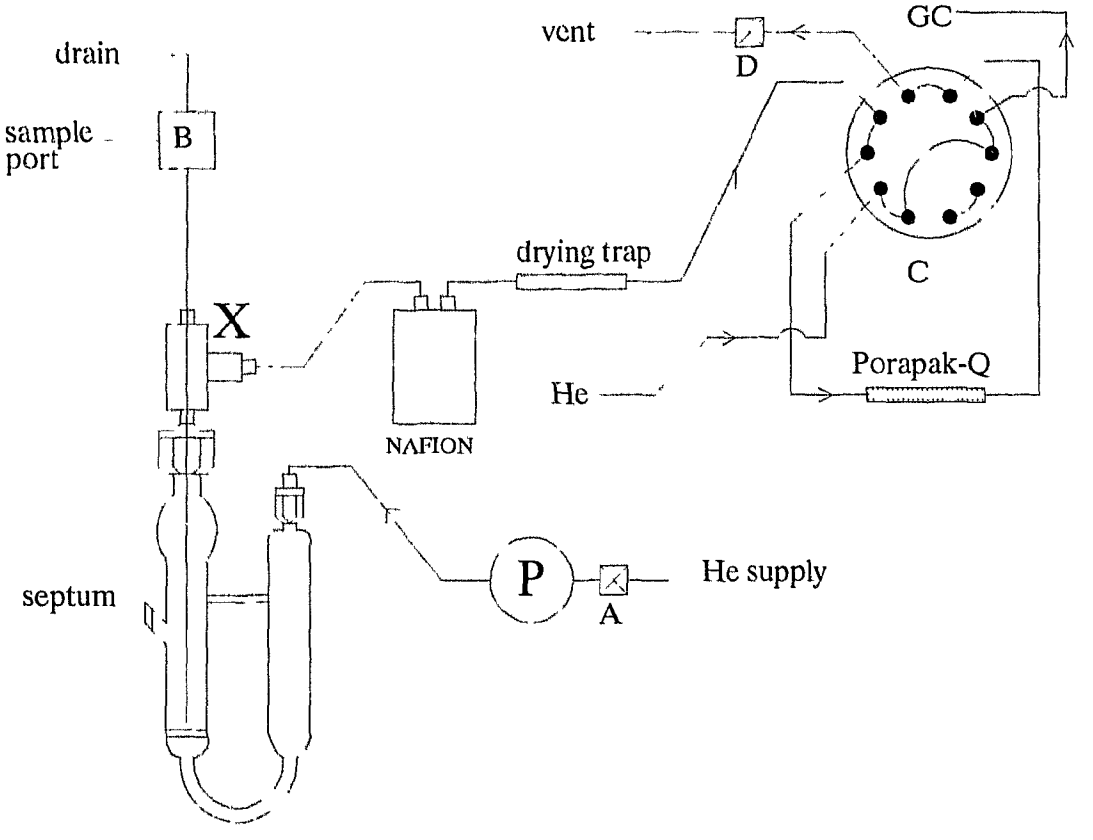


Figure 2.4 Diagram of purge-and-trap System I. A and D = toggle valves, B = distribution valve, C = stainless steel Valco valve, P = pressure regulator. X = position of glass wool plug.

compounds were transferred to the column by immersing the trap in hot water and immediately switching valve C.

A desorption temperature of 100°C will not completely remove less volatile compounds from the Porapak-Q trap. High temperatures (>200°C), or alternatively long time periods, are required to efficiently remove such compounds from the GS-Q. As short a purge time as possible was desired to keep to a minimum the amount of less volatile components reaching the trap and the column. The methyl chloride peak area as a function of volume of purge gas used is shown in Figure 2.5. A purge flow of 40 mL min^{-1} for 5 minutes gave maximum efficiency with minimum trapping of less volatile compounds.

Sequential desorptions showed that the helium carrier flow of 7 mL/min quantitatively removed the methyl chloride from the trap when immersed in hot water.

Initially, only the Nafion drier was used for drying the purge stream. Figure 2.6 (a) shows a chromatogram of a Super-Q (deionized water, Millipore Corp.) water blank with only the Nafion in-line. In Figure 2.6 (b) a nominal CH_3Cl standard had been added to the Super-Q water. A magnesium perchlorate drying trap was inserted after the Nafion drier for the Super-Q blank chromatogram shown in Figure 2.6 (c). When oxygen is present in the gas flow, trace amounts of water cause a decrease in the number of electrons through increased formation of negative ions (Karasek and Kane, 1973) leading to a further increase in baseline level. Incomplete removal of water by the Nafion drier is one possible explanation for the baseline shift seen in Figure 2.6 (a) and (b). Use of a $Mg(ClO_4)_2$ drying trap after the Nafion drier solved the problem. Later runs using the

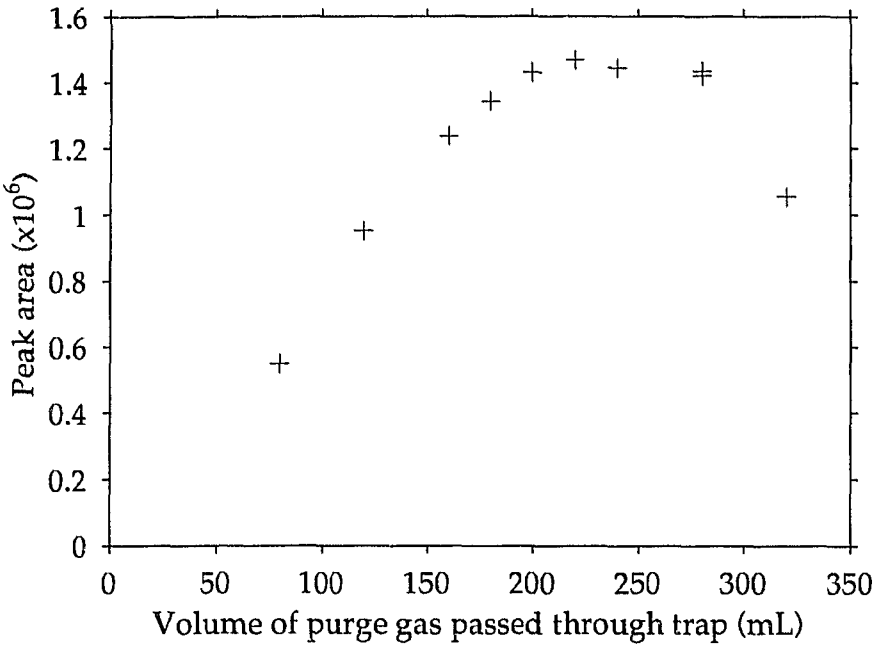


Figure 2.5 Methyl chloride peak area as a function of volume of purge gas passed through a 0.2 mL Porapak trap. Trapping at 0°C, desorption at 100°C.

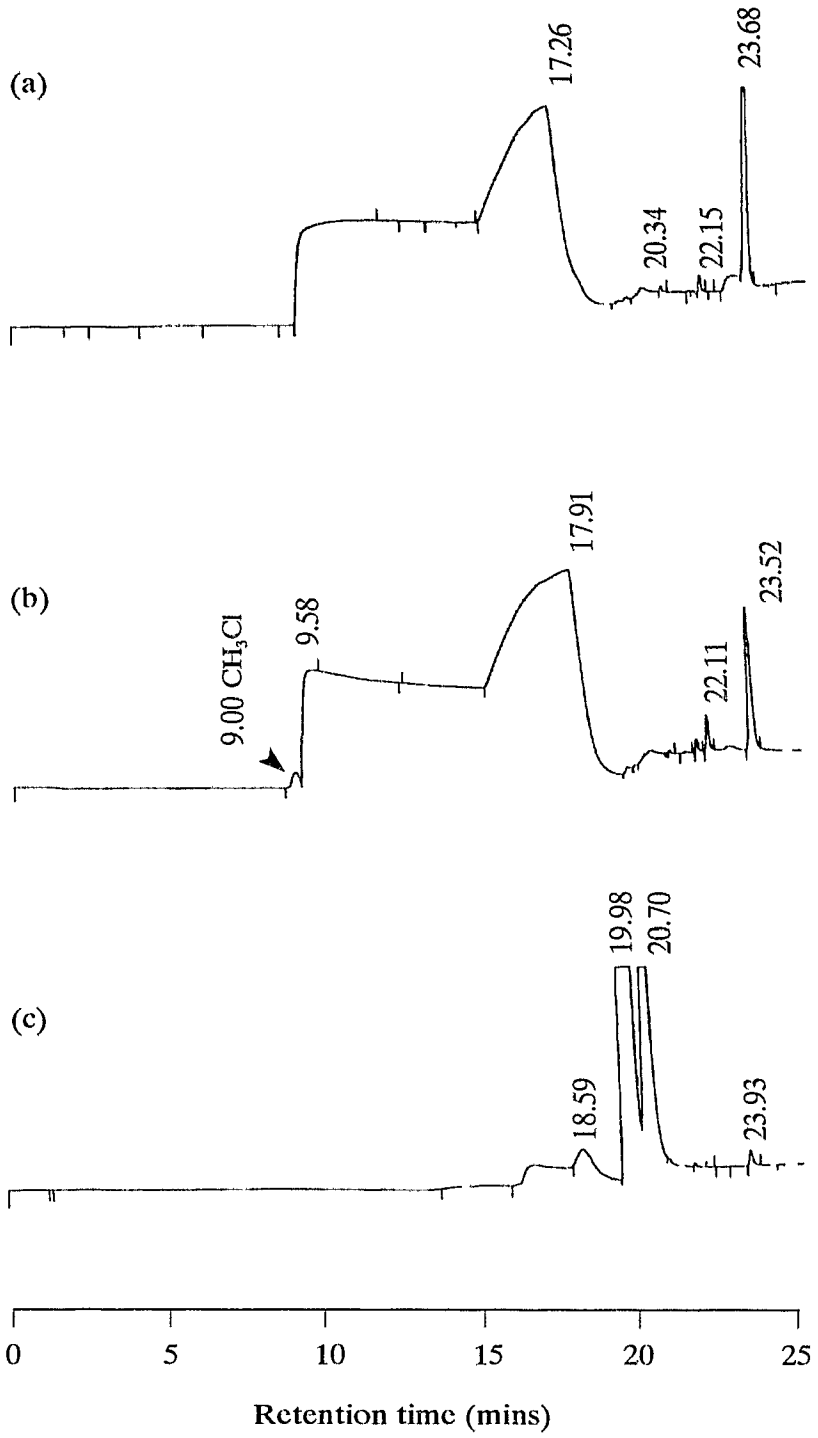


Figure 2.6 Chromatograms of (a) Super-Q using Nafion drier only, (b) Super-Q spiked with CH_3Cl, Nafion only, and (c) Super-Q using both Nafion and $Mg(ClO_4)_2$ trap. Column temperature = 60°C, He flow at 7 mL min^{-1}, System I.

$Mg(ClO_4)_2$ trap alone showed no baseline problems. Use of the Nafion drier was discontinued. Figure 2.6 (c) is the first run after inserting the magnesium perchlorate trap. Although some contaminant peaks are evident around a retention time of 20 minutes, none is present in the earlier part of the chromatogram important for CH_3Cl (retention time = 8.95 minutes for conditions used at this time; He carrier flow 7 mL min^{-1}, column temperature 60°C).

2.6 *Analytical sensitivity and choice of sample volume*

The average surface water CH_3Cl concentration observed by Singh *et al.* (1983) in the eastern Pacific was 229 pM (11.5 ng L^{-1}). Detection of 10 pM (0.5 ng L^{-1}) was considered a reasonable aim for the analytical method sensitivity. If a sample volume of 20 mL was chosen, the required detection limit would be 10 pg, assuming 100% purge and trapping efficiency. Using a larger sample volume, although increasing the amount of methyl chloride available for analysis, would require a total purge flow greater than the breakthrough volume of the trap. With a detector temperature of 275°C, carrier He flow of 7mL min^{-1}, and oxygen-doped UHP N_2 make-up gas flow of 23 mL min^{-1}, the analytical sensitivity was sufficient to determine methyl chloride in Northwest Arm seawater taken from the laboratory tap.

2.7 *Resolution of peaks*

A chromatogram from the analysis of 20 mL of laboratory sea water is shown in Figure 2.7. The peak at 6.2 minutes was identified as CH_3Cl by injecting a spiked sample and also comparison with the standard retention time. With column temperatures below 70°C the methyl chloride peak and the peak at 5.9 minutes were not sufficiently resolved. Optimum separation and peak shape were achieved using a column flow rate of 7mL min^{-1} and temperature of 70-80°C. A column flow rate of 7 mL min^{-1} and temperature of 70°C were used in subsequent analyses. Based on the order of elution of halogenated volatiles on the GS-Q, the peak at 5.9 minutes is tentatively identified as CFC-22 ($CHCl_2CClF_2$). In water samples collected in the field this peak is 5-7 times smaller than in this sample of seawater from the laboratory tap and does not interfere with methyl chloride peak integration.

To check for co-eluting peaks, several natural samples were run using a 60m GS-Q. With a column temperature of 70°C and He flow of 7 mL min^{-1} no additional peaks were observed close to a spike of methyl chloride in a sample of seawater analysed with System I during the "Hudson" cruise. Figure 2.8 (a) shows a System II (see Section 2.8) blank run with the 60m column, 2.8 (b) a 20mL sample of Sackville riverwater, and 2.8 (c) Sackville riverwater spiked with methyl chloride standard. The separation between methyl chloride and the preceding peak on a 60m GS-Q was complete (1.3 minutes). Samples of algal culture showed the same peaks as the sample of riverwater using the 60m GS-Q. The high degree of separation of methyl chloride and "CFC-22" on the 60m

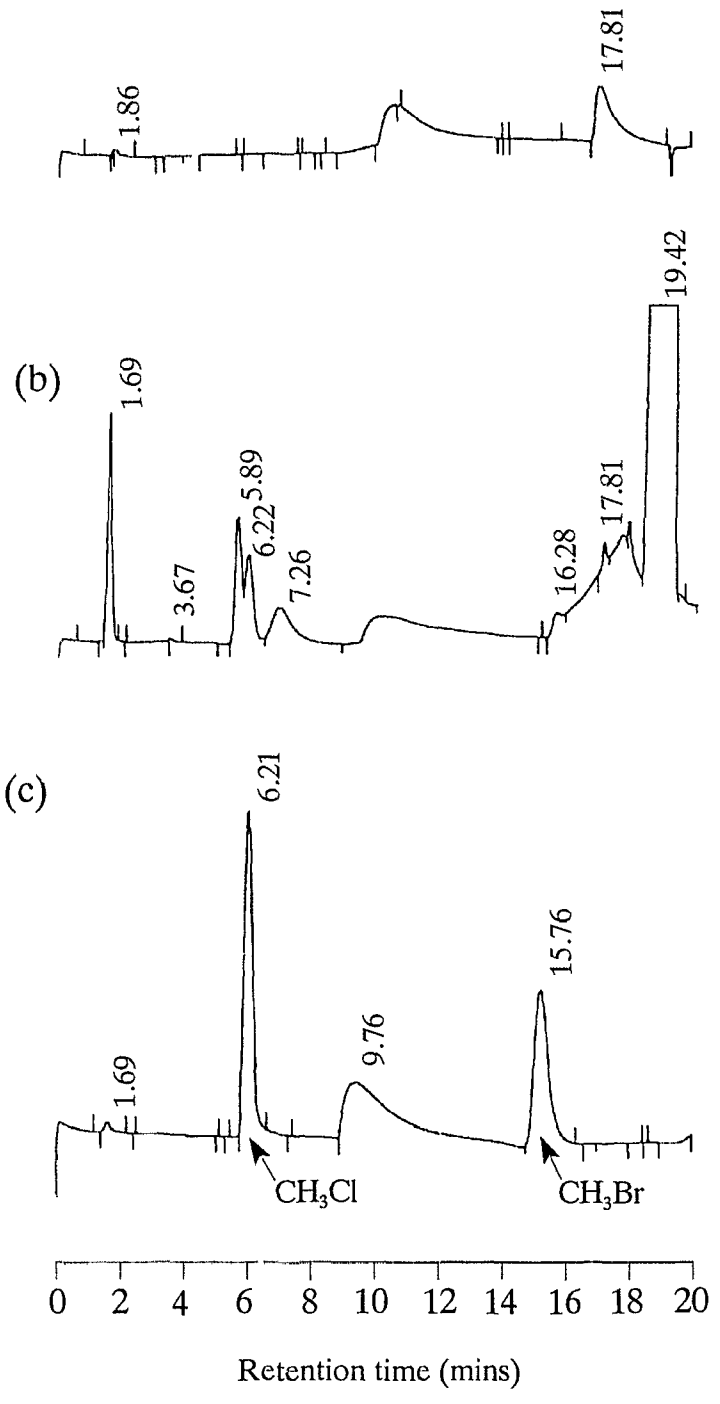


Figure 2.7 Chromatograms of (a) Super-Q blank, (b) 20mL of laboratory seawater, and (c) standard of CH_3Cl and CH_3Br in Super-Q using a 30m GS-Q, column temperature 70°C, He flow 7 mL min^{-1}, System I.

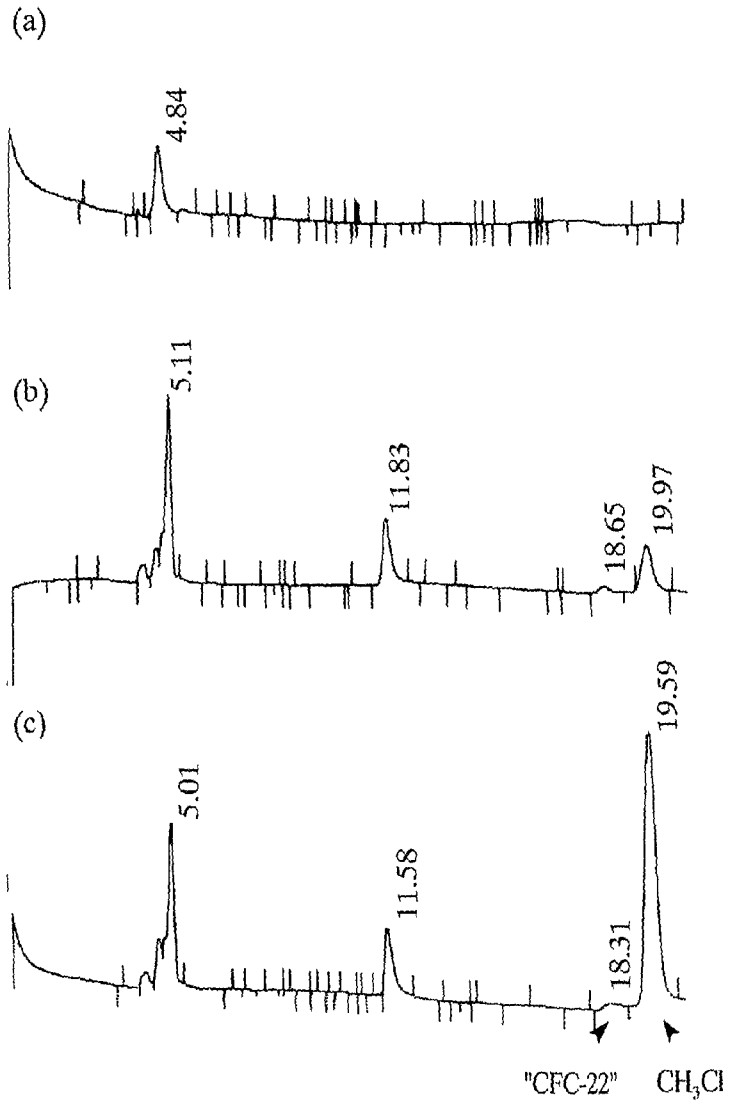


Figure 2.8 Chromatograms of (a) Super-Q blank, (b) a 20mL sample of Sackville riverwater, and (c) a 20mL sample of Sackville riverwater spiked with CH_3Cl, obtained using a 60m GS-Q column at 70°C, He flow at 7 mL min^{-1}, System II.

column without any evidence of additional peaks and the consistency of pattern of eluted peaks was considered strong evidence that no other components were co-eluting with CH_3Cl.

2.8 *Problems arising with System I.*

During sea trials, several problems arose which led to subsequent modification of the system designated as System I. The 1/6" i.d. diameter drying trap was found to block the purge flow when the magnesium perchlorate became wet. To reduce the amount of water reaching the trap, a glass wool plug was inserted within the stainless steel fitting at the exit of the purge vessel (X on Figure 2.4). During the cruise, the purge flow was checked before every sample and standard run, and the drying trap was changed approximately every ten runs. A blank was run before resumption of sample analysis. The Porapak-Q trap was baked periodically using heating tape (200°C) to remove less volatile compounds not desorbed with boiling water.

Although the analysis itself was isothermal (70°C), rapid removal of less volatile compounds from the column required a baking period at a higher temperature. The maximum recommended operating temperature for the GS-Q is 250°C. However, the time for the baseline to return to normal after a short baking period at 200°C was 30 minutes. In order to minimise the duration of the analytical cycle, the column was baked at 150°C for 10 minutes. This eluted the more volatile components but left the less

volatile for subsequent removal by baking at 220°C every 50 or so samples. Total sample analysis time using this temperature programme was 1 hour. On one occasion during the cruise, 20cm was removed from the head of the column to accelerate column clean-up.

2.9 *System II: October 1991 - December 1993*

For easier transport and set-up for possible field applications, the purge system components of System II were firmly mounted on a wooden backboard with a broad wood base. To reduce the possibility of a blockage developing in the drying trap, 1/4" i.d. glass tubing was used in place of the 1/6" i.d. tubing. Care was taken during filling the trap to avoid $Mg(ClO_4)_2$ powder. The trap was changed every morning, and also when evidence of wetness became apparent or purge flow was reduced. Following replacement of the drying trap, the system was dry purged and a blank run to remove contaminants introduced during the replacement. No evidence of interfering contamination from the $Mg(ClO_4)_2$ was observed. Standards run immediately after trap replacement and when moisture effects were becoming visible agreed within the run-to-run precision of the method.

The less volatile compounds collect near the head of the column. Backflushing the column during the bake mode would accelerate the removal of these components. To allow this, the system was modified as shown in Figure 2.9. The rotor in the 10-port

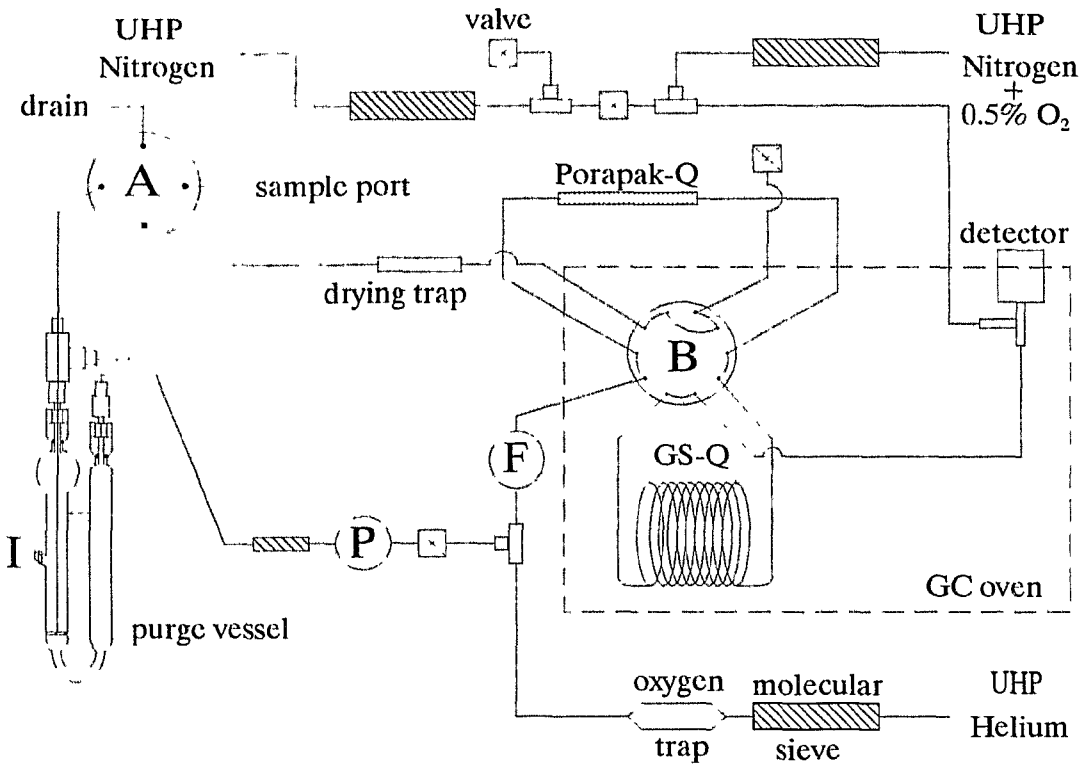


Figure 2.9 Diagram of System II. A = Valco stainless steel distribution valve, B = 10 port Valco valve, P = pressure regulator, I = septum port, □ = toggle valve, F = flow control for carrier gas.

valve (C) was replaced with one capable of withstanding the temperatures in the GC oven(PIN # C10WT). During purging of the next sample, the column was backflushed. Switching valve C for desorption reversed the direction of flow through the column for analysis. This modification reduced the analysis time by 40%. The necessity of high temperature baking of the column every 50 or so samples was also avoided.

The lifetime of the Hamilton distribution valve (valve B in Figure 2.4) was found to be rather short. It was replaced with a Valco distribution valve as shown in Figure 2.9.

2.10 *Standardisation*

2.10.1 Gas standards

During the development of System I and the start of the field study (described in Chapter 3), a primary standard was prepared by a two step sequential dilution of pure CH_3Cl vapour in UHP nitrogen. A vacuum-baked (70-80°C) 500mL gas sampling bulb was flushed with UHP nitrogen for 15 minutes before the Teflon stopcocks were closed. Direct on-column injection of 100μL of the UHP nitrogen in the bulb showed no contaminant peaks in the relevant part of the chromatogram. 500-1000μL of pure CH_3Cl vapour was withdrawn from a lecture bottle into a gas tight syringe through a septum-containing syringe adaptor attached to the pressure regulator. This was injected into the

bulb via a Teflon-coated silicone septum. Based on the diffusion coefficient (0.105 cm^2 s^{-1}) of methyl chloride in air at 25°C, 1 atmosphere pressure, methyl chloride should be well-mixed within the vessel in less than an hour. To make sure that methyl chloride was uniformly distributed within the vessel, it was left for 12 hours, before 500-1000μL volume of this dilution was injected into another identical gas sampling bulb. Twelve to eighteen hours elapsed before 100-200 μL volumes were injected either directly on-column or into the purge vessel. The ambient temperature was noted at each dilution. Volumes of 100-500 μL were injected into pre-purged super-Q or seawater in the purge vessel. Precision (defined as the sample standard deviation over the mean) of repeated injections of gas standards prepared in the laboratory was $\pm$4.5% (n=7). No significant change in peak area was observed after 24 hours. Reusability and lifetime of the Teflon-backed silicone septa was found to be limited. After 10-15 punctures, the peak area showed measurable decrease on time scales of 6-8 hours. Good agreement (within 10%) was found between the limited number of two-step dilution standards run in the laboratory before the cruise. On the cruise however, the precision of injections from a single standard was poor. Further discussion of standardisation during the cruise is given in Chapter 3.

2.10.2 Solution standards

Using a solution standard gives a calibration more representative of the actual sample purging process. Apparatus designed for the preparation of a solution standard

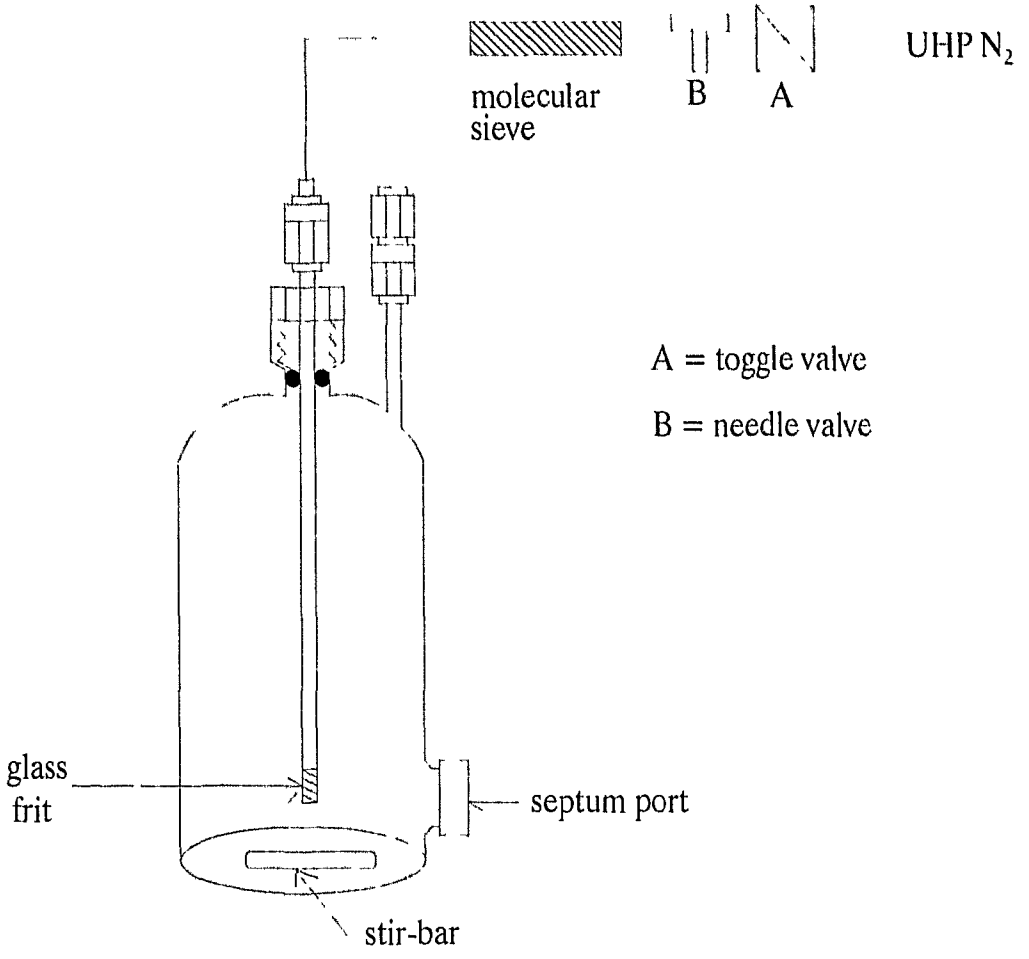


Figure 2.10 Apparatus for preparation of a dilute methyl chloride solution standard.

is shown in Figure 2.10. The volume of Super-Q water contained within the vessel was determined gravimetrically prior to connection with the gas line (typically *ca.* 485 mL). Following 8-12 hours purging with UHP nitrogen with stir-bar agitation, injection of μL quantities of the Super-Q into pre-purged water within the purge vessel of System II showed no detectable methyl chloride. The vessel was sealed and bags containing ice chips were packed around it. 45-60 minutes later, 20 or 25μL of pure methyl chloride vapour was slowly injected just above the stir-bar. Dissolution of the vapour occurred at rates great enough to prevent the small bubbles from reaching the liquid surface. The 25μL gas-tight syringe used for transfer between the lecture bottle syringe adaptor and the glass vessel had a 26s gauge needle with the hole on the side to prevent septum plugging. The mass of methyl chloride added was calculated from the injected volume corrected for both laboratory temperature and atmospheric pressure assuming ideal behaviour. The assumption of ideal behaviour is valid at atmospheric pressures. Due to the high ratio of liquid to gas volume, $<1\%$ of the injected methyl chloride resided in the gas phase at equilibrium. The stir-bar was present to produce rapid mixing within the vessel and also enhance the rate of dissolution of methyl chloride. Sequential standard runs starting less than 5 minutes after addition of the methyl chloride (Figure 2.11) showed no significant change in peak area over a 24 hour period. Run-to-run precision of standard analyses was $\pm 4\%$ (σ_{n-1}/mean; n=11). Peak areas from individual standards prepared throughout a year agreed within 12-20%. Linearity of response extended well beyond the expected range of environmental concentrations (Figure 2.12). The system blank (analysis of previously stripped seawater) was consistently zero.

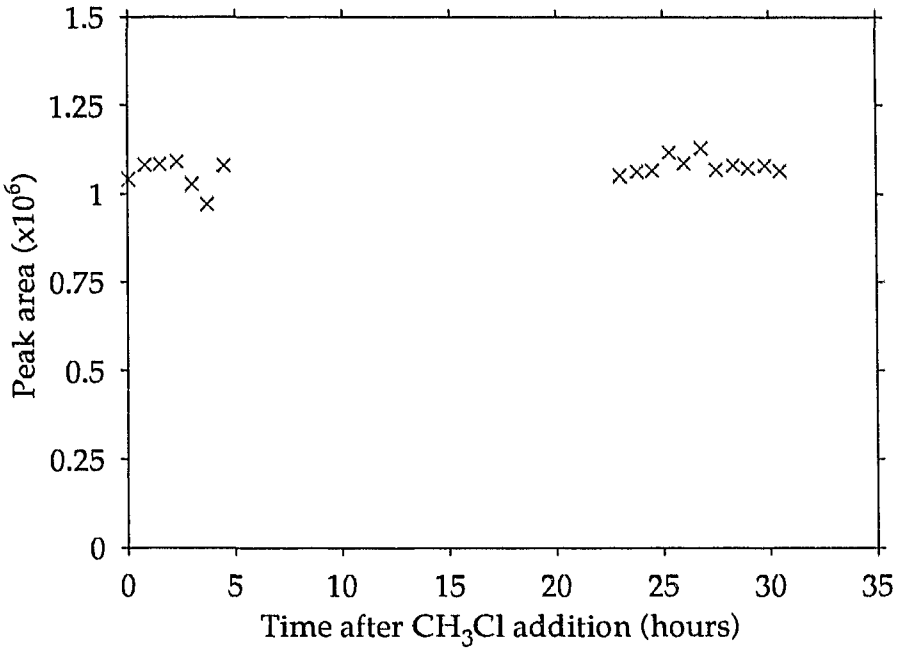


Figure 2.11 Time series following the addition of methyl chloride to the standard vessel. Standard concentration = 190 pM.

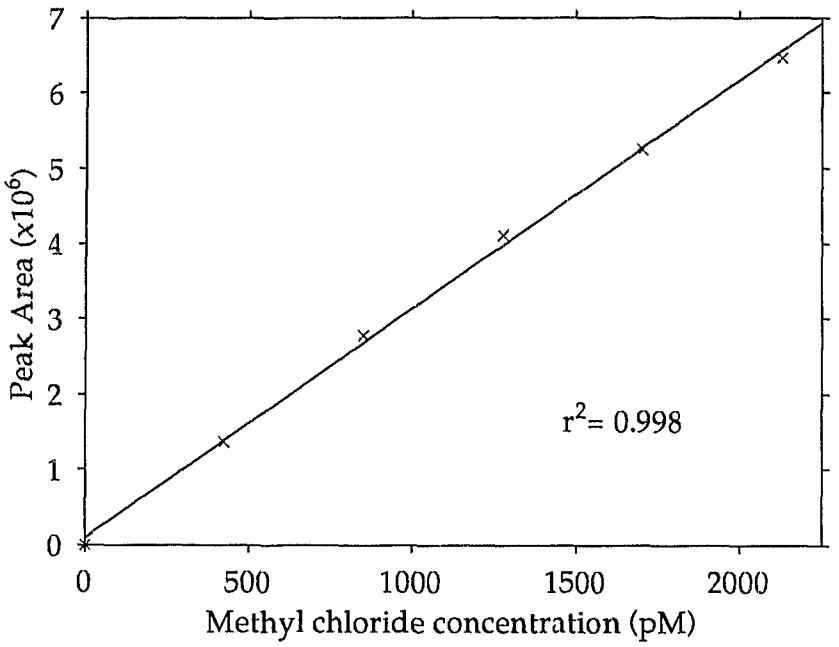


Figure 2.12 Linear dynamic range of detector, System II

Therefore, the detection limit was determined as follows: 319 pM in a 20 mL sample gives a peak area of 1650000, corresponding to an absolute sensitivity of 5108 counts/pg. To prevent integration of baseline noise, the AR REJ (area reject) setting on the HP 3390A had to be set at 10000. Defining the detection limit as peaks three times this size gives a detection limit of 5.8 pM (5.9 pg). Two separate control time series (n=9 and n=11) gave sample standard deviations of 3.3 and 3.2 pM at the 15pM level. The practical detection limit of the system is therefore 6-7 pM (*ca.* 7 pg). This method of standard preparation was used with System II.

2.11 *Sampling and storage*

Good agreement (better than 6%) was found between duplicate seawater samples taken directly from Niskin bottles through a stainless steel adaptor into vacuum-baked (80°C, 12-24 hours) all glass Luer-Lok syringes (syringe volume = 30 or 50 mL). Loss of methyl chloride during transfer of sample from the Niskin bottle to the syringe is considered to be negligible. When necessary, the capped syringes were stored at 4°C in a sealed bucket filled with ambient seawater for short periods until analysis (maximum 12 hours). A time series of samples taken from 50m depth in the Labrador sea (Chapter 3) showed no significant change (±4%) in methyl chloride over a 12 hour period when samples were stored in the laboratory (18-20°C) in this manner.

