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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Emission of iodine containing volatiles by selected microalgae species" *by* U. R. Thorenz et al.

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We thank the Referee for the interest in our study and for the detailed comments. The processing of the raised questions will improve the manuscript. We have tried to do our best to respond in detail to the points raised and to change the manuscript according to that; we appreciate the opportunity to clarify our research results. Each comment by the reviewer is first recalled and then the corresponding replies are given.

1) The emission of halogenated compounds strongly depends on algal species (e.g. Tokarczyk and Moore 1994), growth stage (e.g. Moore et al. 1996) and, at least for macroalgae, on environmental factors such as irradiance (e.g. Laturnus et al. 2004)

and temperature (e.g. Nitschke et al. 2013). Thus, the authors should provide essential and detailed information about the strains examined (strain numbers), the culture/ maintenance and experimental conditions (irradiance: PAR, probably UV [type of bulbs, fluorescent tubes], temperature, photoperiod) and the growth phase which cultures had reached at the time of the experiment (lag, log, stationary?). Since growth of diatoms is silica-dependent, they should also mention that this micronutrient was present (or absent?) in the f/2 growth medium used (concentration?). I am further interested in the fact why species from different geographical regions were chosen (temperate: M. helysia, Antarctic/Arctic: P. glacialis). Are these species key components in their natural habitats (bloom-forming, high abundance, high biomass)? Was the habitat temperature regime considered during maintenance and experiments?

We agree that the emission is strongly dependent on algal species, growth stage and environmental factors. Therefore we give detailed information about the growth of the two diatom cultures, which were cultured before the actual emission experiments stated in our study. Both diatom cultures were personal isolates from the AWI colleagues at Sylt and were cultured in a cooling room at 16 °C in a 12 h light cycle using a Lumilux natural daylight lamp. The culture maintenance is now described with all these details in the experimental section. The different concentrations of the nutrients added to the filtered natural seawater to prepare the F/2 medium are added to the text. We had no possibility to check the growth phase, therefore we do not state it. The two diatoms where chosen in cooperation with our colleagues in Sylt and Helgoland. In an earlier study we investigated Mediopyxis helysia, which is an intensively studied diatom in Helgoland (Kraberg et al. 2012), with promising results. Porosira glacialis was chosen, because we wanted another diatom originating from a different habitat and we were dependent on the isolates present in Sylt. We kept both species using the same growing conditions, although their originating habitat is different, as we had no experimental opportunity to culture them individually. We added the reasons for choosing the species for our experiments to the manuscript in the experimental part.

2) Many algal species do not only release iodide into seawater (e.g. Chance et al. 2009, Nitschke et al. 2013), where it can undergo transformation (e.g. Chance et al. 2009, Bluhm et al. 2010), but they also efficiently absorb it (van Bergeijk et al. 2013). Such iodide uptake may explain the low concentration in the medium as measured by the authors. Iodine uptake is a topic that the authors should address in their discussion to place their findings into a biogeochemical context.

The iodide uptake of algal species is important and therefore added to the discussion, especially for the natural algae sample this leads to an interesting point. The uptake itself was not measured but is now mentioned in the discussion of the low iodocarbon emission and low iodide concentration in the natural plankton concentrate.

3) Regarding the halocarbon emission rates (Table 1), although mean values for CH3I and Ch2ICl differ slightly between "background" (which may be called "blank measurement"), P. glacialis, M. helysia and the natural plankton sample, the actual range of values is quite similar. In order to attribute the emission of these compounds to algal cells present, the authors may back up their data by statistical analyses, meaning they should provide proof that emissions rates were significantly different/higher when algae were present. I would recommend to perform either a simple t-test ("background" against "culture") or, for more information, a one-way ANOVA for each compound. If the assumptions for the t-test and the one-way ANOVA are violated, the authors can perform Mann-Whitney U-tests or Kruskal-Wallis tests, respectively. The term "significant" can only be used when a statistical test revealed a significance. Also, the authors observed the emission of CH2I2 from P. glacialis; this finding contradicts Moore et al.(1996). Any explanation (see the following comments)?

