Response to Reviewer #1 comments

We are grateful to the anonymous Reviewer #1 for the helpful 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 accordingly stated in our answers.

In preparing a revised paper, the authors should include citation to, and data from,the recent relevant publication in Biogeosciences Discussion by Rhew et al. (Large methyl halide emissions from south Texas salt marshes, Biogeosciences Discuss., 11, 9451-9470, 2014) which provides additional data on methyl halide emissions from saltmarshes for the current authors' section on comparing emissions from coastal regions globally. In particular, the recent Rhew et al. work provides further evidence for different magnitudes of methyl halide emissions between temperature and tropical salt marshes.

We fully agree with this suggestion. At the time we prepared our manuskript the latest Rhew et al. study (2014) concerning halocarbon emissions from salt marshes was not available. We now cite the new findings of Rhew et al. in the final manuskript.

Section 2:2. Please provide the dimensions of the chambers, particularly the crosssectional area of the base, and the volume of the enclosure.

The dimensions of the chamber are provided in the final manuscript.
The flux chamber (quartz glass) has an surface area of 0.1 m^2 (7 L enclosure volume). The submersible flux chamber has an surface area of 0.037m^2 (8 L enclosure volume).

P10612, L18: It is not clear what is meant by the phrasing "We observed only occasional blanks for. . .". What is meant by observing a blank? Is what is meant that values above LOD were only occasionally observed for blank samples? Please rewrite to make clear.

The sentence is clarified in the final manuskript. It is now: "The occasionally detected blanks of CH_3Cl and CH_3Br from these determinations were ≤3% to the "real" samples taken from the seagrass meadows during sampling campaigns.

P10613, L15: Equation (2) does not appear to be consistent with the units given for its variables within the text. If the gas exchange velocity used is in units of cm h-1 then there is a factor 100 discrepancy with obtaining a flux, F, value in nmol m-2 h-1.

We are thankful for this comment. The unit is m h^{-1}. This will be corrected in the manuskript.

Section 3.2, and corresponding tables of data: Are 3 significant figures justified for single flux values that demarcate the lower or upper end of a range of individual measurements? Is the

precision in a single measurement that good; I doubt it. (An additional significant figure for calculated summary mean or median values is justifiable.)

Thank you for this advice. We adopted the suggestion and revised the data concerning the significant figures in the mentioned section.

Section 4.2(iii) seasonal trends: The authors should be cautious about statements of seasonal trends given that they have measurements for only a few days in one spring and a few days in one summer.

We agree with this opinion and are more conservative with our statements concerning the seasonal dependence in the final manuskript.
(P10624, lines 18-20) "Overall, these differences observed in periods of air exposure between spring and summer might suggest a certain seasonality in seagrass meadows."
Accordingly, we already stated at the end of the section (P10624, lines 20-22): "However, further studies covering the entire seasoning are necessary to unravel the annual halocarbon emissions from seagrass meadows."

Technical:

P10607, L8: Replace "were" with "have been". done

P10607, L12: Replace "out-weighted" with "unbalanced," (note the addition of a comma also).

done

P10607, L24: Replace "being vital" with "as being important". done

P10608, L2-3: The whole sentence starting "They cover. . .." does not make sense and needs rephrasing. There should be a noun after "intertidal and subtidal". Also it is not clear what the current phrasing "as well in. . ..as in" is comparing what to what.

The sentence is accordingly rephrased.

P10608, L5: Insert "yet" before "sufficiently" and delete the ", yet" from the end of this sentence.

done

P10608, L18: Replace "in" with "into". done

P10609, L10: Insert a noun after "intertidal", e.g. "area"? done

P10609, L12: Insert commas after "Further" and "abundant". done

P10609, L14: Again, insert a noun after "subtidal", e.g. "areas"? done

P10609, L18: Capital "M" for "Marine". done

P10610, L16: Delete the comma after "both". done

P10610, L19: Replace "was" with "were". done

P10611, L3: Insert a noun after "intertidal"; e.g. "area" or "region"? done

P10612, L2: Capital "P" for "Peltier". done

P10613, L4: Delete "commonly", it is not clear what this word is intended to convey here, and is surely superfluous anyway. done

P10613, L11: Insert "of" after "calculation". done

P10613, L14: Delete "common". done

P10613, L24: Replace "were" with "where". done

P10613, L24: Replace "further" with "additionally". done

P10613, L25: Delete the comma after "thus". done

P10615, L5: The word "Punctual" is not the correct word to use here. However, it is not clear what meaning the authors do want to convey here. They should check again with a dictionary and/or thesaurus. punctual was replaced by "discrete"

P10615, L7-L13: There are a number of instances in this block of text where the value given for the lower or upper end of a flux range is discrepant with the corresponding value given in Table 1. For example, in L7 a value of 158 pmol L-1 is quoted in the text for the lower end of the range whilst the entry in Table 1 specifies this value to be 123 pmol L-1. The authors should recheck all quoted values and amend as required.

all quoted values are rechecked and corrected in the manuskript.

P10615, L11: Insert "=" before "0.20".
As suggested by Reviewer#2, we decided to skip the results from the correlation analysis (water samples) due to the small sample size.

P10616, L15: Insert "=" before "0.55".
As suggested by Reviewer#2, we decided to skip the results from the correlation analysis (water samples) due to the small sample size.

P10616, L27: Delete the comma after "both". done

P10617, L23: Rewrite word as "occasionally". done.

P10617, L24: Insert "the" before "summer". done

P10619, L1: Replace "if" with "when". done

P10619, L5: Add a comma after "were" and another comma after the second numerical value quoted. Also, add the part per thousand 'unit' after each of the values quoted. done

P10620, L8: Delete "Accordingly," and start the sentence at "The area. . ." done

P10620, L10: Insert "be" after "to" done

P10620, L19: Replace "like" with "same". done

P10620, L22: Replace "were" with "where". done

P10621, L2: Replace "influence on" with "association with" (a correlation demonstrates association, not causation). done

P10621, L22: Insert "of CH3I" after "correlations". done

P10621, L27: This sentence does not make clear that the subject is emissions of methyl halide fluxes. Rephrase the latter part of the sentence something along the lines of ". . .the main environmental association in salt marsh emissions of CH3Cl and CH3Br was with ambient temperature rather than light." rephrased