Replicate samples of seawater and meltwater from the bottom surface of sea-ice

in Barrow Strait (75°N) were kindly collected by a colleague during sampling near Resolute Bay during spring 1992 and sealed in crimp-top vials with silicone septa. Results from the analysis of these are shown in Figure 2.13. Transport back to the laboratory involved storage periods of 8-12 days (room temperature). Overall, concentrations were high compared with the average open ocean concentration reported by Singh *et al.* (1983). Samples from the period preceding the spring bloom (April 15; Figure 2.13) had concentrations less than those taken during the bloom. Ice meltwater from during the ice-algal bloom (May 10-15) was green with phytoplankton. Analysis of duplicates from during the bloom showed the same trend of higher concentrations close to the ice bottom and lower in the water column. However, a third sample at each depth was kept for a further 6 days to determine the possible effect of storage time on the methyl chloride levels. Concentrations were found to have decreased during this time for all three depths while contaminant peaks had increased. The higher concentrations of methyl chloride in the meltwater compared with the water column suggest that methyl chloride can be produced by organisms present in the ice-algal bloom. However, the concentrations measured back in the laboratory after week-long storage in crimp-top vials are not representative of the environment.

Flame-sealed ampoules are not suitable for storage of water samples for methyl chloride analysis. Methyl chloride was measured in samples of water from the Greenland Sea collected during July and August, 1992 (thanks are due to D. Wallace). Two vessels were used for the storage of samples - glass ampoules sealed using a propane torch and glass ampoules with Swagelok/nylon ferrule seals. From a depth of 1461m, one would

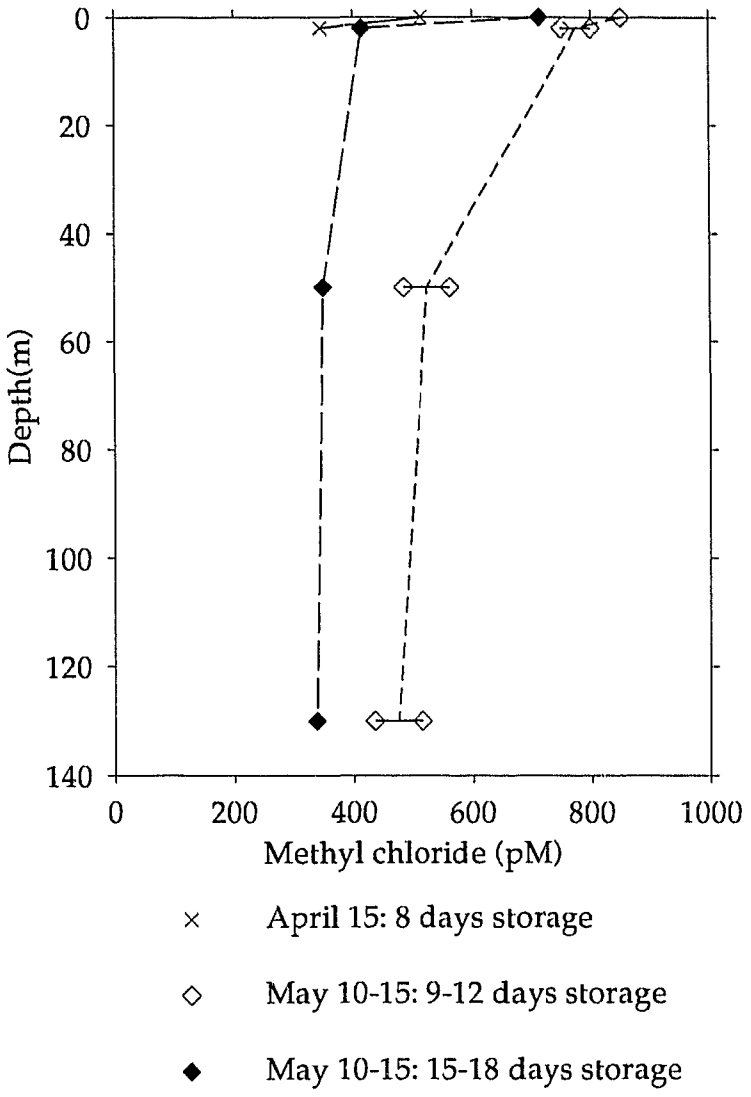


Figure 2.13 Samples stored in crimp-top vials, Resolute, 1992.

expect low concentrations of methyl chloride (see Chapter 3). In the Swagelok-sealed ampoule the concentration was below the detection limit (<7 pM). Both flame-sealed ampoules exhibited high concentrations, in one case exceeding 2000pM (2081 and 474 pM). During a study of methyl chloride during a phytoplankton spring bloom in Bedford Basin, Nova Scotia (described in Chapter 5), concentrations 2-20 times those in the preceding and following weeks were measured in samples stored for a week in flame-sealed ampoules. A subsequent comparison between glass syringe and flame-sealed ampoules with zero storage time showed 3-4 times higher methyl chloride in seawater from the ampoules. Production processes within the seawater itself are another possible contribution to the "excess" methyl chloride found in the stored samples. Swagelok-sealed ampoules did not in this case appear to introduce contamination.

Samples of seawater collected at Resolute during 1993 were stored in Swagelok-sealed ampoules for transport (Figure 2.14). Agreement between replicates was found to be poor. The standard deviation of standards run for the analysis of the samples shown in Figure 2.14 was $\pm 3.9\%$ (n=8).

Immediate analysis of samples on collection is the preferred option.

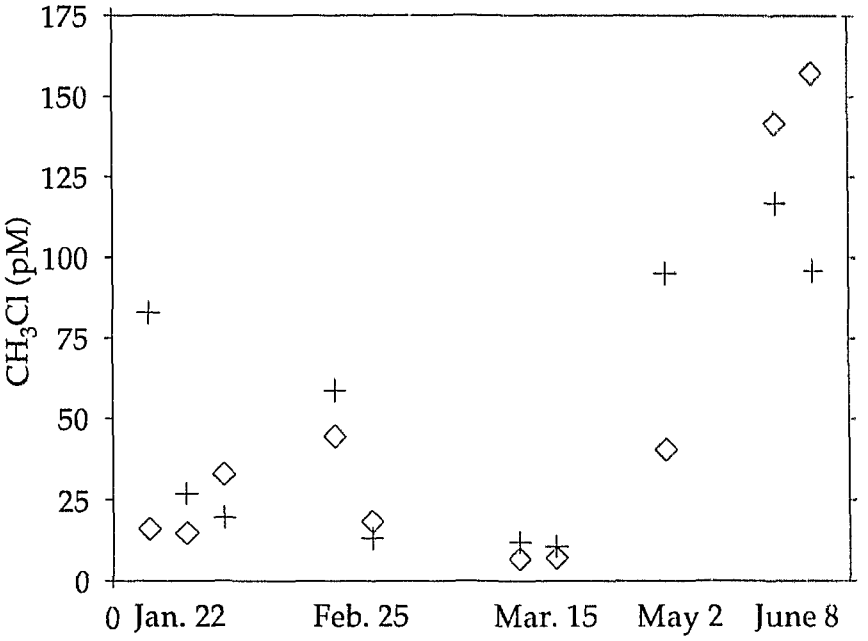


Figure 2.14 Samples stored in Swagelok-sealed ampoules for transport from Resolute, 1993. + = 2m, ◇ = 10m

Chapter 3: Methyl Chloride in the Open Ocean

3.0 *Introduction*

The majority of reported measurements of methyl chloride concentrations in ocean waters were from two studies during the early-to-mid 1980's (Singh *et al.*, 1983; Hoyt and Rasmussen, 1985). The cruise track in the first study covered latitudes 30°S to 30°N in the eastern Pacific while Hoyt and Rasmussen surveyed waters across the Pacific within the latitude band 6°S to 28°N. Both employed the technique of measuring methyl chloride in gas equilibrated with seawater. Therefore, back calculation to the seawater concentration was dependent on the Henry's Law constant, a "constant" of considerable uncertainty (see Chapter 4, section 4.1). The aims of this study were to obtain more information about the distribution of methyl chloride in the oceans using a system capable of its direct measurement in seawater and to examine the distribution in terms of suggested sources and sinks. The results described in this chapter are the first set of methyl chloride measurements from mid-to-high latitudes in the North Atlantic Ocean.

3.1 *Cruise track and station positions*

Figure 3.1 shows the cruise track taken by the C. S. S. "Hudson" from April 28 - June 4, 1991. Samples for the analysis of methyl chloride were taken at the stations indicated.

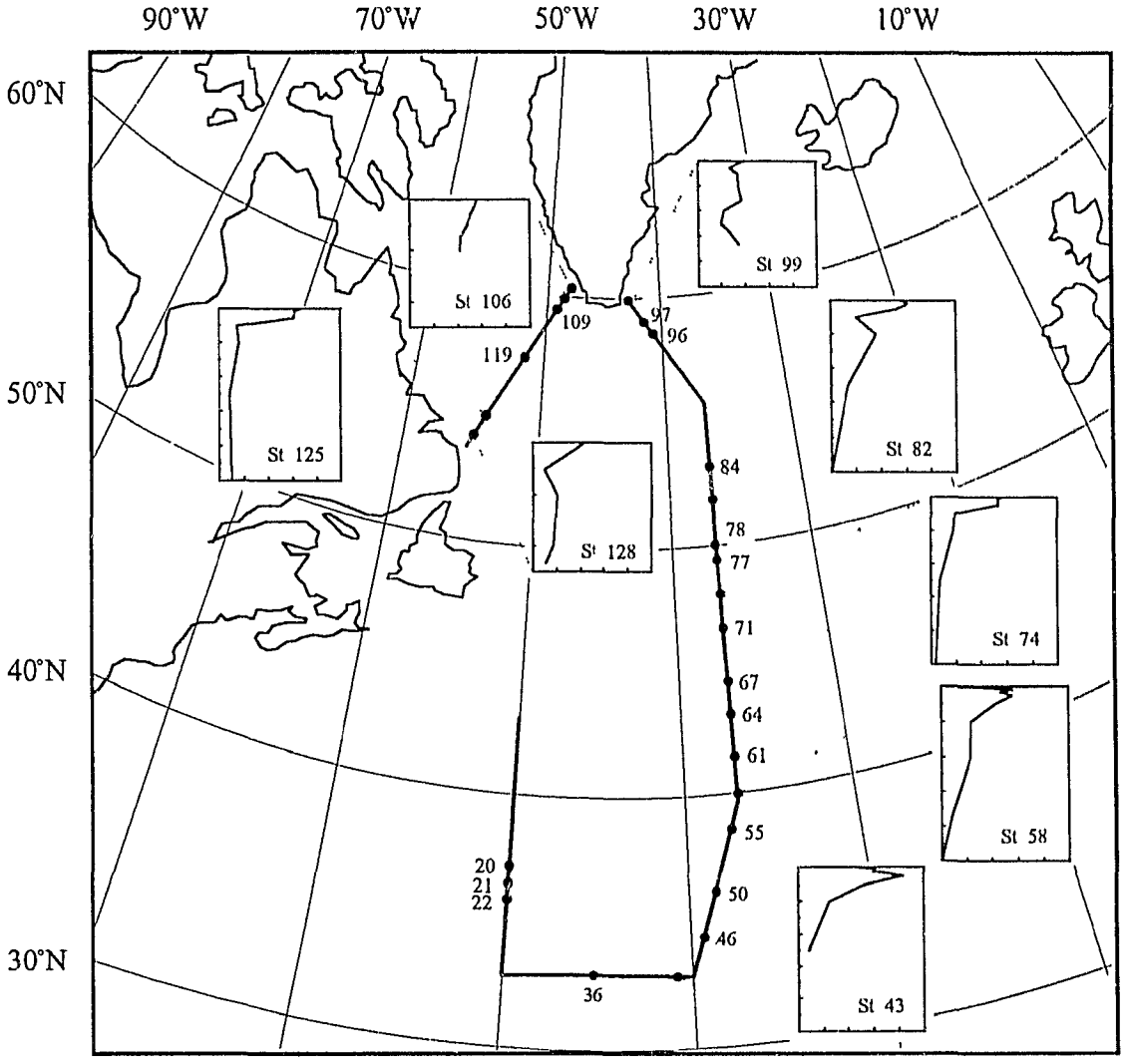


Figure 3.1 Cruise track and station positions. Also shown are several vertical profiles. CH_3Cl is 0 - 500 pM on the x-axis. The depth axis is 0 - 1000m for open ocean stations and 0 - 250 m for nearshore stations 99, 106, and 128

3.2 *Sampling*

3.2.1 Methyl chloride

Upon arrival at the stations, the surface seawater was sampled using a bucket. The bucket was flushed twice with ambient seawater and samples drawn into vacuum-baked (*ca.* 100°C, 8 hours) all-glass Luer-Lok syringes. The syringes were then capped and stored in the collected bucket of seawater. Sub-surface samples were taken directly from the Rosette Niskin bottles via a baked stainless steel adaptor soon after the Rosette arrived on-board. Samples were analysed using System I within 12 hours of collection. A time series to test whether sample integrity was maintained during a 12 hour storage period in the laboratory (temperature 15-25°C) showed no change in methyl chloride concentration (sample standard deviation divided by the mean = 2.2%; n=5) within the run-to-run precision using System I (4-5%).

3.2.2 Complementary measurements used in the methyl chloride data analysis

Data collected by other investigators was kindly made available for the interpretation of the CH_3Cl distribution. A suite of less volatile halocarbons including methyl iodide (CH_3I) and bromoform ($CHBr_3$) were measured by purge-and-trap GC-ECD (Moore and Tokarczyk, 1993).

Chlorophyll-a was sampled at 10 m-depth intervals using a submersible pump

(Herman *et al.*, 1984), collected on Whatman GF/C filters and stored at -20°C for subsequent extraction and fluorometric analysis by the method of Yentsch and Mentzel (1963)(Irwin *et al.*, unpublished results).

3.3 *Standardisation*

During the cruise, the peak areas of injections from individual gas standards prepared as described in Chapter 2 (section 2.9.2) differed by as much as a factor of two. An alternative method of standard preparation was used. Water was collected from greater than 2000m at three stations. Analysis showed undetectable methyl chloride. A gas sampling bulb containing several small glass beads was filled with seawater leaving only 2-3 mL headspace. Ten microlitres of pure methyl chloride vapour was injected into the water using a small volume gas-tight syringe. The bulb was then shaken thoroughly for 10 minutes. The high ratio of liquid to gas volume (*ca.* 250) within the vessel and the value of the Henry's Law constant (H) (0.21; see Chapter 4) ensured that a negligible amount of methyl chloride was partitioned into the gas phase. Precision of solution standard injections was good ($\pm$ 3.5%: sample standard deviation divided by the mean, n=5) as shown in Figure 3.2. A run of a solution standard 24 hours after preparation showed no change in peak area. Reasonable agreement (within 20%) was found between the gas standards prepared in the laboratory prior to the cruise (precision of repeated injections = $\pm$4.5%, n=7) and the solution standards run during the cruise (Figure 3.3).

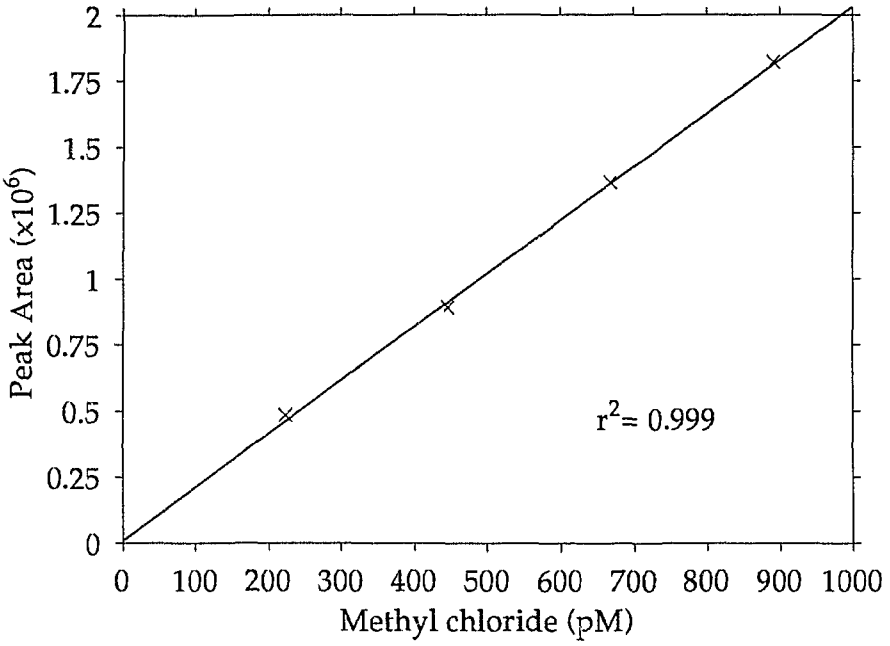


Figure 3.2 Calibration curve of solution standard

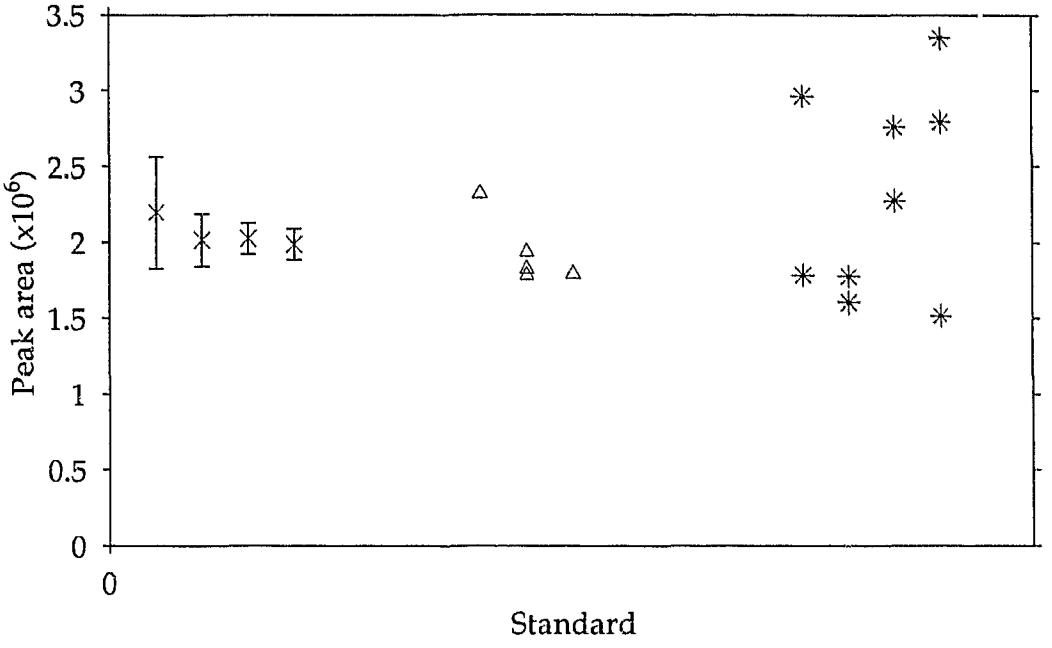


Figure 3.3 Standardisation of System I: × = pre-cruise laboratory gas standard, △= cruise solution standard, ✳= cruise gas standard. Error bars on pre-cruise standards are ±2 standard deviations, n = 4 or 5.

Standardisation of System II (January, 1992) using the solution standard apparatus described in Chapter 2, produced peak areas 70-80% greater than those for equivalent standard concentrations analysed during the cruise. This discrepancy could be due to a change in detector sensitivity, although the reasons for such a change are not clear. The only other instance in which there was a change in detector response in System II occurred due to detector contamination. This was accompanied by a factor of 2-3 increase in baseline. The baseline was not unusually high during the cruise. Another possibility is that the difference is attributable to the different solution standard preparation techniques and apparatus. Without independent evidence supporting either of these suppositions, the average of the cruise solution standards was used to calculate the methyl chloride concentrations during the cruise. The peak areas from the pre-cruise gas standards supported the use of the cruise solution standards for calibration of System I.

Possible reasons for the lack of precision of cruise gas standards have since been considered. The peak areas from gas standard injections are also shown on Figure 3.3. Plugging of syringe needles with septum material was known to have occurred. This could explain peak areas lower than expected. A decrease in atmospheric pressure between dilutions could also result in low peak areas due to loss of methyl chloride during transfer in an open-ended syringe. It is more difficult to account for the higher peak areas. Unless the laboratory air had concentrations in excess of 1000 times outside background concentrations (typically 600-700 pptv), it is unlikely that contamination with methyl chloride occurred during the gas dilutions. Mixing ratios of up to 100 ppbv have

only been observed indoors as a result of cigarette smoking (Edwards *et al.*, 1982). Co-elution of a contaminant peak with methyl chloride could cause erroneously high peak areas. This possibility was addressed by using a 60m GS-Q column (Chapter 2, section 2.6). Although without concurrent mass-selective detection, the possibility cannot be ruled out completely, it appears unlikely. The nature of the gas standard preparation makes over-estimation of the ambient methyl chloride concentrations more likely than under-estimation.

3.4 *Results and Discussion*

3.4.1 Surface concentrations

Surface concentrations of methyl chloride measured during this cruise are shown in Figure 3.4. For comparison, the values from two other published studies are also given. Hoyt and Rasmussen (1985) reported CH_3Cl measurements in air and headspace samples taken during March-June (1983) between 6°S and 28°N in the Central Pacific Ocean. The picomolar values in Figure 3.4 were calculated from the headspace concentrations using H (Henry's Law constant) for methyl chloride determined in Chapter 4 ($H = 5.34 \times 10^3 \exp(-2822/T(K))$). Singh *et al.* (1983) also used a Henry's Law constant in their determination of methyl chloride in seawater samples from the Eastern Pacific (December, 1981; 30°N to 30°S). Error bars on these data include both the

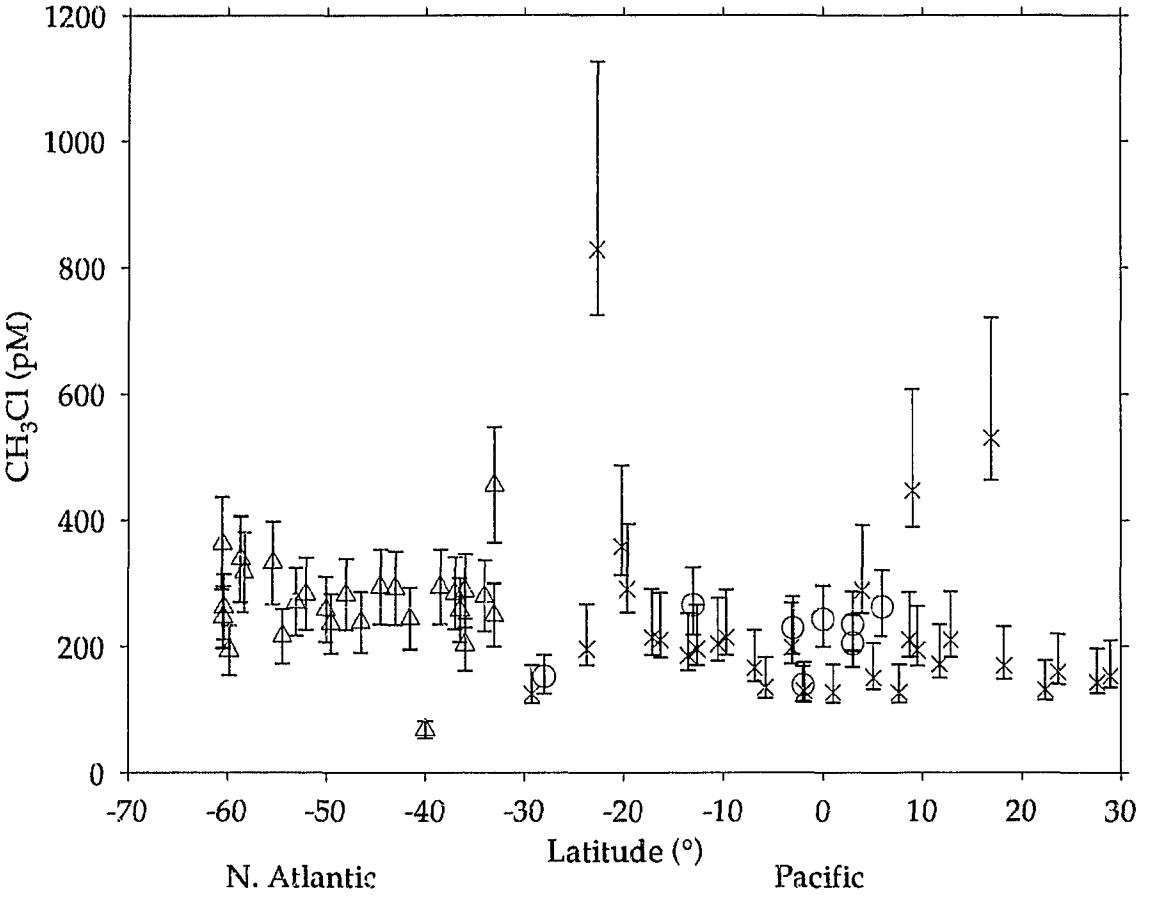


Figure 3.4 Surface ocean concentrations of methyl chloride (pM). ○ = Hoyt and Rasmussen (1985), × = Singh *et al.* (1983), △ = this study. Error bars are described in the text.

analytical precision given in their paper and contributions from uncertainty in H. The average of the measurements in the North-west Atlantic (271pM, σ = 68 pM) was slightly higher than that measured by Singh *et al.* (1983) (229 pM, σ = 146 pM), but the overall variability was less.

Most surface concentrations in this study lie within the range 200-400 pM, except two stations, 36 and 58, at which 455 pM and 69 pM, respectively, were measured. Comparison of temperature, salinity and chlorophyll-a at these stations with those neighbouring offer no obvious explanation for these outlying concentrations.

3.4.2 Coastal versus open ocean waters

Samples were taken at three nearshore stations - 99, 106, and 128. Approach to the shore at stations 99 and 128 was restricted by ice cover. The average concentrations in the top 100m were used to compare coastal stations with those in the open ocean (see Table 3.1). Average rather than surface concentrations were used in the comparisons so as to filter out the effects of air-sea exchange and water column vertical hydrographic structure.

From Table 3.1 it can be seen that at least during the May-June period of the study, any coastal inputs of methyl chloride are not sufficient to produce concentrations greater than those found in pelagic zones. In contrast, the higher methyl iodide concentrations observed in southern Greenland coastal waters, relative to the open ocean, are consistent with a strong, local source. Both compounds however show lower values

Table 3.1 Nearshore concentrations of methyl chloride compared with the open ocean.

Site	Stn.	sea-surface	CH_3Cl mean[a]	CH_3I mean[a]
Greenland east coast	99	30-40% ice	166	5.5
Greenland west coast	106	no ice	260	16.1
Labrador coast	128	40-45% ice	104	<0.2
Open ocean[b]	-	open water	248 (158-340)	2.4 (0.35-5.2)

[a] Concentrations are depth-weighted averages over 0-100m (5 or 6 samples) in pM.

[b] Average value 0-100m, with the range given in parentheses.

close to the Labrador coast (station 128).

3.4.3. Vertical distribution of CH_3Cl

In agreement with the eastern Pacific profiles of Singh *et al.* (1983), elevated concentrations of methyl chloride were found in the surface mixed layer and lower values within the main thermocline (Figure 3.5) of open ocean stations.

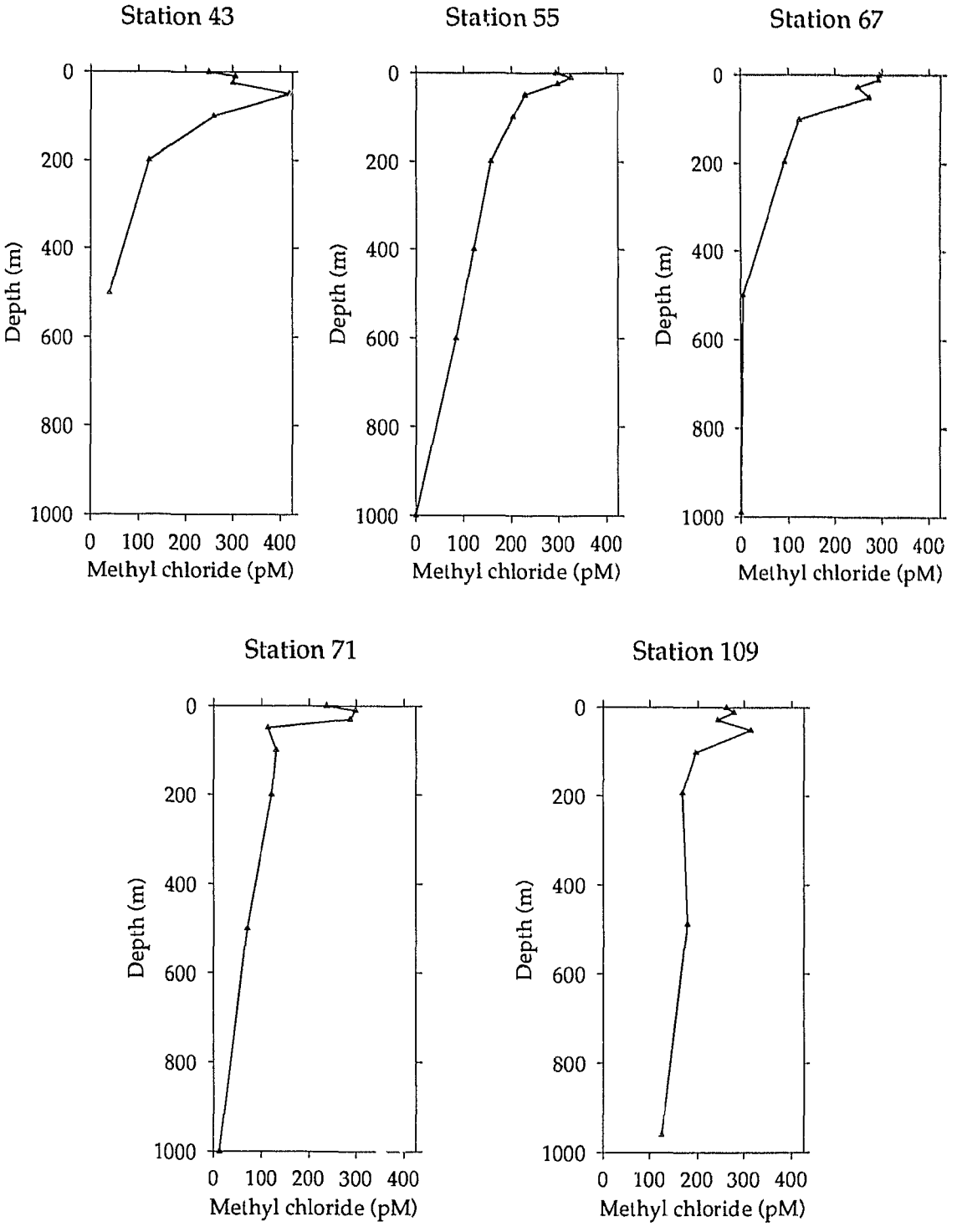


Figure 3.5 Elevated surface layer concentrations of methyl chloride.

3.4.3.1 Near-surface maxima of methyl chloride

Near-surface maxima were observed at 14 out of 18 open ocean stations, the depth and thickness showing strong dependence on the hydrographic structure of the water column. A shallow, sharp maximum at station 61 (Figure 3.8) was restricted by a shallow thermocline under conditions of low wind mixing. The broader maximum seen at station 43 (Figure 3.5) occurred in the presence of a 40m mixed layer.

To maintain a near-surface maximum in the presence of wind-driven transport to the atmosphere requires *in situ* net production of methyl chloride by processes in the upper water column. The highest methyl chloride concentrations were restricted to waters above the thermocline at each station, consistent with net production of methyl chloride concentrated within this surface layer.

Resolution of the smaller scale (10's of metres) water column structure in the CH_3Cl data was dependent on the depths at which Niskin bottle samples were taken relative to the hydrographic features. Multiple maxima were found in upper water column profiles showing complex vertical stratification. The CTD salinity profile at Station 58 (Figure 3.6) shows thin layers of different salinities. From the methyl chloride data, some of these layers also contain distinct concentrations of methyl chloride. Layering within the upper 200m is also evident in the methyl chloride distribution at station 67. At station 96, the two maxima found in the methyl chloride vertical profile were concurrent with a clear step-like feature in the salinity distribution.

Figure 3.7 (a,b) shows two stations at which the surface concentration of methyl

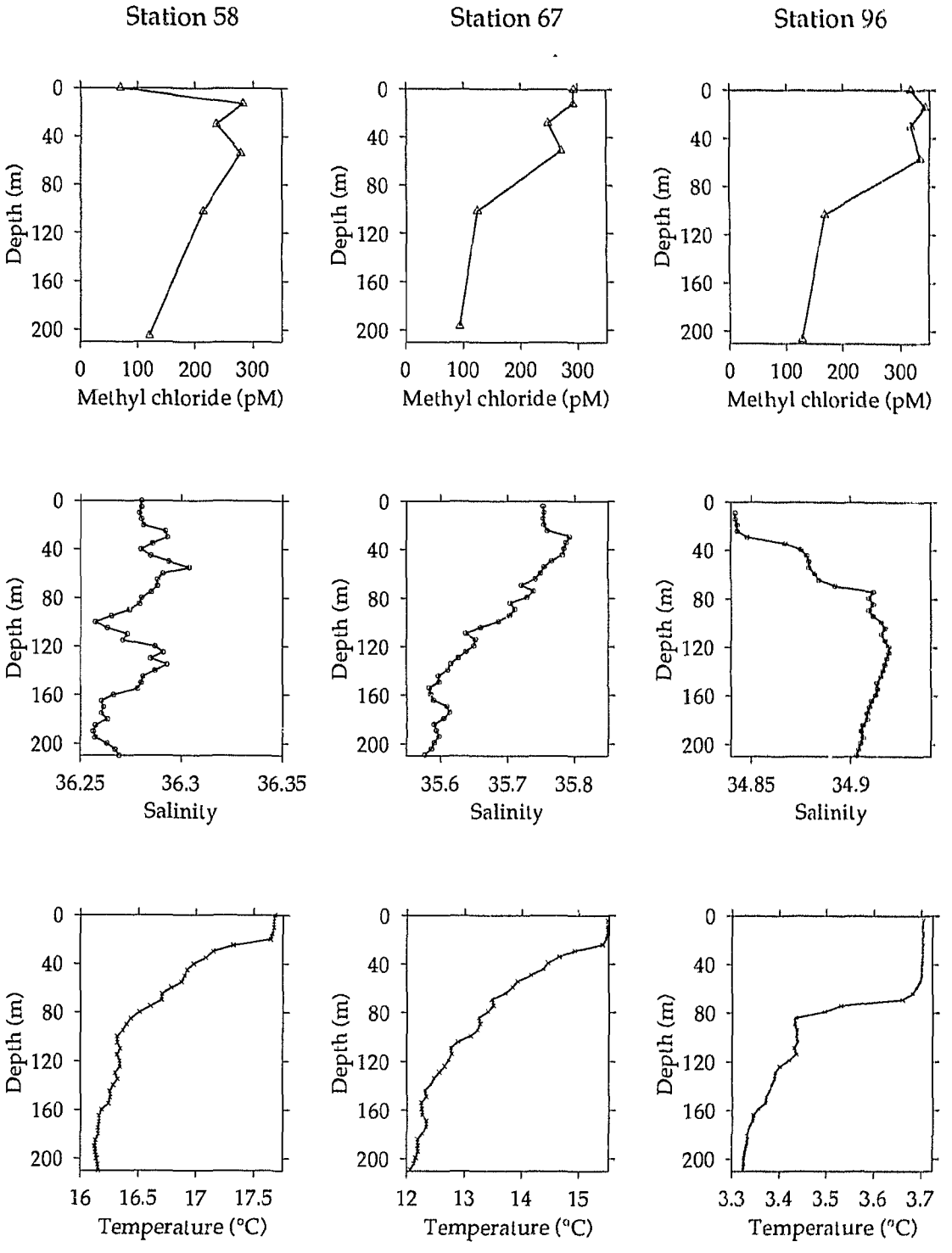


Figure 3.6 Examples of multiple near-surface maxima of methyl chloride.

