Seasonal and spatial variations in methyl chloride in NW Atlantic waters

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[1]   Methyl chloride concentrations were measured in the upper 200 m of the water column of the NW Atlantic during three cruises along the same track in spring, summer and fall of 2003. Distinct seasonality was apparent, with the surface waters being either undersaturated or close to equilibrium with the atmosphere in spring, but with supersaturation of the warmer waters in summer and fall. Cooler waters at the more northerly stations were always undersaturated, thus representing a continual sink for atmospheric methyl chloride. Even on an annual basis, the concentration anomaly (the difference between measured concentration and equilibrium with the atmosphere) was strongly dependent on sea surface temperature (SST). This empirical relationship can be used to extrapolate fluxes globally or to estimate the influence of global warming on ocean-to-atmosphere fluxes of methyl chloride. The global flux of methyl chloride to the atmosphere estimate based on the full-year relationship between concentration anomaly and SST is 17 Gmol/y, and is reduced to 6 Gmol/y if separate seasonal relationships are used. It appears that the ocean component of the flux is highly sensitive to temperature, but the actual source of the methyl chloride in ocean waters remains largely unknown.

1. Introduction

[2]   Methyl chloride is a major carrier of chlorine in the atmosphere and contributor to chlorine flux into the stratosphere. It is present at a mixing ratio of approximately 536 pptv [*Montzka et al.*, 2003], has an almost entirely natural source, an atmospheric residence time of around 1.3 y [*Montzka et al.*, 2003], and its main atmospheric sink is reaction with OH. Of the ca. 8×10^{10} moles added annually to the atmosphere [*Montzka et al.*, 2003] it has been estimated that $6.4-8 \times 10^9$ moles is supplied by the ocean [*Moore*, 2000]. Terrestrial sources include emissions from vegetation and biomass burning. Current estimates of oceanic sources are based on sparse measurements that show that emissions to the atmosphere are non-uniform, typically with release of methyl chloride from low latitude waters and uptake by cooler high latitude waters.

[3]   With predictions of climate change it becomes of interest to determine whether fluxes of gases such as the methyl halides will be altered and to determine the nature of any climate feedbacks. With respect to methyl chloride the question of whether ocean warming would influence its flux to the atmosphere may be approached empirically by determining any relationship between fluxes and temperature or, more fundamentally, by identifying the actual production processes in the ocean and their dependences on critical parameters such as temperature and stratification.

[4]   The only well-established mechanism for CH_3Cl production in the oceans is the reaction of methyl bromide and iodide with chloride ion, but the sources of these precursors are also very uncertain. There is evidence for the production of all three methyl halides from phytoplankton, but the source appears to be weak, and a detailed understanding of the production is lacking. More progress has been made in understanding terrestrial sources of methyl halides with good evidence being found for various types of biological production [*Yokouchi et al.*, 2002; *Rhew et al.*, 2000, 2003; *Redeker et al.*, 2000]. There is also evidence for a marine photochemical source of methyl iodide [*Moore and Zafiriou*, 1994; *Richter and Wallace*, 2004] and, more recently, laboratory experiments have pointed to the possibility of some photochemical CH_3Cl production in coastal waters [*Moore et al.*, 2006].

[5]   As part of the Canadian Surface Ocean Lower Atmosphere Study (C-SOLAS) three cruises were conducted in the NW Atlantic in spring, summer and fall of 2003. Objectives of research done during those cruises included determining the seasonality and spatial variation of methyl halide concentrations and their fluxes between ocean and atmosphere. It is anticipated that knowledge of the regional and depth distributions of these compounds should help to elucidate their sources within the oceans as well as leading to improved estimates of global budgets. Knowledge of the production processes is essential if we are to be able to predict the influence of climate change on the ocean

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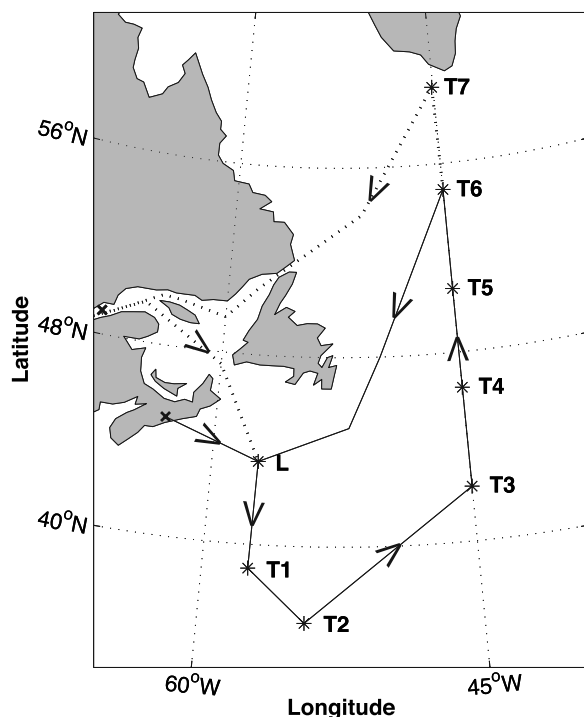
Figure 1. Cruise track followed by the three C-SOLAS cruises in 2003. The stippled line is the track followed in summer and fall between Mont-Joli and the study sites. L denotes the location of the spring Lagrangian study; this was the first station on all cruises. Transect stations are denoted by T.

sources of these and other atmospherically reactive trace gases.