P10622, L3: Insert "a" before "sink". done

P10622, L6: Insert commas after "while" and "general". done

P10622, L23: Delete comma after "Obviously". done

P10623, L2: Delete "an". done

P10623, L15: Replace "as during" with "compared with". done

P10623, L15: Replace "inevitable prove" with "proof". done

P10623, L24: Replace "went along" with "was in parallel". The whole sentence was removed, because we skipped the correlation analysis of halocarbons from water samples (as mentioned above)

P10623, L29: Replace "seasoning of" with "seasonal trend in". done

P10624, L18: Delete comma after "thus". done

P10625, L24: Delete "are". done

P10625, L24; Replace "as" with "compared with". done

P10625, L29: Replace "accompanied" with "accompanying". done

P10626, L17: Replace "as" with "compared with". done

P10626, L21: Insert "to" after "extent". done

P10626, L26: Replace "demanding" with "difficult" and delete "yet" from the end of this sentence.
done

P10627, L20: Replace "as" with "than". done

P10629, L20: Lower case "s" on "southern". done

P10630, L3: Remove hyphen from "species dependent". done

P10630, L6: Insert comma after "sediments". done

P10630, L7: Delete comma after "both" and replace "to act" with "of acting". done

P10639, L1 of caption of Table 1: Replace "General overview" with "Summary". done

P10641, caption of Table 3: State in the caption what is represented by use of bold font for some of the values in the table. done

P10643, caption of Table 5: State in the caption what is represented by use of bold font for some of the values in the table. Done

Response to Reviewer #2 comments

We are grateful to the anonymous Reviewer #2 for the helpful comments on our manuskript. 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 $CHBr_3$ concentration in the water samples was corrceted by the purge efficiency prior to the sea-to-air flux calculations as stated in the manuscript. However, we mistakingly missed to state clearly that the underestimation of $CHBr_3$ fluxes relates only to the fluxes determined by the submergible chamber system (under submerged conditions). We clarified the sentence (10610, L21-23) into "Due to the low purge efficiency of $CHBr_3$ during high tide measurements, the fluxes determined with the submergible 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 $CHBr_3$ during high tide measurements, the fluxes determined with the submergible chamber are underestimated for this compound".

Regarding the low $CHBr_3$ 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 $CHBr_3$ 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) $CHBr_3$ sources exist. Secondly, we would like to mention that the $CHBr_3$ 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 $CHBr_3$ fluxes from the coastal Atlantic being 5-13 nmol m^2 h^{-1}. (flux ranges from seagrass meadows: 1-8 nmol m^2 h^{-1} in summer and 3.8 -23.8 nmol m^2 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 CHBr3 and CH3I 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_3Cl and CH_3Br with about

0.1 % and 0.7 %, respectively. In comparison to the known marine sources for CH_3I and

$CHBr_3$, seagrass meadows are rather small sources."

P10607 L6 "Furthermore, CH3I 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 CH3I (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_3I as precorsor compund 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 manuskript.

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−r2) p(n−2)) of the correlation coefficients
would be approx. (r2=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 the conclusion of the manuscript with the following sentence (in bold):
"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.

Response to Reviewer #3 comments

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 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 CH_3Br 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 $CHBr_3$ during high tide measurements, the fluxes determined with the submergible chamber may be underestimated by 30% to 50% for this compound".

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.

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 saisonality and/or diurnal variations. Unfourtunately, 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 higher productivity may reflect higher enzymatic activity (e.g. methyltransferases) within the organisms of the seagrass community, by which monohalomethanes are presumably formed.** "*

1   *In paragraph "4.3 . . .an isotopic perspective" only some technical comments need to be*
2   *included.*
3
4   done
5
6   *Paragraph 4.4 is nicely written and I like the caution you use when extrapolating your*
7   *measurements to global source strengths.*
8
9   Thanks.
10
11
12 *The conclusions at the end are reasonably drawn and no changes need to be done in my*
13 *opinion. I like the outlook section at the very end of the conclusion paragraph.*
14
15 Thanks.
16
17
18 *Table1: Can you give the air mixing ratios as mean and range in brackets " mean (min-*
19 *max)" as you do it for the water concentrations?*
20
21 We adjusted the table and give mean and ranges for all presented data in this table (as also
22 wished by Reviewer 2).
23
24
25 *Table2: If you like to give the sampling time maybe CET would be better. Maybe you*
26 *think about changing this table to some other graphic (column chart, plot the concentrations*
27 *as column on a map etc. . .)*
28
29 We changed the time to CET. As mentioned above, we prefer to stay with the table as it is.
30
31
32 *Figure 2: Can you give variations of the flux as error bars?*
33
34 done
35
36
37 *Figure3: I cannot read this figure at all. If you want people to read it you have to enlarge it at*
38 *least twice the size it has now. Maybe you can shorten the description by adding the published*
39 *date you adopted the values from to a table inside the graph.*
40
41 This might be an error during formatting since the original figures (one plot per compound)
42 were of very good quality. We however checked the figures and took care on the readability.
43
44
45 *Technical Comments:*
46
47 *P10606L7: Change "..seagrass patches were air exposed and submerged. . ." to "seagrass*
48 *patches were either air exposed or submerged. . ."*
49   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 assumened 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.
In lines 20-21 on page 10615 we already stated that the increased water concentrations of CH_3Cl and CH_3Br was not observed for CH_3I.

P10616L15-L19 and P10617L15-L18: Maybe you can provide correlation scatter plots
in the supplement?
Is 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:

$CH_3X + CH_3SH \rightarrow (CH3)_2S + HX$
$CH_3X + SH \rightarrow CH_3SH + HX$
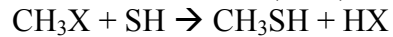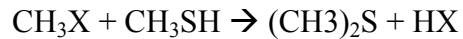
We feel that a full consideration in the manuskript would be too exhaustive. Therefore we would like to only reference the mentioned publication.

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 CH_3Br 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 CH_3Br, enriched in ^{13}C, 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 CH_3Br is strongly influenced by CH_3Br emissions from the surface waters ($\delta^{13}C$ values in water phase (summer): -23±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±8‰ (King and Saltzman 1997: J. Geophys. Res.-Oceans, 102, 18715-18721).
In the current manuscript we referenced this paper and stated: "Accordingly, aqueous CH_3Br 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 concentratios 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 $\delta^{13}C$ values in the lagoon waters in summer are more enriched in ^{13}C as those from the spring campaign.

