

Methyl iodide in the NW Atlantic: Spatial and seasonal variation

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[1] While the global ocean is an important source of atmospheric methyl iodide (CH_3I), the major producers of CH_3I within the ocean remain unclear. During a seasonal study in the NW Atlantic, the relationship between CH_3I and some characteristic phytoplankton pigments was examined in order to identify possible phytoplankton producers of CH_3I . Although no characteristic pigments exhibited a strong positive correlation with CH_3I , in the surface mixed layer, there was a weak correlation ($R = 0.35$, $n = 70$, $p = 0.003$) between the concentrations of CH_3I and zeaxanthin, a pigment characteristic of cyanobacteria in the open ocean. In this study, a moderate correlation was observed between the surface mixed layer CH_3I concentration and depth-averaged daily radiant exposure ($R = 0.61$, $n = 15$, $p = 0.02$), which indicates a positive influence of solar radiation on CH_3I production. However, the results from this study do not conclusively show whether the influence was exerted through photochemistry or other pathways. A positive correlation between the CH_3I concentration and sea surface temperature was also observed ($R = 0.61$, $n = 79$, $p \ll 0.001$).

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1. Introduction

[2] Methyl iodide (CH_3I) is a climatically active trace gas. In the atmosphere, it is rapidly photolyzed releasing iodine radicals, which can effectively catalyze ozone depletion in the troposphere and lower stratosphere [Chameides and Davis, 1980; Solomon et al., 1994]. The mixing ratio of CH_3I in the troposphere ranges from 0.05 to 5 parts per trillion by volume [Yokouchi et al., 1997]. The oceans are regarded as an important source of atmospheric CH_3I , with an annual sea-to-air flux of $1.3\text{--}3.6 \times 10^{11} \text{ g CH}_3\text{I a}^{-1}$, estimated from measured partial pressures of CH_3I in surface waters of the Pacific Ocean, Labrador Sea/North Atlantic, Gulf Stream/Sargasso Sea and average wind speeds from the Comprehensive Ocean-Atmosphere Data Sets [Moore and Groszko, 1999]. However, the major oceanic sources of CH_3I still remain unclear. It has been proposed that marine bacteria may be an indirect source of CH_3I by virtue of their production and release of methylcobalamin which has been shown to react with iodide or molecular iodine in seawater [Manley, 1994]. Some marine macroalgae and microalgae have been identified as CH_3I producers [Gschwend et al., 1985; Manley and Dastoor, 1987, 1988; Nightingale et al., 1995; Manley and de la Cuesta, 1997; Scarratt and Moore, 1999; Murphy et al., 2000; Baker et al., 2001]. With a total global production estimated at less than $3.9 \times 10^9 \text{ g CH}_3\text{I a}^{-1}$ [Manley and Dastoor, 1988; Nightingale et al., 1995; Manley and de la Cuesta, 1997; Scarratt and Moore, 1999; Baker et al.,

2001], the species in these laboratory studies cannot be considered as major CH_3I producers. A recent study has shown that *Prochlorococcus* might be important for oceanic CH_3I production [Smythe-Wright et al., 2006]. There is also evidence for photochemical production of CH_3I in surface ocean [Moore and Zafiriou, 1994; Happell and Wallace, 1996; Richter and Wallace, 2004].

[3] In 2003, a seasonal investigation, the Study of Air-Sea Biogeochemical Interactions in the Northwestern Atlantic (SABINA), was carried out as a part of the Canadian Surface Ocean–Lower Atmosphere Study (C-SOLAS) program. Comprising three cruises, this field campaign provided an unprecedented opportunity to study the seasonal variations of CH_3I in the open ocean. Objectives of the study described here were (1) to examine the seasonal variations of CH_3I concentration and sea-to-air flux in the NW Atlantic; (2) to investigate the spatial variations of CH_3I in distinct biogeochemical provinces of the NW Atlantic; and (3) to study the biological or physical factors that might influence oceanic CH_3I production.

2. Methods

2.1. Cruise Stations

[4] The three SABINA cruises were carried out during 23 April to 16 May, 5–27 July, and 10 October to 3 November 2003. Along similar cruise tracks, eight stations were surveyed (Figure 1) (N. B. Station T7 was not visited during the spring cruise). These stations represent eight distinctive biogeochemical provinces in the NW Atlantic [Longhurst, 1998]: the North West Continental Shelf (NWCS), Slope (Slope), Gulf Stream (GFST), Subtropical Gyre East/West (STGE/STGW), North Atlantic Drift (NADR), Boreal Polar Water (BPLR), and Arctic Water

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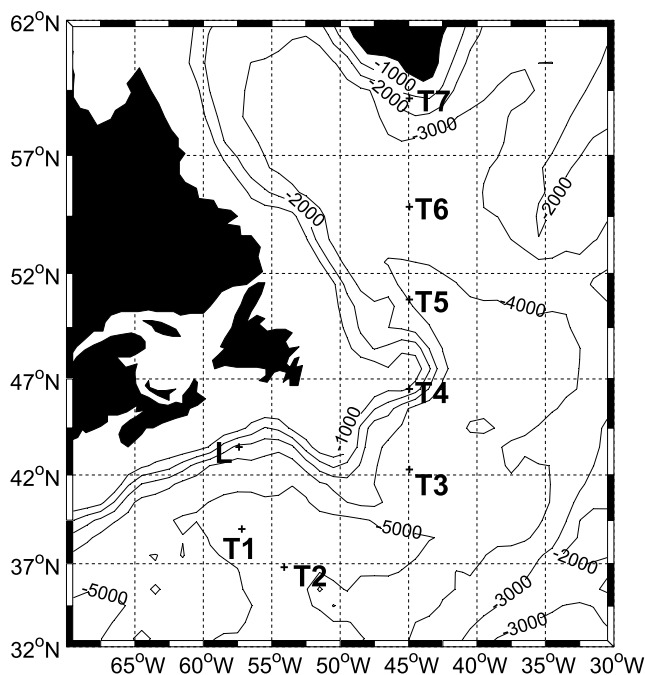


Figure 1. Cruise stations and bathymetry contours during SABINA. The contour lines represent water depths of 1000, 2000, 3000, 4000, and 5000 m.

(ARCT) provinces. The Slope province is a new province defined by *Devred et al.* [2007], representing a transition between the NWCS and GFST provinces. Biogeochemical provinces relate the biological state of a pelagic marine ecosystem to its physical environment. In their study, *Devred et al.* [2007] used a dynamic approach to delineate the provincial boundaries, on the basis of cluster analysis of the remotely sensed sea surface temperature and chlorophyll *a* data averaged over the periods of the SABINA cruises. This approach has provided an effective way to identify the surface water masses (as represented by the biogeochemical provinces) within which the SABINA stations were located (for details, refer to the work by *Devred et al.* [2007]). The designation of biogeochemical provinces at different stations in various seasons is summarized in Table 1 [Longhurst, 1998; *Devred et al.*, 2007].

2.2. Methyl Iodide

[5] When the ship was on station, samples were obtained from 10 L Niskin bottles mounted on a CTD rosette, which routinely sampled 11 depths between 5 and 300 m. When the ship was underway, samples were obtained from its flow through system, which took in water from 3 to 5 m below the sea surface. In each case, water samples were collected using 100 mL glass syringes, which were then sealed, immersed into a bucket of seawater, and covered from direct sunlight for a few hours before analysis.

[6] Dissolved CH_3I was measured using a purge-and-trap, gas chromatography mass spectrometry (GC-MS) method [Moore et al., 1996]. After being filtered through a 25 mm GF75 Whatman filter (particle retention 0.3 μm , to remove microorganisms), the water sample was introduced into a purge-and-trap system, where the dissolved gases were extracted and preconcentrated. The purge-and-trap system

comprises a glass vessel (~ 40 mL), in which the sample, held at 40°C , was purged by a stream of helium (~ 40 mL min^{-1}) for 12 min. Volatiles stripped by the helium stream passed first through a condenser held at 4°C , then through a glass drying tube containing magnesium perchlorate (as desiccant) and Ascarite (as CO_2 absorbent). CH_3I was trapped in a steel tube (~ 30 cm \times 0.8 mm OD) held at -150°C above liquid nitrogen. The preconcentration continued until the end of the purge cycle, when the liquid nitrogen was removed, the trap was heated, and the volatiles were carried by a stream of helium into the GC-MS.

