

Methyl halide production and loss rates in sea water from field incubation experiments

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Abstract

Experiments were conducted in the field to determine the non-chemical loss rate of methyl iodide in seawater and to examine production rates of methyl halides. The loss rate of added C13 labelled methyl iodide, present at concentrations similar to those found in seawater, corrected for chemical loss due to reaction with Cl^- varied from <1 to $18\% \text{ day}^{-1}$, with a mean value of 7%. This rate of loss is much lower than that which was proposed by Bell et al. [Bell, N., Hsu, L., Jacob, D. J., Schultz, M. G., Blake, D. R., Butler, J. H., King, D. B., Lobert, J. M., Maier-Reimer, E., 2002. Methyl iodide: Atmospheric budget and use as a tracer of marine convection in global models, *Journal of Geophysical Research-Atmospheres* 107(D17), 4340-4351.] to account for the large discrepancies between observed and predicted mid-latitude concentrations of CH_3I based on their global photochemical source model. The suitability of several types of container for seawater incubations was studied and only quartz tubes appeared to be free of experimental artifact. Collapsible polyvinyl fluoride containers showed major production of methyl halides on irradiation with simulated sunlight. Polyethylene containers caused spurious production of methyl iodide at lower rates.

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1. Introduction

Halogens exert a major control on stratospheric ozone levels as a result of their catalysis of ozone decomposition. They are also of interest in marine tropospheric chemistry as oxidants (especially Cl) and, in the case of iodine, as a source of ultrafine particles which are precursors of cloud condensation nuclei (O'Dowd et al., 2002; McFiggans et al., 2004). The primary exchangeable reservoir of the halogens is the ocean, but it is trace organohalogen gases rather than the bulk halide ion

which are effective in transporting halogens to high altitude in the atmosphere and in releasing halogen radicals by direct photolysis. Simplest in this class of compounds are the methyl halides (CH_3X), all of which have the ocean amongst their various sources. In the case of CH_3I the ocean is the most important source, while for CH_3Cl it is reported to account for about 15% of the $6\text{--}8 \times 10^{10}$ moles added to the atmosphere annually (Montzka and Fraser, 2003). All three compounds have sinks as well as sources in the ocean; in the case of CH_3Br and CH_3Cl this results in a varied distribution of net source and net sink regions. A well-defined sink for CH_3I and CH_3Br in seawater is the temperature-sensitive reaction with chloride ion, but additional biological sinks have been

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identified for CH_3Br and also CH_3Cl (King and Saltzman, 1997; Tokarczyk et al., 2001, 2003a,b).

At present, research is directed at quantifying the exchanges of all of these gases between ocean and atmosphere, determining spatial and temporal variability, and identifying sources and sinks. In the case of CH_3Br and CH_3Cl , work has been done on quantifying biological loss rates (King and Saltzman, 1997; Tokarczyk et al., 2003a,b) using stable isotope tracers, but to date no results have been reported for CH_3I .

Determining net production or loss rates of trace gases can be done by a mass balance approach provided that their fluxes between the surface mixed layer and both the atmosphere and underlying waters can be estimated. In practice it is difficult to obtain all the data required for such a calculation because measurements of gas concentration and wind speed would be needed over a period of several days within the same body of water, unless a steady state assumption is made. An alternative approach is to measure directly the change in gas concentration in an enclosed sample of water as a function of time. Ideally, this approach would allow the effect of changing various parameters, such as light intensity, to be studied. This paper presents results of methodological studies for determining net production rates of methyl halides using incubators of different kinds. It also presents results on the isotopic determination of loss rates of CH_3I in seawater that are in excess of the known reactions with water and chloride ion.

2. Methods

The work described was done during two cruises in the N. Atlantic during 2003 that formed a part of the Canadian SOLAS programme (Fig. 1). The first was on CCGS Hudson in April–May, and the second on CCGS Martha Black during July. Water samples were either collected in the surface mixed layer using 10 l Niskin bottles or were taken from a continuously pumped supply on board ship. For the study of methyl iodide loss rates, carbon-13 labelled CH_3I was diluted in seawater and added to water samples to give concentrations around 8 pM. This compares with typical natural CH_3I concentrations around 3 pM. The water, unfiltered, was held in collapsible polyethylene Cubitainers® (Hedwin Corporation) within a seawater-filled incubator on the deck of the ship shaded from direct sunlight with a single layer of fine net. Over a period of 3 or 4 days samples were withdrawn using a 100 ml glass syringe. Immediately before analysis by purge and trap and GCMS, all subsamples were filtered through a GFF glass fibre filter. The analytical method used has been described in Moore

