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Key Points:
- A diurnal variation of CH_3I in sunlit samples with maxima in day time
- Daily accumulation was not affected by filtration
- A consequence of large losses of CH_3I by as-yet uncharacterized processes

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A time series of incubation experiments to examine the production and loss of CH_3I in surface seawater

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Abstract In order to investigate production pathways of methyl iodide and controls on emissions from the surface ocean, a set of repeated in vitro incubation experiments were performed over an annual cycle in the context of a time series of in situ measurements in Kiel Fjord (54.3°N, 10.1°E). The incubation experiments revealed a diurnal variation of methyl iodide in samples exposed to natural light, with maxima during day time and losses during night hours. The amplitude of the daily accumulation varied seasonally and was not affected by filtration (0.2 μm), consistent with a photochemical pathway for CH_3I production. The methyl iodide loss rate at nighttime correlates with the concentration accumulated during daytime suggesting a first-order loss mechanism ($R^2 = 0.29$, $p << 0.01$). Daily (24 h) net production (P_{net}) was similar in magnitude between in vitro and in situ mass balances. However, the estimated gross production (P_{gross}) of methyl iodide ranged from -0.07 to 2.24 pmol L^{-1} d^{-1} and was up to 5 times higher in summer than P_{net} calculated from the in situ study. The large excess of P_{gross} over P_{net} in summer revealed by the incubation experiments is a consequence of large losses of CH_3I by as-yet uncharacterized processes (e.g., biological degradation or chemical pathways other than Cl^- substitution).

1. Introduction

Methyl iodide is a major carrier of gas phase iodine from the ocean into the atmosphere. In the atmosphere, CH_3I participates in several catalytic cycles important for air quality and climate [*Solomon et al.*, 1994; *Davis et al.*, 1996; *Carpenter et al.*, 1999; *McFiggans et al.*, 2000; *O'Dowd et al.*, 2002]. Since the first detection of CH_3I in the atmosphere by *Lovelock and Maggs* [1973], many investigations have been performed to identify its sources.

In the ocean, several different potential sources of CH_3I have been proposed. Macroalgae were shown to produce CH_3I in coastal regions [*Lovelock*, 1975a, 1975b; *Manley et al.*, 1992; *Laturnus et al.*, 1995; *Nightingale et al.*, 1995]. For the ocean as a whole, phytoplankton have been hypothesized to be more important than macroalgae in terms of global biological CH_3I production [*Moore and Tokarczyk*, 1993; *Manley and delaCuesta*, 1997; *Shaw et al.*, 2003; *Smythe-Wright et al.*, 2006; *Hughes et al.*, 2011]; however, estimates of such biological sources vary and are controversial. *Smythe-Wright et al.* [2006] estimated global biological production rates of 5.3×10^{11} g yr^{-1} with *Prochlorococcus* as a primary source based on culture experiments and observations in the Atlantic and Indian oceans. However, *Brownell et al.* [2010] calculated a global CH_3I production rate of only 8.5×10^7 g yr^{-1} (equivalent to 0.6 Mmol yr^{-1}) from *Prochlorococcus*, which is 1000-fold lower than estimated by *Smythe-Wright et al.* [2006]. *Hughes et al.* [2011] attempted to reconcile these estimates by suggesting that the rates of CH_3I production by *Prochlorococcus* in culture varies with cell physiological status. Other biological production sources in the ocean have been reported. *Amachi et al.* [2001] reported experiments suggesting that oceanic bacteria (e.g., *Alteromonas macleodii IAM*) are capable of producing CH_3I under environmental concentrations of I^- (0.1 μM). *Klick and Abrahamsson* [1992] argued for the possibility of planktonic CH_3I production based on observation of diatom-rich seawater samples with higher CH_3I concentrations. A set of similar investigations has been conducted which also made the case for CH_3I production by diatoms (>10 μm) [*Moore et al.*, 1996; *Manley and delaCuesta*, 1997; *Xie et al.*, 1999; *Toda and Itoh*, 2011].

A source of CH_3I via photochemical production in surface seawater has been suggested frequently as an alternative to biological production. *Moore and Zafiriou* [1994] presented experimental evidence for a photochemical production pathway based on short-term (maximum 2 h) incubations. Longer-term (>24 h) field incubation experiments with open ocean waters conducted by *Richter and Wallace* [2004] and

Wang et al. [2009] were also interpreted to support photochemical production. The former study included experiments with poisoned and filtered samples. A photochemical mechanism was inferred by *Happell and Wallace* [1996] from their geographical correlation analysis between measured CH_3I concentrations and a number of environmental factors. *Shi et al*. [2014] presented a temporal correlation analysis of seasonal concentration variations in a nearshore environment that was also consistent with photochemical production of CH_3I but which could not rule out a biological source when temporal variability of the net production rate was considered. *Archer et al*. [2007] presented a temporal correlation analysis in shelf waters that noted the similarity of the seasonal trends of CH_3I concentration and light, consistent with a photochemical production mechanism. However, based on their observations of the variations of [CH_3I] in the water column they argued for a biological production pathway. *Ziska et al*. [2013] noted higher CH_3I concentrations in subtropical gyres, which they considered consistent with photochemical production. *Bell et al*. [2002] simulated oceanic and atmospheric concentrations of CH_3I assuming a photochemical CH_3I source dependent on only light and DOC. *Stemmler et al*. [2014] also modeled the CH_3I production globally and suggested that a photochemical process is the best way to explain the global surface concentration variations. However, the relative importance of biological and photochemical production of CH_3I is still debated, perhaps because biological and photochemical processes are likely to be coupled in that a source of organic carbon (as well as light) is required for photochemical production of CH_3I. We note that the highest CH_3I production rates in the above mentioned culture experiments did not explicitly rule out the possibility of abiotic, photochemical production taking place within the cultures.

The main sink of methyl iodide from the surface ocean has generally been considered to be its loss to the atmosphere. Estimates of this global sea-to-air flux vary from 1.9×10^{11} to 1.3×10^{12} g yr^{-1} [*Liss and Slater*, 1974; *Rasmussen et al*., 1982; *Singh et al*., 1983; *Reifenhauser and Heumann*, 1992; *Moore and Groszko*, 1999; *Bell et al*., 2002; *Richter and Wallace*, 2004; *Ziska et al*., 2013]. A second major sink for methyl iodide in seawater is nucleophilic substitution by chloride and bromide, as suggested first by *Zafiriou* [1975]. *Elliott and Rowland* [1993] calculated the temperature dependent chemical loss rate of methyl iodide, with the rate constant for the dominant reaction with chloride at 22°C being 1.0×10^{-6} L mol^{-1} s^{-1}. *Bell et al*. [2002] used these rates to calculate a global in situ sink of CH_3I via reaction with Cl^{-1} of 2.6×10^{11} g yr^{-1}. A third possible sink for CH_3I is biological degradation. *Bell et al*. [2002] hypothesized that an additional biological loss should exist based on their model calculations. *Moore* [2006] estimated a "nonchemical loss" (defined as in situ losses due to processes other than reaction with chloride) from incubation experiments with open ocean surface waters. The loss rates ranged from <1 to 15% d^{-1} assuming a pseudo first-order loss process. In this study, we will refer to this "nonchemical loss" as "nonchloride loss" to allow for the possibility of additional uncharacterized chemical loss processes as well as biological (e.g., microbial) removal processes. Another potential sink of CH_3I from surface seawater is lateral and, especially, vertical mixing with water containing lower concentrations of CH_3I. However, even in open ocean waters where CH_3I concentrations decrease below the euphotic zone, the downward mixing loss has been shown to be negligible in comparison with the sea-to-air flux and chemical loss [e.g., *Richter and Wallace*, 2004].

