

RESEARCH ARTICLE

Seasonal variability of methyl iodide in the Kiel Fjord

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Key Points:

- A seasonal cycle of CH₃I in the Kiel Fjord
- The primary forcing of CH₃I production in surface seawater
- The broad seasonal peak of P_{net} makes it difficult to determine the key factor

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Abstract From October 2008 to November 2010, CH₃I concentrations were measured in the Kiel Fjord together with potentially related biogeochemical and physical parameters. A repeating seasonal cycle of CH₃I was observed with highest concentrations in summer (ca. 8.3 pmol L⁻¹; June and July) and lowest concentrations in winter (ca. 1.5 pmol L⁻¹; December to February). A strong positive correlation at zero lag between [CH₃I] and solar radiation ($R^2 = 0.93$) was observed, whereas correlations with other variables (SST, Chlorophyll *a*) were weaker, and they lagged CH₃I by ca. 1 month. These results appear consistent with the hypothesis that SSR is the primary forcing of CH₃I production in surface seawater, possibly through a photochemical pathway. A mass balance of the monthly averaged data was used to infer mean rates of daily net production (P_{net}) and losses for CH₃I over the year. The sea-to-air flux of CH₃I in the Kiel Fjord averaged 3.1 nmol m⁻² d⁻¹, the mean chemical loss rate was 0.047 pmol L⁻¹ d⁻¹, and P_{net} varied systematically from winter to summer (from 0 to 0.6 pmol L⁻¹ d⁻¹). P_{net} was correlated at zero lag with SST, SSR, and Chl_a ($R^2 = 0.55, 0.67, \text{ and } 0.73$, respectively, $p \ll 0.01$). The lagged cross-correlation analysis indicated that SSR led P_{net} by 1 month, whereas the strongest cross correlations with Chl_a were at lags of 0 to +1 month, and SST lagged P_{net} by 1 month. The broad seasonal peak of P_{net} makes it difficult to determine the key factor controlling CH₃I net production using in situ concentration data alone.

1. Introduction

Iodine plays an important role in the chemistry of reactive gases and particles in the atmosphere. For example, iodine radicals can catalytically destroy tropospheric ozone [Solomon *et al.*, 1994; Davis *et al.*, 1996; Carpenter *et al.*, 1999; Tegtmeier *et al.*, 2013] and participate in aerosol formation in the troposphere [McFiggans *et al.*, 2000]. The ocean has long been recognized as being a major source of iodine to the atmosphere [Miyake and Tsunogai, 1963; Lovelock and Maggs, 1973; Rasmussen *et al.*, 1982; Heumann *et al.*, 1987]. Initially, transport of volatile organoiodine compounds from sea to air was recognized to be important for delivering reactive iodine because the carbon-iodine bond is relatively weak and can be easily broken by solar UV radiation (260–360 nm) to yield, for example, methyl and iodine radicals [Tsao and Root, 1972; Solomon *et al.*, 1994]. Methyl iodide (CH₃I), with its relatively high concentrations in the atmosphere and presumed oceanic source, was considered to be the most important carrier of iodine atoms from sea to air [Lovelock, 1975; Manley *et al.*, 1992; Moore and Zafriou, 1994; Laturnus, 1995; Happell and Wallace, 1996; Richter and Wallace, 2004; Smythe-Wright *et al.*, 2006; Yokouchi *et al.*, 2008; Hughes *et al.*, 2009; Wang *et al.*, 2009]. Recently, the importance of other iodine compounds, such as inorganic iodine and very short-lived iodocarbons (e.g., I₂, CH₂I₂), has also been determined [McFiggans, 2005; O'Dowd and Hoffmann, 2005; Carpenter *et al.*, 2013].

Nevertheless, CH₃I continues to receive attention both because of its role in iodine transport and chemistry, including transport to higher altitudes [Solomon *et al.*, 1994; Tegtmeier *et al.*, 2013], and its potential to be a “model compound” for investigating processes, budgets, and rates related to ocean-atmosphere transfer [Roether, 1983; Richter, 2003]. The production pathways of CH₃I and controls on its sea-to-air flux remain poorly understood. Several investigations have attempted to evaluate the role of macro algae, phytoplankton, and bacteria in producing CH₃I with differing results [Lovelock, 1975; Manley *et al.*, 1992; Moore and Tokarczyk, 1993; Laturnus, 1995; Nightingale *et al.*, 1995; Manley and delaCuesta, 1997; Amachi *et al.*, 2001; Smythe-Wright *et al.*, 2006; Brownell *et al.*, 2010; Hughes *et al.*, 2011]. In contrast, the primary importance of photochemical production of methyl iodide has been demonstrated using incubation experiments [Moore and Zafriou, 1994; Richter and Wallace, 2004] and suggested by correlations [Happell and Wallace, 1996; Yokouchi *et al.*, 2001]. Despite these findings, the relative role of biology and photochemistry as sources of methyl iodide in the global ocean continues to be debated.

Long-term time series observations can reveal indications about the key processes controlling concentration levels as well as constrain overall net rates of production and loss. As part of a study to investigate sources and sinks of methyl iodide in the ocean, seawater samples were collected weekly from the Kiel Fjord of the Baltic Sea, Kiel, Germany, for the measurement of methyl iodide and a range of parameters related to CH_3I production.

2. Methods

Surface water was sampled from the Kiel Fjord (54.3°N, 10.1°E), one to two times per week at approximately 10 A.M. for methyl iodide (sometimes sampled at 2 P.M.), colored dissolved organic matter (CDOM), iodide, iodate, chlorophyll *a* (Chl*a*), and nutrients from October 2008 until July 2010. All samples were collected from the GEOMAR West Shore building pier at a water depth of 0.5 m (maximum depth of inner Kiel Fjord is ca. 12 m). Meteorological data (including light levels) were measured nearby every 8 min over the same time period by the Maritime Meteorology research unit at GEOMAR. Methyl iodide was analyzed using purge and trap gas chromatography with electron capture detection (ECD). For all measurements, a FISON 8000 gas chromatograph (GC), equipped with a capillary column (RTX-VGC; 60 m; 1.4 μm coating, column diameter: 0.25 mm), and helium as carrier gas, was used. Every sample (250 mL) was analyzed in triplicate, and the standard deviation of triplicate measurements was <5%.