Matsson, 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 S$_N$2 Reactions, *J. Org. Chem.*, *70*, 4022-4027, 2005

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

A halocarbon survey from a seagrass dominated subtropical lagoon, Ria Formosa (Portugal): Flux pattern and isotopic composition

Ingo Weinberg, Enno Bahlmann[*], Tim Eckhardt, Walter Michaelis, and Richard Seifert

University of Hamburg, Institute for Biogeochemistry and Marine Chemistry,

Bundesstraße 55, 20146 Hamburg, Germany

[*]corresponding author: enno.bahlmann@zmaw.de

                                 phone: +49-40-42838-5167

                                 fax: +49-40-42838-6347

Abstract

Here we report fluxes of chloromethane (CH_3Cl), bromomethane (CH_3Br), iodomethane (CH_3I), and bromoform ($CHBr_3$) from two sampling campaigns (summer and spring) in the seagrass dominated subtropical lagoon Ria Formosa, Portugal. Dynamic flux chamber measurements were performed when seagrass patches were either air-exposed or submerged. Overall, we observed highly variable fluxes from the seagrass meadows and attributed them to diurnal cycles, tidal effects, and the variety of possible sources and sinks in the seagrass meadows. Highest emissions with up to 130 nmol m^{-2} h^{-1} for CH_3Br were observed during tidal changes from air exposure to submergence and conversely. Furthermore, during the spring campaign, the emissions of halocarbons were significantly elevated during tidal inundation as compared to air exposure.

Accompanying water sampling during both campaigns revealed elevated concentrations of CH_3Cl and CH_3Br indicating productive sources within the lagoon. Stable carbon isotopes of halocarbons from the air and water phase along with source signatures were used to allocate the distinctive sources and sinks in the lagoon. Results suggest CH_3Cl rather originating from seagrass meadows and water column than from salt marshes. Aqueous and atmospheric CH_3Br was substantially enriched in ^{13}C in comparison to source signatures for seagrass

meadows and salt marshes. This suggests a significant contribution from the water phase on the atmospheric CH_3Br in the lagoon.

A rough global upscaling yields annual productions from seagrass meadows of 2.3-4.5 Gg yr^{-1}, 0.5-1.0 Gg yr^{-1}, 0.6-1.2 Gg yr^{-1}, and 1.9-3.7 Gg yr^{-1} for CH_3Cl, CH_3Br, CH_3I, and $CHBr_3$ respectively. This suggests a minor contribution from seagrass meadows to the global production of CH_3Cl and CH_3Br with about 0.1 % and 0.7 %, respectively. In comparison to the known marine sources for CH_3I and $CHBr_3$, seagrass meadows are rather small sources.

1   Introduction

The halocarbons chloromethane (CH_3Cl), bromomethane (CH_3Br), iodomethane (CH_3I), and bromoform ($CHBr_3$) are prominent precursors of reactive halogens which affect the oxidative capacity of the atmosphere and initiate stratospheric ozone destruction (Saiz-Lopez and von Glasow, 2012 and references therein). Therefore, during the last decades, the sources and sinks of these trace gases have been intensively studied.

For CH_3Cl, recent atmospheric budget calculations suggest that the known sinks can be balanced by large emissions from tropical terrestrial sources (Saito and Yokouchi, 2008; Xiao et al., 2010). Nevertheless, these calculations still incorporate large uncertainties. The atmospheric budget of CH_3Br remains still unbalanced, with the known sinks exceeding known sources by about 30% (Yvon-Lewis et al., 2009). The current emission estimates for CH_3I and $CHBr_3$ are assigned with even larger uncertainties (Bell et al., 2002 and reference therein; Quack and Wallace, 2003 and references therein).

Stable carbon isotopes of halocarbons have been applied to further elucidate their sources and sinks by using individual source signatures (Keppler et al., 2005 and references therein). While this was primarily done for CH_3Cl, first isotopic source signatures of naturally-produced CH_3Br were recently reported (Bill et al., 2002; Weinberg et al., 2013). Moreover, the biogeochemical cycling of halocarbons underlies various transformation processes which can be studied by the stable carbon isotope approach in addition to flux and/or concentration measurements.

Coastal zones are reported as being important source regions of halocarbons. In these salt water affected systems halocarbon producers comprise phytoplankton (Scarratt and Moore,

1998), macroalgae (Gschwend et al., 1985), salt marshes (Rhew et al., 2000), and mangroves (Manley et al., 2007).

With a net primary production of ~1200~~11~~ 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). They cover huge areas of the intertidal and subtidal zone in temperate and subtropical/tropical ̶regions. Thus, they may represent an additional source for halocarbons to the atmosphere which is not yet sufficiently studied. Seagrass meadows are highly diverse ecosystems with respect to potential halocarbon producers. Along with the seagrass itself, they comprise epiphytes such as microalgae and diatoms, and sediment reassembling microphytobenthos and bacteria communities. All these constituents of the benthic community have been generally reported to produce halocarbons (Amachi et al., 2001; Blei et al., 2010; Manley et al., 2006; Moore et al., 1996; Rhew et al., 2002; Tokarczyk and Moore, 1994; Urhahn, 2003). While first evidence for the release of halocarbons from seagrass was obtained by incubation experiments (Urhahn 2003), we could recently confirm this production potential in a field study of a temperate seagrass meadow in Northern Germany (Weinberg et al., 2013).

In order to refine these results we conducted two field campaigns in the subtropical lagoon Ria Formosa, Portugal in 2011 and 2012. Here we report the results of these campaigns comprising dynamic flux chamber measurements for halocarbons over seagrass meadows during air exposure and tidal inundation. Using the flux and isotopic data, we present first insights into the environmental controls of halocarbon dynamics within this ecosystem. To complement the chamber-based measurements, the results of a series of air and water samples for dissolved halocarbons and their isotopic composition from both campaigns are discussed. Finally, we compare seagrass meadows emission rates of halocarbons with those of other coastal sources and give a first rough estimation of the seagrass source strength on a global scale.

2   Materials and methods

2.1   Sampling site

The Ria Formosa, covering a surface area of 84 km^2, is a mesotidal lagoon at the South-eastern coast of the Algarve, Portugal (Fig. 1). It is separated from the Atlantic Ocean by a

series of barrier islands and two peninsulas. About 80% of the lagoon is intertidal with a semi-diurnal tidal regime and tidal ranges between 1.3 m during neap tides and 3.5 m during spring tides (Cabaço et al., 2012). Due to negligible inflow of fresh water and high exchange of water with the open Atlantic during each tidal cycle, the salinity within the lagoon is 35 to 36 PSU year round, except for periods of heavy rainfalls. About one-fourth of the intertidal area (13.04 km²) is covered by dense stands of *Zostera noltii Hornem* (Guimarães et al., 2012; Rui Santos, pers. comm.) Further, but much less abundant, seagrass species in the lagoon are *Zostera Marina L*. and *Cymodocea nodosa (Ucria) Ascherson* which are mainly located in shallow parts of the subtidal areas (Santos et al., 2004). About 30% of the lagoon's area is covered with salt marsh communities (Rui Santos, pers. comm.).

