JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 104, NO. C5, PAGES 11,163–11,171, MAY 15, 1999

Methyl iodide distribution in the ocean and fluxes to the atmosphere

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Abstract. Methyl iodide concentrations have been measured in air samples, surface, and subsurface waters of the NW Atlantic, NE Atlantic, and Pacific Oceans. They are shown to be substantially oversaturated in all surface waters. Our best estimate of methyl iodide flux from the ocean to the atmosphere is 0.9 –2.5 x 10^9 mol yr^{-1}, but further substantial and unquantifiable uncertainities exist because of the limited spatial and temporal data on which this flux estimate is based. Pronounced subsurface maxima in methyl iodide concentrations seen in the Pacific Ocean and the Sargasso Sea are thought to result from production and accumulation of the gas in the relatively poorly ventilated waters beneath the surface mixed layer. Our calculations suggest that latitudinal variations in methyl iodide concentrations in the Pacific Ocean are partly controlled by temperature-dependent chemical loss.

1. Introduction

Methyl iodide is of interest as a major carrier of gas phase iodine from the ocean into the atmosphere. The atmosphere, in turn, supplies iodine in precipitation to marine and terrestrial environments, a flux that is relevant to supplying the needs of living organisms for this essential element, particularly in regions far from the ocean. It was *Lovelock et al.* [1973] who first proposed that methyl iodide was produced in the oceans and acted as an important iodine carrier. The gas is known to be produced by marine seaweeds [*Manley and Dastoor*, 1987, 1988], but its possible production by phytoplankton has until recently [*Moore et al*, 1996a; *Manley and de la Cuesta*, 1997] been largely speculative. Laboratory studies have pointed to the possibility that photochemical reactions contribute to the production of methyl iodide in surface seawater [*Moore and Zafiriou*, 1994], support for which was put forward by *Happell and Wallace* [1996] based on their analysis of factors affecting saturation anomalies of CH_3I in the Greenland/Norwegian Seas and the tropical Atlantic.

In the atmosphere, methyl iodide is rapidly broken down by photolysis. A number of studies have considered possible reactions of iodine in the atmosphere, and for a period of time it was thought that the IO radical might play a significant role in the oxidation of dimethyl sulfide. This reaction was subsequently shown to be too slow to be of importance [*Daykin and Wine*, 1990]. *Solomon et al.* [1994] have suggested from modeling studies that there is a potential role for iodine in controlling ozone in the lower stratosphere. It is clear that the kinetics of iodine reactions are conducive to such a role, but the supply of the element to high altitudes demands rapid transport because of the short lifetime of methyl iodide (~5 days [*Zafiriou*, 1974]) with respect to photolysis and of iodine atoms with respect to rain-out as HI.

The nucleophilic reaction of methyl iodide with chloride in seawater has been considered as a source of a part of the methyl chloride produced in the ocean [*Zafiriou*, 1975]. In view of the recent finding [*Moore et al.*, 1996b] that the flux of methyl chloride from the ocean to the atmosphere is very much less than formerly believed, it is worth re-evaluating the potential contribution made to methyl chloride production by this reaction. This paper provides information on the horizontal and vertical distribution of methyl iodide in the oceans, its production rate, and flux to the atmosphere.

Paper number1998JC900073.
0148-0227/99/1998JC900073$09.00

2. Methods

The data presented here were collected during three cruises: in the Labrador Sea and Sargasso Sea in July 1995 (Canadian Scientific Ship *Hudson*), in the Pacific Ocean on a transect between Seattle and Hobart in October/November 1995 (National Oceanic and Atmospheric Administration Ship *Discoverer*), and in the eastern Atlantic off Ireland in June 1996 (Royal Research Ship *Challenger*) (Figure 1).

Water samples were collected in 10 L Niskin bottles (2 L Knudsen bottles in the *Challenger* cruise) or with a bucket and subsampled into glass 100 mL syringes that were stored under water until analysis, a period averaging about 3 hours. On the *Hudson* and *Discoverer* cruises, surface equilibrator samples and ambient air samples were also taken. Two equilibrators were used, one based on the design of R. F. Weiss of Scripps Institution of Oceanography [*Butler et al.*, 1988] and the other a semipermeable membrane equilibrator [*Groszko and Moore*, 1998]. The purge and trap and gas chromatograph-mass spectroscopy (GC-MS) equipment and procedure have been described by *Moore et al.* [1996b].

Calibration was done with a gravimetrically produced standard containing 98.7 parts per billion (ppb) of methyl iodide in nitrogen contained in an Aculife-treated aluminium cylinder. The standard was measured using Hamilton syringes, and volumes between 10 and 200 μL were injected via a septum port. The resulting calibration curves were linear. A blank was established each day by running the system without a water or air sample or by repeatedly purging a water sample so that it was free of dissolved methyl iodide. Average blanks for the water analyses were equivalent to 0.05 and 0.04 pmol L^{-1} for the

