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 #2 for the helpful comments on our manuscript. The suggestions made will surely improve the paper. In some cases there are overlaps with the comments of other reviewers which is accordingly stated in our answers. I miss the discussion of the low recovery rate of bromoform in the discussion of the results. The CHBr3 emissions from seagrass meadows appear to be very low, is how much of this is due to the method? Furthermore, the authors mention that they rely on assumptions in the calculation of sea-air gas-exchange (e.g. in the kw parametrization). What’s the impact of the chosen mean water current velocity on the...
fluxes (how large are variations in the current velocity usually)?

The CHBr3 concentration in the water samples was corrected by the purge efficiency prior to the sea-to-air flux calculations as stated in the manuscript. However, we mistakenly missed to state clearly that the underestimation of CHBr3 fluxes relates only to the fluxes determined by the submersible chamber system (under submerged conditions). We clarified the sentence (10610, L21-23) into “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”.

Furthermore, as also wished by Reviewer#3, we recalled the statement regarding the under-estimate in the results section. “Due to the low purge efficiency of CHBr3 during high tide measurements, the fluxes determined with the submersible chamber are underestimated for this compound”. Regarding the low CHBr3 fluxes, we feel that our fluxes are surprisingly high for a vascular plant ecosystem. The biogenic formation of PHMs proceeds via an halo peroxidases-catalyzed halogenation of organic substrates and to the best of our knowledge haloperoxidases have not been reported from any vascular plants. Thus it is assumed that CHBr3 in the water phase mostly derives from either coastal macroalgae beds or phytoplanktonic communities. With our study from seagrass meadows we presented first evidence that also other (coastal) CHBr3 sources exist. Secondly, we would like to mention that the CHBr3 fluxes we determined from seagrass meadows are in the same range as in other studies. For example, Carpenter et al. (2009, Atm. Chem. Phys., 9, 1805-1816) reported CHBr3 fluxes from the coastal Atlantic being 5-13 nmol m² h⁻¹. (flux ranges from seagrass meadows: 1-8 nmol m² h⁻¹ in summer and 3.8 -23.8 nmol m² h⁻¹ in spring). We share the opinion that the parametrisation is a crucial step to determine the sea-air fluxes of trace gases. Due to the semi-diurnal tidal regime in the lagoon Ria Formosa strong bi-directive currents occur along the channels. The current velocity ranges from zero (during maximum water level) and about 60-90 cm s⁻¹ during maximum incoming and outgoing tide (Christina et al. 2008, ECASA study site report, Ria Formosa, Coastal
Lagoon Portugal). If we assume the maximum current velocity of 90 cm s\(^{-1}\), we would end up with 20-30\% higher CHBr\(_3\) fluxes in comparison to using the mean current velocity (24 cm s\(^{-1}\)). However, due to the strong variations of current velocities in the lagoon, we decided to apply the mean current velocity as a best estimate for the \(k_w\) parametrisation.

Detailed remarks

Abstract, (P10606 L25 ): Mb mention that on a global scale seagrass meadows seem to be rather insignificant emitters of CHBr\(_3\) and CH\(_3\)I on the global scale, as done in conclusion/discussion sections.

We revised the sentences at the end of the abstract. It is now: “This suggests a minor contribution from seagrass meadows to the global production of CH\(_3\)Cl and CH\(_3\)Br with about 0.1 \% and 0.7 \%, respectively. In comparison to the known marine sources for CH\(_3\)I and CHBr\(_3\), seagrass meadows are rather small sources.”

P10607 L6 "Furthermore, CH\(_3\)I may further-contribute to the formation of aerosols .." I think, it is now believed that molecular iodine is the precursor of iodine-mediated ultrafine particles, rather than organic iodine-containing compounds like CH\(_3\)I (see e.g. Saiz-Lopez, A.; Plane, J. M. C.; Baker, A. R.; Carpenter, L. J.; et al. Atmospheric Chemistry of Iodine, Chemical Reviews, 2012, 112, 1773-1804). We skipped the sentence concerning the aerosol formation by CH\(_3\)I as precursor compound from the introductive section.

P10613 You should mention how you get from the mixing ratio to the atmospheric concentration needed in the flux calculation (F2).

The conversion of mixing ratios to pmol L\(^{-1}\) was done using temperature data and the respective molar volume of the ambient air. We clarified this in the manuskipt.

P10615 L5-15 correlation coefficients: I suggest to drop the correlation analysis. Your sample size is too small to give reliable correlation coefficients (the standard error is
relatively high). With a sample size of \( n=9 \) (\( n=10 \)) the standard error (\( SE=p(1-r^2) \frac{n-2}{p(n-2)} \)) of the correlation coefficients would be approx. \( r^2=0.71, 0.2 \) \( SE=0.2, 0.3 \).

We agree with the reviewers’ opinion and skipped the correlation analysis for the water samples.

P10629-10630 The importance of e.g. seagrasses as halocarbon emitters at the global can not be judged only by the absolute amount of substance emitted. It should be noted that vertical transfer in the atmosphere is spatially inhomogeneous and co-location of of vertical motion in air with halocarbon emissions may make low global overall emissions from seagrass matter for e.g. ozone depletion.

We fully agree with the reviewer’s statement. In fact, seagrass meadows have their highest abundance in subtropical and tropical areas where the most effective upward streams occur. We revised this statement. It is now: “On a global scale, seagrass meadows are rather a minor source for halocarbons but will have a certain imprint on the local and regional budgets. This holds in particular true for subtropical and tropical coastlines where seagrass meadows belong to the most abundant ecosystems. In these regions, where strong vertical motions occur, seagrass meadows may be significant contributors to deliver halocarbons to the stratosphere.”

Table 1 caption: drop "General overview". Why are there means and medians for the MR in air and only mean or median (which? specify) for the water concentrations in the table?

According the suggestion of Reviewer 1, we renamed the heading and changed it to “Summary” except of “General overview”. We did not present a median for air mixing ratios (Praia de Faro) and water concentrations, since the sample size is limited (\( n=8 \) – 10). However, we adjusted the table according to Reviewer#3 and give mean and ranges for all presented data in this table.

Fig 3 : Consider arranging the subplots horizontally. We prefer to leave the plots in the
current form. In our opinion this is appropriate.

SI P1: "The analytic procedure is based on those of Bahlmann et al. (2011):"mixture of singular (procedure) and plural (those). We have changed those to that.

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