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Abstract:

We report weekly observations of volatile organic iodocarbons (CH₃I, CH₂ClI and CH₂I₂) over the time-period May 2015 to December 2017 from 4 depths in Bedford Basin, a coastal fjord (70m deep) on the Atlantic coast of Canada. The fjord is subject to winter-time mixing, seasonal stratification and bloom dynamics, subsurface oxygen depletion, local input of freshwater and occasional intrusions of higher density water from the adjacent continental shelf. Near-surface concentrations showed strong seasonal and sub-seasonal variability which is compared with other coastal time-series. The vertical variation of CH₂I₂ and CH₂ClI within the upper 10m is consistent with rapid photolysis of CH₂I₂. Average annual sea-to-air fluxes (46.7 nmol m⁻² day⁻¹) of total volatile organic iodine were similar to those observed in other coastal and shelf time-series and polyiodinated compounds contributed 80% of the total flux. Fluxes were subject to strong interannual variability (a factor of two) mainly due to wind-speed variability. Near-surface net production of CH₃I averaged 1 pmol L⁻¹ day⁻¹ and was similar to rates in the English Channel but an order of magnitude higher than in shallow waters of the Kiel Fjord, Germany, possibly due to higher microbial degradation in the latter. The near-bottom (60 m) time-series showed evidence for CH₃I production associated with organic matter degradation, and a possible “switch” from production of CH₃I via an alkylation pathway to production of CH₂I₂ by a haloform-type reaction. Near-bottom CH₃I production varied strongly between years but was generally ca. 20 times lower than near-surface production.
Keywords: Iodocarbons, iodomethane, chloriodomethane, diiodomethane, air-sea flux, time-series

1. Introduction

Volatile organic iodocarbons (VOIs) such as methyl iodide (CH₃I), chloriodomethane (CH₂ClI) and diiodomethane (CH₂I₂) have a predominantly oceanic source and supply a significant amount of iodine to the atmosphere (see review by Saiz-Lopez and Von Glasow, 2012). These gases, also referred to as VSLS (very short-lived halogenated substances) due to their reactivity and short atmospheric lifetimes, have been implicated in supporting catalytic ozone destruction in the troposphere (Davis et al., 1996; McFiggans et al., 2000) and, potentially in the lower stratosphere (Solomon et al., 1994) as well as aerosol formation in the marine boundary layer (McFiggans et al., 2000, 2004; O’Dowd et al., 2002). Recent modelling of atmospheric reactive iodine (IOx = IO + I) as well as experimental studies (Carpenter et al., 2013; Jones et al., 2010; Mahajan et al., 2010) suggest that the supply of volatile organoiodine represents <50% of the total sea-to-air delivery of reactive iodine, with most being supplied in the form of HOI and I₂. Nevertheless, the potential for localized higher emissions coupled with their relatively long lifetimes (compared to I₂ and HOI) allows the organic compounds to be a significant source of iodine to the free troposphere and even, potentially, to the lower stratosphere in certain regions (Tegtmeier et al., 2013). Further, Mahajan et. al (2012) noted a strong correlation of IOₓ and CH₃I suggesting that the sources of CH₃I and the shorter-lived precursors of IOₓ are closely related or depend on similar variables.

CH₃I is the most abundant VOI species in the atmosphere (Yokouchi et al., 2011) because of its longer lifetime (days) compared to CH₂ClI (hours) and CH₂I₂ (minutes) (Moessinger et al., 1998; Rattigan et al., 1997). However, the total supply of organically-bound iodine to the atmosphere is
several times larger than the CH₃I supply alone (Carpenter et al., 2014) with the bulk of the remainder transported in the form of CH₂I₂ and CH₂ClI (additional iodocabons such as CH₃CH₂I, CH₂BrI and CHI₃ are generally present in much lower concentration). Despite considerable attention on the oceanic distribution and sea-to-air flux of these compounds, in particular CH₃I (Ziska et al., 2013), it is not yet possible to apportion oceanic production of these compounds, unequivocally, to specific mechanisms. Even for CH₃I, controversy remains, for example, as to the relative importance of direct “biological” or “photochemical” production pathways with experimental evidence reported for both, and correlation analysis generally being inconclusive, in part because of the “snapshot” nature of most studies (Stemmler et al., 2014). Comparisons of models to observed distributions have also proven ambiguous, with localized studies suggesting predominance of a biological production pathway (Stemmler et al., 2013) but a global analysis emphasising photochemical production as the dominant mechanism. This diversity of views has been maintained through a variety of experimental studies (Amachi et al., 2001; Brownell et al., 2010; Hughes et al., 2011; Manley and delaCuesta, 1997; Moore and Tokarczyk, 1993; Moore and Zafiriou, 1994; Richter and Wallace, 2004; Shi et al., 2014a; Smythe-Wright et al., 2006).

For compounds other than CH₃I, similar uncertainty exists concerning production pathways, but with fewer underlying studies. Laboratory experiments have shown that the presence of dissolved iodide and dissolved organic matter can lead to production of these compounds in the dark (Martino et al., 2009). Fuse et al. (2003) and Martino et al. (2005) observed that CH₂ClI could be produced by photolysis of CH₂I₂ in artificial and natural seawater. However detailed mechanisms and, especially, their relative importance in the field remain unclear.

Time-series observation can reveal processes and controlling factors underlying production and loss of iodocarbons in the ocean and provide data for testing hypotheses and/or models. However,
only a very few long-term, time series observations of iodocarbons have been reported to date, all from coastal water. Klick (1992) reported 13 months of weekly measurements of CH$_2$I$_2$ and CH$_2$ClI from very shallow (3.5m) water in the Kattegat at the Swedish coast. Orlikowska and Schulz-Bull (2009) reported a year of weekly data for CH$_2$ClI, CH$_2$I$_2$, CH$_3$I and C$_2$H$_5$I from a nearshore (3m depth) site in the Baltic Sea. Archer et al. (2007) reported a seasonal study of CH$_2$ClI, CH$_2$I$_2$, CH$_3$I, C$_2$H$_5$I, and CH$_2$BrI measured weekly at 4 depths (0-50m) in the western English Channel from July 2002 to April 2004. Shi et al. (2014b) reported on the seasonal cycle of CH$_3$I from surface waters of the Kiel Fjord: a shallow (14 m), brackish water body in northern Germany, which was sampled weekly for 2 years. Shimizu et. al (2017) presented a time-series of vertical profiles (0-90m) of CH$_2$I$_2$, CH$_2$ClI, CH$_3$I, and C$_2$H$_5$I from the centre of Funka Bay, Japan, which were measured every 2-4 weeks from March 2012 to December 2014.

Here, we report weekly observations of CH$_3$I, CH$_2$ClI and CH$_2$I$_2$ made over the time-period May 2015 to December 2017 at 4 depths (0-60m) in Bedford Basin: a coastal fjord on the east coast of Canada. We report seasonal to interannual variability of the observed concentrations at different depths in the water column and compare our results with the other time-series. We report daily average fluxes to the atmosphere and use a simple, time-varying mass-balance model for near-surface waters to estimate production rates and their variability. We discuss the observed variability of both concentrations and production rates in the light of earlier studies, potentially correlated variables and suggested production pathways.

2. Methods

Time-series measurements of VOIs were carried out in the Bedford Basin (44.69 °N, -63.63 °E) near Halifax, Canada. Bedford Basin is an 8 km long, 17 km$^2$ fjord with a maximum depth of 71m
and a total volume of 500 km$^3$. The Bedford Basin is connected with continental shelf waters of the Atlantic Ocean through “the Narrows” (a ca. 300 m wide and 20 m deep passage (Fig. 1)). The Basin receives freshwater primarily from the Sackville River at its northwestern end, with a total average freshwater input of 5.41 m$^3$ s$^{-1}$ (Buckley and Winters, 1992). The average near surface salinity within the Basin is 29 which can be compared with salinities of >30 over the adjacent Scotian Shelf. There are only relatively small horizontal gradients of near-surface salinity within the Bedford Basin itself (typically < 2 difference from close to the Sackville River mouth to the Narrows).