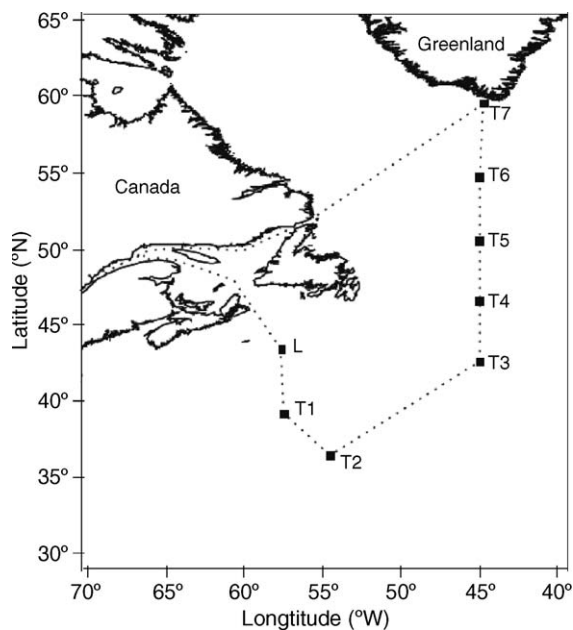


Fig. 1. Cruise track of CCGS Martha Black, July 2003. Station positions for CCGS Hudson cruise same except T7 not occupied.

and Wang, in press. Ions monitored were 142, 143 and 145 originating respectively in natural CH_3I , $^{13}\text{CH}_3\text{I}$, and a fully deuterated methyl iodide internal standard that was added to each sample during analysis with the purpose of allowing correction for any variation in detector sensitivity. Measurement precision for CH_3I was determined on each cruise by measurement of 8 subsamples of water held in glass syringes (100 ml); this gave a coefficient of variation of 2.1%, a value that is assumed to apply also to $^{13}\text{CH}_3\text{I}$. A lower precision must be expected for absolute concentrations in samples measured on different days because of the additional error associated with the daily calibration. This is avoided in the case of the $^{13}\text{CH}_3\text{I}$ measurements by expressing them as the ratio between the detector response for masses 143 and 145. These incubations were done initially in polyethylene Cubitainers which offer the advantage of being collapsible so that no headspace is introduced as subsamples of water are removed. As will be shown, evidence was found for production of CH_3I in Cubitainers as a result of unknown artifacts. While this effect is not expected to influence processes that consume $^{13}\text{CH}_3\text{I}$, some subsequent uptake experiments used glass syringes as incubators. CH_3I production was studied using several types of container including Tedlar® bags (SKC inc.), Cubitainers, glass syringes and quartz tubes.

Water used for incubations to determine production rate of CH_3I was unfiltered, except in an experiment where a comparison was made between unfiltered and

filtered water in which case a glass fibre filter (GFF) was used. Similarly, $^{13}\text{CH}_3\text{I}$ loss experiments used unfiltered water. Water used in experiments on the photochemical production of methyl halides in Tedlar bags had been filtered through a 0.2 μm cartridge filter (Whatman).

Surface irradiance measurements were obtained from a Satlantic multichannel UV–visible detection system that was operated periodically during the cruises. These data were available for the incubations performed in quartz tubes which, it will be demonstrated, provide the most reliable production rates.

3. Results and discussion

The loss of CH_3I in seawater results from chemical reaction with Cl^- , and to a lesser extent OH^- , and an assumed biological component as reported for both CH_3Br and CH_3Cl (Tokarczyk and Saltzman, 2001; Tokarczyk et al., 2003a,b). In the following discussion, the loss rate of CH_3I that is in excess of the known chemical reactions will be referred to as “non-chemical”. This term is applied as a convenient succinct label, and it must be realized that the contributing processes are not known to be entirely biological. For example, while Zika et al. (1984) reported that direct photolysis of CH_3I has a quantum efficiency that is too low for direct photolysis to compete with the loss through reaction with Cl^- , the photolytic loss is not zero. The authors also acknowledged that there could exist in seawater secondary pathways involving natural photosensitizers that could yield significant decomposition of CH_3I .