2. Methods

[6] The three 2003 cruises along the track shown in Figure 1 were carried out on CCGS Hudson (April 23–May 16) and CCGS Martha Black (July 5–July 27, and October 10–November 3). Station T6 was the most northerly sampling point during the spring cruise. During the fall cruise instrument problems resulted in delays of up to 48 hours in measuring samples from stations T3 and T4. On account of possible significant changes in concentration during that time, the data from those stations have not been included in this study. Vertical profiles were collected from up to 8 stations with typical spacing of 5 m in the near surface increasing to 50 m spacing below 100 m; the maximum depth sampled was 350 m. In addition, there was periodic sampling of surface waters while the vessel was under way. In this case the water was collected in syringes from an onboard supply pumped from a depth of 5 m. Samples taken in 100 ml glass syringes were stored in a bucket of surface water until being analyzed usually within about 3 hours. Analysis was by GC-MS on a Finnigan Trace MS after extraction by purge and trap, separation on a pair of DB 624 columns (30 m and 100 m; internal diameter 0.53 mm, film thickness 3 microns, J & W Scientific), with backflushing of unwanted less volatile components, drying over magnesium perchlorate, and trapping at −150°C over liquid nitrogen. Carbon dioxide was stripped from the gas

stream by an Ascarite trap before the drying step. Analytes were desorbed from the cryotrap at 50°C by a stream of warm air. To each sample was added a known volume of a deuterated internal standard so that corrections could be made for variation in the sensitivity of the instrument. Calibration was effected with injections (50–200 μL) via a septum port of a gravimetrically produced standard containing 1961 ppb of methyl chloride in nitrogen stored in an Aculife treated aluminium cylinder. The precision of the measurements was determined by repeated measurements of a single large water sample on each of the the spring and summer cruises giving coefficients of variation 4.5% (7 samples) and 6.5% (8 samples) respectively. Average blank values, determined by running the procedure without injection of a water sample were 2.7 pmol/L. For additional details of the analytical method, see *Moore and Wang* [2006].

[7] Methyl chloride fluxes were extrapolated globally using the same wind speed and sea surface temperature data set as used by *Takahashi et al.* [2002] (provided by R. Wanninkhof). The climatology has 4° latitude by 5° longitude spatial resolution and monthly temporal resolution [*Takahashi et al.*, 2002]. Piston velocities were calculated for each box using the quadratic dependence of piston velocity on wind speed [*Wanninkhof*, 1992].

[8] The concentrations of thirteen algal pigments were measured to study whether certain phytoplankton species were responsible for CH_3Cl production [*Wang*, 2006]. Seawater samples were filtered under vacuum through 25 mm diameter GF75 Whatman filters (particle retention 0.3 μm) to concentrate the phytoplankton cells. The samples were stored in a −80°C freezer on the ship and in liquid nitrogen for transportation from ship to laboratory. The pigments were extracted into 1.7 mL of cold methanol (−18°C) by sonication. The sonicated samples were centrifuged for 10 minutes to separate the dissolved pigments from the filter pulp and were measured by high performance liquid chromatography (HPLC).

[9] For determining whether solar radiation has a direct role in CH_3Cl production, solar irradiances measured at 325 nm, 411 nm, 443 nm, 490 nm, 554 nm, 683 nm, and 700 nm using a Satlantic Multichannel Visible Detector System (MVDS-014) (C. Fichot, personal communication) were converted to daily radiant exposure (E$_d$, units: J m^{-2} nm^{-1} d^{-1}).

3. Results and Discussion

[10] Surface concentrations of CH_3Cl for the profile stations during three seasons are given in Table 1. Of more interest than the measured surface concentrations of CH_3Cl are the differences from equilibrium with the atmosphere. This measure of saturation levels is plotted geographically for the three seasons in Figure 2.

[11] Important features that are illustrated are the widespread undersaturation in spring, and the occurrence in both summer and fall of supersaturated waters in more southerly regions and undersaturated waters at the northerly stations. The average undersaturation at the three northern stations studied in the spring (−38%) is similar to the springtime undersaturation in the Southern Ocean (−37%) reported by *Yvon-Lewis et al.* [2004]. The surface concentrations of

Table 1. Concentrations of CH_3Cl (pM) at Profile Stations During the 3 NW Atlantic C-SOLAS Cruises

	Spring, pM	Summer, pM	Fall, pM
L	90	106	69
T1	60	72	97
T2	64	86	—
T3	55	92	—
T4	82	83	—
T5	60	76	57
T6	79	76	63
T7	—	77	72

CH_3Cl in the three seasons are plotted against temperature in Figure 3 together with the solubility curve which indicates the concentrations that the waters would have in the absence of production and consumption and temporary perturbations resulting from warming or cooling. There are small differences between the curves of equilibrium concentrations, with the summer and fall concentrations being lower than in spring on account of more rapid destruction of atmospheric CH_3Cl when the concentration of hydroxyl radical is higher. This figure well illustrates that in spring the waters were either undersaturated or, in the case of a few samples from the warmest waters, at saturation. In contrast, during the summer cruise, all waters warmer than about 12°C were supersaturated. A closer examination of the figure shows that concentrations were also higher in summer than spring, particularly in the warm waters. The increased summertime concentrations combined with the state of supersaturation can be explained, as detailed below, only by in situ production. The fall concentrations were typically lower than in summer and well-undersaturated in waters of 12°C or cooler. Supersaturation persisted in only the warmest of the measured samples (station T1).