2.2   Sampling

We conducted two sampling campaigns in the western part of the lagoon at the Ramalhete research station (Centre of Marine Sciences (CCMAR), Universidade do Algarve) in the vicinity of Faro (37.0°N, 7.6 W) (Fig. 1). The sampling was carried out from July 23rd – August 7th 2011 and April 17th – April 28th 2012 coinciding with the beginning (2012 campaign) and peak (2011 campaign) of the seagrass reproductive season. Ambient air temperatures were distinctively different between both campaigns ranging from 21 to 27°C (mean 24°C) with almost entirely clear weather in summer and 13 to 23°C (mean 17°C) in spring with frequent strong cloud cover. Mean water temperatures were 25.9°C (summer) and 17.5°C (spring). The prevailing wind direction during both campaigns was West to South-West to with rather low average wind speeds of 4 m s^{-1} during summer and 5 m s^{-1} during spring.

During the two campaigns we used different dynamic flux chamber systems. Firstly, during the 2011 campaign, we measured the halocarbon fluxes during air exposure using a quartz-glass chamber (0.1m^2 bottom surface area, 7 L enclosure volume) as described in Weinberg et al. (2013) with some adjustments. For this study a permanent backup flow (3± 0.2 L min^{-1}) through the flux chamber during sampling and the change of cryotraps was applied to ensure sufficient mixing. Further, to overcome analytical problems with the high humidity in the sampled air, the water content was reduced using a condenser (-15°C). Briefly, the quartz-glass flux chamber was placed on the seagrass patch and sealed with surrounding sediment. Two sampling systems were operated simultaneously measuring inlet and outlet air of the flux

1 chamber (flow rate 1 ± 0.2 L min^{-1}). Prior to sampling, the flux chamber was flushed for about

2 10 min ensuring sufficient equilibration of compounds in the chamber air.

3 During the 2012 campaign, we used a dynamic flux chamber system (0.037 m^2 bottom

4 surface area, 8 L enclosure volume) suitable for flux measurements during both periods of air

5 exposure and tidal immersion. The properties and setup of this dynamic chamber system is in

6 detail described elsewhere (Bahlmann et al., 2014). Since this system acts as an ordinary

7 purge and trap system, the extraction efficiencies were simulated using halocarbon

8 equilibrated artificial seawater. While the results from these tests revealed that

9 monohalomethanes were almost completely extracted ($\geq$90%), the purge efficiencies for

10 CHBr$_3$ were only 33%. Thus the reported CHBr$_3$ fluxes determined from seagrass meadows

11 using the submergible chamber system represent rather an under-estimate.

12 Based on the sampling system for the determination of stable carbon isotopes of halocarbons

13 Bahlmann et al. (2011), we modified the cryogenic trapping system for the measurements of

14 halocarbon mixing ratios, in order to establish a better temporal resolution by reducing the

15 analysis time. This results in a final air volume 28 ± 5 L of air at the inlet and the outlet of the

16 chambers, respectively. The specifications along with the results from test surveys are given

17 in the supplementary.

18 The seagrass species sampled was exclusively *Z. Noltii*. The seagrass patches sampled had an

19 area coverage of >95% and were free of visible epiphytes such as macroalgae. In this low to

20 medium intertidal region the epiphytes of *Z .Noltii* are almost exclusively diatoms whose

21 contribution ranges from 0.5 to 4% of the total seagrass biomass (Cabaço et al., 2009). We

22 further determined the fluxes from an adjacent bare sediment spot during the 2011 campaign.

23 On 2 August 2011, these chamber-based measurements were complemented by atmospheric

24 sampling at a nearby beach (Praia de Faro, upwind site) about 3 km distant from the lagoon

25 during the summer campaign 2011 (Fig. 1). At this time the wind direction was south-

26 westerly reflecting background air from the coastal ocean.

27 Discrete water samples for the determination of dissolved halocarbons concentration and

28 isotopic composition at high tide were taken during both campaigns. The samples were taken

29 directly above the studied seagrass meadow using Duran glass bottles (1-2 L volume). Air and

30 sediment intrusions during water sampling were avoided. The water depth was between 0.3 m

31 and 1 m. On April 24th 2012, a transect cruise through the middle and western part of the

32 lagoon was conducted during rising waters (Fig. 1). The water samples were taken from a

water depth of 1 m. Dissolved halocarbons were extracted from seawater using a purge and trap system. Seawater was purged with helium 5.0 (purge flow 1L min^{-1}) for 30 minutes. After water vapour reduction of the purge gas, the compounds were enriched on cryotraps (submerged in a dry shipper). The shape of the cryotraps used here was the same as those for flux chamber and atmospheric samples. The water samples were usually processed within 30 minutes after sampling. Samples from the transect cruise were stored in the dark at 4°C and analyzed within eight hours. Purge efficiencies of monohalomethanes from lagoon water were ≥95% (1 L and 2 L samples). However, the less volatile $CHBr_3$ was only extracted with 50% (1 L samples) and 30% (2 L samples). Therefore, the results of water concentration were corrected for the respective purge efficiency for this compound.

2.3 Measurement and quantification

The measurement procedure is described in detail in the supplementary. Briefly, compounds enriched on the cryotraps, were thermally desorbed and transferred to Peltier-cooled adsorption tubes. The analytes were further desorbed from the adsorption tubes and refocused cryogenically before injection to the GC-MS system. Air and water samples were measured onsite at Ramalhete research station using a GC-MS system (6890N/5975B, Agilent, Germany) equipped with a CP-PorabondQ column (25 m, 0.25 µm i.d., Varian, Germany). The GC-MS was operated in the electron impact mode. Identification of compounds was executed by retention times and respective mass spectra. Aliquots of gas standard (Scott EPA TO 15/17, 65 compounds, 1 ppm each in nitrogen, Sigma Aldrich, Germany) containing CH_3Cl, CH_3Br, and $CHBr_3$ were applied to quantify the target compounds. During onsite measurements, CH_3I was quantified using the response factor against CH_3Br. The analytical limit of detection was 0.3 ppt for the halocarbons. The accuracy of the entire sampling method (sampling, sample treatment, measurement) was derived from test samples in triplicates. The deviation between the individual samples for CH_3Cl, CH_3Br, CH_3I, and $CHBr_3$ was 5.4%, 6.3%, 15.4% and 6.7%, respectively. A series of procedural blanks (cryotraps and adsorption tubes) were taken during the sampling campaigns. The occasionally detected blanks of CH_3Cl and CH_3Br from these determinations were ≤3% to the "real" samples taken from the seagrass meadows during sampling campaigns. Therefore, the halocarbon fluxes were not blank corrected.