The chemical loss of CH_3I is pseudo first order since the concentration of Cl^- is virtually constant, and the biological loss also is found to be satisfactorily treated as first order. Fig. 2 illustrates the results of a ^{13}C incubation

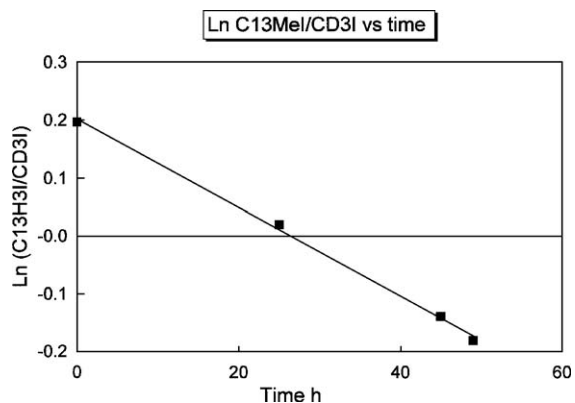


Fig. 2. $\text{Ln } ^{13}\text{CH}_3\text{I}$ normalized to deuterated internal standard in unfiltered seawater incubated on deck in a polyethylene container at ambient temperature (20 °C) as a function of time.

Table 1

Loss rate of $^{13}\text{CH}_3\text{I}$ from unfiltered seawater before and after correction for reaction with Cl^-

Date	Temp °C	Total loss rate % day ⁻¹	Non-chemical loss rate % day ⁻¹
May 4–6	20	18	15
May 8–12	7±2	7	7
May 13–15	7	9	9
July 18–21	11	2	1
July 21–24	Mean 7	<1	<1

in a Cubitainer, and the total and non-chemical loss rates for this and all other incubations are given in Table 1. The combined chemical and biological loss rate is determined from the slope of the graph of $\text{Ln } (^{13}\text{CH}_3\text{I}/\text{CD}_3\text{I})$ vs. time, and the non-chemical loss component was estimated by subtracting the temperature-dependent rate of reaction with Cl^- (Elliott and Rowland, 1993). In the experiment illustrated in Fig. 2, the known chemical loss rate was 3% d⁻¹ which accounts for about one fifth of the total observed loss rate. The high loss rate of 18% d⁻¹ in this first experiment raised the question of whether there could be diffusional loss of the tracer through the Cubitainer walls. This possibility was tested in a second experiment by placing a water sample in a glass syringe in the same incubator as the Cubitainer. After 48 h the decrease in $^{13}\text{CH}_3\text{I}$ in both containers was the same, showing that the loss must be due to in situ processes. Subsequent experiments were done using glass syringes as containers. The mean non-chemical removal rate for all the experiments was 7% d⁻¹, but clearly the springtime data set shows much higher loss rates (7–15% d⁻¹) than seen in the summer (1% d⁻¹). It is apparent that possible errors in the determination of chemical loss rates by Elliott and Rowland (1993) are unlikely to contribute much to the non-chemical loss rates reported here. For even at the highest temperature, the reaction with Cl^- is less than 20% of the observed loss rate, and at the lower temperatures this reaction was negligible.

Bell et al. (2002) modelled marine and atmospheric concentrations of CH_3I with an assumption that the marine source was photochemical with a production rate dependent on both light flux and the modelled concentration of dissolved organic carbon (DOC). The model overestimated the concentrations of CH_3I in some areas, in particular the Labrador Sea during spring and summer, giving values that are higher than observation by 1 or 2 orders of magnitude. This led the authors to conclude that in middle to high latitudes there must exist additional loss processes capable of removing CH_3I at a rate of about 0.24 day⁻¹. They suggested that biological

loss, known to occur in the case of CH_3Br (Tokarczyk and Saltzman, 2001), might be responsible. The results reported here (Table 1) do not support the existence of such a rapid removal process and instead imply that their model overestimates the photochemical production of CH_3I . While there is now independent field evidence for a photochemical source of CH_3I (Richter and Wallace, 2004), it is possible that photochemistry is just one of a number of sources, including direct biological production. Several studies have pointed to some production by marine phytoplankton (Manley and de la Cuesta, 1997; Scarratt and Moore, 1999), although the rates were low in comparison with accepted ranges of CH_3I flux to the atmosphere. While the assumption that photochemical production is proportional to DOC is attractive for its simplicity of application, there is no published evidence that all types of DOC would provide similar substrates for photochemical CH_3I production. Coloured, dissolved organic matter, CDOM, which must be a primary reactant in a photochemical reaction, is known to have a variety of sources, terrestrial and marine (Steinberg et al., 2004), and its properties can be modified by photobleaching (Kieber et al., 1990). Furthermore, DOC comprises CDOM and variable amounts of non-coloured components, so it is likely that DOC concentration is too crude an index of methyl iodide production rate.