[12] It is the case that supersaturations of a gas can sometimes be attributed, partially or totally, to physical effects such as warming of the water. However, we have several lines of evidence that support our argument for in situ production of CH_3Cl. First, with respect to surface waters, we have some measurements of CFC-11 that can be used to estimate the magnitude of physical influences on saturation levels. The group of southerly stations that showed supersaturations of methyl chloride in the summer had an average CFC-11 supersaturation of 7%, while the CH_3Cl was supersaturated by an average of 38%. A small number of air samples collected and analyzed for CFC-11 during the same cruise gave an atmospheric mixing ratio of ca. 260 pptv which is in good agreement with our best literature estimate of the mixing ratio at that time of 258 pptv [*Thompson et al.*, 2003]. Thus we can estimate that warming of the surface waters could have accounted for about one fifth of the supersaturation of CH_3Cl; we conclude that in situ production is responsible for most of the supersaturation and of the resulting flux to the atmosphere. Second, examination of profiles shows cases where the concentrations beneath the mixed layer are far too high to be attributable to physical effects. For example, at Station L in the summer (Figure 5a) there was a subsurface maximum in CH_3Cl of about 158 pmol/L while the saturated concentration at the corresponding temperature would be 69 pmol/L. It is impossible to attribute the measured saturation (230%) to warming, so in situ production is invoked. Furthermore, there is abundant evidence for consumption of CH_3Cl in the water column both from the literature, where biological loss rates have been measured in different areas [*Tokarczyk et al.*, 2003a, 2003b], and from our vertical profiles both in this study and others [e.g., *Moore and Wang*, 2006] which generally show decreases in concentration with depth below about 100 m. This renders it even
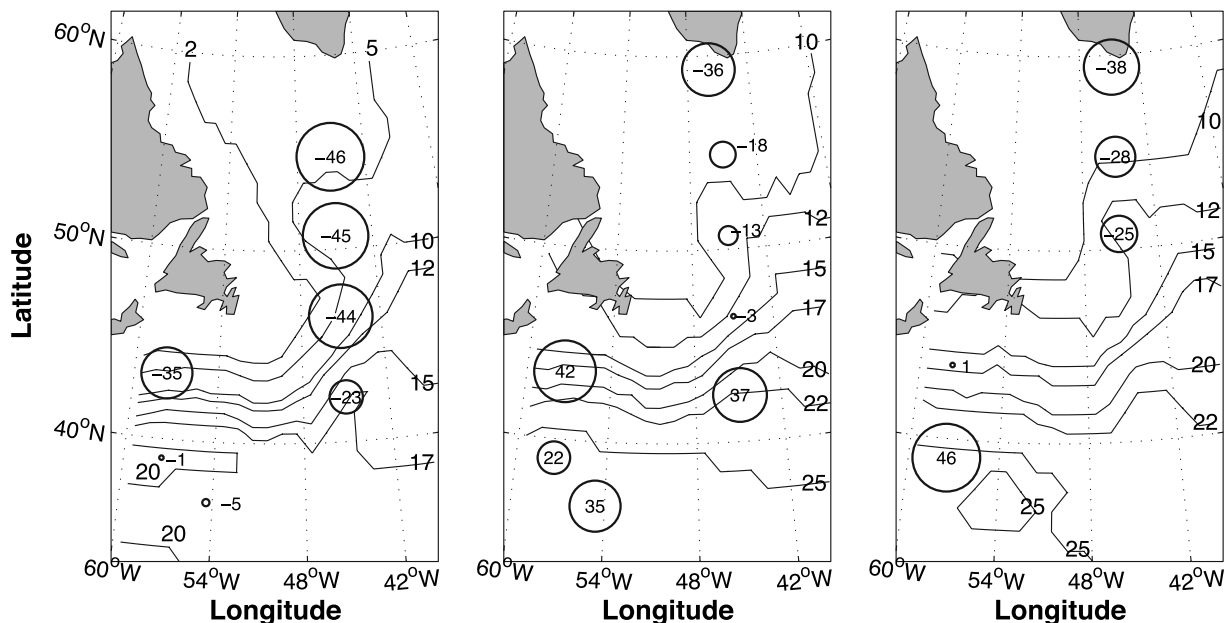
Figure 2. The difference between measured surface water concentration (pM) and concentration corresponding to equilibrium with the atmosphere shown for three seasons: (left) spring, (middle) summer, and (right) fall. Contours are of sea surface temperature (°C).
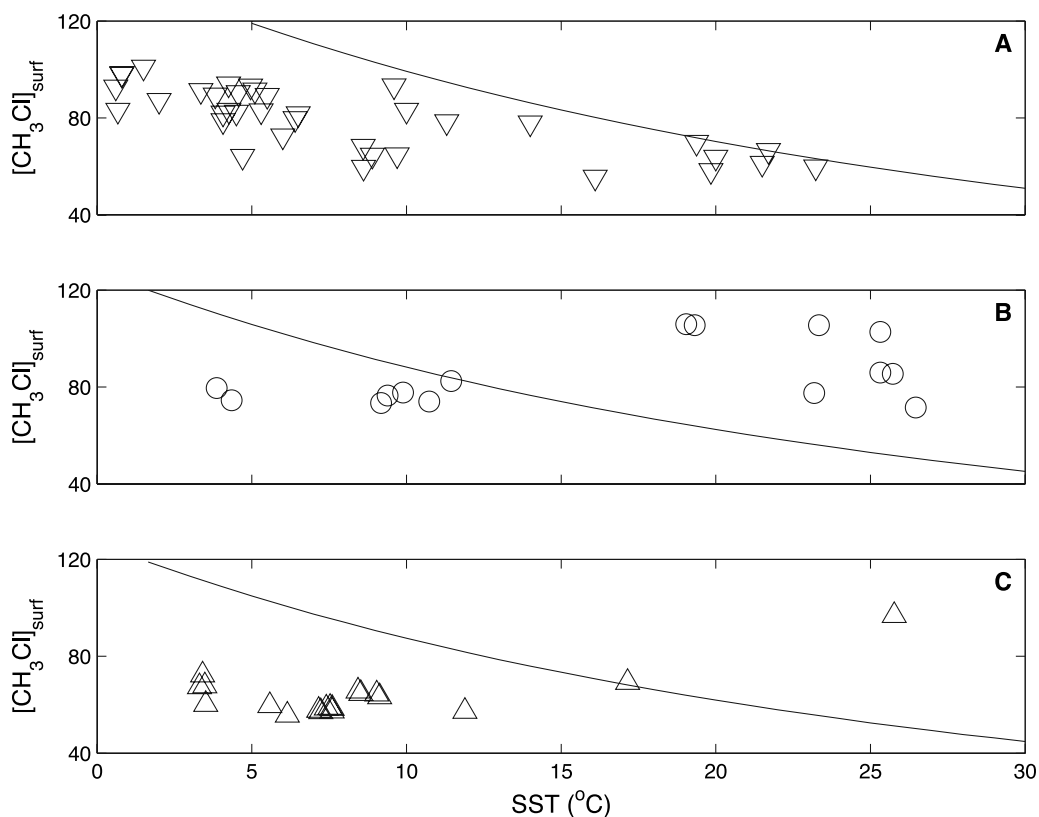
Figure 3. Surface concentrations of CH_3Cl plotted against sea surface temperature for the (a) spring, (b) summer, and (c) fall cruises in the NW Atlantic. The curves indicate the concentrations that would correspond to equilibrium with the atmosphere.

more improbable that physical effects such as warming could account for observed supersaturations.