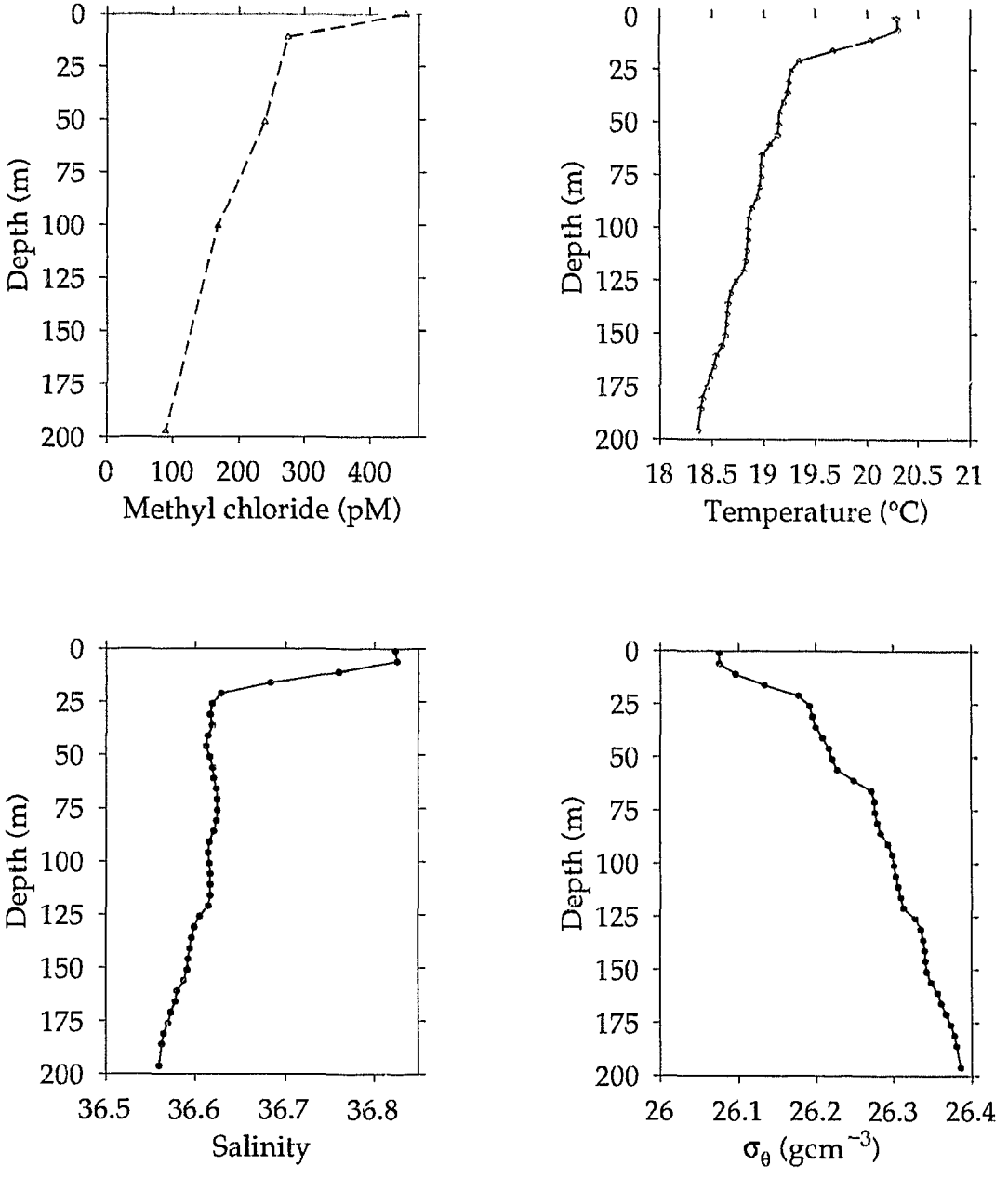


Figure 3.7 (a) Station 36 - methyl chloride (pM), T (°C), S, and σ_θ (mg cm^{-3}) in the upper 200m.

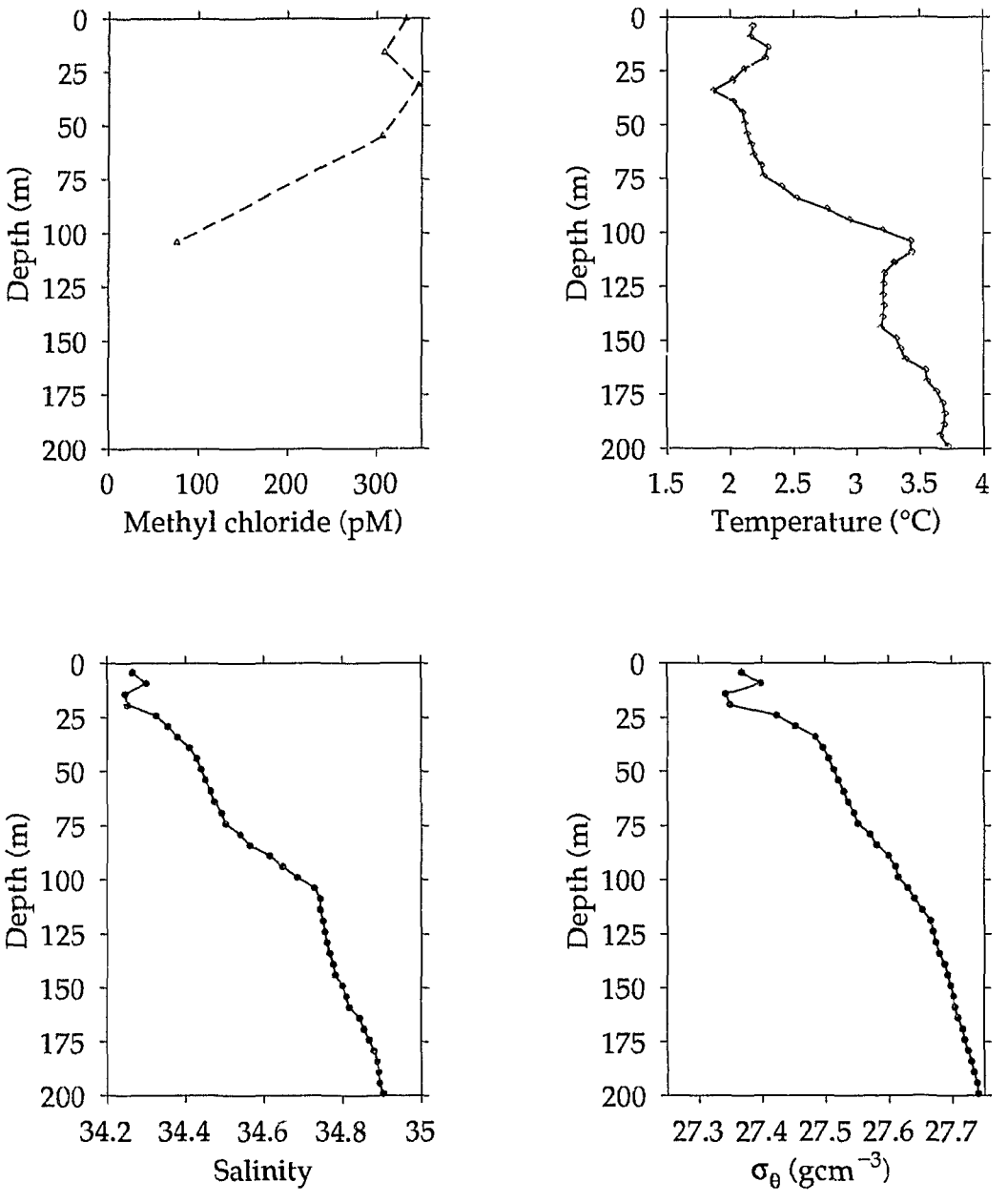


Figure 3.7 (b) Station 125 - methyl chloride (pM), T (°C), S, and σ_θ (mg cm^{-3}) in the upper 200m.

chloride was greater than that measured in the sample below (15m). At both stations there is a thin (*ca.* 10m) surface mixed layer. The only sample taken within these layers was the surface bucket sample. At station 36, the surface layer is warm and saline, due largely to solar heating and evaporation. Restriction of the highest methyl choride concentrations to depths above the thermocline, as suggested by vertical distributions at other stations, would place any near-surface methyl chloride maximum between the samples taken at 0 and 15m. The sampling may, therefore, have missed a shallow near surface maximum. The form of the methyl chloride vertical profile at station 36 is more typical of a compound for which the atmosphere is the source. The very high concentration at the surface (455pM), however, does not support such an interpretation. At station 125 (Figure 3.7), the thin surface layer is relatively cool and fresh compared with the water below and contains higher concentrations than the layer of water below. Station 125 lies within a front between cooler, fresher near-shore waters formed by the seasonal melting of ice and more saline off-shore waters.

3.4.3.2 Mid-depth maxima of methyl chloride

Some profiles exhibited broader and less intense mid-depth maxima (see Figure 3.8 (a)). Maxima were also seen in the oxygen distribution (Figure 3.8 (b)), suggesting more recent contact with the atmosphere than the surrounding waters. Ventilation of the thermocline by sea-surface outcropping of isopycnals is now a widely accepted phenomenon (McCartney and Talley, 1982; McCartney, 1982 and references therein;

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 3.8 (b)) occurring within well-mixed layers at mid-depth (Figure 3.8 (c)) are characteristic of pycnostads formed by winter deep convection. Such pycnostads are a common feature in the 200-800m depth range of the North Atlantic. The temperature and salinity characteristics of the pycnostad 200-400m at station 58 (temperature = 15.9-16.2, salinity = 36.21-36.26, σ_θ=26.7 kg m^{-3}) are intermediate between warmer subtropical mode water and colder subpolar modes (McCartney and Talley, 1982; McCartney and Talley, 1984) and suggest formation within or at the edge of the Gulf Stream between 38-40°N. The denser pycnostad at station 61 (σ_θ=27.1 kg m^{-3}), 400-600m, likely originated further north on the eastern boundary of the North Atlantic Current. Vertical profiles of methyl chloride in the top 1000m of the mid-North Atlantic show indication of *in situ* production of methyl chloride 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 Utilisation Rate (OUR) and density in the Sargasso Sea based on transient tracer measurements. Assuming this relationship holds at Station 58 north-east of the Sargasso Sea, the OUR in the pycnostad between 200 and 400m is approximately 0.112 mL L^{-1} yr^{-1} (σ_θ= 26.7 kg m^{-3}). The observed Apparent Oxygen Utilisation (AOU) of 0.1 mL L^{-1} suggests that the water mass has been isolated from the surface for less than a year. A possible

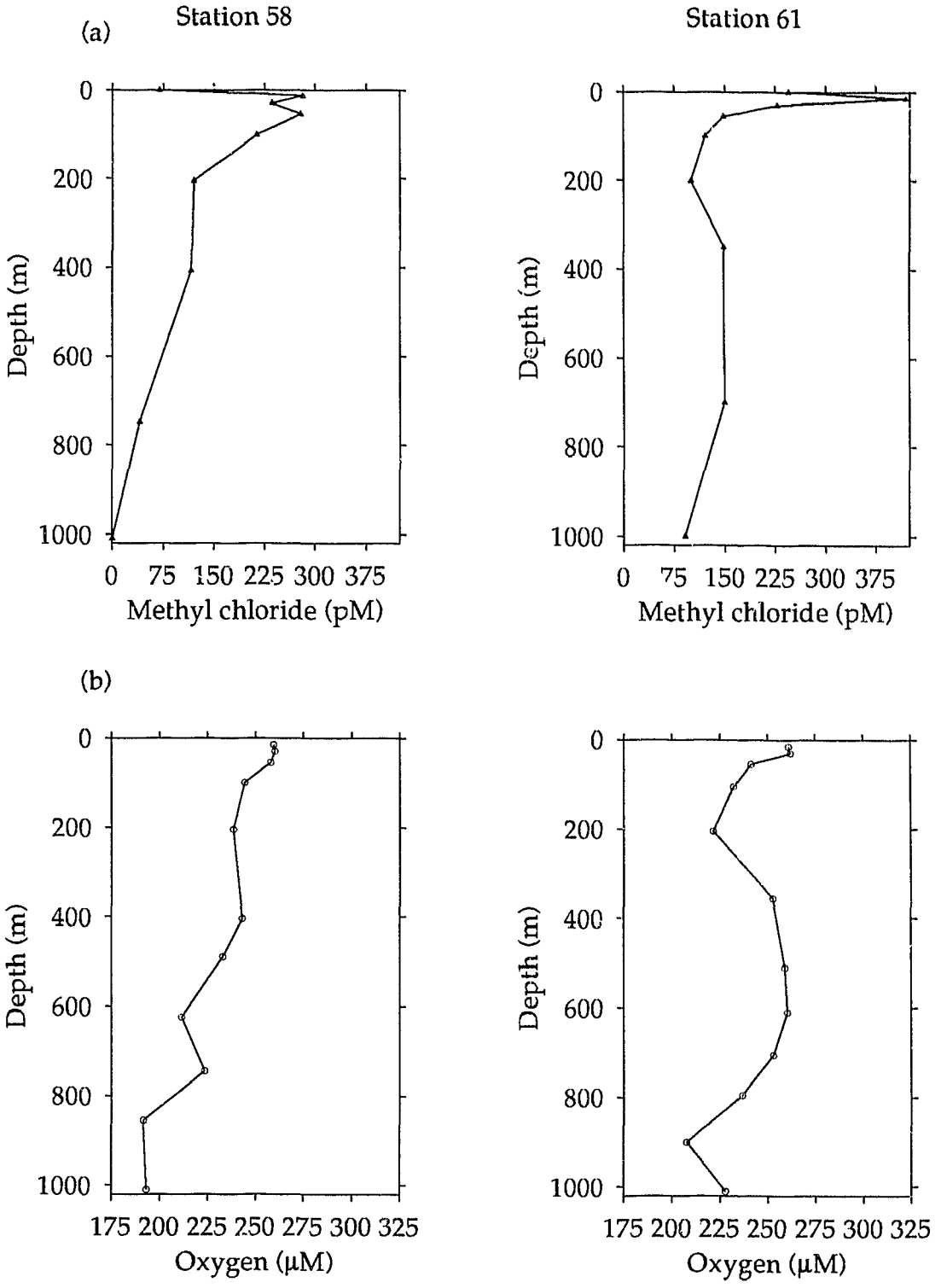


Figure 3.8 (a) Mid-depth maxima of methyl chloride at stations 58 and 61. and (b) Mid-depth maxima of oxygen at stations 58 and 61.

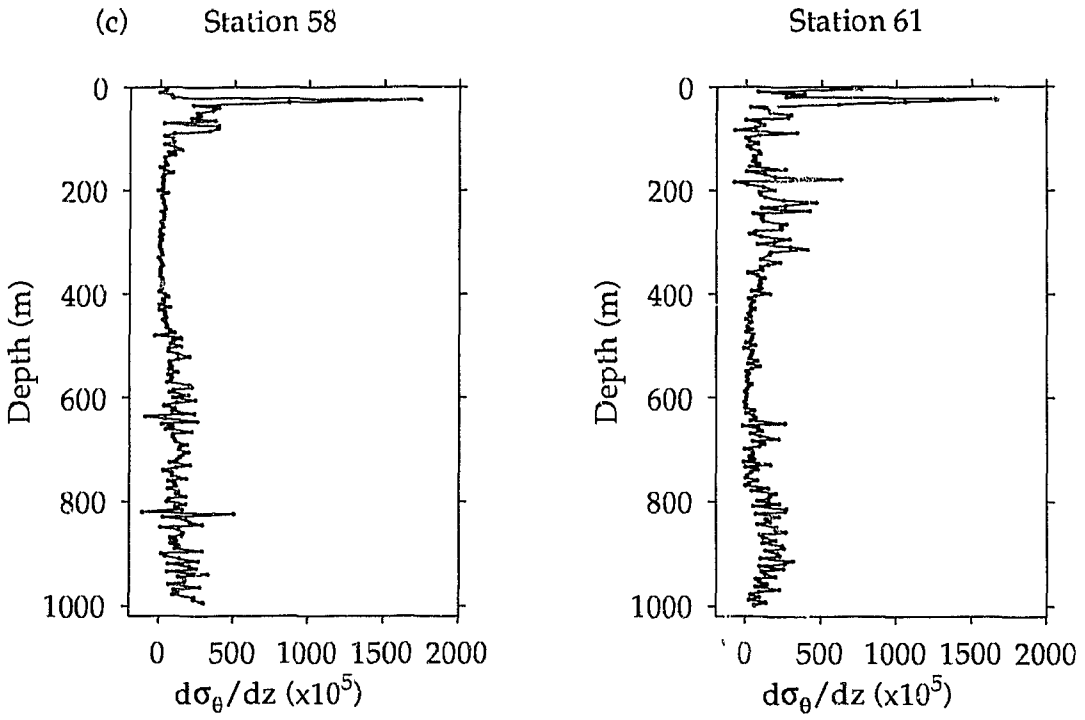


Figure 3.8 (c) Gradients of potential density, stations 58 and 61.

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 during the previous winter. If the convective layer is assumed to have reached equilibrium with the atmosphere during the winter months, the tropospheric boundary layer mixing ratio calculated from its temperature (16°C) and methyl chloride concentration (118 pM) is 890 pptv. Supersaturation within the upper layers must result from methyl chloride produced since the development of the seasonal thermocline.

Station 82 shows an oxygen minimum around 100m (Figure 3.9). The vertical profile of salinity shows that the minimum occurs within a layer of water of relatively high salinity. Methyl chloride (Figure 3.9), methyl iodide and bromoform also exhibit a minimum in this layer. Bromodichloromethane ($CHBrCl_2$) (Figure 3.9) and chlorodibromomethane ($CHClBr_2$) however, show the opposite behaviour. Moore and Tokarczyk (1993) noted that, in contrast to other halocarbons measured including bromoform and methyl iodide, both $CHBrCl_2$ and $CHClBr_2$ increased with depth. Slow production of $CHBrCl_2$ and $CHClBr_2$ from $CHBr_3$ has been demonstrated in laboratory experiments (Geen, 1992), and was suggested by Moore and Tokarczyk (1993) as a possible explanation for the observed increases with depth. These observations suggest that the high salinity layer is an advective feature and has been isolated from the atmosphere for a longer time than the waters above and below.

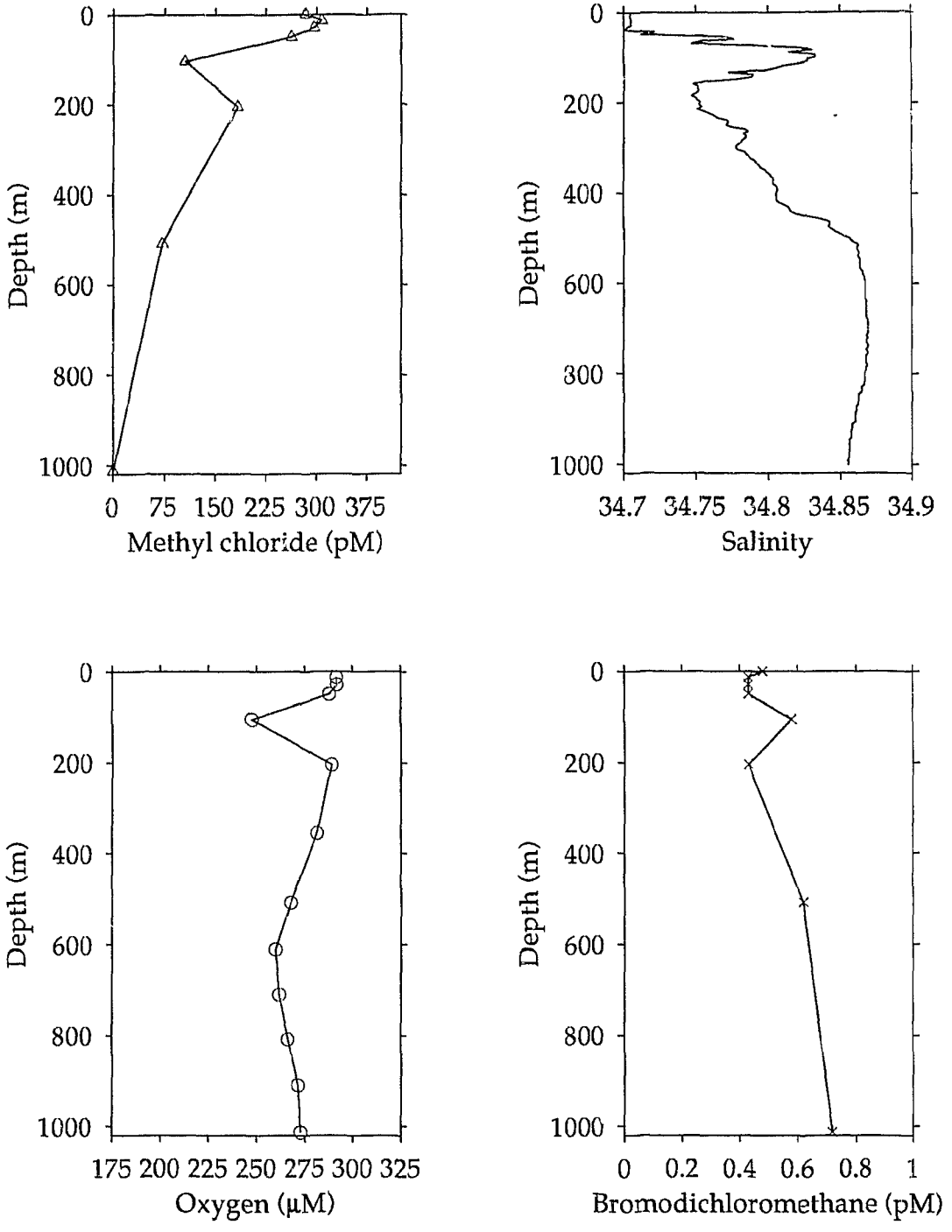


Figure 3.9 Station 82: methyl chloride, salinity, oxygen, and bromodichloromethane.

3.4.4 Methyl chloride and chlorophyll-a

Methyl chloride and chlorophyll-a were measured together at only 8 stations. Figure 3.10 shows chlorophyll-a integrated over 100m depth and methyl chloride over 50m depth along the north-south transect from 33 to 60°N. Two clear blooms are obvious in the chlorophyll-a data; the first is associated with an open-ocean front (Station 78; Figure 3.11), and the second is approaching the ice-edge off the east coast of Greenland (Station 97). Nitrate concentrations in the upper 30m of the water column at Station 78 were not yet totally depleted (1.2-2.4 μM) suggesting that the first bloom was in the middle-to-late stage of development. Nitrate was still greater than 3 μM in samples with elevated chlorophyll-a in the ice-edge zone. In the Labrador Sea, high chlorophyll-a concentrations were seen at station 106 off the Greenland west coast, and also nearing the ice-edge off the coast of Labrador. Nitrate concentrations were around 3.5μM at station 106, and 6-7μM approaching the Labrador coast ice-edge indicating a bloom in the early stages of development. A linear correlation of chlorophyll-a and CH_3Cl integrated over 0-100m depth gives $r = 0.11$ ($n=8$). Higher chlorophyll-a was not consistently accompanied by high methyl chloride, and vice versa, suggesting no simple relationship between the two.

A weak chlorophyll-a maximum was present at a depth of 50m at station 71 (Figure 3.12), within the upper thermocline. Methyl chloride however was highest within the surface mixed layer (depth 20-25m) and was substantially lower in the sample from within the chlorophyll-a maximum. A similar relationship between the two

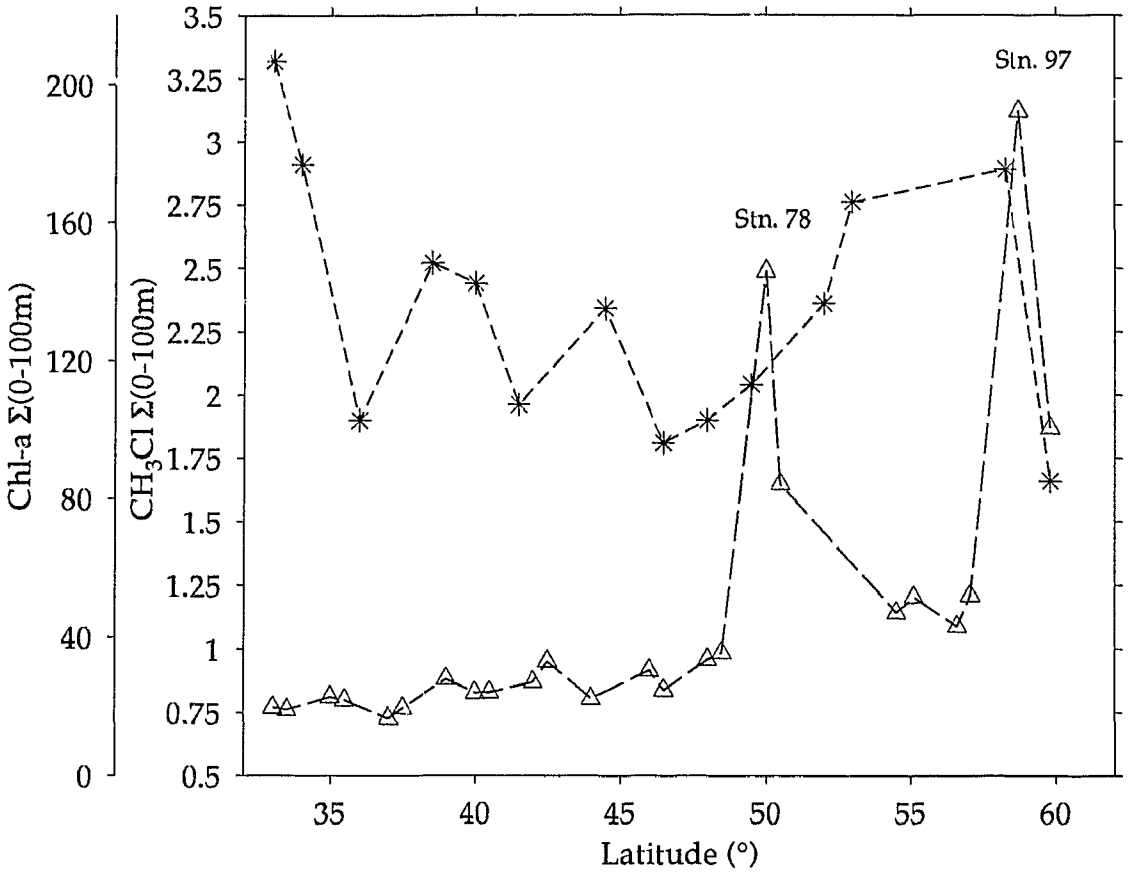


Figure 3.10 Integrated values of chlorophyll-a (△) and methyl chloride (✳) along the mid-Atlantic north-south transect. Units are: chl-a μg m^{-2} ($x10^3$), and methyl chloride moles m^{-2} ($x10^5$).

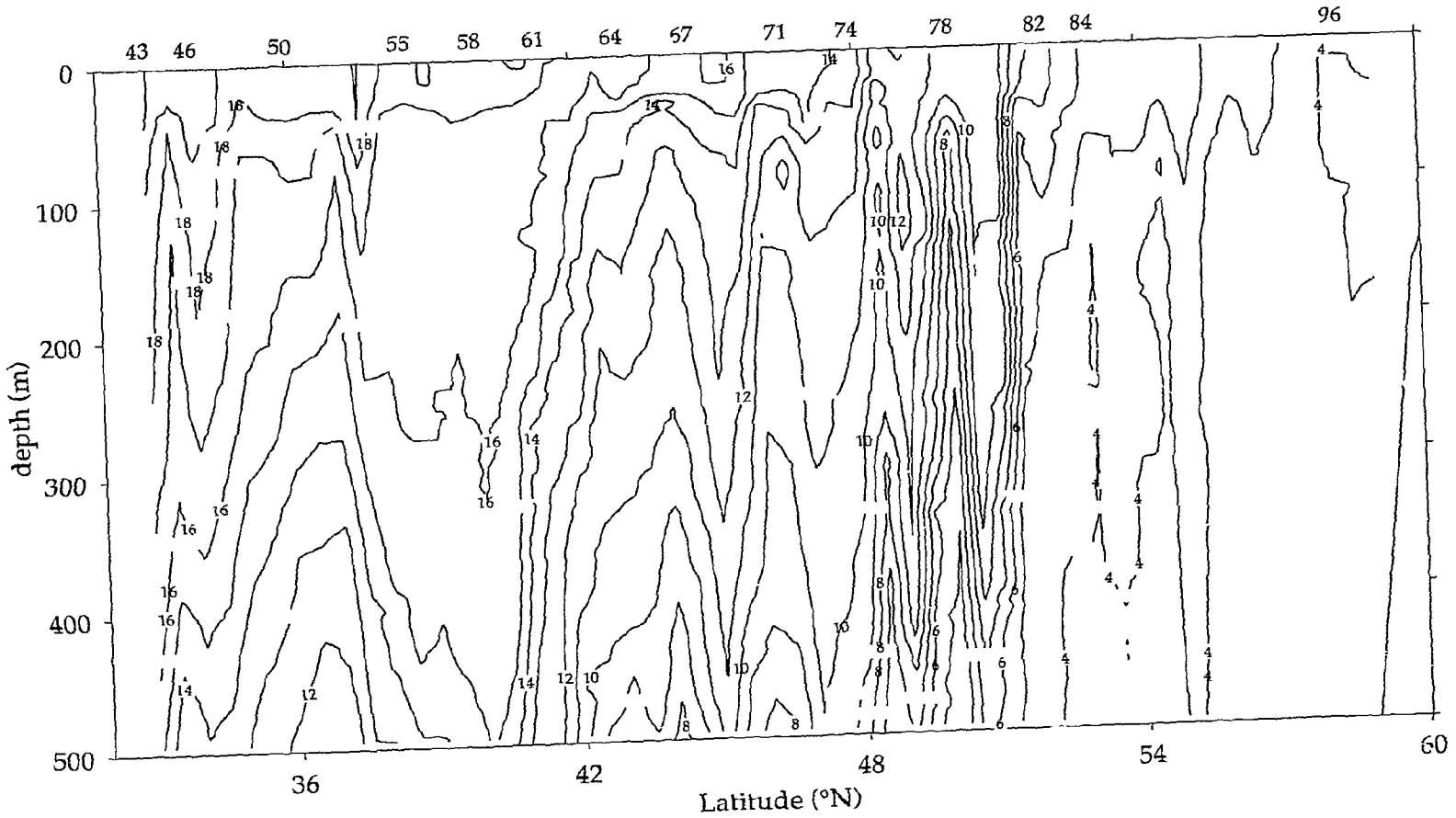


Figure 3.11 Contour plot of temperature along the mid-Atlantic north-south transect. The front in the region of stations 78-82 due to the North Atlantic Current is evident. Station positions are shown on the upper x-axis.

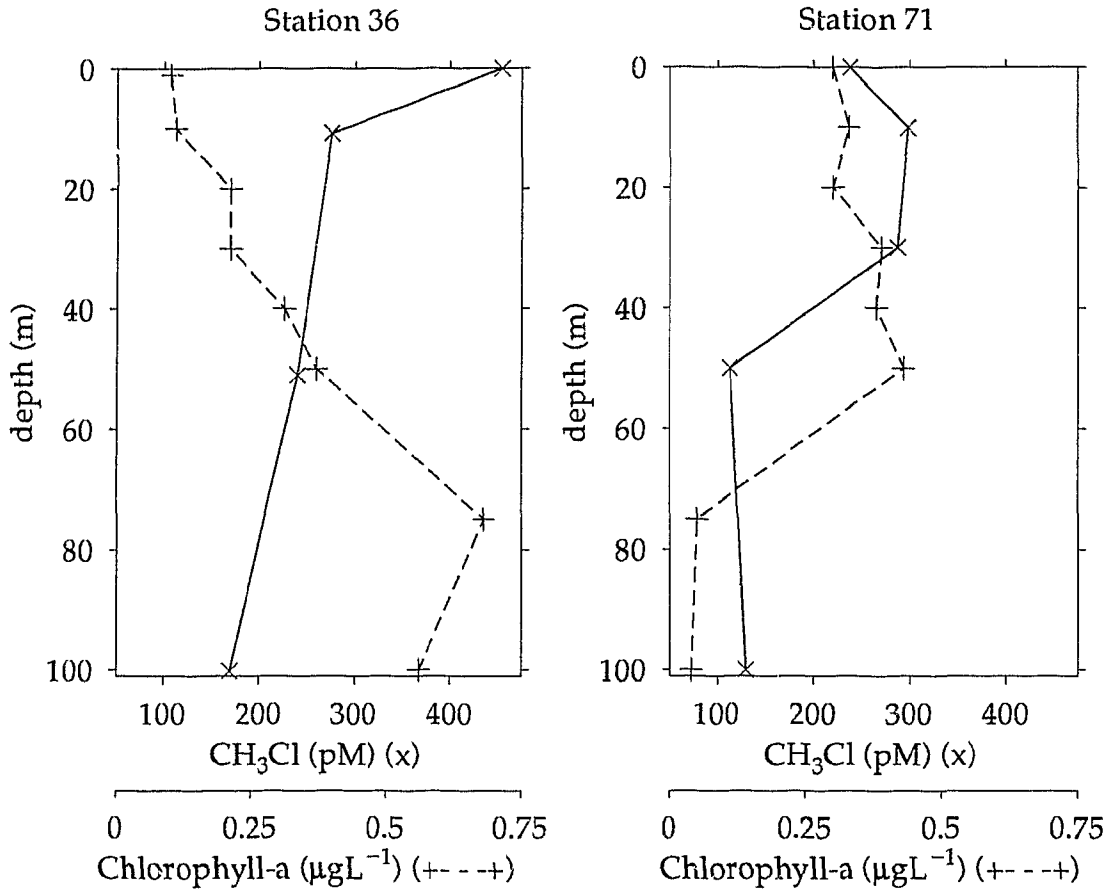


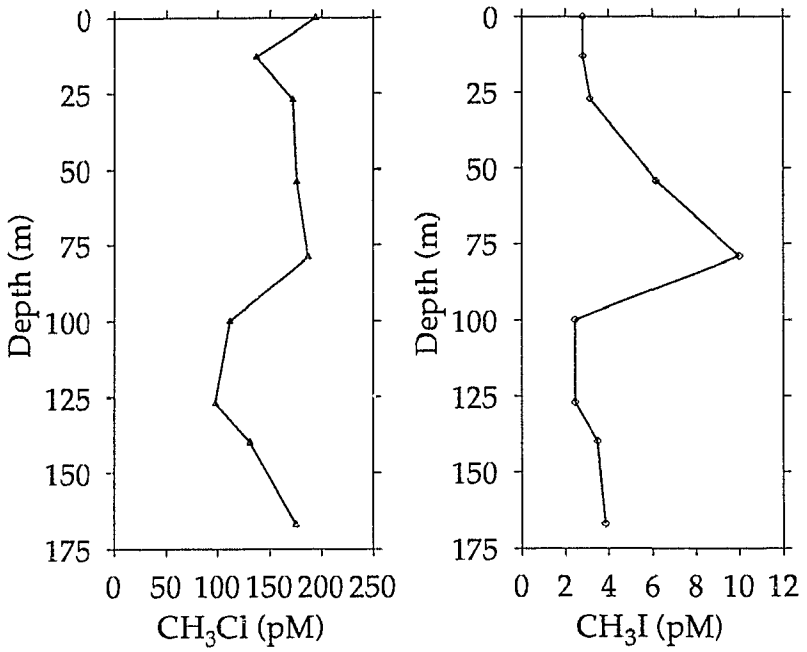
Figure 3.12 Methyl chloride and chlorophyll-a at stations 36 and 71.

variables was observed at low latitude station 36 (Figure 3.12). Physical characteristics of the upper water column show a clearer influence on the methyl chloride distribution than does chlorophyll-a.

3.4.5 The relationship between methyl chloride and methyl iodide

From Table 3.1, it can be seen that methyl chloride was present at concentrations two 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.

There were common features in the distributions of methyl iodide and methyl chloride, suggesting that their sources may be related to some degree. Production appeared to be restricted to the surface layer, and concentrations decreased in water masses isolated from the biologically active upper ocean. Coastal station 106 on the west coast of Greenland had higher concentrations of both compounds compared with station 99 on the east coast (Table 3.1). At station 99, the vertical distributions of the two compounds were related (Figure 3.13). The T-S plot for this station is also shown in Figure 3.13. At least three different water masses were present. Between 40 and 100m the vertical distributions of the methyl halides are consistent with mixing of waters with relatively higher concentrations around 80m with waters containing lower concentrations above and below. Concentrations increased towards the bottom. Without knowledge of the origin of the near-bottom water, a sediment source of methyl chloride and methyl



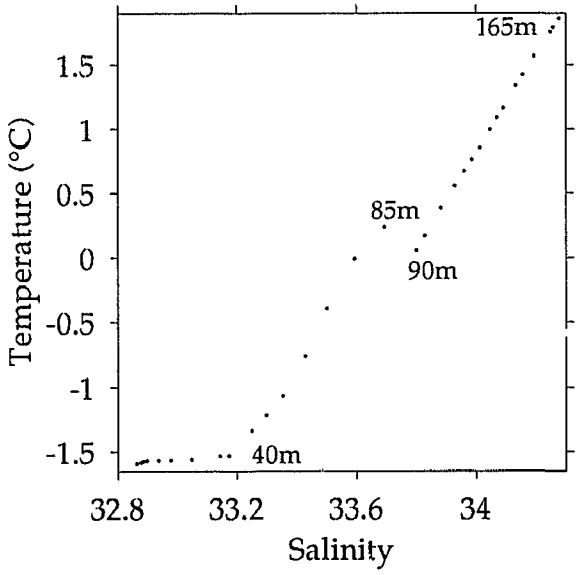


Figure 3.13 Methyl chloride, methyl iodide, and the T-S plot at station 99.

iodide cannot be ruled out.

Conversely, at some stations higher than average methyl chloride concentrations existed in the absence of higher methyl iodide, and vice versa at others. Low surface layer concentrations of methyl iodide were observed at station 96 near the shelf edge off the east coast of Greenland (average 0.35 pM over 0-100m compared with a 0-100m mean of 2.4 pM for all open ocean stations) accompanied by higher than average methyl chloride concentrations (289 and 248 pM, station 96 and open ocean stations average respectively). At this station the water column 100-1000m was dominated by Labrador Sea Water (σ_θ = 27.78 kg m^{-3}) in which methyl iodide could not be detected. For reasons as yet unclear, apparently convective water masses originating in the Labrador Sea contained low levels of both methyl halides. Methyl iodide was below the detection limit of 0.2 pM (0.03 ngL^{-1}) (Moore and Tokarczyk, 1993).