In this work, a set of repeated long-term incubation (in vitro) experiments of $\sim$2.5 days duration were conducted over 1 year using samples of seawater collected from a nearshore, brackish environment, in order to investigate sources and sinks of methyl iodide. Simultaneously, and at the same location, the seasonal cycle and mass balance of in situ methyl iodide concentrations were investigated [*Shi et al*., 2014]. In this paper, production and loss rates of CH_3I are estimated based on the results of the in vitro incubation experiments, and used to calculate the daily mass balance of CH_3I over an annual cycle, which is compared with results from the in situ study.

2. Methods

2.1. Incubation Experiments

Incubation experiments with natural seawater (salinity: 13–16) were conducted from August 2009 to November 2010 in the Kiel Fjord. Seawater was sampled directly from the surface (0.5 m) of the Fjord from a pier in front of GEOMAR's west shore building (54.3°N, 10.1°E). The experiments involved long-term incubations (57 h) of natural seawater samples at natural light levels, as well as in the dark (12 light samples and 8 dark samples per experiment). In this study three treatments of seawater samples were used: natural

seawater samples or "original" untreated samples (O), the "filtered and prepurged samples" (F), and the "nonfiltered and prepurged samples" (NF).

The "filtered and prepurged samples" (F) comprised natural seawater (7 L) which had been filtered stepwise through 20, 5, and finally 0.2 μm membrane filters under 5 bars pressure. After filtration, most of the plankton had been removed, although the samples were not axenic and small bacteria (e.g., <0.2 μm) could have remained. The filtered seawater was bubbled (prepurged) for 5 h with synthetic air (35–45 mL min^{-1}) to reduce the initial concentration of volatile iodinated organic compounds (20–30% of original methyl iodide remained in the seawater). Use of synthetic air assured that dissolved oxygen remained high in the sample (e.g., 150 μmol L^{-1} in original seawater compared to 138 μmol L^{-1} after the 5 h purge). The "nonfiltered but prepurged samples" (NF) represented unfiltered natural seawater that had been bubbled for 5 h with synthetic air at the start of experiment.

After these sample treatments, 20 subsamples (each 300 mL) were placed in sealed quartz bottles. Twelve of the subsamples were exposed to the natural light dark cycle, while eight subsamples were kept in the dark. The quartz-flasks were incubated (upside down) at 0.5 m depth under the sea surface in front of GEOMAR's west shore building in order to keep the experimental conditions as close to natural temperature and light ("sunlit samples") as possible. The "dark samples" were kept in a closed box filled with water of the same temperature. Samples were taken for analysis every 5 h for the light treatments and every 12 h for the dark treatments, corresponding to approximate measurement times of 08:00, 12:00, 17:00, and 22:00 every day. Every sample was analyzed in triplicate, the mean value of each sample (standard deviation <15%) was used in this work.

2.2. Analysis of Halocarbons

A purge and trap (dynamic headspace) method was used for the analysis. The volatile organic compounds (e.g., CH_3I) were released from the seawater samples into the gaseous phase by a continuous 30 mL min^{-1} gas flow of helium for 40 min at a purge temperature of 50–60°C. The purged gas stream was dried by Nafion dryers (50 cm length) and the volatiles were trapped in a glass tube (1/4″ ID) filled with a 25 mm length of glass beads above liquid nitrogen (N_2) at −100°C. The volatiles were released at high temperature (100°C) and trapped again on a deactivated glass capillary (50 cm length, 0.53 mm ID) in liquid nitrogen. The analytes were then injected into the GC at room temperature. For all measurements a FISONS 8000 gas chromatograph (GC) was used, equipped with a RTX-VGC column (60 m long; coated: 1.4 μm, column diameter: 0.25 mm) and electron capture detector (ECD) with helium carrier gas. The temperature program of the GC oven was 25°C for 6 min, increased to 150°C at 6°C/min, and held at 150°C for 1 min.

Calibrations were performed by injecting microliter volumes of liquid standards via a septum port, into the purge vessel containing prepurged tap water and analyzed in the same way as seawater samples. Three stock standard solutions were prepared in 10 mL pentane. The final standards for calibration were then prepared by serial dilutions of the stock solutions into methanol. All chemicals were purchased from Merck, and all stock solutions were stored at −20°C. Every working standard was measured three times. The standard deviation of triplicate measurements ranged from 13% to 23%. The detection limit of the method was 0.06 pmol L^{-1}.

Meteorological data (collected every 8 min), including solar radiation (SSR) and sea surface temperature (SST), were provided by the Maritime Meteorology research unit at GEOMAR (http://www.geomar.de/en/research/fb1/fb1-me/). The annual cycle of SSR and SST are presented in a companion paper [*Shi et al.*, 2014].

3. Results

3.1. Diurnal Variability

The variations of CH_3I concentrations during a 57 h incubation experiment conducted in July 2010 are plotted in Figure 1. The results show a diurnal variation of methyl iodide under irradiation in both nonfiltered (NF) and filtered (F) samples compared with samples that were kept in the dark. The "sunlit" samples showed an increase during daylight hours and a decrease at night. Notably, for "sunlit" samples, almost all of the CH_3I produced in the day was consumed during the night such that a long-term buildup of CH_3I in the flasks was small compared to the diurnal variations. For instance, the CH_3I concentration in the three morning samples (08:00) increased only slightly over the entire incubation experiment (average of increase