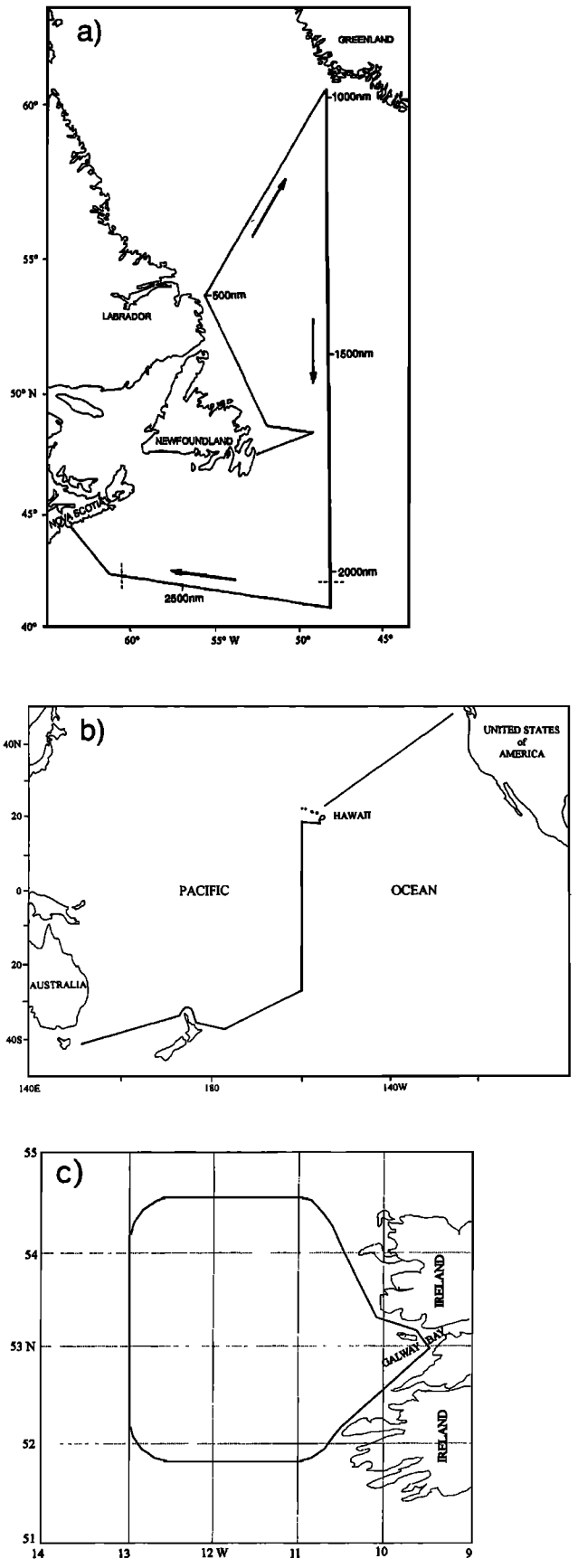

Figure 1. Cruise tracks for (a) CSS *Hudson*, 1995; (b) NOAA Ship *Discoverer*, 1995; and (c) the boundary of the region surveyed in RRS *Challenger* cruise, 1996. In (a) the Gulf Stream boundaries are denoted by dashed lines.

Discoverer and *Challenger* cruises, respectively, but were relatively high at 0.37 pmol L^{-1} for the *Hudson* samples. A possible source of the blank is accumulation of organic matter from water samples in the frit of the purge vessel. Steps taken to reduce this were filtering samples through glass fiber filters held in a stainless steel holder and occasional replacement of the purge vessel. The standard deviation of a set of five replicate measurements of a water sample on the *Discoverer* cruise (2.30 pmol L^{-1}) was 0.04 pmol L^{-1}.

Average blanks for the gas phase (equilibrator and air) measurements were equivalent to partial pressures of about 0.7 patm for the *Hudson* cruise and 0.2 patm for the *Discoverer* cruise, and the detection limit (3 times the standard deviation of the blank) for both cruises was 0.2 patm. Typical equilibrator samples were ~100 times the detection limit, and while several *Discoverer* air samples contained methyl iodide near the detection limit, there was never any difficulty in detecting it in an air sample.

3. Results and Discussion

3.1. Surface concentrations

Figure 2 shows the surface concentrations of methyl iodide together with sea surface temperature and chlorophyll *a* along the cruise track starting in St. John's, Newfoundland, and finishing in Halifax, Nova Scotia. Also shown are the partial pressure of methyl iodide from the equilibrator measurements and its partial pressure in the ambient atmosphere. The cool waters of the Labrador Sea had, with few exceptions, surface methyl iodide concentrations typically less than 2.5 pmol L^{-1}, but higher concentrations were encountered in the warm waters of the Gulf Stream. It is clear from Figure 2 that there is no simple relationship between methyl iodide and chlorophyll *a*; indeed, the Gulf Stream waters, though tending to be relatively high in methyl iodide, had much lower concentrations of chlorophyll *a* than existed in areas of the Labrador Sea.

The data on partial pressure in equilibrator and air samples (Figure 2d) indicate supersaturation of methyl iodide in surface waters along the cruise track, with partial pressures in surface water around 3 to 15 patm in the cold Labrador Sea water, increasing abruptly to ~45 patm at the Gulf Stream boundary. The mean atmospheric mole fraction over the entire *Hudson* cruise track is 1.7±0.2 parts per trillion (ppt).

The surface concentrations of methyl iodide along the Pacific Ocean transect are plotted in Figure 3b as a function of latitude. The main feature is a marked tendency for concentrations to decrease with latitude, a result that seems most likely to be related to water temperature and perhaps irradiance as discussed below. Concentrations lie between 2 and 6 pmol L^{-1}. It should be noted that at 34°S the cruise track passes through coastal waters of New Zealand.

The equilibrator analyses of Pacific surface water (Figure 3c) show ubiquitous supersaturation, with partial pressures typically between 12 and 50 patm. There is one unusually high data point with a partial pressure of 80 patm. This unusual sample was taken at 33°S and 167°W, about 500 nautical miles (926 km) east of New Zealand, and is not one of the coastal samples. The mean atmospheric mole fraction over the entire Pacific cruise was 0.68±0.09 ppt.