[13] There are a number of ways in which relationships between CH_3Cl concentrations and temperature can be used to estimate global fluxes of the gas between ocean and atmosphere. A simple approach used by *Moore et al.* [1996] involved determining the temperature of the transition between undersaturated and supersaturated waters from observations in the NW Atlantic in July 1995. The average flux was determined for both the sampled cool, undersaturated waters and the sampled warm, supersaturated waters. The areas of the ocean having average annual temperatures below and above the threshold ($12°C$) were determined, and the global effluxes and influxes were scaled up to those areas. The same authors pointed out that the oceanic distribution of pCH_3Cl could be approximated by that corresponding to a uniform concentration of 96 pM (using improved solubility data would change that value to 85 pM). This would allow a value of pCH_3Cl to be estimated for any surface water based solely on its temperature. Such information when combined with a knowledge of atmospheric pCH_3Cl as a function of latitude and season can provide the ΔC term in the flux equation, $f = K\Delta C$, where K is the piston velocity (dependent on wind speed and temperature) and ΔC is the difference in concentration of CH_3Cl between the value at equilibrium with the atmosphere and the measured value in surface waters. Thus, with knowledge of wind speed over the ocean and the relationship between wind speed and piston velocity [*Wanninkhof*, 1992], the flux

of CH_3Cl across the ocean surface can be estimated for any location.

[14] We show that the concentration anomaly for our Atlantic data set has a strong linear correlation with temperature Figure 4. It is also apparent that the relationship is similar to that derived from data sets from other regions including the north and south Pacific. The current study gives a clue to the origin of scatter in $\Delta[CH_3Cl]$ data in these relationships with temperature. Waters in the temperature range $20-25°C$ increase their concentration from spring to summer from around $60-70$ pM to $80-110$ pM. Temperature is therefore a good but insufficient predictor of CH_3Cl concentration. It follows that the uncertainty in global estimates of oceanic CH_3Cl fluxes might be reduced if empirical relationships were used that were season-specific. This approach has been adopted in studies of marine methyl bromide fluxes [*King et al.*, 2002; *Tokarczyk and Moore*, 2006].

[15] We have calculated fluxes in two ways: A. using the correlation between all concentration anomalies and sea surfaces temperatures without regard to seasons, and B. using 3 separate seasonal correlations. In the absence of winter data the assumption was made that the undersaturations observed in spring would occur also in winter. In addition to the concentrations measured in this study of the NW Atlantic, our calculations have used data from a Pacific cruise on NOAAS Discoverer in 1995 between Seattle and Hobart [*Groszko*, 1999] and an Atlantic cruise from Halifax to Port of Spain, Trinidad on R/V *Knorr* in July–August 1997 [*Groszko*, 1999]. Concentration anomalies were
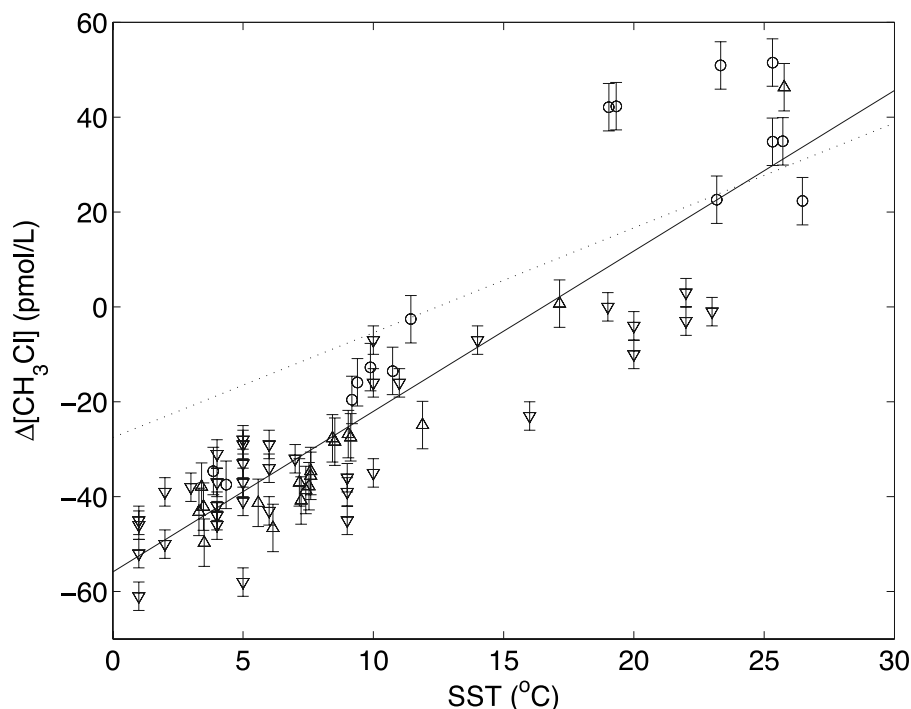
Figure 4. Concentration anomaly of CH_3Cl in surfaces waters for the three seasons plotted against sea surface temperature. Spring data are denoted by downward triangles, summer by circles, and fall by upward triangles. Also shown are the best fit lines for the regression of this data set (solid line), and the combined data from the *Hudson* [1995], *Discoverer* [1995], and *Knorr* [1997] cruises (dotted line).

calculated in $4° \times 5°$ boxes [*Takahashi et al.*, 2002] using the linear relationship between concentration anomaly and sea surface temperature. Net fluxes were calculated as the product of piston velocity and concentration anomaly; the results are presented in Table 2. The bracketed numbers are the uncertainties which were estimated by combining a 25% relative error in piston velocity [*Takahashi et al.*, 2002] and the error in the concentration anomaly-temperature correlation. It should be noted that larger uncertainties in piston velocity (up to a factor of 2) are suggested by comparisons of the different formulations for the wind speed dependence of piston velocity [*Nightingale et al.*, 2000].