4. Methyl halide production rate incubations

A series of deck incubation experiments was conducted during the spring and summer Atlantic cruises with the objective of measuring the production rates of the 3 methyl halides in seawater held at temperature and light conditions similar to the surface mixed layer. In experiments of this kind, because samples of water are to be analyzed as a function of time, it is desirable to use collapsible containers so that there is no headspace. The two such types of container that were used were polyethylene Cubitainers and polyvinyl fluoride Tedlar bags.

Water incubated in Cubitainers showed variable, and sometimes substantial, increases in CH_3I . An example is shown in Fig. 3A for a pair of Cubitainers holding samples of unfiltered and filtered (GFF) water. Here the average rate of increase of CH_3I was $2 \text{ pmol l}^{-1} \text{ h}^{-1}$, a value that would represent a replacement time of CH_3I in the mixed layer of only a few hours, while typical replacement times would be on the order of 10 days based on steady state mass balance in which the main loss was efflux to the atmosphere. To determine whether these results could be artifacts of the Cubitainers, a further time series experiment was conducted which used water in two types of container: Cubitainers and quartz tubes

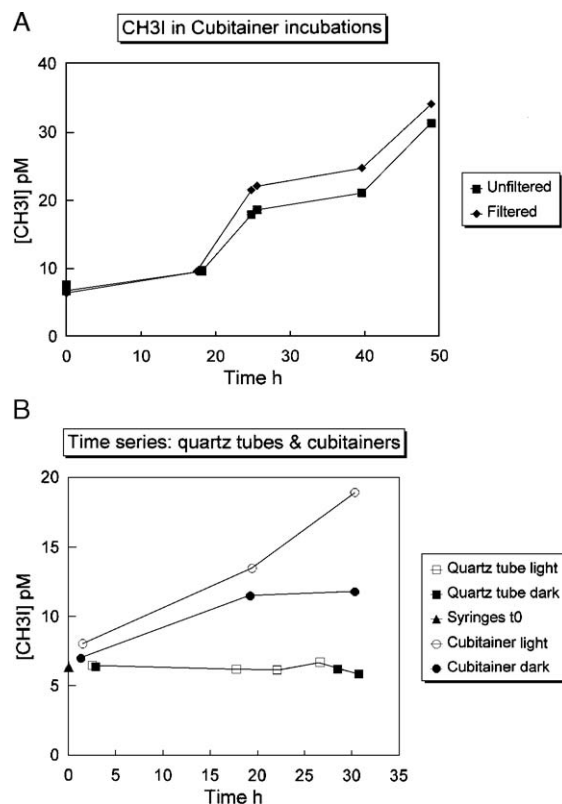


Fig. 3. A. Methyl iodide concentrations as a function of time in a pair of Cubitainers holding filtered and unfiltered water incubated on deck. B. A comparison of CH_3I concentrations as a function of time in Cubitainers and quartz tubes, both irradiated (light) and non-irradiated (dark), also incubated on deck.

(Fig. 3B) all of which were held in the same incubator on deck. Half of the vessels were wrapped to exclude light, and the rest were shielded under a single layer of net to moderate the light intensity. The results strongly suggest that the CH_3I production is an effect of the polyethylene container since the water contained in quartz tubes, dark or light, showed no significant change. Identical behaviour was seen for methyl bromide. Therefore it is concluded that Cubitainers have the potential to interfere in experiments on CH_3I and CH_3Br production by an unknown mechanism and they are not suitable for this type of measurement.

A series of experiments was conducted using Tedlar bags in order to determine their suitability for incubation experiments. One such experiment is described that illustrates contrasting results from these containers and quartz tubes on exposure to simulated sunlight. Filtered ($0.2 \mu\text{m}$) water contained in Tedlar bags and quartz tubes was exposed to light in a solar simulator (intensity: 3 suns). A non-irradiated Tedlar bag served as a control. Also, for comparison, a sample of water was irradiated