Ancillary data were measured using a variety of methods. For CDOM and inorganic iodine species analysis, 50 mL seawater was syringe filtered through 0.2 μm filters (SARSTEDT AG) and stored at -20°C in white high-density polyethylene bottles (HDPE, from Thermo Scientific Nalgene), and in brown HDEP bottles (respectively) at -20°C until laboratory analysis. CDOM absorption coefficients were measured using an Ocean Optics USB4000 UV-VIS spectrophotometer with the same analytical method described in *Heller and Croot* [2010]. Cathode stripping square wave voltammetry with a hanging mercury drop electrode (HMDE) was used to measure iodide according to the method of *Luther et al.* [1988] (as modified by *Campos* [1997]). Iodate was measured by spectrophotometry with a "Unicam" spectrophotometer (UV 300, Thermo-Forma) [Truesdale, 1978]. The analysis steps were the same as described by *Bluhm et al.* [2010, 2011]. A 50 mL volume of nonfiltered seawater was collected for nutrient analysis and stored in white polyethylene bottles at -20°C until laboratory analysis. The autoanalyzer "Quattro" (SEAL Analytical) was used in this study applying the analytical methods for nutrients of *Hansen and Koroleff* [2007]. One liter of water for Chl*a* analysis was collected in polyethylene bottles. The samples were vacuum filtered through 25 mm GF/F filters (Whatman) immediately after sampling with a pressure of <0.2 atm. The filters were frozen at -20°C and kept in the dark prior to analysis. Pigments were analyzed by High-Performance Liquid Chromatography (HPLC) using the procedure described in the Protocols for the Joint Global Ocean Flux Study (JGOFS) Core Measurements, published by UNESCO in 1994 [*Knap et al.*, 1996].

3. Results

3.1. Seasonal Variation of Methyl Iodide Concentrations

The dissolved CH_3I concentrations from the Kiel Fjord time series are plotted in Figure 1. The mean concentration over the entire sampling period (from October 2008 to December 2010) was $5.00 \pm 2.79 \text{ pmol L}^{-1}$ (ranging from 0.45 to $11.20 \text{ pmol L}^{-1}$). The concentrations of CH_3I showed a pronounced seasonal cycle, increasing from February through June, with maximum concentrations in summer (June and July), and decreasing during August

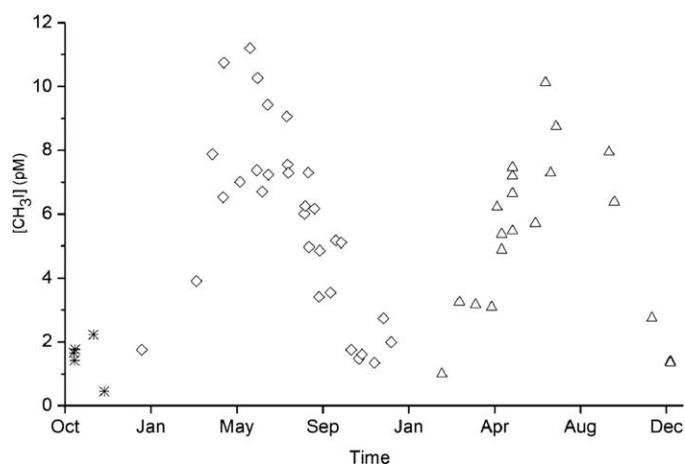


Figure 1. Concentration of CH_3I in the Kiel Fjord between October 2008 and December 2010. Stars (*) indicate 2008, diamonds (\diamond) indicate 2009, and triangles (Δ) indicate 2010.

and September, with minimum values reached during the winter months (November to February). The monthly mean concentrations of CH_3I over the 3 year study increased from $0.99 \pm 0.15 \text{ pmol L}^{-1}$ in February to $8.93 \pm 2.05 \text{ pmol L}^{-1}$ in June, and then gradually decreased again to $1.43 \pm 0.30 \text{ pmol L}^{-1}$ in December (Figure 1).

3.2. Seasonal Variation of Other Parameters

Figure 2 depicts the monthly mean surface concentration of CH_3I together with sea surface temperature (SST), solar radiation (SSR), salinity (SSS), $\text{Chl}a$, CDOM, iodide (I^-), iodate (IO_3^-), and nitrate (NO_3^-). Monthly mean SST remained at $<6^\circ\text{C}$ from November to April, and increased rapidly at the end of April to a maximum of approximately 20°C in late July. There was a noticeable time lag between the seasonal changes of SSR and SST, with the maximum of surface irradiance occurring in June (Figure 2c) and the maximum of SST in July (Figure 2a). The maximum of CH_3I also occurred in June, prior to the maximum in SST (Figure 2). Lower salinity was observed in summer ($S = 13\text{--}14$) compared with winter ($S = 16$) (Figure 2b). This is related to seasonal variation of North Sea water influence in the south-western Baltic, which is generally stronger in winter months. The highest concentrations of $\text{Chl}a$ ($5\text{--}8 \mu\text{g L}^{-1}$, Figure 2d) occurred in June and late September with a minimum ($0.99 \mu\text{g L}^{-1}$) in January.

CDOM absorption varied between 4.2 and 4.6 m^{-1} from December to May, and fell to 3.5 m^{-1} in June. From July to November, the CDOM absorption increased again to 4.2 m^{-1} (Figure 2e). The concentration of iodate in the Kiel Fjord ranged from 100 to 165 nmol L^{-1} (Figure 2f). The variation in iodide was small from January to August (ranging from 100 to 130 nmol L^{-1}), but concentrations increased rapidly in September from 120 to 240 nmol L^{-1} (Figure 2g). Nitrate decreased from January to April ($54\text{--}6 \mu\text{g L}^{-1}$), and then varied between 4 and $10 \mu\text{g L}^{-1}$ from May to December (Figure 2h).

