

Interactive comment on “A three year time-series of volatile organic iodocarbons in Bedford Basin, Nova Scotia: a Northwestern Atlantic fjord” by Qiang Shi and Douglas Wallace

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We also thank reviewer #2, for the careful and useful review and suggestions for improvement. We have responded to all of the changes suggested and feel the text is now clearer and that our discussion is better grounded on the data available.

1. Manuscript format: the manuscript could be improved by more careful attention to the referencing of results. Often the reader is referred to the wrong figure or table. It would also be worth reviewing the sequence in which the results are presented in relation to the sequence of the text.

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Answer: we have corrected and doubled checked the numbering of figures and tables. We also changed the order of figure 2 and 3, the order of figure 7 and 8.

2. Iodide/iodate influence. There is an overemphasis, in my view, on the link between iodide concentration and the production of iodocarbon compounds in relation to what is presented in the paper. Although it is plausible that there may be an influence of iodide concentrations, the authors present no new information to support this, nor do they convincingly link studies that examined iodide/iodate transformation or iodide concentration to their own datasets. For instance, the statement made in the abstract on this issue P1L17-20 has limited bearing on what is actually presented in the paper. The same is true for the sentence in the Conclusion P27L15-17.

Answer: We removed discussion of this point from the abstract as suggested. However, following the recommendation of reviewer #1, we keep a discussion of the hypothesis within the discussion section and mention it in the conclusions. It is true that we have no data about iodide/iodate concentrations in Bedford Basin. However the relationship to the timing of DIN disappearance is notable and may relate closely to behaviour identified in laboratory studies. In general, we believe it is important to try and link findings from laboratory studies to observations in the field, which is why we attempt to connect the two lines of investigation in various sections of the discussion. This attempt reveals very clearly the need to investigate inorganic iodine cycling during these types of time-series, and our future work in Bedford Basin will attempt this so that we can test the ideas and hypotheses presented here. However we think that mentioning the hypothesis will encourage others to do the same. We have reworded some of the discussion to clarify the nature of the relations of iodide formation to organoiodine formation (section 4.2) and also to note the potential of temperature as well as nutrient drawdown to influence production rates including potential effect on reaction kinetics (section 4.3.1, P19L23).

3. Net production of CH₃I: P11L21 it is not clear from the mass-balance calculation of net CH₃I production that the mixed layer depth is taken into account? Not accounting

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for the mixed layer depth may have been appropriate for the study in Kiel Fjord study (Shi et al. 2014) but in the deeper waters of the Bedford Basin for the mass-balance to hold, the net production should account for the full water depth that potentially exchanges CH₃I with the atmosphere. The authors should also explain why the only attempt to estimate the net production of CH₃I and not the other two compounds?

Answer: (see also reply to reviewer #1). We checked the mixed layer of Bedford Basin; due to strong salinity stratification, the mixed layer was shallower than 10 m almost throughout the entire time-series, except for some periods in the winter. In order to simplify the calculation, we calculated the mass balance and net production for the top 10 meter water column consistently. We replotted net production rates of CH₃I (Fig. 6), and no production rates are presented for periods when the layer of uniform density extended deeper than 10 m. For CH₂I₂ and CH₂CII, the loss due to photolysis can be very important and we did not have complete information to estimate it. So we do not show plots of net production rate of CH₂I₂ and CH₂CII (which we include below in this response) but rather we now give estimates of typical production rates (p. 13 line 1-4) and are careful to note the significance of various loss terms underlying our definition of P_{net} for these compounds.

4. Air-sea flux calculation: P10L15. Previously it has been shown that accounting for the air-side resistance to air-sea transfer has an appreciable decrease in the estimated flux of the more soluble volatile iodocarbons. For instance, the flux of CH₂I₂ was reduced by ca. 30% compared to water-side resistance-only calculations (Archer et al. 2007). The authors should state why they do not include the air-side resistance in their calculation, they may have good reason. However, it should be considered when comparing flux estimates of the different compounds and total iodocarbon flux estimates from different studies.