Air and water samples for determining the isotopic composition of halocarbons were transferred to adsorption tubes and stored at -80°C until measurements. The analysis was

conducted using the GC-MS-IRMS system at our home laboratory (Bahlmann et al., 2011). Additional transport and storage blanks were processed which revealed no contamination for all halocarbons studied.

2.4 Calculations

The fluxes were determined with dynamic flux chambers. The principle is as follows: The chamber is positioned on the desired sampling spot and flushed continuously with ambient air. The mixing ratios of compounds at the inlet and outlet air are then measured. The obtained difference along with the flushing rate and the bottom surface area are used for the flux calculation. The net fluxes (F_{Net}, nmol m^{-2} h^{-1}) of the compounds are calculated by

$$F_{Net} = \frac{Q \times (C_{out} - C_{in})}{A \times V \times 1000} \tag{1}$$

Here, Q is the flushing rate of air through the chamber (L h^{-1}), C_{out} and C_{in} are the mixing ratios of target compounds (picomoles mol^{-1}, ppt) at the outlet and the inlet of the flux chamber. A is the enclosed surface area of the flux chamber (m^2) and V is the molar volume (L) at 1013.25 mbar and 298.15 K.

For calculation of the sea-air fluxes from the lagoon water, the inlet samples of the flux chamber were used which reflect the air mixing ratios. Where no corresponding inlet sample was available, the campaign means were applied. After conversion of the air mixing ratios to pmol L^{-1} using temperature data and the respective molar volume of the ambient air, the sea-air fluxes (F, nmol m^{-2} h^{-1}) of halocarbons were calculated by the equation:

$$F = k_w \times (C_w - C_a \times H^{-1}) \tag{2}$$

where k_w is the gas exchange velocity (m h^{-1}), C_w and C_a the water concentration and air concentration (pmol L^{-1}), respectively, and H the dimensionless and temperature dependent Henry's law constant taken from Moore (2000) for CH_3Cl, Elliott and Rowland (1993) for CH_3Br and CH_3I, and Moore et al. (1995) for $CHBr_3$. Several approximations emerged to estimate the relationship between the gas exchange velocity k and the wind speed u for open and coastal oceans (e.g. Nightingale et al., 2000; Wanninkhof, 1992). These estimations rely on assumptions that trace gas exchange is based on wind-driven turbulence. This is not applicable in shallow estuarine and riverine systems where the sea-air gas exchange is

1 additionally driven by wind-independent currents and the bottom turbulence and thus water

2 depth and current velocities further play a major role (Raymond and Cole, 2001). Studying

3 the sea-air exchange in the Ria Formosa, these additional factors have to be considered in

4 addition to wind driven outgassing. Therefore, we used the parameterization of k_w with the

5 assumption that wind speed and water current driven turbulence are additive (Borges et al.,

6 2004):

7 $$k_w = 1.0 + 1.719 \times w^{0.5} \times h^{-0.5} + 2.58 \times u \qquad (3)$$

8 where w is the water current (cm s^{-1}), h the water depth (m) and u the wind speed (m s^{-1}). For

9 the calculations of the sea-air flux in the lagoon a mean water depth of 1.5m (Tett et al., 2003)

10 and a mean water current of 24 cm s^{-1} (Durham, 2000) was used. The Schmidt number (Sc)

11 expresses the ratio of transfer coefficients of the kinematic viscosity of water and gas

12 diffusivity of interest. The gas exchange velocity k_w for each gas was then normalized to a

13 Schmidt number of 660, assuming a proportionality to $Sc^{-0.5}$ (Borges et al., 2004). The

14 individual Schmidt numbers were obtained from Tait (1995) for CH_3Cl, De Bruyn and

15 Saltzman (1997) for CH_3Br and CH_3I, and Quack and Wallace (2003) for $CHBr_3$.

16

3 Results

3.1 Halocarbons in the atmosphere and lagoon water

19 The air mixing ratios in the lagoon were adopted from the inlets of the flux chambers at 1 m

20 above ground during both campaigns. The results of these measurements and those of the

21 upwind site outside the lagoon (Praia de Faro) are presented in Table 1. In summer, the mean

22 air mixing ratios were 828 ppt for CH_3Cl, 22 ppt for CH_3Br, 3 ppt for CH_3I, and 15 ppt for

23 $CHBr_3$. Elevated air mixing ratios of the monohalomethanes were observed during periods of

24 easterly winds when air masses at the sampling site had presumably passed over major parts

25 of the lagoon. These mixing ratios reached up to 1490 ppt for CH_3Cl, 61 ppt for CH_3Br, and

26 11 ppt for CH_3I reflecting a potent source in this system. The mixing ratios at the upwind site

27 (Praia de Faro) were distinctively lower with mean values of 613 ppt (CH_3Cl), 13 ppt

28 (CH_3Br), 1 ppt (CH_3I), and 8 ppt ($CHBr_3$) further indicating a source inside the lagoon. In

29 spring 2012, the mean air mixing ratios in the lagoon were significantly lower than during

30 summer with 654 ppt for CH_3Cl, 12 ppt for CH_3Br, 1 ppt for CH_3I, and 2 ppt for $CHBr_3$.

Discrete water samples were taken above the studied seagrass meadow during tidal inundation (summer n=9; spring n=10). The results are presented in Table 1. In summer, concentrations ranged from ~~158~~ 160 to 30~~1~~0 pmol L^{-1} (CH$_3$Cl), 5 to 11 pmol L^{-1} (CH$_3$Br), 4 to 18 pmol L^{-1} (CH$_3$I), and 67 to 19~~1~~04 pmol L^{-1} (CHBr$_3$). During the spring campaign, the water concentrations were 100~~1~~ to ~~267~~ 270 pmol L^{-1} for CH$_3$Cl, 6 to 28 pmol L^{-1} for CH$_3$Br, 2 to 16 pmol L^{-1} for CH$_3$I, and 39 to ~~133~~ 130 pmol L^{-1} for CHBr$_3$.