A comparison of the partial pressures of methyl iodide in surface water as measured directly using the equilibrator and calculated from the water analyses using the Henry's law

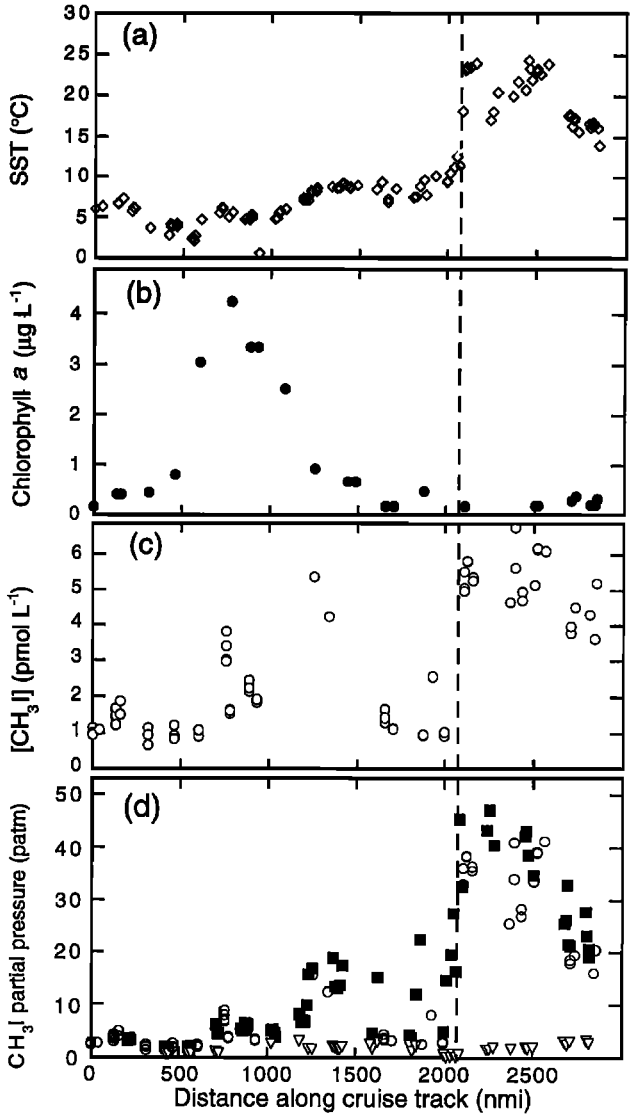

Figure 2. NW Atlantic, (1995) data, including (a) sea surface temperature (b) chlorophyll *a* (c) surface CH_3I concentration, and (d) CH_3I partial pressure in equilibrator (solid squares) and calculated from water analyses (open circles) and atmospheric partial pressures (open triangles), all plotted against distance in nautical miles along the cruise track. The vertical dashed line denotes the position of the Gulf Stream boundary.

constant reported by *Moore et al.* [1995] is illustrated in Figure 2d. For the Pacific data, see Figure 3c. There is general good agreement between the two methods, but in the case of the Atlantic data the equilibrator values between 1500 and 2000 nautical miles (2778 and 3704 km) are scattered, with the lower numbers matching the water analyses. In a portion of the Pacific cruise the equilibrator values are higher than the purge-and-trap measurements.

Data collected in the eastern Atlantic off Ireland during June 1996 are from a limited area (Figure 1) and cannot be usefully plotted against the ship track or latitude because the track was tortuous and frequently crossed itself. The 45 surface purge-and-trap measurements are therefore described in terms of their mean, 3.4 pmol L^{-1}; range, 1.2-8.2 pmol L^{-1}; and standard deviation, 1.7 pmol L^{-1}. No equilibrator was in operation during this cruise. There were indications during the fieldwork that the surface concentrations of methyl iodide were showing some dependence on chlorophyll *a*. However, a plot of these two quantities for the entire data set (Figure 4) does not support the idea of any simple correlation between the two quantities. On the other hand, when a single transect was monitored over a period of 5.5 hours, a time series was obtained (Figure 5) that does suggest some relationship between the two quantities over this relatively small temporal and spatial scale. A possible explanation for these results would be production of methyl iodide by specific organisms, the abundance of which is not necessarily correlated with total chlorophyll.

Our measured atmospheric mole fractions are consistent with those previously reported in the literature. *Reifenhäuser and Heumann* [1992] have tabulated data on atmospheric concentrations of methyl iodide from various sources, and show that typical mole fractions are 1-2.5 ppt, with the higher values being recorded in the Antarctic (their own measurements),