[7] The chromatographic separation was effected on a pair of DB624 columns (30 m and 70 m, ID 0.53 mm, J&W Scientific). Helium was used as the carrier gas at a flow rate of 4 mL min^{-1} . Electron ionization was chosen to ionize and fragment the analyte molecules. The chromatographic conditions are described by Wang [2006]. The mass spectrometer (Finnigan Trace MS system) was equipped with a quadrupole analyzer operating in Selected Ion Monitoring mode. The quantification ion had a mass-to-charge ratio of 142. A calibration curve was determined daily by injecting volumes (50 and 100 μL) of methyl halide standard with a Hamilton gas-tight syringe. The methyl halide standard, consisting of methyl chloride, bromide, and iodide at ppm levels in nitrogen, was prepared gravimetrically. In order to correct any instrument drift, a fixed volume of a deuterated methyl halide mixture was injected into the purge gas downstream from the purge vessel as an internal standard in each measurement. The blanks of CH_3I were in the range of 0.11–0.36 nmol m^{-3} in spring, 0.10–0.37 nmol m^{-3} in summer, and 0–0.25 nmol m^{-3} in fall. The corresponding standard deviations of CH_3I measurements, which were measured on a number (*n*) of samples withdrawn from the same Niskin bottle, were 0.08 (*n* = 8, spring), 0.05 (*n* = 7, summer), and 0.09 (*n* = 4, fall) nmol m^{-3} .

2.3. Phytoplankton Pigments

[8] In conjunction with CH_3I sampling, pigment samples (0.5–1.5 L) were collected from the surface (usually at 5 m) and at the depth of chlorophyll *a* maximum (estimated from the fluorescence profile) when the ship was on station. Underway pigment samples were taken from the ship's flow through system immediately before sampling for CH_3I . Each sample was filtered through a 25 mm GF75 Whatman filter within an hour of collection. The filter was transferred into a cryovial and stored in liquid nitrogen until

Table 1. Biogeochemical Provinces Surveyed by the C-SOLAS 2003 Cruises

	Location	Spring	Summer	Fall
L	43.4°N, 57.7°W	NWCS	Slope	Slope
T1	39°N, 57.5°W	GFST	GFST (STGW) ^a	GFST
T2	36.8°N, 54.4°W	STGE	GFST (STGW) ^a	GFST
T3	42.3°N, 45°W	Slope	Slope	STGE
T4	46.5°N, 45°W	NADR	NADR	NADR
T5	50.7°N, 45°W	NADR	NADR	NADR
T6	54.8°N, 45°W	ARCT	ARCT	NADR
T7	59.3°N, 45°W	-	BPLR	BPLR

^aWaters from the station were also influenced by the waters from the biogeochemical province indicated in the parentheses.

Table 2. Chlorophyll and Carotenoid Pigments in This Study Shown With Their Symbols and Names^a

Symbol	Pigment
chl _a	chlorophyll <i>a</i> (chl <i>a</i>)
chl _b	chlorophyll <i>b</i> (chl <i>b</i>)
chl _{c2}	chlorophyll <i>c</i> ₂ (chl <i>c</i> ₂)
chl _{c3}	chlorophyll <i>c</i> ₃ (chl <i>c</i> ₃)
fuco	fucoxanthin (fuco)
hex	19'-hexanoyloxyfucoxanthin (hex-fuco)
but	19'-butanoyloxyfucoxanthin (but-fuco)
perid	peridinin (perid)
diadino	diadinoxanthin (diadino)
diato	diatoxanthin (diato)
allo	alloxanthin (allo)
caro	β, β-carotene (ββ-car)
zea	zeaxanthin (zea)
pras	prasincoxanthin (pras)

^aThe pigment symbols are patterned after the nomenclature established by the Scientific Committee on Oceanographic Research Working Group 78 [Jeffrey *et al.*, 1997]. Standard abbreviations for the pigments are given in parentheses.

analysis. Storage times were 6, 4, and <1 months for spring, summer, and fall samples.

[9] Phytoplankton pigments were extracted from the filters using cold methanol (1.7 mL) by sonication (less than 1 min). The extracts were centrifuged at 4°C for 10 min at 13200 rpm, and the supernatant transferred into a 2 mL autosampler amber vial and kept at 4°C for analysis. The pigments were measured using high-performance liquid chromatography (HPLC) [Wright *et al.*, 1991; Jeffrey *et al.*, 1997]. A 90 μL sample was injected by the autosampler and analyzed on an Agilent 1100 Series HPLC system. The chromatography column was an Agilent ZORBAX Eclipse XDB-C18 (4.6 × 150 mm). Pigments were separated by programmed gradient elution of the sample with a series of organic solvents: 80:20 (v:v) methanol:0.5 M ammonium acetate (solvent A); 90:10 (v:v) acetonitrile:water (solvent B); ethyl acetate (solvent C). A diode array detector was used for chlorophylls and carotenoids (detected at 436 and 450 nm, respectively) and a fluorescence detector for chlorophyll *a* (excitation wavelength 407 nm; emission wavelength 672 nm). Calibration of the pigments was performed every couple of months. A chlorophyll *a* standard (4 mg/L 90% acetone solution) was inserted before and after each sample set to monitor the occurrence of pigment degradation during analysis.

[10] A suite of 14 phytoplankton pigments were measured in this study: chlorophyll *a* (chl_a), chlorophyll *b* (chl_b), chlorophyll *c*₃ (chl_{c3}), chlorophyll *c*₂ (chl_{c2}), fucoxanthin (fuco), 19'-hexanoyloxyfucoxanthin (hex), 19'-butanoyloxyfucoxanthin (but), peridinin (perid), diadinoxanthin (diadino), diatoxanthin (diato), alloxanthin (allo), β, β-carotene (caro), zeaxanthin (zea), and prasincoxanthin (pras) (Table 2).

2.4. Physical Variables

2.4.1. Water Temperature

[11] Water temperature (*T*, °C) measurements came either from the CTD (for station samples) or from the thermosalinograph connected with the ship's flow through system (for underway samples).

2.4.2. Depth-Averaged Daily Radiant Exposure

[12] A multichannel visible detector system radiometer (MVDS: Satlantic, Halifax) was mounted at the top of the ship's mast. It measured solar irradiance in 7 wavelength channels ($\lambda = 325, 411.4, 442.9, 489.9, 554.3, 682.9$, and 699.7 nm; spectral band width: 10 nm or 20 nm) every 10 s. Assuming no attenuation in solar irradiance between the collection point and the sea surface, the measurements were treated as the downwelling solar irradiance just above the sea surface ($E_d(\lambda, 0+)$, $W m^{-2} nm^{-1}$). The daily radiant exposure at the sea surface ($H(\lambda, 0+)$, $J m^{-2} nm^{-1}$) was computed as the daily integrals of $E_d(\lambda, 0+)$. In order to remove the influence of the varying depth of the surface mixed layer between stations and seasons, the depth-averaged daily radiant exposure at 325 nm ($H_{ave}(325)$, $J m^{-2} nm^{-1}$) and in the photosynthetically available range (i.e., 400–700 nm, $H_{ave}(PAR)$, $J m^{-2}$) in the surface mixed layer were used in the correlation study, which was computed as below:

[13] The diffuse attenuation coefficient of the downwelling irradiance at λ ($K_d(\lambda)$, m^{-1}) was estimated from a regression of $\ln(E_d(\lambda))$ versus depth between 0 and 100 m (or less), where $E_d(\lambda)$ is the downwelling irradiance at a certain depth in $W m^{-2} nm^{-1}$. Assuming no change in $K_d(\lambda)$ during the day and neglecting surface reflection, the daily radiant exposure at wavelength λ nm at depth z m ($H(\lambda, z)$, $J m^{-2} nm^{-1}$) will be

$$H(\lambda, z) = H(\lambda, 0+)e^{-K_d(\lambda) \cdot z} \quad (1)$$

The average radiant exposure in the mixed layer, $H_{ave}(\lambda)$, is obtained by integrating $H(\lambda, z)$ over the surface mixed layer and dividing by the depth of the mixed layer (z_{ML} , m).

$$\begin{aligned} H_{ave}(\lambda) &= \frac{1}{z_{ML}} \int_0^{z_{ML}} H(\lambda, z) dz \\ &= \frac{H(\lambda, 0+)}{z_{ML}} \int_0^{z_{ML}} e^{-K_d(\lambda) \cdot z} dz = \frac{-H(\lambda, 0+)}{z_{ML} K_d(\lambda)} \left(e^{-K_d(\lambda) \cdot z} \right) \Big|_0^{z_{ML}} \end{aligned} \quad (2)$$

$H_{ave}(325)$ was derived using this equation. For PAR, first, values of $H_{ave}(\lambda)$ at wavelengths other than 325 nm were computed individually using equation (2). Then, by assuming the average radiant exposure at 411.4 nm was the same as that at 400 nm, $H_{ave}(PAR)$ was obtained by integrating the computed $H_{ave}(\lambda)$ versus wavelength using trapezoidal integration.

