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1 **A three year time-series of volatile organic iodocarbons in Bedford Basin, Nova Scotia :**
2 **a Northwestern Atlantic fjord.**
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9 **Abstract:**
10
11 We report weekly observations of volatile organic iodocarbons (CH_3I, CH_2ClI and CH_2I_2) over the

12 time-period May 2015 to December 2017 from 4 depths in Bedford Basin, a coastal fjord (70m

13 deep) on the Atlantic coast of Canada. The fjord is subject to winter-time mixing, seasonal

14 stratification and bloom dynamics, subsurface oxygen depletion, local input of freshwater and

15 occasional intrusions of higher density water from the adjacent continental shelf. Near-surface

16 concentrations showed strong seasonal and sub-seasonal variability which is compared with other

17 coastal time-series. Relationships with other properties lead to the hypothesis that near-surface

18 iodocarbon production is linked to reduction of iodate to iodide under conditions of post-bloom

19 phytoplankton senescence, nutrient stress or viral lysis following seasonal disappearance of

20 nutrients. The vertical variation of CH_2I_2 and CH_2ClI within the upper 10m is consistent with rapid

21 photolysis of CH_2I_2.

22 Average annual sea-to-air fluxes (62 nmol m^{-2} day^{-1}) of total volatile organic iodine were slightly

23 higher than observed in other coastal and shelf time-series and polyiodinated compounds

24 contributed 85% of the total flux. Fluxes were subject to strong interannual variability (2-3X) as a

25 result, mainly, of wind-speed variability. Near-surface net production of CH_3I averaged 1.0 pmol

26 L^{-1} day^{-1} and was similar to rates in the English Channel but an order of magnitude higher than in

27 shallow waters of the Kiel Fjord, Germany, possibly due to higher microbial degradation in the

28 latter.

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1   The near-bottom (60 m) time-series showed evidence for CH_3I production associated with organic

2   matter degradation, and a possible "switch" from production of CH_3I via an alkylation pathway to

3   production of CH_2I_2 by a haloform-type reaction. Near-bottom CH_3I production varied strongly

4   between years but was generally ca. 20 times lower than near-surface production. Post-intrusion

5   decreases of iodocarbons at 60m suggested removal timescales of 14, 65 and 70 days for CH_3I,

6   CH_2I_2 and CH_2ClI respectively.

7   **Keywords:** Iodocarbons, iodomethane, chloroiodomethane, diiodomethane, air-sea flux, time-

8   series

9

10   1.   Introduction

11   Volatile organic iodocarbons (VOIs) such as methyl iodide (CH_3I), chloroiodomethane (CH_2ClI)

12   and diiodomethane (CH_2I_2) have a predominantly oceanic source and supply a significant amount

13   of iodine to the atmosphere (see review by Saiz-Lopez and Von Glasow, 2012). These gases, also

14   referred to as VSLS (very short-lived source gases) due to their reactivity and short atmospheric

15   lifetimes, have been implicated in supporting catalytic ozone destruction in the troposphere (Davis

16   et al., 1996; McFiggans et al., 2000a) and, potentially in the lower stratosphere (Solomon et al.,

17   1994) as well as aerosol formation in the marine boundary layer (Mcfiggans et al., 2004;

18   McFiggans et al., 2000b; O'Dowd et al., 2002). Recent modelling of atmospheric reactive iodine

19   ($IOx = IO + I$) as well as experimental studies (Carpenter et al., 2013; Jones et al., 2010; Mahajan

20   et al., 2010) suggest that the supply of volatile organoiodine represents <50% of the total sea-to-

21   air delivery of reactive iodine, with most being supplied in the form of HOI and I_2. Nevertheless,

22   the potential for localized higher emissions coupled with their relatively long lifetimes (compared

23   to I_2 and HOI) allows the organic compounds to be a significant source of iodine to the free

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1   troposphere and even, potentially, to the lower stratosphere in certain regions (Tegtmeier et al.,

2   2013). Further, *Mahajan et. al* (2012) noted a strong correlation of IO_x and CH_3I suggesting that

3   the sources of CH_3I and the shorter-lived precursors of IO_x are closely related or depend on similar

4   variables.

5   CH_3I is the most abundant VOI species in the atmosphere (Yokouchi et al., 2011) because of its

6   longer lifetime (days) compared to CH_2ClI (minutes) and CH_2I_2 (hours) (Moessinger et al., 1998;

7   Rattigan et al., 1997). However, the total supply of organically-bound iodine to the atmosphere is

8   several times larger than the CH_3I supply alone (Carpenter et al., 2014) with the bulk of the

9   remainder transported in the form of CH_2I_2 and CH_2ClI. Despite considerable attention on the

10   oceanic distribution and sea-to-air flux of these compounds, in particular CH_3I (Ziska et al., 2013),

11   it is not yet possible to apportion oceanic production of these compounds, unequivocally, to

12   specific mechanisms. Even for CH_3I, controversy remains, for example, as to the relative

13   importance of direct "biological" or "photochemical" production pathways with experimental

14   evidence reported for both, and correlation analysis generally being inconclusive, in part because

15   of the "snapshot" nature of most studies (Stemmler et al., 2014). Comparisons of models to

16   observed distributions have also proven ambiguous, with localized studies suggesting

17   predominance of a biological production pathway (Stemmler et al., 2013) but a global analysis

18   emphasising photochemical production as the dominant mechanism. This diversity of views has

19   been maintained through a variety of experimental studies (Amachi et al., 2001; Brownell et al.,

20   2010; Hughes et al., 2011; Manley and delaCuesta, 1997; Moore and Tokarczyk, 1993; Moore and

21   Zafiriou, 1994; Richter and Wallace, 2004; Shi et al., 2014a; Smythe-Wright et al., 2006).

22   For compounds other than CH_3I, similar uncertainty exists concerning production pathways, but

23   with fewer underlying studies. Laboratory experiments have shown that the presence of dissolved

1   iodide and dissolved organic matter can lead to production of these compounds in the dark

2   (Martino et al., 2009). *Fuse et al.* (2003) and *Martino et al.* (2005) observed that CH_2ClI could be

3   produced by photolysis of CH_2I_2 in artificial and natural seawater. However detailed mechanisms

4   and, especially, their relative importance in the field remain unclear.

5   Time-series observation can reveal processes and controlling factors underlying production and

6   loss of iodocarbons in the ocean and provide data for testing hypotheses and/or models. However,

7   only a very few long-term, time series observations of iodocarbons have been reported to date, all

8   from coastal water. *Klick* (1992) reported 13 months of weekly measurements of CH_2I_2 and CH_2ClI

9   from very shallow (3.5m) water in the Kattegat at the Swedish coast. *Orlikowska and Schulz-Bull*

10   (2009) reported a year of weekly data for CH_2ClI, CH_2I_2, CH_3I and C_2H_5I from a nearshore (3m

11   depth) site in the Baltic Sea. *Archer et al.* (2007) reported a seasonal study of CH_2ClI, CH_2I_2, CH_3I,

12   C_2H_5I, and CH_2BrI measured weekly at 4 depths (0-50m) in the western English Channel from

13   July 2002 to April 2004. *Shi et al.* (2014b) reported on the seasonal cycle of CH_3I from surface

14   waters of the Kiel Fjord: a shallow (14 m), brackish water body in northern Germany, which was

15   sampled weekly for 2 years. *Shimizu et. al* (2017) presented a time-series of vertical profiles (0-

16   90m) of CH_2I_2, CH_2ClI, CH_3I, and C_2H_5I from the centre of Funka Bay, Japan, which were

17   measured every 2-4 weeks from March 2012 to December 2014.

18   Here, we report weekly observations of CH_3I, CH_2ClI and CH_2I_2 made over the time-period May

19   2015 to December 2017 at 4 depths (0-60m) in Bedford Basin: a coastal fjord on the east coast of

20   Canada. We report seasonal to interannual variability of the observed concentrations at different

21   depths in the water column and compare our results with the other time-series. We report daily

22   average fluxes to the atmosphere and use a simple, time-varying mass-balance model for near-

23   surface waters to estimate production rates and their variability. We discuss the observed

1   variability of both concentrations and production rates in the light of earlier studies, potentially

2   correlated variables and suggested production pathways.

3

4   2.   Method

5   Time-series measurements of VOIs were carried out in the Bedford Basin (44.69 °N, -63.63 °E)

6   near Halifax, Canada. Bedford Basin is an 8 km long, 17 km^2 fjord with a maximum depth of 71m

7   and a total volume of 500 km^3. The Bedford Basin is connected with continental shelf waters of

8   the Atlantic Ocean through "the Narrows" (a ca. 300 m wide and 20 m deep passage (fig. 1). The

9   Basin receives freshwater primarily from the Sackville River at its northwestern end, with a total

10   average freshwater input of 5.41 m^3 s^{-1} (Buckley and Winters, 1992). The average near surface

11   salinity within the Basin is 29 which can be compared with salinities of >30 over the adjacent

12   Scotian Shelf. There are only relatively small horizontal gradients of near-surface salinity within

13   the Bedford Basin itself (typically < 2 difference from close to the Sackville River mouth to the

14   Narrows).

15   Time series observations of physical, chemical and biological parameters have been recorded since

16   1992 (Li, 1998). Our halocarbon samples were collected weekly, in the center of the Bedford Basin,

17   at its deepest point (Figure 1), between May 2015 and January 2018. Samples were collected with

18   10-L Niskin bottles attached to a rosette sampler at 1, 5, 10 and 60 m (10 m samples were collected

19   biweekly from May to September 2015). The upper three water samples covered the majority of

20   the euphotic zone. The 60m water sample was from typically stagnant, near-bottom water which

21   is renewed by vertical mixing events in late winter, and by occasional intrusions of higher-salinity

22   continental shelf water in both summer and winter. Chlorophyll *a* (Chl*a*), dissolved oxygen, and

23   nutrients were measured weekly at the 4 depths as part of the Bedford Basin Monitoring Program

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1   (Details can be found in website: http://www.bio-iob.gc.ca/science/monitoring-monitorage/bbmp-

2   pobb/bbmp-pobb-en.php). In addition to the Niskin bottle sampling, vertically continuous

3   measurements of temperature, salinity, dissolved oxygen and Chl *a* properties were measured with

4   a CTD mounted on the rosette. Additional information concerning the measurements of supporting

5   physical and biological parameters can be found in the paper by *Burt el al.* (2013).

