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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Coastal measurements of short-lived reactive iodocarbons and bromocarbons at Roscoff, Brittany during the RHaMBLe campaign" *by* C. E. Jones et al.

Anonymous Referee #1

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Comments

The paper "Coastal measurements of short-lived reactive iodocarbons and bromocarbons at Roscoff, Brittany during the RHaMBLe campaign" represents a good contribution of new data to scientific progress within the scope of Atmospheric Chemistry and Physics. The scientific approach and the applied methods are valid. The results are overall discussed in an appropriate and balanced way. The manuscript addresses a fairly complex data set of 8 compounds, and discusses the in situ findings based on isolated considerations of complex influencing factors, which can be generally agreed. However it is very hard to follow the discussion and identify the new results and main

points of the paper. A lot of the relevant information is buried in the text. I understand that it is a difficult situation to write the complex story satisfactorily for the reader, but for readability and increasing the relevance of the paper, the authors are asked to restructure the results and discussion section of their paper (mainly 3.1 and 3.2). One suggestion would be to structure the discussion according to conditions and processes which all have been shown to have an influence on the in situ concentrations. Processes should be ordered from general to special, while currently the authors start with special and got more general and jump between compounds and factors. Processes and conditions, which influence the atmospheric concentrations, mentioned in the text are sources, atmospheric lifetimes, light levels, wind direction, topography, tide (normal), tide (influenced by wind direction), macroalgae (biomass) , macro algae (speciation). The processes are not in an appropriate order and the compounds are mixed. sometimes the authors describe this compound while two lines later other compounds and other processes are mentioned, which leaves the reader really puzzled about the significance of the discussed processes for which compound. Already the first paragraph, where the concentrations of six different compounds at five different sites are compared is already too much effort, while the question after reading remains, where is the point of this numeration., while often the discussion reads like a numeration of observations, without firm conclusions. I would strongly suggest to strengthen the manuscript and improve its readability, by elaborating the main points of the discussion and identify one or two key messages of the paper and discuss them for all compounds. Meaning - not order the discussion phenomenological by describing what could be the cause for this observation or for that, but discuss, e.g. which is the influence of the process, in which parameters (compounds) can this be seen. This is one suggestion, however it can also be done for the individual compounds, but then all relevant processes which could have an influence, respectively have been shown to influence the compounds distribution should be discussed. Possibly there can groups of compounds be identified, which undergo the same influencing factors. In addition Roscoff should be discussed first (figures are only and all for Roscoff), before the special conditions of Mace Head are

added. Despite all my concerns and suggestions it could be that I misunderstood the intention of the paper, and the authors intend to say something else with their paper. But even then I would strongly recommend to identify the main points and new findings and key messages and state them clearly in the results and discussion section and the conclusions. One technical addition: there have been a couple of interpretations, based on the compounds lifetime, but they do not appear for all compounds in the text, and some are sprinkled over the text. I recommend to add a table and concentrate the interpretations related to the compounds life times. In general abstract, introduction and method section are good, in addition to the recommended restructuring and refocusing of the paper I add and include some points:

P17128 line 15: considerably less (needs citation)

P17130 L23-P17131 L15; too much comparisons and detail. If the authors intend something with this paragraph they should clearly state what can be seen from this, otherwise the text should be reduced and focused on Mace Head and Roscoff, possibly Breton. It is not obvious, why there should be comparable or even identical concentrations at Dagebüll or even at Spitzbergen-or clarify the scope of this message.

P17131 L16-L19: It is not obvious why sites should only be compared when they have comparable concentrations in the atmosphere- there could be reasons that concentrations in the atmosphere are not comparable. And of course is a good site description very helpful, but not a scientific argument. The comparison can be done but it doesn't need this kind of reasoning.

P17131 L21-L27: There is a lot of detail, for the main point made there (However this could also be due to different wind directions and investigations during different tides): The higher atmospheric maximum concentrations of the short-lived iodocarbons at Mace Head are due to a bigger seaweed source, since sampling sites at Roscoff and Mace Head where in the same distance and height from the seaweed beds (5 m height and 20-25m distance from high tide).

To make it completely correct the authors should exclude different wind directions or tidal conditions between Mace Head and Roscoff as cause for the larger maximum iodocarbon concentrations first and make completely clear that only the seaweed distribution can make the difference and must be the source.

This could possibly be done by resorting the text accordingly. In addition there are only plots from Roscoff. Roscoffs influencing factors should be discussed first. If Roscoff and Mace Head are compared and arguments and obvious possible differences (sampling bias) are omitted the measurement conditions (e.g. Figure 6 could be shown for both sites) are not identical and shouldn't thus yield the same results, should they? Or possibly discuss only Roscoff conditions first – influence of tidal height influence of wind direction on concentrations and then only compare the left over differences between the two sites

P 17131 L27- P 17132 L 21: Main point here is (?): Laminaria digitata, known to be a prolific CH2I2 producer [] is more abundant and closer to the shore at Mace Head () than at Roscoff , which could cause the higher atmospheric CH2I2 levels. (Any other possibilities?). What is the point here to mention Fucus and the other Laminariales? Please clarify.

P17132 L23- P 17133 L5: Main point here is (?): The steep shoreline at Mace Heads favors the conditions for emissions of iodocarbons from Laminaria, since they are exposed to the air by low tide (subjected to oxidative stress), while the shallower shoreline at Roscoff favors the growth of Fucus, which . . .??? (Do they have different emission patterns or what is the point here?)

P 17131 L27 - P 17133 L5: What does this section show? What does it mean for the other compounds (Please clarify your main points, erase non necessary arguments and possibly add more information for other compounds) Since the arguments are not only valid for CH2I2, e.g. Do theses findings have any influence e.g. on CHBr3- or is this meant just as an example for ??)