3. Results

3.1. CH₃I Concentration in the Surface Mixed Layer

[14] Surface mixed layer CH₃I concentrations measured on station and underway in the NW Atlantic in three seasons are displayed in Table 3 and Figure 2. The concentration of dissolved CH₃I in the surface mixed layer ($[CH_3I]_{ML}$) varied seasonally, being high in summer (3.0–12.8 nmol m⁻³), low in spring (0.6–3.6 nmol m⁻³), and intermediate in fall (1.0–7.8 nmol m⁻³). These results are comparable to previous field observations in various seasons in the North Atlantic, which ranged from 0.7 to 22.3 nmol m⁻³ [Tanzer and Heumann, 1992; Moore and

Table 3. Surface Concentrations, Wind Speeds, and Calculated Sea-to-Air Fluxes of CH₃I During the C-SOLAS Cruises

Location	[CH ₃ I] _{ML} (nmol m ⁻³)			u ₁₀ (m s ⁻¹)			F _{CH₃I} (nmol m ⁻² d ⁻¹)		
	Spring	Summer	Fall	Spring	Summer	Fall	Spring	Summer	Fall
L 43.4°N, 57.7°W	1.3, 3.6 ^a	12.8	7.8	8.2, 7.1 ^a	7.5	11.3	4.5, 8.6 ^a	65.4	63.2
T1 39°N, 57.5°W	2.6	4.6	2.9	18.1	4.6	9.9	64.6	8.4	22.6
T2 36.8°N, 54.4°W	3.6	7.0	- ^b	10.6	5.8	- ^b	31.4	18.3	- ^b
T3 42.3°N, 45°W	1.4	6.5	2.9 ^c	12.8	4.4	9.9	13.9	9.5	21.7 ^c
T4 46.5°N, 45°W	0.9	7.1	3.6 ^c	6.1	9.2	8.1	1.4	32.7	13.7 ^c
T5 50.7°N, 45°W	0.7	3.5	2.2	2.8	3.4	14.9	0.3	2.2	26
T6 54.8°N, 45°W	0.6	3.4	3.4	7.6	3.7	16.2	1.3	2.3	44.4
T7 59.3°N, 45°W	- ^b	3.0	1.0	- ^b	1.2	9.7	- ^b	0.4	4.1

^aStation L was visited twice during the spring cruise. The two [CH₃I]_{ML} values are the averages of the measurements during the periods of 28 April to 1 May 2003 and 14–15 May 2003, respectively. The two wind speed and flux values also correspond to the two visits.

^bThere were no measurements at station T7 in spring and at station T2 in fall.

^cThe water samples from stations T3 and T4 in fall were stored for 2 days and 1 day, respectively. Therefore, the measurements should be treated with caution.

Tokarczyk, 1993; Moore and Groszko, 1999; Baker et al., 2000; Hughes, 2001; Richter, 2003; Chuck et al., 2005]. Note that the two measurements of [CH₃I]_{ML} at station L in spring were corresponding to a diatom bloom and post-bloom situation, as observed during the SABINA spring cruise [Lizotte et al., 2008].

[15] Spatial variations in surface mixed layer CH₃I concentration were observed. During spring, there was a pronounced latitudinal pattern, with higher [CH₃I]_{ML} at the four southern stations (L, T1, T2, and T3) than at the three subarctic stations (T4, T5, and T6). This pattern was less obvious in summer and, because of scarcity of data, inconclusive in fall. In general, the Slope, North West Continental Shelf, Subtropical Gyre East/West, Gulf Stream, and North Atlantic Drift provinces were generally associated with high surface mixed layer CH₃I concentrations. The Boreal Polar Water and Arctic Water provinces had low surface mixed layer CH₃I concentrations.

3.2. Estimate of CH₃I Flux

[16] During the SABINA cruises, the atmospheric concentrations of CH₃I were negligible relative to the concentrations of CH₃I in the surface water. Therefore, the sea-to-air flux of CH₃I (F_{CH₃I}, nmol m⁻² d⁻¹) was computed as $F_{CH_3I} = 0.24 k [CH_3I]_{ML}$, where k is the gas transfer velocity in cm h⁻¹; [CH₃I]_{ML} is the concentration of CH₃I in the surface mixed layer in nmol m⁻³; and 0.24 m cm⁻¹ h d⁻¹ is a conversion constant. k was calculated using the Wanninkhof [1992] formula for short-term wind speeds, $k = 0.31u^2 (Sc/660)^{-0.5}$, where u is the wind speed at 10 m in m s⁻¹; Sc is the water-temperature-dependent Schmidt number for CH₃I, given as $Sc = (62.9/52.9)^{0.6} (2004 - 93.5T + 1.39T^2)$ [de Bruyn and Saltzman, 1997]. In this study, the wind speed data were Gaussian Grid Data (4-times daily mean) from NCEP-DOE reanalysis 2 (provided by NOAA-CIRES Climate Diagnostics Center, Boulder, Colorado, USA from <http://www.cdc.noaa.gov>).

[17] The wind speeds at 10 m and calculated sea-to-air fluxes of CH₃I at each station are summarized in Table 3. The seasonal and spatial variations in the estimated flux were not in concert with the variations in the surface mixed layer concentration, mainly because of the great variability in wind speed. Some high values of calculated sea-to-air fluxes during spring and fall arose from high wind speeds, rather than high concentrations of dissolved CH₃I. The

estimates agree with those of Moore and Groszko [1999], which were in the range of 0.3–55 nmol m⁻² d⁻¹ during June and July in the Labrador Sea.

3.3. Vertical Profiles of CH₃I

[18] Figures 3a–3h illustrate the seasonal CH₃I concentration profiles at stations L, T2, and T6. During SABINA, the highest CH₃I concentrations were observed at station L, located near the Scotian Shelf. Station T2 in the Sargasso Sea represented the south end of the transect. Station T6 was one of the subarctic stations in the north. By selecting these representative stations, we hope to provide a snapshot of various CH₃I profiles in distinctive ecological provinces of the NW Atlantic. A subsurface maximum of CH₃I was pronounced at station L in summer and fall, as well as at station T2 in spring and summer, when the surface mixed layer concentrations were relatively high. This subsurface CH₃I maximum was less pronounced at T6 than at the other two stations in corresponding seasons. The occurrence of a subsurface maximum may be accounted for by enhanced subsurface CH₃I production, or accumulation of CH₃I in the less well ventilated zone beneath the mixed layer.

3.4. Biological Variables

[19] The seasonal variations of the phytoplankton pigments in the surface mixed layer are displayed in Figures 4a–4c. Although most of the pigments are common to many phytoplankton groups, a few of them are often regarded as good indicators of certain phytoplankton in the open ocean [Jeffrey et al., 1997]. For example, fucoxanthin (fuco) is a good indicator of diatoms, 19'-hexanoyloxyfucoxanthin (hex) of prymnesiophytes, and zeaxanthin (zea) of cyanobacteria. Therefore, we can draw inferences of the relative abundance of certain phytoplankton groups from the corresponding pigment concentrations. This qualitative estimation was then compared with the cell abundance data (Table 4) of some major phytoplankton groups that have characteristic pigments (i.e., diatoms, prymnesiophytes, dinoflagellates, and cryptophytes) [Jeffrey et al., 1997]. Our goal is to use the measurements of signature pigments as a proxy for the abundance of certain phytoplankton groups, if the former varied consistently with the latter in different seasons at different stations. As can be seen, the patterns in Table 4 can be largely explained by the variations of phytoplankton pigments. For instance, the relatively