6   The concentrations of iodomethane (CH_3I), chloroiodomethane (CH_2ClI) and diiodomethane

7   (CH_2I_2) reported here, as well as of a number of other halocarbons (data not shown), were

8   measured using purge & trap gas chromatography with detection by both mass spectrometry (MS)

9   and electron capture (ECD). All measurements were made using an Agilent Technologies gas

10   chromatograph (GC 7890B), equipped with a capillary column (RTX-VGC; 60 m; 1.4 µm coating,

11   column diameter: 0.25 mm; helium carrier gas 0.5 ml min^{-1}), together with an automated purge

12   and trap system equipped with an autosampler (VSP4000 of IMT, Vohenstrauss, Germany). The

13   GC column was temperature programmed as follows: initial temperature 50 °C for 6 minutes, then

14   ramped to 150 °C at 6 °C min^{-1}; ramped to 200 °C at 10 °C min^{-1}. Water samples (10 ml) were

15   stored in 20 ml vials equipped with an ultra-low-bleed septum, prior to purging with helium (20

16   ml min^{-1} for 18 mins). Every sample was analysed in triplicate. The standard deviation of triplicate

17   measurements (integrated peak area) was <10 % for CH_3I, <15 % for CH_2ClI and <20 % for CH_2I_2.

18   Calibration of the GC system for CH_3I, CH_2ClI and CH_2I_2 was performed using permeation tubes

19   (VICI, Houston, TX, USA) which were maintained at a constant temperature of 23 ºC and weighed

20   every 2 weeks. Dilutions of the permeation tube effluent were made in ultra-high-purity N_2

21   (>99.995 %) with flow rates of 50 to 700 ml min^{-1}, and samples were injected into the purge and

22   trap system (VSP) through a 140 µl loop. Standard deviation of the peak area during these

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1   calibration runs was <5 % for CH_3I and CH_2ClI and <15 % for CH_2I_2. Overall the calibration

2   response varied by less than 15 % over the entire sampling period.

3   Throughout the paper, seasons are defined as follows: summer is June through August; fall is

4   September through November; winter is December through February and spring is March to May.

5   3.   Results and discussion

6   3.1 Environmental Variables from the Bedford Basin

7   Figures 2 and 3 depict time-depth plots of the variation of sea surface temperature (SST), salinity

8   (SSS), dissolved oxygen, total dissolved inorganic nitrogen (DIN), and fluorescence in Bedford

9   Basin over the period of the VOIs sampling. The vertical profiles of temperature and other

10   properties are well-mixed from top to bottom in late winter (Feb-Mar) as a result of wind-mixing

11   and convection (Li, 2001). Temperature is marked by strong seasonality to depths of <30 m. Near-

12   surface temperatures start to rise above winter values of 4 °C, and stratified conditions develop,

13   around early April with temperatures reaching ca. 21 °C by the end of August (fig. 3a). Typically,

14   strongest   irradiance   (data   was   downloaded   from   the   CERES   FLASHFLUX   system:

15   https://power.larc.nasa.gov/cgi-bin/hirestimeser.cgi) occurs in June and July, and highest water

16   temperatures are observed in August (see also fig. 7).

17   Salinity ranges from 23 to 31 through the entire water column, with the lowest salinities occurring

18   very close to the surface (fig. 2b, c and fig. 3b). The near-surface stratification varied both

19   seasonally and between years, primarily in association with variability of precipitation and the

20   discharge   of   the   Sackville   River   (source: Environment   and   Climate   Change   Canada;

21   http://climate.weather.gc.ca/historical_data/search_historic_data_e.html).   For   example,   the

22   salinity at 1m was 1psu lower than at 5m during much of the summer of 2015 (June to September)

23   and summer 2017 (June to August). In summer 2016, however, the salinity at 1m was close to that

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1   at 5m (difference < 0.3) (fig. 2b). The average precipitation in Bedford Basin was 27.6 mm week^{-1}

2   in summer 2015 and was 16 mm week^{-1} in summer 2016 (fig. 2d). Occasional intrusions of more

3   dense water from the Scotian Shelf, results in increased salinity, especially of bottom waters. The

4   intrusions are irregular and tend to occur a few times per year, for instance in early November

5   2016 at which time the salinity of bottom water increased from to 30.9 to 31.3.

6   The dissolved oxygen time-series (fig. 3c) shows the effect of temperature-dependent solubility

7   variations in surface waters as well as intrusions and late-winter vertical mixing in deeper water.

8   In surface water the highest O_2 concentrations occurred between March and April every year in

9   association with lowest SST. The vertical gradient of O_2 concentration was, generally, smallest

10   towards the end of April as a result of vertical mixing. Sub-surface O_2 concentrations (>30 m)

11   generally decreased in summer due to respiration, with occasional interruptions of this O_2 decline

12   (e.g. November 2016) as a consequence of shelf-water intrusions which brought sudden increases

13   in O_2 levels.

14   The seasonal variations of chlorophyll *a* concentration in surface water are plotted in figure 2a.

15   Typically, two blooms (spring and autumn) occur in surface water. For example, in 2016,

16   chlorophyll *a* increased rapidly from March to April (from 5 to 26 µg L^{-1}), and from September to

17   October (from 10 to 28 µg L^{-1}). The vertical variation of chlorophyll *a* (as determined from

18   fluorescence measured on the CTD, see fig. 3d) reached 12 µg L^{-1} during the bloom period. Sub-

19   surface (20- 40 m) fluorescence-derived chlorophyll *a* dropped down to 4 µg L^{-1}. In the near-

20   bottom water chlorophyll *a* ranged between 0 and 2 µg L^{-1} during the whole year and varied only

21   slightly.

22   The seasonal variation of dissolved inorganic nitrogen (DIN=NH_4^+ + NO_2^- + NO_3^-) in surface

23   water is plotted in figure 2b. In winter, when chorophyll *a* levels are very low due to light limitation,

1   DIN concentrations reach ca. 12 µmol L^{-1} but are drawn down to low levels (< 1 µmol L^{-1}) after

2   the spring bloom. Summertime chlorophyll *a* levels are moderate but variable (ca. 3 to 10 µg L^{-1}),

3   likely reflecting continuing nutrient input (e.g. from runoff and/or sewage treatment plants).

4

5   3.2 Variations of Iodocarbons Concentrations in Bedford Basin

6   Iodocarbon concentrations in surface water (1, 5 and 10 m) showed strong seasonality, with lowest

7   concentrations from December through May (1.2 pmol L^{-1} for CH_3I; 1.3 pmol L^{-1} for CH_2ClI and

8   0.3 pmol L^{-1} for CH_2I_2). Concentrations start to increase in late May/ June, reaching levels as high

9   as 45 pmol L^{-1} for CH_3I; 160 pmol L^{-1} for CH_2ClI and ca. 80 pmol L^{-1} for CH_2I_2 (with a single

10   peak of 500.5 pmol L^{-1}; fig. 4). Near-surface, summertime concentrations of all three compounds

11   were characterized by a broad seasonal peak of 6-7 months duration (or shorter for CH_2I_2), on top

12   of which were superimposed ca. 3-4 peaks of shorter (4-5 week) duration. The number, amplitude

13   and timing of these peaks varied amongst the three compounds with CH_3I, notably, showing only

14   one large peak in 2016 and four during the other two years of the time-series (fig. 4a).

15   Concentrations at 60 m were almost always lower, and much less variable, ranging over the year

16   from 1 to 9 pmol L^{-1} for CH_3I (except the Fall/Winter 2015-2016, see below), 1 to 6 pmol L^{-1} for

17   CH_2ClI and 0.4 to 18 pmol L^{-1} for CH_2I_2 (fig. 4d) respectively. Hence, the bottom water (60 m)

18   concentrations of CH_2I_2 and CH_2ClI were always much lower than in near-surface waters

19   throughout the summers. The surface to deep concentration difference was smallest for CH_3I and

20   showed interannual variability. Notably bottom water concentrations reached 26 pmol L^{-1} and were

21   even higher than in contemporary surface waters from September 2015 to March 2016 (fig. 4d).

22   Missing from the bottom water time-series, were the ca. 1 month duration variations seen in

23   summertime surface water.

1   Inter-relations between the iodocarbons in surface seawater were examined with linear regression

2   of both weekly and monthly-averaged concentrations. The resulting correlations are shown in table

3   1. Using weekly data, significant correlations (i.e. $p<0.05$) were found between [CH_3I] and

4   [CH_2ClI] at 1, 5 and 10 m depths with the strongest correlation (0.7) at 10m. The only other

5   significant correlation was between CH_2I_2 and CH_2ClI at 5 m. Use of monthly averaged values

6   gave stronger correlations. Once again, the significant correlations were between CH_3I and CH_2ClI

7   (at 1, 5 and 10m depth) as well as between CH_2ClI and CH_2I_2 at 5 and 10m depth. Table 2 also

8   presents the correlations of iodocarbon concentrations with potentially related variables (discussed

9   in section 4.3).

10   Generally, the concentration of CH_2I_2 was higher than that of CH_2ClI. The average ratio of

11   CH_2I_2/CH_2ClI within the top 10m of the water column over the summer months was 1.4. However,

12   this ratio was significantly lower at 1m depth (average of 0.6) and increased with depth (1.5 at 5

13   m and 2.2 at 10 m, reaching values as high as 2.7 at 60 m).

14

15   3.3 Sea-to-Air Flux

16   Using the concentrations of CH_3I, CH_2ClI and CH_2I_2 at 1m depth (Figure 4a) we estimated the

17   sea-to-air flux of VOIs (F) using the following equations:

18    $$Flux = K\left(C_{aqu} - C_{air} \times H\right)$$

19    $$K = \left(\frac{S_c}{660}\right)^{-0.5} \left(0.222 \cdot u_{10}^2 + 0.333 \cdot u_{10}\right)$$

20   For the calculation of the sea-to-air flux (F) of all three compounds, we assumed that the

21   concentration in the atmosphere (C_{air}) was negligible. *Rasmussen et al.* (1982) reported an average

22   atmospheric mixing ratio of CH_3I of ca. 1 pptv for Cape Meares (45 °N) and *Yokouchi et al.* (2008)

23   presented a mean concentration of 0.98 pptv for Cape Ochiishi (43.2 °N), with both sites sharing

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1   a similar latitude to our sampling location (44.69 °N). If a mixing ratio of 1pptv is applied to our

2   flux calculations, the total annual flux would be reduced by only 5 %. The atmospheric mixing

3   ratios of CH_2ClI and CH_2I_2 are lower than those of CH_3I (reviewed by Carpenter, 2003) and, hence,

4   any overestimation of the fluxes of these compounds will certainly be negligible (Archer et al.,

5   2007).