in a quartz tube under the same light intensity. The results, shown in Fig. 4A, indicate that there was very rapid production of CH_3I in the irradiated Tedlar bag alone. There is evidence from an unreplicated measurement of irradiated water from a quartz tube for some production of CH_3I but at a rate about 15 times lower than in the Tedlar bag. A further experiment was done to test whether the high production rate of CH_3I was due to interaction between the material of the bag (polyvinyl fluoride) and seawater; it used unfiltered water, low in CH_3I , collected from a depth of 150 m. Small strips of Tedlar (total area ca. 10 cm^2) were inserted in one quartz tube containing seawater that was irradiated for 1 h (3 suns). Large increases were seen for all three methyl halides equivalent to factors of 47, 13 and 6 for CH_3I , CH_3Br and CH_3Cl respectively (CH_3I results shown in Fig. 4B). Controls in which the same unfiltered water was irradiated in quartz tubes without Tedlar yielded

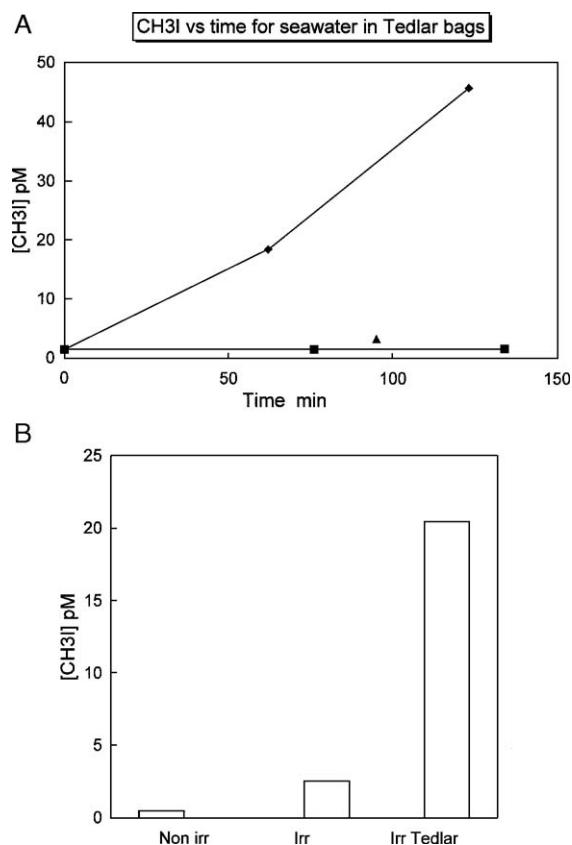


Fig. 4. A: Methyl iodide concentrations as a function of time in irradiated (diamonds) and non-irradiated (squares) Tedlar bags. Filled triangle: a measurement of CH_3I in an irradiated quartz tube. B: A comparison of CH_3I in quartz tubes, irradiated with and without strips of immersed Tedlar, and non-irradiated. The water was unfiltered and collected from 150 m depth. Solar simulator light intensities were 3 suns.

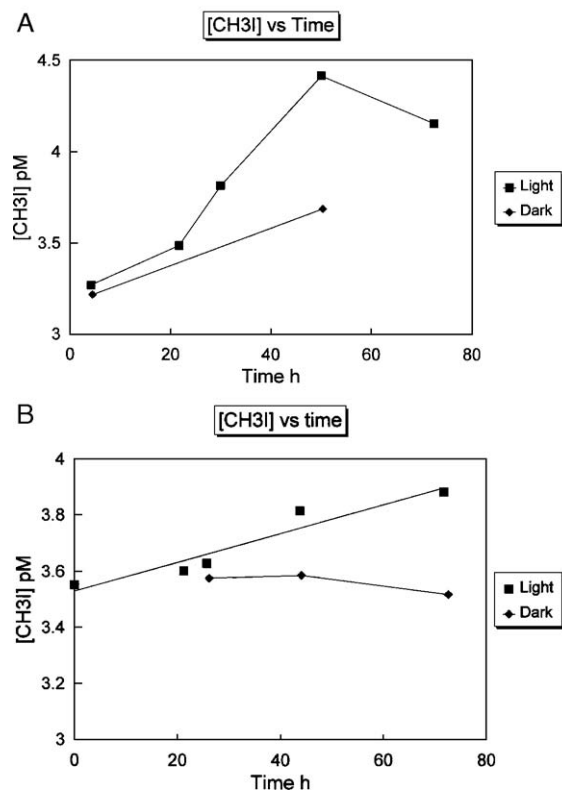


Fig. 5. Results of two incubations of unfiltered water from 1 m depth incubated on deck in quartz vessels both irradiated (light) and non-irradiated (dark). Experiment A, carried out between stations T5 and T6 (water temperature : $9\text{--}13.5\text{ }^\circ\text{C}$). Experiment B, northwards from Station T6 (water temperature $4\text{--}10\text{ }^\circ\text{C}$).

relatively small enhancement in the 3 compounds. This experiment confirms that a serious artifact occurs if a polyvinyl fluoride container is used for seawater in an experiment that involves exposure to sunlight. The mechanism for this effect is unknown.