A scatterplot of CH_3Cl and CH_3I integrated over 0-100m depth is shown in Figure 3.14. The numbers refer to stations. A linear regression of the data gave a low correlation coefficient (r = 0.3, n = 20). Omission of the nearshore stations (99, 106, 128) produced a correlation coefficient only slightly higher (r = 0.41). No simple relationship is evident between concentrations of methyl chloride and methyl iodide. With an observed average methyl iodide concentration of 3.9 pM over 0-100m depth, and average temperature of 15 °C, about 10^9 moles CH_3Cl yr^{-1} can be produced globally by chloride substitution (rate constants from Zafiriou (1975) and Elliott and Rowland (1993)). Assuming a CH_3Br concentration of 5 pM (Singh *et al.* (1983)) over 0-100m, methyl bromide substitution contributes 2 x 10^9 moles CH_3Cl yr^{-1} when the rate constants

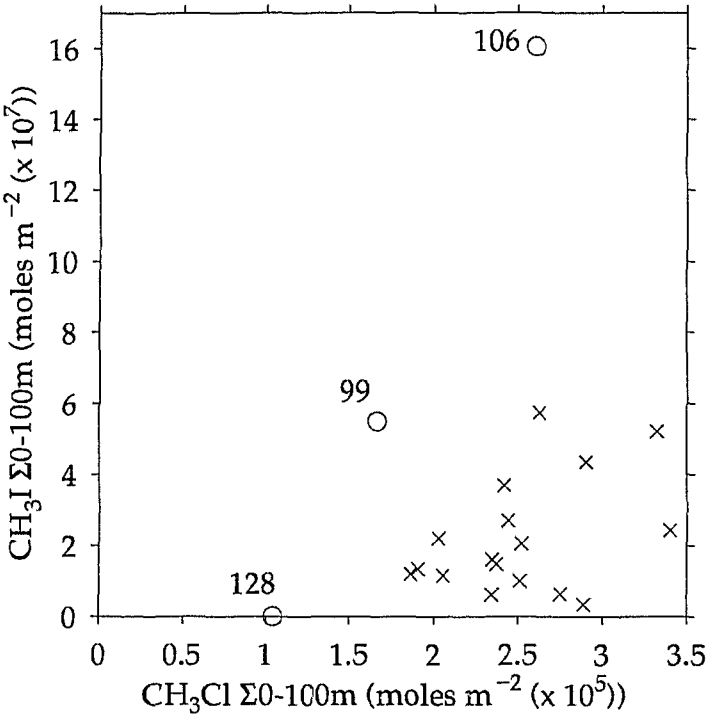


Figure 3.14 Scatter plot of methyl chloride and methyl iodide integrated over 0-100m depth. ○ are nearshore stations (99, 106, 128), × are open ocean stations.

measured by Elliott and Rowland (1993) are applied. Therefore, chloride substitution of methyl iodide and methyl bromide can produce only about 5% of the ocean-to-atmosphere flux of 5.8 - 9.7 x 10^{10} moles CH_3Cl yr^{-1} calculated by Singh *et al.* (1979, 1983). Unless methyl iodide and methyl bromide are transformed to methyl chloride by routes other than simple S_N2 substitution, these compounds cannot be the only source of methyl chloride in the oceans.

3.5 *Summary and conclusions*

During a cruise in the North-west Atlantic (May 1991), methyl chloride was measured directly in seawater using a purge and trap system and gas chromatography with electron capture detection. 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 surface layer indicative of methyl chloride production within upper ocean waters. 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 were not prominent in the area of study, in contrast to methyl iodide. Only a low linear correlation was observed between methyl chloride and methyl iodide ($r = 0.3$; $n = 20$) suggesting no simple relationship between these two compounds. These data also suggest there was no simple relationship between phytoplankton chlorophyll-a ($r = 0.11$; $n = 8$)

and the concentration of methyl chloride. Further work is required to look at direct and indirect mechanisms by which phytoplankton may influence the distribution of methyl chloride in the oceans.

Chapter 4: The Henry's Law Constant and Air-Sea Exchange of Methyl Chloride

4.0 *Introduction*

The flux (F) of a trace gas across the air-sea interface can be estimated using the equation –

$$F = K\,(C_w - C^*) \qquad (2)$$

C_w = concentration in the water phase

C^* = concentration in the water phase at equlilibrium with the gas phase concentration.

(C_w - C^*) is the saturation anomaly and K, having dimensions of [L][θ^{-1}], is called the transfer velocity. C^* ([M][L^{-3}]), the equilibrium concentration, depends on the gas-liquid partition coefficient of the gas through the relationship -

$$C^* = \frac{C_a}{H} \qquad (3)$$

C_a = atmospheric concentration ([M] [L^{-3}])

H = gas-liquid partition coefficient (non-dimensional)

The partition coefficient is often referred to as a dimensionless Henry's Law

constant. An accurate determination of *H* for methyl chloride is required for calculation of air-sea exchange. The measurements of methyl chloride in the surface water of the North Atlantic reported in Chapter 3 have been used to estimate the magnitude and direction of the flux of methyl chloride between the atmosphere and ocean.

4.1 *Literature values for the Henry's Law constant of methyl chloride*

Figure 4.1 provides a summary of previous determinations of $H(CH_3Cl)$ in distilled water. Wilhelm *et al.* (1977) reviewed measurements of the solubility and vapour pressure of over 60 gases including methyl chloride. They calculated the Ostwald coefficient (the volume of gas at system temperature and system partial pressure dissolved per unit volume of solvent) for methyl chloride in distilled water over the temperature range 5-80°C. The dimensionless Henry's Law constant (*H*) is the reciprocal of the Ostwald coefficient. Pearson and McConnell (1975) reported a value of 0.30 for *H* at 20°C calculated from solubility and vapour pressure data. In a more recent review, Mackay and Shiu (1981) recommended a value of 0.95 ± 0.05 (kPa m^3 mol^{-1}) at 25°C which when converted to *H* by division by RT (R = the ideal gas constant = 8.314×10^{-3} kPa m^3 mol^{-1} K^{-1}, T = Kelvin temperature) gives a value of 0.39 ± 0.02. Gossett (1987) and Elliott and Rowland (1993) measured *H* in distilled water using equilibration methods. Gossett (1987) used an EPICS method (Equilibrium Partitioning in Closed Systems). Two serum bottles were filled with different volumes of distilled water. *H*

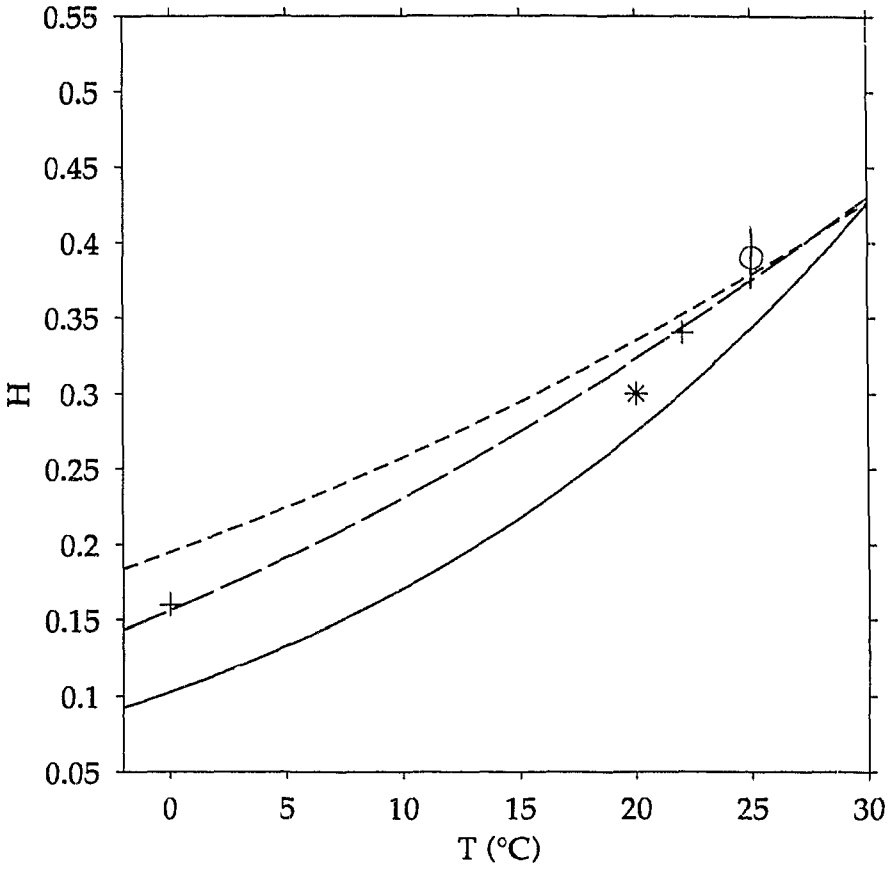


Figure 4.1 Literature values for the Henry's Law constant of methyl chloride in distilled water. (+) Elliott and Rowland, 1993; (*) Pearson and McConnell, 1975; (○) Mackay and Shiu, 1981; (— —) Glew and Moelwyn-Hughes, 1953; (- - - -) Wilhelm *et al.*, 1977; (——) Gossett, 1987.

was determined by measuring the concentration of the volatile compound in the headspace of each bottle after equilibration and applying the following equation -

$$H = \frac{V_{w2} - r\ V_{w1}}{r V_{g1} - V_{g2}} \qquad (4)$$

V_{w1}, V_{w2} = volumes of liquid in bottles 1 and 2, respectively.

V_{g1}, V_{g2} = volumes of gas in bottles 1 and 2.

$$r = \frac{C_{g1} / M_1}{C_{g2} / M_2} \qquad (5)$$

C_{g1}, C_{g2} = headspace concentrations (mol L^{-1})

M_1, M_2 = total moles of volatile compound added to bottles 1 and 2.

Elliott and Rowland (1993) equilibrated a known initial gas phase concentration of methyl chloride with water and calculated H by mass balance from a measurement of the resulting equilibrium gas phase concentration. The literature values for H at higher temperatures show reasonable agreement (10%), but at low temperatures they differ by as much as a factor of 2 (Figure 4.1).

A Henry's Law constant in seawater can be calculated from H measured in pure

water by multiplying by a constant, γ. γ depends on the ionic strength (I) of the solution according to the equation -

$$\log_{10}\gamma = k_s I \qquad (6)$$

I is in moles L^{-1}

k_s, the salting-out coefficient is in L $mole^{-1}$.

(Gossett, 1987).

Gossett (1987) determined the salting-out coefficient for six chlorinated aliphatic hydrocarbons. k_s ranged from 0.213 L $mole^{-1}$ for tetrachloroethylene to 0.107 L $mole^{-1}$ for dichloromethane. The measured values of k_s for these compounds showed a general trend of decreasing magnitude with increasing volatility of the molecule. k_s for methyl chloride was not determined. Elliott and Rowland (1993) measured H for methyl chloride in distilled water and seawater. γ calculated from their results is 1.06. The ionic strength of seawater was calculated using the equation -

$$I = 0.5 \sum_i m_i z_i^2 \qquad (7)$$

m_i = concentration of ion, i, in moles L^{-1}

z_i = charge of ion, i

(Drever, 1982)

- (0.7 moles L^{-1}). Thus, k_s for γ = 1.06 is ~ 0.04 L $mole^{-1}$. This value is less

than that measured by Gossett (1987) for dichloromethane, consistent with the trend of decreasing k_s with increasing volatility. The 20% increase in H assumed by Singh *et al.* (1983) overestimated H in seawater.

The measurement of H directly in seawater avoids the uncertainty associated with applying a "salt-effect" to values determined in distilled water.

4.2 *Measurement of the Henry's Law constant for methyl chloride directly in seawater using a gas-stripping method.*

4.2.1 Theory

A gas-stripping method for the measurement of Henry's Law constants for hydrophobic pollutants was developed by Mackay *et al.* (1979). A column of liquid containing the dissolved pollutant of interest is bubbled with a steady flow of inert gas. The concentration of the pollutant (C) decreases with time (t) according to the equation -

$$V\frac{dC}{dt} = -HFC \qquad (8)$$

V = volume of liquid in column (mL)

F = flow rate of purge gas (mL/min)

With an initial boundary condition of $C = C_o$ at $t = 0$, equation 8 can be integrated to give -

$$\ln\left(\frac{C_t}{C_o}\right) = -\frac{HF}{V}\,t \qquad (9)$$

Thus a plot of ln C_t versus t will give a straight line with slope equal to - $H\,F/V$. This treatment assumes that the sampling removes negligible volumes of the liquid, i.e., V remains constant. Equation 9 can be adapted to include the effect of the decrease in volume due to sampling (Lincoff and Gossett, 1984).

$$\ln\left(\frac{C_i}{C_o}\right) = -HF\sum_i\left(\frac{\Delta t_i}{V_i}\right) \qquad (10)$$

C_i = concentration at the end of the ith time interval

Δt_i = duration of ith time interval (min)

V_i = volume of liquid during the ith time interval (mL)

Six conditions must be met for the mathematical description of the stripping process given in equation 10 to be valid.

(1) The vapour must behave ideally. Ideal vapour behaviour can be assumed at environmental pressures for the low concentrations of dissolved CH_3Cl used.

(2) The liquid phase must be well-mixed.

(3) Henry's Law must be obeyed over the concentration range.

(4) The partial pressure of the dissolved pollutant must be small compared with

the total pressure. At high dissolved pollutant partial pressures, behaviour may deviate from ideal.

(5) The system must be isothermal.

(6) The pollutant must have reached an equilibrium distribution between the liquid phase and the bubbles of purge gas by the time it reaches the top of the liquid column.

4.2.2 Method

A gas-stripping column (Figure 4.2) built for the determination of H for some less volatile compounds over the temperature range 0-20°C (Moore *et al.*, 1994) was used for the measurement of H for methyl chloride. A volume of seawater in a glass column was purged with a steady stream of UHP N_2 introduced via a sparger (porosity 10-20 μm). Evaporation was kept to a minimum by saturating the gas stream with water vapour prior to entering the column. The temperature of the seawater was carefully controlled ($\pm$ 0.05°C) by a water jacket with surrounding foam insulation and measured using a platinum resistance thermometer. The sparging itself ensured rapid mixing within the column. The salinity of the seawater (measured using a Guildline Autosal) was 30.4 based on the Practical Salinity Scale. A Tylan mass flow controller was used to maintain a constant flow of gas. The flow was checked before and during the experiments with a bubble flow meter. The volume of liquid in the column could be calculated from a scale on the side of the column and was typically *ca.* 190 mL.

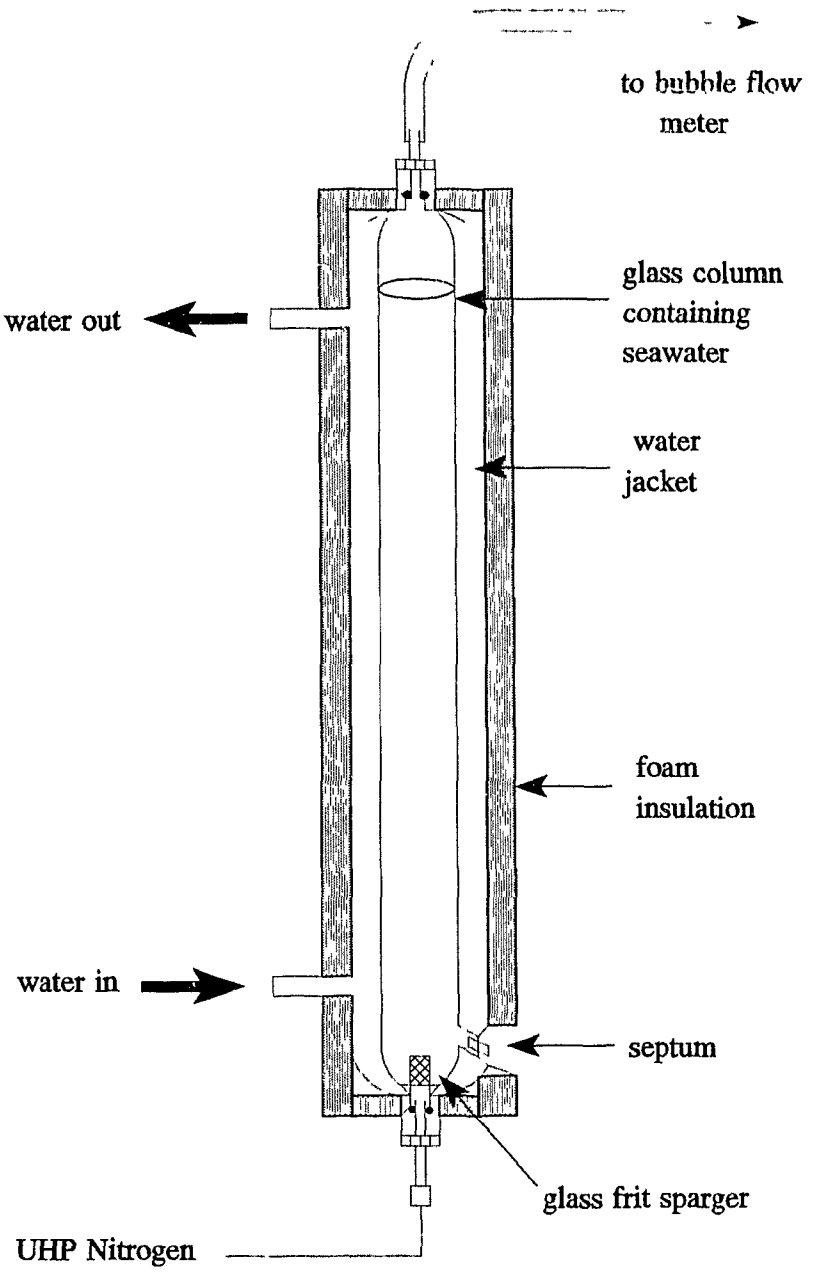


Figure 4.2 Gas stripping column used for the measurement of H for methyl chloride in seawater. Height = 52 cm, diameter = 2.25cm.

A solution of methyl chloride in distilled water (1.7μM) was prepared in the solution-standard vessel described in Chapter 2. One millilitre of this was added to the column via the septum directly into the bubbling zone. The initial concentration in the column was *ca.* 9 nM (nanomolar), 40-50 times sea-surface concentrations. The resulting maximum partial pressure of methyl chloride in the gas phase is negligible (*ca.* 10^{-9}) compared with the total pressure. After allowing sufficient time for complete mixing within the column (5-10 minutes), approximately 1 mL was withdrawn into a previously weighed gas-tight syringe. The syringe plus sample was then weighed to determine the exact volume removed from the column, the plunger adjusted to one millitre volume, and the sample injected into 20 mL of pre-purged Super-Q water in the purge and trap system for analysis. The syringe was then weighed again to accurately ascertain the volume of sample injected. The initial concentration of 9 nM was necessary to make sure that the concentrations throughout the experiment were within the tested linear range of the analysis method. Further samples of 1 mL were withdrawn from the column at 45 minute intervals.

Prior use of this apparatus for the determination of H for other volatile halocarbons had shown that assumption (6), equilibrium between the gas and aqueous phases, was met at values of H less than 0.22 (CH_3I at 20°C) for a column height of 46cm (liquid volume of 190 mL). The rate of approach to equilibrium within the column depends on three factors - H, the overall liquid mass transfer coefficient K_l, and the area of gas/liquid interface within the column, A (Mackay *et al.*, 1979). A low value of H i.e. high solubility, and high values of K_l and A favour rapid equilibration between the

gas and liquid phases in the column. The overall liquid mass transfer coefficient for CH_3Cl is a factor of 2 greater than that for CH_3I (Liss and Slater, 1974). The first determination of H was done at 0°C. Extrapolating to 0.22 using the temperature dependence of H in distilled water determined by (Wilhelm *et al.*, 1977) suggested that H for methyl chloride would reach 0.22 at 7.5°C. Further measurements were done at 3°C and 6°C. The higher value of K_l supports the assumption of equilibrium at these temperatures.

Table 4.1 Experimental values of Henry's Law constant for CH_3Cl in seawater (S=30.4)

Temperature (°C)	slope (-*HF*)	r^2	standard error of slope (%)	*H* (± uncertainty[a])
0	-1.3003	0.9981	2.2	0.173 ± 2.5%
3	-1.4422	0.9995	1.5	0.198 ± 2%
6	-1.6458	0.9997	1.8	0.219 ± 2%

[a] - Uncertainty limits were calculated by combining variances from the observed uncertainty in F (± 0.3%), and the standard error of the slopes obtained from the regressions of $ln(C_i/C_o)$ versus $\Sigma(\Delta t_i/V_i)$ assuming errors were normally distributed.

4.2.3 Results

Table 4.1 contains the results of determinations of H at 0, 3, and 6 °C. Plots of $ln(C_i/C_o)$ versus $\Sigma(\Delta t_i/V_i)$ for these experiments are shown in Figure 4.3.

Regression of ln H versus $1/T$ (T = absolute temperature (K)) for these three temperatures produces the equation -

$$\ln H = 9.163 - \frac{2981}{T} \;;\therefore H = 9.54 \times 10^3 \exp\left(\frac{-2981}{T}\right) \qquad (11)$$

(Figure 4.4)

The solid line on Figure 4.5 shows H as a function of T (converted to °C) calculated using equation 11. For comparison, H used by Singh *et al.* (1983) and that measured by Elliott and Rowland (1993) are also shown. Singh *et al.* (1983) calculated H using the equation -

$$H = 1.2\ H_{25}^{\circ} \exp\left(0.0334\ (T-25)\right) \qquad (12)$$

H_{25}° = H in distilled water at 25 °C. (A value of 0.393 was calculated from Wilhelm *et al.*(1977)).

T = temperature in °C;

1.2 = "salt effect"

Singh *et al.*'s calculated values are 10-20% higher than those obtained from equation 11 over the temperature range 0-30 °C, with the greatest difference occurring at

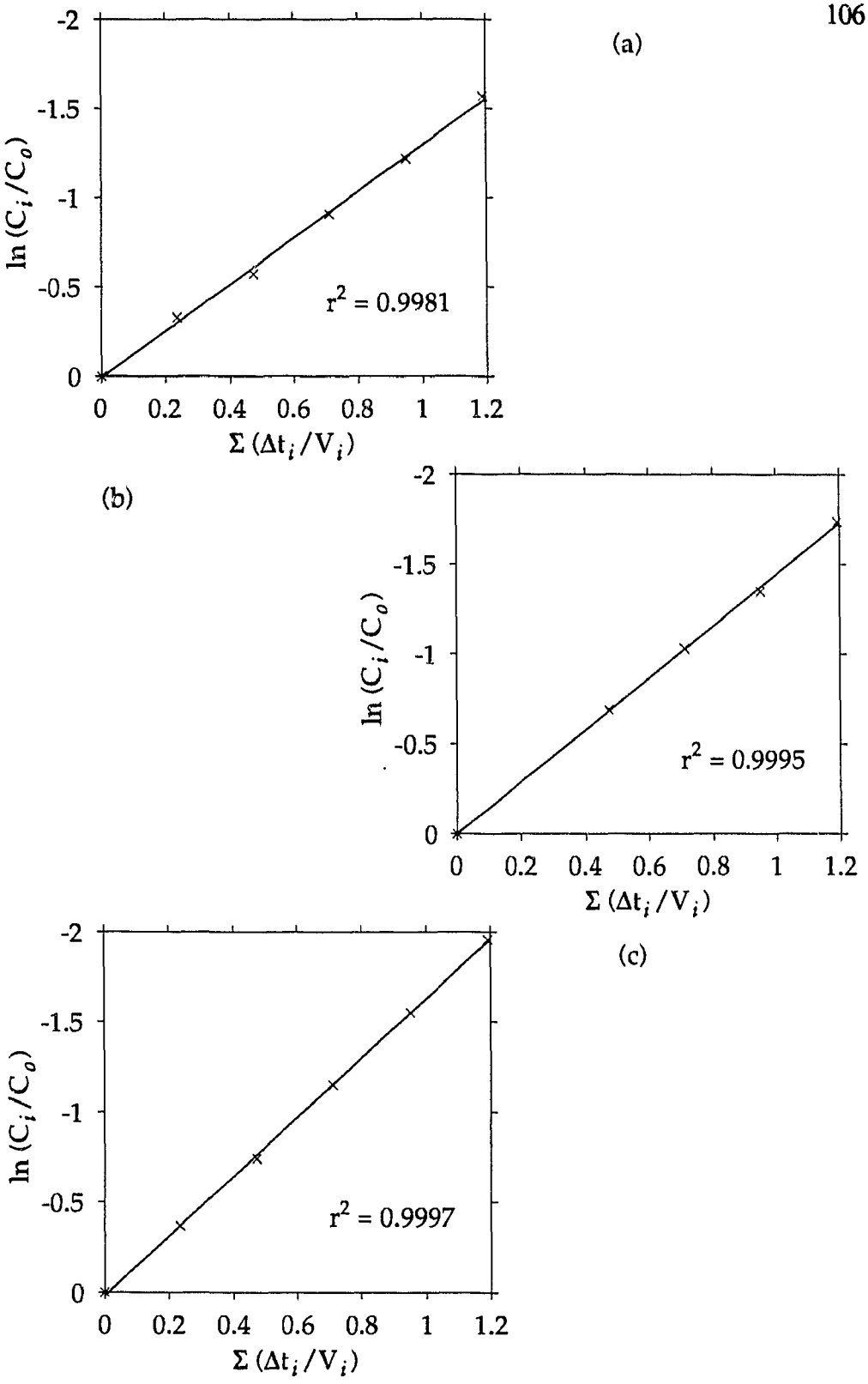


Figure 4.3 Results of experiments to determine H at (a) 0°C, (b) 3°C and (c) 6°C.

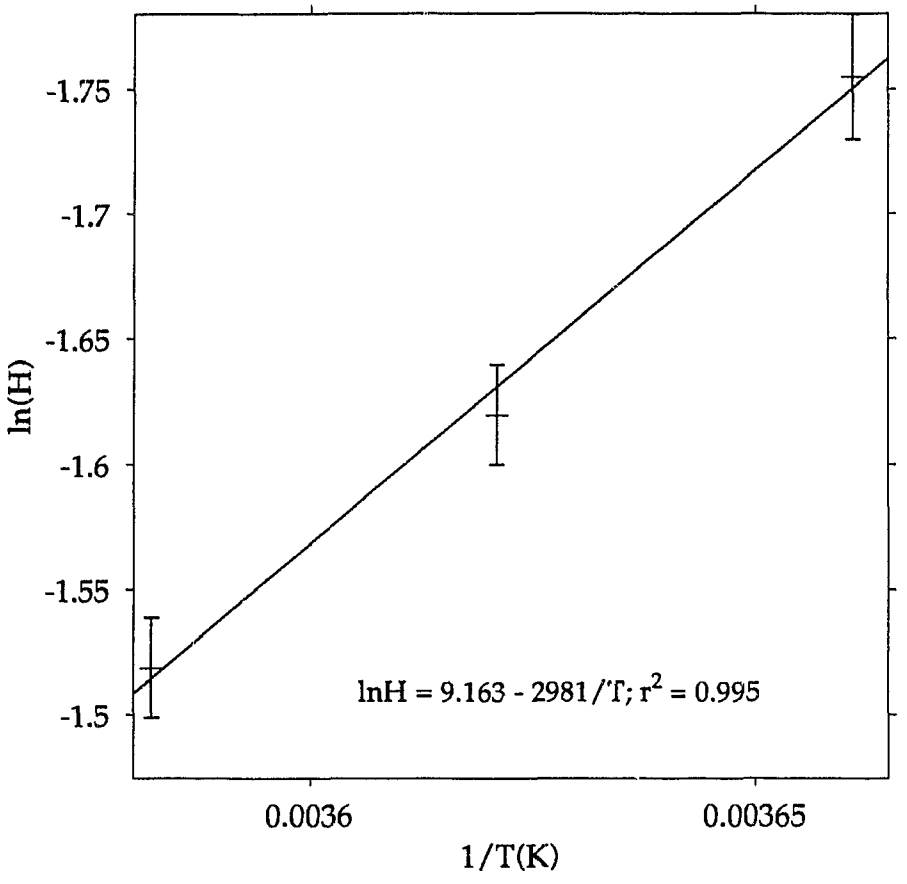


Figure 4.4 Regression of experimental values of $\ln H$ against 1/T (K). Error bars are uncertainty limits given in Table 4.1.

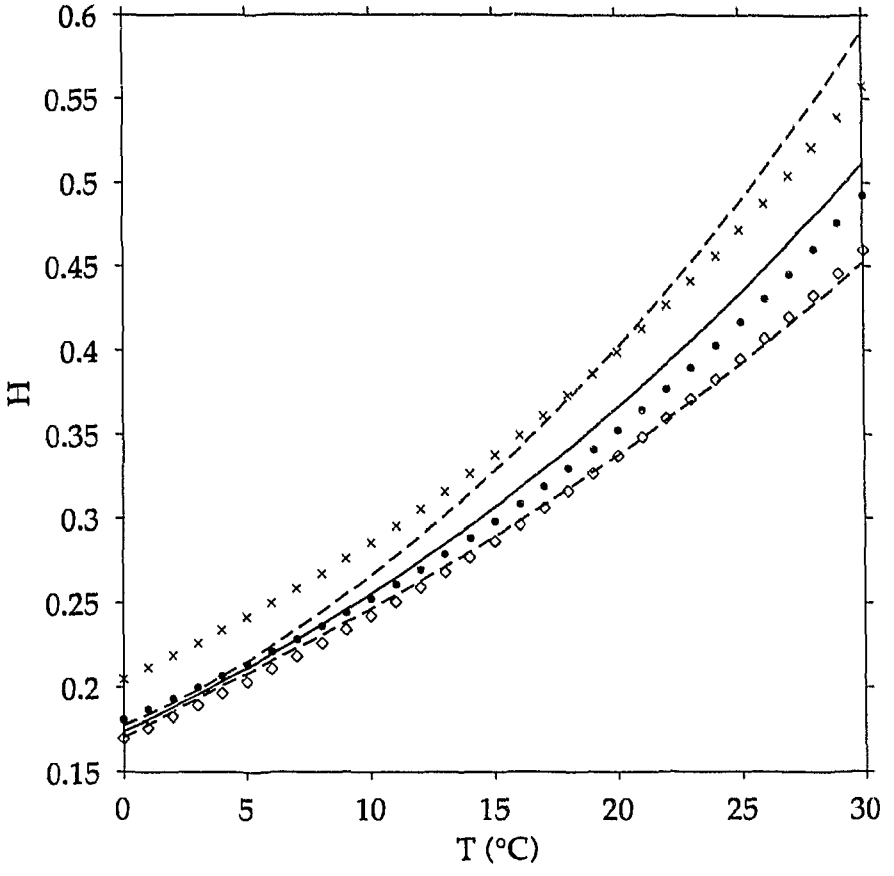


Figure 4.5 H as a function of temperature for methyl chloride in seawater. (———) present study with uncertainty (– – – –) estimated as described in the text. (◇ ◇ ◇) Elliott and Rowland, 1993; (× × ×) Singh *et al.*, 1983; (• • •) Singh *et al.*, 1983, assuming a 6% salt effect.

low temperatures. Some of the discrepancy can be explained through Singh *et al.*'s assumption of a 20% salting out in seawater compared to distilled water. Inserting a salt effect of 1.06 in place of 1.2 in equation 12 gives values of H within 5% of those determined in the present study between 0 and 30°C. Elliott and Rowland (1993) calculated an equation describing the temperature dependence of H for methyl chloride in seawater from measurements at 0°C and 22°C -

$$H = 4.00 \times 10^3 \exp\left(\frac{-2750}{T}\right) \qquad (13)$$

H from the present study was greater than Elliott and Rowland (1993). The difference was less than 2.5% at 0°C and increased to 10% by 30°C.

The equations for the temperature dependence of H produced from both this study and that of Elliott and Rowland (1993) are based on very few data points (3 and 2, respectively). Elliott and Rowland estimated the uncertainty of their measurements to be <0.01. This translates to a $\pm$3-5% uncertainty in their two measured values of H. The present study is subject to a second limitation - the restricted temperature range over which measurements were made. The uncertainty in the values of H derived from the linear regression of the three data points increases at temperatures outside the experimental range. The dashed lines on Figure 4.5 show upper and lower limits of H calculated using estimates of the standard error of the slope and intercept obtained from the uncertainty estimates for the individual data points. The $\pm$2-2.5% uncertainty in the measured values of H produces an uncertainty of $\pm$9% at 20°C. The two studies,

however, show good agreement within the calculated uncertainty limits of the experimental methods.

Figure 4.5 shows that with a 6% salt effect, the temperature dependence of H calculated from vapour pressure and distilled water solubility data (Wilhelm *et al.*, 1977; Singh *et al.*, 1983) is in good agreement with those determined by direct measurement in seawater by both equilibration (Elliott and Rowland, 1993) and dynamic stripping (present study) methods. The data from all three sources were combined to obtain the best estimate of H (CH_3Cl) in seawater -

$$H = 5.34 \times 10^3 \exp\left(\frac{-2822}{T}\right) \qquad (14)$$

- with an estimated uncertainty of $\pm 10\%$ over the temperature range 0 to 30°C.

4.3 *Calculation of a global sea-air flux of methyl chloride.*

4.3.1 The saturation anomaly (C_w - C^*)

Calculation of the saturation anomaly at a particular site requires concurrent measurements of the methyl chloride concentration in both the air and water phases as well as an accurate value for H. To estimate the air-sea exchange using the surface concentrations reported in Chapter 3, an assumed tropospheric boundary layer mixing ratio derived from published values was used. CH_3Cl mixing ratios measured in the

lower marine troposphere in the northern hemisphere range from 530 pptv to greater than 1 ppbv (Koppmann *et al.*, 1993; Singh *et al.*, 1977). Some of the highest values (*ca.* 800 pptv) over the open ocean were observed at low latitudes by Rasmussen *et al.* (1980). At higher latitudes, tropospheric boundary layer mixing ratios were closer to 600 pptv. Hov *et al.* (1984), however, measured an average of 730 pptv at Spitsbergen. Several investigators report average tropospheric boundary layer mixing ratios in the range 600-650 pptv (Khalil and Rasmussen, 1981; Singh *et al.*, 1983; Hoyt and Rasmussen, 1985). It has been decided to adopt a mixing ratio of 625 pptv for the calculation of an air-sea flux of methyl chloride. The average saturation anomaly (i.e. supersaturation) calculated is then 168%.

4.3.2 The transfer velocity, *K*

One of the early approaches to air-sea exchange employed a two-layer stagnant film model (Liss and Slater, 1974). The atmosphere and ocean were assumed to be well-mixed reservoirs each separated from the interface by a thin layer through which molecular diffusion occurred. An overall mass transfer coefficient, (*K*), was calculated from the individual transfer coefficients in the diffusion layers on either side of the interface according to -

$$\frac{1}{K} = \frac{1}{\alpha k_w} + \frac{1}{k_g H} = r_w + r_g \qquad (15)$$

k_w = the transfer coefficient in the diffusion layer on the water side of the interface

k_g = transfer coefficient on the gas side.

α = enhancement factor due to chemical reaction with the water *e.g.* dissociation

r_w, r_g = resistance to gas transfer in the water and gas phases, respectively.

For an unreactive gas such as methyl chloride, $\alpha = 1$. This model predicts that 94-97% of the total resistance to methyl chloride transfer over the temperature range of 0 to 20°C is found in the liquid phase. Therefore, the overall exchange velocity is relatively insensitive to the value of H. The stagnant film model predicts a linear relationship between K (dimensions [L] [θ^{-1}]) and the molecular diffusion coefficient of the gas, D ([L^2] [θ^{-1}]) -

$$K = \frac{D}{z} \qquad (16)$$

- where z ([L]) is the thickness of the stagnant film.

Later studies have addressed the effect of wind speed on K (e.g. Liss and Merlivat, 1986). However, not only wind speed, but also duration, fetch and variability affect the rate of gas exchange. These factors determine the development of the wave field and the distribution of white caps which have been found to affect the rate of air-sea exchange (Asher *et al.*, 1992). The overall transfer velocity of a particular gas is also

related to its Schmidt number, S_c (S_c = the kinematic viscosity of seawater (ν) / diffusion coefficient of the gas (D), both of which are functions of temperature (Wanninkhof, 1992)). Experimental evidence suggests that $K \propto S_c^n$ with n varying between -0.7 and -0.3 depending on the amount of foam due to breaking waves (Asher *et al.*, 1992). Wanninkhof (1992) reviewed relationships between K and wind speed derived from direct measurements of K. At a wind speed of 6 ms^{-1}, K varies by a factor of 3 between studies.

In the estimation of annual sea-air fluxes of trace gases, K is normally chosen by assuming an annual average wind speed and applying a relationship between the two variables derived from experimental data. The average wind speed measured at sea during the "Hudson" cruise was *ca.* 6.5 ms^{-1}. This value will be used in the calculation.

Wanninkhof (1992) derived equations for the Schmidt number temperature dependence for several gases including CO_2, CFC-11, and CFC-12. An equation for methyl chloride can be obtained similarly. D ($cm^2\ s^{-1}$) for methyl chloride in pure water was calculated using the Wilke-Chang empirical correlation for diffusion coefficients in dilute solution -

$$D = 7.4 \times 10^{-8} \frac{(\phi M_w)^{0.5}\, T}{\eta_w V_a^{0.6}} \qquad (17)$$

ϕ = association factor of water = 2.26 (Reid *et al.*, 1977).