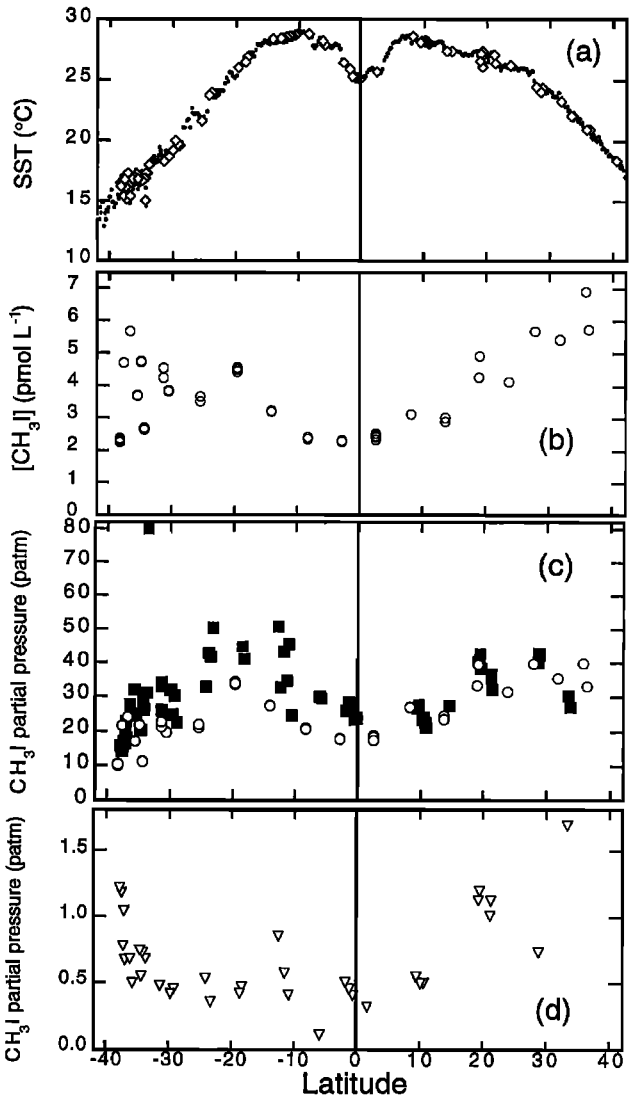

Figure 3. Pacific data of (a) sea surface temperature, with diamonds denoting locations where samples were collected, and other points from the hourly log, (b) surface concentrations of CH_3I (c) partial pressure of CH_3I in equilibrator (solid squares) and calculated from water analyses (open circles), and (d) partial pressure of CH_3I in atmosphere on an expanded scale, all plotted against latitude.

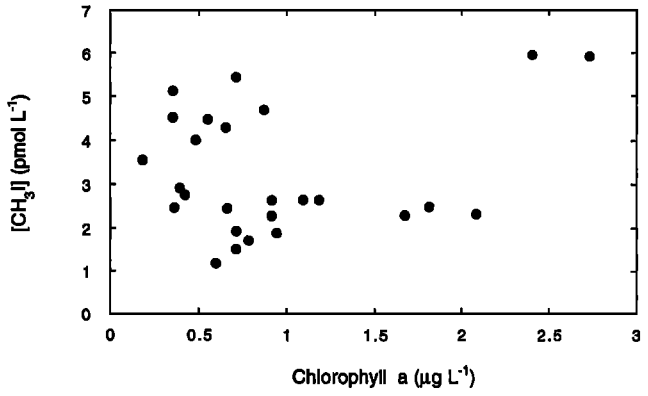

Figure 4. East Atlantic data, 1995, of CH_3I concentration plotted against chlorophyll *a* for all surface samples.

Tasmania, and Hawaii [*Rasmussen et al.*, 1982]. *Happell and Wallace* [1996] reported atmospheric mole fractions over the Greenland-Norwegian Sea area in November of 2.4±0.1 ppt. *Oram and Penkett* [1994] measured mole fractions in East Anglia that were typically less than 2 ppt, but with occasional peaks as high as 43 ppt (1989) and 29 ppt (1990).

The large supersaturations of methyl iodide in surface waters of the Labrador Sea found in this study are in contrast with methyl chloride [*Moore et al.*, 1996b] and bromide [*Moore and Webb*, 1996], both of which were measured at the same time and found to be undersaturated. However, the mean lifetime of methyl iodide in the atmosphere is very short because of its ready photolysis, and this tends to keep atmospheric concentrations very low, thereby promoting supersaturation in waters where any production occurs.

3.2. Flux Estimates

Flux estimates have been made in two independent ways using first, the water analyses and second, the equilibrator data. Since a typical seawater methyl iodide concentration of 3 pmol L^{-1} has an equivalent partial pressure of 8-18 patm at temperatures from 5-28°C, and atmospheric partial pressures measured in this work are of the order of 1 patm, it is apparent that typical concentrations of methyl iodide in surface ocean waters are greatly supersaturated. Consequently, the ocean-to-atmosphere flux is given by the product of the surface water concentration and a piston velocity. The latter may be calculated from the wind speed u, (m s^{-1}) and the Schmidt number for the gas (Sc) at the appropriate temperature using one of the formulas given by *Wanninkhof* [1992]:

$$k = 0.31\ u^2\ (Sc/660)^{-0.5}$$
$$k = 0.39\ (u_{av})^2\ (Sc/660)^{-0.5}$$

where u_{av} is a long-term average wind speed.

Since the molecular diffusion coefficient of methyl iodide in seawater appears not to have been measured, its Schmidt number has been estimated from that for methyl bromide [*De Bruyn and Saltzman*, 1997], by assuming that the ratio of the diffusivities is inversely proportional to the ratio of the molar volumes V_b (at the normal boiling point) to the power 0.6 [*Wilke and Chang*, 1955]. The molar volumes V_b for methyl iodide and methyl bromide were taken to be 62.9 and 52.9 $cm^3\ mol^{-1}$, respectively [*Reid et al.*, 1987]. The resulting formula for calculating the Schmidt number of methyl iodide is given below:

$$Sc(CH_3Br) = 2004 - 93.5\ T + 1.39\ T^2$$

[*De Bruyn and Saltzman*, 1997]

$$Sc(CH_3I) = (62.9 / 52.9)^{0.6}\ (Sc(CH_3Br))$$

where T is the temperature in degrees Celsius. This method of approximating the Schmidt number of methyl iodide is discussed in greater detail by *Groszko* [1999].

First, we give flux estimates based on the water analyses. The exchange velocities have been calculated using the spot wind speeds. The fluxes for the Pacific data set are shown in Figure 6; the average is 16.0 (range 1.8-64) nmol $m^{-2}\ d^{-1}$. Average fluxes for the Labrador Sea and eastern Atlantic data sets are 11.9 (range 0.3-55) and 25 (range 0.3-108) nmol $m^{-2}\ d^{-1}$, respectively. It should be noted that the wide range in each case is to be expected in view of the temporal variability in wind speed during the cruises. Extrapolating the Pacific fluxes to a global ocean area of 3.6 x $10^{14} m^2$ yields a flux of 2.1 x 10^9 mol yr^{-1} (290,000 t yr^{-1}). While this figure would have increased by 11% if the average of all three data sets had been used or decreased by 25% if the Labrador and Sargasso Seas had been used, these uncertainties are much smaller than that due to selection of the relationship between exchange velocity and wind speed. Use of the *Liss and Merlivat* [1986] relationship would reduce the fluxes by about half [*Yvon and Butler*, 1996].