6   We calculated the fluxes of the three compounds using the transfer velocity (K) parameterization

7   (Nightingale et al., 2000), where Sc is the temperature-dependent Schmidt number, as estimated

8   by *Groszko* (1999) and Henry's Law constants (H) were from *Moore et al.* (1995). The wind speed

9   data (daily averages, fig. 2e) were measured at the nearby Halifax Dockyard (fig. 1) (source:

10   Environment and Climate Change Canada; http://climate.weather.gc.ca/index_e.html).

11   The calculated daily emissions ranged from 0.3 to 78.9 nmol m^{-2} d^{-1} for CH_3I (annual average of

12   8.7 nmol m^{-2} d^{-1}), 0.3 to 203.2 nmol m^{-2} d^{-1} for CH_2ClI (annual average of 19.6 nmol m^{-2} d^{-1}) and

13   0.1 to 240.6 nmol m^{-2} d^{-1} for CH_2I_2 (annual average of 16.7 nmol m^{-2} d^{-1}). Figure 5 presents the

14   combined flux of organically-bound iodine, F_{Iorg}, as stacked bar charts, where $F_{Iorg} = (F_{CH3I} +$

15   $F_{CH2ClI} + 2*F_{CH2I2})$. (Note that values plotted in Figure 5 represent daily flux estimates specific to

16   days on which sampling took place, and are based on the daily-average wind-speed and

17   concentration for those specific days.) Seasonal and annual average fluxes of the individual

18   compounds and of I_{org} are presented in table 4. Clearly the sea-to-air flux is highest in summer and

19   fall and is dominated by the flux of the dihalomethanes rather than CH_3I.

20

21   3.4 Net Production of CH_3I

22   Making use of the air-sea flux calculations (section 3.3), we used a mass balance approach to

23   estimate the production rate of CH_3I from the concentration time-series (see also Shi et al., 2014b).

1   Using the annual cycle of near-surface CH_3I concentrations (average of concentrations at 1, 5 and

2   10 m; Fig. 4a), we examined the mass balance of CH_3I in the top 10 m of the water column

3   according to:

4
$$\Delta C = P_{net} - L_{sea-to-air} - L_{SN2} - L_{mix}$$

5   where ΔC is the daily accumulation of VOIs in near-surface seawater; P_{net} is the net production

6   rate (i.e. the net of gross production minus any additional, uncharacterized losses such as microbial

7   degradation); $L_{sea-to-air}$ is the sea-to-air flux (section 3.3) and L_{SN2} is the 'chemical' loss due to

8   nucleophilic substitution of Cl^- for I^- which was calculated based on reaction kinetics (Elliott and

9   Rowland, 1993; Jones and Carpenter, 2007) using the corresponding temperature, salinity and

10   mean concentration of CH_3I. L_{SN2} averaged 0.1 pmol L^{-1} day^{-1}. L_{mix} is the loss due to downward

11   mixing and has been shown in several studies to be negligible compared with other loss terms e.g.

12   (Richter and Wallace, 2004). This assumption will not be valid in winter when mixed layers deepen,

13   however most production of iodocarbons appears to occur during summer and fall.

14   The net production rate of CH_3I over the 3-year time-series is shown in figure 6. The annual

15   average production rate of CH_3I was 1.0 pmol L^{-1} day^{-1} (ranging from -1.6 to 8.5pmol L^{-1} day^{-1}).

16   A significant peak of the net production rate occurred from August to September in every year.

17   The net production rate of CH_3I in summer and fall averaged 1.6 pmol L^{-1} day^{-1} and was 5 times

18   larger than the net production rate in winter of ca. 0.3 pmol L^{-1} day^{-1}.

19

20   4. Discussion

21   In the following we discuss the Bedford Basin data in comparison with other studies that have

22   reported concentrations of multiple iodocarbons and especially those that have reported time-series

23   covering an annual cycle (see citations in the introduction). All of these time-series are from mid-

1 latitude (40-60 °N) nearshore or continental shelf environments subject to strong seasonal

2 variations of light, temperature and biological productivity. There are no reported time-series of

3 seawater concentrations from low latitudes.

4

5 4.1 Potential influence of nearshore and /or macroalgal sources

6 The potential of nearshore macroalgae to cause elevated coastal iodocarbon concentrations has

7 been mentioned in a number of studies (Giese et al., 1999; Manley and delaCuesta, 1997; Schall

8 et al., 1994). We investigated this in July 2017, by sampling at 5 nearshore sites around Bedford

9 Basin (fig. 1) and comparing nearshore concentrations with values measured at the regular

10 sampling site in the center of the Basin (table 3). The results show no significant difference

11 between sampling locations. *Klick* (1992) also compared measurements on samples collected

12 directly over a rich bed of macroalgae with samples collected further away from direct contact

13 with macroalgae: whereas they observed significantly higher concentrations of bromocarbons in

14 proximity to the macroalgae, there was no difference observed for CH_2I_2 and CH_2ClI. *Shimizu et*

15 *al.* (2017) sampled a number of nearshore regions around Funka Bay, including rocky shores with

16 extensive macroalgae, and also found concentrations to be similar at both nearshore and central

17 Bay locations. We therefore conclude that any direct impact of macroalgae on measured

18 organoiodine levels is small, even in coastal regions, which lends strong support to the conclusion

19 by *Saiz-Lopez and Von Glasow* (2012) that macroalgae are only a minor global source of these

20 compounds to the atmosphere.

21

22 4.2 Concentrations and relative abundance of iodocarbon compounds

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1   The average concentration of total volatile organic iodine I_{org} (where I_{org} = [CH_3I] + [CH_2ClI] +

2   2[CH_2I_2]) and the relative contributions of the different compounds to I_{org} from this and other

3   studies is shown in Figure 8. The combined concentrations of the three iodocarbons are highest

4   but also highly variable ([I_{org}] = 25 to 281 pmol L^{-1}) in summertime coastal waters (loosely defined

5   here as within a few kms of land). Continental shelf waters have lower concentrations of I_{org}

6   averaging 32 pmol L^{-1}, with open ocean waters having comparable or lower concentrations

7   (average I_{org} = 17 pmol L^{-1}). This distribution is contrary to the global distribution of CH_3I reported

8   by *Ziska et. al* (2013) who noted a tendency for the open ocean to have higher concentrations than

9   coastal waters (their definition of "coastal" was within 1 degree latitude or longitude of land and

10   therefore much broader than ours). As noted by *Ziska et al.* (2013), this may reflect higher CH_3I

11   concentrations in tropical and sub-tropical open ocean waters, as their general pattern was reversed

12   in the Northern Hemisphere. The coastal waters depicted in Figure 8 are largely from mid-latitudes

13   of the Northern Hemisphere.

14   The relative contribution of the dihalomethanes to I_{org} also varies between regions, with the ratio

15   of dihalomethane-I to I_{org}, ([CH_2ClI]+2*[CH_2I_2])/[I_{org}], averaging 0.71, 0.69 and 0.55 in coastal,

16   shelf and open ocean waters, respectively. The elevated contribution of dihalomethanes in coastal

17   waters is consistent with the report by *Jones et al.* (2010).

18   *Klick* (1992), *Jones et al.* (2010) and *Shimizu et al.* (2017) reported concentrations of volatile

19   organic iodine in summertime coastal waters that are comparable to, or higher than those observed

20   in Bedford Basin (i.e. average I_{org} concentrations >100 pmol L^{-1}). Our results from Bedford Basin

21   correspond closely with the concentrations and relative contributions reported by *Shimizu et al.*

22   (2017) for coastal water in Funka Bay, Japan (fig. 8). In these coastal surface waters, the CH_2I_2

23   concentration and contribution was highest on average, followed by CH_2ClI and the lowest was

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1   CH_3I. In open ocean waters, the relative contribution of $[CH_3I]$ to I_{org} is higher and reaches over

2   50% in some cases (see fig. 8), with the contribution of CH_2I_2 generally being much lower in the

3   open ocean than in coastal waters.

4   In laboratory studies, *Fuse et al.* (2003) demonstrated that relatively large amounts of CH_2I_2 and

5   I_2 together with smaller but still significant amounts of CH_2ClI and CHI_3 can be produced,

6   presumably abiotically, in dark incubations of (filtered) spent culture media with suspended

7   bacterial cells and added $[I^-]$. The CH_2I_2/CH_2ClI production ratio was ∼35 and no mono-iodinated

8   CH_3I was produced in these experiments. The implication was that dissolved organic compounds

9   within spent media were key to production of polyiodinated compounds. In the absence of spent

10   culture media, additions of oxaloacetic acid also resulted in formation of CH_2I_2 and CH_2ClI (with

11   a lower ratio of CH_2I_2/CH_2ClI of ∼10) suggesting that organic acids may be a substrate for their

12   formation. The mechanistic role of the suspended bacterial cells was not clear, however they may

13   have supplied haloperoxidases required for oxidation of I^- (see also Hill and Manley, 2009).

14   *Martino et. al* (2009) demonstrated that, alternatively, oxidation of dissolved iodide to I_2 and HOI

15   by reaction with ozone (e.g. Garland et al., 1980) in filtered (0.2 μm) seawater containing natural

16   levels of dissolved organic matter also resulted in formation of polyiodinated compounds (CH_2I_2,

17   CH_2ClI and CHI_3) with CH_2I_2/CH_2ClI production ratios ranging from 2 to 4. They suggested that

18   the yield of various iodocarbons depends on "the abundance and perhaps on the nature of the

19   organic substrate" which "can vary widely both temporally and spatially". We could not, however,

20   find any obvious relationship of near-surface iodocarbon concentrations with local measurements

21   of atmospheric ozone near Bedford Basin (results not shown).

22   We therefore suggest that higher levels of CH_2I_2 observed in coastal waters reflect a higher supply

23   rate of HOI and/or I_2 and/or abundance of organic precursor compounds suitable for formation of

1 polyiodinated compounds. Iodide is also implicated as the source of reactive iodine for the

2 photochemical formation of CH_3I (Moore and Zafiriou, 1994), yet *Shi et. al* (2014b) found no

3 positive correlation of $[I^-]$ with seasonal CH_3I production in the Kiel fjord. They noted however

4 that there may always have been sufficient iodide available to support the observed production of

5 pM levels of CH_3I. Given that it is the formation rate of reactive iodine (e.g. iodine atoms, HOI

6 and/or I_2) that is likely the key control, there is no *a priori* reason that iodocarbon production

7 should correlate positively with the concentration of I^-. Indeed, formation of HOI, for example as

8 a result of the action of haloperoxidases or ozone, might lead to transient depletions of iodide.

9 Ultimately, however, iodocarbon production is likely to be controlled by the production of iodide

10 as this, in turn, determines the potential for production of HOI and other reactive inorganic iodine

11 species.

12 Relatively small quantities of CH_2ClI were produced in several of the experiments cited above,

13 yet observations in Bedford Basin show average CH_2I_2/CH_2ClI ratios of 1.4 in the top 10 m of the

14 water column. Production ratios in experiments clearly vary, as noted above, but laboratory studies

15 have also shown that photolysis of CH_2I_2 can be an important source of CH_2ClI in surface waters

16 with a yield of 25 % to 35 % (Jones and Carpenter, 2005; Manuela Martino et al., 2005). The

17 correlations between $[CH_2ClI]$ and $[CH_2I_2]$ in Bedford Basin (table 1) are consistent with this

18 photochemical transformation but may also reflect the original production ratios which could, in

19 turn, be substrate-dependent. In both cases however, DOM quality and quantity (possibly

20 associated with terrestrial supply) and/or elevated supply of I^- are likely to be underlying reason(s)

21 for the high concentrations of dihalomethanes observed in Bedford Basin and other coastal waters.