[16] It is apparent that the net flux of CH_3Cl from the ocean to the atmosphere, which amounts to only 3.5% of the total supply to the atmosphere, is substantially lower when calculated using seasonal data rather than annual. A major contributor to the difference comes from the assumption that winter conditions are the same as in spring, that is, waters are undersaturated everywhere. This tends to give a larger influx to undersaturated regions and also to reduce the efflux from supersaturated areas.

[17] The approach used above for estimating global ocean-atmosphere exchanges of CH_3Cl can, with caution, be applied to the problem of estimating the influence of a warming of ocean waters on CH_3Cl fluxes. The caution is necessary because, in the absence of knowledge of how the gas is produced, it cannot be assumed that the link between temperature and saturation anomaly is causal. It is found that for a $1°C$ warming the annual net global flux to the atmosphere from the ocean would increase by $6 (\pm14) \times 10^9$ moles. This change comprises an increased flux from warm regions of $4 (\pm9) \times 10^9$ moles y^{-1}, and a decreased

uptake by cold waters of $2 (\pm8) \times 10^9$ moles y^{-1}. The non-season-specific correlation gives almost the same result: $6 (\pm9) \times 10^9$ moles/y. This appears to be potentially significant in comparison with the net marine flux to the atmosphere of $6.4–8 \times 10^9$ moles y^{-1} reported by *Moore* [2000], but small relative to the combined marine and terrestrial sources 8×10^{10} moles y^{-1}.

[18] The basis for the temperature relationship between CH_3Cl concentration anomaly is currently not understood. It is apparent that there is net production in warm waters and it is also known that consumption occurs in both warm and cold waters [*Tokarczyk et al.*, 2003a, 2003b] but outweighs production in cold waters. There are several factors that could lead to greater production in warm than cold waters. The rates of reaction of both CH_3I and CH_3Br with Cl^- in seawater are much faster in warm waters but the origins of these two other methyl halides are as poorly understood as CH_3Cl itself. It is possible that CH_3Cl is produced biologically from organisms whose distribution is dependent on

Table 2. Estimates of Global Influxes and Effluxes Calculated From the Data Sets Listed in the Text Using a Single Relationship Between Concentration Anomaly and SST (Line 1) and Separate Relationships for Each Season[a]

	Threshold T, °C	Influx, Gmol/y	Efflux, Gmol/y	Total Flux, Gmol/y
Annual	15	13.5 (6.2)	30.2 (11.5)	16.6 (13.1)
Spring/Winter	18	11 (5.1)	11.1 (4.2)	0.1 (6.8)
Summer	14	2.6 (1.2)	7.7 (3.0)	5.1 (3.2)
Fall	18	5.6 (2.6)	6.3 (2.4)	0.8 (3.5)
Total		19.2 (5.8)	25.2 (5.7)	6.0 (8.1)

[a]The last line gives the sum of the seasonal fluxes.
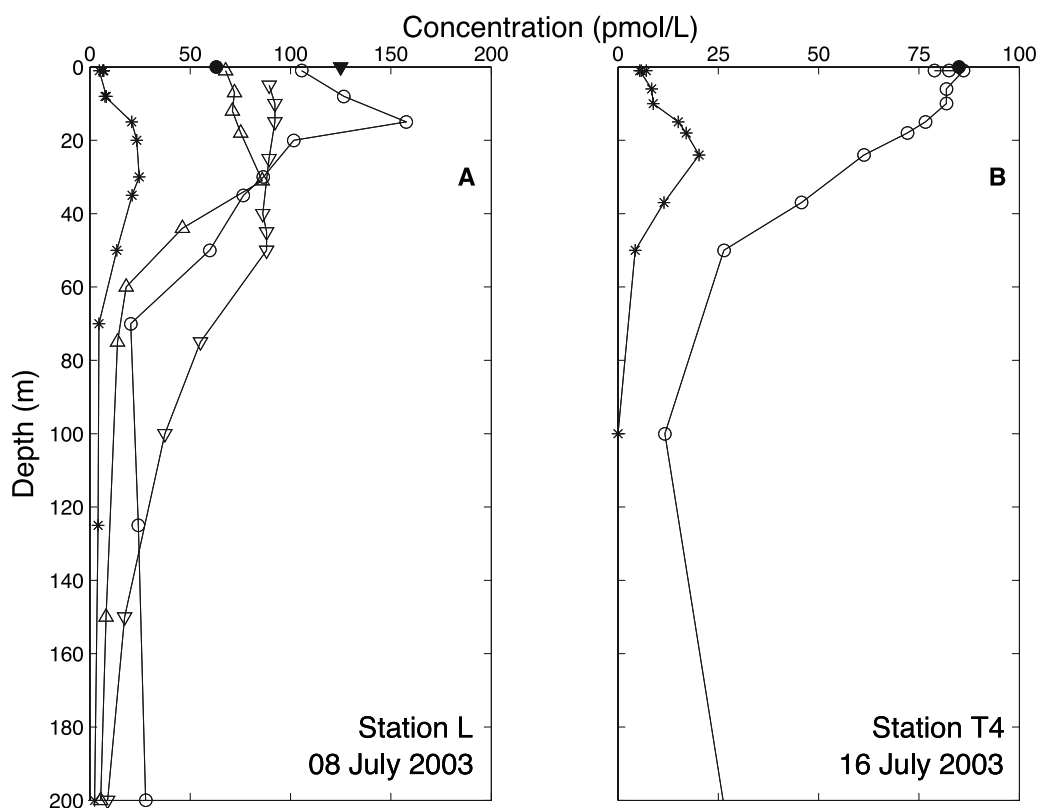
Figure 5. (a) The seasonal variation in methyl chloride profiles at station L; spring data are indicated by downward triangles, summer by circles, and fall by upward triangles. Also shown is the summer profile of isoprene (stars); (b) methyl chloride and isoprene profiles measured in summer at station T4. Saturation values are indicated by solid symbols at the surface.