V_a = molar volume of CH_3Cl at its normal boiling temperature (50.6 cm^3 $g\text{-}mol^{-1}$; Reid *et al.*, 1977: p552)

M_w = molecular weight of water (g)

T = absolute temperature (K)

η_w = dynamic viscosity of pure water (cP = 10^{-2} g cm^{-1} s^{-1})

At 20°C, $D(CH_3Cl)$ calculated using this method is 1.31 x 10^{-5} cm^2 s^{-1}. It is assumed that diffusion coefficients in seawater are *ca.* 5% lower than in pure water based on the measured diffusion coefficients of helium and hydrogen in the two media (Jahne *et al.*, 1987). A third order polynomial was fitted to calculated Schmidt numbers over the temperature range 0 to 30°C giving an $r^2 > 0.999$. Table 4.2 contains the values of S_c for methyl chloride between 0-30°C calculated using the derived equation -

$$S_c(CH_3Cl) = 2869.6 - 187.99\,T + 5.8573\,T^2 - 0.07292\,T^3 \quad (18)$$

Over the temperature range 0-30°C, S_c for CO_2 varies by a factor of 5 (Jahne *et al.*, 1987) while the calculated S_c for methyl chloride varies by a factor of 6. The Schmidt number, and therefore K, for methyl chloride shows a strong temperature dependence.

For CO_2 (S_c = 600 at 20°C) and wind speed of 6.5 ms^{-1}, K is 13.1 cm h^{-1} using the wind speed dependence suggested by Wanninkhof (1992) for wind speeds measured by shipboard anemometers (see Table 4.3). K for CH_3Cl, assuming a dependence on $S_c^{-0.5}$ (Watson *et al.*, 1991; Wanninkhof, 1992), is 11.4 cm h^{-1} at 20°C, 10-15% smaller. Over the range of temperatures encountered during the cruise (-1.5 - 20.5°C), K varies by a factor of 2 (5.9 - 11.5 cm h^{-1}).

4.3.3 Flux calculation

Table 4.3 contains a summary of the parameters used in the calculation of a sea-air flux of CH_3Cl from the surface concentrations measured during spring 1991 in the North Atlantic. F was calculated for each surface concentration. The average value of F was 4 x 10^{-12} moles m^{-2} s^{-1} (2.00 x 10^{-10} g m^{-2} s^{-1}). Extrapolating this value to the global oceans and assuming no seasonality, produces an annual sea-to-air flux of 4.5 x 10^{10} moles yr^{-1} (2.3 x 10^{12} g yr^{-1}). Omitting the dependence of K on the Schmidt number for methyl chloride increases the estimate by 50%.

Singh *et al.* (1983) calculated that 9.7 x 10^{10} moles (4.9 x 10^{12} g) of methyl chloride would be released from the oceans per year. The transfer velocity used in this calculation was estimated using the two-layer resistance approach described by Liss and Slater (1974). The flux can be re-evaluted using more recent information on the value of H and also on the wind speed and temperature dependence of the transfer velocity. When the Henry's Law constant measured in this chapter is used, a decrease of only 3.3% results. Inclusion of the wind speed and temperature dependence of the transfer velocity (Wanninkhof, 1992), however, reduces the calculated flux by 40% to 6.2 x 10^{10} moles yr^{-1} (3.1 x 10^{12} g yr^{-1}). A large source of uncertainty in the flux calculated in the present study is due to the question of the wind speed dependence of K ($\pm$ 50-60%). A $\pm$20% uncertainty in the measurement of C_w (Chapter 3) would result in $\pm$40% uncertainty in the calculated flux. The validity of extrapolating a flux based on measurements made in late spring to the whole year must also be questioned. The

absence of sampling particularly during winter months is a source of bias in the reported measurements.

Table 4.2 Calculated Schmidt Numbers for methyl chloride. Schmidt Numbers for carbon dioxide measured by Jahne *et al.* (1987) are included for comparison.

Temperature (°C)	S_c (CH_3Cl)[a]	S_c (CO_2)[b]	Difference (%)
0	2870	2070	-38
5	2065	1530	-35
10	1500	1135	-32
15	1120	860	-30
20	870	665	-30
25	690	525	-32
30	530	400	-32

[a] - Diffusion coefficients calculated using Wilke-Chang correlation with water association factor = 2.26.

[b] - From measurements by Jahne *et al.* (1987) reported in third order polynomial equation form by Wanninkhof (1992).

Table 4.3 Parameters used in calculation of the air-sea exchange of methyl chloride.

Parameter			Source
K	U_{10}	6.5 ms^{-1}	average observed during cruise
	$K(U_{10})$	13.1 cm h^{-1}, 20 °C, $S_c = 660$.	Wanninkhof (1992)
	$K \propto S_c^{-0.5}$	$0.31U_{10}^2(S_c/660)^{-0.5}$	Wanninkhof (1992), Watson *et al.* (1991)
	- D	Wilke-Chang correlation (equation 17)	Reid *et al.* (1977)
	- ν		Jahne *et al.* (1987), Wanninkhof (1992)
C_w			Chapter 3
C^*	C_a	625 pptv	**
	H	$H = 5.34x10^3exp(-2822/T)$	section 4.2.3

** Koppmann *et al.* (1993), Hoyt and Rasmussen (1985), Hov *et al.* (1984), Singh *et al.* (1983), Rasmussen *et al.* (1980).

4.4 *Conclusions*

The Henry's Law constant (H) for methyl chloride was measured directly in seawater using a dynamic gas-stripping method. Results are in reasonable agreement with those from a recently reported equilibration method (Elliott and Rowland, 1993). An equation describing the temperature dependence -

$$\ln H = 9.163 - \frac{2981}{T}$$

- was calculated using measurements at 0, 3, and 6 °C.

The air-sea exchange of methyl chloride was estimated from surface concentrations in the North-west Atlantic. The average supersaturation (170% with respect to an assumed boundary layer mixing ratio of 625 pptv) drives a flux from ocean-to-atmosphere. The transfer velocity (K) was corrected for wind speed according to the relationship suggested by Wanninkhof (1992) and temperature through the Schmidt number. Extrapolation of the average flux of 4.0×10^{-12} moles m^{-2} s^{-1} (2.0×10^{10} g m^{-2} s^{-1}) to the global ocean yields an annual transfer of 4.5×10^{10} moles (2.3×10^{12} g) from the surface ocean to the lower troposphere. Omission of the temperature correction through the Schmidt number dependence of K increases the calculated flux by 50%. The sea-air flux calculated in this study is 45-50% lower than that estimated by Singh *et al.* (1983). The ocean source estimated from the measurements of Singh *et al.* (1983) was re-evaluated by inclusion of wind speed and temperature dependences of K. The resulting flux (6.2×10^{10} moles yr^{-1}; 3.1×10^{12} g yr^{-1}) was 40% lower than that originally reported.

Chapter 5: Methyl Chloride in a Coastal Environment

5.0 *Introduction*

Concentrations of methyl chloride were measured at depths between 0 and 30m in Bedford Basin, Nova Scotia, from February to June, 1992, throughout the course of a spring phytoplankton bloom. The aims of the study were to assess whether phytoplankton influenced the distribution of methyl chloride in the Bedford Basin, and if so, whether increases in methyl chloride were associated with a particular stage of bloom development. The study was also intended to provide measurements of methyl chloride from a temperate coastal environment (45°N) for comparison with open ocean concentrations measured in the North-west Atlantic (30 - 60°N).

5.1 *Study area*

The Bedford Basin (Figure 5.1) is a coastal inlet of maximum depth 70m which exchanges with the ocean via Halifax Harbour. The Harbour is a shallow (20m), narrow channel (minimum 400m wide) which acts as a sill, restricting ventilation of waters below 20m within the Basin. The major freshwater input is from the Sackville River. Surface salinity ranges from 15 - 30 (based on the Practical Salinity Scale) (Platt and Conover, 1971). The Basin also receives treated and untreated sewage from surrounding

communities. Riverflow, tides, and wind are the major driving forces flushing the upper 20m of the water column within the Basin (Platt *et al.*, 1970; Platt and Conover, 1971). Ventilation of the deeper waters may occur by the sinking of dense oxygenated ocean waters intruding over the sill and wind or convection driven mixing events. Photosynthesis is restricted to depths above about 15m.

5.2 *Sampling*

Figure 5.1 is a map of the Bedford Basin showing the sampling sites - the D.N.D. barge (1) and the Compass Buoy (2). From February 11 to April 22, samples were taken at the D.N.D. barge. On three occasions the bottle cast was done from M.V. "Sigma-T" moored alongside the barge. Water was taken from a 12-l Niskin bottle directly into all-glass syringes and stored in a bucket of surface seawater for transport back to the laboratory. Samples taken from 0.5m depth inside and outside the barge agreed within 5%. On one occasion, samples were sealed in glass ampoules using a propane torch and analysed the following week. These numbers were omitted from the data set due to apparent contamination (see Chapter 2). All other data are from samples analysed within 12-24 hours of collection. Bucket samples were not taken in the barge due to the possibility of contamination from surface debris. After April 22, circumstances required a change of sampling site. For the remainder of the study sampling was done from the "Sigma-T" moored alongside Compass Buoy (site 2; Figure 5.1). Although lateral

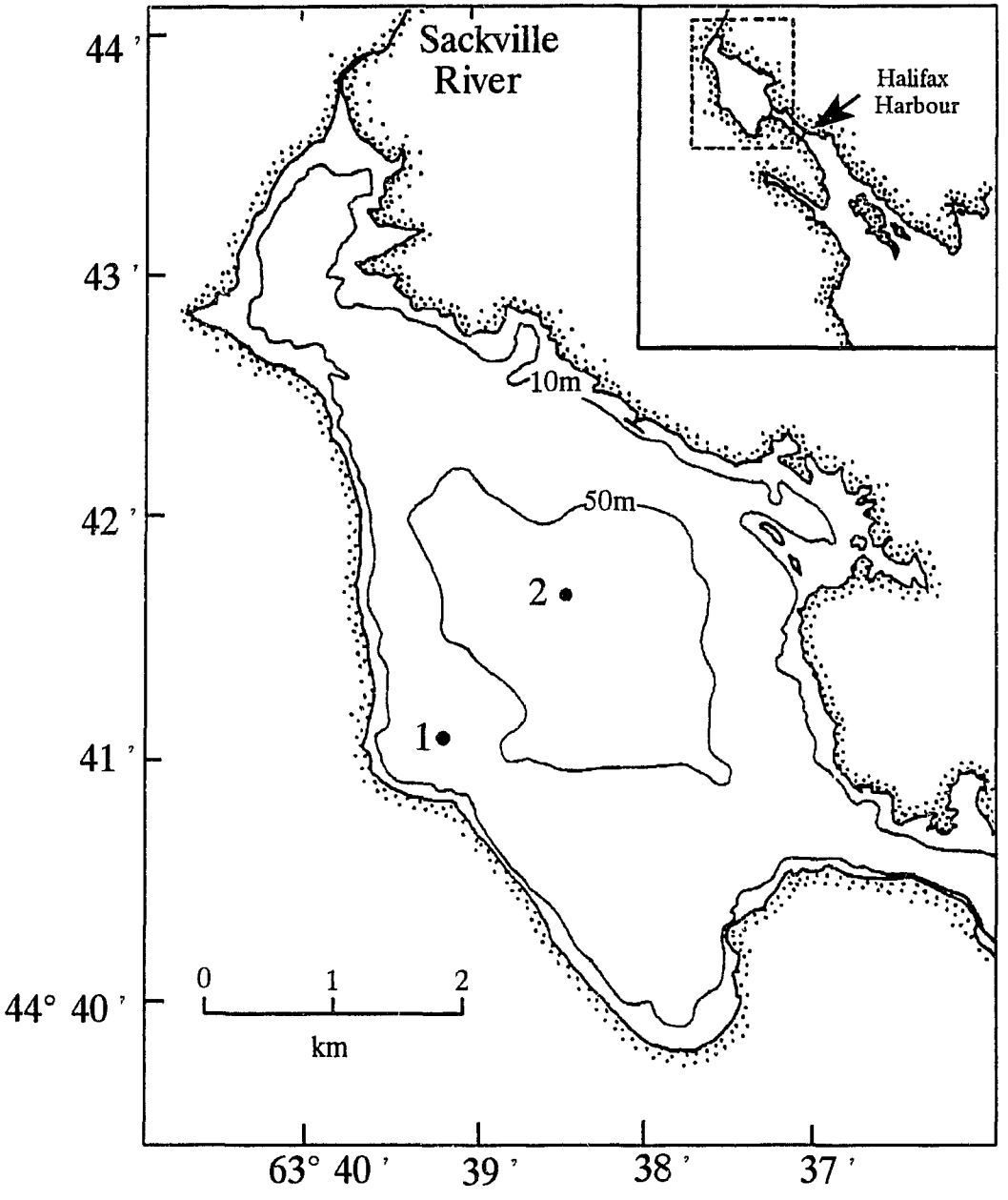


Figure 5.1 The study area - Bedford Basin, Nova Scotia. 1 = D.N.D. barge; 2 = Compass Buoy.

heterogeneity in chlorophyll-a concentrations occurs within the Basin, Platt and Conover (1971) observed that differences at a station were as great as between stations. The change in sampling site is unlikely to affect the overall picture of the time course of bloom development in the Basin.

Temperature and salinity were measured using a Seabird® CTD. P. Clement at the Bedford Institute determined concentrations of nitrate + nitrite, phosphate, and silicate by standard spectrophotometric methods using a Technicon autoanalyser. Chlorophyll-a was measured using the method of Holm-Hansen *et al.* (1965). The Sackville River discharge data were provided by the Water Resources Branch of Environment Canada (A. Gilmore), and monthly meteorological summaries were obtained from Atmospheric Environment Service (D. Porter).

5.3 *Results*

5.3.1 Temperature, salinity, and oxygen

Contour plots of the CTD temperature and salinity distributions are shown in Figures 5.2 (a) and (b). Days on which salinity and temperature were measured are marked as "x" on the upper x-axis. Only bottle salinities were available prior to Day 70. Figure 5.3 shows the mean daily wind speed and Sackville River volume discharge.

During February to mid-April (days 42-105) the magnitude of freshwater inflow,

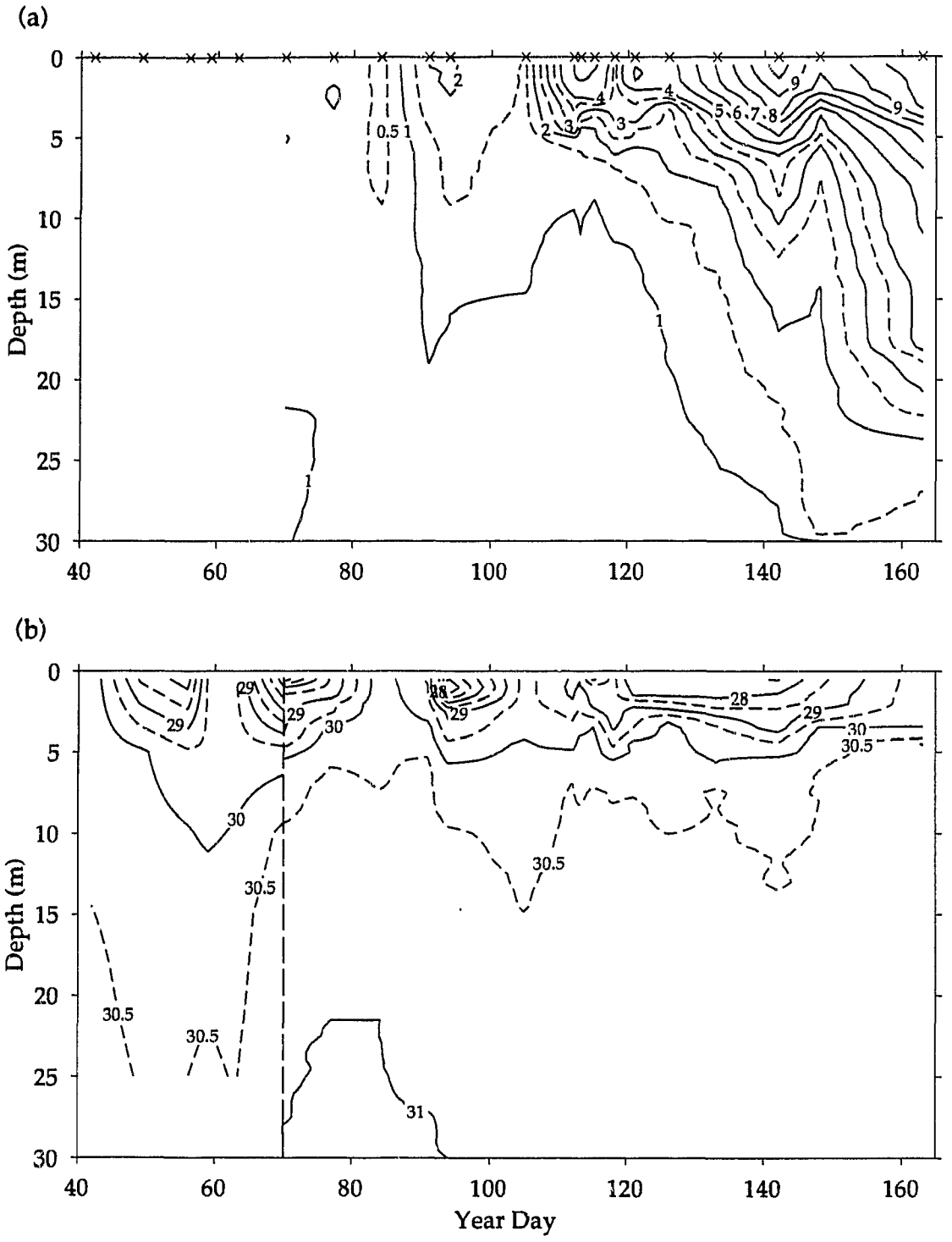


Figure 5.2 Contour plots of (a) CTD temperature (°C) and (b) bottle and CTD salinity. "x" on the upper x-axis marks sampling days.

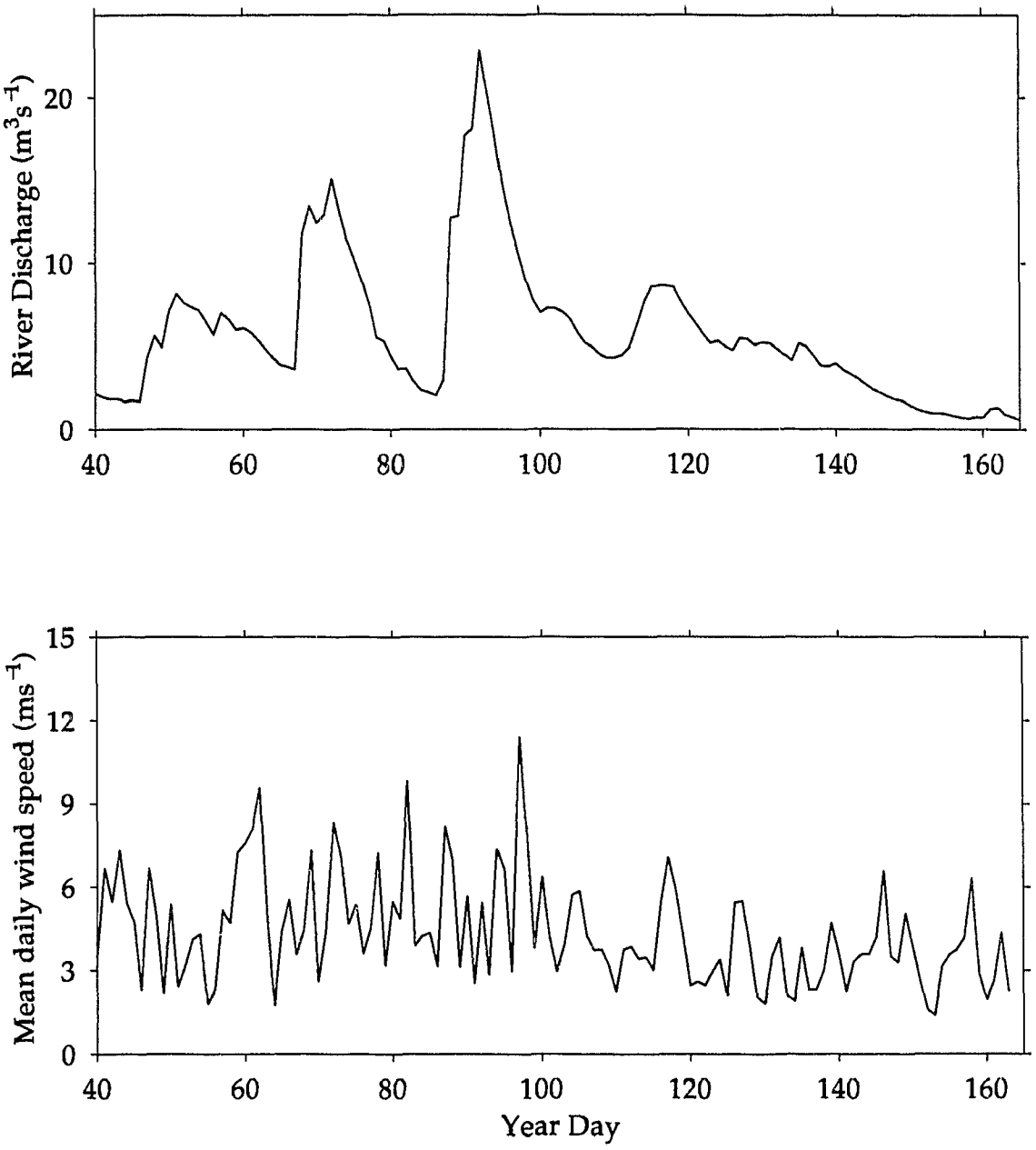


Figure 5.3 Sackville River volume discharge and mean daily wind speed during the study period.

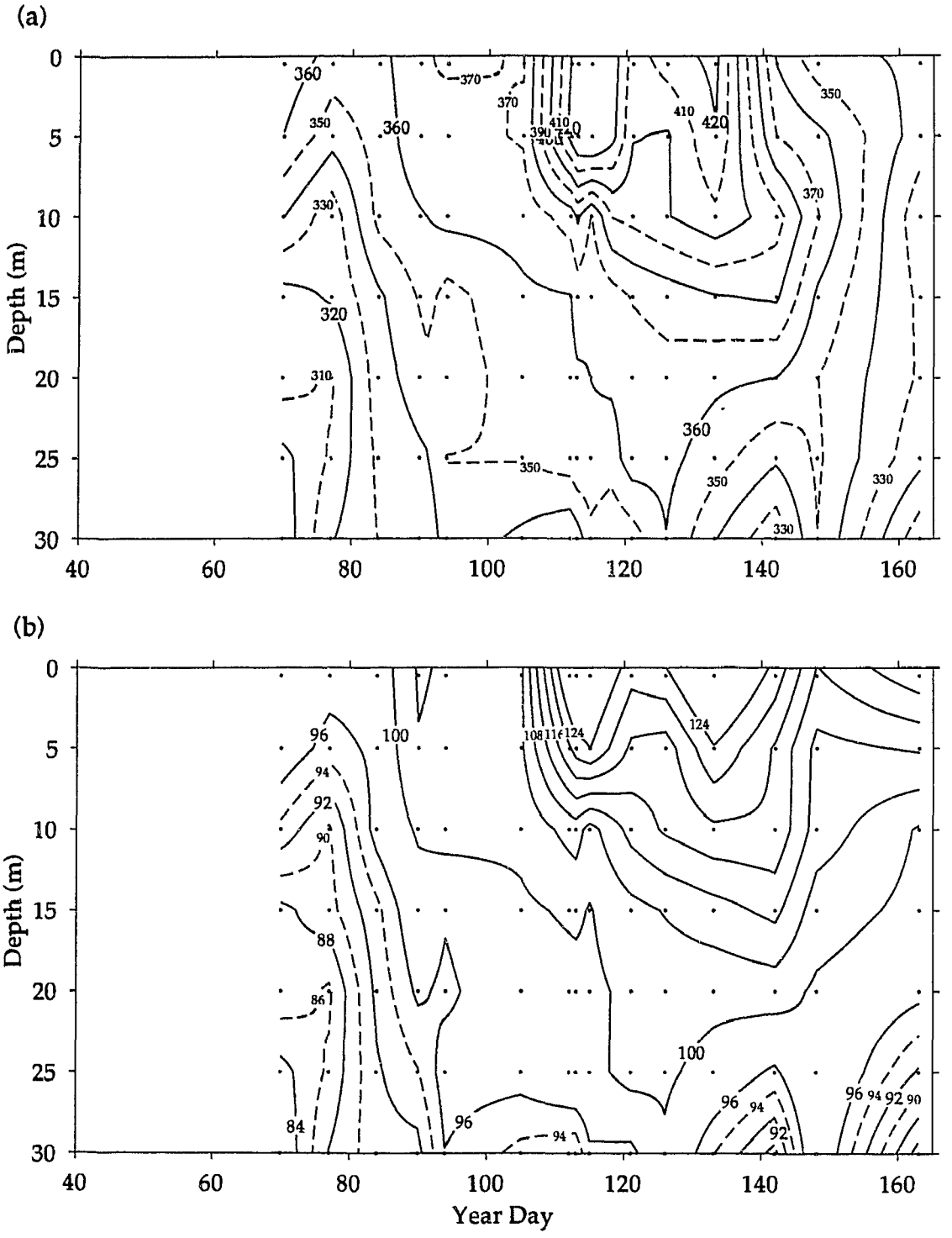


Figure 5.4 Contour plots of (a) oxygen concentration (μM) and (b) oxygen saturation (%).

dominated by the Sackville River, was the major factor controlling the salinity distribution within the upper 5-10m of the Bedford Basin (Figures 5.2 and 5.3). Whereas river inputs produced vertical gradients of salinity, winds drove mixing of the water column. Following a period of sustained high winds, a comparatively homogeneous vertical salinity profile was observed on day 63. High winds and low run-off preceded the well-mixed water column found on day 84.

A shallow thermocline had developed by day 105, which persisted for the remainder of the study with only a temporary interruption around day 118 (Figure 5.2 (b)). The passage of a storm caused greater wind-induced mixing and freshwater run-off at this time (Figure 5.3). By *ca.* day 140, the 1 $^{\circ}$C isotherm had reached close to 30m due to surface heating. Decreased wind-driven vertical mixing of near-surface waters with colder waters below the sill depth could also contribute to the warmer temperatures.

Oxygen concentrations and saturations within the upper water column are shown in Figure 5.4. Between days 70 and 90, higher salinities and lower oxygen concentrations were observed from 10-30m consistent with the upward penetration of denser, older waters from below the sill depth within the Basin. Less pronounced episodes of upwards penetration of deeper waters occurred between days 133 and 142 and on day 163. During the bloom (days 105-142), phytoplankton photosynthesis resulted in oxygen supersaturation within the upper 20m of the water column.

5.3.2 Macronutrients and chlorophyll-a

Macronutrient distributions (phosphate, nitrate + nitrite, silicate in μM) are shown in Figures 5.5 (a) to (c). Prior to depletion due to uptake by phytoplankton, nutrient distributions in the upper 20m reflect a riverine source. Higher concentrations of nutrients were found between 20 and 30 m around day 70 within the water intruding from below. A temporary reversal in the downward progression of the nutrient contours on day 115 during the bloom can also be seen in the chlorophyll-a distribution (Figure 5.6) and to a lesser extent the oxygen distribution (Figure 5.4).

Chlorophyll-a concentrations remained below 3 μgL^{-1} from days 42-84 (Figure 5.6). On day 94 chlorophyll-a concentrations were greater than 3 μgL^{-1} at 5m. A subsequent decrease in chlorophyll-a followed an event of high freshwater run-off from the Sackville River and high winds which flushed the surface layer of the Basin. Periods of high riverflow flushing the surface layer of the Basin and increased vertical mixing of the water column by winds delayed the establishment of the bloom until mid-April.

During the bloom, maximum concentrations of chlorophyll-a ranged from 11 - 14.9 μgL^{-1}. The dominant species of phytoplankton contributing to this bloom have been reported by Head *et al.* (1994). Diatom species *Chaetoceros concavicornis, C. socialis,* and *Skeletonema costatum* were three of the most abundant within the chlorophyll maximum. The peak of the bloom was around day 115. As the material sank out of the surface layer in the later stages of the bloom, the chlorophyll maximum became progressively deeper.

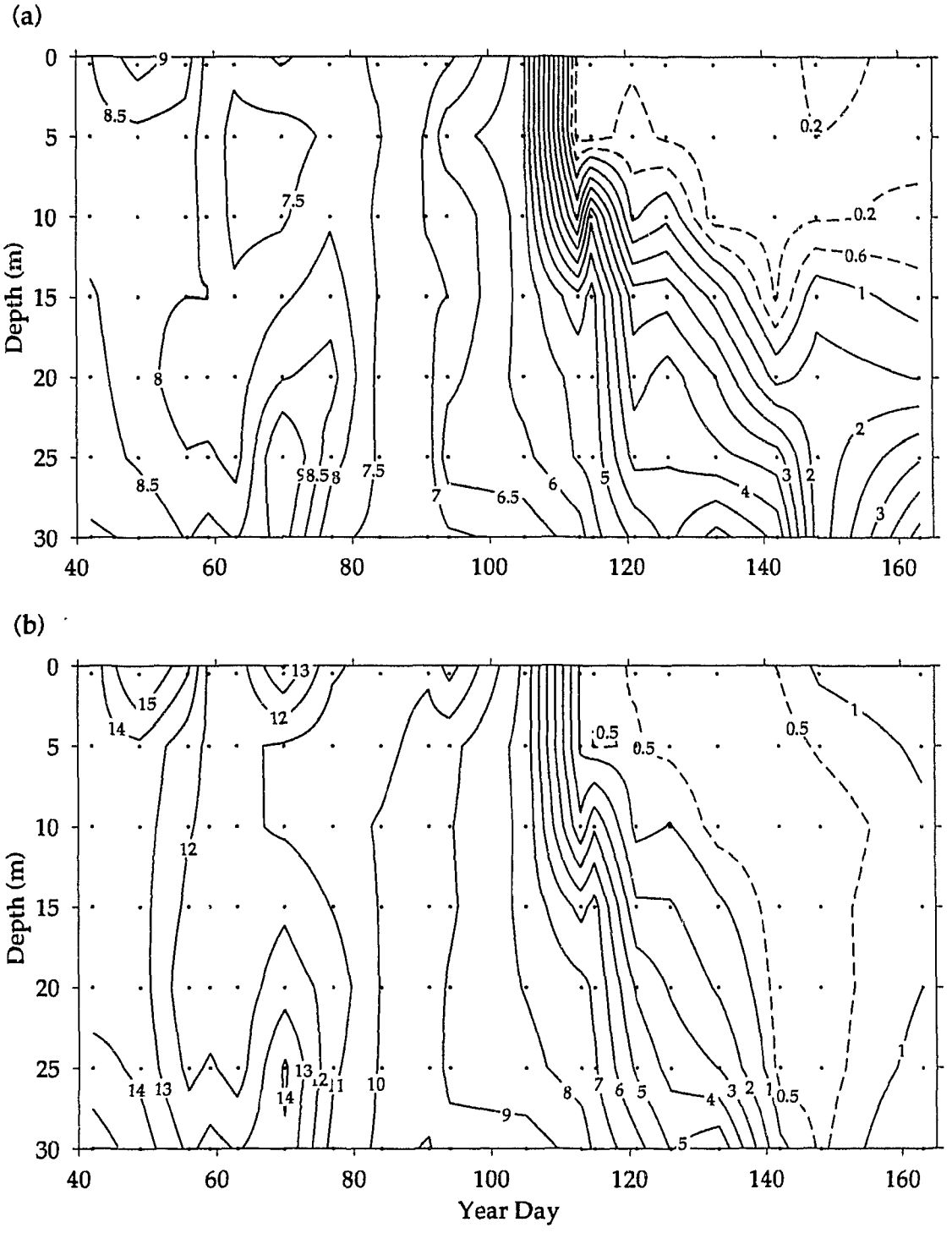


Figure 5.5 Contour plots of (a) nitrate + nitrite and (b) silicate (μM).

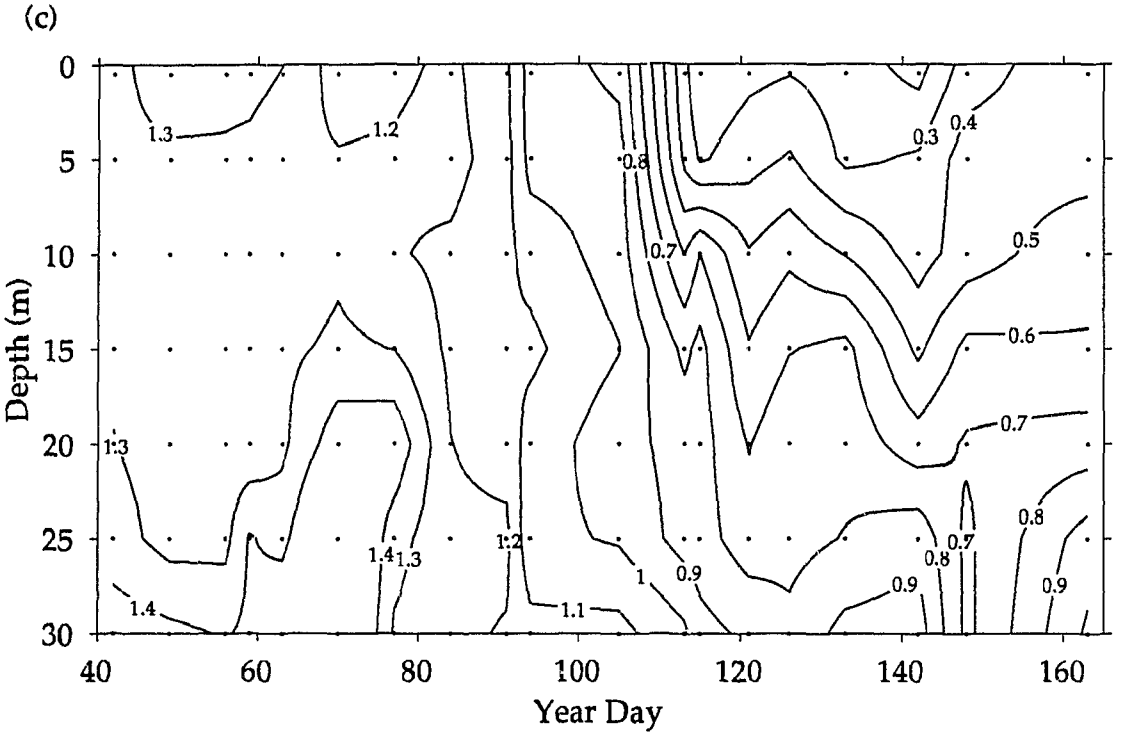


Figure 5.5 (contd.) and (c) phosphate (μM). Bullets mark data points.

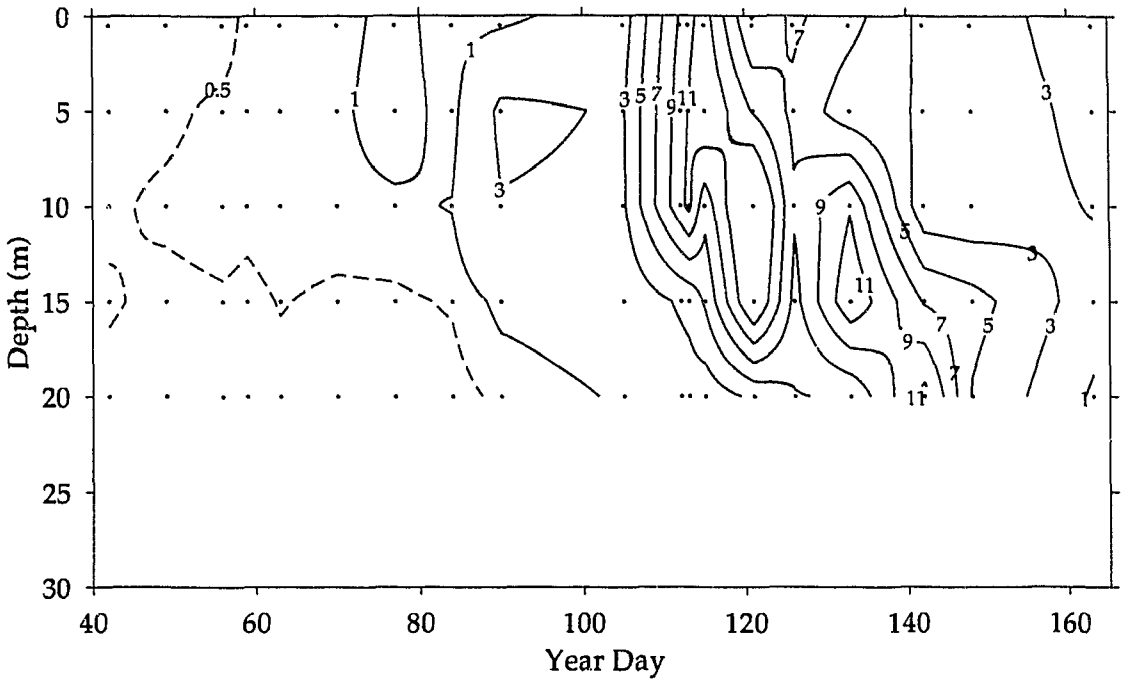


Figure 5.6 Concentrations of chlorophyll-a between 0 and 20m in μgL^{-1}.

