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Interactive comment on “A halocarbon survey from a seagrass dominated subtropical lagoon, Ria Formosa (Portugal): flux pattern and isotopic composition” by I. Weinberg

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We are grateful to the anonymous Reviewer #3 for the valuable comments on our manuskript. The suggestions made will surely improve the paper. In some cases there are overlaps with the comments of other reviewer's which is stated accordingly in our answers.

I suggest removing the seasonal dependence in section “4.2 Flux pattern from seagrass meadows”. Sampling in April in 2012 and in July/August in 2011 (25 days) is not enough two discuss seasonal changes. I like the other points you raise in this section like diurnal cycles, tidal effects, temperature dependence or flux dependence on solar

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radiation, so maybe you can restructure this section.

We understand the concerns regarding the seasonal dependence section. It is well known from other plant-based systems such as coastal salt marshes that the strength of halocarbon emissions depends on the season (e.g. Blei et al .2010, Biogeosciences, 7, 3657–3668; Cox et al. 2004, Atm. Env. 38, 3839–3852). Since this is the first detailed study on halocarbon emissions from seagrass meadows and we could derive indications for a seasonal dependence from our data, we prefer to not remove it completely from the manuskript. However, we considered the concerns by making now a more cautious statement in the final manuskript. (See also answers to Rev#1)

Specific Comments:

The abstract is a comprehensive summary of the paper. If you remove the seasonal dependence of halocarbon fluxes in section 4.2, you should remove it here too.

This point is not mentioned in the abstract.

The expression in line 20 on page 10606 “a significant contribution of the water column to the atmospheric CH₃Br” seems a bit strange to me. The water column cannot emit halocarbons to the atmosphere. Emissions take place at the water surface, maybe you can change this sentence to clarify what you mean.

We clarified the sentence. It is now: “ This suggests a significant contribution from the water phase on the atmospheric CH₃Br in the lagoon.”

I like the precise introduction and the material and method section and have only one comment: You explain the extraction efficiency of CHBr₃ clearly but when you discuss the results you do not mention that it is an underestimate. Maybe you can recall this fact in the result section again. A brief comment is now given in the results section. “Due to the low purge efficiency of CHBr₃ during high tide measurements, the fluxes determined with the submersible chamber may be underestimated by 30% to 50% for this compound”.

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The result section is an extensive list of air mixing ratios measured, fluxes calculated and results of stable isotope analysis in water samples. Although the descriptions are good in this whole section the authors might think about using a different way of showing results than tables. (Table2 could be a column chart, maybe on a map?) This is just a thought not a mandatory change in the paper. Actually, we thought about to merge table 2 (results water sampling, transect) and Figure 1 (Map of the lagoon). But in our opinion, the bundle of information (isotopic values and water concentration for each of the four compounds) would overload the figure and decrease the readability.

I would like a different start for the Discussion section; “Despite the short residence time. . .” is not a nice start. Paragraph “4.1 Dissolved halocarbons “would benefit if you start with the comparison (L21) and add lines 14-20 at the end of this paragraph.

We rearranged this section. It now starts with line 21 (P10619) to line 14 (P10620) and is followed by lines 14 to 20 (P10619) and the conclusion of this section (line 15 and 16, P10620)

The second paragraph “4.2 Flux pattern. . .” should be changed (as highlighted above). It is impossible to investigate seasonal behavior with the limited measurements.

This is modified as mentioned above.

Maybe you can add the discussion about atmospheric lifetimes of the different halocarbons in the part (i) diurnal variations? We did not discuss the atmospheric lifetime in terms of seasonality and/or diurnal variations. Unfortunately, we cannot get the point.

In “(ii) Tidal effects” you discuss the primary productivity; maybe you can add a sentence to the production mechanism of halocarbons and its connection to primary productivity.

We added the sentence (in bold): “Nevertheless, in accordance with our results from halocarbon measurements we also observed higher primary productivity by increased CO₂ uptake during submerged conditions (Bahlmann et al., 2014). Therefore, the

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higher productivity may reflect higher enzymatic activity (e.g. methyltransferases) within the organisms of the seagrass community, by which monohalomethanes are presumably formed. “

In paragraph “4.3 . . .an isotopic perspective” only some technical comments need to be included. done

Paragraph 4.4 is nicely written and I like the caution you use when extrapolating your measurements to global source strengths. Thanks.

The conclusions at the end are reasonably drawn and no changes need to be done in my opinion. I like the outlook section at the very end of the conclusion paragraph. Thanks.

Table1: Can you give the air mixing ratios as mean and range in brackets ” mean (min-max)” as you do it for the water concentrations?

We adjusted the table and give mean and ranges for all presented data in this table (as also wished by Reviewer 2).

Table2: If you like to give the sampling time maybe CET would be better. Maybe you think about changing this table to some other graphic (column chart, plot the concentrations as column on a map etc. . .) We changed the time to CET. As mentioned above, we prefer to stay with the table as it is.

Figure 2: Can you give variations of the flux as error bars? done

Figure3: I cannot read this figure at all. If you want people to read it you have to enlarge it at least twice the size it has now. Maybe you can shorten the description by adding the published date you adopted the values from to a table inside the graph.

This might be an error during formatting since the original figures (one plot per compound) were of very good quality. We however checked the figures and took care on the readability.

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Technical Comments:

P10606L7: Change “..seagrass patches were air exposed and submerged. . .” to “seagrass patches were either air exposed or submerged. . .” done

P10606L10: Change “Furthermore, at least” to “Furthermore, during the. . .” done

P10608L1: Please explain in more detail “most productive ecosystem”

The sentence is now: “With a net primary production of 1200 g C m⁻² yr⁻¹ seagrass meadows are one of the most productive ecosystems with a similar global abundance as mangroves and salt marshes (Duarte et al., 2005).”