temperature. It is also possible that photochemistry plays a role in its production. There are literature reports of such a source for CH_3I [*Moore and Zafiriou*, 1994; *Richter and Wallace*, 2004], and a recent report of photochemical production of CH_3Cl in chloride-containing waters that have a high concentration of colored dissolved organic matter (CDOM) [*Moore et al.*, 2006]. The question of correlations between CH_3Cl and indices of algal abundance and radiant exposure is addressed further below.

[19] Depth profiles typically show low concentrations of CH_3Cl at depths of 200–300 m, and higher concentrations near the surface, constant through the mixed layer. The highest concentrations occur within a maximum beneath the mixed layer: this feature was found to be most common and pronounced during summer when the highest surface concentrations were also seen, and virtually absent in spring when surface waters were undersaturated. The seasonal variation at station L is illustrated in Figure 5a. For comparison the summer profile of the trace gas, isoprene is also shown. This gas is known to be biogenic and has been shown to be widely produced by phytoplankton. Its maximum is interpreted as an effect of restricted ventilation coupled with decreasing production with depth and background consumption that is probably microbial. The concentration maxima of the methyl halides should similarly not be regarded as evidence for higher production rates than at shallower depths, but rather less efficient loss to the atmosphere of gases in these waters beneath the mixed layer. Based on this proposed explanation for the existence

of subsurface maxima, reasons why they are not always seen (as in the springtime profiles) would be that there is no net production at that depth, or the system is not in a steady state and the maximum has not developed beneath a recently established surface mixed layer. Maxima were frequently observed to coexist for methyl chloride and iodide, but were typically much more intense for the latter probably due to its much lower atmospherically supported background concentration. Correlations between the different methyl halides are discussed below.

[20] Although the isoprene and CH_3Cl profiles are similar, it can be demonstrated that there are major differences in the source by reference to more northerly stations, for instance T4 (Figure 5b), where isoprene retains the same type of profile but CH_3Cl shows no maximum. The difference in sources of the gases was illustrated in *Moore and Wang* [2006] in an iron fertilization experiment in the NE Pacific where it was shown that stimulation of increased production of isoprene was not matched by measurable change in the methyl halides. It is possible that CH_3Cl, like isoprene, does have an algal source, but as suggested by laboratory experiments [*Scarratt and Moore*, 1996, 1998] there is a lag between active growth and CH_3Cl release, perhaps resulting from the involvement of degradation processes.

[21] During these cruises, measurements were made of methyl bromide [*Tokarczyk and Moore*, 2006] and methyl iodide [*Wang*, 2006] in addition to methyl chloride. A comparison of the distributions of the 3 compounds could perhaps shed some light on their origin or, at least indicate
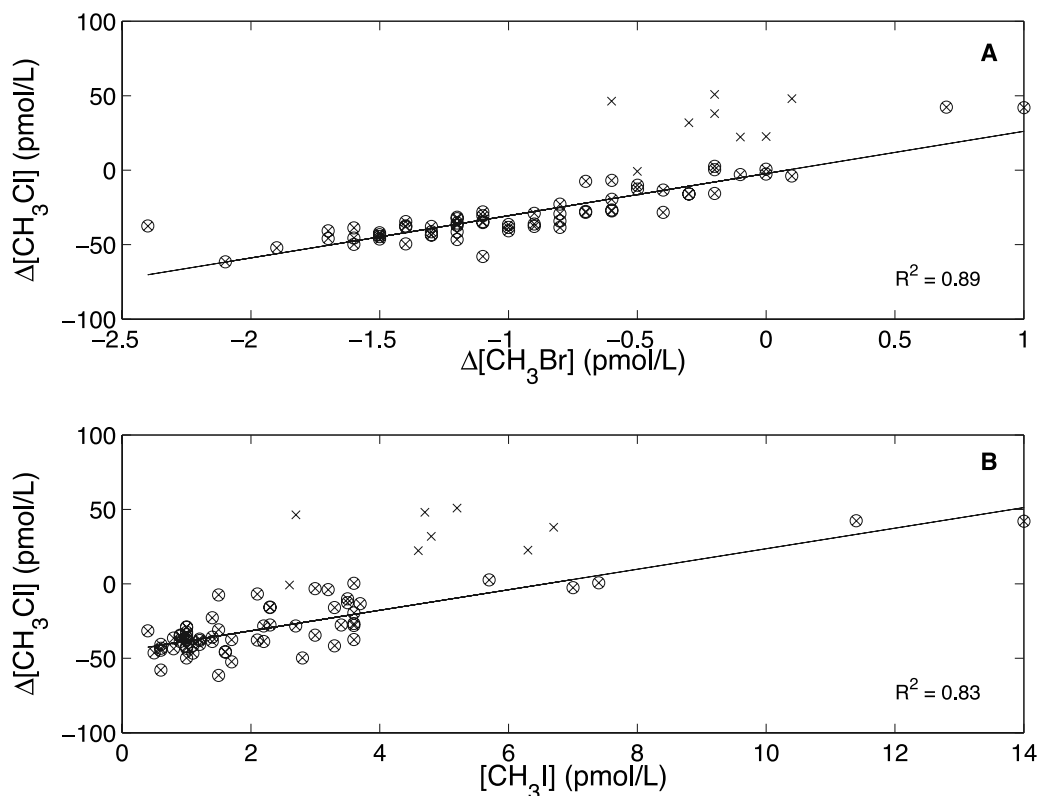
Figure 6. (a) Plot of saturation anomaly of CH_3Cl against saturation anomaly of CH_3Br, and (b) saturation anomaly of CH_3Cl against concentration of CH_3I. Crosses represent all data points, and circled symbols are those for water temperatures less than 23°C.