Bullets show data points.

5.3.3 Methyl chloride

Figure 5.7 shows contour plots of methyl chloride concentration and saturation (calculated assuming an atmospheric mixing ratio of 580 pptv - please see later discussion). Bullets on the contour plots show the depths at which samples were taken. Methyl chloride concentrations over the 0.5-30m depth interval ranged from 50 to 216 pM, with most measurements lying within the 75-150 pM range (Figure 5.7). At 0.5m, concentrations varied from 93 to 216 pM with an average of 139 pM, 50% lower than the average surface concentrations reported for the North-west Atlantic in Chapter 3.

5.4 *Discussion*

Concentrations of dissolved compounds within the upper 30m of the Bedford Basin are controlled by a variety of time dependent processes. Flushing of the surface 20-30m is driven by river runoff, tides, and wind (Platt *et al.*, 1970) all of which vary in time. The extent of mixing of surface waters with those from greater depths will also influence the upper water concentrations of compounds involved in biological processes. This was observed for the macronutrients and oxygen (Figures 5.5 and 5.6). For a dissolved trace gas such as methyl chloride, the fluctuating rate of wind-driven air-sea exchange must also be considered. The approximate weekly sampling intervals, however, cannot be expected to resolve all the shorter timescale tidal and weather-driven fluctuations.

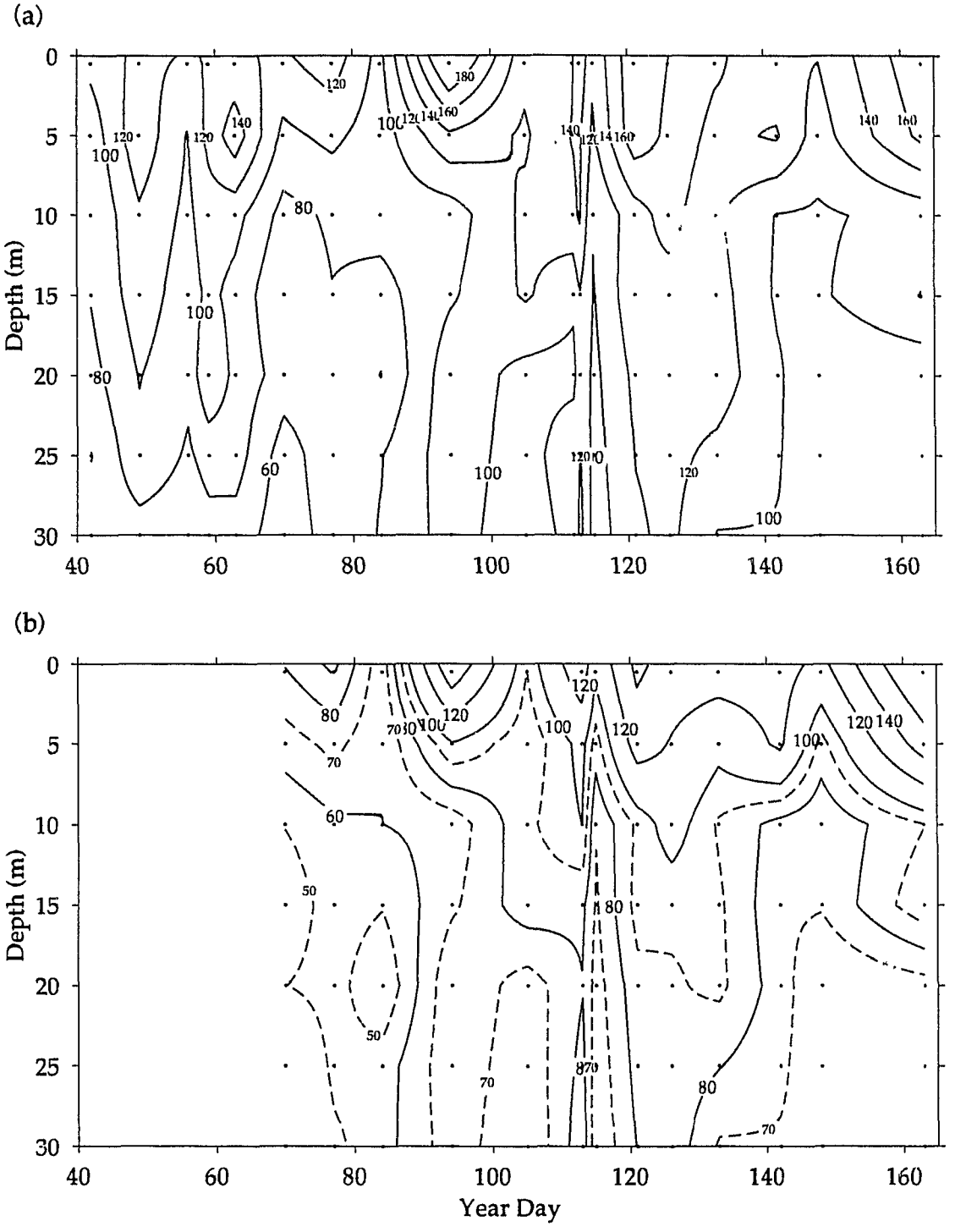


Figure 5.7 Contour plots of methyl chloride (a) concentrations (pM) and (b) saturation (%).

5.4.1 Methyl chloride during the pre-bloom period (days 42-105, Feb.11 - Apr.14).

The distribution of methyl chloride in the upper 30m of the Bedford Basin during the pre-bloom period exhibited features consistent with a fluctuating riverine input of methyl chloride. High runoff from the Sackville River (Figure 5.3) was accompanied by higher near-surface concentrations of methyl chloride (Figure 5.7). Waters containing lower concentrations of oxygen intruding from below the sill-depth between days 70 and 90 contained low concentrations of methyl chloride (2-3 times lower than near-surface concentrations). Methyl chloride saturations were as low as 50% in this intrusion (Figure 5.7 (b)). A period of high winds (mean wind speed 9.8 ms^{-1}) on day 82 (April 22) concurrent with low river run-off (Figure 5.3) further contributed to the upward penetration of waters from greater depth, indicated by the relatively low oxygen (Figure 5.4), high salinities, and low temperatures (Figure 5.2). Methyl chloride concentrations in samples collected on day 84 were low (59 - 93 pM) throughout the water column. In general, concentrations of methyl chloride between 20 and 30m were lower during the pre-bloom period than later in the study. The higher wind speeds during this time (Figure 5.3) would contribute to enhanced mixing of waters depleted in methyl chloride from deeper in the Basin with the near-surface waters.

During the study the water temperature below 30m ranged from 0.6 to 1.0°C. Chemical hydrolytic loss calculated using the rate constants of Moelwyn-Hughes (1938, 1953) proceeds at about 1.3% per year at these temperatures. At this rate, close to 50 years would be required to deplete the methyl chloride concentration by 50%. The water

concentration at equilibrium with an atmospheric mixing ratio of 580 pptv is 140 pM at 1 °C. To produce the concentrations of 50-70 pM observed at 30m on days 70 and 77 requires either isolation from the atmosphere for 80 years, inconsistent with the residence time of waters below the sill depth (months to 1 or 2 years; Platt *et al.*, 1970), or loss processes occurring at rates considerably faster than can be accounted for by the hydrolysis rate constants determined in distilled water by Moelwyn-Hughes (1938, 1953).

As discussed in Chapter 3, section 3.4.6, the greater ionic strength of seawater may lead to a greater rate of neutral S_N2 hydrolysis of methyl chloride in seawater compared to that measured in distilled water. Restricted exchange of waters below the sill depth can lead to the occurrence of oxygen depletion within the Bedford Basin (Platt *et al.*, 1970). Oxygen saturations close to 0% have been observed at 60m during late autumn and winter (Platt *et al.*, 1970). The degree of stagnation of the bottom waters, and hence the oxygen depletion, is determined by the frequency and density of sporadic intrusions of saline water over the sill and wind and convective mixing events (Platt *et al.*, 1970) and is therefore variable from year to year. Water below 30m is, however, consistently undersaturated with respect to oxygen due to respiratory processes. Microbial decomposition of polyhalogenated methanes occurs at greater rates under conditions of oxygen-limitation (Cobb and Bouwer, 1991). Methane-oxidising bacteria found in sub-oxic conditions can degrade methyl chloride through the action of the enzyme methane monooxygenase (Stirling and Dalton, 1980; Patel, 1984). Biological consumption of CH_3Cl has been observed in anaerobic saltmarsh sediments (Oremland *et al.*, 1994) and in the presence of both aerobic (Hartmans *et al.*, 1986) and anaerobic

bacteria (Traunecker *et al.*, 1991; Braus-Stromeyer *et al.*, 1993). Microbial degradation of methyl chloride in the presence of the reduced levels of oxygen within the water column or sediments is another possible contribution to the high apparent loss rates of methyl chloride within waters below the sill depth in Bedford Basin. If rapid rates of microbial destruction of methyl chloride occur in waters containing low levels of oxygen, the oxygen minimum layers in the open ocean could represent a sink of methyl chloride which has not been considered previously in the cycling of this compound within the ocean.

Samples of Sackville riverwater analysed during spring/summer 1993 showed a trend of decreasing concentration with increasing temperature (Figure 5.8), consistent with the decreasing solubility of methyl chloride in water. Supersaturation of methyl chloride in freshwaters has not been reported, although traces may result from water chlorination (Edwards *et al.*, 1982). The measurements of H in Chapter 4 were corrected for a 6% "salting-in" (Elliott and Rowland, 1993) to calculate atmospheric mixing ratios assuming these river-waters were at equilibrium with the atmosphere. The average was 580 pptv and range 430-700 pptv. These values lie at the lower end of reported atmospheric mixing ratios (400 pptv - >1 ppbv (Singh *et al.*, 1977; Koppmann *et al.*, 1993)). It is unlikely, therefore, that the riverwaters were supersaturated with methyl chloride. Changes in volume discharge (Figure 5.3), temperature, and the atmospheric mixing ratio will control the riverine input of methyl chloride into the Basin. Considering the 0 to 24 $^{\circ}$C range of riverwater temperatures encountered and atmospheric boundary layer mixing ratios of 400 - 700 pptv, the saturated concentration of methyl

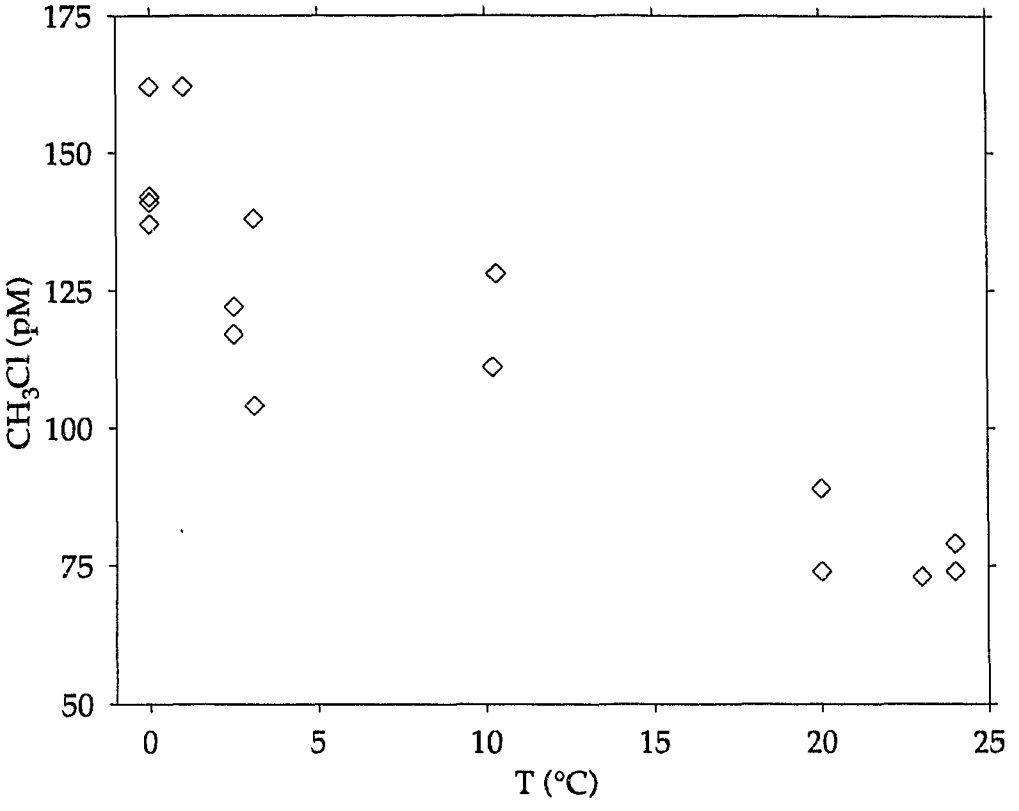


Figure 5.8 Methyl chloride (pM) measured in Sackville riverwater during the period February to June,1993.

chloride within the riverwater varies by a factor of 4-5 (40 to 190 pM).

Chlorophyll-a concentrations had increased on day 91, indicative of the onset of bloom development. The highest concentration of methyl chloride (216 pM) was observed at 0.5 m on day 94 which was during a period of high river runoff. Although measurements of chlorophyll-a in samples from the Niskin bottle were not available for day 94, comparison of the chlorophyll-a calculated from the CTD fluorometer data showed that the amount of chlorophyll-a from 0-20m on day 94 was twice that on day 84. Chlorophyll-a levels had, however, decreased compared with day 91. A further decrease in concentrations of chlorophyll-a and lower levels of methyl chloride were observed on day 105 following the passage of a storm from the north-west (days 97-98) (Figure 5.3) which flushed the surface layers of the Basin.

5.4.2 The bloom (days 105-142; April 14 - May 27) and post-bloom periods (days 142-163; to June 11)

Stable vertical stratification was evident on day 113 (Figure 5.2) and chlorophyll-a concentrations had risen to 11 μgL^{-1}. Phytoplankton growth had already depleted nutrients in the surface 5-10m of the water column by this time (Figure 5.5) and oxygen levels were supersaturated due to photosynthesis (Figure 5.4(b)). Methyl chloride concentrations had also increased near the surface coincident with the establishment of the phytoplankton bloom (145 pM and 117 pM at 5 m depth on days 113 and 105 respectively).

On day 115 during the bloom, a temporary reversal in the downward trend of nutrient and oxygen contours was observed (Figures 5.4 and 5.5) at depths greater than 5m. (i.e. lower oxygen concentrations and higher nutrient concentrations were present at shallower depths than on the preceding sampling day). Increased river runoff and wind speeds also occurred at this time (Figure 5.3). These features are coincident with a reduction in methyl chloride concentrations throughout the water column. One possible explanation for the reduction in methyl chloride concentrations is that the higher winds resulted in greater rates of air-sea exchange, driving surface waters towards equilibrium with the atmosphere. This explanation would require supersaturation prior to the wind event (Table 5.1, days 113 and 115; 135% and 105% saturations respectively). Greater wind-driven mixing of the surface waters with deeper water, as suggested by the spike in the nutrient and oxygen contours, could also contribute to a reduction in methyl chloride concentration.

The next sampling day (121) was during a period of calmer winds. Methyl chloride concentrations had increased (Figure 5.7; 174 pM at 0.5m). By day 142, the chlorophyll maximum had sunk below 20m and concentrations of chlorophyll-a from 0-10m were <3 μgL^{-1}. Methyl chloride concentrations had also decreased in the upper 10m of the water column. A subsequent increase in oxygen saturation and chlorophyll-a on day 163 at 0.5 and 5m was accompanied by higher levels of methyl chloride. Samples analysed on day 163 exhibited the highest supersaturations of methyl chloride (Figure 5.4(b)).

Methyl chloride concentrations between 20-30m were generally higher later in the

study period. This increase could result from the decreased wind-induced mixing of deeper waters with near-surface waters but may also reflect an increase in the concentration within the saline inflow through the Halifax Harbour. One possible source of methyl chloride in the saline inflow is the release by macroalgae within Halifax Harbour and along the adjoining coastline. Macroalgae within the Basin itself are another possible source of methyl chloride.

Lovelock (1975) reported high concentrations of methyl iodide in a bed of *Laminaria digitata*. This species is abundant on exposed sites in the Halifax region (MacFarlane and Bell, 1933). The distribution of macroalgae within the Bedford Basin itself has been little studied. A survey in 1930-1932 (MacFarlane and Bell, 1933) included inlets around the Bedford Basin. Abundant species included *Enteromorpha* spp., *Chordaria* sp., *Fucus* spp., *Ascophyllum nodosum*, *Polysiphonia* spp., and *Porphyra* sp., all typical of eastern Canadian shores (South, 1976). The effects that the increasing inputs of both industrial and urban pollution to the Bedford Basin during intervening years may have had on the macroalgal population is not documented. Beds of attached macrophytes (*Laminaria* and *Fucus* spp.) can be seen in Bedford Basin and throughout Halifax Harbour on exposed rock and cobble bottom in the depth range 5-15m (B. Hargrave, pers. comm.). A recent report (Hargrave *et al.*, 1989) includes observations of macroalgal species near the entrance to Halifax Harbour Narrows and the adjoining coastline. Representatives of *Laminaria, Ulva, Fucus, Desmarestia, Agarum,* and *Corallina* were present. Manley *et al.* (1992) report the release of CH_3I from both kelp and non-kelp species including members of *Laminaria, Ulva,* and *Enteromorpha* spp.

Methyl chloride was measured in seawater samples taken from between the fronds of *Fucus vesiculosis* and *Ascophyllum nodosum* at two sites on the Eastern shore of Nova Scotia in June 1992. One site was an exposed, rocky shore, the second a sheltered, calm tidal inlet. No significant difference was observed between the two sites. All samples were close to saturation with respect to an atmospheric mixing ratio of 600 pptv. Any production of methyl chloride by these macroalgae was not sufficient to maintain supersaturation.

Summer maxima and winter minima have been observed in concentrations of polybrominated organohalogens released from *F. vesiculosis* (Klick, 1992). A seasonal cycle in presence of bromoperoxidase isolated from *A. nodosum* fruiting bodies has been reported (Wever *et al.*, 1991). Haloperoxidase enzymes do not, however, catalyse the production of the monohalomethanes (Wuosmaa and Hager, 1990). At a nearshore site (Kimmeridge, on the south shore of England) rich in kelp, Lovelock (1975) observed a 3-4 fold increase in methyl chloride in May relative to samples collected earlier in the year. Data are not available to permit evaluation of a possible time-dependent source of methyl chloride from macroalgae within Bedford Basin or nearby Halifax Harbour.

An increasing methyl chloride concentration within the saline inflow cannot explain the concurrent increases of chlorophyll-a and methyl chloride at the onset of the bloom and the decrease following the bloom. No relationship was observed between methyl chloride concentrations and the state of the tide at the time of sampling.

A succession of phytoplankton species is observed in temperate coastal waters during spring and summer, controlled to some extent by the availability of

macronutrients. The spring bloom in Bedford Basin in 1992 was dominated by diatoms (Head *et al.*, 1994). Dinoflagellates such as *Ceratium* and *Peridinium* spp. (Taguchi, 1981) are prevalent in the nutrient-depleted waters during the summer months following the diatom spring bloom in Bedford Basin. A species dependence in methyl chloride production would lead to only a loose correlation between methyl chloride and the bulk phytoplankton biomass index, chlorophyll-a.

Figure 5.9 shows a scatter plot of methyl chloride and chlorophyll-a integrated over 0-20m depth. The overall sample correlation coefficient (r) is 0.65. The null hypothesis that the two variables show no linear association is rejected at the 1% level of significance. Linear regression of the data divided into pre-bloom and bloom periods gives sample correlation coefficients of 0.37 and 0.4 respectively. Short-term changes in methyl chloride within the surface layer of the Bedford Basin are clearly influenced by the rate of air-sea exchange which is a function of wind speed and also vertical mixing. In the presence of such complex interactions, the existence of a strong linear correlation between methyl chloride and chlorophyll-a might not be expected despite a bloom-related source of methyl chloride.

A contour plot of methyl chloride saturations calculated assuming a tropospheric boundary layer mixing ratio of 580 pptv (based on the riverwater concentrations measured during 1993) is shown in Figure 5.7 (b). Percentage saturations at 0.5 m are shown in Table 5.1. The average 0.5m saturation during the full course of the study was 120% (range 63 - 188%); averages during the pre-bloom and bloom periods were 97% and 129% respectively. The warmer temperatures during the pre-bloom period contribute to

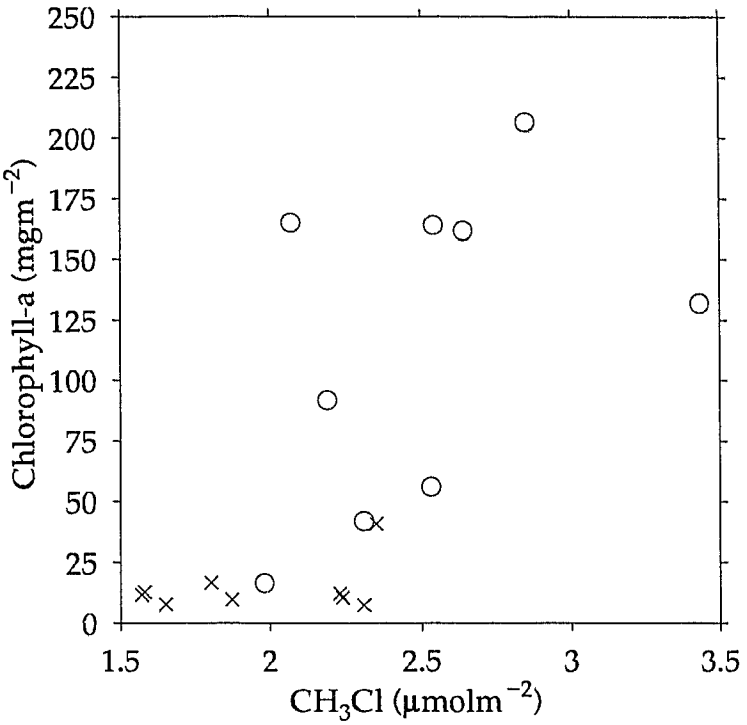


Figure 5.9 Scatter plot of methyl chloride and chlorophyll-a integrated over 0-20m depth in Bedford Basin during February to June,1992.

the higher saturations during that time. Supersaturation may result from both in situ production and warming of the surface waters. Between day 105 and 113, approximately 60% of the observed increase in saturation is due to the increase in concentration. Atmospheric measurements concurrent with surface water sampling would be required to accurately determine the degree of saturation.

5.4.3 Calculation of the average air-sea exchange of methyl chloride

The average mean daily wind speed during the study period was 4.5 ms^{-1}. This translates to a exchange velocity of 7 cm h^{-1} (S_c=600, 20°C) using the wind speed dependence suggested by Wanninkhof (1992). The average temperature at 0.5m during the study was 4.6°C. Thus, the exchange velocity corrected to S_c = 2120 for CH_3Cl at 4.6°C is 3.7 cm h^{-1} (see Chapter 4; section 4.3.2). The average flux of methyl chloride to the troposphere from the Bedford Basin was 2.5 x 10^{-13} moles m^{-2} s^{-1} (1.25 x 10^{-11} g m^{-2} s^{-1}), 16 times smaller than the estimated flux for the north-west Atlantic (4 x 10^{-12} moles m^{-2} s^{-1}). The lower concentrations (50%), lower wind speed (4.5 ms^{-1} compared with 6.5 ms^{-1}), and lower average temperature in the Bedford Basin compared with the North-west Atlantic study are factors contributing to the difference.

Table 5.1 Surface saturations assuming an atmospheric mixing ratio of 580 pptv.

Date	Year Day	Temperature (°C)	CH_3Cl (pM)	Saturation (%)	comment
March 10	70	0.66	117	81	pre-bloom
March 17	77	0.94	133	93	pre-bloom
March 24	84	0.34	93	63	pre-bloom
March 31	91	2.02	-	-	-
April 3	94	2.06	216	158	higher chl-a
April 14	105	1.46	127	91	surface layer flushed
April 22	113	5.65	158	135	bloom
April 24	115	5.22	125	105	bloom, following wind event
April 30	121	4.96	174	145	bloom
May 5	126	4.6	160	131	bloom
May 12	133	7.12	145	131	bloom
May 21	142	10.53	123	128	post-bloom
May 27	148	8.14	121	114	post-bloom
June 11	163	11.04	176	188	post-bloom

5.5 *Conclusions*

Prior to the onset of the spring phytoplankton bloom, methyl chloride concentrations in the upper 10-15m of the Bedford Basin showed increases during periods of high river discharge. Concentrations of methyl chloride in Sackville riverwater showed a decrease with increasing temperature consistent with the decreasing solubility of methyl chloride. As the inputs of freshwater became warmer and decreased in volume later in the time series, the magnitude of the riverine input of methyl chloride to the Basin decreased. Storm-driven mixing of surface waters with those deeper in the Basin resulted in a decrease in the observed concentrations of methyl chloride. Methyl chloride loss rates calculated using rate constants for its chemical hydrolysis in distilled water (Moelwyn-Hughes, 1938, 1953) cannot account for the low concentrations of methyl chloride observed in waters from below the sill depth. Enhanced rates of hydrolysis in seawater compared with distilled water and high rates of microbial destruction in waters or sediments containing low levels of oxygen are suggested as possible explanations.

With respect to an atmospheric mixing ratio of 580 pptv, based on the assumption of riverwaters being saturated with methyl chloride, the average saturation of the near-surface waters during the study period was 120%. Colder waters prior to the bloom were generally undersaturated, while for the warmer waters during the bloom saturations were $>100\%$. The sea-air flux calculated from this data set was 2.5×10^{-13} moles m^{-2} s^{-1}, an order of magnitude less than that estimated for the North-west Atlantic (Chapter 3).

Methyl chloride concentrations increased coincidentally with the development of

the phytoplankton bloom. It is proposed that a subsequent reduction in methyl chloride levels resulted from increased sea-air exchange due to higher wind speeds and also an increase in warm river runoff associated with the passage of a frontal system. Methyl chloride and chlorophyll-a integrated over 0-20m depth showed a moderate positive correlation ($r=0.65$; $n=18$), evidence supporting the hypothesis that phytoplankton contribute to methyl chloride concentrations in Bedford Basin. The correlation cannot be considered conclusive evidence, however, due to the possibility of a seasonally increasing macroalgal source of methyl chloride coincident with the phytoplankton bloom development.

Chapter 6 : Methyl chloride production in phytoplankton cultures

6.0 *Introduction*

Studies using the giant kelp *Macrocystis pyrifera* (Manley and Dastoor, 1987) have already demonstrated that some marine macroalgae can produce methyl chloride. Macroalgal sources of methyl chloride cannot, however, explain the widespread supersaturations observed in field studies of open ocean waters (Singh *et al.* 1983; Hoyt and Rasmussen, 1985; Chapter 3). The vertical distribution of methyl chloride in the North Atlantic (Chapter 3) shows near-surface maxima and a general decrease with depth, consistent with production predominantly in the biologically active surface layer. High concentrations of methyl chloride were measured in samples of melted ice containing ice-microalgae collected during a bloom at Resolute in May 1992 (Chapter 2). Samples taken from an open ocean phytoplankton bloom did not contain concentrations appreciably greater than samples from less productive waters. Measurements of methyl chloride during a spring bloom in Bedford Basin (Chapter 5), although higher during the bloom period, did not provide conclusive evidence of a phytoplankton source of methyl chloride.

Monospecific incubations of phytoplankton offer a more controlled environment in which to investigate the possibility of a phytoplankton contribution to the oceanic methyl chloride pool. The initial aim of the following experiments was to determine whether any methyl chloride release could be detected. Several species of phytoplankton were sampled periodically throughout their growth curve to look at possible species and

growth stage dependence of CH_3Cl release and to address the question of direct versus indirect production.

6.1 *Materials and Methods*

Table 6.1 Species of phytoplankton examined for methyl chloride production

Phytoplankton species	T(°C)
Porosira glacialis	4
Nitzschia seriata	4
Nitzschia sp. CCMP 580	4
Odontella mobiliensis	20
Thalassiosira weissflogii	20
Phaeodactylum tricornutum	20
T. *Isochrysis galbana*	20

The phytoplankton species studied are shown in Table 6.1. All species except *Nitzschia seriata* were originally obtained from the Provasoli-Guillard Centre for the Culture of Marine Phytoplankton. *Nitzschia seriata* was obtained from Dr. R. Smith.

Approximately 450 mL of autoclaved f/2 (Guillard, 1975) or f/8 medium in a glass vessel (Figure 6.1) was purged with a zero air/CO_2 mixture (*ca.* 0.1% CO_2) for 36 hours to remove halocarbon contaminants. Following inoculation with 2-3 mL algal culture, gentle purging was continued for a further 3 hours, then the vessel was sealed. The pH at the time of inoculation in all cultures was between 7.6 and 7.9. The media were not buffered. Warm water species were incubated at 20°C under cool white fluorescent tubes (*ca.* 70 μmol PAR m^{-2} s^{-1}) with a light:dark cycle of 16:8. Cold (4°C) water phytoplankton were held under constant illumination of 10 μmol PAR m^{-2} s^{-1}. The vessels were agitated gently to disperse cells every 2-3 days. Ten millilitre samples of medium were withdrawn every 2-3 days through a metal needle into vacuum-baked (100°C, minimum 24 hours) glass syringes for immediate injection into the purge and trap system. During sample removal, a low flow of air/CO_2 was maintained to prevent entrance of contamination from the atmosphere. The gas flow was continued for a further 3 minutes to supply CO_2. Care was taken to minimise the number of phytoplankton cells removed from the vessel. For the cold water species and *O. mobiliensis*, the cells settled to the bottom of the vessel and negligible numbers were drawn up through the needle. *T. weissflogii, P. tricornutum,* and *I. galbana*, however, were dispersed throughout the medium and removal of cells could not be avoided. During the late stationary phase when the medium volume had been depleted but cells

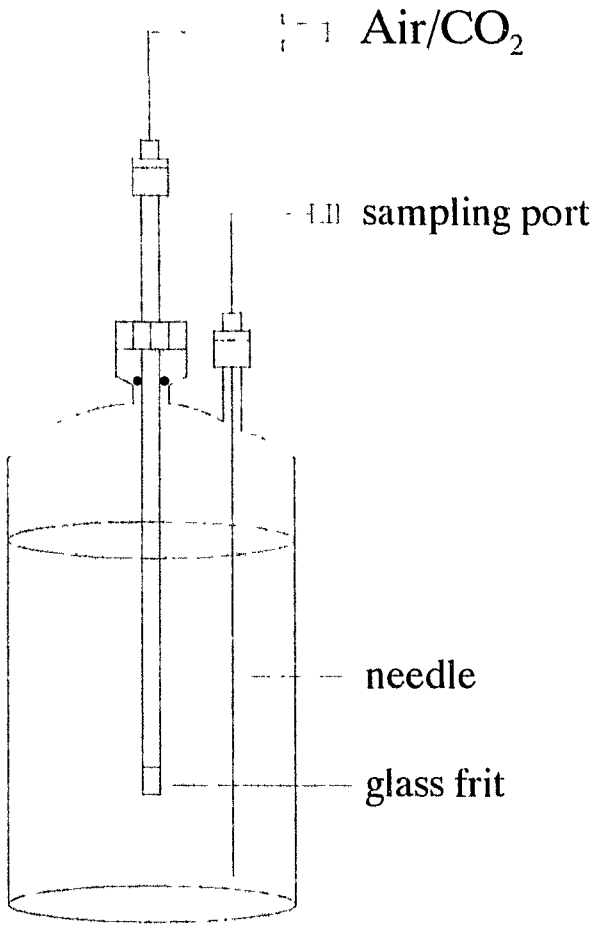


Figure 6.1 Glass vessel (volume approximately 600 mL) used for the culturing of phytoplankton under halocarbon-clean conditions.

were still abundant, the fraction of cells removed could have been as high as 10%. It is not known whether the vigorous, though brief, purging during analysis of a sample containing phytoplankton cells results in release of CH_3Cl. The purge vessel was cleaned frequently (chromic/sulphuric acid for 12 hours) to remove any biological material which remained in the system. Daily system blanks were consistently below the detection limit indicating that any phytoplankton or bacteria which entered the purge system did not interfere with analysis.

After gentle agitation to disperse the cells, samples were also taken for light microscope (magnification x400 for *O. mobiliensis*, *N. seriata*, *P. glacialis*, and CCMP 580) or Coulter counter (Coulter Electronics Inc. Model ZF) (*I. galbana*, *P. tricornutum*, *T. weissflogii*) cell counts. Samples counted using the Coulter counter were also examined under the light microscope to determine the percentage of living cells. Precisions of cell counts (expressed as sample standard deviation divided by the mean) for data shown in the figures are given in Table 6.2. Samples for bacteria number determinations were withdrawn through the metal needle into sterile plastic Luer-lok syringes (B-D). When necessary, these samples were diluted by addition of sub-mL amounts to autoclaved septum-capped vials containing 0.2 μm filtered medium. Bacteria were counted using the acridine orange epifluorescence microscopy method of Hobbie *et al.* (1977). A 1-2 mL sample was filtered onto a rinsed (0.2 μm Super-Q) Irgalan Black stained 0.2 μm Nuclepore mounted on a 0.2 μm cellulose acetate Millipore filter. After staining for 3 minutes with 1 mL of acridine orange (Esbe Laboratory Supplies, Canada) solution (0.05-0.1% in sterile Super-Q fixed with 2% formalin), the damp filter was

mounted on a slide and examined within 3-4 hours by immersion (Cargille Type A immersion oil) epifluorescence microscopy (Wild Leitz 20EB microscope, Leitz filter pack I2: exciter 450-490 nm, beam splitter 510 nm, suppression filter 515 nm; magnification x1250). Twenty fields were counted on each filter. Duplicate samples agreed to within 5% for young cultures at the 10^5/mL level, and to ± 20% for 10^2 bacteria/mL. During late stationary phase and senescence, phytoplankton cells became covered with bacteria leading to a highly heterogeneous distribution over the filters which made counting difficult.

Table 6.2 Precision of phytoplankton cell number counts

Species	Level (cells mL^{-1})	Estimated precision of counting (sample standard deviation divided by sample mean (%))
O. mobiliensis	10^3-10^4	±11: n=4
P. tricornutum	10^5	±3: n=6
	10^6	±2: n=6
T. weissflogii	4 x 10^5	±4: n=6
T. *I. galbana*	10^5-10^6	±7: n=6
Nitzschia sp. CCMP-580	10^5-10^6	±12-15: n=7

No fungi were seen in the phytoplankton cultures.

6.2 *Results and Discussion*

The first measurements of methyl chloride in phytoplankton culture medium were from a senescent *Odontella mobiliensis* culture. Concentrations in excess of 2000pM were observed, an order of magnitude greater than those found in open ocean surface waters. Preliminary measurements on media from other cultures resulted in the detection of methyl chloride in a dead *Nitzschia seriata* culture and a dying *Isochrysis galbana* culture. Methyl chloride production has been found in cultures of all phytoplankton species examined to date (Table 6.1).

6.2.1 Time series of methyl chloride in cultures of cold water phytoplankton.

The high methyl chloride concentrations in the samples from Resolute, 1992 (Chapter 2, section 2.11) suggested that some species of ice microalgae may have the capacity to produce methyl chloride. The first time series to be completed were from incubations of *N. seriata, Porosira glacialis,* and CCMP 580 *Nitzschia* sp., three cold water species which were simultaneously studied for the production of less volatile halocarbons, in particular bromoform (Tokarczyk and Moore, 1994). Results are reported as total methyl chloride in the medium and headspace (picomoles) calculated assuming an equilibrium distribution between the two phases. These units were chosen

in preference to concentration in the medium alone due to the partitioning of methyl chloride into the gas phase. As sampling progressively decreases the ratio of liquid to headspace volume, the fraction of the total methyl chloride partitioned into the headspace increases. Using the change in total methyl chloride should give a better representation of changes in the rate of methyl chloride production throughout the time series than the concentration in the liquid phase alone. After 10 days, methyl chloride levels in the 3 vessels containing microalgae were significantly greater (3-6 times) than in the control (Figure 6.2). The highest production of methyl chloride, largely restricted to the stationary phase, was observed in the vessel containing CCMP 580. Methyl chloride production ceased as the number of healthy phytoplankton fell. Prior to the stationary phase, medium from all 3 vessels showed similar increases of CH_3Cl. The absolute production rate during the stationary phase of CCMP 580 (45 ± 4 pmol L^{-1} dy^{-1}) was 15-20 times greater than in incubations of either *N. seriata* or *P. glacialis*.

After 30 days, the level of methyl chloride in the control vessel was significantly different from zero. There are two possible explanations for this. Outer air may have entered the vessel during sampling or due to slow leakage. Alternately, methyl chloride production was taking place within the control medium itself. A slow growth of contaminant peaks found in the cold room air was observed in successive chromatograms. However, at the end of the experiment, bacteria were present at numbers greater than the detection limit of the method (1500 bacteria mL^{-1}: average blank + 2 σ) in the control vessel. It cannot be concluded whether the increase in methyl chloride seen in the control was due to chemical contamination or biological production.