4. Discussion

4.1. CH_3I Concentration Ranges and Their Seasonality

Reported concentrations of CH_3I in coastal and shelf sea environments range from 0.6 to 61 pmol L^{-1} [Love-lock, 1975; Manley *et al.*, 1992; Moore and Tokarczyk, 1993; Happell and Wallace, 1996; Moore and Groszko, 1999; Carpenter *et al.*, 2000; Chuck *et al.*, 2005; Archer *et al.*, 2007; Wang *et al.*, 2009]. CH_3I concentrations in the Kiel Fjord from October 2008 to December 2010 fall within this range ($0.45\text{--}11.20 \text{ pmol L}^{-1}$) and are similar to those measured from the shelf seas of the western English Channel ($0.6\text{--}14.6 \text{ pmol L}^{-1}$) [Archer *et al.*, 2007].

The repeating seasonal cycle of CH_3I found in this study is similar to the seasonal pattern of CH_3I concentrations observed in the western English Channel with a summer maximum and winter minimum [Archer *et al.*, 2007]. Wang *et al.* [2009] reported seasonality of CH_3I in the open ocean for the first time with maximum concentrations also observed in summer (Table 1). Seasonal variation of atmospheric CH_3I (based on nine observation stations from 82.5°N to 68.5°S in both hemispheres) was also reported by Yokouchi *et al.* [2008]. The seasonality was interpreted to imply that there was a seasonal variation of the oceanic source of methyl iodide with the maximum inferred sea-to-air flux in summer-autumn.

4.2. Correlations of CH_3I With Other Parameters

The correlations of the seasonal variability of CH_3I in the Kiel Fjord with corresponding $\text{Chl}a$ data and physical data can provide information useful for understanding the factors that influence oceanic CH_3I production in temperate regions. An analysis based on scatterplots and linear regression was used initially to investigate the relationship between the monthly mean values of the surface water concentrations of CH_3I and the other measured parameters. The seasonal variation of methyl iodide concentration was most strongly correlated with SSR ($R^2 = 0.93$) and weakly correlated with SST ($R^2 = 0.58$) and $\text{Chl}a$ ($R^2 = 0.51$). Inverse correlations were observed with salinity ($R^2 = 0.46$) and nitrate ($R^2 = 0.51$). No significant correlations were observed with CDOM ($R^2 = 0.20$), iodide ($R^2 = 0.04$), and iodate ($R^2 = 0.12$; in Table 2). Using the weekly average data, similar qualitative results were observed but with weaker correlations. The weaker correlations might result, in part, from the fact that samples for $\text{Chl}a$ and nutrient analysis were collected 1–2 days later than the CH_3I data as well as reflecting analytical and high-frequency “noise” in the data. In order to focus on seasonal variations and avoid possible noise associated with day-to-day variability and/or analytical error, we focus on the monthly averaged data in the remainder of this study.