whether they show evidence for having a common source (or sources), or sinks. At the outset it is known that CH_3Cl has a portion of its production in the reaction of the other two compounds with chloride ion, particularly in warm waters. It is proposed that, if the methyl halides have a significant source in common, their distributions should show some similarities. Both CH_3Cl and CH_3Br have surface concentrations that are in part imposed by their presence in the atmosphere, so their concentrations will be considered in terms of concentration anomaly in order to reduce the atmospheric influence (Figures 6a and 6b). The atmospheric concentration of CH_3I being much lower, the comparison with this gas will be made simply using its concentration in seawater (Figure 6b). It is seen that there are strong correlations when waters cooler than 23°C are arbitrarily selected to reduce the influence of CH_3Cl production by nucleophilic reactions of CH_3Br and CH_3I.

[22] The strongest correlation was observed between $\Delta[CH_3Cl]$ and $\Delta[CH_3Br]$ but, over most of temperature range in which the correlation occurred, CH_3Cl and CH_3Br were undersaturated, that is, the waters were acting as a net sink, with supply coming at least in part from the atmosphere. The correlation may be due to the existence of common loss processes, probably microbial, as supported by the limited studies that have been made of loss rates of these gases in the ocean [*Tokarczyk et al.*, 2003a]. The slightly weaker correlation between $\Delta[CH_3Cl]$ and CH_3I is difficult to explain. It appears that net consumption of CH_3Cl is occurring alongside net production of CH_3I. The few measurements that were made of CH_3I loss rates

[*Moore et al.*, 2006] were low for cold waters (1–9% day^{-1}). The highest concentrations of all three gases in waters cooler than 23°C occurred in the same samples; these were from station L in the summer.

[23] Attention is given to two possible sources: algal and photochemical. The first is considered because there is substantial evidence for production, albeit at low levels, of methyl halides from phytoplankton in laboratory cultures [*Manley and de la Cuesta*, 1997; *Scarratt and Moore*, 1996, 1998], and the second because there is some evidence for the production of CH_3I in laboratory and field studies [*Moore and Zafiriou*, 1994; *Richter and Wallace*, 2004]. Considering the possible algal source, it has been shown [*Moore et al.*, 1996] that there is no simple correlation between CH_3Cl and chlorophyll a, but it is possible that production could be significant from selected groups of algae that can be characterized by other pigments. Correlations were examined between net production of CH_3Cl (moles m^{-3} d^{-1}) and 13 algal pigments where net production is given by:

$$\text{Net production} = K \times \Delta[CH_3Cl]/MLD + (K_I[CH_3I] + K_{Br}[CH_3Br])[Cl^-]$$

where K is the piston velocity, MLD the mixed layer depth, K_I, K_{Br}, the rate constants for reaction of CH_3I and CH_3Br with chloride ion [*Elliott and Rowland*, 1993]. This assumes that the concentration of CH_3Cl at the surface is at steady state with respect to production and loss to the atmosphere. No positive correlation was found for the data set that combined all

seasons, but negative correlations emerged for alloxanthin, chlorophyll c_2, and diatoxanthin. The first of these pigments is characteristic of Cryptophytes, an algal class that also possesses chlorophyll c_2 [*Jeffrey et al.*, 1997]. The inverse correlation might arise from the fact that Cryptophytes were found to be more abundant in the cooler more northerly waters (M. Levasseur, personal communication) which were also characterized by lower saturation levels of CH_3Cl.

[24] Regarding possible photochemical production of CH_3Cl, the same measure of net production rate was found not to be significantly correlated with the depth-averaged daily radiant exposure in the mixed layer. This finding does not support the idea that CH_3Cl has a major photochemical source in ocean waters.

4. Summary/Conclusions

[25] The concentration of CH_3Cl and its level of saturation in the NW Atlantic were found to be strongly seasonal and to vary spatially. During spring no supersaturation was observed while, in summer, warm waters had higher concentrations and were supersaturated. During the fall concentrations were lower and only the warmest waters (in a more limited data set) were supersaturated.

[26] The concentration anomaly of CH_3Cl shows a strong dependence on temperature and the relationship is of value in global extrapolation of limited data sets. There is potential for improving predictions of methyl chloride concentration anomaly if seasonality is taken into account.

[27] There was a strong correlation between the concentration anomalies of CH_3Cl and CH_3Br in waters cooler than 23°C suggesting the existence of similarities in production and/or loss of the gases. Since the waters concerned were undersaturated in both gases it is clear that both must have had an atmospheric source component, and both are likely to experience microbial loss. There was a slightly weaker correlation between the concentration anomaly of CH_3Cl and the concentration of CH_3I.

[28] No positive correlation was found between production of CH_3Cl and the concentration of algal pigments, but there was a negative correlation with alloxanthin, chlorophyll c_2, and diatoxanthin. This might be attributable to the observation that the cooler northerly waters were not favorable to CH_3Cl production but did support greater abundances of Cryptophytes. No correlation was found with surface radiant exposure; this suggests that photochemical production is not the major source, or that other factors, such as the presence of a suitable organic substrate, exert a major control over any such process.