Time series observations of physical, chemical and biological parameters have been recorded since 1992 (Li, 1998). Our halocarbon samples were collected weekly, in the center of the Bedford Basin, at its deepest point (Fig. 1), between May 2015 and January 2018. Samples were collected with 10-L Niskin bottles attached to a rosette sampler at 1, 5, 10 and 60 m (10 m samples were collected biweekly from May to September 2015). The upper three water samples covered the majority of the euphotic zone. The 60m water sample was from typically stagnant, near-bottom water which is renewed by vertical mixing events in late winter, and by occasional intrusions of higher-salinity continental shelf water in both summer and winter. Chlorophyll $a$ (Chla), dissolved oxygen, and nutrients were measured weekly at the 4 depths as part of the Bedford Basin Monitoring Program (Details can be found in website: http://www.bio-iob.gc.ca/science/monitoring-monitorage/bbmp-pobb/bbmp-pobb-en.php). In addition to the Niskin bottle sampling, vertically continuous measurements of temperature, salinity, dissolved oxygen and Chl $a$ properties were measured with a CTD mounted on the rosette. Additional information concerning the measurements of supporting physical and biological parameters can be found in the paper by Burt et al. (2013). **Nutrients were measured using a Skalar SAN$^{++}$ autoanalyzer, the precisions of NO$_2^-$, NO$_3^-$ and NH$_4^+$ were ± 0.01**
µmol L⁻¹, ± 0.14 µmol L⁻¹ and ± 0.14 µmol L⁻¹ respectively. Chl a concentration was analyzed using a fluorescence technique (Turner Design Model 10 Fluorometer) with the root mean square error (RMSE) being 0.23 µg L⁻¹. Dissolved oxygen concentrations were determined at 4 depths using Winkler titration with a precision of ± 0.5 µmol kg⁻¹. The resulting between-lab agreement is approaching the specifications for repeat hydrography required by the Global Ocean Observing System (http://www.goosocean.org/components/com_oc/oe.php?task=download&id=35904&version=2.0&lang=1&format=1). The concentrations of iodomethane (CH₃I), chloriodomethane (CH₂ClI) and diiodomethane (CH₂I₂) reported here, as well as of a number of other halocarbons (data not shown), were measured using purge & trap gas chromatography with detection by both mass spectrometry (MS) and electron capture (ECD). All measurements were made using an Agilent Technologies gas chromatograph (GC 7890B), equipped with a capillary column (RTX-VGC; 60 m; 1.4 µm coating, column diameter: 0.25 mm; helium carrier gas 0.5 ml min⁻¹), together with an automated purge and trap system equipped with an autosampler (VSP4000 of IMT, Vohenstrauss, Germany). The GC column was temperature programmed as follows: initial temperature 50 °C for 6 minutes, then ramped to 150 °C at 6 °C min⁻¹; ramped to 200 °C at 10 °C min⁻¹. Water samples (10 ml) were stored in 20 ml vials equipped with an ultra-low-bleed septum, prior to purging with helium (20 ml min⁻¹ for 18 mins). Every sample was analysed in triplicate. The standard deviation of triplicate measurements (integrated peak area) was <10 % for CH₃I, <15 % for CH₂ClI and <20 % for CH₂I₂. Calibration of the GC system for CH₃I, CH₂ClI and CH₂I₂ was performed using permeation tubes (VICI, Houston, TX, USA) which were maintained at a constant temperature of 23 °C and weighed every 2 weeks. Dilutions of the permeation tube effluent were made in ultra-high-purity N₂.
(>99.995 %) with flow rates of 50 to 700 ml min\(^{-1}\), and samples were injected into the purge and trap system (VSP) through a 140 µl loop. Standard deviation of the peak area during these calibration runs was <5 % for CH\(_3\)I and CH\(_2\)ClI and <15 % for CH\(_2\)I\(_2\). Overall the calibration response varied by less than 15 % over the entire sampling period.

Throughout the paper, seasons are defined as follows: summer is June through August; fall is September through November; winter is December through February and spring is March to May.

3. Results and discussion

3.1 Environmental Variables from the Bedford Basin

The vertical profiles of temperature, salinity, dissolved oxygen and fluorescence (Fig. 2) are well-mixed from top to bottom in late winter (Feb-Mar) as a result of wind-mixing and convection (Li, 2001). Temperature is marked by strong seasonality to depths of <30 m. Near-surface temperatures start to rise above winter values of 4 °C, and stratified conditions develop, around early April with temperatures reaching ca. 21 °C by the end of August (Fig. 2a).

Salinity ranges from 23 to 31 through the entire water column, with the lowest salinities occurring very close to the surface (Fig. 2b and Fig. 3c). The near-surface stratification varied both seasonally and between years, primarily in association with variability of precipitation and the discharge of the Sackville River (source: Environment and Climate Change Canada; http://climate.weather.gc.ca/historical_data/search_historic_data_e.html). For example, the salinity difference between 1m and 5m was >1 during much of the summer of 2015 (June to September) and summer 2017 (June to August). In summer 2016, however, the salinity at 1m was close to that at 5m (difference < 0.3) (Fig. 3c). Occasional intrusions of more dense water from the Scotian Shelf, results in increased salinity, especially of bottom waters. The intrusions are irregular
and tend to occur a few times per year, for instance in May 2016 at which time the salinity of bottom water increased from 30.8 to 31.0 (Fig. 2b), and in early July 2017 when the salinity of mid-depth water increased from 30.5 to 31 (see marked circle in Fig. 2b).

The dissolved oxygen time-series (Fig. 2c) shows the effect of temperature-dependent solubility variations in surface waters as well as intrusions and late-winter vertical mixing in deeper water. In surface water the highest O\textsubscript{2} concentrations occurred between March and April every year in association with lowest seawater temperature. The vertical gradient of O\textsubscript{2} concentration was, generally, smallest towards the end of April as a result of vertical mixing. Sub-surface O\textsubscript{2} concentrations (>30 m) generally decreased in summer due to respiration, with occasional interruptions of this O\textsubscript{2} decline (e.g. November 2016) as a consequence of shelf-water intrusions which brought sudden increases in O\textsubscript{2} levels.

Fig. 3 depicts time-depth plots of the variation of chlorophyll \(a\), total dissolved inorganic nitrogen (DIN = [NH\textsubscript{4}\textsuperscript{+}] + [NO\textsubscript{2}\textsuperscript{-}] + [NO\textsubscript{3}\textsuperscript{-}]), salinity, precipitation, windspeed and solar irradiance in Bedford Basin over the period of the VOIs sampling. The seasonal variations of chlorophyll \(a\) concentration in surface water (Fig. 3a) show that two blooms (spring and autumn) occur in surface water. For example, in 2016, chlorophyll \(a\) increased rapidly from March to April (from 5 to 26 \(\mu\text{g} \text{ L}^{-1}\)), and from September to October (from 10 to 28 \(\mu\text{g} \text{ L}^{-1}\)). The vertical variation of chlorophyll \(a\) (as determined from fluorescence measured on the CTD, see Fig. 2d) reached 12 \(\mu\text{g} \text{ L}^{-1}\) during the bloom period. Sub-surface (20- 40 m) fluorescence-derived chlorophyll \(a\) dropped down to 4 \(\mu\text{g} \text{ L}^{-1}\). In the near-bottom water chlorophyll \(a\) ranged between 0 and 2 \(\mu\text{g} \text{ L}^{-1}\) during the whole year and varied only slightly.

The seasonal variation of dissolved inorganic nitrogen(DIN) in surface water is plotted in Fig. 3b. In winter, when chorophyll \(a\) levels are very low due to light limitation, DIN concentrations reach
ca. 12 µmol L⁻¹ but are drawn down to low levels (< 1 µmol L⁻¹) after the spring bloom. Summertime chlorophyll a levels are moderate but variable (ca. 3 to 10 µg L⁻¹), likely reflecting continuing nutrient input (e.g. from runoff and/or sewage treatment plants). The average precipitation in Bedford Basin was 27.6 mm week⁻¹ in summer 2015 and was 16 mm week⁻¹ in summer 2016 (Fig. 3d). Typically, strongest irradiance (data was downloaded from the CERES FLASHFLUX system: https://power.larc.nasa.gov/cgi-bin/hirestimeser.cgi) occurs in June and July (see Fig. 3f), and highest water temperatures are observed in August.

3.2 Variations of Iodocarbons Concentrations in Bedford Basin

Iodocarbon concentrations in surface water (1, 5 and 10 m) showed strong seasonality, with lowest concentrations from December through May (1.2 pmol L⁻¹ for CH₃I; 1.3 pmol L⁻¹ for CH₂ClI and 0.3 pmol L⁻¹ for CH₂I₂). Concentrations start to increase in late May/ June, reaching levels as high as 45 pmol L⁻¹ for CH₃I; 160 pmol L⁻¹ for CH₂ClI and ca. 80 pmol L⁻¹ for CH₂I₂ (with a single peak of 500.5 pmol L⁻¹; Fig. 4). Near-surface, summertime concentrations of all three compounds were characterized by a broad seasonal peak of 6-7 months duration (or shorter for CH₂I₂), on top of which were superimposed ca. 3-4 peaks of ca. 1 month duration. The number, amplitude and timing of these peaks varied amongst the three compounds with CH₃I, notably, showing only one large peak in 2016 and four during the other two years of the time-series (Fig. 4a).