A separate flux estimate was made using the equilibrator partial pressure analyses, along with average wind speeds from the Comprehensive Ocean-Atmosphere Data Sets (COADS) data set [*Woodruff et al.*, 1987]. It is apparent from inspection of Figures 2d and 3c that the cold waters of the Labrador

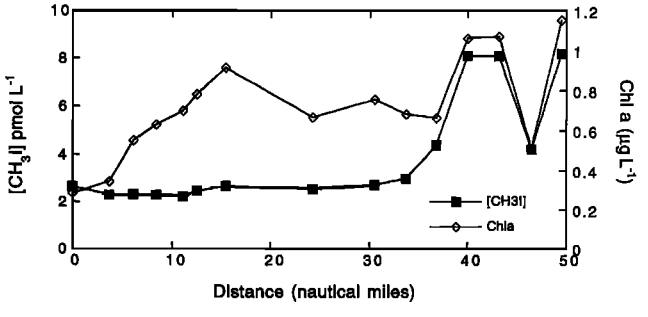

Figure 5. East Atlantic 1995, data of CH_3I and chlorophyll *a* concentrations measured along a transect through strong chlorophyll gradients plotted as a function of distance (nautical miles).

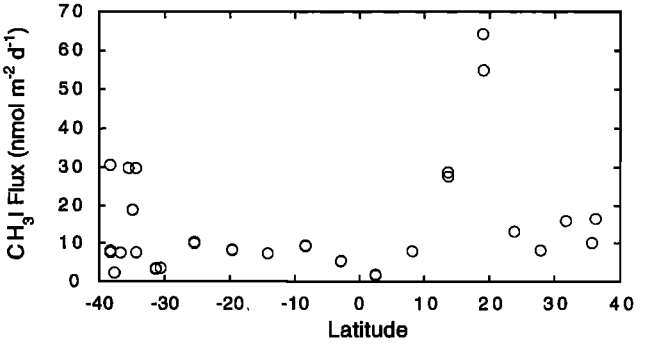

Figure 6. Methyl iodide fluxes plotted against latitude in the Pacific Ocean.

Sea/North Atlantic have significantly lower supersaturations of methyl iodide than either the warm Gulf Stream/Sargasso Sea or central Pacific waters. On the basis of this observation, for the purpose of this flux estimate the colder, high-latitude regions were considered separately from the rest of the ocean. The cold, high-latitude regions were taken to be those areas of the ocean with an annual average sea surface temperature (SST) less than 12°C (based on the *Hudson* cruise SST data of Figure 2a), and the flux from this cold region was assumed to be represented by the average of the fluxes calculated for the Labrador Sea (5.3 nmol $m^{-2} d^{-1}$). According to the World Ocean Atlas [*Levitus and Boyer*, 1994], 25% of the ocean is in this category. The rest of the ocean, 12°C and above, was represented by the combined average of fluxes calculated for the Pacific and the Gulf Stream/Sargasso Sea (18.9 nmol $m^{-2} d^{-1}$). On the basis of this set of assumptions, the annual ocean-atmosphere flux of methyl iodide was estimated to be 2.0 x 10^9 mol yr^{-1} (290,000 t yr^{-1}). A higher estimate of 2.5 x 10^9 mol yr^{-1} (360,000 t yr^{-1}) would result if the average flux from the Pacific (19.4 nmol $m^{-2} d^{-1}$) had been extrapolated to the entire ocean.

Thus, taking our various estimates, we propose that the global ocean source of methyl iodide to the atmosphere is in the range 2.0 - 2.5 x 10^9 mol yr^{-1}. The range of uncertainty is extended to ~0.9 - 2.5 x 10^9 mol yr^{-1} when we take into account uncertainties resulting from selection of the wind speed dependence of gas exchange, but additional uncertainties resulting from the limited spatial and temporal coverage of our data exist but are not easy to quantify. Indeed, other researchers have reported methyl iodide concentrations outside the ranges that we report here. For example, *Happell and Wallace* [1996] reported that the Greenland-Norwegian Sea area in November was undersaturated with respect to methyl iodide, a result perhaps linked to the low light intensities. In contrast, *Reifenhäuser and Heumann* [1992] report substantially higher concentrations of methyl iodide in the Southern Ocean in springtime (average 18 pmol L^{-1}, range: 2 - 53 pmol L^{-1}). Wintertime studies of trace gas concentrations in the surface ocean are very uncommon and lead to further uncertainty in global extrapolations.

An early estimate of the flux of methyl iodide from the ocean to the atmosphere was made by *Rasmussen et al.* [1982]. Their value of 90 x 10^9 mol yr^{-1} was strongly influenced by their supposition that highly productive waters, accounting for 10% of the ocean area, would supply about 70 x 10^9 mol yr^{-1}, a value which was derived from *Lovelock's* [1975] measurements of around 150 pmol L^{-1} for a region off SW Ireland, since they did not have measurements themselves for productive regions. Recent work on the production of methyl iodide by marine microalgae [*Manley and de la Cuesta*, 1997] suggests that the particular species present would be important, not just the overall productivity; furthermore, it may be shown that species of marine zooplankton are also producers of halocarbons.

Reifenhäuser and Heumann [1992] estimated a global ocean source of methyl iodide to the atmosphere of 6 x 10^9 mol yr^{-1} based on their average concentration of 18 pmol L^{-1} in Antarctic waters. In view of the much higher surface concentrations that they report, it is not surprising that their extrapolated global flux is 4 times higher. Surface Atlantic measurements (30°S-45°N) made by *Tanzer and Heumann* [1992] are more similar to the values reported in this study: mean, 4.2 pmol L^{-1}; range, 1.4-8.5 pmol L^{-1}. It seems clear that methyl iodide concentrations are highly variable geographically and perhaps also seasonally.