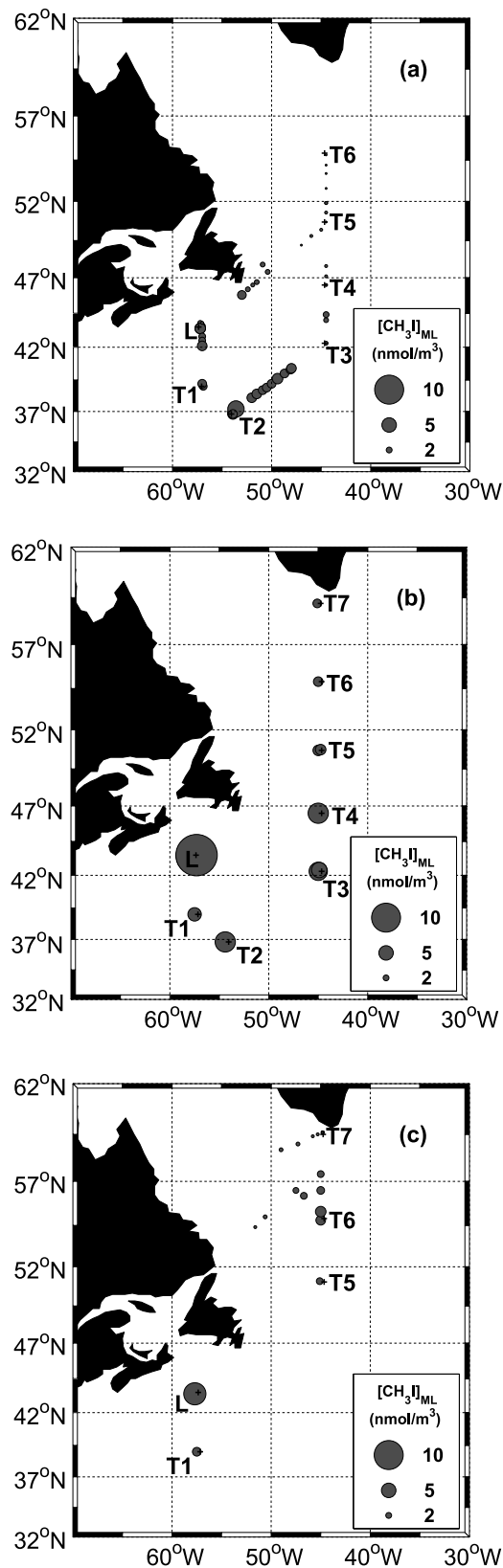


Figure 2. Maps of $[\text{CH}_3\text{I}]_{\text{ML}}$ (nmol m^{-3}) during (a) spring, (b) summer, and (c) fall. The diameter of the circle indicates the magnitude of the concentration. Station T7 was not visited in spring. There was no measurement at station T2 in fall. Because of the extensive sample storage period, measurements for stations T3 and T4 in fall are not plotted here.

high diatom abundance at L and T3 in spring and at T7 in summer is consistent with the observed high fucoxanthin concentrations. Since the data in Table 4 were obtained by other research groups, and since the abundance data are mostly unpublished, in this paper we use our own pigment measurements wherever possible as a measure of the abundance of phytoplankton groups.

[20] In Figure 4, the relatively high concentrations of fucoxanthin ($[\text{fuco}]_{\text{ML}}$) at L and T3 in springtime indicate the abundance of diatoms. In all three seasons, the abundance of prymnesiophytes was evidenced by the level of 19'-hexanoyloxyfucoxanthin concentration ($[\text{hex}]_{\text{ML}}$) at the three subarctic stations (T4–T6). The relatively high peridinin concentrations ($[\text{perid}]_{\text{ML}}$) at some of the subarctic stations are indications of relatively high dinoflagellate abundance. The increase in zeaxanthin concentration ($[\text{zea}]_{\text{ML}}$) at most stations from spring to summer and fall suggests an increasing abundance of cyanobacteria. At most stations, the seasonal variations in pigments as a whole reflect a shift from a large-cell phytoplankton community (more diatoms) in spring to a small-size one (more prymnesiophytes and cyanobacteria) toward summer and fall in the surface mixed layer.

3.5. Correlations Between CH_3I and Some Physical and Biological Variables

[21] The coefficients of Spearman rank correlation between CH_3I concentration ($[\text{CH}_3\text{I}]_{\text{ML}}$) and water temperature (T), depth-averaged daily radiant exposure ($H_{\text{ave}}(325)$ and $H_{\text{ave}}(\text{PAR})$), and some characteristic phytoplankton pigment concentrations ($[\text{zea}]_{\text{ML}}$, $[\text{hex}]_{\text{ML}}$, $[\text{perid}]_{\text{ML}}$, $[\text{allo}]_{\text{ML}}$) in the surface mixed layer are shown in Table 5. Moderate correlations were found between $[\text{CH}_3\text{I}]_{\text{ML}}$ and T ($R = 0.61$, $n = 79$, $p \ll 0.001$), $H_{\text{ave}}(325)$ ($R = 0.58$, $n = 15$, $p = 0.02$) and $H_{\text{ave}}(\text{PAR})$ ($R = 0.64$, $n = 15$, $p = 0.01$). The positive correlation between CH_3I and sea surface temperature is in agreement with the studies of Baker *et al.* [2000] ($R = 0.71$; n and p not reported) in the Eastern Atlantic, and Chuck *et al.* [2005] ($R = 0.67$, $n = 122\text{--}250$, $p < 0.01$) in the Eastern and tropical Atlantic and Southern Ocean. Positive correlations between CH_3I and PAR [Baker *et al.*, 2000] or surface CH_3I saturation anomaly and PAR [Happell and Wallace, 1996] have also been reported.

[22] Weak correlations between $[\text{CH}_3\text{I}]_{\text{ML}}$ and $[\text{zea}]_{\text{ML}}$ ($R = 0.35$, $n = 70$, $p = 0.003$), $[\text{CH}_3\text{I}]_{\text{ML}}$ and $[\text{perid}]_{\text{ML}}$ ($R = -0.41$, $n = 70$, $p = 0.0004$) were observed in this study. While positive correlation between surface concentrations of CH_3I and hex ($R = 0.48$, $n = 14$, $p = 0.08$) was observed by Hughes [2001] along a 43°N transect of the North Atlantic in August/September, such a correlation was not observed in this study. Because of the lack of correlation between $[\text{CH}_3\text{I}]_{\text{ML}}$ and $[\text{fuco}]_{\text{ML}}$, the latter is not included in Table 5.

4. Discussion

[23] This study marks the first time that the seasonality of CH_3I has been investigated in the open ocean. At most stations, CH_3I in the surface mixed layer demonstrated an obvious variation between different seasons, with the occurrence of highest CH_3I concentrations during summer. The seasonal and spatial variability of CH_3I in the NW