22

23 4.3 Temporal variations of iodocarbons in near-surface water

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1   The following discussion of temporal variability is separated into consideration of seasonal, sub-

2   seasonal and interannual variations.

3   4.3.1 Seasonal Variations

4   All of the reported iodocarbon time-series showed strong seasonality, with minimum, sometimes

5   undetectable concentrations in winter, and higher concentrations in summer. Near-surface (0-10

6   m) concentrations of all three iodocarbons in Bedford Basin, including CH_3I, remained low until

7   mid-May to mid-June, with their subsequent increase coincident with initial warming of near-

8   surface waters from wintertime minimum temperatures of ca. 1-2 °C (lag < 1 month; fig. 7a). Hence

9   the initial appearance of all three iodocarbons occurred more than 3 months after the seasonal

10   increase in solar radiation, ca. 1-2 months after the Spring Bloom (fig. 7d), and after near-surface

11   nitrate had been drawn down to low levels (fig. 7e).

12   In the western English Channel (Archer et al., 2007), a gradual increase of CH_3I commenced in

13   February, coincident with the seasonal increase in solar radiation. Summertime values remained

14   high, with some higher-frequency variation, and then decreased in September/October. The

15   increase of CH_2ClI and CH_2I_2 started later, in April, more or less coincident with both the Spring

16   Bloom and initiation of near-surface warming from a wintertime minimum temperature of ca. 8

17   °C. Summertime values of CH_2ClI and CH_2I_2 showed periodic variations similar to those observed

18   in Bedford Basin (section 3.2).

19   The lower temporal resolution of the study in Funka Bay (Shimizu et al., 2017), with sampling

20   only every 1 or 2 months, precluded detailed examination of timing. A gradual increase in CH_3I

21   appeared to start in March, during or towards the end of the Spring Bloom when surface water

22   temperatures were still close to their wintertime minimum of -1 to 2.5 °C. The seasonal increase

23   of CH_2I_2 and CH_2ClI occurred later (May-June) at a time of rising water temperatures and low

1 nutrient levels with concentrations remaining elevated through the summer and decreasing to

2 wintertime levels in October.

3 The initial CH_3I increase at a shallow station in the Kiel Fjord (Shi et al., 2014b) occurred in March,

4 and was closely linked in time to seasonal increases of solar radiation, temperature (winter

5 minimum of 0 °C) as well as Chl a and the springtime drawdown of nitrate. Lagged correlation

6 analysis showed similarly strong correlations of CH_3I with both temperature and solar radiation.

7 However, the springtime increase of CH_3I, and its annual cycle, lagged temperature by ca. 1 month

8 leading *Shi et al.* (2014b) to attribute causality to solar radiation.

9 The observation of a rapid increase in the production rate of I^- within phytoplankton cultures

10 (diatoms and prymnesiophytes) when they enter stationary and, especially, senescent phases

11 (Bluhm et al., 2011) is potentially relevant to the observed seasonality of iodocarbon formation.

12 The reduction of iodate to iodide was suggested to be due to release of precursors, such as reduced

13 sulphur species, to surrounding culture medium in association with a loss of membrane integrity

14 by stressed cells or as a result of viral lysis. *Hughes et al.* (2011) also reported studies with cultures

15 of *Prochlorococcus marinas* in which accumulation of CH_3I commenced when cultures became

16 senescent. We note that significant iodocarbon accumulation in Bedford Basin was confined to

17 summertime when DIN was depleted (see fig. 2) and when cells may have been stressed or subject

18 to viral lysis, perhaps similar to later stages of batch culture experiments.

19 We therefore hypothesize that seasonal nitrate drawdown leads to increased supply of iodide to

20 surface waters which can, in turn, lead to increased formation of iodine atoms, HOI and I_2 as

21 precursors for iodocarbon formation by both photochemical and haloform reaction pathways

22 (Martino et al., 2009; Moore and Zafiriou, 1994). Whereas the supply of iodide may be one key

23 control, it is likely that variations in light intensity and water temperature also contribute to the

1   overall seasonality of the production rate of methyl iodide. For example, light can influence

2   formation of CH_3I directly (e.g. Moore and Zafiriou, 1994; Richter and Wallace, 2004). Light can

3   also influence iodocarbon production indirectly, for example by producing oxidants such as H_2O_2

4   to promote oxidation of iodide by haloperoxidases (Hill and Manley, 2009) or by altering the

5   quality of dissolved organic matter. The time-series of CH_2I_2 and CH_2ClI from very shallow (< 4

6   m), nearshore waters of the Kattegat, Sweden (Klick, 1992) and the Baltic Sea, Germany

7   (Orlikowska and Schulz-Bull, 2009) showed peaks in April/ May and again in September/October,

8   with low concentrations throughout summer. This contrasts with the deeper water columns of

9   Bedford Basin, Funka Bay and the English Channel where concentrations remain elevated

10   throughout summer. This likely reflects dominance of photolytic loss over production within very

11   shallow water columns exposed to summertime light intensities and long periods of daylight. Sub-

12   surface production coupled with vertical mixing may explain the summertime persistence in

13   deeper water columns.

14   4.3.2 Sub-seasonal periodicity

15   The key feature at the sub-seasonal scale during summer is periodicity of near-surface iodocarbon

16   concentrations which was observed in both the English Channel and Bedford Basin. There was no

17   obvious pattern linking maxima and minima of the three compounds. For example, whereas in

18   Bedford Basin, peaks in all three compounds tend to coincide, their relative amplitudes are variable.

19   In the English Channel, peaks of CH_2I_2 and CH_2ClI also appeared to coincide, however CH_3I

20   variability was largely decoupled (Archer et al., 2007). The periodicity of iodocarbon

21   concentrations may be a consequence of the internal coupling of iodine cycling reactions, together

22   with depth- and light-dependent photolytic degradation, as much as the result of external forcing.

23   4.3.3 Interannual variability

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1   The Bedford Basin time-series is unique in having high temporal resolution sampling (weekly)

2   over three annual cycles which allows interannual variability to be examined for the first time. The

3   most obvious interannual difference was in the behavior of methyl iodide. In particular, 2016 was

4   markedly different in that only a single peak was observed in late August, whereas the summers

5   of 2015 and 2017 were marked by 3-4 quasi-periodic, multi-week maxima. As noted already, the

6   English Channel time-series of CH_3I did not exhibit this behavior. The shallow-water time-series

7   of CH_3I in the Kiel Fjord and coastal Baltic Sea (Orlikowska and Schulz-Bull, 2009; Shi et al.,

8   2014b) also did not exhibit this type of variability. Because the cause of the periodicity itself is not

9   understood or explained, discussion of reasons for its interannual variation must be highly

10 speculative. One clear difference of 2016 relative to the other two years, was the lower

11 summertime precipitation and associated lack of near-surface salinity stratification. The temporal

12 behavior of CH_3I in 2016 might therefore be related to altered near-surface mixing dynamics

13 within Bedford Basin, or alternatively, to decreased delivery of key precursors (e.g. DOM) from

14 land via rivers and wastewater.

15

16 4.4 Vertical distributions and subsurface temporal variability

17 Figure 4 shows the near-surface concentration variations of the VOIs. For CH_3I, concentrations

18 were almost always uniform between 1, 5 and 10 m. For CH_2ClI, the concentrations at 1 and 5m

19 were usually very similar (average difference -4.1 %; median -2.5 %), however concentrations at

20 10m depth were noticeably lower for periods of time. For CH_2I_2, the highest concentrations were

21 observed at a depth of either 5 or 10 m, with concentrations at 5 m occasionally peaking at very

22 high levels (e.g. 250-350 pmol L^{-1}) for short periods (less than one week). Concentrations at 1 m

23 were almost always lower than at 5 m, with the percentage reduction relative to 5 m averaging 52 %

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1   in summer. Concentrations at 10 m, on the other hand, were generally the same or higher as those

2   measured at 5 m (with the exception of the previously mentioned, short-lived peaks).

3   These results are consistent with earlier studies of vertical profiles in the open ocean (e.g. (Moore

4   and Tokarczyk, 1993; Yamamoto et al., 2001)) as well as with model predictions (Jones et al.,

5   2010; Martino et al., 2006). In particular, our results are consistent with the quantitative predictions

6   of a mixed-layer model (Jones et al., 2010) that CH_2ClI would typically be near-uniform within

7   the upper 6 m of the water column, whereas photolytic decay could remove up to 100 % of the

8   CH_2I_2 over that depth range, depending on time of day and conditions.

9

10   4.5 Temporal variability in near-bottom water (60 m)

11   Temporal variations of VOIs in near-bottom waters (60 m), were of lower amplitude except for

12   the already noted variation of CH_3I during the winter of 2015-2016 (fig. 4d). From June to

13   December 2015, $[CH_3I]$ increased steadily (concentration change, $\Delta C = 20$ pmol L^{-1}) so that

14   concentrations exceeded those in surface waters from October 2015 until end of March 2016. This

15   did not occur in the two subsequent years, with $[CH_3I]$ remaining constant through the remainder

16   of 2016 and showing a smaller seasonal increase ($\Delta C = 8$ pmol L^{-1}), confined to early summer, in

17   2017.

18   Concentrations of CH_2ClI remained almost constant at <5 pmol L^{-1} throughout the time-series with

19   the notable exception of abrupt (<1 week) increases in May and November 2016 and December

20   2017. These increases ($\Delta C = 2$-5 pmol L^{-1}) corresponded with increases of salinity (and O_2)

21   indicating that they were linked to intrusions of saltier, near-surface waters from offshore. The

22   subsequent concentration declines (with estimated half-life, assuming 1st order kinetics, of order

23   70 days) reflects loss due to mixing or, more likely, by reaction or microbial degradation within

1   the water column and/or sediments. The same three intrusions drove abrupt increases of CH_2I_2

2   with amplitude ca. $1.5 - 2$ times higher than those for CH_2ClI, consistent with near-surface

3   concentration ratios (see section 3.2). However, CH_2I_2 showed additional, higher amplitude

4   variability, unrelated to the bottom water intrusions, which is discussed in detail below.