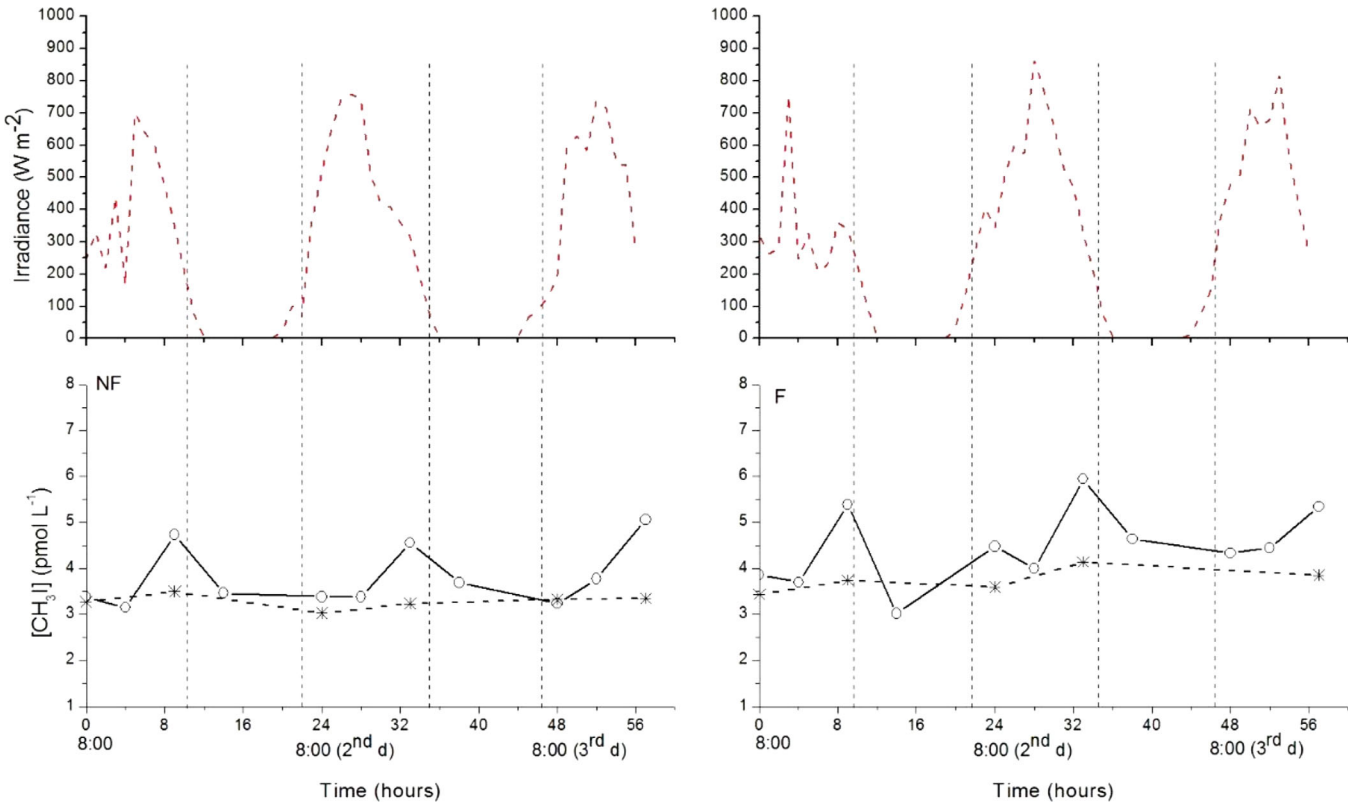

Figure 1. Variation of CH_3I concentrations in (left) nonfiltered samples (NF) and (right) filtered samples (F) for incubations conducted in July 2010: Sunlit samples—solid line with circles; dark samples—dashed line with stars. Vertical hatched lines denote light dark cycles. The red dashed lines (top plots) present the variation of irradiance during each experiment. Each experiment started at 08:00.

over 24 h of ~0.05 pmol L^{-1} for NF samples and ~0.5 pmol L^{-1} for F samples (Figure 1), compared to daytime variation of 1.35 pmol L^{-1} for NF sample and 1.53 pmol L^{-1} for F sample (from 08:00 to 17:00).

Both the concentration measured at each time-point (overall range of 0.67–5.84 pM) and the amplitude of the daytime increase (range of 0.18–1.53 pM from 08:00 to 17:00) varied from experiment to experiment. In order to characterize a typical daily cycle, the results from all (NF, F, and O samples) experiments (n = 24) were normalized for each 24 h time period (from 08:00 to 08:00 on second day, and 08:00 on second day to 08:00 on third day). The normalized concentrations for the different time-points over a 24 h period were calculated as

$$[CH_3I]_{nor} = \frac{[CH_3I] - [CH_3I]_{initial}}{[CH_3I]_{peak} - [CH_3I]_{initial}}, \quad (1)$$

where $[CH_3I]_{nor}$ is the normalized concentration of CH_3I, $[CH_3I]$ is the concentration measured at an individual time-point, $[CH_3I]_{initial}$ is the concentration in the "sunlit" samples analyzed at 08:00 for that 24 h time period, and $[CH_3I]_{peak}$ is the maximum concentration measured during the 24 h time period in the "sunlit" samples. For the "dark" samples, $[CH_3I]_{initial}$ is the concentration in the "dark" samples analyzed at 08:00 for each 24 h time period, and $[CH_3I]_{peak}$ is the maximum concentration in the "sunlit" samples during the same 24 h time period. Subsequently, average values of these normalized concentrations were calculated for each daily sampling time from all 24 incubation experiments.

The normalization procedure yields the typical daily cycle for the "sunlit" samples during incubations based on data collected over an entire annual cycle (Figure 2a). From early morning (08:00), the CH_3I concentration increases to a maximum at 17:00 within the "sunlit" samples. Hence, the maximal daily value of $[CH_3I]$ lagged the maximum of SSR in cycle by ~5 h. Sometime around 17:00 the CH_3I concentration started to decrease rapidly until near midnight (22:00). From 22:00 to 08:00 of the next day, the concentration of CH_3I

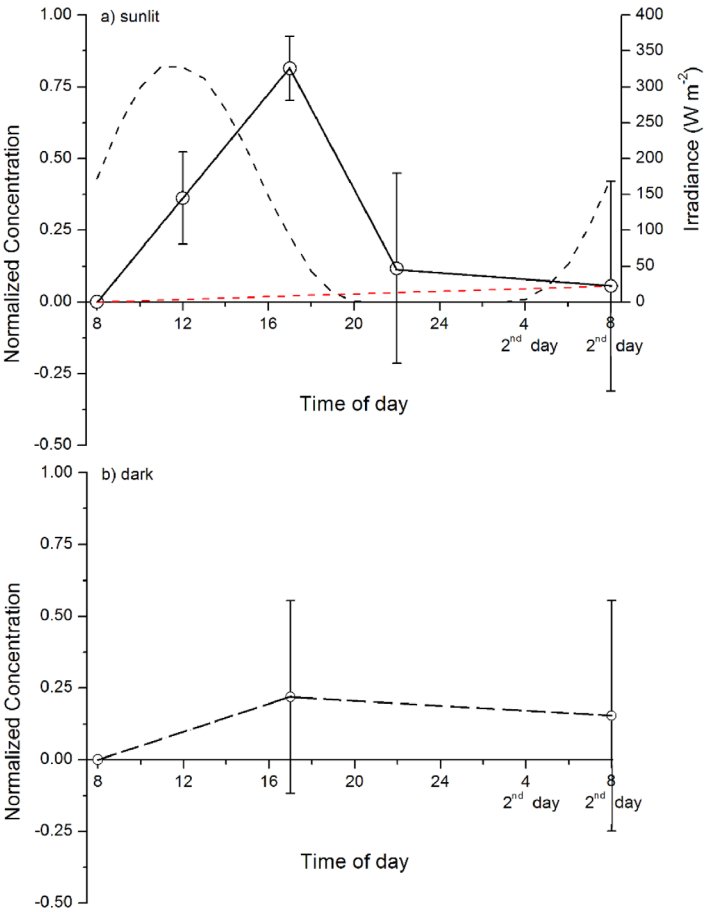

Figure 2. Normalized daily cycle of CH_3I based on all 24 experiments in (a) the sunlit samples (solid line) and (b) in the dark samples (dashed line). The red dashed line represents, schematically, that the net daily accumulation over a 24 h period is small. The black dashed line represents the annual average of the daily variation of irradiance in Kiel. The error bars are 95% confidence intervals. No error bar is shown for the first point, because the normalized concentration for the first time-point was always zero by definition, for all 24 h periods.