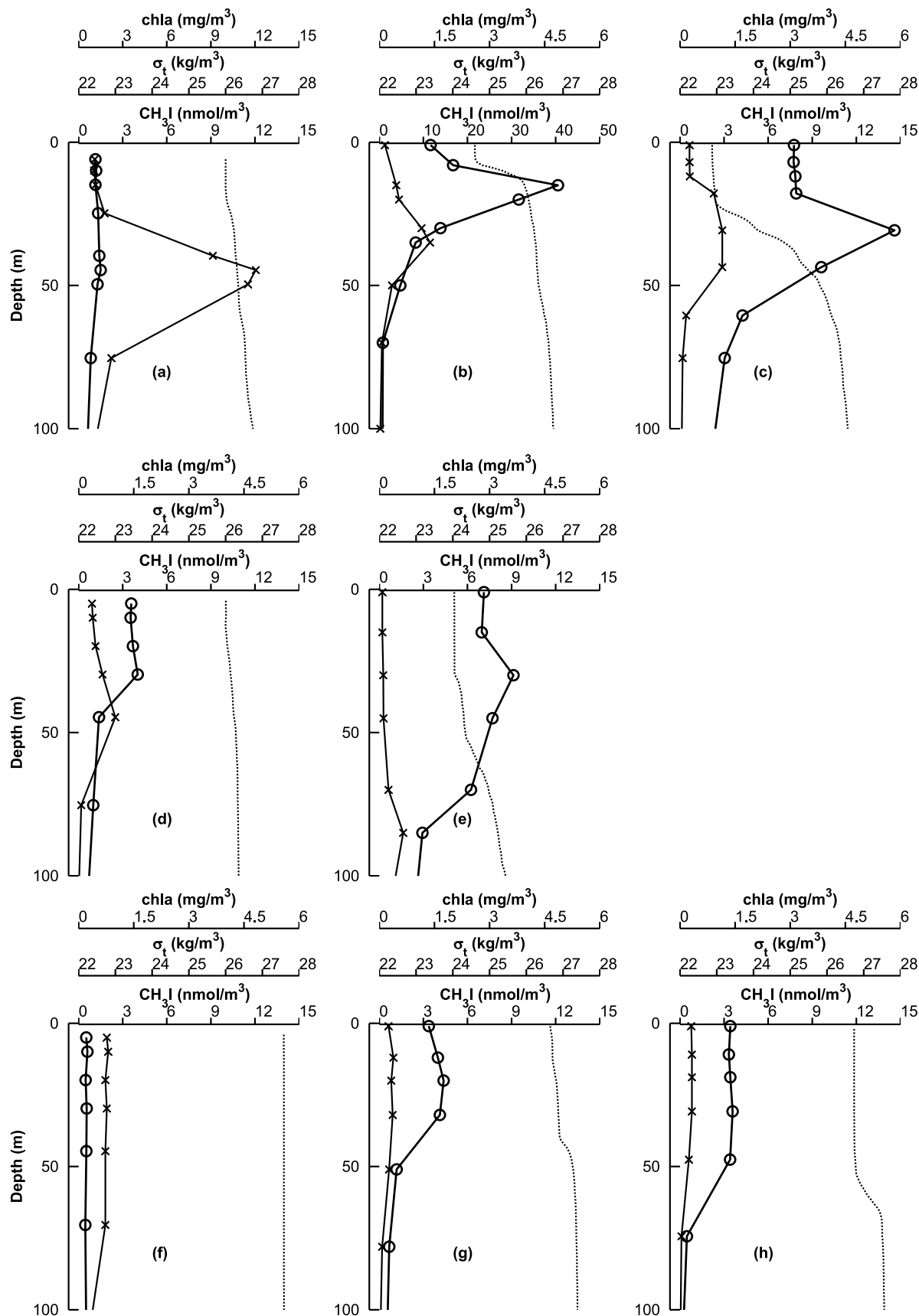


Figure 3

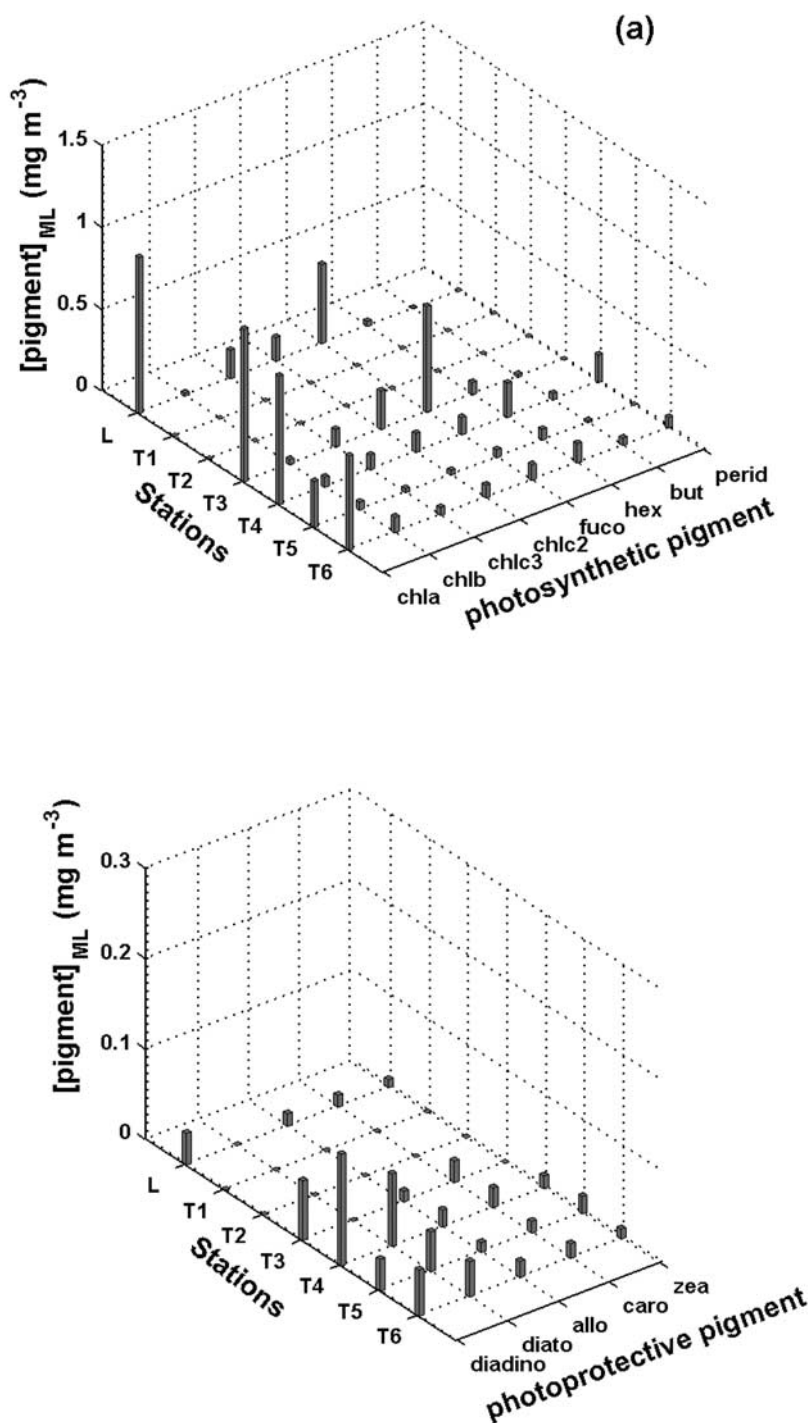


Figure 4. Compositions of phytoplankton pigments ($[\text{pigment}]_{\text{ML}}$, mg m^{-3}) in the surface mixed layer during (a) spring, (b) summer, and (c) fall. Note that there were no pigment measurements during spring at stations T1 and T2 and during fall at station T2.

Figure 3. Depth profiles of $[\text{CH}_3\text{I}]$ (nmol m^{-3} , circles), $[\text{chl a}]$ (mg m^{-3} , crosses) (based on the fluorometric determination of chl a on discrete samples extracted in 90% acetone; data courtesy of M. Gosselin (2003)), and density (σ_t , in kg m^{-3} , dotted line) at stations L, T2, and T6 during SABINA. (a–c) Station L in spring, summer, and fall. (d and e) Station T2 in spring and summer (no CH_3I measurement was performed at T2 in fall). (f–h) Station T6 in spring, summer, and fall. Note that at station L, the spring chl a concentration (in Figure 3a) and summer CH_3I concentration (in Figure 3b) have different scales from the others.

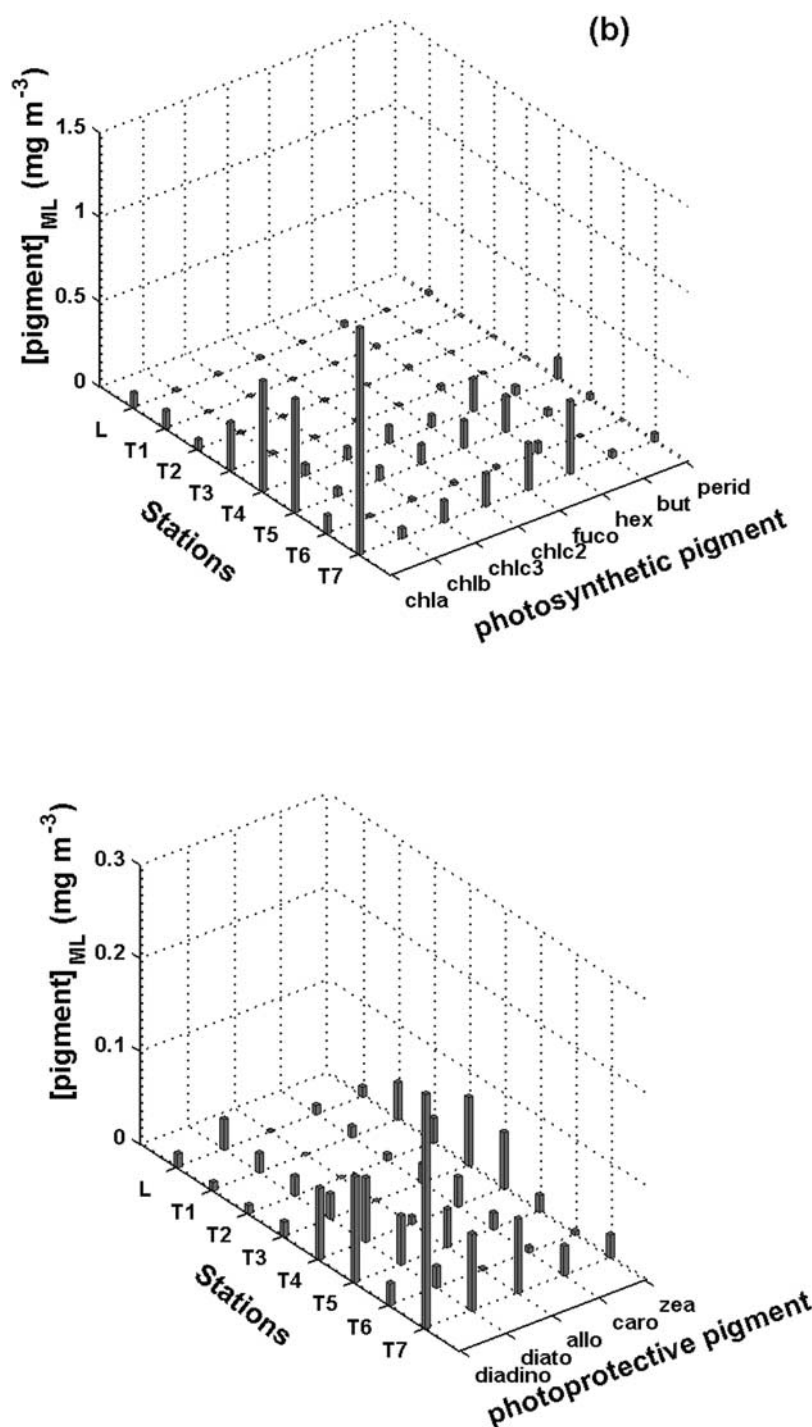


Figure 4. (continued)

Atlantic, along with the corresponding biological and physical data, are expected to provide information useful to the study of the factors that influence oceanic production of CH_3I .