5   In 2015, a gradual but high-amplitude increase of CH_3I ($\Delta C = 20$ pmol L^{-1}) from June through

6   October, paralleled a steady decline in oxygen, suggesting CH_3I production linked to degradation

7   of organic matter (apparent production rate of 0.06 pmol L^{-1} day^{-1} from June to December). This

8   is ca. 20 times lower compared with the annual averaged P_{net} of CH_3I (see section 3.4) in surface

9   water of ca. 1 pmol L^{-1} day^{-1}. This initial part of the time-series is consistent with results from

10   short-term incubation experiments (3 days duration) conducted by *Hughes et al.* (2008) with

11   biogenic marine aggregates. They observed increasing concentrations of mono-iodinated

12   iodocarbons, including CH_3I, but no corresponding increase in the dihalogenated compounds such

13   as CH_2I_2 and CH_2ClI. The results suggested alkylation of inorganic iodine or breakdown of higher

14   molecular mass organohalogens as production pathways and, following *Amachi et al.* (2001), it

15   was suggested that microbial degradation increases the supply of precursors.

16   However, as O_2 concentrations declined further from October through late December, the

17   concentration of CH_3I stabilized and the CH_2I_2 concentration increased markedly from ca. 2 to 12

18   pmol L^{-1}. From January through April 2016, CH_3I levels decreased rapidly, in concert with

19   increasing O_2 concentrations and decreasing salinity (see fig. 4) as a result of progressive vertical

20   mixing with overlying waters with lower CH_3I concentrations. Over this period, the CH_2I_2

21   concentrations at 60 m remained almost constant (due to the smaller vertical gradient of

22   concentration), before decreasing again in summer, in parallel with the seasonal decline of O_2.

1 The combined time-series is suggestive of a switch of production mechanism from an alkylation

2 pathway producing mono-iodinated compounds (CH_3I) to a haloform-type reaction which

3 produces CH_2I_2. The apparent "switch" took place in October, when oxygen concentrations

4 dropped below ca. 90 μmol kg^{-1}, although whether the switch was related to redox conditions in

5 the water column or sediments, the speciation and availability of iodine, or the availability of

6 suitable organic precursors and/or enzymes cannot be determined.

7 There was no significant near-bottom iodocarbon production throughout 2016, especially for CH_3I,

8 and therefore no "switch", for reasons that are not clear given that O_2 concentrations declined

9 through most of the summer and fall, until interrupted by an intrusion in November. It can only be

10 speculated that the lack of production might be linked to the limited and time-restricted period of

11 production of CH_3I in near-surface waters (fig. 4a) in 2016. In 2017, there was moderate sub-

12 surface production of CH_3I, associated with O_2 consumption, and again an apparent "switch" to

13 CH_2I_2 production as marked by a plateau of CH_3I concentrations at the same time as CH_2I_2

14 concentrations started to increase. The switch took place earlier in the year and at significantly

15 higher O_2 concentrations (175 μmol kg^{-1}) than in 2015. Closer examination suggests, however,

16 that the CH_3I and CH_2I_2 time-series in 2017 may have been impacted more by intrusions and

17 mixing of water with different origins than by changing reaction mechanisms, as explained below.

18 Figure 4 shows that the moderate increase of CH_3I at 60m, observed from April through early July

19 2017, was followed by a concentration plateau lasting ca. 6 weeks and a subsequent decrease to

20 background levels over a period of <4 weeks. Close inspection of figure 4 suggests that the plateau

21 of CH_3I was linked with a mid-depth intrusion of salty, offshore waters (as denoted by the 31

22 salinity contour). The period from the beginning of July to mid-August 2017 was marked by a

23 pronounced increase in the rate of warming at 60 m, a switch from declining to increasing salinity,

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1   and a reduction in the rate of oxygen concentration decline. The mid-depth salinity maximum must

2   have been due to an intrusion of saltier water from offshore. Generally, intruding waters are dense

3   enough to sink to the bottom of Bedford Basin so that they mix with and displace the low-oxygen

4   waters that develop there, as seen at other times in the time-series. However, the altered trends in

5   T, S and O_2 at 60m over the 6-week period in 2017 are consistent with mixing between a newly-

6   introduced offshore end-member at mid-depth and the pre-existing deeper water of Bedford Basin.

7   It is therefore likely that mixing also contributed to the sudden increase of CH_2I_2 and the "plateau"

8   of CH_3I concentrations, which both occurred at exactly the same time. A very small but significant

9   increase in CH_2ClI (ΔC=1-2 pmol L^{-1}) commenced at the same time. At the end of this period, in

10   mid-August, the rate of warming and salinity increase at 60 m decreased again, and the rate of

11   oxygen decline increased, suggesting that the intrusion's impact at 60 m had lessened. At this time,

12   CH_2I_2 and CH_3I concentrations decreased immediately, returning to background levels within

13   about 1 month (1st order half-life of 65 days for CH_2I_2 and 14 days for CH_3I). A corresponding

14   decrease in $[CH_2ClI]$ concentration appeared to start 4-6 weeks later with the rate of decline

15   matching that observed after the three intrusions discussed earlier (1st order half-life of 70 days).

16   This detailed discussion of the observed temporal variability emphasizes that a variety of

17   underlying physical and biogeochemical mechanisms are responsible for the observed seasonal,

18   sub-seasonal and interannual variability of the three iodocarbons. The high amplitude signals

19   observed in Bedford Basin suggest that these complex and variable processes could be resolved,

20   in detail, with more targeted, higher-resolution sampling, and would be amenable to examination

21   with models, so that the variability itself would be useful for model validation. Separation of the

22   multiple contributing factors and processes that underlay observed temporal variability will,

23   however, require a seasonally-resolved time-series of experimental studies that are linked to a

1   physical model that can represent both mixing dynamics and key aspects of aquatic iodine

2   chemistry.

3

4   4.6 Sea-to-air fluxes

5   The temporal variation of the sea-to-air flux of I_{org} and its relative contribution from the three

6   iodocarbons is shown in figure 5 and table 4.

7   Consistent with earlier time-series (excluding those from very shallow waters, see section 4.2), the

8   sea-to-air flux of iodocarbons is generally highest in summer/fall. However, high wintertime fluxes

9   are also possible, as shown in 2017 when there was a large efflux of CH_2I_2 (averaging 41 nmol m^{-}

10   ^{2} d^{-1}; table 4), due to both strong winds and relatively high concentrations. The fluxes of CH_3I and

11   of CH_2ClI, on the other hand, were always higher in summer (ca. 3-5X and 10X higher,

12   respectively). Similar results were presented by *Shimizu et. al* (2017) with the total iodine flux in

13   Funka Bay in summer being > 5 times that in winter.

14   Our estimated fluxes of CH_3I (8.7nmol m^{-2} d^{-1}, table 5) are in the range of emissions calculated for

15   coastal and continental shelf water in similar latitudes (9.6 and 11.9 nmol m^{-2} d^{-1}; Archer et al.,

16   2007; Shimizu et al., 2017 respectively). The average flux of CH_3I reported by Jones et. al (2010),

17   from the west of Ireland, was 4 times higher but based on a sampling period of only 1 month during

18   summer only. Sea-to-air fluxes of CH_2ClI from the same studies were very similar to the fluxes

19   from Bedford Basin that we calculated. For CH_2I_2, the annual averaged flux (17.8 nmol m^{-2} d^{-1}) in

20   Bedford Basin is 5 times higher than in west English Channel, and similar as in Funka Bay, Japan.

21   The total, annual I_{org} sea-to-air flux from Bedford Basin averaged 62 nmol m^{-2} d^{-1}, approximately

22   8 times higher than the flux of CH_3I. This flux is ca. 40% higher than the annual fluxes reported

23   for the Western English Channel and Funka Bay, Japan (Archer et al., 2007; Shimizu et al., 2017)

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1   and the relative contribution of polyiodinated compounds to the total flux was also slightly higher

2   in Bedford Basin (table 5).

3   As shown in figure 5 and table 4, however, the total I_{org} flux is subject to significant interannual

4   variability, which could not be assessed in earlier studies. Notably, the I_{org} flux in 2016 was 2-3X

5   lower than in 2015 and 2017. A comparison of wind-speeds and concentrations showed that

6   although both factors contributed to interannual flux variation, the effect of wind speed dominated,

7   with winds during summer/fall of 2016 being 1-2 m s^{-1} lower than average.

8

9   4.7 Production rate of CH$_3$I

10   The annual mean production rate of CH$_3$I in this study, estimated using equation 1, was 1.0 pmol

11   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

12   with the global average production rate estimated by *Stemmler et al.* (2013) (1.64 pmol L^{-1} day^{-1}),

13   for which 70% was produced via a photochemical mechanism. Based on data presented by *Archer*

14   *et al.* (2007), the annual mean production rate of CH$_3$I in the western English Channel was ca. 2

15   pmol L^{-1} day^{-1} (range: -0.2 to 6 pmol L^{-1} day^{-1}). Here it should be noted, that their "minimum gross

16   production rate" is equivalent to P_{net} in this study and in *Shi et al.* (2014a). In contrast, *Shi et al.*

17   (2014b) estimated a considerably lower annual mean net production rate in the Kiel Fjord of ca.

18   0.1 pmol L^{-1} day^{-1} (maximum of 0.8 pmol L^{-1} day^{-1}). The maximum production rates from the Kiel

19   Fjord study were based on monthly average concentrations, and therefore expected to be smaller.

20   However, *Shi et al.* (2014a) also conducted weekly incubation experiments in Kiel Fjord which

21   gave *in vitro* values of P_{net} which were closely comparable with the field-based estimates.

1   The lower values of P_{net} in the Kiel Fjord compared with both Bedford Basin and the English

2   Channel must reflect either differences in gross production (e.g. due to differences in the supply

3   of precursors and reactants such as iodide) or differences in other, uncharacterized losses. An

4   additional, poorly characterized loss process, possibly microbial degradation, was in fact observed

5   in the Kiel Fjord incubation experiments (Shi et al., 2014a). On the other hand, incubation

6   experiments conducted with additions of labelled methyl iodide ($^{13}CD_3I$) to Bedford Basin surface

7   waters (data not shown) showed no such losses. We therefore hypothesize that the lower P_{net} in

8   Kiel Fjord is a result of higher microbial degradation of CH_3I in that very shallow (12 m deep),

9   nearshore environment.

10

11 5.   Conclusions, Implications and Further Work

12 The key findings of the time-series sampling of Bedford Basin are as follows:

13 Iodocarbon concentrations in near-surface waters showed strong seasonal variability and

14 similarities and differences in their correlation with temporal variations of potentially-related

15 properties and causal factors in comparison to other coastal time-series. Based on the time-series

16 and lab studies, we hypothesize that the production of iodocarbons is linked to accelerated

17 reduction of iodate to iodide under conditions of post-bloom phytoplankton senescence, nutrient

18 stress and/or viral lysis following the seasonal disappearance of nutrients.

19 The observed vertical variation of CH_2I_2 and CH_2ClI within the upper 10m is consistent with the

20 more rapid photolysis of CH_2I_2 and is affected by near-surface stratification and mixing associated

21 with variable freshwater input.