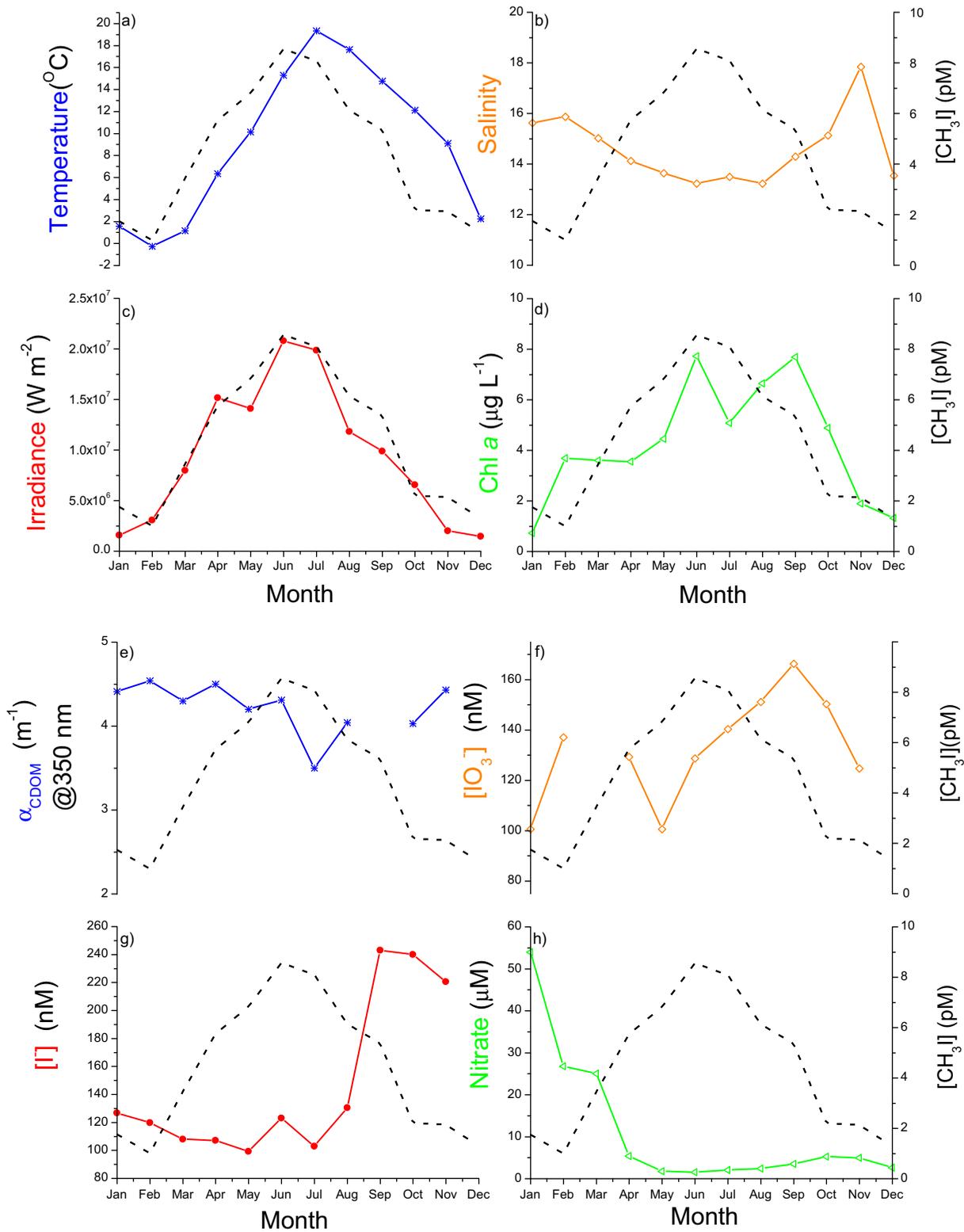


Figure 2. Annual variation of (a) SST, (b) SSS, (c) SSR, (d) Chl a, (e) CDOM, (f) iodate, (g) iodide, and (h) nitrate in the Kiel Fjord. The black dashed line depicts the annual cycle of methyl iodide. The data presented are monthly mean values for data collected from October 2008 to December 2010.

Table 1. Seasonal Variation of CH₃I in Surface Water and the Atmosphere From This and Previous Studies^a

Reference	Latitude	Site	[CH ₃ I] (pM) (mean)			
			Spring	Summer	Fall	Winter
<i>In Water</i>						
Tessier et al. [2002]		Scheldt Estuary	24.0	2.4	9.2	3.2
		Gironde Estuary		3.5	1.3	1.4
		Rhine Estuary	5.6		2.9	2.7
Archer et al. [2007]	50.25°N	Western English Channel	4.9	11.1	6.5	1.8
Wang et al. [2009]	43.4°N	Labrador sea	1.3	12.8	7.8	
	46.5°N	NW Atlantic	0.9	7.1	3.6	
<i>This Study</i>						
2009–2010	54.3°N	Kiel Fjord	5.03	6.95	2.18	1.39
<i>In Air</i>						
			[CH ₃ I] (ppt) (mean)			
Carpenter et al. [1999]	53.2°N	Mace Head	0.43	3.4		
Krummel et al. [2007]	40.4°S	Cape Grim	0.84	1.20	1.43	1.21
Yokouchi et al. [2008]	43.2°N	Cape Ochi-ishi	0.77	1.59	1.09	0.48

^aHere spring is defined as being from March to May, summer from June to September, October and November are the fall, and from December to February is winter.

The strongest positive temporal correlation between CH₃I and incident solar radiation ($R^2 = 0.93$) is consistent with the spatial correlations reported in Greenland/Norwegian Seas by Hoppel and Wallace [1996]. The latter reported a linear relationship between open ocean CH₃I saturation anomaly and incident photosynthetically active radiation (PAR) ($R^2 = 0.79$). This was interpreted to suggest that CH₃I production in the open ocean was controlled primarily by the amount of solar radiation reaching the sea surface and likely by a photochemical mechanism. Wang et al. [2009] observed a moderate positive correlation of CH₃I and PAR ($R^2 = 0.37$) in the NW Atlantic and suggested also that solar radiation (SSR) may be responsible for the production of CH₃I. However, it is also possible that the correlation with SSR exists because SSR correlates with the light-dependent growth of specific CH₃I-producing phytoplankton species (see below).

A moderately strong positive correlation observed between CH₃I and SST ($R^2 = 0.58$) might indicate that SST plays a role in controlling the production of CH₃I in the surface ocean. However, since the temporal variation in SST is determined strongly by the input of solar radiation, the positive correlation with SST could also reflect the influence of light on both variables and remain consistent with CH₃I production via a photochemical mechanism [Chuck et al., 2005; Wang et al., 2009]. Groszko [1999] observed that the sea-air concentration anomaly of CH₃I increased with SST < 15°C (described by an empirical fourth-order polynomial function; $R^2 = 0.64$). Above 18°C, CH₃I had no strong trend with temperature in their study. In this study, CH₃I concentrations continued to increase with SST even for waters up to 21.7°C. Further, the empirical fourth-order polynomial function of Groszko [1999] did not fit our data for waters < 15°C. SST can also influence the accumulation of methyl iodide through its control on the chemical loss reaction rate of methyl iodide [Elliott and Rowland, 1993; Moore, 2006] and decreases in solubility with increases in SST, so that warming can lead to an increase of the sea-to-air loss rate of methyl iodide [DeBruyn and Saltzman, 1997; Yamamoto et al., 2001; Yokouchi et al., 2001, 2008]. Finally, increased temperature also tends to enhance the growth rate of phytoplankton and bacteria (up to a temperature limit) [Eppley, 1972; Rhee and Gotham, 1981; Ratkowsky et al., 1982], including, potentially, the growth of organisms that might produce methyl iodide in seawater [Amachi et al., 2001]. It has been hypothesized that some species of cyanobacteria produce CH₃I (see discussion below) [Smythe-Wright et al., 2006; Brownell et al., 2010; Hughes et al., 2011] and

Table 2. Correlations Between [CH₃I] and Other Parameters Based on Monthly and Weekly Average Data

		Correlation With [CH ₃ I]				
		SST	SSR	SSS	Chla	NO ₃ ⁻
[CH ₃ I] Monthly (n = 12)	P value	0.04	≪0.01	≪0.01	0.42	0.17
	R ² (at zero lag)	0.58	0.93	0.46	0.51	0.51
	Time lag (months) ^a	+1 m	0		+1 m	
[CH ₃ I] Weekly (n = 39)	P value	≪0.01	≪0.01	0.36	≪0.01	
	R ² (at zero lag)	0.43	0.68	0.31	0.23	
	Time lag (weeks) ^a	+5 w	-1 w		+9 w	

^aNegative lag implies that the correlated variable (e.g., SSR) leads CH₃I.