changed only slightly. Note however that the exact timing of peak and minimum concentrations are not well-defined due to the still-limited time resolution of the sampling. On average, over 24 h of incubation, the CH_3I concentration changed only slightly and the daily accumulations were small (see above and Figure 2a, red dashed line). The daytime increase and the net daily accumulation will be discussed in sections 3.2 and 4.2. Figure 2b illustrates the mean, normalized concentrations for the "dark" samples. The CH_3I concentration in the "dark" samples varied only very slightly over the entire 24 h period. Comparison of the "sunlit" samples and "dark" samples (Figure 2) indicates that samples exposed to sunlight had much higher daytime accumulations compared to samples kept in the dark.

Based on this "typical" average daily cycle, we calculated the daytime accumulation ($\Delta[CH_3I]_{day}$) in the "sunlit" samples for each experiment as the CH_3I concentration increase over the 9 h interval between 08:00 and 17:00. Similarly, the nighttime loss ($\Delta[CH_3I]_{night}$) was calculated as the concentration decrease measured between 17:00 and 08:00 on the second day.

3.2. Seasonal Variability and Filtration Effects

Incubation experiments were conducted from spring through winter in order to examine seasonal variations of the CH_3I production. The *daytime accumulations* of CH_3I ($\Delta[CH_3I]_{day}$) from the 2.5 day incubation experiments (NF, F, and O samples) conducted from February to November were averaged and are shown in Figure 3d. The $\Delta[CH_3I]_{day}$ in sunlit samples ranged from 0.04 to 2.05 pmol L^{-1} and from −0.33 to 0.45 pmol L^{-1} in the dark samples. A seasonal cycle of $\Delta[CH_3I]_{day}$ with a clear maximum in summer and early fall (from June to September) and a minimum in winter (from November to February) was observed for the sunlit samples, whereas there was no apparent seasonality for the dark samples (Figure 3d).

For the Nonfiltered samples (NF), a maximum value of $\Delta[CH_3I]_{day}$ of 1.53 pmol L^{-1} was observed in July with the minimum value of 0.04 pmol L^{-1} observed in November (Figure 3a) (No incubation experiments with NF samples were conducted in August and September). The seasonal variation from the more limited number of experiments conducted with filtered samples (F) were consistent with the results of the nonfiltered (NF) experiments (Figure 3b). A maximum accumulation of 1.35 pmol L^{-1} of CH_3I in filtered samples was observed in July (summer), whereas only 0.21 pmol L^{-1} of CH_3I accumulated in experiments conducted at the end of October (fall). For experiments with the original samplers (O), the highest value of $\Delta[CH_3I]_{day}$ (2.05 pmol L^{-1}) was observed in September, with lower values found in winter time (from November to February).

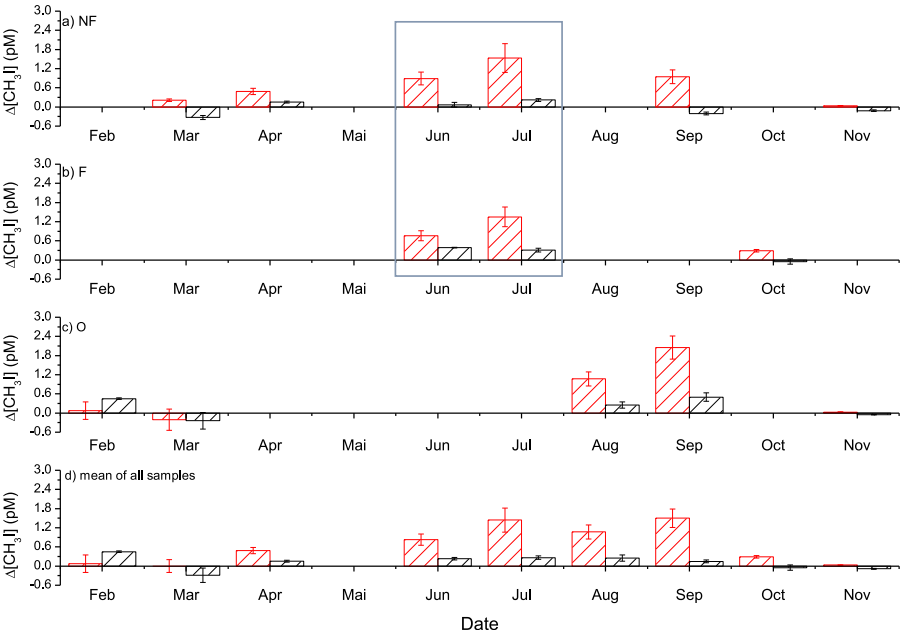

Figure 3. Daytime accumulation of CH_3I ($\Delta[CH_3I]_{day}$) (see definition in section 3.1) during incubation experiments conducted over a year for (a) Nonfiltered samples (NF), (b) Filtered samples (F), (c) Original samples (O), and (d) the mean of all samples. Red shading denotes the "sunlit" samples, black shading denotes samples kept in the dark. Error bars represent 95% confidence intervals; each incubation experiment resulted in three values for daytime accumulation.

Similar magnitudes of diurnal variability of CH_3I were observed for both NF and F samples during the incubations (Figure 3, in blue frame). In June, the $\Delta[CH_3I]_{day}$ for NF samples was 0.89 and 0.76 pmol L^{-1} for the F samples. The difference of $\Delta[CH_3I]_{day}$ between the NF and F samples was small, with overlapping error bars (95% confidence).

4. Discussion

4.1. Diurnal Variation

The incubation experiments revealed a diurnal cycle of CH_3I in "sunlit" samples that appears closely linked to the daily light cycle but with a time-lag of ~5 h. A link to irradiance is consistent with the seasonal observations of in situ concentrations in the Kiel Fjord reported in the companion paper [*Shi et al.*, 2014]. The ~5 h time-lag between peak irradiance and maximum daily $[CH_3I]$ likely reflects a balance between light-dependent production and concentration-dependent loss processes (see below section 4.4).

Richter and Wallace [2004] and *Moore* [2006] also conducted incubation experiments in sealed bottles, but they did not resolve diurnal variability, because they analyzed the incubation samples over longer intervals (24 and 15 h, respectively). Our study has higher temporal resolution (5 h) than previous studies and can give new insight into diurnal production and cycling of methyl iodide. To our knowledge, there has been only one prior study to have examined diurnal variability of CH_3I concentrations in a natural system [*Ekdahl et al.*, 1998]. They observed two maxima of CH_3I concentrations over 24 h (from 16:00 to 18:00 and from 2:00 to 5:00) in a rock pool containing macroalgae. They suggested that the first maximum was associated with photosynthesis by the algae in daytime and the second was suggested to have been associated with macroalgal respiration during nighttime.