The results obtained from samples of the transect cruise covered in 2012 (Fig. 1) are given in Table 2. We observed an about two-fold increase of concentration for CH$_3$Cl (from 121 to 241 pmol L^{-1}) and CHBr$_3$ (from 26 to 55 pmol L^{-1}) between position 1 (Faro-Olhão inlet) and position 2 (near to the seagrass meadows studied). The increase was less pronounced for CH$_3$Br (5 to 7 pmol L^{-1}) and not notable for CH$_3$I. The seawater at positions 6 and 7, the nearest to the Ancão inlet, revealed rather low concentrations for all compounds. We further observed rising concentrations for all halocarbons along positions 3, 4, and 5 with increasing distance to the Ancão inlet. They increased from 96 to 180 pmol L^{-1} for CH$_3$Cl, from 9 to 19 pmol L^{-1} for CH$_3$Br, 2 to 14 pmol L^{-1} for CH$_3$I, and 21 to 95 pmol L^{-1} for CHBr$_3$. The difference in concentration along the transect was accompanied by variations in the carbon isotopic composition of all compounds. The most ^{13}C depleted values of CH$_3$Cl, CH$_3$Br, and CH$_3$I were detected at the position furthest from the inlet. Interestingly, CHBr$_3$ showed the opposite trend with more ^{13}C enriched values in the lagoon (-25.8‰ vs. ~ -18‰).

3.2 Fluxes from seagrass meadows, sediment, and sea-air exchange

The mean fluxes and ranges of CH$_3$Cl, CH$_3$Br, CH$_3$I, and CHBr$_3$ from seagrass meadows, sediment, and from sea-air exchange calculations obtained from the two sampling campaigns are given in Table 3.

During the summer campaign (air exposure), we observed highly variable emission and deposition fluxes ranging from -49 to 74 nmol m^{-2} h^{-1} and -5.7 to 130 nmol m^{-2} h^{-1} for CH$_3$Cl and CH$_3$Br, respectively. The variability was less pronounced for CH$_3$I (0.5 to 2.8 nmol m^{-2} h^{-1}) and CHBr$_3$ (-0.6 to 5.7 nmol m^{-2} h^{-1}) where predominantly emissions were measured. Strongly elevated fluxes up to 130 nmol m^{-2} h^{-1} for CH$_3$Br were recorded in conjunction with tidal change from air exposure to inundation and conversely. These high fluxes were substantiated by a concurrent enhanced atmospheric mixing ratios ranging from 23 ppt to ~~118~~ 120 ppt (campaign median 14 ppt). Omitting these compound-specific tidal phenomena, the

1   fluxes of CH_3Cl and CH_3Br were positively correlated to each other (R^2 0.55, p< 0.05).

2   However, CH_3I and $CHBr_3$ fluxes correlated neither with each other nor with any of the other

3   investigated halocarbons. Due to the inherent high variability of the fluxes, a direct

4   comparison of halocarbon fluxes with solar radiation revealed a rather low correlation ($R^2 \leq$

5   0.20).

6   The flux chamber measurements over the sediment during air exposure revealed

7   predominantly emissions of all four halocarbons (n=5). These fluxes were 3.6±4.3 nmol m^{-2} h^{-1}

8   (CH_3Cl), 0.6±0.5 nmol m^{-2} h^{-1} (CH_3Br), 0.2±0.2 nmol m^{-2} h^{-1} (CH_3I), and 0.8±1.0 nmol m^{-2}

9   h^{-1} ($CHBr_3$). Hence, the bare sediment may contribute to the overall emissions above the

10   seagrass by about 10 to 20% for the monohalomethanes and 45% for $CHBr_3$.

11   During the 2012 spring campaign the halocarbon fluxes from seagrass meadows were

12   determined during both periods of air exposure and periods of tidal immersion. Furthermore,

13   the measurements were complemented by other trace gases including hydrocarbons and

14   sulphur containing compounds. High-time resolution CO_2 and methane flux measurements

15   were further conducted to gain insights in the biogeochemistry and tidal controls in this

16   system. These measurements along with other trace gases are reported in more detail in

17   Bahlmann et al. (2014). As in the summer campaign, the seagrass meadows were a net source

18   for all halocarbons studied, but on a lower level. The individual ranges of air exposure

19   measurements were -30 to 69 nmol m^{-2} h^{-1} (CH_3Cl), -0.8 to 3.9 nmol m^{-2} h^{-1} (CH_3Br), -0.6 to

20   2.6 nmol m^{-2} h^{-1} (CH_3I), and -0.5 to 1.3 nmol m^{-2} h^{-1} ($CHBr_3$). On average, the seagrass

21   meadows were a net source also under submerged conditions ranging from -58 to 100 nmol

22   m^{-2} h^{-1} for CH_3Cl, -1.6 to 8.3 nmol m^{-2} h^{-1} for CH_3Br, 0.1 to 8.0 nmol m^{-2} h^{-1} for CH_3I, and -

23   0.4 to 10.6 nmol m^{-2} h^{-1} for $CHBr_3$. Due to the low purge efficiency of $CHBr_3$ during high tide

24   measurements, the fluxes determined with the submergible chamber are underestimated for

25   this compound. Despite this high variability in production/decomposition during air exposure

26   and inundation, the monohalomethanes were significantly correlated to each other ($R^2 \geq 0.50$).

27   These correlations were enhanced compared to those found when the seagrass meadows were

28   air-exposed ($R^2 \geq 0.50$). In this case, only CH_3I and CH_3Br were significantly correlated (R^2

29   0.51). $CHBr_3$ was only slightly correlated to the monohalomethanes.

30   While deposition fluxes of CH_3Cl and CH_3Br of air-exposed seagrass meadows occurred

31   predominantly during periods of low irradiance in summer, no obvious relation to the time of

32   day and/or solar radiation was observed during spring when deposition fluxes were frequently

detected. For CH_3I and $CHBr_3$, uptake was only occasionally observed and situations of emission clearly dominated.