Concentrations at 60 m were almost always lower, and much less variable, ranging over the year from 1 to 9 pmol L⁻¹ for CH₃I (except the Fall/Winter 2015-2016, see below), 1 to 6 pmol L⁻¹ for CH₂ClI and 0.4 to 18 pmol L⁻¹ for CH₂I₂ (Fig. 4d) respectively. Hence, the bottom water (60 m) concentrations of CH₂I₂ and CH₂ClI were always much lower than in near-surface waters throughout the summers. The surface to deep concentration difference was smallest for CH₃I and showed interannual variability. Notably bottom water concentrations reached 26 pmol L⁻¹ and were
even higher than in contemporary surface waters from September 2015 to March 2016 (Fig. 4d). Missing from the bottom water time-series, were the ca. 1 month duration variations seen in summertime surface water.

Inter-relations between the iodocarbons in surface seawater were examined with linear regression of both weekly and monthly-averaged concentrations. The resulting correlations are shown in Table 1. Using weekly data, significant correlations (i.e. p<0.05) were found between \([\text{CH}_3\text{I}]\) and \([\text{CH}_2\text{ClI}]\) at 1, 5 and 10 m depths with the strongest correlation \((R=0.7)\) at 10m. The only other significant correlation was between \(\text{CH}_2\text{I}_2\) and \(\text{CH}_2\text{ClI}\) at 5 m. Use of monthly averaged values gave stronger correlations. Once again, the significant correlations were between \(\text{CH}_3\text{I}\) and \(\text{CH}_2\text{ClI}\) (at 1, 5 and 10m depth) as well as between \(\text{CH}_2\text{ClI}\) and \(\text{CH}_2\text{I}_2\) at 5 and 10m depth. Table 2 also presents the correlations of iodocarbon concentrations with potentially related variables (discussed in section 4.3).

Generally, the concentration of \(\text{CH}_2\text{I}_2\) was higher than that of \(\text{CH}_2\text{ClI}\). The average ratio of \(\text{CH}_2\text{I}_2/\text{CH}_2\text{ClI}\) within the top 10m of the water column over the summer months was 1.4. However, this ratio was significantly lower at 1m depth (average of 0.6) and increased with depth (1.5 at 5 m and 2.2 at 10 m, reaching values as high as 2.7 at 60 m).

3.3 Sea-to-Air Flux

Using the concentrations of \(\text{CH}_3\text{I}, \text{CH}_2\text{ClI}\) and \(\text{CH}_2\text{I}_2\) at 1m depth (Fig. 4) we estimated the sea-to-air flux of VOIs (F) using the following equation and the parameterization of Nightingale et al., 2000) for the water-side transfer velocity:

\[
\text{Flux} = K(C_{aqu} - C_{air} \times H)
\]  

\[
K_w = \left(\frac{S}{660}\right)^{-0.5} (0.222 \cdot u_{10}^2 + 0.333 \cdot u_{10})
\]
where $u_{10}$ is wind speed at 10 m height, $Sc$ is the temperature-dependent Schmidt number, as estimated by Groszko (1999) and Henry’s Law constants (H) were from Moore et al. (1995). The air-side resistance has been shown by Archer et al. (2007) to be significant for soluble gases such as CH$_2$ClI and CH$_2$I$_2$. Hence $K$ in equation 1 is calculated as follows (Liss and Slater, 1974):

$$\frac{1}{K} = \frac{1}{K_w} + \frac{1}{HK_a}$$

(3)

where the air-side transfer velocity was calculated according to Duce et al. (1991).

$$K_a = \frac{u_{10}}{(770 + 45(MW)^{1/3})}$$

(4)

with MW being the molecular weight of the gas of interest.

Daily averaged wind speed was measured at the nearby Halifax Dockyard (Fig. 1) (source: Environment and Climate Change Canada; [http://climate.weather.gc.ca/index_e.html](http://climate.weather.gc.ca/index_e.html)). Seawater temperature and surface iodocarbon concentrations were interpolated linearly between the weekly measurements in order to coincide with the wind speed data and generate daily flux estimates.

Following Archer et al. (2007) and Shimizu et al. (2017), we applied an atmospheric concentration of zero for calculating the flux of all three compounds. Rasmussen et al. (1982) reported an average atmospheric mixing ratio of CH$_3$I of ca. 1 pptv for Cape Meares (45 °N) and Yokouchi et al. (2008) presented a mean concentration of 0.98 pptv for Cape Ochiishi (43.2 °N), with both sites sharing a similar latitude to our sampling location (44.69 °N). If a mixing ratio of 1pptv had been used for our calculations, the total annual flux of CH$_3$I would be reduced by only 5 %. Atmospheric mixing ratios of CH$_2$ClI and CH$_2$I$_2$ are generally lower (reviewed by Carpenter, 2003) so that any overestimation of the fluxes of these compounds due to this assumption will certainly be negligible (Archer et al., 2007).

Fig. 5 presents the weekly averaged combined flux of organically-bound iodine, $F_{\text{org}}$, as stacked bar charts, where $F_{\text{org}} = (F_{\text{CH3I}} + F_{\text{CH2ClI}} + 2*F_{\text{CH2I2}})$. The calculated emissions of individual
compounds ranged from 0.9 to 39.2 nmol m\(^{-2}\) d\(^{-1}\) for CH\(_3\)I (annual average of 8.4 nmol m\(^{-2}\) d\(^{-1}\)), 0.9 to 78.0 nmol m\(^{-2}\) d\(^{-1}\) for CH\(_2\)ClI (annual average of 17.4 nmol m\(^{-2}\) d\(^{-1}\)) and 0.3 to 78.0 nmol m\(^{-2}\) d\(^{-1}\) for CH\(_2\)I\(_2\) (annual average of 10.3 nmol m\(^{-2}\) d\(^{-1}\)). Seasonal and annual average fluxes of the individual compounds and of I\(_{org}\) are presented in Table 3. Clearly the sea-to-air flux is highest in summer and fall and is dominated by the flux of the dihalomethanes rather than CH\(_3\)I.

3.4 Net Production of CH\(_3\)I
We used a mass balance approach to estimate the production rate of CH\(_3\)I within the uppermost 10m of the water column, based on the concentration time-series (see also Shi et al., 2014b). Using the annual cycle of average near-surface CH\(_3\)I concentrations (Fig. 4a), we examined the mass balance of CH\(_3\)I for this fixed depth interval according to:

\[
\Delta C = P_{net} - L_{sea-to-air} - L_{SN2} - L_{mix} \tag{5}
\]

where \(\Delta C\) is the daily change of the average CH\(_3\)I concentration in the near-surface seawater (0-10 m); \(P_{net}\) represents the net of gross production minus any additional, uncharacterized losses such as microbial degradation; \(L_{sea-to-air}\) is the sea-to-air flux (section 3.3) and \(L_{SN2}\) is the ‘chemical’ loss due to nucleophilic substitution of Cl\(^{-}\) for I\(^{-}\) which was calculated based on reaction kinetics (Elliott and Rowland, 1993; Jones and Carpenter, 2007) using the corresponding temperature, salinity and mean concentration of CH\(_3\)I. \(L_{SN2}\) averaged 0.1 pmol L\(^{-1}\) day\(^{-1}\). \(L_{mix}\) is the loss due to downward mixing and has been shown in several studies to be negligible compared with other loss terms e.g. (Richter and Wallace, 2004). The latter assumption will not always be valid in winter and, especially, when mixed layers deepen to >10m. However most production of iodocarbons occurs during summer and fall when there is strong stratification within the upper 10m (see Fig. 3c), and
we excluded from our mass balance calculations the limited periods of time when density was uniform in this depth interval.

The net production rate of CH$_3$I over the 3-year time-series is shown in Fig. 6. The annual average production rate of CH$_3$I was 1.0 pmol L$^{-1}$ day$^{-1}$ (ranging from -1.6 to 8.5 pmol L$^{-1}$ day$^{-1}$). A significant peak of P$_{net}$ occurred from August to September in every year. The net production rate of CH$_3$I in summer and fall averaged 1.6 pmol L$^{-1}$ day$^{-1}$ and was 5 times larger than wintertime rates (ca. 0.3 pmol L$^{-1}$ day$^{-1}$). Net production rates for CH$_2$ICl and CH$_2$I$_2$ were also calculated (results not shown), with typical summertime values being 3.2 and 1.3 pmol L$^{-1}$ day$^{-1}$, respectively. Photolytic loss can be very significant for these compounds and has not been estimated, so these P$_{net}$ values represent the net of gross production minus uncharacterized losses including photolysis as well as microbial degradation.