An estimate of the emission of iodine to the atmosphere based on the concentration of iodine in rainwater was made by *Miyake and Tsunogai* [1963]. Their value of 4 x 10^9 mol yr^{-1} is reasonably consistent with our estimate of the methyl iodide flux to the atmosphere, bearing in mind the limited geographic range of their rain samples (from 21 stations in Japan) and the fact that other, less well quantified sources of gaseous iodine exist, such as chloroiodomethane, diiodomethane, iodopropanes and butanes [*Klick and Abrahamsson*, 1992].

3.3. Vertical Profiles

Vertical profiles of methyl iodide were measured along the three cruise tracks, with the purpose of providing information on production and consumption. Figure 7 illustrates the dramatic difference between vertical profiles from the Labrador Sea and Sargasso Sea, the latter being characterized by much higher concentrations of CH_3I and a very pronounced subsurface maximum. It should be noted that subsurface maxima do occur in some of the Labrador Sea profiles, but they are less prominent. A number of other trace gases, e.g., methyl chloride and isoprene, were found to show similar maxima, not only in the Sargasso Sea profiles but also in profiles from the North Pacific. Figure 8 provides examples of three vertical profiles, two of which show pronounced subsurface maxima. In this figure are indicated the temperatures of the water at the depths of the respective CH_3I maxima. Profiles measured in the east Atlantic were generally similar to those of the Labrador Sea, being characterized by roughly uniform concentrations over a depth of about 50 m and decreasing into the deep waters. Occasional small maxima were seen.

The locations that showed large maxima in methyl iodide are those that show a deep chlorophyll maximum. This feature is

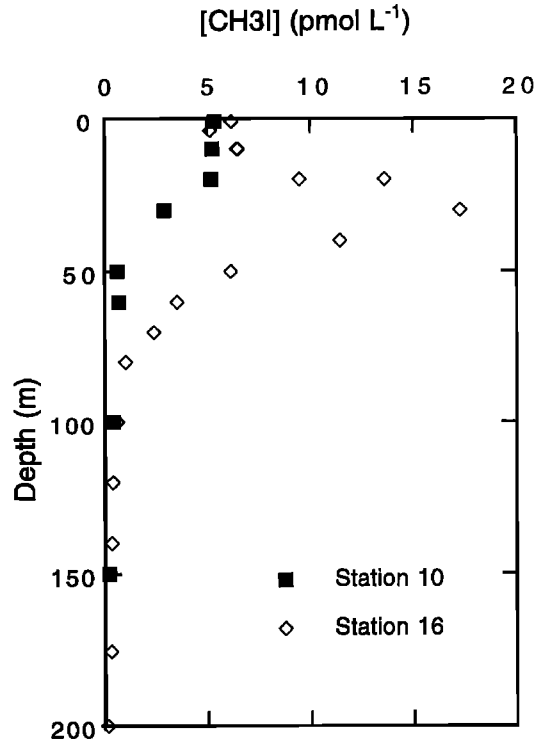

Figure 7. Vertical profiles of methyl iodide concentrations, from the Labrador Sea (solid squares) and the Sargasso Sea (open diamonds).

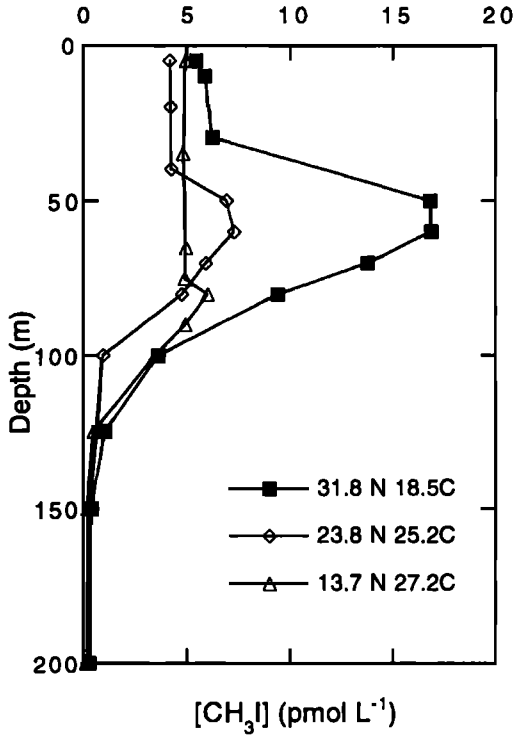

Figure 8. Vertical profiles of CH_3I concentrations at three stations in the Pacific Ocean. Temperatures at the depth of each CH_3I maximum are indicated in the key.

located within the density gradient at the base of the mixed layer and represents algal biomass that is prevented from mixing vertically. While the maximum in chlorophyll might suggest the presence of higher levels of plant biomass, it must be remembered that cells held in dimly illuminated layers compensate for the low light level by producing higher inventories of photosynthetic pigments [e.g., *Moore et al.*, 1995]. The chlorophyll *a* profile does not therefore match the algal biomass profile, and primary production at the chlorophyll maximum in the Caribbean Sea and western Atlantic was found by *Taguchi et al.* [1988] to be not significantly different from that in the mixed layer.

The stability of the water column, which allows cells that are acclimatized to low light to remain at the base of the mixed layer, can also account for the occurrence of elevated concentrations of trace gases that are produced in situ. For, whereas gas production at shallower depths is balanced by loss processes including ventilation to the atmosphere, production occurring in the deep chlorophyll maximum is subject to a relatively low vertical mixing flux into the layers above or below.