22 Seasonality of iodocarbon concentrations in Bedford Basin is similar to that observed in coastal

23 time-series from the English Channel and Funka Bay, Japan, but does not exhibit the mid-summer

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1   minimum in the concentration of polyiodinated compounds observed in very shallow time-series

2   (<10m), which likely reflect the dominance of photolytic decay in such shallow water columns.

3   Quasi-periodic variability of all three compound with a characteristic timescale of 4-5 weeks was

4   observed in summertime near-surface waters and is similar to variability observed in the western

5   English Channel.

6   Near-surface interannual variability was particularly pronounced for CH_3I, with only one, short-

7   lived near-surface concentration maximum occurring in 2016. The reasons for the variability are

8   unclear but may be a consequence of anomalously low rainfall and an associated reduction in the

9   supply of terrestrial organic matter during that summer.

10   A lack of spatial variation of near-surface iodocarbon concentrations within Bedford Basin is

11   consistent with earlier studies and confirms that air-sea fluxes are not influenced directly by

12   macroalgal sources, even in nearshore waters.

13   Average annual sea-to-air fluxes (62 nmol m^{-2} d^{-1}) of total volatile organic iodine (I_{org}) were

14   comparable to or slightly higher than those oberved in Funka Bay, Japan, and the English Channel.

15   The polyiodinated compounds contributed ca. 85 % of the total flux which was also higher than in

16   the other two time-series and confirms that the sea-to-air flux of polyiodinated compounds such as

17   CH_2I_2 and CH_2ClI are larger than those of CH_3I in coastal waters. The fluxes were subject to strong

18   interannual variability (2-3X) as a result, mainly, of wind-speed variability but also variability of

19   surface concentrations.

20   Concentrations and temporal variability were smaller in near-bottom waters (60 m). However, the

21   60m time-series showed evidence for CH_3I production associated with the decay of sinking organic

22   matter. There was a suggestion in the time-series that iodocarbon production could "switch" from

23   CH_3I production (e.g. by alkylation of organic matter) to production of CH_2I_2 (e.g. by a haloform

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1   type reaction), after a period of ca. 5 weeks. Other increases in CH_2I_2 and CH_2ClI at 60m were

2   associated with intrusions of saltier, near-surface waters carrying higher iodocarbon concentrations.

3   Concentrations decreased following these intrusions with half-lives, assuming 1st order kinetics,

4   of 14 days (CH_3I), 65 days (CH_2I_2) and 70 days (CH_2ClI). These half-lives are likely lower bounds

5   for chemical/ microbial degradation of these compounds given that concentrations might also be

6   reduced as a result of vertical mixing.

7   Net production rates of CH_3I averaged 1.0 pmol L^{-1} day^{-1} and were similar to rates estimated in

8   the English Channel but an order of magnitude higher than rates estimated and measured in shallow,

9   nearshore waters of the Kiel Fjord. The low net production in the Kiel Fjord is hypothesized to be

10 the result of high microbial degradation rates, as suggested by *in vitro* incubations. These were not

11 observed in Bedford Basin,

12 In general, the time-series confirms that there are at least two pathways of CH_3I production

13 (photochemical and production via an alkylation pathway) operating in coastal waters, and the

14 photochemical production rate in near surface water is more than one order of magnitude higher

15 than the alkylation pathway rate in near-bottom water. Coastal waters can also support high rates

16 of production of polyiodinated compounds. The seasonality and variability of production of both

17 mono- and poly-iodinated compounds may be a function of the rate of supply of iodide. The higher

18 rates of CH_2I_2 and CH_2ClI production in comparison with offshore waters may, additionally,

19 reflect a greater supply of organic precursor compounds (e.g. from land). Alternatively, it may

20 reflect differences in inorganic iodine cycling between coastal and offshore waters.

21 The very high amplitude concentration variations encountered in Bedford Basin, coupled with its

22 relative accessibility for high-frequency sampling and constrained, yet variable, physical

23 exchanges make Bedford Basin a useful location to investigate complex iodine cycling dynamics.

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1   To-date, the multiple production pathways and relative complexity of iodine biogeochemistry have

2   hindered progress towards understanding the underlying dynamics that result in varying spatial

3   and temporal fluxes of iodine between the ocean and atmosphere.

4   Based on these results, we suggest that progress in detailed understanding can now be made

5   through the implementation of a more comprehensive sampling strategy (higher vertical resolution

6   and inclusion of inorganic iodine speciation measurement), coupled to a biogeochemical model of

7   Bedford Basin that includes iodine chemistry (e.g. Stemmler et al, 2013) and a time-series of

8   targeted experimental studies conducted in the context of the time-series (see Shi et al., 2014b). In

9   other words, Bedford Basin may be an ideal location and time-series upon which to base a multi-

10   investigator campaign focused on understanding environmental controls on volatile iodine cycling

11   and improving their representation in models.

12

20

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1   **Table 1.** correlations between individual iodocarbons based on weekly data and monthly average.

	weekly			monthly		
	CH_3I	CH_2ClI	CH_2I_2	CH_3I	CH_2ClI	CH_2I_2
CH_3I (1m)	1.0			1.0		
CH_2ClI (1m)	0.4	1.0		0.7	1.0	
CH_2I_2 (1m)	0.0	0.3	1.0	0.1	0.4	1.0
CH_3I (5m)	1.0			1.0		
CH_2ClI (5m)	0.4	1.0		0.5	1.0	
CH_2I_2 (5m)	0.1	0.4	1.0	0.1	0.6	1.0
CH_3I (10m)	1.0			1.0		
CH_2ClI (10m)	0.7	1.0		0.7	1.0	
CH_2I_2 (10m)	0.1	0.3	1.0	0.2	0.4	1.0

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1   **Table 2.** correlations between iodocarbons and potentially relevant parameters.

1m	weekly			monthly		
	CH_3I	CH_2ClI	CH_2I_2	CH_3I	CH_2ClI	CH_2I_2
SST	0.5	0.4	0.0	0.7	0.6	0.1
SSS	0.1	0.0	0.0	0.1	0.1	0.0
Oxygen	0.3	0.2	0.1	0.3	0.2	0.1
Flu	0.0	0.0	0.0	0.1	0.0	0.0
PAR	0.1	0.1	0.0	0.1	0.3	0.0

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1 **Table 3.** Concentration (pmol L^{-1}) of iodocarbons in various measured at near shore locations of

2 Bedford Basin in 2017 (see Fig. 1a).

	CH_3I	CH_2ClI	CH_2I_2
[1]Tufts cove	5.8	35.5	8.8
[2]Wrights cove	6.7	20.6	12.5
[3]Sackville	3.8	6.5	4.9
[4]Mill cove	8.3	28.0	18.6
[5]Fairview cove	6.2	26.3	6.4
Middle of Bedford Basin	6.1	37.6	6.3

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1   **Table 4.** Seasonal variation of total sea-to-air fluxes of iodocarbons (nmol m^{-2} d^{-1}). In spring 2015,

2   we have substituted the flux of iodocarbons based on the average values from spring 2016 and

3   spring 2017. Higher flux values of iodocarbons in each year are marked in red.

4

year	season	CH$_3$I	CH$_2$ClI	CH$_2$I$_2$	Total iodine
2015	*Spring	3.0	5.0	8.1	24.2
	Summer	17.6	42.0	25.7	110.8
	Fall	13.7	38.1	28.6	109.1
	Winter	2.8	3.6	13.8	34.0
	Annual	13.8	34.8	25.0	98.6
2016	Spring	3.0	7.6	15.2	40.9
	Summer	9.9	27.7	11.2	60.0
	Fall	5.6	6.9	2.1	16.8
	Winter	3.2	2.6	8.7	23.2
	Annual	5.7	12.2	9.1	36.2
2017	Spring	3.1	3.0	2.5	11.1
	Summer	12.2	26.3	21.0	80.4
	Fall	13.9	27.3	17.3	75.8
	winter	5.3	15.4	40.7	102.0
	Annual	8.7	17.8	19.2	64.9

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1   **Table 5.** Comparison of sea-to-air flux (nmol m^{-2} d^{-1}) of total organic iodine in different studies.

2   Data from Archer et al. (2007) is 1 year annual average, from Shimizu et al. (2017) is 3 years

3   annual average, from Shi et al. (2014b) is 2 years annual average (only the flux of CH$_3$I) and from

4   our study is ca. 3 years average.

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| | English Channel | | Funka Bay | | Kiel Fjord | | Bedford Basin | |
| | Archer et al.(2007) | | Shimizu et al. (2017) | | Shi et al. (2014) | | This Study | |
Season	Total	%-CH$_3$I	Total	%-CH$_3$I	Total	%-CH$_3$I	Total	%-CH$_3$I
Spring			12.3	46.7	2.8		23.6	12.7
Summer			79.3	14.0	5.2		82.4	15.8
Fall			51.7	36.0	2.2		67.2	16.5
Winter			18.0	27.0	0.2		60.7	6.8
Annual	42.6	27.9	43	22.3	3.3		61.7	14.1