References

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

Groszko, W. (1999), An estimate of the global air-sea flux of methyl chloride, methyl bromide, and methyl iodide, Ph.D. thesis, Dalhousie Univ., Halifax.

Jeffrey, S. W., R. F. C. Mantoura, and S. W. Wright (1997), Phytoplankton pigments in oceanography: Guidelines to modern methods, U. N. Educ., Sci., and Cult. Org., Paris.

King, D. B., J. H. Butler, S. A. Yvon-Lewis, and S. A. Cotton (2002), Predicting oceanic methyl bromide saturation from SST, *Geophys. Res. Lett.*, 29(24), 2199, doi:10.1029/2002GL016091.

Manley, S. L., and J. L. de la Cuesta (1997), Methyl iodide production from marine phytoplankton cultures, *Limnol. Oceanogr.*, 42(1), 142–147.

Montzka, S. A., et al (2003), Controlled substances and other source gases, in *Scientific Assessment of Ozone Depletion: 2002, Rep. 47*, chap. 1, Global Ozone Res. and Monit. Proj., Geneva.

Moore, R. M. (2000), The solubility of a suite of low molecular weight organochloride compounds in seawater and implications for estimating the marine source of methyl chloride to the atmosphere, *Chemosphere Global Change Sci.*, 2, 95–99.

Moore, R. M., and L. Wang (2006), The influence of iron fertilization on the fluxes of methyl halides and isoprene from ocean to atmosphere in the SERIES experiment, *Deep Sea Res., Part II*, 53, 2398–2409.

Moore, R. M., and O. C. Zafiriou (1994), Photochemical production of methyl iodide in seawater, *J. Geophys. Res.*, 99(D8), 16,415–16,420.

Moore, R. M., W. Groszko, and S. J. Niven (1996), Ocean-atmosphere exchange of methyl chloride: Results from NW Atlantic and Pacific Ocean Studies, *J. Geophys. Res.*, 101(C12), 28,529–28,538.

Moore, R. M., P. Wan, and E. Arctander (2006), A proposed mechanism for the production of methyl halides by light-induced reactions of CDOM, *Eos Trans. AGU*, 87(36), Ocean Sci. Meet. Suppl., Abstract OS53K-02.

Nightingale, P. D., G. Malin, C. S. Law, A. J. Watson, P. S. Liss, M. I. Liddicoat, J. Boutin, and R. C. Upstill-Goddard (2000), In situ evaluation of air-sea gas exchange parameterizations using novel conservative and volatile tracers, *Global Biogeochem. Cycles*, 14(1), 373–387.

Redeker, K. R., N.-Y. Wang, J. C. Low, A. McMillan, S. C. Tyler, and R. J. Cicerone (2000), Emissions of methyl halides and methane from rice paddies, *Science*, 290, 966–969.

Rhew, R. C., B. R. Miller, and R. F. Weiss (2000), Natural methyl bromide and methyl chloride emissions from coastal salt marshes, *Nature*, 403, 292–295.

Rhew, R. C., L. Østergaard, E. S. Saltzman, and M. F. Yanofsky (2003), Genetic control of methyl halide production in Arabidopsis, *Curr. Biol.*, 13, 1809–1813.

Richter, U., and D. W. R. Wallace (2004), Production of methyl iodide in the tropical Atlantic Ocean, *Geophys. Res. Lett.*, 31, L23S03, doi:10.1029/2004GL020779.

Scarratt, M. G., and R. M. Moore (1996), Production of methyl chloride and methyl bromide in laboratory cultures of marine phytoplankton, *Mar. Chem.*, 54, 263–272.

Scarratt, M. G., and R. M. Moore (1998), Production of methyl bromide and methyl chloride in laboratory cultures of marine phytoplankton II, *Mar. Chem.*, 59, 311–320.

Takahashi, T., et al. (2002), Global sea-air CO_2 flux based on climatological surface ocean pCO_2, and seasonal biological and temperature effects, *Deep Sea Res., Part II*, 49, 1601–1622.

Thompson, T. M., et al. (Eds.) (2003), Halocarbons and other atmospheric trace species, *Clim. Monit. Diagn. Lab. Summary Rep. 27*, pp. 115–135, Earth Syst. Res. Lab., Natl. Oceanic and Atmos. Assoc., Boulder, Colo.

Tokarczyk, R., and R. M. Moore (2006), A seasonal study of methyl bromide concentrations in the North Atlantic (35°–60°N), *J. Geophys. Res.*, 111, D08304, doi:10.1029/2005JD006487.

Tokarczyk, R., K. D. Goodwin, and E. S. Saltzman (2003a), Methyl chloride and methyl bromide degradation in the Southern Ocean, *Geophys. Res. Lett.*, 30(15), 1808, doi:10.1029/2003GL017459.

Tokarczyk, R., E. S. Saltzman, R. M. Moore, and S. A. Yvon-Lewis (2003b), Biological degradation of methyl chloride in coastal seawater, *Global Biogeochem. Cycles*, 17(2), 1057, doi:10.1029/2002GB001949.

Wang, L. (2006), Spatial and seasonal variation of methyl iodide in the NW Atlantic, Master's thesis, Dalhousie Univ., Halifax.

Wanninkhof, R. (1992), Relationship between wind speed and gas exchange over the ocean, *J. Geophys. Res.*, 97(C5), 7373–7382.

Yokouchi, Y., M. Ikeda, Y. Inuzuka, and T. Yukawa (2002), Strong emission of methyl chloride from tropical plants, *Nature*, 413, 163–165.

Yvon-Lewis, S. A., D. B. King, R. Tokarczyk, K. D. Goodwin, E. S. Saltzman, and J. H. Butler (2004), Methyl bromide and methyl chloride in the Southern Ocean, *J. Geophys. Res.*, 109, C02008, doi:10.1029/2003JC001809.

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