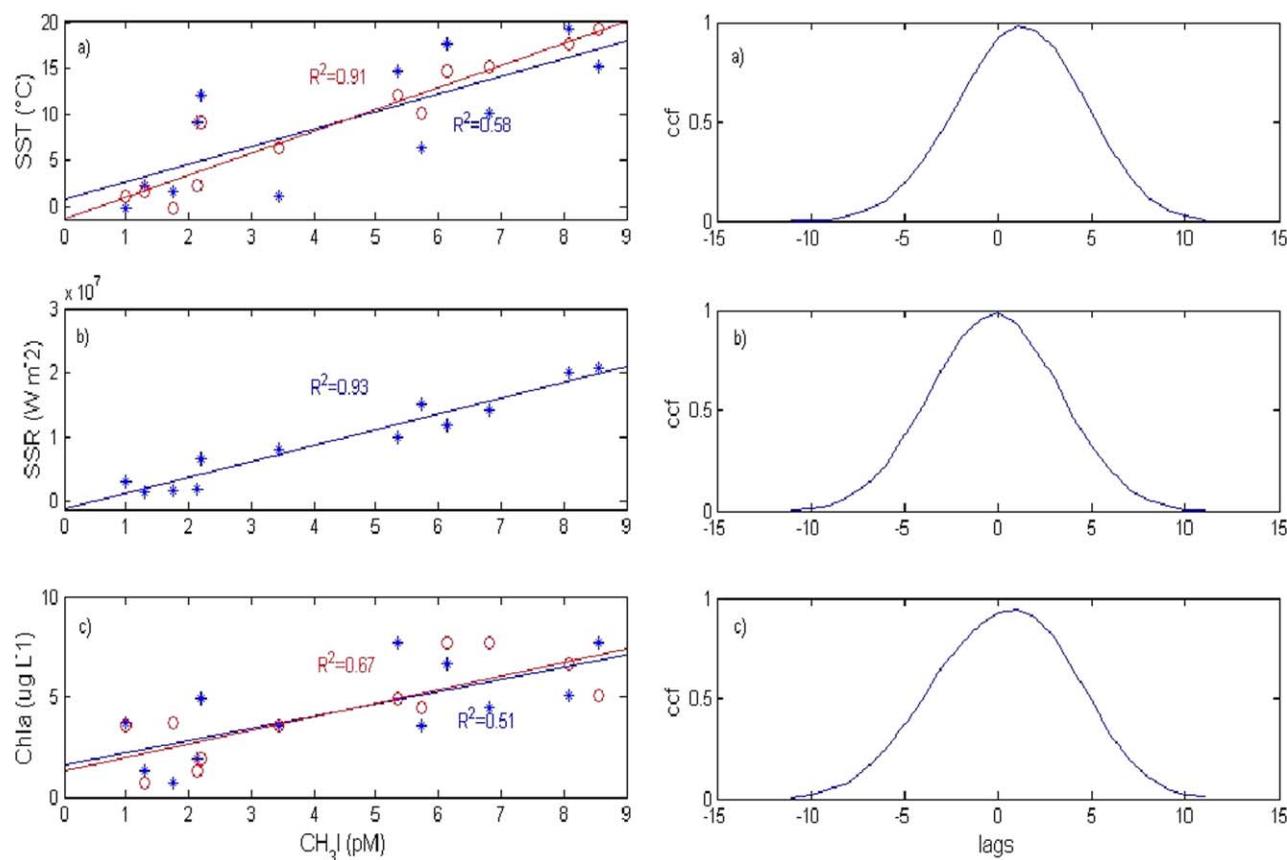


Figure 3. (left) Scatterplots of monthly mean CH₃I concentrations versus the monthly means of (a) SST, (b) SSR, and (c) Chla. Blue stars and lines indicate the data and regression at zero lag, red circles indicate the data after time shifting. (right) Lagged cross correlations (ccf) between [CH₃I] and the three parameters. Based on these cross-correlation results, the data were time shifted and regressions recalculated. The time-shifted results are shown on the left plots as red circles and lines.

these are restricted to certain temperature ranges. Therefore, SST can have both positive and negative, direct and indirect influence on CH₃I concentrations.

A positive correlation between Chla and CH₃I ($R^2 = 0.51$) was observed, which might imply CH₃I production via a biological production pathway. However, positive correlations with Chla were not observed in the studies of *Chuck et al.* [2005] ($R^2 = 0.006$) and *Happell and Wallace* [1996]. Indeed our observed correlation between Chla and CH₃I concentration may be spurious because seasonal Chla variability in the Kiel Fjord is also correlated with solar radiation. As noted above, evidence for biological production of CH₃I by *Prochlorococcus* has been suggested and debated [*Smythe-Wright et al.*, 2006; *Brownell et al.*, 2010; *Hughes et al.*, 2011] or diatoms [*Klick and Abrahamsson*, 1992; *Moore et al.*, 1996; *Manley and delaCuesta*, 1997; *Xie et al.*, 1999; *Toda and Itoh*, 2011]. The Kiel Fjord lies outside of the region of *Prochlorococcus* habitat [*Urbach et al.*, 1992; *Partensky et al.*, 1999], however, diatoms are observed there [*Sommer*, 1996]. Nonetheless, the relatively weak ($R^2 = 0.51$) correlation between CH₃I and Chla is not compelling evidence for direct biological production of CH₃I in the Kiel Fjord, although it cannot be ruled out completely (see below).

An inverse correlation between CH₃I and nitrate ($R^2 = 0.51$) was observed. *Chuck et al.* [2005] observed a strong inverse correlation ($R^2 = 0.72$) between surface CH₃I concentration and nitrate in the open ocean. They suggested lower CH₃I concentrations in the pelagic Southern Ocean could be a result of low biological activity (e.g., high nitrate) or through a proposed mechanism involving nitrate reductase. Based on the work of *Campos et al.* [1999], nitrate reductase can reduce iodate (IO₃⁻) to iodide (I⁻), the latter being a prerequisite for CH₃I production. While we did observe an apparent anticorrelation between iodide and nitrate (Figure 2), the lack of a significant correlation between iodide and CH₃I in our study argues against this being an important control. Furthermore, this correlation may also be spurious as nitrate is inversely correlated with light levels over seasonal time scales.