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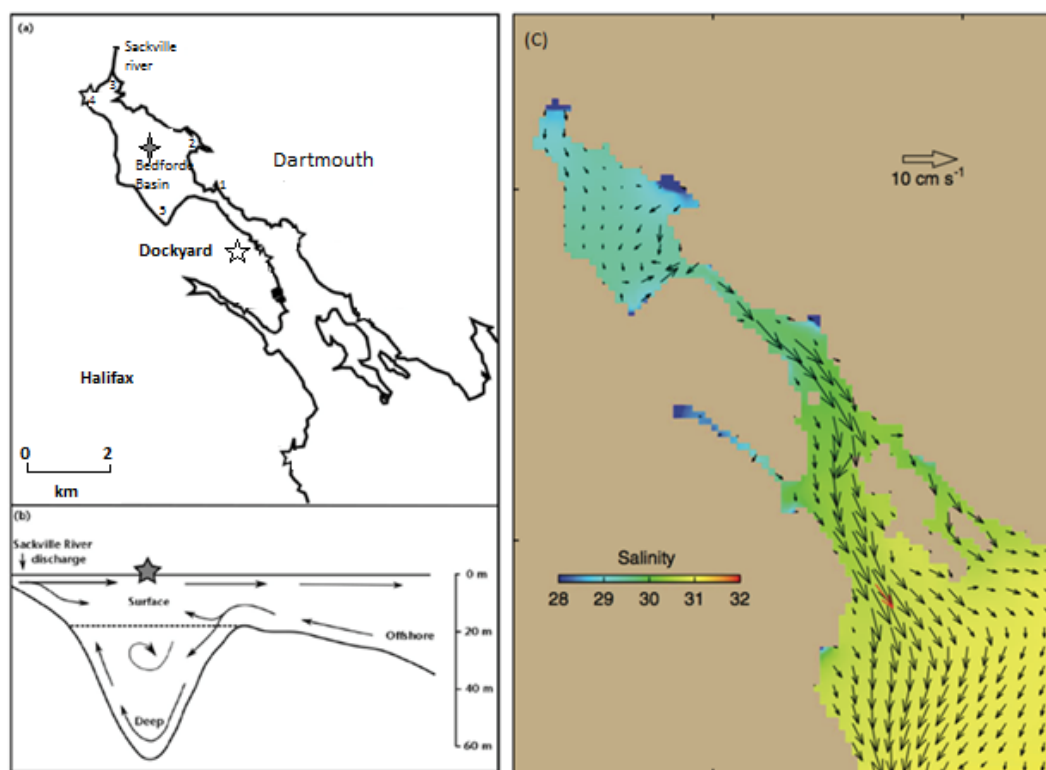
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3   **Figure 1.** (a): Main sampling location (grey star) and near-shore sampling locations 1-5 (1: Tufts
4   cove; 2: Wrights cove; 3: Sackville; 4: Mill cove; 5: Fairview cove) in Bedford Basin; (b): two
5   layered flow in Halifax Harbour, adapted from *Kerrigan et al.* (2017); (c): horizontal circulation
6   of water in Halifax Harbour from *Shan et al.* (2011), using annual mean currents and velocities.
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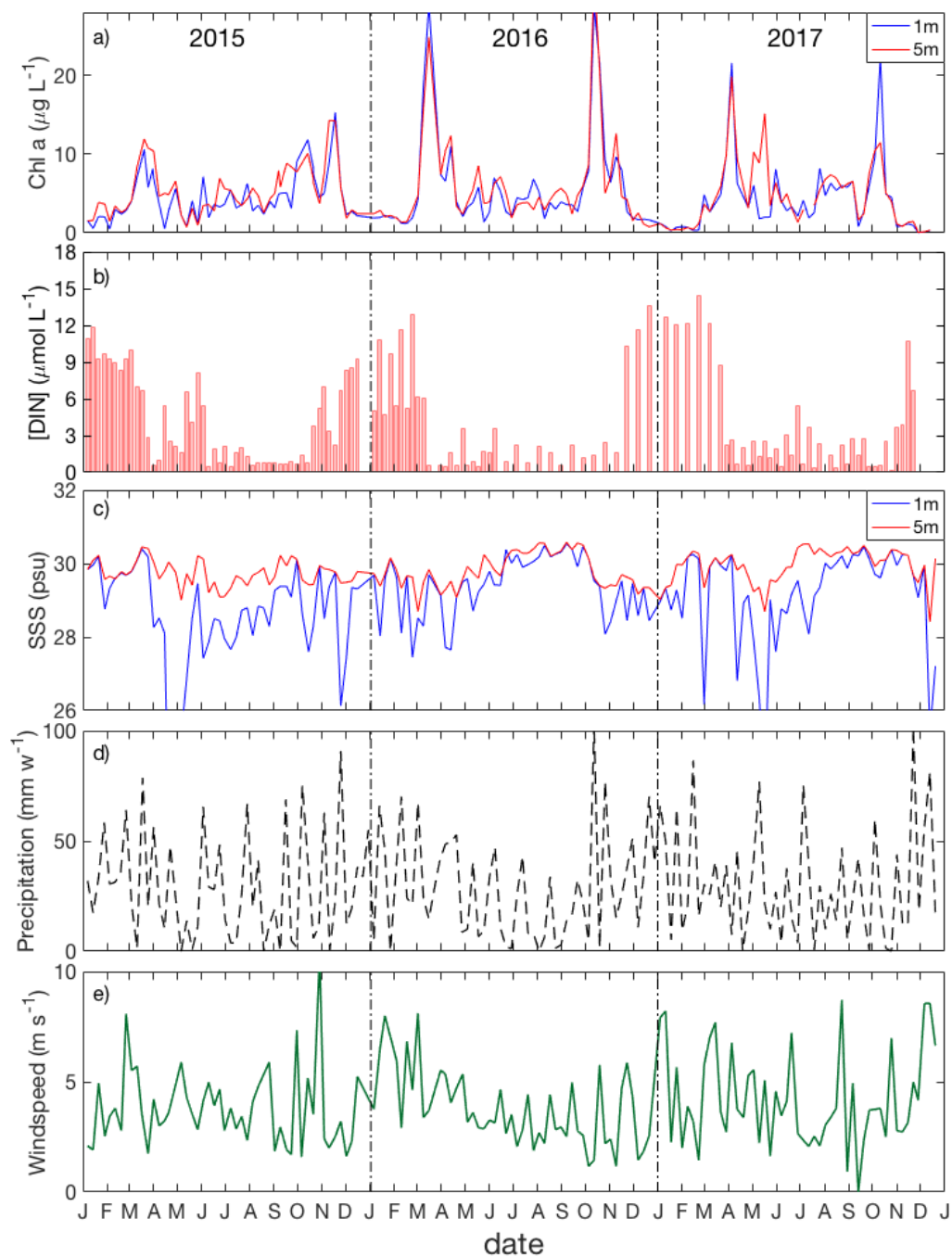
Figure 2. Seasonal variation of (a) chlorophyll *a* (blue line for 1 meter and red line for 5 meter);
(b) DIN; (c) near surface salinity, (d) precipitation and (e) windspeed in Bedford Basin from
January 2015 to Dec 2017.
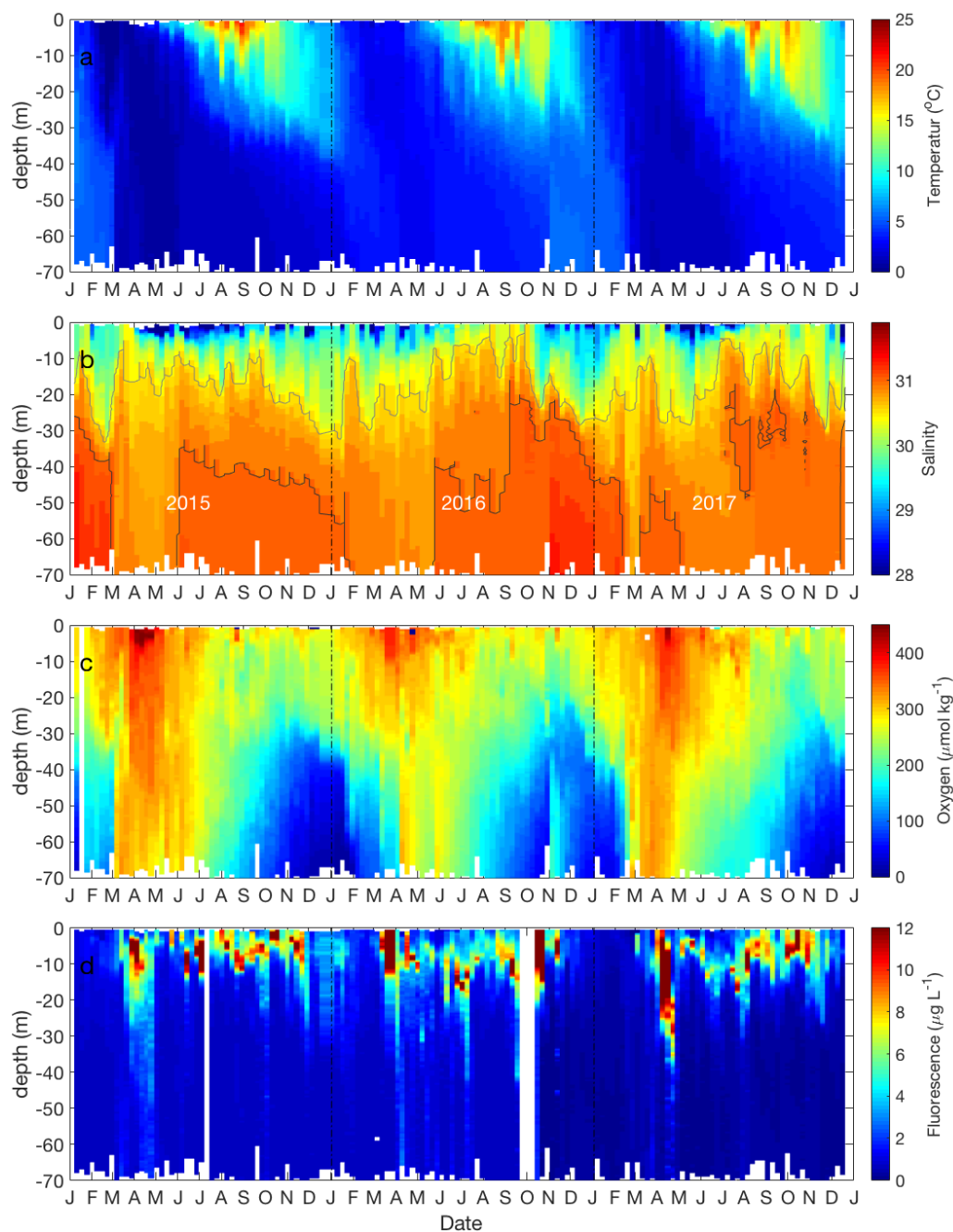
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Figure 3. Seasonal patterns of environmental and biological variables in Bedford Basin from
January 2015 to Dec 2017. (a) temperature; (b) salinity (showing contour lines for 30.5 and 31);
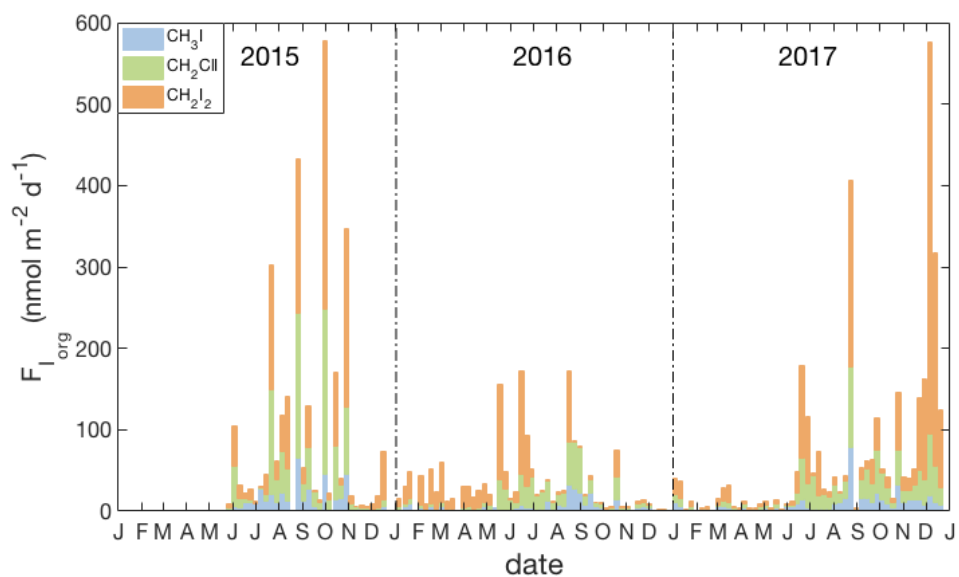(c) dissolved oxygen; (d) chlorophyll fluorescence.

