

Response to Referee #1

We would like to thank the reviewer for the time spent reviewing the manuscript, and for the helpful and generous comments – always greatly appreciated. Our specific responses are given below in italics:

[Referee] This study examined the effect of acidification on the response of halocarbons in the Arctic using the mesocosm experiments. The area of study is of particular interest, because rapid environmental change is likely to be observed in this region. The general experimental set-up selected for this study seems sufficient for the objective to assess the effect of increased pCO₂ treatment on the production or decomposition of halocarbons. My main concern is related with the low concentrations (about 1 pmol/L) of CH₂I₂ observed in the most samples with the exception of some anomalous spikes. The results suggested that the production of CH₂I₂ was observed, but not significant, in the mesocosm experiments

Please see our comments below with regard to the low concentrations of CH₂I₂ observed during this experiment.

[Referee] This study shows that pCO₂ concentration showed no or some correlations to halocarbon concentrations or dynamics but these data are important and valuable for the development of the knowledge about the oceanic halocarbon dynamics. I consider the paper “Response of halocarbons to ocean acidification in the Arctic” by Hopkins et al., acceptable after minor revision.

We thank the reviewer for their positive comments.

[Referee] P8200, line 14-17 “Diiodomethane (CH₂I₂) displayed a number of strong relationships with biological parameters. Furthermore, the concentrations, the rate of net production and the sea-to-air flux of CH₂I₂ showed a significant positive response to pCO₂.”: P8212, line 20 “3.3 Halocarbons and pCO₂”: P8215, line 19 “4.1.2 Diiodomethane (CH₂I₂)”: The values of CH₂I₂ observed in the samples were small as compared to the ranges of CH₂I₂ in the water column, for example, 1.7 – 8.2 pmol/L in the Southern Ocean (Carpenter et al., Mar. Chem., 103, 227-236, 2007) and <0.1–22.2 pmol/L in the western North Pacific Ocean (Kurihara et al., Mar. Chem., 118, 156-170, 2010).

Low concentration (about 1 pmol/L) of CH₂I₂ could imply that the production of CH₂I₂ was observed, but not significant, in these mesocosm experiments. It would be useful for readers to present this more clearly.

We feel the low concentrations of CH₂I₂ observed during this experiment do not detract from the importance of this compound, and do not invalidate its inclusion in the discussion of this dataset. There are a number of reasons for this:

- 1. The concentrations of CH₂I₂ we report fall within the range of concentrations measured in the open ocean (which the reviewer has demonstrated in their comments).*
- 2. CH₂I₂ is considered to be the most important iodocarbon emitted from the oceans to the atmosphere, which is stated in the text (see P8201, L26 – P8202, L3 and P8217, L21-25).*

3. *The Arctic atmosphere is particularly pristine – thus even relatively small changes to the sea-to-air flux of reactive compounds could have significant implications for atmospheric chemistry and climate processes (See Mauritsen et al. Atmos. Chem. Phys. 11, 165-173, 2010).*
4. *Significant net production rates of CH₂I₂ were observed during this study (Table 3) and significant relationships with pCO₂ concentration were also identified (Figure 4). The mesocosms are a tool that represents the open ocean, and these results suggest a possible effect of elevated CO₂ on the production of this compound. Thus the relative change, rather than the absolute change is of interest in this experimental context.*

[Referee] P8210, line 6-8 “Peaks occurred following nutrient addition and in parallel with the chl a peak on t19 in PII, and during the rapid rise in chl a observed during PIII.”: Fig. 1A
Could the author show the possible source of the rapid rise in chl a observed during PIII? I’d like to see the authors elucidate the possible source of this rise in chl a during PIII a bit more.

The rapid increase in chl a observed during PIII was attributable to increased growth of diatoms, prasinophytes, and to a certain extent haptophytes (see Schulz et al. Biogeosciences, 10, 161-180, 2013). Text has been added to the manuscript to this effect.