4. Discussion

In the following we discuss the Bedford Basin data in comparison with other studies that have reported concentrations of multiple iodocarbons and especially those that have reported time-series covering an annual cycle (see citations in the introduction). All of these time-series are from mid-latitude (40-60°N) nearshore or continental shelf environments subject to strong seasonal variations of light, temperature and biological productivity. There are no reported time-series of seawater concentrations from low latitudes.

4.1 Potential influence of nearshore and /or macroalgal sources

The potential of nearshore macroalgae to cause elevated coastal iodocarbon concentrations has been mentioned in a number of studies (Giese et al., 1999; Manley and delaCuesta, 1997; Schall
et al., 1994). We investigated this in July 2017, by sampling at 5 nearshore sites around Bedford Basin (Fig. 1) and comparing nearshore concentrations with values measured at the regular sampling site in the center of the Basin (Table 4). The nearshore results were consistently within one standard deviation of mean concentrations of VOIs measured at the center of Bedford Basin during July, indicating no significant difference. Klick (1992) also compared measurements on samples collected directly over a rich bed of macroalgae with samples collected further away from direct contact with macroalgae: whereas they observed significantly higher concentrations of bromocarbons in proximity to the macroalgae, there was no difference observed for CH$_2$I$_2$ and CH$_3$ClI. Shimizu et al. (2017) sampled a number of nearshore regions around Funka Bay, including rocky shores with extensive macroalgae, and also found concentrations to be similar at both nearshore and central Bay locations. We therefore conclude that any direct impact of macroalgae on measured organoiodine levels is small, even in coastal regions, which lends strong support to the conclusion by Saiz-Lopez and Von Glasow (2012) that macroalgae are only a minor global source of these compounds to the atmosphere.

4.2 Concentrations and relative abundance of iodocarbon compounds

The average concentration of total volatile organic iodine I$_{org}$ (where I$_{org}$ = [CH$_3$I] + [CH$_2$ClI] + 2(CH$_2$I$_2$)) and the relative contributions of the different compounds to I$_{org}$ from this and other studies is shown in Fig. 7. The combined concentrations of the three iodocarbons are highest but also show highest variability ([I$_{org}$] = 25 to 281 pmol L$^{-1}$) in summertime coastal waters (loosely defined here as within a few kms of land). Continental shelf waters have lower concentrations of I$_{org}$ averaging 32 pmol L$^{-1}$, with open ocean waters having comparable or lower concentrations (average I$_{org}$ = 17 pmol L$^{-1}$). Despite the differences in I$_{org}$ concentration ranges evident for
different regions in Fig. 7, a 1-way ANOVA showed no significant differences between the means for the three regions. However after pooling of shelf and open ocean results to make only two populations, a t-test did reveal a significant difference with coastal waters for at the 95% confidence level.

The distribution of I$_{org}$ is contrary to the global distribution of CH$_3$I reported by Ziska et al. (2013) who noted a tendency for the open ocean to have higher concentrations than coastal waters (their definition of “coastal” was within 1 degree latitude or longitude of land and therefore much broader than ours). As noted by Ziska et al. (2013), this may reflect higher CH$_3$I concentrations in tropical and sub-tropical open ocean waters, as their general pattern was reversed in the Northern Hemisphere. The coastal waters depicted in Fig. 7 are largely from mid-latitudes of the Northern Hemisphere.

The relative contribution of the dihalomethanes to I$_{org}$ also appears to vary between regions, with the ratio of dihalomethane-I to I$_{org}$, ([CH$_2$ClI]+2*[CH$_2$I$_2$])/[I$_{org}$], averaging 0.71, 0.69 and 0.55 in coastal, shelf and open ocean waters, respectively. While an elevated contribution of dihalomethanes in coastal waters is consistent with the report by Jones et al. (2010), regional differences apparent in Fig. 7 are not significant at the 95% confidence level when tested with a 1-way ANOVA.

Klick (1992), Jones et al. (2010) and Shimizu et al. (2017) reported concentrations of volatile organic iodine in summertime coastal waters that are comparable to, or higher than those observed in Bedford Basin (i.e. average I$_{org}$ concentrations >100 pmol L$^{-1}$). Our results from Bedford Basin correspond closely with concentrations and relative contributions reported by Shimizu et al. (2017) for coastal water in Funka Bay, Japan (Fig. 7). In these coastal surface waters, the CH$_2$I$_2$ concentration and contribution was highest on average, followed by CH$_2$ClI and the lowest was
CH₃I. In open ocean waters, the relative contribution of [CH₃I] to Iₐorg appears higher, reaching over 50% in some cases (see Fig. 7), with the contribution of CH₂I₂ generally being lower in the open ocean than in coastal waters. However, once again, these apparent regional differences are not significant at the 95% confidence level.

In laboratory studies, Fuse et al. (2003) demonstrated that relatively large amounts of CH₂I₂ and I₂ together with smaller but still significant amounts of CH₂ClI and CHI₃ can be produced, presumably abiotically, in dark incubations of (filtered) spent culture media with suspended bacterial cells and added [I⁻]. The CH₂I₂/CH₂ClI production ratio was ~35 and no mono-iodinated CH₃I was produced in these experiments. The implication was that dissolved organic compounds within spent media were key to production of polyiodinated compounds. In the absence of spent culture media, additions of oxaloacetic acid also resulted in formation of CH₂I₂ and CH₂ClI (with a lower ratio of CH₂I₂/CH₂ClI of ~10) suggesting that organic acids may be a substrate for their formation. The mechanistic role of the suspended bacterial cells was not clear, however they may have supplied haloperoxidases required for oxidation of I⁻ (see also Hill and Manley, 2009).

Martino et al. (2009) demonstrated that, alternatively, oxidation of dissolved iodide to I₂ and HOI by reaction with ozone (e.g. Garland et al., 1980) in filtered (0.2 μm) seawater containing natural levels of dissolved organic matter also resulted in formation of polyiodinated compounds (CH₂I₂, CH₂ClI and CHI₃) with CH₂I₂/CH₂ClI production ratios ranging from 2 to 4. They suggested that the yield of various iodocarbons depends on “the abundance and perhaps on the nature of the organic substrate” which “can vary widely both temporally and spatially”. We could not, however, find any obvious relationship of near-surface iodocarbon concentrations with local measurements of atmospheric ozone near Bedford Basin (results not shown).
We therefore suggest that the higher levels of CH$_2$I$_2$ observed in coastal waters, including Bedford Basin, reflect a higher supply rate of HOI and/or I$_2$ and/or of the organic precursors suitable for formation of polyiodinated compounds. Ultimately, reduction of seawater iodate to reduced forms, such as iodide, likely supports the potential for organoiodine formation. Addition of iodide has been identified, in short-term experiments, as a source for reactive iodine (iodine atoms) which can stimulate photochemical formation of CH$_3$I (Moore and Zafiriou, 1994). However, Shi et al. (2014b) found no positive correlation of [I$^-$] with seasonal CH$_3$I production in a field study in Kiel fjord, noting that background iodide levels may have been always sufficient to support production of pM levels of CH$_3$I. Indeed, there is no a priori reason to expect a positive correlation of [I$^-$] with iodocarbon production if supply of more reactive iodine species (iodine atoms, HOI and/or I$_2$) is the key, proximate control. The short-term formation rate of reactive species from a background reservoir of I$^-$, and hence production of iodocarbons, may depend more on availability of haloperoxidases, various oxidants and/or temperature-dependent kinetics. The conversion of I$^-$ to these reactive species could even lead to inverse correlations between I$^-$ and iodocarbons.

Relatively small quantities of CH$_2$ClI were produced in several of the experiments cited above, yet observations in Bedford Basin show average CH$_2$I$_2$/CH$_2$ClI ratios of 1.4 in the top 10 m of the water column. Production ratios in these experiments vary, as noted above, but laboratory studies have also shown that photolysis of CH$_2$I$_2$ can be an important source of CH$_2$ClI in surface waters with a yield of 25 % to 35 % (Jones and Carpenter, 2005; Martino et al., 2005). We observed significant correlation between [CH$_2$I$_2$] and [CH$_2$ClI] at 5 and 10 m depth (but not at 1m) (Table 1), which is consistent with a fraction of the CH$_2$I$_2$ production being transformed photochemically (The lack of correlation at 1m may be due to the very rapid photolysis). However the correlation may also reflect the original production ratio of the individual compounds (which laboratory
experiments suggest may be substrate-dependent). In both cases however, dissolved organic matter (DOM) quality and quantity (possibly associated with terrestrial supply) and/or elevated supply of I are likely to be underlying reason(s) for the high concentrations of dihalomethanes observed in Bedford Basin and other coastal waters.