If vigorous vertical mixing extends to below the euphotic zone, a deep chlorophyll maximum would not be expected to develop. These conditions are also not conducive to the establishment of trace gas maxima because there is not a poorly ventilated zone within the euphotic zone in which the gases, produced in situ, may accumulate. It was observed that methyl iodide and chloride maxima existed in the North Pacific transect only at the sampling sites north of 2.5°N. The most obvious change that occurred coincidentally with the disappearance of the methyl iodide maximum was a deepening of the pycnocline from about 40 to about 95 m. This results in a large reduction in the light intensity in the zone beneath the mixed layer where water column stability is relatively high.

If it is correct to assume that a methyl iodide maximum lying within the pycnocline beneath the surface mixed layer represents a zone in which rates of loss by vertical mixing and efflux to the atmosphere are minimized, it follows that the production rate within the zone of the maximum may be estimated by equating production with known chemical loss rates. This will provide a lower estimate of the local production rate because it will neglect other loss processes (e.g., biological, as has been identified for methyl bromide [*King and Saltzman*, 1997], vertical diffusion, and nonsteady state, when $d[CH_3I]/dt$ may be greater than 0). This calculation has been done for profiles from the Sargasso Sea and North Pacific (Table 1), using the temperature-dependent rate constants for reaction between methyl iodide and chloride reported by *Elliott and Rowland* [1993].

From Table 1 it is seen that for waters above 17°C, the estimated minimum production rate of methyl iodide at the depth of the maximum is 0.4 - 0.7 pmol L^{-1} d^{-1}. The values for the higher temperatures are more reliable because the chemical loss rate is higher and therefore will tend account for a larger proportion of the losses (the other loss processes are not included in the calculation).

It is not known a priori whether these rates of production occur at depths other than the base of the mixed layer. Photosynthetic organisms occurring at this depth tend to be specialized so as to efficiently utilize the low light flux, e.g., *Prochlorococcus marinus* [*Moore et al.*, 1995], so in the absence of information on the actual sources of the methyl iodide, we do not know whether these production rates are typical of the water column. If these minimum production rates

Table 1. Calculation of Minimum Production Rates of Methyl Iodide in the Subsurface Maxim to Balance the Loss due to Chemical Reaction With Cl.

Latitude, Longitude, deg	Maximum $[CH_3I]$, pmol L^{-1}	Depth, m	Temperature, °C	Estimated Production Rate of CH_3I, pmol L^{-1} d^{-1}
42.0N, 57.3W	17.3	30	21.7	0.70
42.5N, 61.4W	8.7	25	13.5	0.09
43.9N, 62.9W	8.7	20	6.9	0.03
36.3N, 140.8W	19.0	50	16.3	0.33
31.8N, 146.1W	18.5	55	17.8	0.40
23.8N, 154.8W	7.3	60	25.2	0.51
19.1N, 159.1W	4.7	65	27.2	0.44
13.7N, 160W	6.6	60	24.7	0.42

are extrapolated to the surface, we find production rates of 20-30 nmol m^{-2} d^{-1} for the waters above 17°C.

Using the estimate that has been made of the production rate of methyl iodide, it is possible to address the question of whether the variation of CH_3I with latitude in the Pacific may be attributable to temperature variations. The procedure is to assume a steady state between production and loss, with the latter being made up of contributions from chemical degradation and efflux to the atmosphere, both of which are a function of the concentration in the water column. Supply of methyl iodide equals chemical loss plus flux to the atmosphere.

$$Sz = [CH_3I]_s (L_c z + k)$$

$$[CH_3I]_s = Sz/(L_c z + k)$$

where S is supply (mol m^{-2} d^{-1}), z is the mixed layer thickness (meters), L_c is the chemical loss rate (d^{-1}), $[CH_3I]_s$ is surface concentration of methyl iodide, and k is piston velocity. The calculation of $[CH_3I]_s$ as a function of latitude has been done in two ways, differing only in whether a constant value of the mixed layer depth is taken (50 m) or, alternatively, a value indicated by the density profiles at each station. For the piston velocity a value of 3.4 m d^{-1}, the average for the Pacific data set, has been used. Figure 9a shows the results for a constant mixed layer depth. The shape of the curve for methyl iodide concentration nicely matches the data, except that a predicted higher concentration in the cooler waters near the equator (due to a lower chemical loss rate) is not seen in the data. When the actual mixed layer depths are used, the main difference is to give lower predicted methyl iodide concentrations in higher latitude stations, especially those around 30°S. This is related to the mixed layer depth being less than 50 m at those sites which means that the production of CH_3I per unit area of mixed layers is less, the flux to the atmosphere must consequently be lower, and this will be driven by a lower surface concentration.

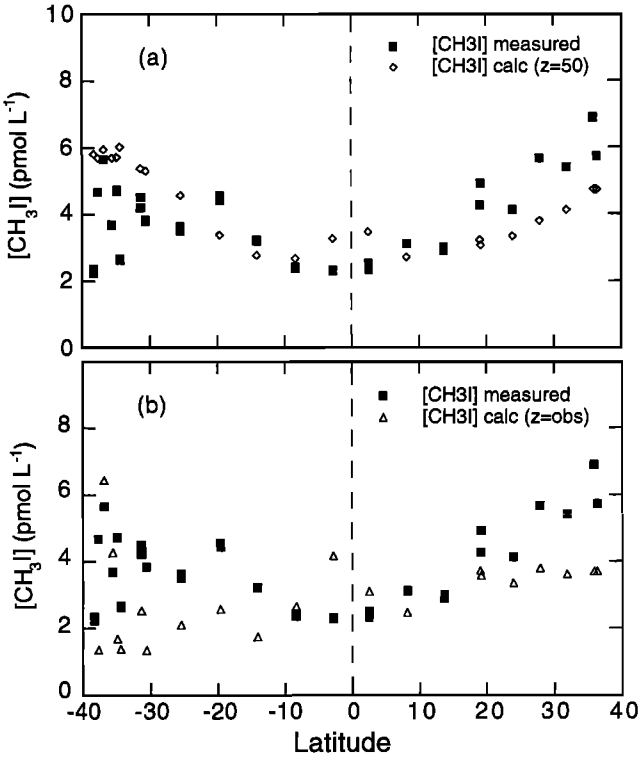

Figure 9. Comparison of observed and calculated CH_3I concentrations plotted against latitude in the Pacific for a mixed layer depth (a) of 50 m and (b) the observed value of mixed layer depth.