[Referee] P8210, line 20-23 “M1 displayed significantly higher concentrations over almost the entire duration of the experiment, with a maximum and seemingly anomalous value of 2.5 pmol l⁻¹ on t19 (ANOVA F = 2.52, df=8, η^2 = 0.014, p < 0.05).”: P8211, line 13-18
“Concentrations of CH₂BrCl (Fig. 2i) were low (<0.1 pmol l⁻¹) and stable, with the exception of a small 15 number of anomalous data points in PI and PII. CH₂BrI showed little variability as the experiment progressed (overall mean=0.35 pmol l⁻¹), with the exception of some anomalous spikes in concentration during PI and II, and little response to nutrient addition or phytoplankton growth (Fig. 2j).”: Were these anomalous spikes in concentration of halocarbons also observed in the procedure blanks? Because many of the halocarbons are used in laboratories, it would be useful to the readers to know how the potential problem (contamination of halocarbon) has been solved by the authors.

All efforts were made to minimise the possibility of contamination of samples with halocarbon standards. Calibrations were performed separately to the seawater analyses; therefore the opportunity for cross-contamination of samples with standards was minimal. Standards were stored in a freezer in a separate laboratory to which the analyses were performed. Separate glassware was used for standard runs and sample runs. Similar spikes in concentrations were not encountered during calibration runs or procedural blanks, indicating that there was no problem of contamination with the standards themselves. We can conclude that spikes in concentrations may have been caused by the inclusion of aggregates/large cells in samples which caused artificially elevated concentrations in certain samples (See Hughes et al. 2008, Limnol. Oceanogr. 52 (2), 867-872). Text to this effect has been added to the methods section as follows:

2.3 Quantification of halocarbon compounds

“In order to prevent the possibility of contamination of natural samples with halocarbon standards, all working standards were stored at -20°C in a separate laboratory to where analyses were carried out, and handling of standards was undertaken in a fume hood. Additionally, separate glassware was used for standard runs and sample runs. Instrumental and procedural blanks were performed daily before the commencement of sample analyses, and the system was invariably found to display no contamination”.

4 Discussion

“For a number of halocarbons, anomalous spikes in concentrations were observed on a small number of occasions (Fig 2). Excluding the likelihood of contamination of the analytical system (see Section 2.3), it is possible that these elevated concentrations were caused by aggregates of biogenic material, known to be “hotspots” of halocarbon production, incidentally included in particular samples (Hughes et al. 2008)”.

[Referee] P8211, line 25-P8212, line 2 “To simplify these analyses and to give an overview of general trends, the halocarbons were assigned to three groups based on their common biological production pathways: (1) I-monohalocarbons (CH₃I, C₂H₅I, 2-C₃H₇I, 1-C₃H₇I), potentially formed via methyl transferase activity,”: It would be useful for readers unfamiliar with methyl transferase that C₂H₅I, 2-C₃H₇I, 1-C₃H₇I potentially formed via methyl transferase activity is presented more clearly. Please cite a reference or experimental data.

We agree that this information needs some better substantiation. To address this, we have inserted a relevant citation, as shown here:

“To simplify these analyses and to give an overview of general trends, the halocarbons were assigned to three groups based on their common biological production pathways (Manley 2002):”

[Referee] P8216, line 16 “Fig. 5b, c” would be “Fig. 5b”.

This has been changed.

[Referee] Fig. 4 and Fig. 5 Note that the amounts of CH₂I₂ produced were small in comparison with the maximum concentration of CH₂I₂ observed in the open ocean. So I don't think that changes in concentrations of CH₂I₂ would be significant, or is worth mentioning. Overall I am unclear as to the relevance of these Figures.

Fig.5 and accompanying text has been removed.

[Referee] Fig. 6A The Y-axis title “net loss rate – flux t₂₁ - t₂₇” would be “net loss rate t₂₁ - t₂₇”.

This has been changed.