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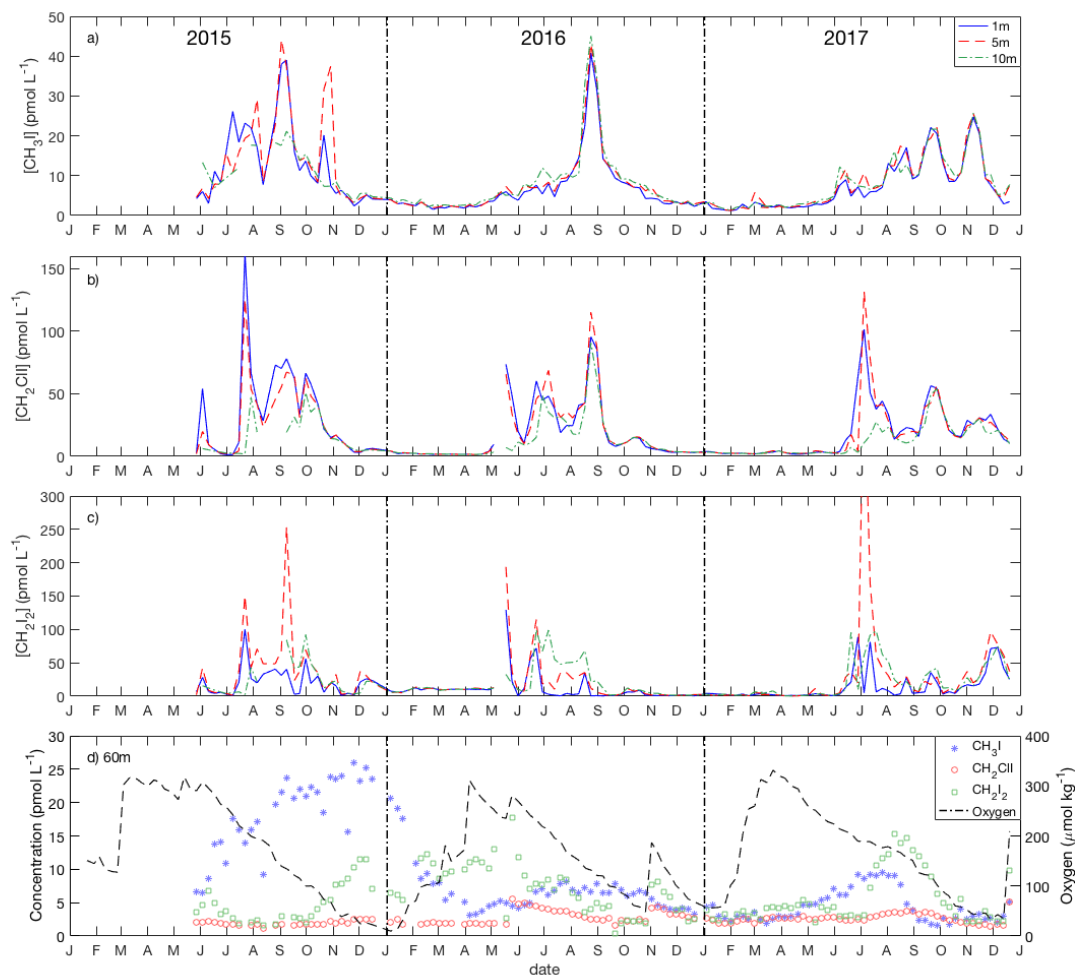
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4   **Figure 4.** Seasonal variation of Iodocarbons in the Bedford Basin at 1 meter (blue line), 5 meter
5   (red line) and 10 meter (green line) from May 2015 to December 2017: (a) CH$_3$I; (b) CH$_2$ClI and
6   (c) CH$_2$I$_2$. (d): time-series of near-bottom water (60m) of iodocarbons and dissolved oxygen.
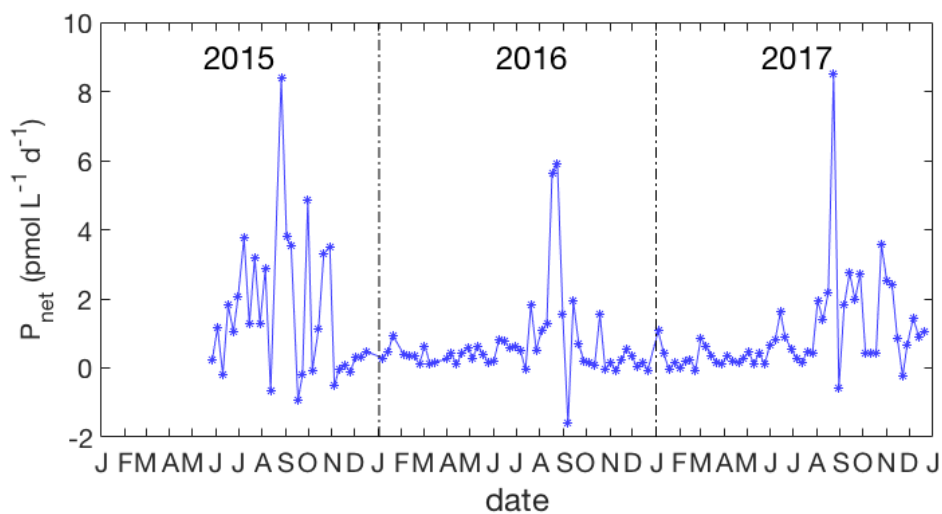7

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Figure 5. Sea-to-air flux of I_{org}: including relative contributions of individual compounds and using the parameterization for transfer velocity of Nightingale et al. (2000).

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2 **Figure 6.** Variation of net production rate of CH$_3$I from 2015 to 2017.
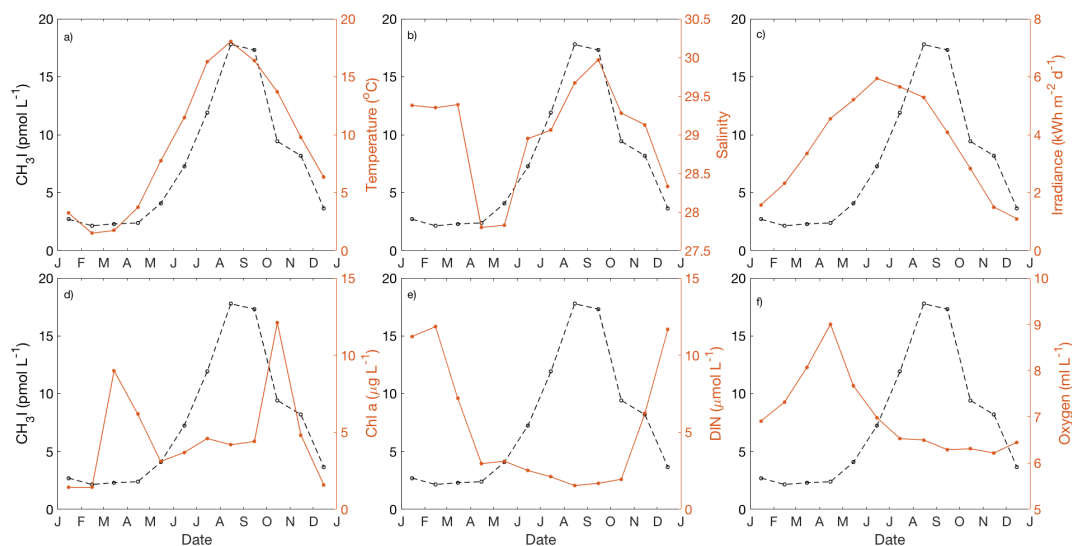
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4 **Figure 7.** Annual cycle of (a) temperature, (b) salinity , (c) irradiance, (d) Chl *a*, (e) dissolved
5 inorganic nitrogen (DIN) and (f) dissolved oxygen for near-surface water (1-5 m) in Bedford Basin.
6 The black dashed line depicts the annual cycle of CH3I. The figures present the monthly mean
7 values based on the data collected from May 2015 to December 2017.
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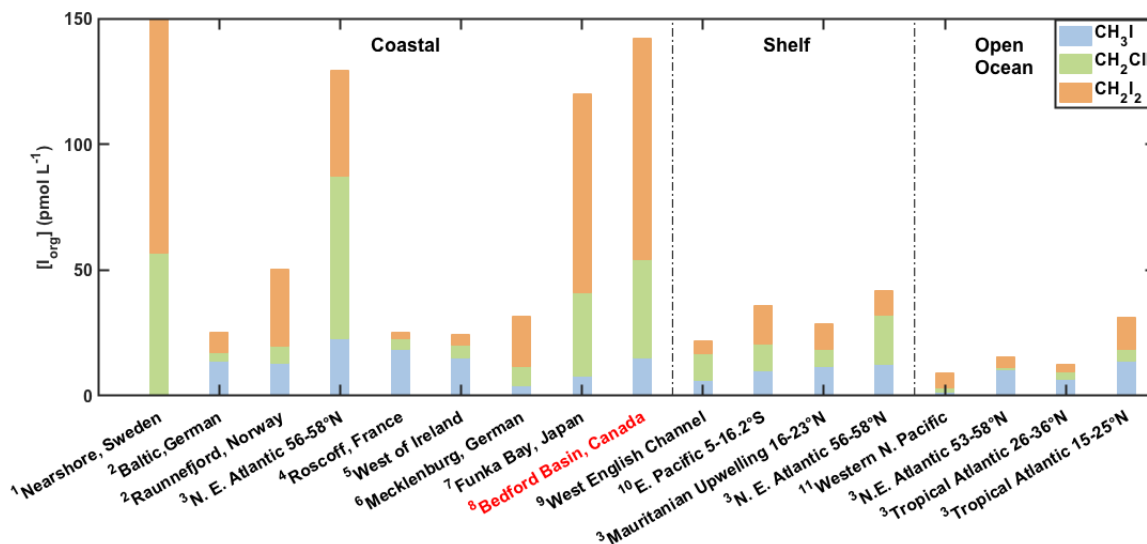
Figure 8. Contribution of Iodocarbons to total organic iodine (Iorg) in surface seawater from different regions and studies:

1 : Klick, 1992; 2: Orlikowski et al., 2015; 3: Jones et al., 2010;4: Jones et al. 2009; 5: Carpenter et al., 2000; 6: Orlikowski & Schulz-Bull, 2009; 7: Shimizu et al.,2017; 8: this study; 9: Archer et al., 2007; 10: Hepach et al., 2016; 11: Kurihara et al., 2010.