The simple model indicates reasonably good agreement when a production rate of 0.5 pmol L^{-1} d^{-1}, estimated earlier, is used. One might inquire whether the agreement between the calculated and observed concentrations is the result of circularity in the calculations. In fact, the production rates were estimated from only a few methyl iodide maxima, and the model suggests that those production rates seem to be generally applicable or are correct to within a factor of about 2. The results do suggest that the latitudinal variation in methyl iodide concentrations are in part controlled by temperature-dependent chemical loss.

In this treatment of the data, photolytic loss of methyl iodide has not been included since *Zika et al.* [1984] reported that methyl iodide loss is dominated by the SN2 reaction with Cl^-, except in high-latitude cold waters, where the half-life with respect to this reaction is greater than ~ 50 days. They also point out that the rate of photolysis decreases sharply with depth on account of the extinction of light having wavelengths less than 340 nm. Only the samples from south of 34°S in this data set would have a methyl iodide lifetime with respect to reaction with Cl^- longer than this value and so might have some significant photochemical loss.

4. Methyl Iodide as Source of Methyl Chloride

From the observed concentrations of methyl iodide in the mixed layer an estimate can be made of the production rate of methyl chloride, again using the reaction rates of *Elliott and Rowland* [1993]. It is found that north of 25°S, the average production rate is 15 nmol m^{-2} d^{-1}, which may be compared with ocean-to-atmosphere fluxes of 100 nmol m^{-2} d^{-1} that were reported to be typical of this region of the Pacific [*Moore et al.*, 1996b]. Other sources of methyl chloride in the ocean include the equivalent reaction of methyl bromide, which has been quantified by *Lobert et al.* [1995], and direct production by phytoplankton [*Scarratt and Moore*, 1996].

4.1. Origin of Marine Methyl Iodide

Efforts have been made to determine whether macrophytes and phytoplankton are producers of methyl iodide and to quantify any production. *Manley and Dastoor* [1987, 1988] have shown that the giant kelp, *Macrocystis pyrifera,* is a source of methyl iodide, but its direct production is insignificant at 4 x 10^6 mol yr^{-1}. They speculated that bacterial decay of kelp could potentially substantially increase this source, but it should be noted that this would constitute only a coastal source.

Moore et al. [1996a] reported that a laboratory culture of a marine diatom (*Nitzschia* sp.) did produce methyl iodide. *Manley and de la Cuesta* [1997] have examined 15 species of marine phytoplankton and report that in five cases the cultures showed increases in the amount of methyl iodide present. They have made estimates of the global production of methyl iodide by marine phytoplankton based on laboratory rates for those species that were the most prolific on a per cell basis: they range from 6.7 x 10^3 to 25 x 10^6 mol yr^{-1}, with a mean of 8.4 x 10^6 mol yr^{-1}. These values are insignificant in comparison with the 2 x 10^9 mol yr^{-1} global flux estimated here.

As shown above from the east Atlantic data set (Figure 4), there is no clear general correlation between methyl iodide concentrations and chlorophyll *a*, but on a smaller space scale (Figure 5) there are indications of a relationship, suggesting that CH_3I has a biological source, direct or indirect. At this stage it is not possible to ascertain whether this source is from phytoplankton or zooplankton. The existence of CH_3I maxima at depths of up to 65 m demonstrates in situ production and establishes that the compound can be formed at low light levels.

Moore and Zafiriou [1994] provided evidence from laboratory experiments for a photochemical source of methyl iodide. *Happell and Wallace* [1996] reported that light intensity explained significant variance in methyl iodide saturation anomalies which they measured in the Greenland and Norwegian Seas, and argued that this supports the notion of a photochemical source. It could, however, be questioned whether light intensity played a role through biology rather than by direct photochemistry.

5. Summary

Methyl iodide was found to be substantially supersaturated in all surface ocean waters, a result that is in part due its short lifetime in the atmosphere, where it is lost by photolysis. Our best estimate of its ocean-to-atmosphere flux is 0.9 – 2.5 x 10^9 mol yr^{-1}, where the lower limit is based on exchange velocities from *Liss and Merlivat*, [1996] and the upper limit is from exchange velocities of *Wanninkhof* [1992]. The uncertainty range is larger than this because we have limited spatial and temporal sampling of the oceans. Pronounced subsurface maxima in methyl iodide concentrations have been found in waters of the Pacific and the Sargasso Sea. We have calculated that in these maxima the production rate is at least 0.5 pmol L^{-1} d^{-1}, the level required to balance loss due to reaction with chloride ions. Latitudinal variation in methyl iodide concentrations in the Pacific Ocean are controlled in part by temperature-dependent chemical loss.

Acknowledgments. This work was supported by an NSERC Strategic Grant to R.M.M. and by the NERC (UK) Thematic Programme ACSOE. The authors wish to thank S. A. Penkett for his support; the chief scientists, G. Harrison, T. Bates, and W. Broadgate, and the officers and crews of CSS *Hudson*, NOAA Ship *Discoverer*, and RRS *Challenger*. We appreciate the helpful comments of J. Lobert and of anonymous reviewers. This research is a contribution to the International Global Atmospheric Chemistry (IGAC) core project of the International Geosphere-Biosphere Programme (IGBP) and is a part of the IGAC Aerosol Characterization Experiments (ACE).

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(Received April 10, 1998; revised October 10, 1998;
accepted November 2, 1998.)