4.2. Daytime and Daily Accumulation

The incubation experiments were conducted over a full seasonal cycle, and the amplitude of $\Delta[CH_3I]_{day}$ showed a clear seasonal pattern (see Figure 3). It was notable that most of the CH_3I produced in sunlit samples during the day was subsequently degraded at night. In contrast, CH_3I concentrations remained invariant in samples that were kept in the dark (Figure 2b). The daily accumulation ($\Delta[CH_3I]_{24h}$) was calculated as the variation of $[CH_3I]$ between 08:00 and 08:00 of the following day and monthly averages are presented

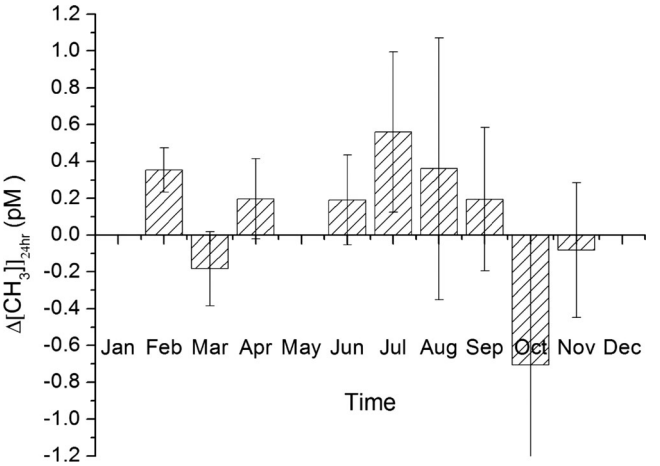

Figure 4. Seasonal variation of the monthly average daily accumulations ($\Delta[CH_3I]_{24h}$) calculated from the incubation experiments. Error bars represent 95% confidence intervals. The method of calculation is presented in the main text.

in Figure 4. Note, that there were 2 × 24 h cycles so that two values of $\Delta[CH_3I]_{24h}$ were resolved per incubation experiment. Overall, daily accumulation values in the sunlit samples were positive; however, the monthly averages were not statistically different from zero in most months, so that a seasonal signal could not be clearly identified.

The observation of higher daytime and daily accumulation in sunlit samples is consistent with the observations from prior incubation experiments reported by *Richter and Wallace* [2004] and *Moore* [2006]. Richter and Wallace found that the accumulation of methyl iodide in dark samples over a 24 h period was only 0.72 pmol L^{-1} (mean) compared with 4.08 pmol L^{-1} (mean) in samples exposed to a natural light dark cycle [*Richter and Wallace*, 2004]. *Moore* [2006] reported CH_3I accumulation of 0.02 pmol L^{-1} in dark samples after a 48 h incubation and 10 times higher accumulation of CH_3I in samples exposed to a natural light dark cycle [*Moore*, 2006]. All of these studies provide evidence that solar radiation promotes production of CH_3I in surface seawater. However, as noted, the earlier studies did not resolve possible diurnal variation of $[CH_3I]$.

The *daytime* accumulation rate was calculated based on the accumulation during the daytime period ($\Delta[CH_3I]_{day}$) only (i.e., over 9 h; from 08:00 to 17:00), whereas the *daily* accumulation rate was calculated based on the accumulation of methyl iodide over 24 h ($\Delta[CH_3I]_{24h}$), such that

$$\mathrm{Rate}_{day} = \frac{\Delta[CH_3I]_{day}}{9h} \text{ or } \mathrm{Rate}_{24h} = \frac{\Delta[CH_3I]_{24h}}{24h}. \quad (2)$$

Both the *daytime* accumulation rates and the *daily* accumulation rates of different samples in different seasons were calculated as hourly rates and are presented in Tables 1 and 2. Here it should be noted that the *daytime* accumulation rates were 10 times higher than the *daily* accumulation rates because methyl iodide produced during day was degraded during night.

The *daytime* accumulation rates ($Rate_{day}$) in summer during this study (0.1–0.2 pmol L^{-1} h^{-1}) are lower than the 1.0–1.5 pmol L^{-1} h^{-1} reported for short-term (<2 h) incubations conducted under artificial light by *Moore and Zafiriou* [1994]. The latter used artificial light with an intensity of 1325 W m^{-2} over 280–1100 nm. In our study, the strongest light level (in summer) was 498 W m^{-2} over 310–2800 nm (average from 08:00 to 17:00). The different light intensities might be one reason to explain the difference of the daytime (or short-term) accumulation rates in the presence of light (Table 1).

Table 1. Comparison of *Daytime* Accumulation Rates ($Rate_{day}$ in pmol L^{-1} h^{-1}) in Nonfiltered Samples (NF) or Filtered Samples (F)

$Rate_{day}$	*Moore and Zafiriou* [1994]		This Study (2009–2010)	
Incubation time	2 h		9 h	
Sample source	Coastal North seawater		Coastal Kiel Fjord water	
Latitude	52.6°N		54.3°N	
Irradiance (W m^{-2})	1325 (artficial)[a]		498 (summer)[b]	
Samples	Light	Dark	Light	Dark
F (pmol L^{-1} h^{-1})	1.11	0.15	0.14	0.04
NF (pmol L^{-1} h^{-1})			0.17	0.04

[a]At a solar zenith angle of 48°, over 280–1100 nm.
[b]Average from 08:00 to 17:00 over 310–2800 nm.

Table 2. Comparison of *Daily* Accumulation Rates ($Rate_{24h}$ in pmol L^{-1} h^{-1}) in Nonfiltered Samples (NF) or Filtered Samples (F)

$Rate_{24h}$	*Moore* [2006]		*Richter and Wallace* [2004]		This Study (2009–2010)	
Incubation time	50 h		24 h		24 h	
Sample source	Offshore water		Tropical Atlantic		Coastal Kiel Fjord water	
Latitude	50°N–55°N		10°N		54.3°N	
Irradiance (W m^{-2})	0.5 (with fog)[a]		500–590 (daily mean)[b]		498 (summer)[c]	
Samples	Light	Dark	Light	Dark	Light	Dark
F (pmol L^{-1} h^{-1})	0.005–0.015	0.0004	0.1	0.02	0.03	0.01
NF (pmol L^{-1} h^{-1})			0.17	0.03	0.008–0.01	−0.006 to 0.002

[a]Average over 12 h, light intensity at 411 nm.
[b]Daily average (12 h) for latitude range of global horizontal irradiation map by *SolarGIS* [2014].
[c]Average from 08:00 to 17:00 over 310–2800 nm.

The *daily* accumulation rates ($Rate_{24h}$) in this study ranged from 0.008 to 0.03 pmol L^{-1} h^{-1} (in Table 2). Our results are similar in magnitude to the results of multiday incubations reported by *Moore* [2006]. *Moore* [2006] conducted two incubation experiments using offshore waters (station T5: 50°N, 45°W) during two cruises in the North Atlantic in spring and summer of 2003. They observed daily accumulation rates ($Rate_{24h}$) of only 0.005 to 0.015 pmol L^{-1} h^{-1} in "sunlit" samples (>50 h incubation). However, both sets of rates are ~10 times lower than *daily* rates reported by *Richter and Wallace* [2004] (0.17 pmol L^{-1} h^{-1} for NF samples and 0.10 pmol L^{-1} h^{-1} for F samples) in the tropical Atlantic. *Moore* [2006] explained their lower daily accumulation rates possibly due to the average light level during their incubations being reduced by frequent fog.