Answer: yes, the air-side resistance should be considered during the calculation of the flux. We recalculated fluxes including air-side resistance, and the reduction of the flux of CH₂I₂ averaged 24%, 10% for CH₂CII and 2% for CH₃I. The revised text is

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presented in section 3.3. We also were careful to adjust the flux estimates of Shimizu et al. (2017), prior to comparing with our estimates and those of Archer et al. (2007). The adjustments are significant and, interestingly, lead to closer correspondence of the annual air-sea fluxes of Iorg from the three environments (see Table 5).

5. Deep-water section. Section 4.5, P21 L10 to P25 L2. ‘temporal variability in near bottom water (60m)’ could be usefully reduced in length in order to make it more readable and the messages more clear. The switch from alkylation processes that produce mono-iodinated compound to a haloform-type process (P25L1) that is possible linked to oxygen concentrations, is interesting but the message is lost in the complexity of the explanation of changing iodocarbon concentration and hydrography that follows.

Answer: In section 4.5 ‘temporal variability in near bottom water (60m)’, we added figure 9 to help clarify the discussion. Special events labelled 1 to 9 present the timing of switching from alkylation processes to a haloform-type reaction, and of intrusions. We completely rewrote the description of these events and while still substantial, the text has been shortened considerably and is, we feel, much easier to follow.

6. Unclear conclusions. (Section 5) At present, the concluding section consists of a series of largely unconnected points that have been extracted from the discussion and that lack a coherent structure. It would be more useful if the really important points were picked out and their significance described in the narrative. The easiest to read, conclusion-like comments come at the end of the section.

Answer: We restructured and shortened the conclusion section, dispensing with some minor points, and emphasising the more general conclusions towards the end.

7. Figure and Table legends. The figure legends and table legends could be more informative in general.

Answer: We added more information to the captions.

Additional points:

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1. P3L5, At some point the authors should point out that the three compounds they focus on are not the only volatile iodocarbons that are likely to be present, with minor contributions to the total from several other compounds including CH₃CH₂I, CH₂BrI and CHI₃.

Answer: yes, VOIs also include CH₃CH₂I, CH₂BrI and CHI₃, although they are usually minor contributions compared with other three compounds. We added this to line 2 of page 3.

2. P7L7: Temperature is the first environmental parameter described but does not appear in Figure 2. It would be clearer if the sequence in the text and figures corresponded. Plus, SST is not shown in either figure but is referred to in the text.

Answer: We changed the sequence of figures. The new figure 2 is about seasonal patterns of environmental and biological variables in Bedford Basin, and temperature is shown in fig 2a. And SST is corrected to temperature in the text (P7L23).

3. P7L13: No information on the seasonality of irradiance is provided until figure 7c, but it is an important part of the explanations that the author provides for seasonal trends in both polyiodinated compounds and CH₃I. I recommend removing SSS from the current figure 2, as it is effectively repeated in figure 3, and replacing it with irradiance information.

Answer: We added seasonality of irradiance in figure 3f. For sea surface salinity we refer to this now as “salinity” in section 3.1, so we kept the figure (figure 3c). These data are especially important for showing the near-surface stratification.

4. P8L1: Figure 2b shows DIN not SSS, similarly for P&L18.

Answer: We corrected this in the text (see P7L9).

5. Table 1: Please explain what the numbers actually are in the legend, Pearson's correlation coefficient? An indication of the statistical significance would also be useful.

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Answer: They are the R² values (Pearson's correlation coefficient) while p is < 0.05. We added more information in the caption.

6. Table 2: Again, more information required in the legend that describes exactly what data is being correlated and the significance of the correlations.

Answer: They are the R² values (Pearson's correlation coefficient) while p is < 0.05. We added more information in the caption.

7. Table 3: The legend needs rephrasing, plus more information on when these samples were obtained would put the results in context with the seasonal study. The sequence of tables does not match the text. The information in table 3 is not addressed until the discussion, after table 4. How was the lack of significant differences between measurements determined (P13L10)?