A Mann-Whitney U test was performed (which I know as Wilcoxon rank sum test) to investigate whether or not the increases in CH3I, CH2I2 and CH2ICl are significant. To investigate the significance the whole sample dataset was used, all 6 replicates for the iodocarbons. The test proves the significant increase in iodocarbons when diatoms are present. This discussion is now added to the manuscript. In our discussion we still

include other probable formation pathways as considered by the reviewer in the following comments. Regarding that Moore et al. did not observe that P. glacialis produces CH2I2 we refer to the publication when Moore et al state: " P. glacialis produced CH2I2 either in insignificant quantities or it was not possible to say that the quantities were substantially different from the control treatment. This does not mean that this organism is unable to produce CH2I2." Therefore, we do not see a contradiction with Moore et al.. The sampling and experimental conditions are very different for the presented study and the study of Moore et al, as they measured production using a purge and trap system, while we measure emissions using a chamber system with a constant flow and adsorption tubes which are analyzed later. One reason why we measured CH2I2 when Moore et al. did not, aside from the experimental differences, could be the different strains of the micro algae, different environmental conditions in the medium or other environmental factors. All these points are interesting, but are not the primary scope of the presented study (abiotic formation and emission of I2 from natural seawater to the atmosphere) However, we feel that these points make a good case for investigating the production of iodocarbons by different micro algae strains in more detail and with the presented method again.

4) Were halocarbons potentially present in the growth medium? They may not originate from algal cells. Where did the seawater used for media preparation originate from? For example, concentrations of organic iodine species can be high in coastal or nearshore waters (Wong and Cheng 1998); a fact that is neglected by the authors (see p 14581, l 10) and should be addressed.

To be aware of emission from the growth medium we used the medium in our emission experiment as we used the diatom cultures, which we explain now in more detail in the experimental part. The halocarbons emitted from the growth medium were stated in Table 1 in the row f/2 medium background. To emphasize the emission from the background we add the discussion about emission of halocarbons from natural seawater as suggested by the referee.

5) Also, some bacteria are known to take up, release and emit iodine species (Amachi et al. 2001, Amachi et al. 2003). The presence of bacteria in the growth medium and/or in association with algae might have influenced the results presented. For example, the authors show that halocarbons were also emitted from pure growth medium without algal cells (Table 1: f/2 medium "background" range). Any explanation? Was the f/2 medium sterilised before usage? Were the algal strains axenic?

Bacteria that are able to take up, release and emit iodine cannot be excluded in our emission experiment; therefore we add them to our discussion. The emission from the medium without algal cells is discussed now for both emissions due to halocarbons in the seawater used to produce the medium and for bacteria.

6) Regarding the determination of I2 emission rates, was the experimental set-up (Fig. 1) characterised for potential wall losses? I2 is quite "sticky" and large surfaces can potentially act as efficient sink for I2, implying that I2 emission rates are probably underestimated. How was this issue addressed?

Wall losses have been evaluated for the set up described in Fig. 1 in the lab using a I2 diffusion source. We measured the I2 mixing ratios after diluting the source flow (500ppt I2) and compared it to the mixing ratios at the end of the glass chamber described in Fig. 1 using the same flows as described in the micro algae experiment. We could not observe wall losses larger than our analytical precision (RSD =5%). We also checked losses to the water surface by adding ultra pure water, and again we did not observe any losses to the water surface. We include our results on wall losses for I2 in the experimental description.

7) Chlorophyll concentration can vary with environmental factors and under stress conditions; it represents therefore not the best proxy for biomass. Chlorophyll a data may be supported by cell numbers.

We agree that Chlorophyll a concentrations are not the best proxy for biomass. We did not have the opportunity to count the cells at the AWI in List, Sylt or to measure the dry

weight or anything else, therefore we cannot state cell numbers or other proxys for the biomass. Since chlorophyll a is the only possibility to relate the emissions of volatile iodine compounds to the biomass, we use this proxy in our manuscript.

8) The study is placed into the field of biology and the link to atmospheric processes is relatively weak. Thus, I am not sure that ACP is a suitable journal for the work presented. In any case, before publication, the authors should address the above points.

We disagree with the referee in this point. The study is placed in the field of atmospheric processes, since the emission of molecular iodine and iodocarbons from the hydrosphere to the atmosphere is important for many atmospheric processes (ozone depletion, particle formation, perturbation of oxidative cycles in the atmosphere, (Carpenter et al., 2013)). We tried to clarify the atmospheric relation of the study in the text, by clarifying that the study is not an incubation study but an emission study. Additionally we clarified the importance of the emission of I2 (which is formed abiotically) versus the emission of iodocarbons (which are related to the field of biology). We also tried to reduce the biological language (by reducing the use of biology related vocabulary like F/2 medium) to clarify that the study is not related to biology in the first place, but we still kept all the explanations of micro algal processes, since one goal of the study was to relate the biological formation of iodide from iodate by microalgae and the atmospheric relevant process of I2 formation at the air/water interface.

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