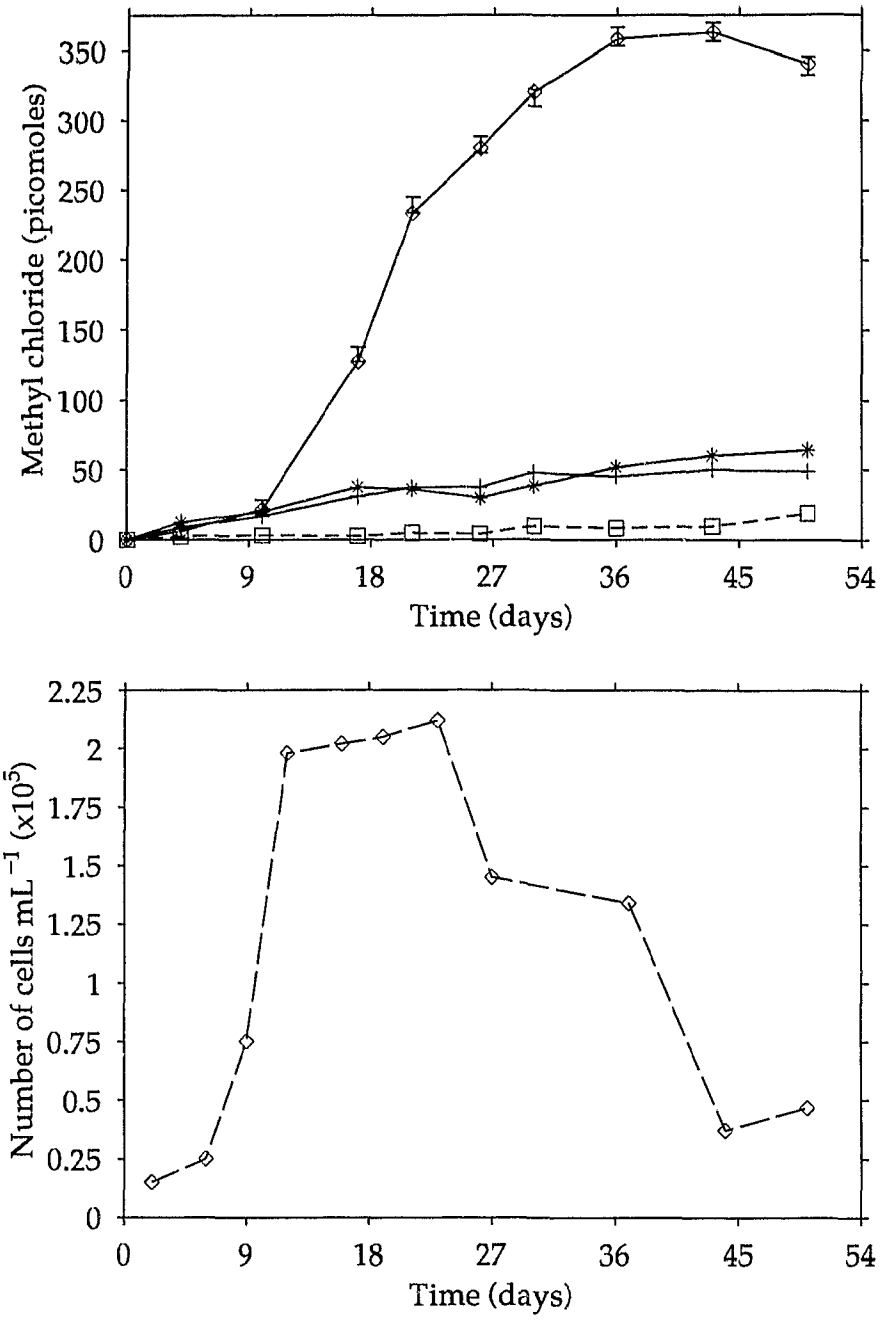


Figure 6.2 Time series of methyl chloride (upper panel) in cultures of cold water phytoplankton; □ = control, + = *N. seriata*, ∗ = *P. glacialis*, ◇ = CCMP 580. Error bars or symbol size give combined run-to-run and standard precision. Lower panel gives CCMP 580 cell numbers.

Bacteria were prolific in all three microalgal incubations at the end of the experiment. The initial inocula were not axenic. Although the cessation of methyl chloride production on senescence of the CCMP 580 culture suggests that the phytoplankton themselves were involved, a bacterial role in the production cannot be ruled out. Knowledge of changes in bacterial numbers throughout the time series would contribute to clearer interpretation of possible phytoplankton and/or bacterial components of the observed methyl chloride production.

As discussed in Chapter 3 (section 3.4.5), chloride substitution of methyl iodide is a mechanism of CH_3Cl formation in seawater (Zafiriou, 1975; Elliott and Rowland, 1993). CH_3I was not significantly different from the control in medium from cultures of both *N. seriata* and *P. glacialis*, and only slightly higher in *Nitzschia* sp. CCMP 580 (R. Tokarczyk, unpublished results). Unless the reaction occurs intracellularly, with subsequent release of the methyl chloride, or more rapid alternative pathways of CH_3I transformation to CH_3Cl exist, it is unlikely that CH_3I is the source of the CH_3Cl observed in these cultures.

6.2.2 Indirect versus direct production of methyl chloride

Medium from a senescent culture of *O. mobiliensis*, a tropical diatom of widespread distribution (Round *et al.*, 1990) contained high CH_3Cl concentrations. Bacteria numbers were monitored in an incubation of this species (Figure 6.3). The batch culture from which the initial inoculum was taken was found to contain bacteria.

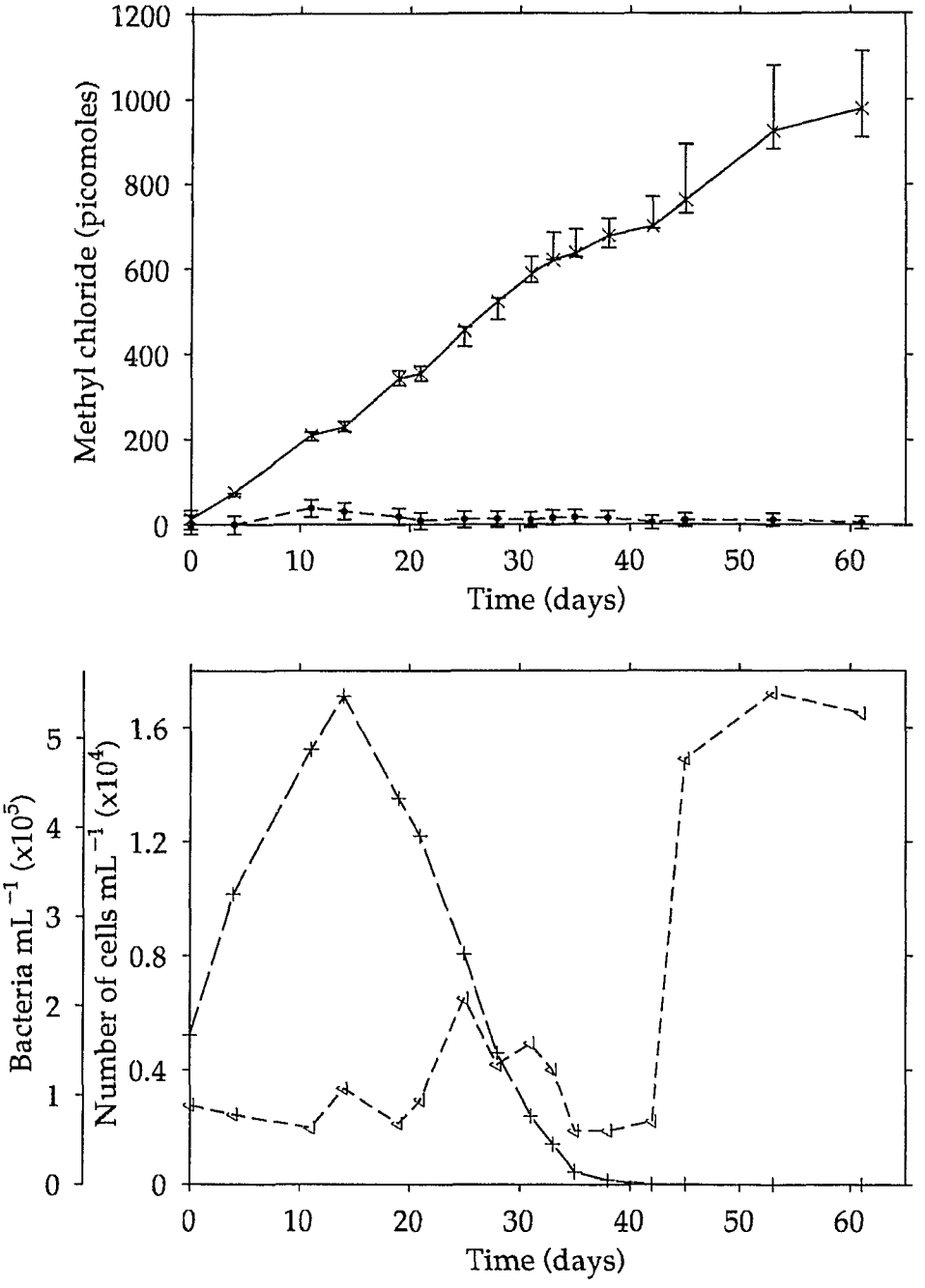


Figure 6.3 Methyl chloride in a culture of *O. mobiliensis* (×) and in a control incubation (•) (upper panel). Error bars show combined run-to-run and standard precision. (+) Cell numbers and (◁) numbers of bacteria are shown in the lower panel.

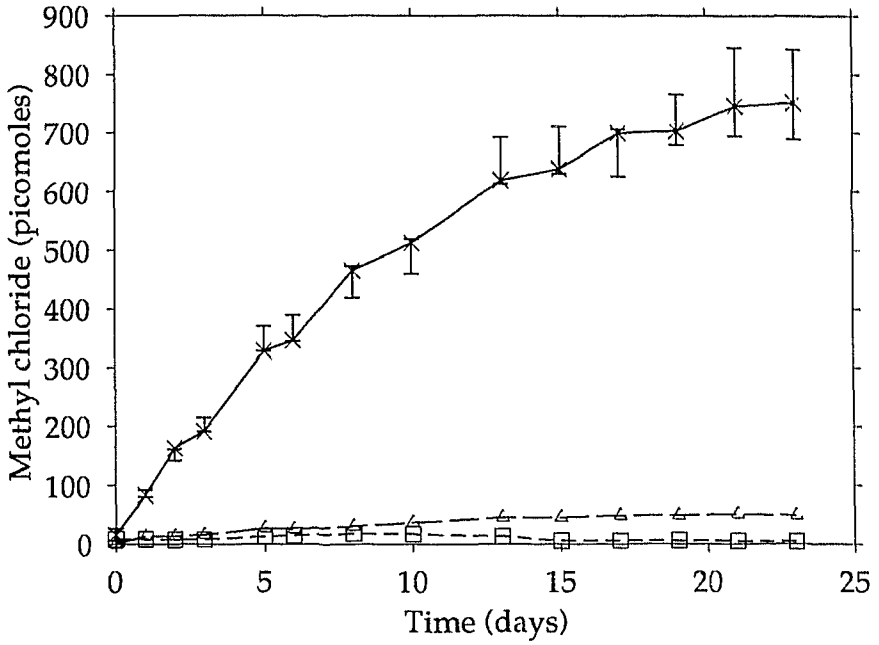


Figure 6.4 Methyl chloride production in filtrate (△) from a full culture (×) of *O. mobiliensis*. □ = control.

However, in contrast to the CCMP 580 incubation, methyl chloride production in the incubation of *O. mobiliensis* started from time zero, and did not show a clear growth stage dependence. Moreover, CH_3Cl continued to rise within the vessel after the death of all the phytoplankton cells.

Production of methyl chloride as a by-product of *O. mobiliensis* metabolism cannot be ruled out during the early part of the time series. Indirect biotic or abiotic mechanisms are required to explain the continued increase in the absence of viable phytoplankton cells. Net CH_3Cl production was observed in 5μm (Nuclepore) filtrate from a dense *O. mobiliensis* culture purged and then incubated alongside the full culture (Figure 6.4). Bacteria numbers in the filtrate were 10-20% of those in the full culture, possibly due to adhesion of bacteria to the phytoplantkon cells retained by the filter. A similarly filtered control medium showed no significant CH_3Cl production over the same time period. In the full culture, production of methyl chloride proceeded at an order of magnitude greater rate than in the filtrate. However, the increase in the filtrate confirms the occurrence of "indirect" methyl chloride production due to either chemical reaction of organic matter from the *O. mobiliensis* or production by bacteria supported by the organic matter.

6.2.3 Time series of CH_3Cl in cultures of warm water phytoplankton

Incubations of *T. weissflogii* and *P. tricornutum* in f/8 are shown in Figure 6.5 (a) and (b). Both showed that concentrations of methyl chloride increased throughout the

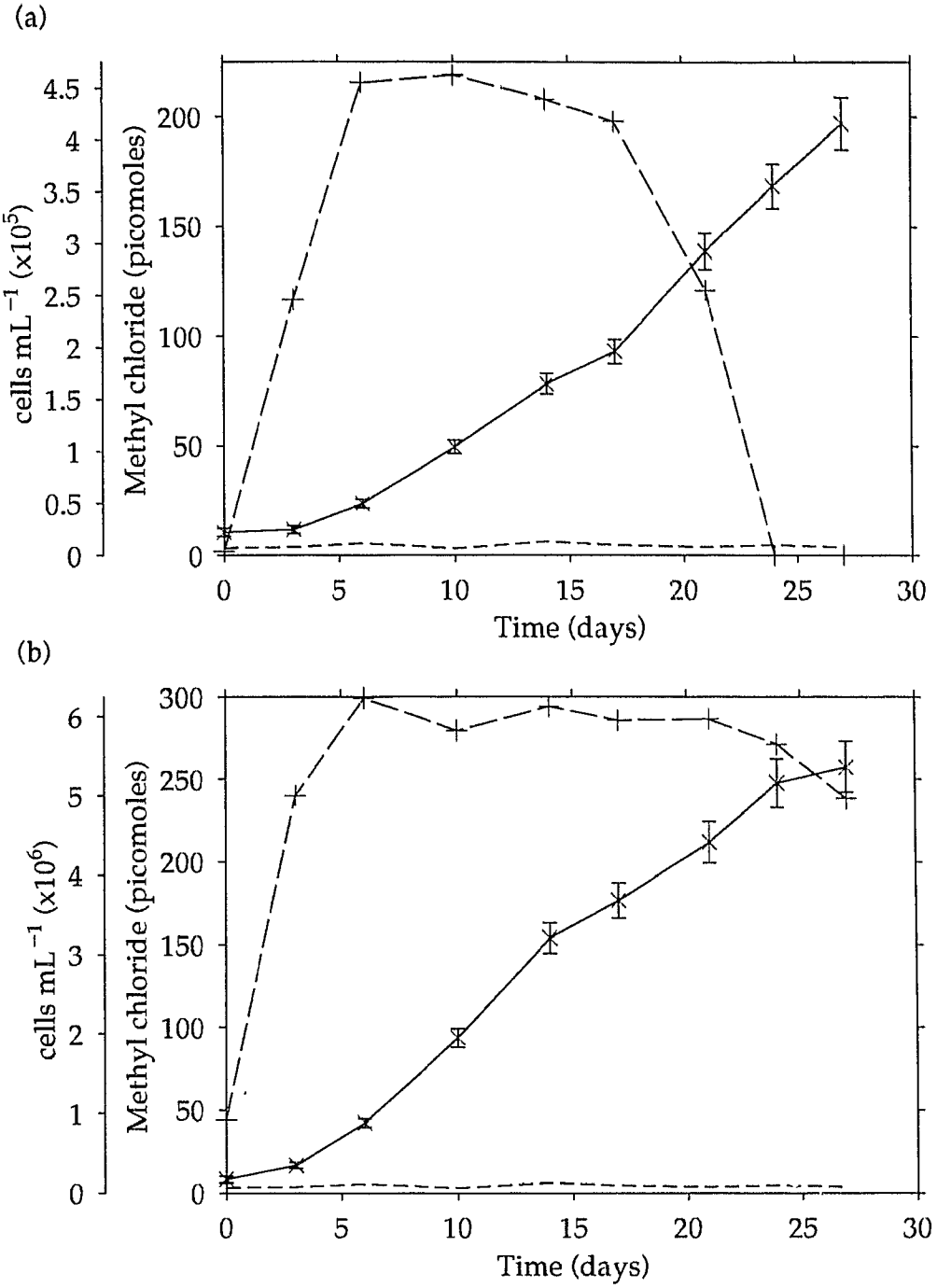


Figure 6.5 Methyl chloride (×) and cell numbers (+) in cultures of (a) *T. weissflogii* and (b) *P. tricornutum* (– – –) is the methyl chloride in a control vessel containing only medium.

experiment. During the exponential and stationary phases of cell growth in the *T. weissflogii* culture, the rate of methyl chloride production increased with the number of phytoplankton in the vessel. There was no significant change in the rate of methyl chloride production expressed on a per cell basis. When the number of phytoplankton began to decline, however, the absolute rate of methyl chloride production increased by a factor of approximately 2, while the rate per cell increased by a factor of 3. The number of bacteria in the vessel increased dramatically at this time. As in the *O. mobiliensis* time series, methyl chloride continued to increase after the death of all the *T. weissflogii* cells. The *P. tricornutum* incubation (Figure 6.5 (b)) also showed increasing CH_3Cl production with increasing phytoplankton numbers. This culture had an extended stationary phase, and did not reach senescence during the time period of the experiment. The number of bacteria in this culture increased gradually throughout the incubation (2.1×10^4 mL^{-1} to 4.2×10^4 mL^{-1}).

Separation of the bacterial and phytoplankton roles in methyl chloride production will require time series incubations using axenic phytoplankton cultures. With care, the apparatus described can be used to maintain axenic conditions in the control medium over a period of 3-4 weeks. However, the requirement of opening the vessel for sampling increases the risk of bacterial contamination.

An order of magnitude difference in maximum absolute rates of stationary phase methyl chloride production has been observed in incubations of different phytoplankton species (*N. seriata* - 2 pmol $L^{-1}d^{-1}$, CCMP 580 - 45 pmol $L^{-1}d^{-1}$, *O. mobiliensis* - 75 pmol $L^{-1}d^{-1}$). When normalised to the number of phytoplankton cells in the vessel rates of *ca.*

4×10^{-9}, 2×10^{-7}, and 6×10^{-6} pmol cell^{-1} d^{-1} are obtained for *N. seriata*, CCMP 580, and *O. mobiliensis* respectively. In the absence of a better direct measure of phytoplankton biomass than cell numbers, cell carbon was estimated using the experimental results of Sicko-Goad *et al.* (1991). Sicko-Goad *et al.* used electron microscopic methods to measure relative volumes of frustule, vacuole, and cytoplasm in several species of diatoms. For the smaller cells (volumes less than 1270 μm^3), cytoplasm volume was close to 50% of the total cell volume in all seven species studied. Larger species contained relatively smaller cytoplasmic volumes (20-41%). Cytoplasm in *O. mobiliensis* was assumed to occupy 30% of the total cell volume and 50% in CCMP 580 and *N. seriata*. Multiplication of the cytoplasm volume (μm^3) by 0.11 gives a reasonable estimate of cell carbon (pg) (Sicko-Goad *et al.*, 1991; Strathmann, 1967). The results are shown in Table 6.3. Sources of uncertainty in these values include estimation of the cell and cytoplasmic volume. Cell carbon calculated using the relationship between cultured phytoplankton cell carbon and cell volume determined by Strathmann (1967) lie within these uncertainty limits. Despite the estimated uncertainty in these calculations, the difference between methyl chloride production rates in *N. seriata* and CCMP 580 cultures cannot be simply explained by the different amounts of biomass.

Neither *O. mobiliensis* nor CCMP 580, which exhibited high absolute rates of methyl chloride production, is readily available in axenic culture for further study. *T. weissflogii* and *P. tricornutum* showed maximum rates of methyl chloride production of 30 and 60 pmol L^{-1} d^{-1} under non-axenic conditions. Axenic inocula of both of these species can be easily obtained.

Table 6.3 Methyl chloride production rates normalised to estimated total phytoplankton cell carbon.

Species	approximate cell volume (μm^3)	carbon/cell (pg)	CH_3Cl production rate (pmol CH_3Cl pgC^{-1} d^{-1}
O. mobiliensis	9.5×10^4	3000 ± 1000	8×10^{-10} - 1.7×10^{-9}
N. seriata	8	1.1 ± 0.7	$2.1 - 9.6 \times 10^{-9}$
CCMP 580	100	9 ± 4	$1.6 - 4.3 \times 10^{-8}$

6.2.4 Possible influence of culture conditions and bacteria on methyl chloride production

The high nutrient concentrations used for culturing the phytoplankton in these experiments (f/2 nitrate 800μM) supported cell densities 100-1000 times those found in the environment. Such high cell densities may result in carbon limitation of the phytoplankton, a state atypical of the environment. The pH was monitored throughout the *T. weissflogii* and *P. tricornutum* incubations. During the exponential and stationary phases it reached as nigh as 9.0, indicating a depletion of CO_2 available for phytoplankton photosynthesis.

Light intensity (Beardall and Morris, 1976) and spectral composition (Wallen and Geen, 1971) affect phytoplankton photosynthesis. The 70 μmol PAR m^{-2} s^{-1} measured outside the glass vessel in the 20°C culture room corresponds to a depth of roughly 25-30 m in open ocean conditions. High cell densities may contribute to self-shading and result in a gradient of light intensity and spectral composition throughout the vessel.

Over large areas of the ocean, phytoplankton growth may be limited by nitrate availability (Ryther and Dunstan, 1971). In the culture experiments, the high nutrient concentrations themselves may directly affect the phytoplankton, producing potentially different physiological behaviour from that displayed in the environment.

The methyl chloride production observed must be described as net production due to the possibility of both production and consumption of methyl chloride by bacteria. Production of methyl iodide by microbes from decaying kelp has already been demonstrated (Manley and Dastoor, 1988). Bacterial consumption of methyl chloride under both aerobic and anaerobic conditions has also been observed (please see Chapter 1, section 1.2.2).

Depending on the species assemblage, it is possible that bacteria may act as a net source or sink of methyl chloride. The changing conditions of pH within the closed vessel through the growth cycle may also have favoured a succession of bacterial species. In addition, separate phytoplankton inocula may contain different bacterial populations.

6.2.5 Extrapolation of rates measured in the laboratory to the environment

Considering the previous discussion, it is unlikely that the rates of methyl chloride production observed in these laboratory culture experiments are representative of those occurring in the ocean. A rough calculation has, however, proved informative. Assuming a cell chlorophyll-a content of 10 pg $cell^{-1}$ (see Post *et al.* (1985) for *T. weissflogii* in f/2 medium, 17 °C, under illumination of 72 μmol quanta m^{-2} s^{-1}), the concentration of chlorophyll-a in the *T. weissflogii* culture during the stationary phase was 4500 μg L^{-1}. Chlorophyll-a during the 1991 C.S.S. "Hudson" cruise (Chapter 3) was 0.5 μg L^{-1} or less throughout much of the upper 50m , 3-4 orders of magnitude smaller than in the *T. weissflogii* culture. Assuming an average chlorophyll-a concentration of 0.5 μg L^{-1} over a 50m layer gives a global mass of chlorophyll-a of 9.0×10^{15} mg. 250mL *T. weissflogii* culture during the stationary phase contained 1.125 mg chl-a and produced methyl chloride at a rate of 7 pmol d^{-1} (Figure 6.5 (a)). An average absolute CH_3Cl production rate from all the culture experiments was *ca.* 10 pmol d^{-1} (40 pmol L^{-1} d^{-1}). If the laboratory rate of methyl chloride production is scaled using the calculated masses of chlorophyll-a in the culture and the surface ocean, only 2×10^7 moles (1×10^9 g) of methyl chloride can be produced per year, less than 0.1% of sea-air flux estimates (4.5 - 9.7 x 10^{10} moles (2.3 - 4.9 x 10^{12} g) yr^{-1} (Singh *et al.*, 1979, 1983; this study, Chapter 4 section 4.3.3).

6.3 *Conclusions*

Net methyl chloride production has been detected in xenic unialgal cultures of warm and cold water phytoplankton. Incubations of cultures of six species exhibited methyl chloride production. The magnitude of the production varied by a factor of 10 between species. Highest absolute rates of production were observed in cultures of *Phaeodactylum tricornutum* and *Odontella mobiliensis*.

Methyl chloride continued to increase in incubated culture solutions after the death of all the phytoplankton cells in experiments with both *O. mobiliensis* and *T. weissflogii*. Chemical and/or bacterial mechanisms transforming algal-released organic compounds is required to explain this result. Experiments using axenic microalgal cultures will be necessary to further study the contribution of phytoplankton to methyl chloride production in the oceans. The role of bacteria, whether as source and/or sink of methyl chloride, cannot be determined from the presently available data.

When scaled using chlorophyll-a, the rates measured in the laboratory can account for $<0.1\%$ of estimates of sea-air fluxes of methyl chloride. The species studied or other microalgal species more prolific in the open ocean may exhibit different rates under the conditions of light and levels of nutrients and inorganic carbon found in their natural environment.

Chapter 7: Summary and Synthesis

7.1 *Summary*

An analytical system was developed for the direct determination of methyl chloride in aqueous samples. Methyl chloride was stripped from a 10 or 20 mL sample of water by purging with helium and trapped on Porapak-Q (0°C). Thermal desorption (100°C) was followed by gas/solid chromatographic separation (30m GS-Q column, 70°C) and oxygen-doped electron capture detection (275°C, 0.38% O_2). Initially, standards were prepared by sequential dilutions of methyl chloride in UHP nitrogen. Subsequent use of a dilute solution standard resulted in improved precision.

The system was used to measure methyl chloride at depths from 0 to 1000m in the North-west Atlantic during May, 1991. Concentrations were higher above the seasonal thermocline and showed a general decrease with depth. Near-surface maxima were a common feature. The thickness and depth of the near-surface maxima were related to the vertical hydrographic structure of the water column. Broad, mid-depth maxima within the main thermocline were coincident with maxima in the oxygen distribution, evidence for more recent contact with the atmosphere than the waters above and below. No simple relationship was observed between phytoplankton biomass, measured as chlorophyll-a, and methyl chloride concentrations in the open ocean. Surface waters in the North-west Atlantic were supersaturated with respect to an assumed atmospheric mixing ratio of 625 pptv. The average saturation was 268 %.

A sea-to-air flux was calculated using the measurements in the North-west Atlantic. The transfer velocity, *K*, was estimated using an average wind speed and the wind-speed dependence suggested by Wanninkhof (1992). *K* also included a correction for temperature through the Schmidt number. The Henry's Law constant, *H*, was measured using a dynamic stripping method. The results showed that, when increased by 6% to account for salinity, values of *H* calculated from methyl chloride vapour pressure and solubility in distilled water give a good estimate of *H* in seawater. The sea-to-air flux calculated using the measurements in the North-west Atlantic was 4.5×10^{10} moles yr^{-1} (2.3×10^{12} g yr^{-1}), 50-60% less than that estimated by Singh *et al.* (1983) from measurements in the eastern Pacific.

Methyl chloride was also measured in a coastal environment, Bedford Basin, Nova Scotia, during February to June, 1992. The average concentration at 0.5m was 139 pM. Prior to the onset of the spring diatom bloom, concentrations in the upper 10-15m exhibited features related to the magnitude of river discharge. Waters brought upwards by wind-driven vertical mixing of the water column contained lower levels of methyl chloride than could be accounted for by chemical hydrolysis based on reported rates for distilled water. Higher rates of chemical hydrolysis in seawater and microbial destruction of methyl chloride in the oxygen depleted waters below the sill depth are possible explanations. Linear correlation of methyl chloride with chlorophyll-a integrated over 0-20m depth gives $r = 0.65$ ($n = 18$). Testing the null-hypothesis that there was no linear association between the variables resulted in rejection at the 1% level of significance. This correlation suggested that some relationship did exist between methyl

chloride concentrations and chlorophyll-a. It could not, however, be considered conclusive evidence of phytoplankton production of methyl chloride due, in particular, to lack of information on the contribution of another possible source of methyl chloride in the Basin, macroalgae.

Net production of methyl chloride was observed in xenic unialgal cultures of cold and warm water phytoplankton. In extended time series of warm water diatoms, *T. weissflogii* and *O. mobiliensis*, methyl chloride continued to increase following the death of all the phytoplankton cells. Chemical and/or bacterial pathways converting organic substrates released by the phytoplankton to methyl chloride are required to explain this occurrence. The role of bacteria in these cultures, whether as source or sink of methyl chloride, was not resolved.

Rates of methyl chloride production measured in the laboratory cultures were extrapolated to the environment. This was done recognising that the culture conditions were not representative of the environment and that only a few species of phytoplankton had been examined, most of which were diatoms. When scaled using levels of chlorophyll-a, the laboratory rates can account for $<0.1\%$ of the estimate of the oceanic emission of methyl chloride calculated in Chapter 4.

7.2 *Discussion*

7.2.1 A phytoplankton source of methyl chloride?

Net production of methyl chloride was clearly demonstrated in xenic laboratory cultures of several species of phytoplankton. Although release as a by-product of phytoplankton metabolism may have contributed to the observed production, further increases in methyl chloride following the death of all the phytoplankton indicated transformation of organic precursors, abiotically or by bacteria, to methyl chloride. Field studies have not produced conclusive evidence of direct phytoplankton production of methyl chloride. An increase in methyl chloride concentrations during the spring bloom in Bedford Basin, Nova Scotia, could not be conclusively linked to phytoplankton. No simple relationship was observed between phytoplankton biomass, measured as chlorophyll-a, and methyl chloride along the cruise track in the North-west Atlantic. If the dominant source of methyl chloride in ocean waters were direct production by phytoplankton, some correlation would be expected. Near-surface maxima observed in the North-west Atlantic were clearly supersaturated (~ 250-400% saturation) with methyl chloride requiring *in situ* production. Further laboratory culture experiments under axenic conditions are necessary to resolve the role of the bacteria from that of the phytoplankton in producing methyl chloride. The effects of the culture conditions (light levels, nutrients, inorganic carbon, and temperature) on methyl chloride production in the presence of different species should also be examined.

At present, identified sources of methyl chloride in the oceans (chloride substitution of methyl iodide (Zafiriou, 1975) and methyl bromide, macroalgae (Manley and Dastoor, 1987)), cannot explain more than 5 - 10% of the estimated sea-to-air flux. Rates of methyl chloride release by phytoplankton are several orders of magnitude smaller the estimated flux. The higher concentrations above the seasonal thermocline and existence of near-surface maxima, however, are evidence suggestive of a link to biological activity. Marine fungi, bacteria, and higher organisms have not yet been examined for methyl chloride production.

7.2.2 The magnitude of the ocean-to-atmosphere flux of methyl chloride

The flux calculated from the measurements reported in Chapter 4, 4.5 x 10^{10} moles CH_3Cl yr^{-1} (2.3 x 10^{12} g yr^{-1}), is the lowest to date and is equivalent to 70% of the estimated tropospheric sink due to reaction with hydroxyl radicals. There are several sources of uncertainty in the sea-air flux calculation. Measurements of methyl chloride made during May in the North-west Atlantic were assumed to be representative of the global ocean in all seasons. The central gyre regions typified by low nutrient concentrations, warm temperatures, and high fluxes of solar radiation are under-represented in available data sets. Whether or not such conditions might favour methyl chloride production is not yet known. The data are also biased towards spring. Production as a result of biological processes would lead to higher methyl chloride during spring and summer at temperate latitudes. An annual sea-air flux calculated from

measurements made at this time of year would then overestimate the actual flux. Better spatial and temporal sampling of ocean surface waters would allow a more accurate assessment of the sea-air exchange of methyl chloride. The lack of clear explanation for the 80% greater apparent sensitivity in System II compared with System I throws some doubt on the calibration used for calculating the concentrations in the North-west Atlantic. It was suggested that the relatively high mid-depth (200-400 m) concentrations of methyl chloride at Station 58 were the result of a convective layer formed the previous winter. If it is also assumed that this layer had reached equilibrium with the atmosphere, the tropospheric boundary layer mixing ratio would have been 890 pptv, 40% greater than the 625 pptv average extracted from the literature. Measurements of winter surface layer concentrations of methyl chloride are not available to verify the assumption that the apparently convective layer at Station 58 had been at equilibrium with the atmosphere. Methyl chloride production in ocean waters is not yet sufficiently understood to conclude that no production occurs during the winter. Convective and wind-driven deepening of the mixed layer during winter, however, can lead to undersaturation. It is also surprising, perhaps, that the near-surface concentrations in Bedford Basin were found to be a factor of 2 smaller than those in the North-west Atlantic. These observations suggest that the concentrations may have been overestimated. An overestimation of the surface concentrations of methyl chloride in the North-west Atlantic would lead to an overestimation of the sea-air flux.

The value of K, the transfer velocity, is another source of uncertainty in the flux calculation. Combining a ± 1 ms^{-1} estimated uncertainty in the average wind speed value

of 6.5 ms^{-1}, the uncertainty in the wind speed dependence of the transfer velocity (*ca.* ±50-60%), and the ±10% uncertainty in the best estimate of *H* results in a ±70-80% uncertainty in the estimated flux (1.7×10^{10} - 8.1×10^{10} moles yr^{-1} = 8.7×10^{11} - 4.1×10^{12} g yr^{-1}).

7.2.3 The tropospheric budget of methyl chloride

Figure 7.1 is a diagram summarising available information on the tropospheric budget of methyl chloride.

The tropospheric mixing ratio of methyl chloride is generally assumed to be invariant on decadal time scales. Under this assumption inputs must balance losses. Attack of hydroxyl radicals, estimated to consume 6 - 8 x 10^{10} moles CH_3Cl yr^{-1} (3 - 4 x 10^{12} g CH_3Cl yr^{-1}) (Singh *et al.*, 1979; Warneck, 1988; Koppmann, 1993), is the dominant removal process in the troposphere. Estimates of the air-sea exchange of methyl chloride by Singh *et al.* (1977, 1983) suggested that the flux from the ocean surface could account for this loss. The sea-air emission estimate from the present study (4.5×10^{10} moles/2.3×10^{12} g yr^{-1}) supports the existence of an ocean source. At this point, present estimates of the sources and sinks of methyl chloride do not balance. Values for biomass burning emissions of methyl chloride range from 1.8 - 7.1 x 10^{10} moles CH_3Cl yr^{-1} (0.9 to 3.6 x 10^{12} g yr^{-1}) (Andreae, 1993), with contributions from both natural (*e.g.* wildfires) and anthropogenic (*e.g.* slash-and-burn agriculture) combustion processes. Uncertainty in this estimate can be found in the CH_3Cl/CO_2 emission ratio and

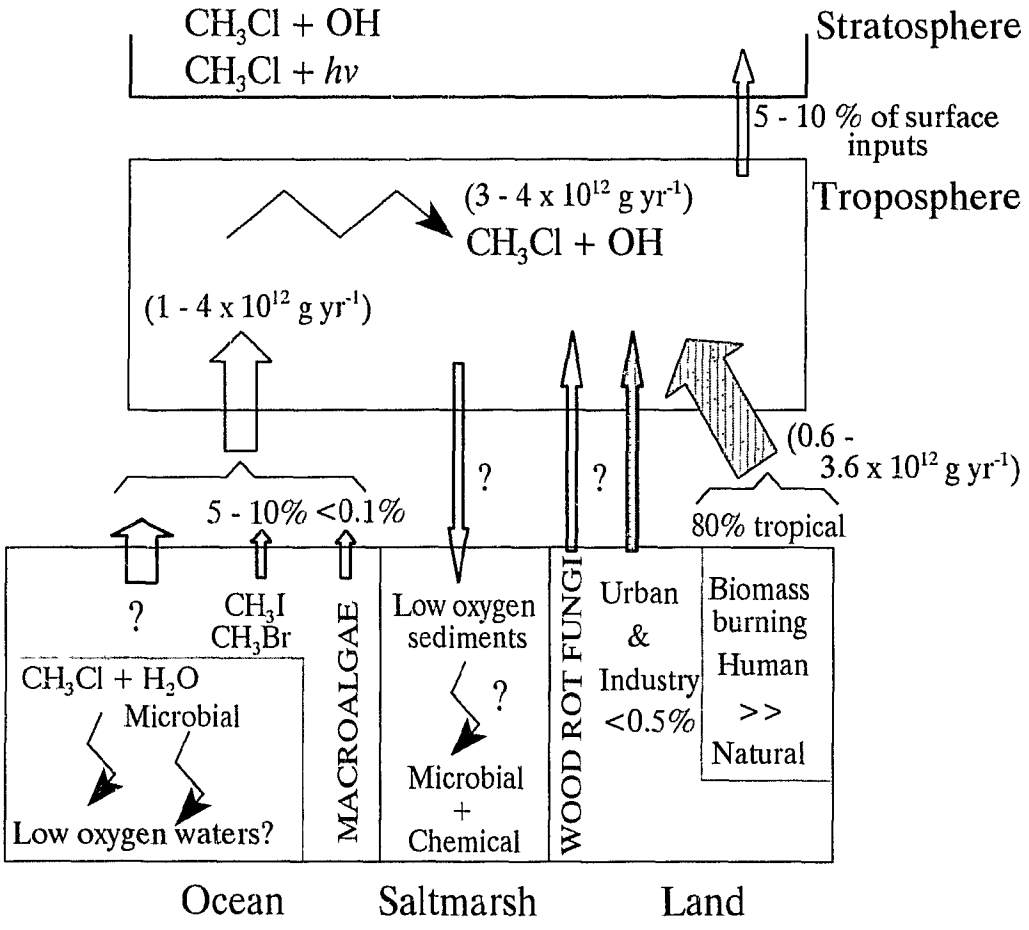


Figure 7.1 The tropospheric budget of methyl chloride

also the value for global CO_2 release from biomass burning. Together, oceanic emissions and biomass burning sources appear to be greater than losses due to reaction with hydroxyl radical. There is also evidence of a terrestrial biological source from some species of wood-rot fungi (Harper, 1993) which has not yet been quantified. Three possibilities are suggested to account for the discrepancy. First, the tropospheric budget of methyl chloride may not be balanced, in which case the validity of assuming a constant methyl chloride mixing ratio on decadal time scales is brought into question. Second and third, sources may have been overestimated or conversely, sinks underestimated.