There were several differences between all of these studies. As noted above, the different light intensities might be one factor. *Richter and Wallace* [2004] conducted incubation experiments at 10°N under clear skies. They did not report actinic measurements; however, the irradiation at 10°N is typically 8 times higher than at 50°N. The difference might also be attributable, at least in part, to the different water types used in these studies. In our study, coastal water was used, compared with offshore North Atlantic water used by *Moore* [2006] and oligotrophic water of the tropical Atlantic used by *Richter and Wallace* [2004]. The different water types might have impacted light absorption and/or photochemical precursor concentrations and hence production rates, but they might also have impacted chemical or biological loss processes (see below section 4.4).

4.3. Filtration Effects

As discussed in section 1, the relative importance of abiotic and biotic processes underlying methyl iodide production in the ocean continues to be debated [*Stemmler et al.*, 2014]. In order to determine if methyl iodide production is mainly associated with biological activity or photochemistry, a comparison between incubations of filtered and unfiltered natural seawater samples was performed. Note that whereas our sampling location lies well outside the natural region of *Prochlorococcus* occurrence [*Urbach et al.*, 1992; *Partensky et al.*, 1999], diatoms are present in Kiel Fjord [*Sommer*, 1996].

No significant difference of the daytime accumulations of CH_3I ($\Delta[CH_3I]_{day}$) was observed between NF and F samples (Figure 3, blue frame). June and July were chosen for the filtered/nonfiltered comparison, because these months experience strongest solar radiation intensity and also higher biological activity. Our observations appear to be consistent with the arguments expressed in earlier studies [e.g., *Moore and Zafiriou*, 1994; *Happell and Wallace*, 1996; *Richter and Wallace*, 2004; *Moore*, 2006; *Stemmler et al.*, 2014; *Shi et al.*, 2014] that the production of methyl iodide in the ocean is not directly biological (i.e., metabolic) but rather photochemical. Nonetheless, *Richter and Wallace* [2004] observed that the CH_3I accumulation in filtered samples from the tropical Atlantic was ~30% lower than in untreated samples. They suggested this may have been a result of organic precursor removal via filtration, rather than a difference in biological activity due to filtration per se. Compared with the 0.1 μm membrane filter used in their study, a 0.2 μm membrane filter was used in our study. The daily accumulation ($\Delta[CH_3I]_{24h}$) in filtered samples was 11% (mean) lower than that in the unfiltered samples but this difference was not statistically significant.

4.4. Loss Processes

In our experiments, the loss of CH_3I during nighttime was much larger in samples that had been incubated in the light. As a consequence, the daily accumulation of CH_3I over a full 24 h period ($\Delta[CH_3I]_{24h}$) was low (Table 2 and Figures 1 and 4). Figure 5 shows the correlation between CH_3I concentrations and loss rates in

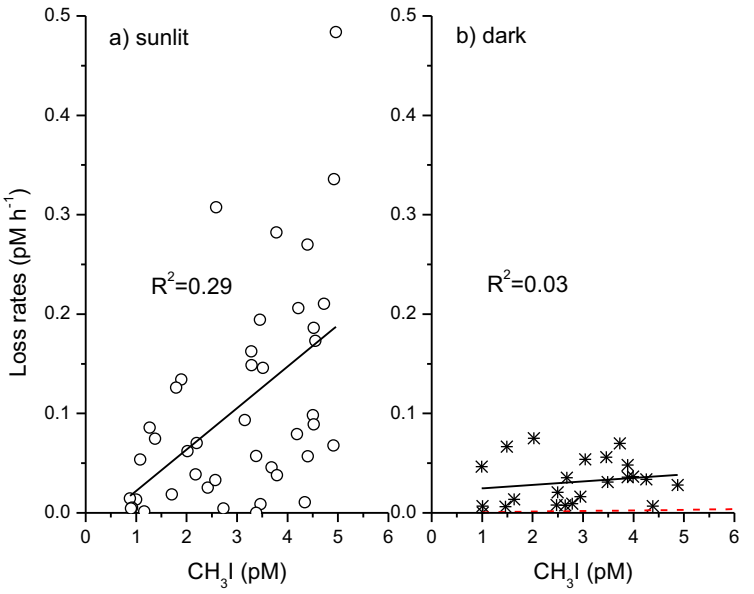

Figure 5. Loss rates of CH_3I as a function of peak daytime concentrations in both (a) "sunlit" samples (circles) and (b) "dark" samples (stars). Solid lines represent linear regressions. The dashed line in Figure 5b depicts the loss rates expected due to chloride substitution as calculated for the maximum temperatures (20°C) encountered during the study.

the "sunlit" samples and the "dark" samples ($R^2 = 0.29$, $p << 0.01$ and $R^2 = 0.03$, $p = 0.45$, respectively). The loss rate of CH_3I correlated with its concentration for the "sunlit" samples. The correlation, while significant, exhibits a lot of scatter which may be a result of the limited time-resolution of our data, other measurement uncertainty, and the possibility that additional factors may affect loss rates (e.g., temperature, CDOM, etc.).

The commonly considered losses for CH_3I in field studies are the sea-to-air flux and nucleophilic substitution [*Elliott and Rowland*, 1993; *Nightingale et al*., 2000; *Richter and Wallace*, 2004; *Moore*, 2006; *Archer et al*., 2007]. Of these two loss processes, the sea-to-air flux tends to dominate for surface waters [*Nightingale et al*., 2000; *Richter and Wallace*, 2004; *Chuck et al*., 2005; *Moore*, 2006; *Archer et al*., 2007]. However, during our incubation experiments, a sea-to-air loss was excluded because the flasks were sealed. Using the reaction rates of *Elliott and Rowland* [1993], nucleophilic substitution rates by chloride ion were calculated. The average for Kiel Fjord waters from May 2009 to July 2010 was 0.002 pmol L^{-1} h^{-1} (range: 4.2×10^{-5} to 0.006 pmol L^{-1} h^{-1}, as a result of the different temperatures in summer of 21°C and winter of −0.5°C), which is equivalent to 0.047 pmol L^{-1} d^{-1} and a range of 0.001–0.147 pmol L^{-1} d^{-1}. However, the observed nighttime loss rate of CH_3I from our "sunlit" incubation flasks was 1–2 orders of magnitude higher, averaging 0.11 pmol L^{-1} h^{-1} (range: 0.0001–0.48 pmol L^{-1} h^{-1}). For the "dark" samples, loss rates were also higher than predicted from chloride substitution, averaging 0.03 pmol L^{-1} h^{-1} (range: 0.003–0.07 pmol L^{-1} h^{-1}). These results suggest that additional loss pathways were operating during our incubations. There are two main possibilities:

1. Bacterial degradation: some bacteria are likely to have passed through the 0.2 μm filters or remained on bottle walls, and our incubation experiments were not axenic. As noted above, *Moore* [2006] reported "non-chloride loss" rates ranging from <1 to 15% d^{-1} (mean: 7%) based on incubation experiments using ^{13}C labeled methyl iodide in open ocean waters. However, the nighttime loss rates for our "sunlit" incubations were >80% d^{-1}. Bacterial degradation is one possible mechanism to explain this large loss. *Richter and Wallace* [2004] conducted incubation experiments with alternative treatments, including samples that had been filtered in parallel to samples that had been poisoned with mercury (II) chloride (the poisoned water still contained bacterial cells and organic matter, but without metabolism). Their poisoned samples had slightly higher CH_3I accumulation, which might have been consistent with reduced bacterial degradation, but the difference was not statistically significant. They speculated that removal of organic precursors led to the decreased accumulation of CH_3I in their filtered samples. However, their experiments were not designed to resolve diurnal variability. As a result, the experiments did not provide any information on nighttime losses.

2. Chemical degradation: alternatively, CH_3I might be lost via an additional, as-yet unknown, chemical degradation pathway. Figure 5 suggests first-order (or higher) kinetics for the loss process in the "sunlit" samples, but not in the "dark" samples. We find this difference between the sunlit and dark incubations hard to reconcile with a bacterial degradation process. We speculate that the higher removal rates in the "sunlit" samples may be the result of reaction with an unknown, photochemically produced, reactive species. Clearly, an explanation for this behavior requires further experimental investigation.

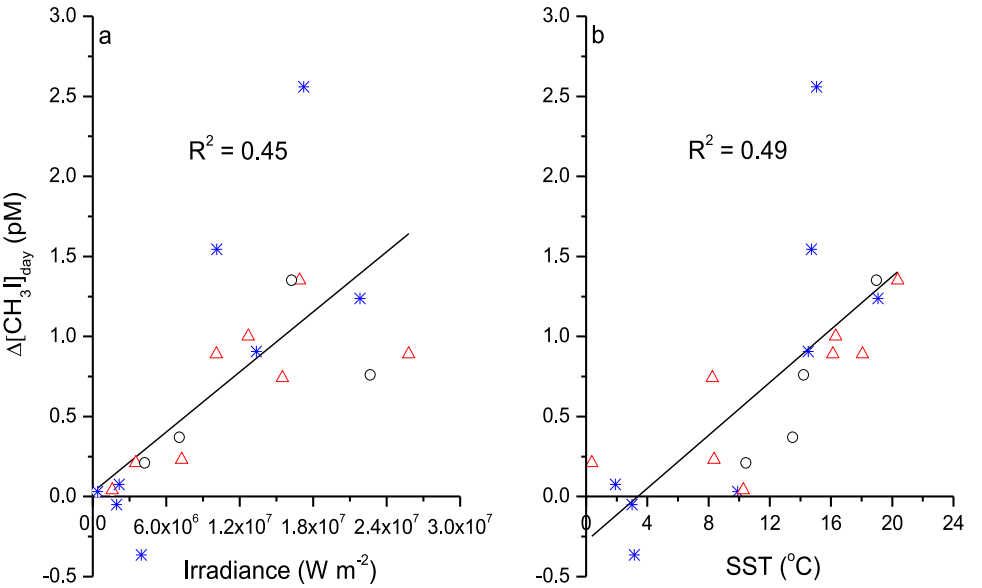

Figure 6. Scatterplots of the daytime accumulation of CH_3I ($\Delta[CH_3I]_{day}$) versus (a) SSR and (b) SST during the incubations. Red triangles denote NF-samples, black circles are F-samples, and blue stars are O-samples.

4.5. Correlations With Seasonally Varying Parameters

The time series of incubation experiments presented here were conducted over the same time period as a study of in situ variations published in the companion paper of *Shi et al.* [2014]. The annual cycles of irradiance, CDOM, nutrients, SST, salinity, and Chl*a* for the same sampling location are presented in *Shi et al.* [2014], where they were used to investigate correlations with monthly mean concentrations of in situ [CH_3I] and estimates of daily production rates. They found that solar radiation had the strongest positive correlation ($R^2 = 0.93$) of all variables with [CH_3I], which appeared to be consistent with the hypothesis that SSR is the primary forcing of CH_3I production in surface seawater, through a photochemical pathway. However, they also found that the daily net production rates (P_{net}) of CH_3I derived from the seasonal time series was correlated at zero lag with SST, SSR, and Chl*a* (there was no correlation of [CH_3I] or P_{net} with nutrients, salinity, or CDOM). The broad seasonal peak of P_{net} made it impossible to distinguish the key factor controlling CH_3I net production using the in situ concentration data alone.

During our incubation experiments, $\Delta[CH_3I]_{day}$ also showed a pronounced seasonal cycle with higher daytime accumulations in summer months (Figure 3). Weak but significant correlations were observed of $\Delta[CH_3I]_{day}$ with both SSR and SST ($R^2 = 0.45$ and 0.49, respectively, $p << 0.01$, Figure 6). These regressions confirm that SSR and/or SST are closely linked to the daily production of methyl iodide in the incubation experiments. As discussed in the companion paper of *Shi et al.* [2014], the temporal (and geographical) variation in SST is determined strongly by irradiance. Thus, the positive correlation with SST could also be due to the influence of light and remain consistent with SSR as the primary forcing of CH_3I production. In the case of this incubation study, the lack of difference of $\Delta[CH_3I]_{day}$ between F and NF samples lends some further support for the photochemical production pathway.

4.6. Insight Into the Mass Balance of CH_3I in the Kiel Fjord

A seasonal mass balance of CH_3I in the Kiel Fjord was examined using monthly in situ time series study [*Shi et al.*, 2014], collected in parallel with these incubation studies. The results of the incubation experiments can be compared with this in situ mass balance. In *Shi et al.* [2014], the daily (24 h) mass balance for CH_3I for surface waters in Kiel Fjord was given as

$$\Delta[CH_3I]_{24h} = P_{net} - L_{sea-air} - L_{SN_2} - L_{Mix}, \quad (3)$$

where $L_{sea\text{-}air}$ is the daily sea-to-air flux of CH_3I, L_{SN2} is the "chemical" loss due to nucleophilic substitution of Cl^- for I^-. P_{net} is the daily net production of CH_3I (in units of pmol L^{-1} over a 24 h period). However, the diurnal data from the incubation experiments revealed additional, uncharacterized losses that are not