4.1. Phytoplanktonic Production of CH_3I

4.1.1. Phytoplankton and CH_3I Concentration

[24] During the SABINA cruises, variations in surface mixed layer CH_3I concentration with seasons and biogeochemical conditions were observed. As shown in Table 3, wind speed in the studied areas also varied seasonally. This

physical force can affect the stratification of the water column. Light wind speeds in summer in general were associated with strengthened stratification and thus shallow surface mixed layers as indicated by the σ_t profile. As a result, the effluxes of CH_3I into the atmosphere were reduced significantly. However, this weakened sea-to-air gas exchange is not sufficient to explain the significantly elevated CH_3I concentrations in summer, particularly in view of the extremely high concentrations observed beneath the mixed layer (e.g., 40.5 nmol m^{-3} at station L in Figure 3b, which was the highest measured anywhere during this

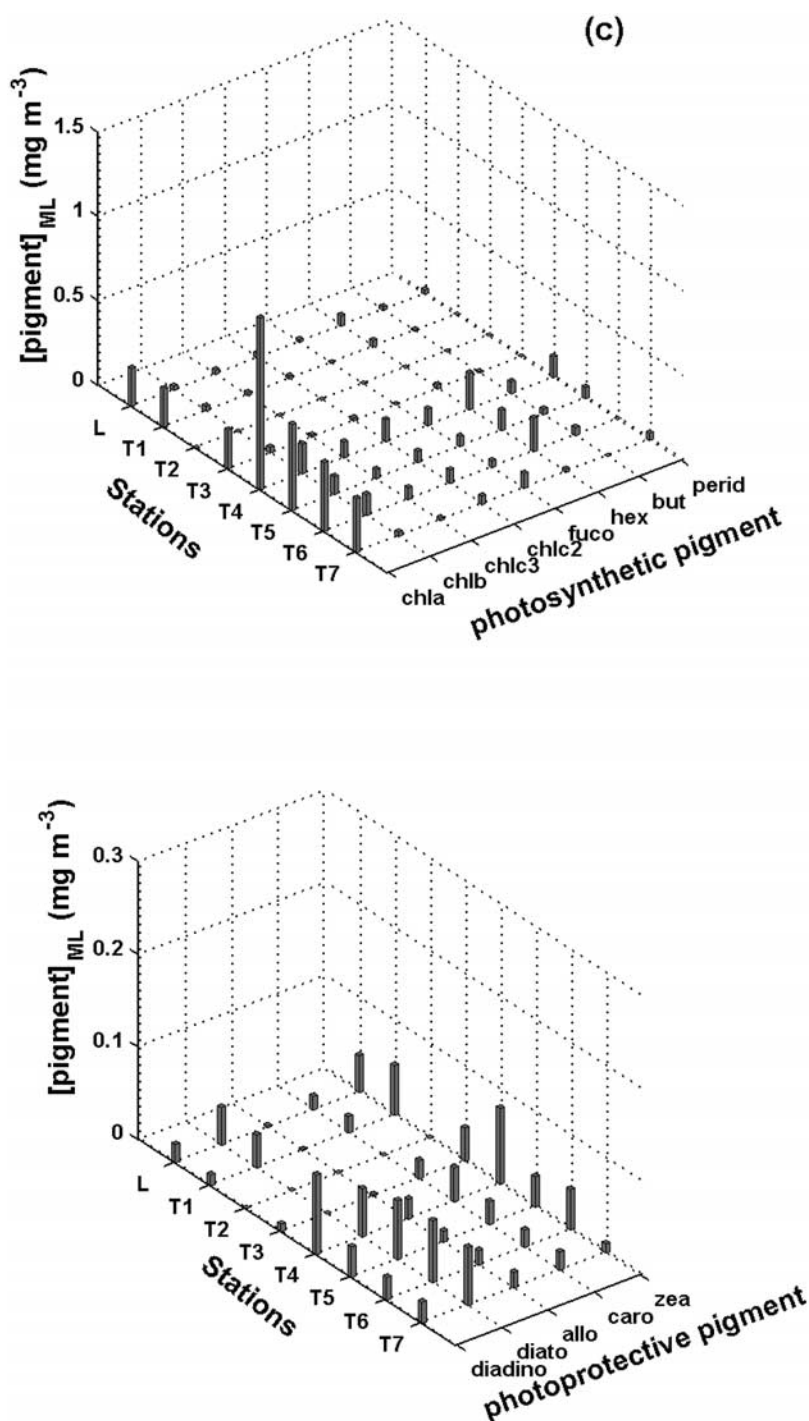


Figure 4. (continued)

study). On the other hand, stations T5 and T6 experienced much higher wind speeds in fall than in spring. The concentrations of CH_3I were nonetheless several fold higher in fall than in spring. These observations suggest that the physical controls affecting the gas exchange, such as wind speed and stratification, sometimes are not the dominant factors that influence the surface mixed layer concentration of CH_3I .

[25] The observed seasonal and spatial variations in oceanic CH_3I concentration may be influenced by biological factors that change with season and biogeochemical

province, such as the composition of the phytoplankton community. As mentioned above, the subsurface CH_3I maximum became prominent when the water column CH_3I concentrations reached the seasonal high. This concentration maximum occurred at depths where the PAR was significantly attenuated to 5–30% of the surface level (from in situ radiometer measurements, data not shown). Associated with higher K_d values than the PAR, the ultraviolet (UV) portion of the solar radiation would be more strongly attenuated. As a result, photochemical reactions at the depth of the CH_3I concentration maximum would likely be

Table 4. Abundance of Major Phytoplankton Groups in the Surface Mixed Layer^a

Location	Diatoms			Prymnesiophytes			Dinoflagellates			Cryptophytes		
	Spring	Summer	Fall	Spring	Summer	Fall	Spring	Summer	Fall	Spring	Summer	Fall
L 43.4°N, 57.7°W	139,720, 17,520 ^b	3,200	560	11,895, 271,815 ^b	175,243	190,071	83,825, 162,849 ^b	113,202	65,129	61,437, 208,288 ^b	20,713	2,2627
T1 39°N, 57.5°W	124,320	1,640	2,360	129,072	79,702	76,244	48,104	32,440	28,040	37,923	12,807	7,106
T2 36.8°N, 54.4°W	27,640	1,600	3,360	144,019	54,626	58,515	38,652	32,160	36,680	65,207	8,615	5,668
T3 42.3°N, 45°W	762,303	2,480	3,360	144,652	52,443	84,230	45,922	29,560	29,064	43,439	10,053	23,133
T4 46.5°N, 45°W	25,104	292,938	36,280	382,448	205,950	398,335	156,353	176,753	304,449	169,821	67,224	160,765
T5 50.7°N, 45°W	20,144	101,480	52,144	140,427	416,299	184,294	40,080	133,628	133,729	127,457	105,062	58,277
T6 54.8°N, 45°W	22,424	1,120	32,840	122,386	225,965	181,653	58,080	7,224	75,873	118,689	19,913	120,638
T7 59.3°N, 45°W	- ^c	191,622	8,240	- ^c	273,089	28,386	- ^c	22,273	34,600	- ^c	249,055	46,368

^aAbundance is measured in cells per liter. Spring data at Station L are from *Lizotte et al.* [2008]. All phytoplankton taxonomic data, which have currently been integrated into the Canadian SOLAS data set, were provided by S. Lessard and M. Scarratt (Fisheries and Oceans Canada, Maurice Lamontagne Institute, 2004).