P17133 L2- P 17133 L5: What is the point here? Please clarify relevance?

P 17133 L6-P17134 L 8: Correlation should be treated in a separate section, which could be termed as indications for common and different sources of brominated and iodinated compounds- and all compounds should be correlated (table?)- and then only some significant ones or ones with extra and elaborated meanings should be shown in a figure. It is not clear whether it is spoken about atmosphere or water in the last section (bromocarbons)

P17134 L 10 - P17135 L 3 The tidal influence should be treated as one of the first processes-possibly after wind direction.

The first lines should be reordered, reading:

Table 2 shows the ratios of mean low tide to mean high tide halocarbon concentrations. For these purposes low tide concentrations were taken to be those measured made while the tide height was <4.25m and high tide concentrations are the concentrations observed while the tide height was >6.5 m. A statistical t-test was carried out on the high tide and low tide data sub-sets for each halocarbon to determine whether there were significant differences in their concentrations during the two periods (see Table 2). The only halocarbons which showed statistically significant elevated ambient air concentrations during periods of low tide relative to high tide were those with the shortest tropospheric lifetimes, i.e. CH2I2 and CH2IBr. Figure 4 shows the CH2I2 and CH2IBr concentrations in air during the RHaMBLe campaign overlaid with the tide height. On a number of occasions there was a significant increase in the CH2IBr (and to a lesser extent CH2I2) concentration which coincided with low tide i.e. when the surface footprint around the site contained the most exposed macroalgae. The most significant difference between low tide and high tide concentrations of these dihalomethanes occurred during the period from the 5–14 September, when the site was subjected to easterly winds over the channel between Roscoff and Ile de Batz (see Figs. 4 and 6). This period includes the spring tides on the 9 and 10 September when the inter-tidal range

was greatest, and exposed the highest seaweed biomass.

P17135 L 3 - P17136 L 7: In the next lines wind speed, direction and tidal height influences on halocarbon atmospheric concentrations are lumped together. This section is not readable, since site specialties, related to wind direction and tidal heights related to time are presented with insufficient focus on the actual points of this chapter. Also here is a source mechanism included- which refers to light levels- which does not seem to belong here-or does it- then please clarify the intention of the chapter? Other source mechanisms are buried in other chapters.(correlations) -also the last sentence L5-L7 should be underlined with correlations. (see above)

P 17136 L15: which site?

Reordered: During the 11 and 25 September a limited number of seawater samples were analyzed 10 for halocarbons, alongside the ambient air measurements. Samples were taken from a range of locations between the site and Ile de Batz, at a range of tide heights. Theobserved halocarbon concentrations are summarized in Table 3. The seawater concentrations at Roscoff (typically a few pmoldm$-$3 of most halocarbons and up to several hundred pmoldm$-$3 CHBr3) were comparable with other coastal water measurements of these gases (Klick, 1992; Carpenter and Liss, 2000; Carpenter et al., 2000). All halocarbons exhibited elevated concentrations in seawater during low tide compared to high tide and, with the exception of CH3I, the highest concentrations were consistently observed in water directly over kelp beds approximately mid-way between the site and the island, a region characterized by the presence of the seaweeds Laminaria digitata, Laminaria saccharina and Laminaria ochroleuca (McFiggans et al., 2009). Conversely, seawater closer to the site and to the southern shore of Ile de Batz contained relatively lower levels of halocarbons. Figure 8 shows correlations between the seawater concentrations of several bromocarbons and iodocarbons. CHBr3 and CH2Br2 are exceptionally well correlated,supporting the theory of a common source for these gases. The ratio of CH2Br2 to CHBr3 in seawater is not dissimilar to the slope of 0.09 determined by Carpenter and Liss (2000) for higher concentrations of these

bromocarbons (slope=0.063, see Fig. 8).CH2I2 and CH2IBr were less well correlated in seawater than in air (R2=0.68, and at lower concentrations there was no strong relationship at all), however the correlation observed between these dihalomethanes broadly supports the hypothesis of related emission rates for these gases. CH2ICl in seawater was found to correlate well with both iodocarbons and bromocarbons, in particular CH2IBr (R2=0.87) and C2H5I (an apparent polynomial relationship with R2=0.95). Incubation studies have demonstrated that while Laminaria digitata appears to be the most prolific producer of CH2I2 and CH2IBr, Laminaria saccharina produces the highest concentrations of both C2H5I and CH2ICl (Carpenter et al., 2000). [Does this support the correlation-what does it means for CH2CLI especially the statement about Lamniaria digitata?] The apparent correlation between C2H5I and CH2ICl in seawater implies that these gases may possess a common source in coastal waters, although these gases were not well correlated within the MBL. This missing correlation could potentially be explained by differences in their gas phase photolytic lifetimes [please add lifetimes in table see above]

P 17138 L4, L14: reference to table of photolysis rates needed

P 17138 L4, L20-L28: Based on these findings a calculation, based on some assumptions could be performed as well.

P 17139: The conclusion section should be rewritten, possibly refocused, depending on the findings after restructuring of the chapters 3.1 and 3.2.

To summarize my suggestions: The results and discussion section should be restructured and refocused – first discuss processes individual for Roscoff (figures are only for Roscoff) then compare Mace Head and Roscoff differences (seaweed exposure and taxonomy), then address sources. If the authors feel that this goes beyond or besides the scope of this paper, they should address the scope more concisely in their results and discussion section, and focus their interpretations accordingly. The suggestions are for increasing the significance of the paper by elaborating the relevant scientific

question, the presentation of their novel ideas and data and the achievement of substantial conclusions and interpretations by refocusing on the main points and some key messages of the paper, which are already partly addressed in the abstract and also partly the conclusion but are lost and buried in the results and discussion section.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 17125, 2009.