4.3 Temporal variations of iodocarbons in near-surface water

The following discussion of temporal variability is separated into consideration of seasonal and interannual variations.

4.3.1 Seasonal Variations

All of the reported iodocarbon time-series showed strong seasonality, with minimum, sometimes undetectable concentrations in winter, and higher concentrations in summer. Near-surface (0-10 m) concentrations of all three iodocarbons in Bedford Basin, including CH$_3$I, remained low until mid-May to mid-June, with their subsequent increase coincident with initial warming of near-surface waters from wintertime minimum temperatures of ca. 1-2 °C (lag < 1 month; Fig. 8a). Hence the initial appearance of all three iodocarbons occurred more than 3 months after the seasonal increase in solar radiation, ca. 1-2 months after the Spring Bloom (Fig. 8d), after near-surface nitrate had been drawn down to low levels (Fig. 8e) and almost coincident with the seasonal temperature increase (Fig. 8a).

In the western English Channel (Archer et al., 2007), a gradual increase of CH$_3$I commenced in February, coincident with the seasonal increase in solar radiation. Summertime values remained high, with some higher-frequency variation, and then decreased in September/October. The increase of CH$_2$ClI and CH$_2$I$_2$ started later, in April, more or less coincident with both the Spring Bloom and initiation of near-surface warming from a wintertime minimum temperature of ca. 8
°C. Summertime values of CH₂ClI and CH₂I₂ showed periodic variations similar to those observed in Bedford Basin (section 3.2).

The lower temporal resolution of the study in Funka Bay (Shimizu et al., 2017), with sampling only every 1 or 2 months, precluded detailed examination of timing. A gradual increase in CH₃I appeared to start in March, during or towards the end of the Spring Bloom when surface water temperatures were still close to their wintertime minimum of -1 to 2.5 °C. The seasonal increase of CH₂I₂ and CH₂ClI occurred later (May-June) at a time of rising water temperatures and low nutrient levels with concentrations remaining elevated through the summer and decreasing to wintertime levels in October.

The initial CH₃I increase at a shallow station in the Kiel Fjord (Shi et al., 2014b) occurred in March, and was closely linked in time to seasonal increases of solar radiation, temperature (winter minimum of 0 °C) as well as Chl a and the springtime drawdown of nitrate. Lagged correlation analysis showed similarly strong correlations of CH₃I with both temperature and solar radiation, with the annual cycle of CH₃I lagging temperature by ca. 1 month, however the very close correspondence of multiple seasonal cycles led the authors to note that “the use of correlation analysis to infer causality has likely reached its limit in this analysis”.

The observation of a rapid increase in the production rate of I⁻ within phytoplankton cultures (diatoms and prymnesiophytes) when they enter stationary and, especially, senescent phases (Bluhm et al., 2011) is potentially relevant to the observed seasonality of iodocarbon formation. The reduction of iodate to iodide was suggested to be due to release of precursors, such as reduced sulphur species, to surrounding culture medium in association with a loss of membrane integrity by stressed cells or as a result of viral lysis. Hughes et al. (2011) also reported studies with cultures of Prochlorococcus marinas in which accumulation of CH₃I commenced when cultures became
senescent. We note that significant iodocarbon accumulation in Bedford Basin was confined to summertime when DIN was depleted (see Fig. 3b) and when cells may have been stressed or subject to viral lysis, perhaps similar to later stages of batch culture experiments.

We therefore hypothesize that seasonal nitrate drawdown leads to increased supply of iodide to surface waters which can, in turn, lead to increased formation of iodine atoms, HOI and I₂ as precursors for iodocarbon formation by both photochemical and haloform reaction pathways (Martino et al., 2009; Moore and Zafiriou, 1994). Whereas the supply of iodide may be one key control, it is likely that variations in light intensity and water temperature also contribute to the overall seasonality of the production rate of CH₃I (e.g. through temperature influence on reaction kinetics). For example, light can influence formation of CH₃I directly (e.g. Moore and Zafiriou, 1994; Richter and Wallace, 2004). Light can also influence iodocarbon production indirectly, for example by producing oxidants such as H₂O₂ to promote oxidation of iodide by haloperoxidases (Hill and Manley, 2009) or by altering the quality of dissolved organic matter. The time-series of CH₂I₂ and CH₂ClI from very shallow (< 4 m), nearshore waters of the Kattegat, Sweden (Klick, 1992) and the Baltic Sea, Germany (Orlikowska and Schulz-Bull, 2009) showed peaks in April/May and again in September/October, with low concentrations throughout summer. This contrasts with the deeper water columns of Bedford Basin, Funka Bay and the English Channel where concentrations remain elevated throughout summer. This likely reflects dominance of photolytic loss over production within very shallow water columns exposed to summertime light intensities and long periods of daylight. Sub-surface production coupled with vertical mixing may explain the summertime persistence in deeper water columns.

In addition to the broad seasonal variation, a number of maxima with duration of ca. 1 month, were observed, and appear similar to short-period fluctuations observed in the English Channel time-
series (Archer et al., 2007). There does not appear to be any consistent pattern linking the maxima and minima of the three compounds in the two studies, so that the underlying causes for these shorter period variations are unclear.

4.3.2 Interannual variability

The Bedford Basin time-series is unique in having high temporal resolution sampling (weekly) over three annual cycles which allows interannual variability to be examined for the first time. The most obvious interannual difference was in the behavior of CH\textsubscript{3}I. In particular, 2016 was markedly different in that only a single peak was observed in late August, whereas the summers of 2015 and 2017 were marked by 3-4 quasi-periodic, multi-week maxima. As noted already, the English Channel time-series of CH\textsubscript{3}I did not exhibit this behavior. The shallow-water time-series of CH\textsubscript{3}I in the Kiel Fjord and coastal Baltic Sea (Orlikowska and Schulz-Bull, 2009; Shi et al., 2014b) also did not exhibit this type of variability. Because the cause of the periodicity itself is not understood or explained, discussion of reasons for its interannual variation must be highly speculative. One clear difference of 2016 relative to the other two years, was the lower summertime precipitation and associated lack of near-surface salinity stratification. The temporal behavior of CH\textsubscript{3}I in 2016 might therefore be related to altered near-surface mixing dynamics within Bedford Basin, or alternatively, to decreased delivery of key precursors (e.g. DOM) from land via rivers and wastewater.

4.4 Vertical distributions and subsurface temporal variability

Fig. 4 shows the near-surface concentration variations of the VOIs. For CH\textsubscript{3}I, concentrations were almost always uniform between 1, 5 and 10 m. For CH\textsubscript{2}ClI, the concentrations at 1 and 5 m were
usually very similar (average difference -4.1%; median -2.5%), however concentrations at 10m depth were noticeably lower for periods of time. For CH$_2$I$_2$, the highest concentrations were observed at a depth of either 5 or 10 m, with concentrations at 5 m occasionally peaking at very high levels (e.g. 250-350 pmol L$^{-1}$) for short periods (less than one week). Concentrations at 1 m were almost always lower than at 5 m, with the percentage reduction relative to 5 m averaging 52% in summer. Concentrations at 10 m, on the other hand, were generally the same or higher as those measured at 5 m (with the exception of the previously mentioned, short-lived peaks).

These results are consistent with earlier studies of vertical profiles in the open ocean (e.g. Moore and Tokarczyk, 1993; Yamamoto et al., 2001) as well as with model predictions (Jones et al., 2010; Martino et al., 2006). In particular, our results are consistent with the quantitative predictions of a mixed-layer model (Jones et al., 2010) that CH$_2$ClI would typically be near-uniform within the upper 6 m of the water column, whereas photolytic decay could remove up to 100% of the CH$_2$I$_2$ over that depth range, depending on time of day and conditions.