As in the summer campaign, we observed some remarkable tidal effects on halocarbon fluxes during the spring campaign. Firstly, the highest fluxes of all halocarbons were measured when the lagoon water was just reaching the sampling site. Occasionally this was also observed from air exposure to tidal inundation, although less pronounced. However, these short-timed effects were not as strong as during the summer campaign. Secondly, we observed deposition fluxes for CH_3Cl and CH_3Br at tidal maximum. Though uptake was not always observed for CH_3I and $CHBr_3$, their emissions turned out to decline in any case. Before and after this period emission fluxes during incoming tide and ebb flow dominated.

The lagoon water was a net source for all investigated halocarbons to the atmosphere during both campaigns. In summer, the flux ranges were 13-45 nmol m^{-2} h^{-1} (CH_3Cl), 0.6-1.7 nmol m^{-2} h^{-1} (CH_3Br), 0.5-3.2 nmol m^{-2} h^{-1} (CH_3I), and 1.0-8.0 nmol m^{-2} h^{-1} ($CHBr_3$). The respective fluxes in spring were 3.5-32 (CH_3Cl), 0.5-4.1 (CH_3Br), 0.3-3.7 (CH_3I), 3.8-24 ($CHBr_3$).

3.3 Stable carbon isotopes of halocarbons

Stable carbon isotope ratios of halocarbons were determined for selected samples of both campaigns (Table 4). Isotopic source signatures from seagrass meadows for CH_3Cl and CH_3Br were calculated using a coupled isotope and mass balance without integration of a possible sink function (Weinberg et al., 2013).

In 2011, the difference in atmospheric mixing ratios of CH_3Cl and CH_3Br between within the lagoon and the upwind position (Praia de Faro) was accompanied by a shift of $\delta^{13}C$ values. More ^{13}C depleted values were found for CH_3Cl in the lagoon (-42±2‰) compared to the upwind position (-39±0.4‰). In contrast, the $\delta^{13}C$ values of CH_3Br were significantly enriched in ^{13}C by about 10‰ inside the lagoon (-29±5‰) as compared to the upwind site (-38±3). These $\delta^{13}C$ values found in air samples in the lagoon roughly correspond to the $\delta^{13}C$ values of CH_3Cl (-43±3‰) and CH_3Br (-23±3‰) found in samples of lagoon waters.

Atmospheric CH_3Cl and CH_3Br were on average more enriched in ^{13}C in spring than in summer by 4 and 6‰, respectively. While the $\delta^{13}C$ values of CH_3Cl in the lagoon water were quite similar between both periods of the year, those of CH_3Br were on average more depleted in ^{13}C during spring suggesting certain changes in production/decomposition processes. The

1   isotopic composition of CH_3I in lagoon water was quite similar between summer (-39± 9‰)

2   and spring (mean -37±7‰). As for CH_3Br, the $\delta^{13}C$ values of $CHBr_3$ were more enriched in

3   ^{13}C in summer when compared with those of the spring campaign.

4   Using the fluxes and $\delta^{13}C$ values from the inlet and outlet of the flux chamber we were able to

5   calculate the source signatures of seagrass covered areas. The resulting source signatures of

6   CH_3Cl from seagrass meadows were, with -51±6‰ and -56±2‰, similar between both

7   campaigns and independent from the strength of emission. For CH_3Br, we observed most

8   depleted $\delta^{13}C$ values of -53‰ and -58‰ at increased emission fluxes in summer, but values

9   of -26‰ and -29‰ during periods of low emission. This corroborates the findings of

10   isotopically heavy CH_3Br produced within the seagrass meadows (-29‰) in spring 2012

11   when all samples analysed for the isotopic composition were taken at situations of low

12   emission.

13

14   **4   Discussion**

15   **4.1   Dissolved halocarbons**

16   A comparison of halocarbon concentrations in the lagoon water to other measurements of the

17   coastal Atlantic found in the literature is displayed in Table 5. The lagoon waters appeared to

18   be highly enhanced in CH_3Cl. Except one early study of Tait et al. (1994), our measurements

19   gave the most elevated concentrations for this compound. Enhanced concentrations in the

20   lagoon waters were also found for CH_3Br. Given the mean concentrations from other coastal

21   Atlantic studies (Baker et al., 1999; Carpenter et al., 2000; Hu et al., 2010), we recorded

22   higher concentration by a factor of 2 to 3 at our sampling site. The average water

23   concentrations in the lagoon of CH_3I were in the same range as reported from other parts of

24   the Atlantic (Moore and Groszko 1999; Zhou et al., 2005). However, especially those regions

25   where macroalgae are the dominating source organisms possess higher maximum values

26   (Bravo-Lineares and Mudge, 2009; Jones et al., 2009). This is even more pronounced for

27   $CHBr_3$, for which the seawater concentration within or in the vicinity of macroalgae beds are

28   strongly elevated (Bravo-Lineares and Mudge, 2009; Carpenter et al., 2000; Jones et al.,

29   2009). The area occupied by the prevalent macroalgae species *Enteromorpha spp.* and *Ulva*

30   *spp.* in the Ria Formosa is estimated to be 2.5 km^2 (Duarte et al., 2008), considerably below

31   that of other abundant sources such as seagrass meadows. We cannot exclude that

1   phytoplankton contributes significantly to the water concentration of halocarbons, but the

2   predominantly low chlorophyll a concentrations (3.~~106~~ µg L^{-1} from long-term measurements,

3   Brito et al., 2012) and low water volumes seem to limit the impact from this source.

4   Despite the short residence time of the lagoon water masses of which 50-75% is exchanged

5   during one tidal cycle (Brito et al., 2010), the transect cruise along the main channels revealed

6   a successive enrichment of halocarbon concentration in the water with increasing distance

7   from the main inlets (Fig. 1 and Table 2). Therefore, the halocarbon net production in the

8   lagoon appears to clearly exceed that outside the lagoon. This is supported by the distinctively

9   increased air mixing ratios of halocarbons in the lagoon as compared to the upwind site

10 (Table 1).

11 Overall, the lagoon seems to comprise highly potent halocarbon sources into the water

12 column for CH_3Cl and CH_3Br rather than for CH_3I and $CHBr_3$.

4.2   Flux pattern from seagrass meadows

14 The halocarbon fluxes from seagrass meadows were characterized by a high variability with

15 deposition and emission fluxes occurring at all sampling spots. The same was observed within

16 other studies investigating halocarbon fluxes in coastal environments (e.g. Blei et al., 2010;

17 Manley et al., 2006; Rhew et al., 2000). Halocarbon dynamics in coastal systems where

18 multiple sources and sinks interact are apparently quite complex. It should be noted that the

19 fluxes discussed here refer to the entire benthic community constituting the seagrass

20 meadows. Thus, some variability may relate to the activity of distinct source organisms which

21 may be stimulated by different environmental factors. To gain insights into the common

22 environmental controls for this ecosystem we discuss the following factors i) diurnal

23 variations ii) tidal effects and iii) seasonal dependence.