P10609L9: which unit for salinity? ppt ? We prefer to use PSU. This is added to the manuskript

P10610 L3-L23: Please state the footprint/surface area of the flux chamber. done.

P10611L2: can you give coverage also as area in m²? During both sampling campaigns the sampled seagrass meadow was very densed (>95%). Therefore, we assumed that the chamber area is equivalent to the seagrass area. We don't think that providing the coverage area in m² would improve the manuscript.

P10611L7: Is Praia de Faro upwind or downwind from the other sampling locations? It is the upwind site. This information is added in the manuskript.

P10611L14: How do you avoid air and sediment intrusions? The water was sampled with the bottle opening in the direction of the current, about 30 cm to the ground in order to minimize sediment instrusions.

P10612L1-24: Can you state a limit of detection for the method used? The analytical limit of detection was 0.3 ppt for the halocarbons. Now stated in the manuskript in the Measurement and quantification section.

P10615L23: CH3I is smaller at sampling points 6 and 7 compared to sampling point 3.

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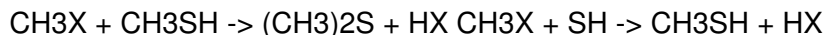


In lines 20-21 on page 10615 we already stated that the increased water concentrations of CH₃Cl and CH₃Br was not observed for CH₃I.

P10616L15-L19 and P10617L15-L18: Maybe you can provide correlation scatter plots in the supplement? The scatter plots are now provided in the supplement.

P10623 L7: Is physiological stress higher during the change in water level or when the seagrass is exposed over a longer time to the oxidative atmosphere? From several macroalgae species it is known that they emit higher quantities of halogenated compounds under oxidative stress conditions (Pedersén et al. 1996, Sci. Mar., 60, 257-263) such as air exposure at coastlines (Carpenter et al. 1999, J. Geophys. Res, 104, 1679-1689). However, to the best of our knowledge, for seagrass meadows nothing is known whether oxidative stress and/or physiological stress reactions will result in enhanced emissions of halocarbons. Our statement was rather a assumption based on our observation and was stated cautious.

P10623L13: Please describe the degradation mechanism you propose. The proposed mechanisms are based on the work of (Barbash and Reinhard ,1989, Reactivity of sulfur Nucleophiles toward halogenated organic compounds in natural waters, in Biogenic Sulfur in the Environment, edited by Saltzman, E., Cooper, W .J., 101-137, American Chemical Society, Washington D .C.). Potential reactions include but are not limited to:



We feel that a full consideration in the manuskript would be too exhaustive. Therefore we would like to only reference the mentioned publication.

P10624L19-L23: You can delete this if you do not use a seasonal dependence anymore. Will would like to keep this sentence (as mentioned above)

P10625L27: which degradation processes? We assumed that CH₃Br is degraded in the sediments as e.g. reported by Miller et al. (2004) by methylotrophic bacteria (Miller et al. 2004: Geochim. Cosmochim. Ac., 68, 3271-3283) The remaining portion of

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CH₃Br, enriched in ¹³C, is then emitted into the atmosphere. The sentence in lines 27-28 (page 10625) has been changed: “This shift can most likely be explained by simultaneous microbial degradation processes at the sediment surfaces.”

P10626L7: it is hard for me to understand how the water column influences the atmosphere? Maybe you mean emissions from the water surface? Clarified in the manuskript. It is now: “Therefore, it is most likely that the atmospheric CH₃Br is strongly influenced by CH₃Br emissions from the surface waters ($\delta^{13}\text{C}$ values in water phase (summer): $-23\pm 3\%$.”

P10626L13: Transhalogenation, exchanging Cl with Br, would also influence the isotopic ratios of ¹³CHCl and ¹³CHBr. Is there any information about isotopic fractionation for this process? Yes, King and Saltzman (1997) reported fractionation factors for hydrolysis + transhalogenation of about $69\pm 8\%$ (King and Saltzman 1997: J. Geophys. Res.-Oceans, 102, 18715-18721). In the current manuscript we referenced this paper and stated: “Accordingly, aqueous CH₃Br appears to become rapidly degraded by biotic/abiotic processes such as hydrolysis, transhalogenation, and microbial degradation with strong isotopic fractionation (King and Saltzman, 1997). In this context we will additionally reference the above mentioned Miller et al. 2004 publication. The transhalogenation of chloromethane (Reaction with Br- and I-) is assigned with a similar large isotopic fractionation (Mattson et al. 2005), With the reaction rate constants being fourfold smaller (Baesman et al, 2005) and the much smaller bromide concentrations in seawater these reactions can be assumed to be negligible in seawater. These decomposition mechanisms are temperature dependent with increasing destruction with increasing seawater temperature. This is most likely the reason why the $\delta^{13}\text{C}$ values in the lagoon waters in summer are more enriched in ¹³C as those from the spring campaign.

Mattson, O., Dybala-Defratyka, A., Rostkowski, M., Paneth, P. and Westaway, K.C.: A Theoretical Investigation of α -Carbon Kinetic Isotope Effects and Their Relationship to the Transition-State Structure of SN₂ Reactions, J. Org. Chem., 70, 4022-4027, 2005

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Baesman S.H., Miller L.G.: Laboratory Determination of the Carbon Kinetic Isotope Effects (KIEs) for Reactions of Methyl Halides with Various Nucleophiles in Solution, *Journal of Atmospheric Chemistry* 52: 203–219, DOI: 10.1007/s10874-005-1904-0, 2005

P10628L14: which season was the campaign in Northern Germany? The season was late summer. This is added in the manuskript

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