4.5 Temporal variability in near-bottom water (60 m)

The time-series of VOIs in near-bottom waters (60 m) are presented in detail in Fig. 9a,b,c, with specific events labelled 1 through 9. Variability was generally of lower amplitude than in surface waters, except for CH$_3$I during the winter of 2015-2016 (Fig. 4d). From June to December 2015, [CH$_3$I] increased steadily (concentration change, $\Delta C = 20$ pmol L$^{-1}$) (event 1 to 3; Fig. 9a), exceeding surface water concentrations from October 2015 until the end of March 2016. No comparable increase was observed during 2016 (Fig. 9b), and a smaller increase ($\Delta C = 8$ pmol L$^{-1}$) was confined to the early summer of 2017 (Fig. 9c).
Concentrations of CH$_2$ClI remained almost constant at <5 pmol L$^{-1}$ throughout, with the notable exception of abrupt (<1 week) increases in May and November 2016 (events 4 and 5; Fig. 9b) and December 2017 (event 9; Fig. 9c). These increases ($\Delta C = 2$–5 pmol L$^{-1}$) coincided with sudden increases of salinity (and O$_2$) and reflect intrusion of saltier, near-surface waters from offshore, rather than local production. The subsequent concentration declines reflect loss due to mixing or, more likely, reaction and/or microbial degradation within the water column and sediments. The same three intrusions also drove abrupt increases of CH$_2$I$_2$ with amplitude ca. 1.5 – 2 times higher than those for CH$_2$ClI, consistent with near-surface concentration ratios (see section 3.2). However, CH$_2$I$_2$ also showed higher-amplitude variations unrelated to the bottom water intrusions (see below).

The increase of CH$_3$I from June through October 2015 (event 1 through 3; Fig. 9a), paralleled a steady decline in oxygen, suggesting that production was linked to degradation of organic matter. The accumulation rate of ca. 0.06 pmol L$^{-1}$ day$^{-1}$ was 20 times smaller than typical P$_{net}$ for CH$_3$I in surface waters (see section 3.4). The increase appears consistent with results from short-term (3-day) incubation experiments with biogenic marine aggregates reported by Hughes et al. (2008) in which concentrations of mono-iodinated iodocarbons, including CH$_3$I, increased but with no corresponding increase in dihalogenated compounds. Their results suggested alkylation of inorganic iodine or breakdown of higher molecular mass organohalogens as production pathways and, following Amachi et al. (2001), they suggested that microbial degradation increased the supply of precursors.

However, as O$_2$ concentrations declined further from October through late December (event 2 to 3; Fig. 9a), the concentration of CH$_3$I stabilized and CH$_2$I$_2$ concentration increased markedly from 2 to 12 pmol L$^{-1}$. From January through April 2016, CH$_3$I levels decreased (following event 3; Fig. 23)
9a, b), in concert with increasing O\textsubscript{2} concentrations and decreasing salinity, reflecting the effects of progressive vertical mixing with overlying waters which had lower CH\textsubscript{3}I concentrations. Over this same period, CH\textsubscript{2}I\textsubscript{2} concentrations at 60 m remained almost constant (Fig. 9a, b) due to the smaller vertical concentration gradient, until increasing due to an intrusion (event 4). This was followed by a gradual decrease over summer months, in parallel with the seasonal decrease of O\textsubscript{2} (fig 9b).

The data from 2015 and 2017 are suggestive of a “switch” of production mechanism from an alkylation pathway producing mono-iodinated compounds (CH\textsubscript{3}I) to a haloform-type reaction producing CH\textsubscript{2}I\textsubscript{2}. The “switch” took place in October 2015 (event 2; Fig. 9a), when oxygen concentrations dropped below 90 \(\mu\text{mol} \text{ kg}^{-1}\), although whether the switch was related to redox conditions in the water column or sediments, speciation and availability of iodine, or availability of suitable organic precursors and/or enzymes cannot be determined.

There was almost no near-bottom iodocarbon production during 2016 (Fig. 9b), and therefore no “switch”, for reasons that are not clear given that O\textsubscript{2} declined through summer and fall, until interrupted by an intrusion in November (event 5; Fig. 9b). We speculate that the lack of production in near-bottom water might be linked to the relatively short period of CH\textsubscript{3}I production in near-surface waters during that year (fig 4a).

In 2017, there was moderate sub-surface production of CH\textsubscript{3}I, associated with O\textsubscript{2} consumption (April through July; event 6 to 7), and, again, an apparent “switch” to CH\textsubscript{2}I\textsubscript{2} production marked by plateauing of CH\textsubscript{3}I concentrations (event 7) at the same time as CH\textsubscript{2}I\textsubscript{2} concentrations started to increase (Fig. 9c). This was followed by a subsequent decrease to background levels over a period of about a month. The apparent “switch” in production took place earlier in the year and at higher O\textsubscript{2} concentrations (175 \(\mu\text{mol} \text{ kg}^{-1}\)) than in 2015.
However close inspection of Fig. 2 shows that the plateauing of CH$_3$I in near-bottom waters (event 7) also coincided with the appearance of a mid-depth intrusion of saltier water (as denoted by the salinity contour; see blue circled area in Fig. 2). The same period (between events 7 and 8) was marked at 60m by a change from declining to increasing salinity, reduction in the rate of oxygen concentration decline (Fig. 9c) and an increase in the rate of warming (not shown). The mid-depth salinity maximum in Bedford Basin must reflect intrusion of saltier water from offshore. The subsequent trends in temperature, salinity and dissolved oxygen at 60m, between events 7 and 8 (Fig. 9c), are consistent with mixing of pre-existing near-bottom water with this intrusion. It therefore cannot be ruled out that mixing with this intrusion contributed in some way to the near-bottom increase of CH$_3$I$_2$, plateauing of CH$_3$I concentrations as well as the small but significant increase in CH$_2$ClI ($\Delta C$=1-2 pmol L$^{-1}$), and hence to the apparent “switch”, which all occurred at the same time.

At the end of this period, in mid-August (event 8), the rate of warming and salinity increase at 60m decreased again and the rate of oxygen decline increased (Fig. 9c), suggesting that the intrusion’s impact had lessened. At this time, CH$_3$I$_2$ and CH$_3$I concentrations started to return to background levels with estimated half-life, assuming 1st order kinetics, of ca. 65 days (CH$_3$I$_2$) and 14 days (CH$_3$I). A decrease in [CH$_2$ClI] started about a month later with 1st order half-life of ca. 70 days. Similar rates of decline of [CH$_2$ClI] and [CH$_3$I$_2$] were observed following sudden concentration increases associated with other intrusions, discussed earlier.

This very detailed discussion of the temporal variability emphasizes that a variety of physical and biogeochemical mechanisms can contribute to interannual, seasonal, and short-term variability of the three iodocarbons. The high amplitude variability observed in Bedford Basin could prove useful for validation of models representing complex iodine cycling as well as physical mixing.
dynamics. However, separation of multiple potential contributing factors and processes underlying temporal variability may require a data set with higher vertical resolution and, ideally, a seasonally-resolved time-series of experiments (compare Shi et al., 2014a).

4.6 Sea-to-air fluxes

The temporal variation of the sea-to-air flux of I$_{org}$ and the relative contribution from the three iodocarbons are shown in Fig. 5 and Table 3. Similar to the findings of Archer et al. (2007), air-side resistance leads to significant reductions in calculated, annual average fluxes for CH$_2$ClI and CH$_2$I$_2$ of 10% and 24%, respectively, relative to calculations when it is ignored. The study by Shimizu et al. (2017) did not consider air-side resistance, so Table 5 presents both their original reported fluxes, as well as fluxes adjusted for its likely impact based on our study and that of Archer et al. (2007). The following discussion makes use of the adjusted fluxes.

Consistent with earlier time-series (excluding those from very shallow waters, see section 4.2), the sea-to-air flux of iodocarbons is generally highest in summer/fall. However, high wintertime fluxes are also possible, as seen in 2017 when there was a large efflux of CH$_2$I$_2$ (averaging 9.1 nmol m$^{-2}$ d$^{-1}$; Table 3), due to both strong winds and relatively high concentrations. The fluxes of CH$_3$I and CH$_2$ClI, on the other hand, were always higher in summer/fall (ca. 3-5 times and 10 times higher, respectively). Similar findings were presented by Shimizu et al. (2017) with the total iodine flux in Funka Bay in summer being > 4 times that in winter.

Our estimated emissions of CH$_3$I (8.4 nmol m$^{-2}$ d$^{-1}$, Table 5) are in the range calculated previously for coastal and continental shelf water in similar latitudes (11.9 and 7.7 nmol m$^{-2}$ d$^{-1}$; Archer et al., 2007; Shimizu et al., 2017 respectively). The average flux of CH$_3$I reported by Jones et. al (2010), from the west of Ireland, was 4 times higher but based on a sampling period of only 1
month during summer. Sea-to-air fluxes of CH$_2$ClI from Funka Bay and English Channel were similar to our calculated fluxes from Bedford Basin. However the highest variation is observed in the annual averaged flux of CH$_2$I$_2$, ranging from 3.5 nmol m$^{-2}$ d$^{-1}$ (the west English Channel), 10.3 nmol m$^{-2}$ d$^{-1}$ (Bedford Basin) and 12.6 nmol m$^{-2}$ d$^{-1}$ (Funka Bay, Japan). The total, annual I$_{org}$ sea-to-air flux from Bedford Basin averaged 46.7 nmol m$^{-2}$ d$^{-1}$, which was approximately 5 times larger than the flux due to CH$_3$I alone. The total annual flux was similar between all three locations.