Following these tests of the two types of collapsible container, time series incubations were done using sets of quartz tubes stored in flowing seawater in an incubation vessel on deck while the vessel was underway. This approach has the disadvantage of limiting the number of time points that can be measured, but appears to avoid spurious methyl halide production. Results of such an experiment done between stations T5 and T6 (Fig. 1) using unfiltered water collected at 1 m are plotted in Fig. 5A. This shows an increase in CH_3I over 50 h, followed by a decline to 73 h. Light intensities during this period were reduced by frequent fog; averaged over 12 h, the light intensity at 411 nm was ca. $50\ \mu\text{W cm}^{-2}\ \text{nm}^{-1}$. The intensity experienced by the incubations was further reduced by ca. 50% by a layer of net. A linear regression over the first 50 h yields an

increase of CH_3I of $0.015 \text{ pmol L}^{-1} \text{ h}^{-1}$, that is an increase of $0.5\% \text{ h}^{-1}$. If the results are calculated by the more direct method of monitoring the change in ratio of CH_3I to the added internal standard, the result is almost the same: $0.4\% \text{ h}^{-1}$. The rate of net production of CH_3I in the mixed layer was calculated using a steady state mass balance approach in which the production rate is assumed to equal the flux to the atmosphere and loss due to chemical reaction with Cl^- . The value for the period of this experiment is $0.036 \text{ pmol L}^{-1} \text{ h}^{-1}$ which, given the uncertainties in both calculation and measurement, is in reasonable accord with the incubation result.

A second time series experiment to determine net production rate was done from station T6 northwards, using quartz tubes filled with unfiltered water from a depth of 1 m, again including both light and dark samples with the former partially shielded from direct sunlight by a layer of mesh. The results for CH_3I shown in Fig. 5B indicate a net production rate of $0.005 \text{ pmol L}^{-1} \text{ h}^{-1}$ for the “light” samples (equivalent to an increase of $3.5\% \text{ day}^{-1}$) and no change in concentration for the dark ones. Calculated net production rates for this period are in the range $0.004\text{--}0.04 \text{ pmol L}^{-1} \text{ h}^{-1}$. The light intensity was approximately the same as in the first of this pair of experiments. Such low rates of production are a challenge to measure but do suggest an influence of light. This is interpretable in two ways, either the effect occurs through the influence of light on photosynthetic organisms, or there is a photochemical effect that is independent of primary influence by algae. There is evidence for both types of process yielding CH_3I , but laboratory studies have not demonstrated algal production at a rate that would be required to account for typical ocean–atmosphere fluxes (Manley and de la Cuesta, 1997). While evidence for photochemical production is sparse, Richter and Wallace (2004) argue that the process can account for about 50% of the production at their tropical Atlantic site. Their estimate of photochemical production rate was ca. $1 \text{ pmol L}^{-1} \text{ h}^{-1}$, greatly in excess of any production at our high latitude site. This could be attributable, at least in part, to the large differences in light intensity during these studies; while Richter and Wallace have not reported actinic measurements, their studies at 10°N were conducted under clear skies.

5. Conclusions

Non-chemical losses of CH_3I were measured in the range of <1 to $15\% \text{ d}^{-1}$, with the highest value occurring in the warmest temperature (20°C). No evidence was found for biological loss rates of the magnitude deemed necessary by Bell et al. (2002) to

balance modelled photochemical production at mid-latitudes in the N. Atlantic.

The experiments described here point to serious artifacts when containers of polyethylene or polyvinyl fluoride are used and exposed to light. In the absence of any information on the mechanism it cannot be certain whether such vessels will always yield compromised results in experiments of this kind. Where incubations were done in quartz containers there was no evidence for interferences and the CH_3I production rates were in the range calculated for surface waters using a steady state mass balance of CH_3I . However, the waters in which these incubations were done were characterized by production rates of CH_3I far below average for the ocean, consequently the experiments revealed little about the mechanisms responsible for CH_3I production.

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