Biologically mediated consumption of methyl chloride (and methyl bromide) has been observed in anaerobic saltmarsh sediments (Oremland *et al.*, 1994). It was also suggested that microbial processes in anaerobic soils consumed methyl bromide. It appears likely that methyl chloride would also be degraded under such conditions. Abiotic consumption of methyl chloride and methyl bromide also occurs under anoxic conditions due to substitution reactions with sulphur nucleophiles (Oremland *et al.*, 1994). It remains to be assessed whether terrestrial and coastal wetland sinks of methyl chloride are important in the tropospheric budget.

The waters in Bedford Basin in which low concentrations of methyl chloride were observed were 80 - 85% saturated with oxygen. Assuming a 1 year residence time of the waters behind the sill and initial equilibrium with the atmosphere, the rate of methyl chloride destruction is *ca.* 50 times that predicted from hydrolysis rate constants (Moelwyn-Hughes, 1938, 1953). Whether the low concentrations of methyl chloride resulted from consumption within these aerobic waters themselves and/or within anoxic

sediments on the Basin bottom is not clear. If high rates of microbial consumption occur only under sub-oxic (< *ca.* 40 μM oxygen) and anoxic (< *ca.* 7 μM oxygen) conditions, methyl chloride losses in aquatic environments will be restricted to specific areas such as the oxygen minimum zones of the Pacific and Indian oceans and anoxic basins and estuaries. Such areas may act as a net sink for tropospheric methyl chloride.

Aerobic microbial consumption of methyl chloride has implications for a widespread sink of methyl chloride throughout upper ocean waters. In order to generate the flux that is estimated to come from the oceans, processes producing methyl chloride within seawater would have to be occurring at an even greater rate to account for this.

As discussed in the previous section, there are huge uncertainties associated with estimates of the ocean emission of methyl chloride calculated using the simple two-layer diffusion model. Measurement of methyl chloride concurrently in air and surface seawater in a variety of locations and seasons would improve the uncertainty in C_w and C_a. The uncertainty in the value of K will reduce as understanding of air-sea exchange progresses and knowledge of the global wind field increases. At present, however, estimates of the oceanic emission of methyl chloride using the two-layer model are not sufficiently accurate to resolve the dilemma of the importance of the oceanic source in the methyl chloride budget.

Anderson, J. G., D. W. Toohey, and W. H. Brune (1991), Free radicals within the Antarctic Vortex: The role of CFC's in Antarctic ozone loss, *Science*, *251*, 39-46.

Andreae, M. O. (1990), Ocean-atmosphere interactions in the global biogeochemical sulphur cycle, *Mar. Chem*, *30*, 1-29.

Andreae, M. O. (1993), The influence of tropical biomass burning on climate and the Atmospheric environment, pp113-150 in *Biogeochemistry of Global Change: Radiatively Active Trace Gases*, Proc. Tenth Int. Symp. on Environmental Biogeochemistry, San Francisco, August 1991, ed. R. S. Oremland, Chapman and Hall, New York.

Asher, W. E., P. J. Farley, R. Wanninkhof, E. C. Monahan and T. S. Bates (1992), Laboratory and field experiments on the correlations of fractional area whitecap coverage with air-sea gas transport, pp815-828 in *Precipitation Scavenging and Atmosphere-Surface Exchange* , Vol. 2, *The Semonin Volume*, eds. S. E. Schwartz and W. G. N. Slinn, Hemisphere, Washington.

Atkinson, R., D. L. Baulch, R. A. Cox, R. F. Hampson, J. A. Kerr and J. Troe (1992), Evaluated kinetic and photochemical data for atmospheric chemistry: Supplement IV, *Atmos. Environ., 26A*, 1187-1230.

Austin, B. (1988), Taxonomy of marine micro-organisms, chapter 4 in *Marine Microbiology*, Cambridge University Press, Cambridge.

Beardall, J. and I. Morris (1976), Concept of light intensity adaptation in marine phytoplankton: Some experiments with *Phaeodactylum tricornutum*, *Mar. Biol.*, *37*, 377-387.

Blaustein, A. R., P. D. Hoffman, D. G. Hokit, J. M. Kiesecker, S. C. Walls, and J. B. Hays (1994), UV repair and resistance to solar UV-B in amphibian eggs: A link to population declines, *Proc. Nat. Acad. Sci USA, 91*, 1791-1795.

Bouwer, E. J., B. E. Rittmann, and P. L. McCarty (1981), Anaerobic degradation of halogenated 1- and 2-carbon organic compounds, *Environ. Sci. Technol., 15*, 596-599.

Bouwer, E. J. and P. L McCarty (1983a), Transformation of 1- and 2-carbon halogenated aliphatic compounds under methanogenic conditions, *Appl. Environ. Microbiol.*, *45*, 1286-1294.

Bouwer, E. J. and P. L. McCarty (1983b), Transformation of halogenated organic compounds under denitrification conditions, *Appl. Environ. Microbiol, 45*, 1295-1299.

Brasseur, G. P. (1991), A deepening, broadening trend, *Nature, 352*, 667-668.

Brasseur, G. P., C. Granier and S. Walters (1990), Future changes in stratospheric ozone and the role of heterogeneous chemistry, *Nature, 348*, 626-628.

Braus-Stromeyer, S. A., A. M. Cook and T. Leisinger (1993), Biotransformation of chloromethane to methanethiol, *Environ. Sci. Technol., 27*, 1577-1579.

Chipperfield, M.(1991), Stratospheric ozone depletion over the Arctic, *Nature, 349*, 279-280.

Cicerone, R. J. (1987), Changes in stratospheric ozone, *Science, 237*, 35-42.

Class, T. J. and K. Ballschmiter (1987), Chemistry of organic traces in air IX: Evidence of natural marine sources of chloroform in regions of high primary production,

Fres. Z. Anal. Chem., 327, 40-41.

Class, T. J. and K. Ballschmiter (1988), Chemistry of organic traces in air VIII: Sources and distributions of bromo- and bromochloro-methanes in marine air and surface water of the Atlantic, *J. Atmos. Chem., 6,* 35-46.

Clemons, C. A. and A. P. Altshuller (1966), Responses of electron-capture detector to halogenated substances, *Anal. Chem., 38,* 133-136.

Cobb, G. D. and E. J. Bouwer (1991), Effects of electron acceptors on halogenated organic compound biotransformations in a Biofilm Column, *Environ. Sci. Technol., 25,* 1068-1074.

Cowan, M. I., A. T. Glen, S. A. Hutchison, M. E. MacCartney, J. M. Mackintosh, and A. M. Moss (1973), Production of volatile metabolites by the species of fomes, *Trans. Br. Mycol. Soc., 60,* 347-360.

Cox, R. A., R. G. Derwent, A. E. J. Eggleton and J. E. Lovelock (1976) Photochemical oxidation of halocarbons in the troposphere, *Atmos. Environ., 10,* 305-308.

Cronn, D. R., R. A. Rasmussen, E. Robinson and D. E. Harsch (1977), Halogenated compound identification and measurement in the troposphere and lower stratosphere, *J. Geophys. Res., 82,* 5935-5944.

Crutzen, P. J., L. E. Heidt, J. P. Krasnec, W. H. Pollock, and W. Seiler (1979), Biomass burning as a source of atmospheric trace gases CO, H_2, N_2O, NO, CH_3Cl, and COS, *Nature, 282,* 253-256.

Crutzen, P. J. and L. T. Gidel (1983), A two-dimensional photochemical model of the

atmosphere 2, the tropospheric budgets of the anthropogenic chlorocarbons, CO, CH4, CH_3Cl, and the effect of various NOx sources on tropospheric ozone, *J. Geophys. Res., 88,* 6641-6661.

Crutzen, P. J. and F. Arnold (1986), Nitric Acid cloud formation in the cold Antarctic stratosphere: a major cause for the springtime ozone hole, *Nature, 324,* 651-655.

Crutzen, P. J., R. Müller, Ch. Brühl and Th. Peter (1992), On the potential importance of the gas phase reaction of CH_3O_2 + ClO → ClOO + CH_3O and the heterogeneous reaction HOCl + HCl → H_2O + Cl_2, *Geophys. Res. Lett., 19,* 1113-1116.

Dickerson, R. R., G. J. Huffman, W. T. Luke, L. J. Nunnermacker, K. E. Pickering, A. C. D. Leslie, C. G. Lindsey, W. G. N. Slinn, T. J. Kelly, P. H. Daum, A. C. Delany, J. P. Greenberg, P. R. Zimmerman, J. F. Boatman, J. D. Ray and D. H. Stedman, Thunderstorms: An important mechanism in the transport of air pollutants, *Science, 235,* 460-465.

Drever, J. I. (1982), *The Geochemistry of Natural Waters,* first edition, p22, Englewood Cliffs, N. J., Prentice-Hall.

Edwards, P. R., I. Campbell, and G. S. Milne (1982), The impact of chloromethanes on the environment, Part 2 Methyl chloride and methylene chloride, *Chem. Ind. (London),* 619-622.

Ehman, P. J., W. O. Walker and W. R. Rinelli (1964), Methyl chloride, pp100-110 in *Kirk-Othmer Encyclopedia of Chemical Technology,* 2nd edition, executive editor

A. Standen, Wiley Interscience.

Elliott, S. and F. S. Rowland (1993), Nucleophilic substitution rates and solubilities for methyl halides in seawater, *Geophys. Res. Lett.*, *20*, 1043-1046.

Farman, J. C., B. G. Gardiner, and J. D. Shanklin (1985), Large losses of total ozone in Antarctica reveal seasonal ClO_x/NO_x interaction, *Nature, 315*, 207-210.

Fenical, W. (1975), Halogenation in the Rhodophyta - A review, *J. Phycol.*, *11*, 245-259.

Fenical, W. (1982), Natural products chemistry in the marine environment, *Science, 215*, 923-928.

Fogelqvist, E. (1985), Carbon tetrachloride, tetrachloroethylene, 1,1,1-trichloroethane, and bromoform in Arctic seawater, *J. Geophys. Res.*, *90*, 9189-9193.

Geen, C. (1992), Selected marine sources and sinks of bromoform and other low molecular weight organobromines, M.Sc. Thesis, Dalhousie University.

Geigert, J., S. L. Neidleman, S. K. deWitt and D. J. Dalietos (1984), Halonium ion-induced biosynthesis of chlorinated marine metabolites, *Phytochem.*, *32*, 287-290.

Gentile, I. A., L. Ferraris and S. Crespi (1989), The degradation of methyl bromide in some natural freshwaters. Influence of temperature, pH, and light, *Pestic. Sci.*, *25*, 261-272.

Glew, D. N. and E. A. Moelwyn-Hughes (1953), Chemical statics of the methyl halides in water, *Disc. Far. Soc.*, *15*, 150-161.

Glombitza, K. -W. (1979), Antibiotics from algae, pp310-341 in *Marine Algae in Pharmaceutical Science*, eds. H. A. Hoppe, T. Levring and Y. Tanaka, walter

de Gruyter, Berlin, New York.

Gossett, J. M. (1987), Measurement of Henry's Law constants for C_1 and C_2 chlorinated hydrocarbons, *Environ. Sci. Technol., 21,* 202-208.

Graedel, T. E. (1979), The kinetic photochemistry of the marine atmosphere, *J. Geophys. Res., 84,* 273-286.

Graedel, T. E. and D. L. Allara (1976), Tropospheric halocarbons: Estimates of atmospheric chemical production, *Atmos. Environ., 10,* 385-388.

Grimsrud, E. P. and D. A. Miller (1978), Oxygen doping of carrier gas in measurement of halogenated methanes by gas chromatography with electron capture detection, *Anal. Chem., 50,* 1141-1145.

Grimsrud, E. P. and D. A. Miller (1980), Non-linear responses of the electron-capture detector to alkyl monochlorides, *J. Chromatogr., 192,* 117-125.

Grimsrud, E. P., D. A. Miller, R. G. Stebbins and S. H. Kim (1980), Alteration of the electron-capture detector response to polycyclic aromatic hydrocarbons by oxygen doping of the carrier gas, *J. Chromatogr., 197,* 51-58.

Grimsrud, E. P. and R. A. Rasmussen (1975), Survey and analysis of halocarbons in the atmosphere by gas chromatography-mass spectrometry, *Atmos. Environ., 9,* 1014-1017.

Grimsrud, E. P. and R. G. Stebbins (1978), Effect of oxygen on the response if a constant-current ^{63}Ni electron-capture detector, *J. Chromatogr., 155,* 19-34.

Gschwend, P. M., J. K. MacFarlane and K. A. Newman (1985), Volatile halogenated organic compounds released to seawater from temperate marine algae, *Science,*

227, 1033-1035.

Gschwend, P. M. and J. K. MacFarlane (1986), Polybromomethanes: A year-round study of their release to seawater from *Ascophyllum nodosum* and *Fucus vesiculosis*, pp314-322 in *Organic Marine Geochemistry*, ed. M. L. Sohn, ACS Symp. Ser. 305, ACS, Washington D. C..

Guillard, R. R. L. (1975), Cultures of phytoplankton for feeding marine invertebrates, pp46-53 in *Culture of Marine Invertebrate Animals*, eds. W. L. Smith and M. H. Chanley, Plenum Press.

Hargrave, B. T., D. L. Peer and H. F. Wiele (1989), Benthic biological observations, pp37-45 in *Investigations of Marine Environmental Quality in Halifax Harbour*, Can Tech. Rep. Fish. Aquat. Sci., 1693, ed. H. B. Nicholls.

Harper, D. B. (1985), Halomethane from halide ion - a highly efficient fungal conversion of environmental significance, *Nature*, *315*, 55-57.

Harper, D. B. (1993a), Biogenesis and metabolic role of halomethanes in fungi and plants, chapter 11 in *Biological Properties of Metal Alkyl Derivatives*, eds. H. Sigel and A. Sigel, Volume 29 of *Metal Ions in Biological Systems*, Marcel Dekker, New York.

Harper, D. B. (1993b), Biosynthesis and metabolic role of chloromethane in fungi, presented at the Int. Conf. on Naturally-Produced Organohalogens, Sep 14-17, 1993. TNO Zuidpolder Delft, The Netherlands.

Hartmans, S., A. Schmuckle, A. M. Cook and T. Leisinger (1986), Methyl chloride: Naturally occurring toxicant and C-1 growth substrate, *J. Gen. Microbiol.*, *132*,

1139-1142.

Head, E. J. H., B. T. Hargrave, and D. V. Subba Rao (1994), Accumulation of a pheophorbide *a*-like pigment in sediment traps during late stages of a spring bloom: A product of dying algae?, *Limnol. Oceanogr., 39*, 176-181.

Herman, A. W., M. R. Mitchell and S. W. Young (1984), A continuous pump sampler for profiling copepods and chlorophyll in the upper oceanic layers, *Deep Sea Res., 31*, 439-450.

Hobbie, J. E., R. J. Dalye and S. Jasper (1977), Use of Nuclepore filters for counting bacteria by fluorescence microscopy, *Appl. Environ. Microbiol., 33*, 1225-1228.

Hoffmann, D. J. and T. Deschler (1991), Evidence from balloon measurements for chemical depletion of stratospheric ozone in the Arctic winter of 1989-1990, *Nature, 349*, 300-305.

Holm-Hansen, O., C. J. Lorenzen, R. W. Holmes and J. D. H. Strickland (1965), Fluorometric determination of chlorophyll, *J. du Conseil, 30,* 3-15.

Hov, O., S. A. Penkett, I. S. A. Isaksen and A. Semb (1984), Organic gases in the Norwegian Arctic, *Geophys. Res. Lett, 11*, 425-428.

Hoyt, S. D. and R. A. Rasmussen (1985), Determining trace gases in air and seawater, chapter 3 in *Chemical Mapping Strategies in Oceanography,* ed. A. Zirino, American Chemical Society.

Hyman, M. R. and P. M. Wood (1984), Bromocarbon Oxidations by *Nitrosomonas europaea,* pp49-52 in *Microbial Growth on C1 Compounds,* Proceedings of the 4th International Symposium, American Society for Microbiology, Washington

D. C..

Jähne, B., G. Heinz and W. Dietrich (1987), Measurement of the diffusion coefficients of sparingly soluble gases in water, *J. Geophys. Res.*, *92*, 10767-10776.

Jenkins, W. J. (1980), Tritium and ^{3}He in the Sargasso Sea, *J. Mar. Res.*, *38*, 533-569.

Jenkins, W. J. (1982), On the climate of a subtropical ocean gyre: Decade timescale variations in water mass renewal in the Sargasso Sea, *J. Mar. Res, 40 (suppl.)*, 265-290.

Karasek, F. W. and D. M. Kane (1973), Effect of oxygen on response of the electron-capture detector, *Anal. Chem.*, *45*, 576-580.

Khalil, M. A. K. and R. A. Rasmussen (1981), Atmospheric methyl chloride (CH_3Cl), *Chemosphere, 10*, 1019-1023.K

Khalil, M. A. K. and R. A. Rasmussen (1983), Gaseous tracers of Arctic Haze, *Environ. Sci. Technol.*, *17*, 157-163.

Khalil, M. A. K., R. A. Rasmussen and R. Gunwardena (1993), Atmospheric methyl bromide: trends and global mass balance, *J. Geophys. Res.*, *98*, 2887-2896.

Klick, S. (1992), Seasonal variations of biogenic and anthropogenic halocarbons in seawater from a coastal site, *Limnol. Oceanogr.*, *37*, 1579-1585.

Kollias, N., A. Baqrem, I. Sadiq and R. M. Sayre (1992), *In vitro* and *in vivo* ultraviolet-induced alterations of oxy- and deoxyhemoglobin, *Photochem. Photobiol.*, *56*, 223-227.

Koppmann, R., F. J. Johnen, C. Plass-Dulmer and J. Rudolph (1993), Distribution of methyl chloride, dichloromethane, trichloroethene, and tetrachloroethene over the

North and South Atlantic, *J. Geophys. Res., 98*, 20517-20526.

Lincoff, A. H. and J. M. Gossett (1984), The determination of Henry's Law constants for volatile organics by equilibrium partitioning in closed systems, pp17-25 in *Gas Transfer at Water Surfaces*, eds. W. Brutsaert and H. Jirka, Reidel.

Liss, P. S. and L. Merlivat (1986), Air-sea gas exchange rates: Introduction and synthesis, pp113-127 in *The Role of Air-Sea Exchange in Geochemical Cycling*, ed. P. Buat-Ménard, Reidel.

Liss, P. S. and P. G. Slater (1974), Flux of gases across the air-sea interface, *Nature, 247,* 181-184.

Lovelock, J. E. (1963), Electron absorption detectors and technique for use in quantitative and qualitative analysis by gas chromatography, *Anal. Chem., 35*, 474-481.

Lovelock, J. E. (1975), Natural halocarbons in air and sea, *Nature, 256,* 193-194.

Lovelock, J. E. and S. R. Lipsky (1960), Electron affinity spectroscopy - A new method for the identification of functional groups in chemical compounds separated by gas chromatography, *J. Amer. Chem. Soc., 82,* 431-433.

Luyten, J. R., J. Pedlovsky, and H. Stommel (1983), The ventilated thermocline, *J. Phys. Oceanogr., 13,* 292-309.

MacFarlane, C. and H. P. Bell (1933), Observations of the seasonal changes in marine algae in the vicinity of Halifax, with particular reference to winter conditions, *Proc. Trans. N. S. Inst. Sci., 18,* 134-176.

Mackay, D., W. Y. Shiu, and R. P. Sutherland (1979), Determination of air-water

Henry's Law constants for hydrophobic pollutants, *Environ. Sci. Technol.*, *13*, 333-337.

Mackay, D. and W. Y. Shiu (1981), A critical review of Henry's Law constants for chemicals of environmental interest, *J. Phys. Chem. Ref. Data.*, *10*, 1175-1199.

Manley, S. L. and M. N. Dastoor (1987), Methyl halide (CH_3X) production from the giant kelp, *Macrocystis*, and estimates of global CH_3X production by kelp, *Limnol. Oceanogr.*, *32*, 709-715.

Manley, S. L. and M. N. Dastoor (1988), Methyl iodide production by kelp and associated microbes, *Mar. Biol.*, *98*, 447-482.

Manley, S. L., K. Goodwin and W. J. North (1992) Laboratory production of bromoform, methylene bromide, and methyl iodide by macroalgae and distribution in nearshore southern California waters, *Limnol. Oceanogr.*, *37*, 1652-1659.

Manö, S. and M. O. Andreae (1994), Emission of methyl bromide from biomass burning, *Science, 263,* 1255-1256.

Manthey, J. A. and L. P. Hager (1981), Purification and propoerties of bromoperoxidase from *Penicillus capitatus*, *J. Biol. Chem.*, *256*, 11232-11238.

March, J. (1992), Aliphatic Nucleophilic Substitution, chapter 10 (pp298-300 and 357-362) in *Advanced Organic Chemistry*, Fourth edition, Wiley & Sons, New York.

McCartney, M. D. (1982), The subtropical recirculation of Mode Waters, *J. Mar. Res, 40 (suppl),* 427-464.

McCartney, M. D. and L. D. Talley (1982), The Subpolar Mode Water of the North Atlantic ocean, *J. Phys. Oceanogr.*, *12,* 1169-1188.

McCartney, M. D. and L. D. Talley (1984), Warm-to-cold water conversion in the northern North Atlantic ocean, *J. Phys. Oceanogr., 14,* 922-935.

McConnell, O. J. and W. Fenical (1977), Halogen chemistry of the red alga *Asparagopsis*, *Phytochemistry, 16,* 367-374.

McConnell, O. J. and W. Fenical (1979), Antimicrobial agents from marine red algae of the family *Bonnemaisoniaceae*, pp403-427 in *Marine Algae in Pharmaceutical Science*, eds. H. A. Hoppe, T. Levring, and Y. Tanaka, Walter de Gruyter, Berlin, New York.

McElroy, M. B., R. J. Salawitch, S. C. Wofsy and J. A. Logan (1986), Reductions in Antarctic ozone due to synergistic interactions of bromine and chlorine, *Nature, 321*, 759-762.

Megie, G., M.-L. Chanin, D. Ehhalt, P. Fraser, J. F. Frederick, J. C. Gille, M. P. McCormick, and M. Schoeberl (1990), Global trends, p249 of chapter 2 in *Scientific Assessment of Stratospheric Ozone*, WMO Report 20, 1989.

Moelwyn-Hughes, E. A. (1938), The hydrolysis of the methyl halides, *Proc. Roy. Soc. Lond. A, 164*, 295-306.

Moelwyn-Hughes, E. A. (1949), The kinetics of certain reactions between methyl halides and anions in water, *Proc. Roy. Soc. Lond. A, 196*, 540-553.

Moelwyn-Hughes, E. A. (1953), The kinetics of hydrolysis, *Proc. Roy. Soc. Lond. A., 220*, 386-396.

Molina, M. J. and F. S. Rowland (1974), Stratospheric sink for chlorofluoromethanes: Chlorine atom catalysed destruction of ozone, *Nature*, *249*, 801-814.

Molina, L. T. and M. J. Molina (1987), Production of Cl_2O_2 from self-reaction of the ClO radical, *J. Phys. Chem., 91,* 433-436.

Moore, R. M. and R. Tokarczyk (1993), Volatile halocarbons in the Northwest Atlantic, *Global Biogeochemical cycles, 7,* 195-210.

Moore, R. M., R. Tokarczyk, V. K. Tait, M. Poulin and C. Geen (1994), Marine phytoplankton as a natural source of volatile organohalogens, Proc. Int. Conf. on Naturally-Produced Organohalogens, Sep 14-17, 1993. TNO Zuidpolder Delft, The Netherlands.

Moore, R. M., C. Geen, and V. K. Tait (1994), Determination of Henry's Law constants for a suite of naturally occurring halogenated methanes in seawater, *Chemosphere*, in press.

Nightingale, P. D. (1991), Low molecular weight halocarbons in seawater, Ph.D. Thesis, University of East Anglia.

Oremland, R. S., L. G. Miller and F. E. Strohmaler (1994), Degradation of methyl bromide in anaerobic sediments, *Environ. Sci. Technol., 28,* 514-520.

Palmer, T. Y. (1976), Combustion sources of atmospheric chlorine, *Nature, 263,* 44-46.

Patel, R. N. (1984), Methane mono-oxygenase from *Methylobacterium* sp. strain CRL-26, pp83-90 in *Microbial Growth on C1 Compounds*, Proceedings of the 4th International Symposium, American Society for Microbiology, Washington D. C..

Pearson, C. R. and G. McConnell (1975), Chlorinated C_1 and C_2 hydrocarbons in the marine environment, *Proc. Roy. Soc. Lond. B., 189,* 305-332.

Penkett, S. A., R. G. Derwent, P. Fabian, R. Borchers, and U. Schmidt (1980), Methyl

chloride in the stratosphere, *Nature*, *283*, 58-60.

Perdue, E. M. and N. L. Wolfe (1983), Prediction of buffer catalysis in field and laboratory studies of pollutant hydrolysis reactions, *Environ. Sci. Technol.*, *17*, 635-642.

Pierotti, D., R. A. Rasmussen, and R. Dalluge (1980), Measurements of N_2O, CF_2Cl_2, $CFCl_3$, CH_3CCl_3, CCl_4, and CH_3Cl in the troposphere and lower stratosphere over North America, *J. Geomag. Geoelectr.*, *32*, 181-205.

Platt, T., R. J. Conover, R. Loucks, K. H. Mann, D. L. Peer, A. Prakash and D. D. Sameoto (1970), Study of a eutrophicated marine basin, FAO Technical Conference on Marine Pollution and its Effects on Living Resources and Fishing, Rome, Dec. 1970.

Platt, T. and R. J. Conover (1971), Variability and its effect on the 24h chlorophyll budget of a small marine basin, *Mar. Biol.*, *10*, 52-65.

Post, A. F., Z. Dubinsky, K. Wyman and P. G. Falkowski (1985), Physiological responses of a marine planktonic diatom to transitions in growth irradiance, *Mar. Ecol. Progr. Ser.*, *25*, 141-149.

Post, A. and A. W. D. Larkum (1993), UV-absorbing pigments, photosynthesis and UV exposure in Antarctica: Comparison of terrestrial and marine algae, *Aquat. Bot.*, *45*, 231-243.

Prinn, R. G. (1988), How have the atmospheric concentrations of halocarbons changed?, pp33-48 in *The Changing Atmosphere,* eds. F.S. Rowland and I.S.A. Isaken, Wiley and Sons.

Prinn, R., D. Cunnold, P. Simmonds, F. Alyea, R. Boldi, A. Crawford, P. Fraser, D. Gutzler, D. Hartley, R. Rosen, and R. A. Rasmussen (1992), Global average concentration and trend for hydroxyl radicals deduced from ALE/GAGE trichloroethane (Methylchloroform) data for 1978-1990, *J. Geophys. Res.*, *97*, 2445-2461.

Rahn, K. A., R. D. Borys and R. A. Duce (1976), Tropospheric halogen gases: Inorganic and organic components, *Science, 192*, 549-550.

Rasche, M. E., M. R. Hymam and D. J. Arp (1990), Biodegradation of halogenated hydrocarbon fumigants by nitrifying bacteria, *Appl. Environ. Microbiol.*, *56*, 2568-2571.

Rasmussen, R. A., L. E. Rasmussen, M. A. K. Khalil, and R. W. Dalluge (1980), Concentration distribution of methyl chloride in the atmosphere. *J. Geophys. Res.*, *85*, 7350 - 7356.

Rasmussen, R. A., M. A. K. Khalil, R. Gunwardena and S. D. Hoyt (1982), Atmospheric methyl iodide (CH_3I), *J. Geophys. Res.*, *87*, 3086-3090.

Reichardt, C. (1988), Qualitative theory of solvent effects on reaction rates, pp 136-147 *Solvents and Solvent Effects in Organic Chemistry*, Second edition, VCH, Weinheim, Germany.

Reid, R. C., J. M. Prausnitz and T. K. Sherwood (1977), Diffusion coefficients, chapter 11 in *The Properties of Gases and Liquids*, third edition, McGraw-Hill, New York.

Robbins, D. E. (1976), Photodissociation of methyl chloride and methyl bromide in the

atmosphere, *Geophys. Res. Lett., 3,* 213-216.

Rodriguez, J. M., M. K. W. Ko and N. D. Sze (1991), Role of heterogeneous conversion of N_2O_5 on sulphate aerosols in global ozone losses, *Nature, 352,* 134-137.

Ryther, J. H. and W. M. Dunstan (1971), Nitrogen, phosphorus, and eutrophication in the coastal marine environment, *Science, 171,* 1008-1013.

Setlow, R. B. (1974), The wavelengths in sunlight effective in producing skin cancer: A theoretical analysis, *Proc. Nat. Acad. Sci. USA, 71,* 3363-3366.

Schauffler, S. M., L. E. Heidt, W. H. Pollock, T. M. Gilpin, J. F. Vedder, S. Solomon, R. A. Hueb, and E. L. Atlas (1993), Measuremnts of halogenated organic compounds near the tropical tropopause, *Geophys. res. Lett., 20,* 2567-2570.

Sicko-Goad, L. M., C. L. Schelske and E. F. Stoermer (1984), Estimation of the intracellular carbon and silica content of diatoms from natural assemblages using morphometric techniques, *Limnol. Oceanogr., 29,* 1170-1178.

Sieburth, J. McN., P. W. Johnson, V. M. Church and D. C. Laux (1993), C_1 bacteria in the water column of Chesapeake Bay, USA III. Immunologic relationships of the type species of marine monomethylamine- and methane-oxidising bacteria to wild estuarine and oceanic cultures, *Mar. Ecol. Progr. ser., 95,* 91-102.

Singh, H. B., L. Salas, H. Shigeishi, and A. Crawford (1977), Urban non-urban relationships of halocarbons, SF_6, N_2O, and other atmospheric trace constituents, *Atmos. Environ., 11,* 819-828.

Singh, H. B., L. J. Salas, H. Shigeishi, and E. Scribner (1979), Atmospheric halocarbons and sulphur hexafluoride: Global distributions, sources, and sinks, *Science, 203,* 889-903.

Singh, H. B., L. J. Salas, and R. E. Stiles (1983), Methyl halides in and over the Eastern Pacific, *J. Geophys. Res., 88,* 3684-3690.

South, G. R. (1976), A check-list of marine algae of Eastern Canada - First revision, *J. Mar. Biol. Ass. U.K., 56,* 817-843.

Stirling, D. I. and H. Dalton (1979), The fortuitous oxidation and cometabolism of various carbon compounds by whole-cell suspensions of *Methylococcus capsulatus* (Bath.), *FEMS Microbiol. Lett., 5,* 315-318.

Stirling, D. I. and H. Dalton (1980), Oxidation of dimethyl ether, methyl formate, and bromomethane by *Methylococcus capsulatus* (Bath), *J. Gen. Microbiol., 116,* 277-283.

Strathmann, R. R. (1967), Estimating the organic carbon content of phytoplankton from cell volume or plasma volume, *Limnol. Oceanogr., 12,* 411-418.

Sturges, W. T., G. F. Cota and P. T. Buckley (1992), Bromoform emission from Arctic ice algae, *Nature, 358,* 660-662.

Sturges, W. T., C. W. Sullivan, R. C. Schnell, L. E. Heidt and W. H. Pollock (1993), Bromoalkae production by Antarctic ice algae, *Tellus, 45B,* 120-126.

Symonds, R. B., W. I. Rose and M. H. Reed (1988), Contribution of Cl- and F-bearing gases to the atmosphere by volcanoes, *Nature, 334,* 415-418.

Taguchi, S. (1981), Seasonal studies of the dinoflagellate *Ceratium longipes* (Bailey)

Gran in the Bedford Basin, Canada, *J. Exp. Mar. Biol. Ecol., 55*, 115-131.

Theiler, R., J. C. Cook and L. P. Hager (1978), Halohydrocarbon synthesis by bromoperoxidase, *Science, 202*, 1094-1096.

Tokarczyk, R. and R. M. Moore (1994), Production of volatile organohalogens by phytoplankton cultures, *Geophys. Res. Lett., 21*, 285.

Tolbert, M. A., M. J. Rossi and D. M. Gloden (1988); Heterogeneous interactions of chlorine nitrate, hydrogen chloride, and nitric acid with sulphuric acid surface at stratospheric temperatures, *Geophys. Res. Lett., 15*, 847-850.

Traunecker, J., A. Preuß and G. Dieckert (1991), Isolation and characterisation of a methyl chloride utilising strictly anaerobic bacterium, *Arch. Microbiol., 156*, 416-421.

Turner, E. M., M. Wright, T. Ward, D. J. Osborne, and R. Self (1975), Production of ethylene and other volatiles and changes in cellulase and laccase activtities during the life cycle of the cultivated mushroom, *Agaricus bisporus*, *J. Gen. Microbiol., 91*, 167-176.

Turner, S. M., G. Malin, and P. S. Liss (1989), Dimethyl sulphide and (dimethylsulphonio)propionate in European coastal and shelf waters, chapter 12 in *Biogenic Sulphur in the Environment,* eds. E. S. Saltzman and W. J. Cooper American Chemical Society Symposium Series, Washington D.C.

Van de Wiel, H. J. and P. Tommassen (1972), Effect of oxygen on electron capture detection, *J. Chromatogr., 71,* 1-7.

Vilter, H. (1984), Peroxidases from Phaeophyceae: A Vanadium(V)-dependent peroxidase

from *Ascophyllum nodosum*, *Phytochemistry*, *23*, 1387-1390.

Wanninkhof, R. (1992), Relationship between wind speed and gas exchange over the ocean, *J. Geophys. Res.*, *97*, 7373-7382.

Wallen, D. G. and G. H. Geen (1971), Light quality in relation to growth, photosynthetic rates and carbon metabolism in two species of marine plankton algae, *Mar. Biol.*, *10*, 34-43.

Warneck, P. (1988), Halocarbons, pp267-277 in *Chemistry of the Natural Atmosphere*, *Int. Geophys. Ser.*, *41*, Academic Press, Orlando.

Warner, M. J. and R. F. Weiss (1985), Solubilities of chlorofluorocarbons 11 and 12 in water and seawater, *Deep Sea Res.*, *32*, 1485-1497.

Watson, A. J., R. C. Upstill-Goddard, and P. S. Liss (1991), Air-sea exchange in rough and stormy seas measured by the dual-tracer technique, *Nature, 349,* 145-147.

Weisenstein, D. K., M. K. W. Ko, and N-D. Sze (1992), The chlorine budget of the present-day atmosphere: A modeling study, *J. Geophys. Res.*, *97,* 2547-2559.

Wentworth, W. E., E. Chen and J. E. Lovelock (1966), The pulse-sampling technique for the study of electron-attachment phenomena, *J. Phys. Chem.*, *70*, 445-458.

Wever, R. (1988), Ozone destruction by algae in the Arctic atmosphere, *Nature, 335*, 501.

Wever, R., E. de Boer, H. Plat, and B. E. Krenn (1987), Vanadium - an element involved in the biosynthesis of halogenated compounds and nitrogen fixation, *F.E.B.S.Lett.*, *216*, 1-3.

Wever, R., M. G. M. Tromp, B. E. Krenn, A. Marjani and M. Van Tol (1991),

Brominating activity of the seaweed *Ascophyllum nodosum*: Impact on the biosphere, *Environ. Sci. Technol.*, *25*, 446-449.

White, R. H. (1982), Analysis of dimethylsulphonium compounds in marine algae, *J. Mar. Res.*, *40*, 529-536.

Wilhelm, E., R. Battino and R. J. Wilcock (1977), Low-pressure solubility of gases in liquid water, *Chemical Reviews, 77,* 219-262.

Wilke, C. R. and P. Chang (1955), Correlation of diffusion coefficients in dilute solutions, *A.I.Ch.E. Journal, 1,* 264-270.

Woodin, S. A., M. D. Walla and D. E. Lincoln (1987), Occurrence of brominated compounds in soft-botton benthic organisms, *J. Exp. Mar. Biol. Ecol.*, *107*, 209-217.

Wuosmaa, A. M. and L. P. Hager (1990), Methyl chloride transferase: A carbocation route for the biosynthesis of halometabolites, *Science, 249,* 160-162.

Zafiriou, O. C. (1975), Reactions of methyl halides with seawater and marine aerosols, *J. Mar. Res., 33,* 75-81.

Zika, R. G., L. T. Gidel, and D. D. Davis (1984), A comparison of photolysis and substitution decomposition rates of methyl iodide in the ocean, *Geophys. Res. Lett, 11*, 353-356.