Fig. 5 and Table 3 show that the total I$_{org}$ flux is subject to significant interannual variability, which could not be assessed by the earlier studies. Notably, the I$_{org}$ flux in 2016 was ca. 2 times smaller than in 2015 and 2017. A comparison of wind-speeds and concentrations showed that the influence of wind speed was dominant, due to winds during summer/fall of 2016 being 1-2 m s$^{-1}$ lower.

4.7 Production rate of CH$_3$I

The annual mean production rate (P$_{net}$) of CH$_3$I in this study, estimated using equation 1, was 1.0 pmol L$^{-1}$ day$^{-1}$ (ranging from -1.6 to 8.5 pmol L$^{-1}$ day$^{-1}$, see section 3.4 and Fig. 6). This is comparable with the global average production rate estimated by Stemmler et al. (2013) (1.64 pmol L$^{-1}$ day$^{-1}$), for which 70% was produced via a photochemical mechanism. Based on data presented by Archer et al. (2007), the annual mean production rate of CH$_3$I in the western English Channel was ca. 2 pmol L$^{-1}$ day$^{-1}$ (range: -0.2 to 6 pmol L$^{-1}$ day$^{-1}$). Here it should be noted, that their “minimum gross production rate” is equivalent to P$_{net}$ in this study and in Shi et al. (2014a).

In contrast, Shi et al. (2014b) estimated a considerably lower annual mean net production rate in the Kiel Fjord of ca. 0.1 pmol L$^{-1}$ day$^{-1}$ (maximum of 0.8 pmol L$^{-1}$ day$^{-1}$). The maximum production rates from the Kiel Fjord study were smaller as they were based on monthly average (and therefore “smoothed”) concentrations. However, Shi et al. (2014a) also conducted weekly incubation
experiments which gave in vitro values of $P_{\text{net}}$ which were closely comparable with the field-based estimates in Kiel Fjord.

The lower values of $P_{\text{net}}$ in the Kiel Fjord compared with both Bedford Basin and the English Channel must reflect either differences in gross production (e.g. due to differences in the supply of precursors and reactants such as iodide) or differences in other, uncharacterized losses. Evidence for a poorly characterized loss process, possibly microbial degradation, was in fact observed in the Kiel Fjord incubation experiments (Shi et al., 2014a). On the other hand, incubation experiments conducted with additions of labelled methyl iodide ($^{13}$CD$_3$I) to Bedford Basin surface waters (data not shown) during the course of this study showed no such losses. We therefore hypothesize that the lower $P_{\text{net}}$ in Kiel Fjord is a result of higher microbial degradation of CH$_3$I in that very shallow (<12 m), nearshore environment.

5. Conclusions, Implications and Further Work

The 3-year time-series of weekly iodocarbon concentrations from Bedford Basin shows overall seasonality similar to that observed in coastal time-series from both the English Channel and Funka Bay, Japan. There was no mid-summer minimum in the concentration of polyiodinated compounds as observed in some time-series from very shallow water (<10m), which likely reflects dominance of photolytic decay in such shallow water columns. Interannual variability in near-surface water concentrations was particularly pronounced for CH$_3$I, with only a single, short-lived concentration maximum observed in 2016, possibly as a result of anomalously low rainfall and consequently reduced supply of terrestrial organic matter during that summer.

Based on the time-series as well as published lab studies, we hypothesize that seasonal, near-surface production of iodocarbons is linked to accelerated reduction of iodate to iodide under post-
bloom conditions, following disappearance of nutrients and possibly also influenced by water
temperature. The observed vertical variation of CH$_2$I$_2$ and CH$_2$ClI is consistent with the more rapid
photoysis of CH$_2$I$_2$.

The average annual sea-to-air flux of total volatile organic iodine (46.7 nmol m$^{-2}$ d$^{-1}$) is almost
identical to that observed in Funka Bay, Japan, and the English Channel. The polyiodinated
compounds contributed ca. 80 % of the total flux which was similar to that in the other two time-
series and confirms that the sea-to-air flux of polyiodinated compounds dominates in coastal
waters. The fluxes were variable on interannual timescales (factor of 2) as a result, mainly, of
wind-speed variability.

The near-bottom water (60m) time-series was impacted by episodic intrusions of water from
offshore and showed evidence for CH$_3$I production associated with decay of organic matter, albeit
with a production rate more than an order of magnitude lower than in surface waters. The time-
series showed evidence for a possible “switch” from CH$_3$I production (e.g. by alkylation of organic
matter) to production of CH$_2$I$_2$ (e.g. by a haloform type reaction), after periods of about 1 month.

The very high amplitude concentration variations encountered in Bedford Basin, coupled with its
relative accessibility for high-frequency sampling and constrained, yet variable, physical
exchanges make Bedford Basin a useful location to investigate iodine cycling. To-date, the
complexity of iodine biogeochemistry has hindered progress towards understanding the controls
on spatial and temporal fluxes of iodine between the ocean and atmosphere. We suggest that
progress can now be made through more comprehensive sampling (higher vertical resolution and
inclusion of inorganic iodine speciation measurement), coupled to a biogeochemical model of
Bedford Basin that includes iodine chemistry (e.g. Stemmler et al, 2013) and a time-series of
experimental studies conducted in the context of the time-series (see Shi et al., 2014a). In other
words, Bedford Basin may provide an ideal location and time-series upon which to base a multi-investigator campaign to understand environmental controls on volatile iodine cycling and improve its representation in models.

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Figure 1. (a): Main sampling location (grey star) and near-shore sampling locations 1-5 (1: Tufts cove; 2: Wrights cove; 3: Sackville; 4: Mill cove; 5: Fairview cove) in Bedford Basin; (b): two layered flow in Halifax Harbour, adapted from Kerrigan et al. (2017); (c): horizontal circulation of water in Halifax Harbour from Shan et al. (2011), using annual mean currents and velocities.
Figure 2. Seasonal patterns of environmental and biological variables in Bedford Basin from January 2015 to Dec 2017. (a) temperature; (b) salinity (grey contour line for S=30.5; white contour line for S=31). The blue circle (A) highlights a mid-depth intrusion. (c) dissolved oxygen; (d) chlorophyll fluorescence.
**Figure 3.** Seasonal variation of (a) chlorophyll $\alpha$: 1 m (blue line) and 5 m (red line); (b) DIN; (c) salinity in the surface layer: 1 m (blue line), 5 m (red line) and 10 m (black line); (d) weekly precipitation and (e) daily averaged windspeed (shown here only for sampling days); (f) weekly average PAR from January 2015 to December 2017.

**Figure 4.** Seasonal variation of iodocarbons in the Bedford Basin at 1 m (blue line), 5 m (red line) and 10 m (green line) from May 2015 to December 2017: (a) CH$_3$I; (b) CH$_2$ClI and (c) CH$_2$I$_2$. (d): time-series from near-bottom water (60m) of iodocarbons and dissolved oxygen.
**Figure 5** Weekly averages of daily sea-to-air flux estimates of $I_{org}$ (see section 3.3): including relative contributions of individual compounds (blue: CH$_3$I, green: CH$_2$ClI and orange: CH$_2$I$_2$) and using the parameterization for transfer velocity ($k_w$) of Nightingale et al. (2000) and for the airside transfer velocity ($k_a$) of Duce et al. [1991].
Figure 6. Variation of the net production rate of $\text{CH}_3\text{I}$ in the upper 10 m from 2015 to 2017. No data are plotted when the layer of uniform density extended below 10 m.
Figure 7. Contribution of iodocarbons to total organic iodine (I$_{org}$) in surface seawater from different regions and studies:
Figure 8. Annual cycle of (a) temperature, (b) salinity, (c) irradiance, (d) Chl a, (e) dissolved inorganic nitrogen (DIN) and (f) dissolved oxygen for near-surface water (1-5 m) in Bedford Basin. The black dashed line depicts the annual cycle of CH$_3$I. The figures present the monthly mean values based on the data collected from May 2015 to December 2017.
Figure 9. Detailed time-series from near-bottom waters in (a) 2015, (b) 2016 and (c) 2017. For each year, the upper panel shows variability of salinity (red dash-dot line) and dissolved oxygen (black dashed line); the lower panel shows iodocarbons (CH$_3$I: blue stars; CH$_2$ClI: red open circles and CH$_2$I$_2$: green open squares). The vertical bold, dashed lines (1 to 9) represent special events discussed in section 4.5.