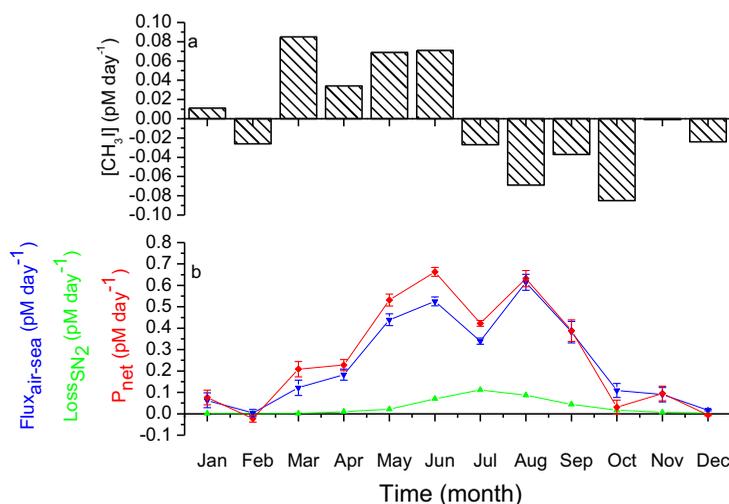


Figure 4. (a) Monthly average values of the daily accumulation/loss rates ($\Delta[\text{CH}_3\text{I}]_{24\text{hr}}$) of CH_3I based on the time series data set (October 2008 to December 2010) shown in Figure 1. (b) Variation of the terms in equation (1) over an annual cycle (L_{mix} is assumed to be negligible). Values represent daily rates calculated from monthly averages. Shown are P_{net} (red diamonds), $L_{\text{air-sea}}$ (blue triangles), and L_{SN_2} (green triangles). pM means pmol L^{-1} . The error bars on the flux estimate represent the range calculated when atmospheric mixing ratios of 3 and 0.5 ppt were used.

In the proposed photochemical pathway of CH_3I production via a radical mechanism [Moore and Zafriou, 1994; Hoppel and Wallace, 1996; Richter and Wallace, 2004], the iodine atoms are formed from the oxidation of iodide. In support of this, Manley et al. [1992] and Moore et al. [1994] found that addition of iodide enhanced CH_3I production during incubations. A lack of correlation between CH_3I and iodide in this study could be a consequence of the concentration of iodide ($>100 \text{ nmol L}^{-1}$) being always at least 10,000 times higher than the CH_3I concentration (maximum of 10 pmol L^{-1}). Similarly, over the annual cycle no correlation was observed between iodate and CH_3I . If iodate participates in the production of methyl iodide in the seawater, iodate first needs to be reduced to molecular iodine (I_2). As noted above, there may always have been sufficient iodide available in the Kiel Fjord (100 nmol L^{-1}) to produce the relatively low levels of methyl iodide measured.

In order to examine the underlying causality for these correlations, we performed a lagged cross-correlation analysis between monthly mean values of CH_3I and SSR, SST and Chla using the Mat lab code “xcorr” and an autoregressive model (AR) (Figure 3, right). The strongest correlation with SSR was found at zero lag, whereas the strongest correlations with both SST and Chla were observed with a lag of +1 month (i.e., CH_3I leading SST and Chla). Regression of CH_3I against time-shifted SST and Chla resulted in much improved correlations (R^2) of 0.91 for SST and 0.67 for Chla . The lagged correlation analysis suggests that neither SST nor Chla are the cause of CH_3I variations, but rather that they are both related to SSR with a time lag of the order +1 month. On the other hand, within the time resolution of the monthly averaged data used here, there is no apparent lag between SSR and CH_3I variability. Taken together, the correlation strength and the lack of a time lag are suggestive of a primary forcing of CH_3I variations by light variability. Using the weekly data (Table 2), SSR led CH_3I with strongest correlation observed at “-1” week lag. SST and Chla lagged CH_3I by +5 and +9 weeks, respectively. Compared to the results with monthly average data, the lag times and correlations were slightly different, however, the overall results (i.e., SSR leads CH_3I which leads SST and Chla) were similar. The correlations of weekly average data illustrate again that neither SST nor Chla appear to be the primary forcing of CH_3I concentration variation.

4.3. The Seasonal Mass Balance of CH_3I in the Kiel Fjord and CH_3I Production

The prior analysis focused on observed concentration variations rather than rates of production and loss. In this section, we use a mass balance approach to estimate these rates from the temporal concentration data. Based on the average annual cycle (Figure 1), the averaged accumulation (or loss) rates of CH_3I in different months ranged from -0.09 to $0.09 \text{ pmol}\cdot\text{L}^{-1}\cdot\text{d}^{-1}$ (Figure 4a). Using the annual cycle of monthly mean

concentrations, we can examine monthly and seasonal variations in the mass balance of CH₃I in the Kiel Fjord according to:

$$\Delta[\text{CH}_3\text{I}]_{24\text{hr}} = P_{\text{net}} - L_{\text{sea-air}} - L_{\text{SN}_2} - L_{\text{Mix}} \quad (1)$$

where $\Delta[\text{CH}_3\text{I}]_{24\text{hr}}$ is the average daily accumulation or loss of CH₃I which is calculated from the changes of the monthly mean concentrations shown in Figure 2, and P_{net} is the average daily net production of CH₃I. Conceptually, P_{net} represents the difference between gross (or total) production of CH₃I (e.g., due to photochemical and/or biological processes) and losses due to any additional, uncharacterized loss processes that are not represented in the mass balance equation (e.g., microbial degradation). $L_{\text{sea-air}}$ is the average daily sea-to-air flux of CH₃I calculated with the gas exchange relationship of *Nightingale et al.* [2000]. L_{SN_2} is the “chemical” loss due to nucleophilic substitution of Cl[−] for I[−] and is calculated based on published reaction kinetics [*Elliott and Rowland, 1993*]. L_{mix} is the loss due to mixing, either lateral or vertical, with waters with lower concentrations of CH₃I.