Answer: We swapped the order of Table 3 and 4 and added more information in the caption of Table 4. The goal of these measurements was to look for potential influence of nearshore, macroalgal production. The highest concentration of CH₂I₂ (18.6 pmol/L). We added a sentence to section 4.1 (P13L18), which compares the nearshore measurements to the mean and standard deviation of measurements made at the central Basin sampling site during the month of July. Compared to the very significant differences of bromocarbons measured close to or far from macroalgal beds (e.g. Klick, 1992), the difference of iodocarbons was certainly not significant.

8. Figure 5: Please add an explanation of what the bars actually show, weekly data presumably but from single surface iodocarbon values, wind speed averaged over the week, water temperature from a single measurement during the week, these all impact on the flux value.

Answer: This is a useful point. We added more information in the caption and also in the text (section 3.3) to explain how we calculated the fluxes and what the averages represent. We recalculated the fluxes so that the bars in figure 5 represent weekly

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averages of daily flux estimates (based on daily average wind speeds and interpolated daily values based on weekly water sampling). This is now explained clearly in the text.

9. The ratio of dihalomethanes to the total volatile organic iodine is interesting but would a stronger point if backed up with a statistical test of significance and/ or an indication of the range of values between regions.

Answer: We assume here that the reviewer was referring to the results shown in Fig. 7. We have added a little more text on the comparison between regions to the text in section 4.2 on both pages 14 and 15. Basically a 1-way ANOVA showed no significant difference between means for the three regions for either total organoiodine content (Iorg) or for the percentage of the total given by different compounds. On the other hand, if we pooled results into only two regions (coastal and shelf+open ocean) then a t-test showed a significant difference for Iorg at the 95% confidence level. Although Fig. 7 appears to reveal differences in the relative contributions of different compounds between regions, we now state clearly that the overall differences are not statistically significant.

10. P15L22: this paragraph makes some interesting points but seems to have a mixed message regarding the potential limitation of iodide concentrations on volatile iodocarbons formation rates.

Answer: We rewrote this paragraph to clarify the description and we hope the arguments about potential for inverse correlations of iodocarbons with iodide are now clearer.

11. P18L3-8: this paragraph describes what happened in the Kiel Fjord study, but what is the relevance to the current study. Were lagged correlations used for the Bedford Basin. Answer: We did not use lagged correlation analysis for the Bedford Basin as the end-result of the earlier study in the Kiel Fjord was that detailed correlation analysis may have reached its practical limit of utility for identifying causation. This paragraph was rewritten (line 1-7, page18) to make this point. 12. P19L14: Section 4.3.2. Please

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clarify the points that are being made in this section, at present it is confusing.

Answer: we removed this separate section and now simply refer to maxima of ca. 1 month duration.

13. P26L9: CH3I production etc. of the environmental variables shown for Bedford Basin, there is a similar pattern to the temporal change of water temperature and CH3I concentration (Table 2, figure 7). Yet this receives little attention, despite the fact it appears to be considerably more closely related to the CH3I temporal pattern than irradiance? Why this may be the case would be worth considering.

Answer: We changed the sequence of Fig. 7 and 8, and added a reference to Fig. 7a in section 4.3.1. We had already discussed the temperature influence in Page 19 line 23, and emphasise the correlation between CH3I production and temperature.

14. P27L13: The sentence beginning ‘iodocarbon concentrations...’ is difficult to interpret.

Answer: We rewrote the whole conclusion and removed this sentence from the conclusion.

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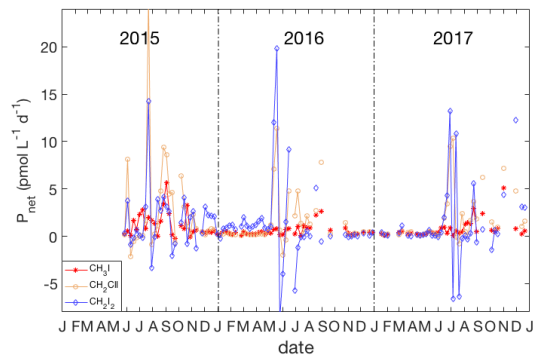


Fig. 1. Variation of the net production rate of VOIs in the upper 10 m from 2015 to 2017. No data are plotted when the layer of uniform density extended below 10 m.

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