^bStation L was visited twice during the spring cruise. The two abundance values are the averages of the daily measurements during the periods of 28 April to 1 May 2003 and 14–15 May 2003, respectively.

^cThere were no measurements at station T7 in spring.

relatively insignificant. If indeed biological and photochemical processes are overall the main oceanic sources of CH₃I, the high concentrations seen in some subsurface maxima (e.g., 40.5 nmol m⁻³ at station L during summer) could lend support to the importance of biological sources.

[26] Production of CH₃I by certain algal species has been observed in both laboratory and field studies. The macroalgae, including kelps and some red and green seaweeds identified by *Lovelock* [1975], *Manley and Dastoor* [1987, 1988], *Manley et al.* [1992], *Nightingale et al.* [1995], and *Baker et al.* [2001], cannot be major CH₃I producers on a global scale, because of their restricted distributions in coastal waters and limited annual production rates (less than 3×10^8 g CH₃I a⁻¹, on the basis of *Manley and Dastoor* [1988], *Nightingale et al.* [1995], and *Baker et al.* [2001]). Phytoplankton are considered to be potentially more important than macroalgae in terms of producing CH₃I, given their wide distribution. Some non-*Prochlorococcus* phytoplankton have been identified in laboratory studies as CH₃I producers [*Moore and Tokarczyk*, 1993; *Manley and de la Cuesta*, 1997; *Scarratt and Moore*, 1999]. However, compared with the sea-to-air flux of $1.3\text{--}3.6 \times 10^{11}$ g CH₃I a⁻¹ [*Moore and Groszko*, 1999], production of CH₃I by these phytoplankton ($9.5 \times 10^5\text{--}3.6 \times 10^9$ g a⁻¹, with a mean rate of 1.2×10^9 g a⁻¹ [*Manley and de la Cuesta*, 1997]) can only account for a small fraction of the oceanic CH₃I production. From their laboratory and field studies, *Smythe-Wright et al.* [2006] reported that some *Prochlorococcus* species were an important source of CH₃I, with an estimated global production rate of 4.3×10^9 mol CH₃I a⁻¹ (equal to 6.1×10^{11} g CH₃I a⁻¹). For the following reasons, this value may be regarded as an upper limit of CH₃I production

by *Prochlorococcus*. First, the estimate of biological flux by the authors, 109.5 nmol m⁻² d⁻¹, is a fairly high value for the North Atlantic (between 20 and 40°N, May 1998) and Indian Ocean (between 8 and 20°S, June 2002), compared with about 27.5 nmol m⁻² d⁻¹ nonphotochemical flux and 53 nmol m⁻² d⁻¹ total flux reported by *Richter and Wallace* [2004], and less than 71.1 nmol m⁻² d⁻¹ in this study at stations located south of 40°N. Second, *Prochlorococcus* may not be the sole biological source of CH₃I as assumed by the authors. During the SABINA cruises, there were significantly elevated water column CH₃I concentrations at station L (43.4°N, 57.7°W) in summer. While *Prochlorococcus* is ubiquitous at latitudes lower than 45° [*Partensky et al.*, 1999], some other phytoplankton species may account for the biological sources. In fact, the flow cytometry data provided by R. Rivkin (unpublished data, 2006) showed the existence of another cyanobacterial species, *Synechococcus*, and an absence of *Prochlorococcus* in the water column at station L during the SABINA summer cruise.

[27] During SABINA, the occurrence and decline of a spring diatom bloom (dominated by centric diatoms [*Lizotte et al.*, 2008]) were captured at station L. The surface mixed layer CH₃I concentration was low during the course of the bloom, indicating that centric diatoms are not important CH₃I producers. This result agrees with the observations from two previous iron fertilization experiments, during which diatom blooms were artificially stimulated. One observation came from the Southern Ocean Iron Enrichment Experiment (SOFEX), during which the average of CH₃I concentrations within and outside the iron-enriched patch were 0.22 and 0.29 nmol m⁻³ [*Wingenter et al.*, 2004]. Inside

Table 5. Spearman Rank Correlation of [CH₃I]_{ML} With the Depth-Averaged Daily Radiant Exposure, the Water Temperature, the Concentrations of Zeaxanthin, 19'-Hexanoyloxyfucoxanthin, Peridinin, and Alloxanthin in the Surface Mixed Layer^a

	H _{ave} (325)	H _{ave} (PAR)	T	[zea] _{ML}	[hex] _{ML}	[perid] _{ML}	[allo] _{ML}
R	0.58	0.64	0.61	0.35	-0.06	-0.41	-0.30
p value	0.02	0.01	≤0.001	0.003	0.64	0.0004	0.01

^aCH₃I, in nmol m⁻³; depth-averaged daily radiant exposure, H_{ave}(325), in J m⁻² nm⁻¹, and H_{ave}(PAR), in J m⁻²; water temperature, T, in °C; zeaxanthin, [zea]_{ML}, in mg m⁻³; 19'-hexanoyloxyfucoxanthin, [hex]_{ML}, in mg m⁻³; peridinin, [perid]_{ML}, in mg m⁻³; and alloxanthin, [allo]_{ML}, in mg m⁻³. H_{ave}(325), *n* = 15; H_{ave}(PAR), *n* = 15; T, *n* = 79; [zea]_{ML}, *n* = 70; [hex]_{ML}, *n* = 70; [perid]_{ML}, *n* = 70; [allo]_{ML}, *n* = 70.

the patch, the growth of a pennate diatom (*Pseudo-nitzschia* spp.) was enhanced [Coale *et al.*, 2004]. Another observation was from the Subarctic Ecosystem Response to Iron Enrichment Study (SERIES) in the NE Pacific, during which the surface mixed layer CH₃I concentrations showed no apparent difference between regions within (4.3–6.3 nmol m⁻³) and outside (4.4–6.6 nmol m⁻³) the iron-enriched patch [Moore and Wang, 2006]. Inside the iron patch, the abundance of large diatoms (>20 µm) increased constantly, dominated by pennate (*Pseudo-nitzschia*, *Neodenticula* and *Thalassiothrix*) and centric (*Chaetoceros*, *Rhizosolenia*, and *Proboscia*) species [Marchetti *et al.*, 2006]. In contrast, during another iron fertilization experiment, EisenEx in the Southern Ocean, a greater increase in CH₃I concentration was observed inside the iron-enriched patch than outside the patch [Liss *et al.*, 2005]. Nevertheless, CH₃I concentrations were at a low level, less than 2.6 nmol m⁻³ throughout the experiment [Liss *et al.*, 2005]. On the basis of our observations from the SABINA and SERIES cruises, we do not regard diatoms as important CH₃I producers.

[28] At station L in spring, the surface mixed layer CH₃I concentration started to increase after the decline of the diatom bloom. Simultaneously, small-sized phytoplankton (such as prymnesiophytes and cryptophytes) [Lizotte *et al.*, 2008] began to dominate the phytoplankton community. While the increase in the abundance of prymnesiophytes (from around 10,000 to >260,000 cell/L [Lizotte *et al.*, 2008]) was coincident with the elevated CH₃I concentration in the surface mixed layer, we cannot conclude that prymnesiophytes are important CH₃I producers. This can be demonstrated by examining the results from other seasons at station L. As compared with the summer and fall results at this station, the CH₃I concentrations were lowest during spring when prymnesiophytes were most abundant (Table 4). Similarly, at station T4, higher CH₃I concentrations occurred in summer, when the abundance of prymnesiophytes was almost half that in spring and fall (Table 4). In contrast, at station T5, highest CH₃I concentration coincided with highest prymnesiophyte abundance (Table 4).

[29] During the course of SABINA, enhancement in the abundance of other phytoplankton during a specific season was also observed. For example, at station T7 in summer, cryptophyte abundance reached >240,000 cell/L, and at station T4 in fall, the abundance of dinoflagellates was >300,000 cell/L (Table 4). In both cases, the concentrations of CH₃I were not correspondingly high.

[30] Clearly, if phytoplanktonic production of CH₃I is important, the rate may be influenced by other factors. As proposed by Nightingale *et al.* [1995], CH₃I production by macroalgae could be affected by light availability, tissue age, and grazing. The decoupling of CH₃I concentration from the phytoplankton abundance in the surface mixed layer may be due to similar reasons that are associated with light availability, cell physiological status, and zooplankton grazing.