In open ocean waters, CH₃I concentrations decrease below the euphotic zone, however, the downward mixing loss has been shown to be negligible in comparison with the sea-to-air flux [e.g., *Richter and Wallace, 2004*]. In the Kiel Fjord, which is only 2 m deep at the sampling site and 12 m deep at the deepest location, we assume that this mix loss pathway is negligible. Horizontal exchanges, on the other hand, depend on horizontal gradients which we did not measure. We assume that in the absence of tides and significant estuarine flow, that this loss pathway is also negligible.

L_{SN_2} is calculated using the corresponding monthly mean temperature, salinity and CH₃I concentration. The “chemical” loss rate was calculated to be an average of 0.047 pmol L^{−1} d^{−1} in this study. Compared with the mean chemical loss rate of 0.12 pmol L^{−1} d^{−1} in the western English Channel [*Archer et al., 2007*] and of 1.0 pmol L^{−1} d^{−1} in the tropical Atlantic [*Richter and Wallace, 2004*], the chemical loss rate in Kiel Fjord was much lower. This is most likely due to the differences in SST and SSS, where in the Kiel Fjord SST and SSS were lower (in tropical Atlantic, SST: 27–29°C, SSS: 35), resulting in lower concentrations of chloride and a lower reaction rate.

$L_{\text{sea-air}}$ is calculated in this study using 24 h averages of wind speed as measured at GEOMAR, and assuming a constant atmospheric CH₃I mole fraction of 3 ppt, equivalent to the mean concentration at Mace Head in summer (53.2°N, similar latitude to this sampling location) reported by *Bassford et al.* [1999]. *Yokouchi et al.* [2008] reported the global atmospheric CH₃I value was around 0.5 ppt in the wintertime at middle and high latitudes. *Campos et al.* [1996] reported an atmospheric mixing ratio CH₃I of 0.5 ppt in February and March (originally from *Oram and Penkett* [1994]). We calculated the error range of the flux using atmospheric concentrations of 3 and 0.5 ppt (Figure 4b). The transfer velocity parameterization was corrected for the temperature-dependent Schmidt number estimated by *Groszko* [1999]. Based on this approach the calculated sea-to-air flux in this study averaged 3.1 nmol m^{−2} d^{−1} and ranged from −0.4 to 5.9 nmol m^{−2} d^{−1} (assuming an average depth of 10 m for the Kiel Fjord, this flux is equivalent to an average rate of concentration change of 0.31 pmol L^{−1} d^{−1} with a range of −0.04–0.59 pmol L^{−1} d^{−1}). The sea-to-air flux in this study was almost 9 times lower than the 45.8 nmol m^{−2} d^{−1} calculated by *Archer et al.* [2007] in August in the western English Channel and 4 times lower than the mean flux of 23 nmol m^{−2} d^{−1} in the tropical Atlantic [*Richter and Wallace, 2004*]. The major reasons for these differences are the different wind speed regimes and different concentration gradients for the different studies.

Strong seasonality, with higher rates of production and loss in summer and lower rates in winter, were observed for all terms in equation (1) (Figure 4b). The sea-to-air flux is the major known loss process for CH₃I. Cl[−] substitution is responsible for only approximately 14% of the total known loss. Based on equation (1), the average daily net production of CH₃I (P_{net}) in the Kiel Fjord can be estimated from the field time series data (Figure 4b, red diamonds). P_{net} also showed strong seasonality ranging from 0 (November to February) to 0.6 pmol L^{−1} d^{−1} (August). Compared with the maximum production rates of 2–6 pmol L^{−1} d^{−1} (from mid-July to mid-August in 2003) in the western English Channel [*Archer et al., 2007*], the production rate of CH₃I in the Kiel Fjord was 5–10 times lower. The difference of P_{net} between the Kiel Fjord and the western English Channel could be the result of either lower gross production in the Kiel Fjord or larger additional uncharacterized loss processes (e.g., greater microbial or chemical degradation) in a nearshore shallow environment.

Table 3. Correlations Between P_{net} and Other Parameters

		Correlation With Pnet				
		SST	SSR	SSS	Chla	NO_3^-
P_{net} Monthly (n = 12)	P value	<<0.01	<<0.01	0.02	<<0.01	0.13
	R^2 (at zero lag)	0.55	0.67	0.43	0.73	0.21
	Time lag (months) ^a	+1 m	-1 m		0 to +1 m	
	P value(after time shift)	<<0.01	<<0.01		<<0.01	
	R^2 (after time shift)	0.80	0.70		0.74	

^aNegative lag implies that the correlated variable (e.g., SSR) leads P_{net} .

We repeated the correlation analysis to examine the relative influence of various environmental factors on P_{net} variation. The results are shown in Table 3 and Figure 5. Without time shifting of the data, P_{net} was correlated ($p < 0.01$) with SST, SSR, and Chla with R^2 values of 0.55, 0.67, and 0.73, respectively (Figure 5a). Hence, the monthly net production rates of CH_3I appears to be most strongly correlated with Chla and most weakly correlated with SST. We then performed a time-lagged cross-correlation analysis after prewhitening of the data using an autoregressive model. This revealed the strongest cross correlation of P_{net} with SST, SSR, and Chla at lags of +1, -1, and 0 to +1 month, respectively (Figure 5b). This suggests that only SSR leads the seasonal variability of P_{net} , whereas SST lags behind the seasonal variation of P_{net} . The situation for Chla is less clear in that the cross-correlation function is broad with indistinguishable correlation at lags of 0 and +1 month. Application of these time shifts resulted in (time shifted) correlation coefficients of P_{net} with SST, SSR, and Chla of 0.80, 0.70, and 0.74, respectively (Table 3).