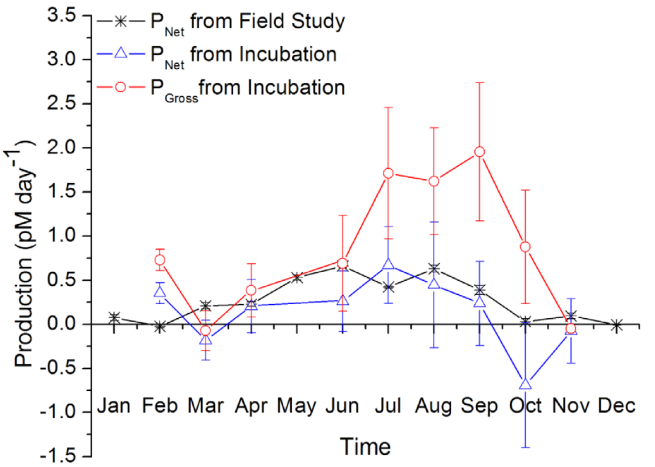

Figure 7. Seasonal variations of gross CH_3I production (P_{gross}) based on incubation experiments (red line; see equation (6)), P_{net} derived from the incubation experiments (blue line; see equation (4)), and P_{net} based on the field sampling (black line) (as calculated in *Shi et al.* [2014]). The production estimates are for daily production amounts (i.e., over 24 h period). Note that here, P_{gross} is expressed on a per day basis; however, we have assumed that all production takes place during the daytime hours.

represented in equation (3), which implies that the overall production of CH_3I must be considerably larger than P_{net}. In analogy with biological production we refer to this as gross production (P_{gross}) defined as

$$P_{gross} = P_{net} + L_{other}. \quad (4)$$

When applying equation (3) to the sealed flasks of the incubation experiments it is obvious that $L_{air\text{-}sea} = L_{mix} = 0$, so that equation (3) reduces to

$$\Delta[CH_3I]_{24hr} = P_{net} - L_{SN_2}, \quad (5)$$

where L_{SN2} is calculated using the corresponding daily average temperature, salinity, and CH_3I concentration. Although the monthly averages of CH_3I accumulation over 24 h ($\Delta[CH_3I]_{24h}$) were not statistically significant in most months because of experimental and measurement error, an estimate of P_{net} was calculated using equation (5) in order to allow comparison with the P_{net} values calculated from the in situ study.

Further, the accumulation in the incubation flasks during the daytime can be defined as

$$\Delta[CH_3I]_{day} = P_{gross(day)} - L_{other)} - L_{SN_2(day)}, \quad (6)$$

where $\Delta[CH_3I]_{day}$ represents accumulation during the daytime period only (i.e., over 9 h; approximately from 08:00 to 17:00). Note that here, $L_{other(day)}$ and $L_{SN2(day)}$ are calculated for a 9 h period rather than for a 24 h period as in equation (3). For the remaining nighttime period, we assume that $P_{gross} = 0$ and that the loss rate remains unchanged so that

$$\Delta[CH_3I]_{night} = -L_{SN_2(night)} - L_{other(night)} \quad (7)$$

Here $L_{other(night)}$ and $L_{SN2(night)}$ are calculated for a 15 h period (from 17:00 to 08:00 of the second day). $L_{other(night)}$ can therefore be estimated directly from the nighttime decreases in CH_3I concentration observed during the incubations. While the loss rate from "sunlit" samples appears to correlate with CH_3I concentration (Figure 5), the estimate of $L_{other(night)}$ represents an average loss rate for the range of CH_3I concentrations present in the flasks over the nighttime period. The daytime concentration increase and range of CH_3I concentrations is similar to the nighttime concentration decrease/range and we therefore assume that average $L_{other(night)}$ is appropriate also for the loss over the daytime period, $L_{other(day)}$, as well. Given these assumptions, P_{gross} was calculated using equation (6) and its monthly average values are plotted in Figure 7 (red line).

The values of P_{net} derived from the incubation experiments can be compared with P_{net} values derived from the field time series study. The latter exhibited strong seasonality, varying from near-zero in winter months to maximum values of 0.57 ± 0.15 pmol L^{-1} d^{-1} in summer (Figure 7, black line). P_{net} derived from incubation experiments (Figure 7, blue line) was 0.46 ± 0.19 pmol L^{-1} d^{-1} in summer (June to August) and 0.14 ± 0.33 pmol L^{-1} d^{-1} in winter (November to February). Hence, although it was not possible to detect a seasonal cycle, the overall magnitude of P_{net} derived from the incubations is in good agreement with P_{net} values derived from the field study [*Shi et al.*, 2014]. P_{gross} is much higher than both estimates of P_{net} in summer (from July to October). The difference reflects the excess of CH_3I production over loss by uncharacterized processes, such as those listed and discussed in section 4.4. Both the incubation experiments and the time series revealed a close, seasonal relationship between CH_3I production and light intensity.

5. Summary

"Whole-bottle" (quartz-flask) long-term (57 h) incubation experiments were conducted to examine the production of methyl iodide in nearshore, brackish waters from July 2009 to July 2010. A strong diurnal variation of methyl iodide was observed in the samples incubated under natural light conditions. This has not been observed before, likely because prior incubation experiments did not resolve the diurnal cycle. On average, the concentration of methyl iodide in the sunlit samples increased between 08:00 and 17:00, and decreased from 17:00 to 08:00. Compared to these sunlit samples, the CH_3I concentration in dark control samples varied only slightly over 24 h. This, and lack of a significant difference between filtered and nonfiltered samples implies that solar radiation plays an important role in the CH_3I production process.

Methyl iodide loss during nighttime was unexpectedly large in the "sunlit" samples. The large nighttime losses caused the daily net accumulation of CH_3I over 24 h periods to be low. During our incubation experiments, the calculated loss rate due to chloride substitution was 1–2 orders of magnitude lower than the observed loss rate of CH_3I. The loss rates of CH_3I correlated with its concentrations in the sunlit samples, but not in the dark samples. For the dark samples, loss rates were also higher than predicted due to chloride substitution alone. These results suggest that additional loss pathways were operating during our incubations. One possibility is bacterial degradation, because our incubation flasks were not axenic. However, the difference of loss rates between the sunlit and dark incubations is hard to reconcile with a bacterial degradation processes alone. Another possibility for the higher removal rates in the sunlit samples may be reaction with an unknown, photochemically produced, reactive species. The mechanisms of loss during nighttime require further experimental investigation.

A mass balance for CH_3I was calculated based on the results of incubation experiments, assuming that P_{gross} is zero in the night, and L_{other} is an average loss rate for the range of $[CH_3I]$ during nighttime, which is also appropriate as daytime loss rate. Given these assumptions, P_{gross} and P_{net} were calculated on a monthly basis. P_{gross} showed a strong seasonal variation with a maximum in summer and a minimum in winter, but it was not possible to resolve seasonal variable in P_{net}. The values of P_{net} ranged from -0.69 to 0.67 pmol L^{-1} d^{-1}, consistent with P_{net} values derived from the accompanying field study [*Shi et al.*, 2014]. P_{gross} is much higher than both estimates of P_{net}, especially in summer months. The difference implies an additional (uncharacterized) loss pathway for CH_3I, such as microbial degradation or "nonchloride" chemical degradation.

In summary, the diurnal variability observed in the incubation flasks shows that short-term production (and loss) rates can be very much higher than the rates estimated from long-term, low frequency trends and budgets. This has important implications for the interpretation of rates calculated from prior incubation studies using natural light, which have not resolved the diurnal cycle, as well as for the design of future field and experimental studies.

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