Atmos. Chem. Phys. Discuss., 14, C7919–C7922, 2014
www.atmos-chem-phys-discuss.net/14/C7919/2014/

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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Received and published: 13 October 2014

Received and published: 13 August 2014

We thank the Referee for the interest in our study and for the helpful comments that will improve the manuscript and its comprehensibility. We have tried to do our best to respond to the points raised and to change the manuscript accordingly and we appreciate the opportunity to clarify our research objectives and results. Each comment by the reviewer is first recalled and then the corresponding replies are given.

- For stoichiometrically comparing production rates, it would be desirable to compute the rates for halocarbons and iodine (not only for iodide and iodate) in moles (Table 1).

To make it easier to stoichiometrically compare the halocarbon emission rates, they were computed to pico moles. Table 1 was changed accordingly. The summed emission rates in the text were kept in ng min-1 m-2, since the comparison with the literature is easier in this dimension. The emission rate of iodine, shown in the Figures 2 and 3, were also changed to pico moles. Therefore, it is now straightforward to compare the emission rates of iodocarbons and I2 as reported in this study with emission or production rates from other studies.

- Also, for comparing rates between species, it would be desirable to express them on a basis per g (or mg) chlorophyll a or maybe even g fresh weight (or dry weight) – if the conversion factor between chlorophyll and biomass is known (Table 1).

Since the conversion factor is not known the emission rates cannot be expressed on fresh or dry weight basis. The summed iodocarbon emission rates of the three algae suspensions were expressed on the basis per g chlorophyll a, this information was added to table 1. We think it is inappropriate to discuss the iodocarbon emission expressed on the basis of chlorophyll a in the text, since the reader could misinterpret emission as formation. Chl a is a concentration measured for the algae suspension, the iodocarbons were measured in the gas phase passing above the surface of the algae suspensions. This study is not a classical incubation study to investigate the formation of halocarbons by microalgae and to measure the concentrations built up in the water. The study presented here is an emission study to investigate the emission of iodocarbons by aqueous suspensions containing different microalgae. As a consequence we prefer not to discuss emission rates based on chlorophyll a in the text, however, for comparison to other studies the sum of iodocarbon emission based on chlorophyll a is stated in Table 1.

- There seems to be a discrepancy between the text and Table 1. Is the iodate concentration actually going up or down over time in a batch culture? And, if it does go down (in case it is reduced as the text suggests) can the differential amount of moles iodine be traced – in other words, does that iodate become iodide, molecular iodine, iodocarbons, or a combination of all these?

Since we did not measure the iodate and iodide concentrations during the course of the experiment we are unable to comment this issue. The concentrations were measured after the cultures had 4 weeks for growing. The F/2 medium was treated the same way, however, without any micro algae cultures in it. We therefore assume that the background is a representative background for the iodide and iodate concentrations in the plankton samples and is comparable to the samples before the micro algae were grown.

When we compared the iodide and iodate concentrations of the different samples and stated that the iodate concentrations were in the same range for all samples, we presume that the amount of iodate which the micro algae are able to reduce to iodide is not measurable, since the concentration differences are too low to be measured with the analytical precision of the methods used. When we discuss the slightly elevated iodide concentrations in the micro algae cultures compared to the background, we are aware that this observation is not statistically significant, however, at least an indication that the microalgae indeed reduced iodate to iodide, as expected from previous studies.

The iodate concentrations are between 397 and 538 nmol L-1 for the different samples, about two orders of magnitude higher than the iodide concentrations. Therefore, the reduction of iodate falls within our analytical precision. For the iodide measurements the analytical precision is much higher and the natural variability of the concentrations lower, therefore, we believe that the discussion of the formation of iodide is scientifically sound.

To improve this part of the manuscript, we introduced changes in the individual sections on iodide and iodate in the results and discussion part.

- A particularly interesting question which the manuscript does not address or even raise at all: Actually do the data tell us or suggest anything, which is the precursor (iodine source) for the formation of iodocarbons – iodide or iodate?

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This is indeed an interesting question, however, we think it is not possible to answer this question based on the results and experimental set up chosen for this study. We measured the iodocarbons in the gas phase and it is obvious that they are released from the different algae solutions. The emission rates of iodocarbons measured for the background sample suggests that iodocarbons were already present in the seawater which was used to prepare the media to grow the diatoms. The emissions rate of iodocarbons in the diatom samples are elevated compared to the background, therefore we assume that diatoms are capable of producing iodomethanes, however, we cannot judge based on our experiments if they use iodate or iodide. We know that iodide is favoured for the biotic (SAM, haloperoxidase) and abiotic (photochemical formation with DOM (Moore and Zafirou, 1994)) formation reactions, since iodine has the same oxidation state in iodide as it has in iodocarbons (-1), however, whether the micro algae reduce iodate to iodide to form the halocarbons or if they us the iodide directly which is already present in the water cannot be resolved. What we can assume is the discrepancy in the emission of iodocarbons and I2. The iodocarbon emissions are not related to the formation of I2 at the air/water interface, since the formation of iodocarbons is not different for high and low ozone conditions. This conclusion was added to the I2 emission section in the manuscript.

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 14575, 2014.