Given the broad seasonal peak of P_{net} , it is difficult to use correlation analysis to infer causality of CH_3I production by the other time-varying factors. The correlated coefficients of P_{net} with SST, SSR, and Chla are all quite similar, especially with the time-shifted data. It is notable that SST variation lags P_{net} by 1 month suggesting that temperature variation does not drive CH_3I production. However, it is harder to distinguish the relative influence of SSR and Chla on P_{net} . On the one hand, SSR is the only parameter that appears to lead

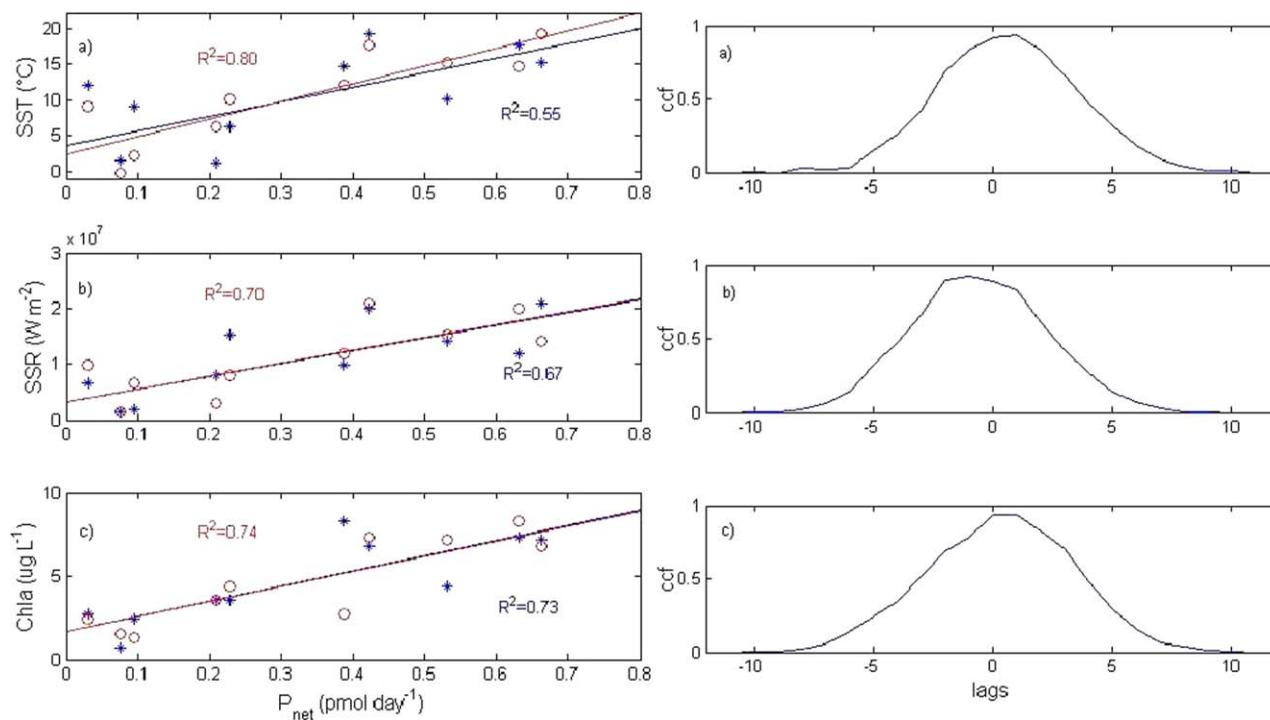


Figure 5. (left) Scatterplots of monthly production rates of CH_3I (P_{net}) versus the monthly means of (a) SST, (b) SSR, and (c) Chla. Blue stars and lines indicate the data and regressions at zero lag, red circles indicate the data after time shifting based on observed lags from the cross-correlation functions. (right) Lagged cross correlations (ccf) between P_{net} and these three parameters.

P_{net} on the other hand the cross-correlation analysis shows strong correlation of P_{net} with Chl a at zero lag (as well as lag of +1 month). It remains possible that the positive correlation between P_{net} and Chl a might be due to them both being forced, independently, by SSR variations. However, within the time resolution of the data and the analysis, we cannot exclude the possibility that SSR forces Chl a variability and that the Chl a variability forces P_{net} variations. The Chl a correlation could, in turn, reflect either a "direct" biological contribution to P_{net} (e.g., metabolic production of CH $_3$ I), or an indirect contribution (e.g., production of precursor compounds that go on to form CH $_3$ I via a photochemical mechanism).

5. Conclusions

The time series (October 2008 to December 2010) observations of CH $_3$ I in the Kiel Fjord showed a repeating seasonal cycle of CH $_3$ I with highest concentrations in summer (June and July) and lowest concentration in winter (December to February). Irradiance had the strongest positive correlation ($R^2 = 0.93$, $n = 12$, $p \ll 0.01$) of all measured variables with [CH $_3$ I]. SST and Chl a were also correlated. However, time-lagged cross analysis appeared consistent with the hypothesis that SSR being the primary forcing of CH $_3$ I production in the Kiel Fjord.

A mass balance for CH $_3$ I in the Kiel Fjord, using the annual cycle of monthly mean concentrations, was used to estimate variations in the daily net production rates of CH $_3$ I (P_{net}). These varied seasonally, from 0 to 0.6 pmol L $^{-1}$ d $^{-1}$ in winter and summer months, respectively. Our P_{net} estimates were lower than estimates from a prior study in the western English Channel, either as a result of lower gross production in the Kiel Fjord or larger uncharacterized (e.g., bacterial) loss processes in the nearshore environment. P_{net} was correlated ($p \ll 0.01$) with SST, SSR, and Chl a . Lagged cross-correlation analysis showed that SSR preceded P_{net} whereas Chl a correlation with P_{net} was highest at lags of 0 and +1 month. The broad maximum of P_{net} in summer makes it difficult to infer causal relationships with the time-varying factors. We conclude that the use of correlation analysis to infer causality has likely reached its limit in this analysis, and that it is necessary to use manipulative experimentation, where forcing parameters can be independently varied, to make further progress.

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