Table 1. $R^2$ value (Pearson’s correlation coefficients, p<0.05) for the individual iodocarbon data based on both weekly data and monthly average.

<table>
<thead>
<tr>
<th></th>
<th>weekly</th>
<th>monthly</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CH$_3$I</td>
<td>CH$_2$ClI</td>
</tr>
<tr>
<td>CH$_3$I (1m)</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>CH$_2$ClI (1m)</td>
<td>0.4</td>
<td>1.0</td>
</tr>
<tr>
<td>CH$_2$I$_2$ (1m)</td>
<td>0.0</td>
<td>0.3</td>
</tr>
<tr>
<td>CH$_3$I (5m)</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>CH$_2$ClI (5m)</td>
<td>0.4</td>
<td>1.0</td>
</tr>
<tr>
<td>CH$_2$I$_2$ (5m)</td>
<td>0.1</td>
<td>0.4</td>
</tr>
<tr>
<td>CH$_3$I (10m)</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>CH$_2$ClI (10m)</td>
<td>0.7</td>
<td>1.0</td>
</tr>
<tr>
<td>CH$_2$I$_2$ (10m)</td>
<td>0.1</td>
<td>0.3</td>
</tr>
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Table 2. $R^2$ value (pearson’s correlation coefficients, $p<0.05$) for iodocarbons and potentially relevant parameters based on both weekly data and monthly average.

<table>
<thead>
<tr>
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<th>monthly</th>
</tr>
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<tr>
<td></td>
<td>$CH_3I$</td>
<td>$CH_2ClI$</td>
</tr>
<tr>
<td>SST</td>
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<td>0.4</td>
</tr>
<tr>
<td>SSS</td>
<td>0.1</td>
<td>0.0</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.3</td>
<td>0.2</td>
</tr>
<tr>
<td>Flu</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>PAR</td>
<td>0.1</td>
<td>0.1</td>
</tr>
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</table>
Table 3. Seasonal variation of total sea-to-air fluxes of iodocarbons (nmol m\(^{-2}\) d\(^{-1}\)). Highest flux values of iodocarbons in each year are marked in red.

<table>
<thead>
<tr>
<th>year</th>
<th>season</th>
<th>CH(_3)I</th>
<th>CH(_2)ClI</th>
<th>CH(_2)I(_2)</th>
<th>I(_{org})</th>
</tr>
</thead>
<tbody>
<tr>
<td>2015</td>
<td>Spring</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Summer</td>
<td>13.9</td>
<td>29.3</td>
<td>15.4</td>
<td>74.0</td>
</tr>
<tr>
<td></td>
<td>Fall</td>
<td>13.1</td>
<td>30.7</td>
<td>13.7</td>
<td>71.2</td>
</tr>
<tr>
<td></td>
<td>Winter</td>
<td>3.6</td>
<td>3.0</td>
<td>8.6</td>
<td>23.7</td>
</tr>
<tr>
<td></td>
<td>Annual</td>
<td>11.9</td>
<td>25.9</td>
<td>14.0</td>
<td>65.9</td>
</tr>
<tr>
<td>2016</td>
<td>Spring</td>
<td>3.4</td>
<td>11.8</td>
<td>16.5</td>
<td>48.2</td>
</tr>
<tr>
<td></td>
<td>Summer</td>
<td>12.0</td>
<td>33.2</td>
<td>9.4</td>
<td>64.0</td>
</tr>
<tr>
<td></td>
<td>Fall</td>
<td>7.2</td>
<td>9.4</td>
<td>1.8</td>
<td>20.2</td>
</tr>
<tr>
<td></td>
<td>Winter</td>
<td>3.2</td>
<td>3.0</td>
<td>1.7</td>
<td>9.6</td>
</tr>
<tr>
<td></td>
<td>Annual</td>
<td>6.6</td>
<td>14.4</td>
<td>8.2</td>
<td>37.3</td>
</tr>
<tr>
<td>2017</td>
<td>Spring</td>
<td>3.0</td>
<td>2.7</td>
<td>1.7</td>
<td>9.0</td>
</tr>
<tr>
<td></td>
<td>Summer</td>
<td>7.8</td>
<td>22.1</td>
<td>12.1</td>
<td>54.1</td>
</tr>
<tr>
<td></td>
<td>Fall</td>
<td>19.7</td>
<td>31.3</td>
<td>15.9</td>
<td>82.8</td>
</tr>
<tr>
<td></td>
<td>Winter</td>
<td>3.2</td>
<td>4.5</td>
<td>9.1</td>
<td>25.9</td>
</tr>
<tr>
<td></td>
<td>Annual</td>
<td>8.5</td>
<td>15.9</td>
<td>10.1</td>
<td>44.7</td>
</tr>
</tbody>
</table>
Table 4. Concentration (pmol L⁻¹) of iodocarbons measured at near shore locations around Bedford Basin as well as at the regular sampling location on July 19, 2017 (1: Tufts cove, 2: Wrights cove, 3: Sackville (rive), 4: Mill cove and 5: Fairview cove) (see Fig. 1a). “Centre” refers to the regular sampling site for the weekly time-series.

*Centre Mean for July: the average (and std. deviation) of measurements at the regular, weekly sampling location during the month of July 2017 (n=4).

<table>
<thead>
<tr>
<th>Location</th>
<th>CH₃I</th>
<th>CH₂Cl</th>
<th>CH₂I₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tufts cove</td>
<td>5.8</td>
<td>35.5</td>
<td>8.8</td>
</tr>
<tr>
<td>Wrights cove</td>
<td>6.7</td>
<td>20.6</td>
<td>12.5</td>
</tr>
<tr>
<td>Sackville</td>
<td>3.8</td>
<td>6.5</td>
<td>4.9</td>
</tr>
<tr>
<td>Mill cove</td>
<td>8.3</td>
<td>28.0</td>
<td>18.6</td>
</tr>
<tr>
<td>Fairview cove</td>
<td>6.2</td>
<td>26.3</td>
<td>6.4</td>
</tr>
<tr>
<td>Middle of Bedford Basin</td>
<td>6.1</td>
<td>37.6</td>
<td>6.3</td>
</tr>
<tr>
<td>*Centre Mean for July</td>
<td>5.9±0.9</td>
<td>58.5±25.2</td>
<td>26.1±32.0</td>
</tr>
</tbody>
</table>
Table 5. Comparison of sea-to-air flux (nmol m\(^{-2}\) d\(^{-1}\)) of total organic iodine from different studies.

English Channel is an average for 1 year; Funka Bay value is average over 3 years; Kiel Fjord is average over 2 years but for CH\(_3\)I only; Bedford Basin (this study) is an average over 3 years.

Seasons as defined in this study (see section 2). For Funka Bay, values in parentheses represent fluxes that have been adjusted from the original reported values to take into account effect of air-side resistance, using correction factors of 12 and 28 % for CH\(_2\)ClI and CH\(_2\)I\(_2\) respectively (based on average effects reported in Archer et al. (2007) and this study; see section 4.6).

<table>
<thead>
<tr>
<th>Season</th>
<th>English Channel</th>
<th>Funka Bay</th>
<th>Kiel Fjord</th>
<th>Bedford Basin</th>
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<tr>
<td></td>
<td>Archer et al. (2007)</td>
<td>Shimizu et al. (2017)</td>
<td>Shi et al. (2014)</td>
<td>This Study</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td>%-CH(_3)I</td>
<td>Total</td>
<td>%-CH(_3)I</td>
</tr>
<tr>
<td>Spring</td>
<td>15.3 (12.8)</td>
<td>33.8 (40.3)</td>
<td>2.8</td>
<td>28.6</td>
</tr>
<tr>
<td>Summer</td>
<td>113.3 (86.6)</td>
<td>4.7 (6.2)</td>
<td>5.2</td>
<td>64.0</td>
</tr>
<tr>
<td>Fall</td>
<td>47.6 (41.1)</td>
<td>32.5 (37.6)</td>
<td>2.2</td>
<td>58.1</td>
</tr>
<tr>
<td>Winter</td>
<td>27.5 (22.5)</td>
<td>22.3 (27.2)</td>
<td>0.2</td>
<td>19.7</td>
</tr>
<tr>
<td>Annual</td>
<td>42.6</td>
<td>27.9</td>
<td>54.8 (43.5)</td>
<td>14.0 (17.6)</td>
</tr>
</tbody>
</table>