4.1.2. Using Phytoplankton Pigments to Identify CH₃I Producers

[31] As mentioned, some characteristic phytoplankton pigments can be used as the indicators of certain phytoplankton groups [Jeffrey *et al.*, 1997]. In this study, the compositions of phytoplankton pigment were measured in conjunction with dissolved CH₃I measurements. The aim

was to use characteristic pigments as indicators to identify phytoplankton groups that may be responsible for CH₃I production. As pointed out above, none of the fourteen pigments examined showed a significant correlation with CH₃I concentration in the surface mixed layer. The lack of correlation between CH₃I and fucoxanthin again suggests that diatoms are unlikely to be major producers of CH₃I. There was also a lack of correlation between the concentrations of CH₃I and 19'-hexanoyloxyfucoxanthin, indicating that even if prymnesiophytes are CH₃I producers, their production may be affected by other factors that could mask an obvious correlation between the concentrations of CH₃I and hex.

[32] Negative correlations were observed between the concentrations of peridinin and CH₃I ($R = -0.41$, $n = 70$, $p = 0.0004$), and alloxanthin and CH₃I ($R = -0.30$, $n = 70$, $p = 0.01$). In the open ocean, peridinin and alloxanthin are characteristic for dinoflagellates and cryptophytes, respectively [Jeffrey *et al.*, 1997]. Their negative correlations with CH₃I may suggest that the environmental conditions favoring the growth of dinoflagellates and cryptophytes are unfavorable to CH₃I production. It is also possible that these phytoplankton are associated with CH₃I consumption.

[33] Zeaxanthin concentration showed a weak positive correlation with CH₃I concentration in the surface mixed layer ($R = 0.35$, $n = 70$, $p = 0.003$). From spring to summer and fall, there was an obvious enhancement in zeaxanthin concentration at most stations. In the open ocean, zeaxanthin is the characteristic pigment of cyanobacteria [Jeffrey *et al.*, 1997], which include the most abundant phytoplankton in the ocean, *Prochlorococcus* and *Synechococcus*. This positive correlation between zeaxanthin and CH₃I suggests that cyanobacteria might be producers of CH₃I. However, since the HPLC column used in this study could not differentiate divinyl chlorophyll *a* (produced exclusively by *Prochlorococcus*) from chlorophyll *a*, it was not possible to estimate the proportion of *Prochlorococcus* zeaxanthin to total zeaxanthin on the basis of only the pigment data. To account for the observed positive correlation between zeaxanthin and CH₃I, it is, however, also possible that the environmental conditions that favor cyanobacteria also favor CH₃I production.

[34] It has to be noted that using pigments as an indicator of phytoplankton group has limitations. The pigment composition of phytoplankton could vary between different species of the same phytoplankton group [Lutz, 1999]. Even for a given species, its pigmentation can change under different light fields [Lutz, 1999]. These variations could lead to a decoupling of the phytoplankton abundance from the characteristic pigment and thus make the latter an unsatisfactory indicator for the former.

4.2. Solar Radiation and CH₃I Concentration

[35] During the SABINA cruises, the depth-averaged daily radiant exposure ($H_{\text{ave}}(325)$ and $H_{\text{ave}}(\text{PAR})$) showed a moderate positive correlation with the concentration of CH₃I in the surface mixed layer ($R = 0.58$, $n = 15$, $p = 0.02$ for the former, $R = 0.64$, $n = 15$, $p = 0.01$ for the latter). These positive correlations indicate that solar radiation may favor the production of CH₃I, in agreement with the field observations of Happell and Wallace [1996] and Richter and Wallace [2004]. However, there is no convincing

evidence in this study showing which portion of the solar radiation more effectively influences the CH_3I production. The UV portion of the solar radiation could affect the CH_3I concentration by facilitating the release of CH_3 radicals from the chromophore-containing dissolved organic matter (CDOM), if CH_3 radicals are involved in the photochemical production of CH_3I [Moore and Zafiriou, 1994]. The PAR portion could positively affect the CH_3I concentration by enhancing the growth of CH_3I -producing phytoplankton. Or, if CH_3I formation by macroalgae can be enhanced under elevated UV radiation, as noted by Laturnus *et al.* [2004], a positive correlation between the solar exposure and CH_3I concentration may also exist for phytoplankton.

4.3. Water Temperature and CH_3I Concentration

[36] A positive correlation between CH_3I concentration and water temperature ($R = 0.61$, $n = 79$, $p \ll 0.001$) suggests that increase in water temperature may favor the production of CH_3I . As we know, temperature positively affects the two major loss processes of CH_3I in the surface mixed layer, enhancing its nucleophilic reaction with Cl^- by raising the reaction rate computed as $7.78 \times 10^{13} e^{-13518/T}$ [Elliott and Rowland, 1993] and enhancing its sea-to-air efflux by increasing the Schmidt number as shown in section 3.2 [de Bruyn and Saltzman, 1997]. Thus, the positive correlation implies that one or more production processes of CH_3I have to be enhanced by increased temperature in order to counteract the above mentioned negative effects. Since the major oceanic CH_3I production processes still remain uncertain, the reason for the positive effect of temperature can only be speculated on. Biologically, it could be achieved through the enhancement in the growth of phytoplankton producers of CH_3I , which was also briefly mentioned by Baker *et al.* [2000]. Photochemically, there are a few possible ways in which temperature could have an indirect effect. For example, higher temperature could promote growth of phytoplankton and bacteria and hence CDOM formation. Alternatively, if the production of CH_3I is a secondary photochemical process, its rate of production could be positively influenced by temperature.

4.4. Biogeochemical Province and CH_3I Concentration

[37] Each biogeochemical province is associated with distinctive sea surface temperature and chl *a* signatures [Devred *et al.*, 2007]. As discussed before, both sea surface temperature and phytoplankton can affect CH_3I production in the ocean. We, therefore, evaluated the effectiveness of using the biogeochemical province information to predict the level of CH_3I concentration in the surface mixed layer.

[38] As shown in Figure 2, during a specific season, the lowest CH_3I concentrations in the surface mixed layer were observed in the Boreal Polar Water and Arctic Water provinces (T6 in spring and summer, T7 in summer and fall). Compared with the other provinces, lower temperature in these two provinces should be one factor contributing to this result. The compositions of their local phytoplankton communities, as represented by their compositions of photosynthetic pigments, should also be important. In most provinces, measured CH_3I concentration varied with season. For instance, the highest CH_3I concentrations were observed in the Slope province in summer (station L). During spring and fall, CH_3I concentrations in this province

were much lower (T3 in spring and L in fall). Such variations of surface mixed layer CH_3I concentration were also observed in the NADR province (stations T4 and T5). Again, both water temperature and phytoplankton compositions may have played important roles in this seasonal variation.

[39] It is noticeable that the CH_3I concentration could be very different even in the same province during the same season. For example, in summer, the surface mixed layer CH_3I concentration at L was almost twice that at T3, although both stations belonged to the Slope province. Consequently, on the basis of merely the biogeochemical properties of each province, we cannot predict whether CH_3I concentration in the surface mixed layer will be high or not. In other words, only knowing the biogeochemical province designation of an area or water mass is not sufficient to predict its surface mixed layer CH_3I concentration. The distribution of CH_3I in the surface mixed layer is a combined result of many biological (e.g., phytoplankton compositions) and physical (e.g., water temperature, solar radiation, and wind speed) controls.

[40] It has become increasingly common for oceanographers to relate patterns in ecological or biogeochemical properties to biogeochemical provinces. Often, reference to the framework helps to explain variability. In our study, the assignment of biogeochemical provinces did not explain the dominant patterns observed. We feel that this mildly negative result (subject to the limitations of a relatively small number of samples) should be reported to help with the overall assessment of biogeochemical provinces as an oceanographic construct.

5. Summary

[41] We acknowledge that our results from one or a few visits to a specific station in one season may not be representative, and that to show the seasonal variation of CH_3I , we would need more detailed time series studies. Nonetheless, this study clearly indicates such seasonality of CH_3I variation in the open ocean, and it is also clear that the surface mixed layer concentration of CH_3I varied between the distinctive biogeochemical provinces of the NW Atlantic. Although the observations imply the existence of biological sources for high CH_3I concentrations at some stations, no phytoplankton group appeared to be solely and directly responsible for its biological production. The production of CH_3I by phytoplankton may be affected by environmental conditions, such as water temperature and solar radiation. To evaluate the influence of other factors, such as cell physiological status or grazing, on CH_3I production, we would need extra data (e.g., phaeopigment data) from other SABINA participants. The relationship between zeaxanthin-containing phytoplankton and CH_3I warrants further studies. During SABINA, no confirmative evidence was found for photochemical production of CH_3I .

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