24 i) Diurnal variations. The correlation analysis with solar radiation resulted in only a weak

25 association with the magnitude of fluxes. However, after grouping by daytime, our data

26 provide some indication for a diurnal pattern (Fig. 2). For CH_3Cl, there was the most obvious

27 relationship between time of day and actual emissions. Highest emissions were observed

28 during day periods with increased sunlight (midday and afternoon). In contrast, deposition

29 fluxes were exclusively recorded during periods of low radiation and nighttimes. The same

30 was also observed for CH_3Br. However, highest mean emissions of this compound seemed to

31 be shifted towards the afternoon. CH_3I was constantly emitted from the seagrass covered spot

revealing a weak diurnal dependence. The emissions did not cease during periods of low irradiance and darkness. Nevertheless, elevated mean emissions were observed in the afternoon. Except one occasion, $CHBr_3$ was emitted throughout the sampling periods. Mean emissions were higher around midday and afternoon as during night.

Several studies especially from salt marshes reported a diurnal trend of halocarbon emissions initiated by irradiance (Dimmer et al., 2001; Rhew et al., 2000, 2002; Drewer et al., 2006). The flux data of halocarbons from the summer campaign with elevated fluxes during midday and afternoon suggest a similar pattern also in seagrass meadows. However, this was more obvious for CH_3Cl and CH_3Br than for CH_3I and $CHBr_3$. The lower production of CH_3I during the time of highest light intensity cannot fully be explained. Possibly, the emissions might derive from sources within the benthic community different from those of other halocarbons. This is also supported by the rather low correlations of CH_3I to CH_3Br and CH_3Cl. For example, Amachi et al. (2001) reported microbial production of CH_3I which may not relate to solar irradiance. $CHBr_3$ emission which peaked during midday and afternoon did not instantly cease when radiation becomes low. This could be an effect of the low volatility of the compound resulting in a time-delayed release from the system.

Blei et al. (2010) reported that the main environmental association in salt marsh emissions of CH_3Cl and CH_3Br was with ambient temperature rather than light. However, during the summer campaign, temperature variations (day/night) were too low to explain the observed emission/deposition pattern of CH_3Cl and CH_3Br.

It is known that coastal sediments can act as a sink for CH_3Cl and CH_3Br mainly due to microbial degradation (Miller et al., 2004; Oremland et al. 1994). This would support our findings of the deposition fluxes during night times where production above the sediment is presumably lower than during daytime (summer campaign). While, in general, the deposition fluxes of CH_3Cl and CH_3Br occurred more frequently during spring, they did not exhibit a certain day-night-relationship. Moreover, the dependence of light intensity on the magnitude of emission fluxes of halocarbons seemed to have a minor effect during this period of the year.

ii) Tidal effects. During the spring campaign, mean fluxes derived from submerged seagrass meadows were remarkably elevated by factors of 17 (CH_3Cl), 5 (CH_3Br), 3 (CH_3I), and 8 ($CHBr_3$) when compared to the average fluxes during air exposure. This clearly higher production of halocarbons under submerged conditions was quite unexpected. In general it is

28

believed that the production of trace gases during low tide exceeds that during inundation. For halocarbons this was suggested for example by Carpenter et al. (1999) and Jones et al. (2009) from atmospheric measurements over intertidal macroalgae beds in Mace Head, Ireland. Nevertheless, in accordance with our results from halocarbon measurements we also observed higher primary productivity by increased CO_2 uptake during submerged conditions (Bahlmann et al., 2014). Therefore, the higher productivity may reflect higher enzymatic activity (e.g. methyltransferases) within the organisms of the seagrass community, by which monohalomethanes are presumably formed. Furthermore, the correlation analysis revealed a different behaviour of halocarbons between the two tidal states with stronger correlations between monohalomethanes during tidal inundation than air exposure. Obviously the change in environmental conditions was accompanied with a shift in the halocarbon production-decomposition pattern of the benthic community and/or different source organisms were stimulated.

An interesting outcome of both campaigns is the observation of strongly elevated halocarbon fluxes during tidal change from air exposure to submergence and reversely (Table 3). Continuous high-time resolution CO_2 and methane flux measurements performed in spring 2012 (Bahlmann et al., 2014) principally support this observation. At the particular moment when the water reached the sampling site, we observed a distinct peak flux of methane and CO_2. This may be evidence for processes in the sediments attributable to changes in hydrodynamic pressures resulting in the release of trace gases trapped in sedimentary pore spaces (Bahlmann et al., 2014). On the other hand, these most likely sedimentary driven emission processes can hardly explain our observation of enhanced emissions also when the water was leaving the sampling site. Perhaps these emission increases relate to physiological stress reaction of the benthic community to the short-timed changing environmental conditions at the transition from inundation to air-exposure.

The remarkable deposition flux of CH_3Cl and CH_3Br during the maximum water level (Table 3) was accompanied by highest emissions of other trace gases such as methanethiol and hydrogen sulfide as discussed by Bahlmann et al. (2014). These compounds are effective nucleophiles which could have contributed to the degradation of halocarbons as described in Barbash and Reinhard (1989). This suggests a significantly different biogeochemistry during this period compared with incoming tide and ebb flow. Although we actually have no proof for an existence of light dependence under these submerged conditions, it is however possible

that production of photoautotrophic sources is reduced during this high tide state where solar irradiance is presumably the lowest.

Overall, while there is evidence for a tidal control on halocarbon production and decomposition, additional research is needed to further elucidate these phenomena.

iii) Seasonal dependence. There are considerable differences between the results from spring and summer. We observed elevated mixing ratios for all halocarbons in ambient air as well as higher water concentrations for CH_3Cl, CH_3I, and $CHBr_3$ compounds in summer (Table 1). This observed signal of general increased halocarbon production in the lagoon during summer might even be attenuated by assumedly enhanced degradation in the water phase and sediments at higher temperatures. Nevertheless, given the calculated sea-air flux there is only little evidence for a pronounced seasonal trend in halocarbon volatilisation to the atmosphere from the lagoon water. While the fluxes of CH_3Cl appeared to be enhanced in summer, those of CH_3Br and CH_3I seemed to be quite similar between spring and summer. $CHBr_3$ emissions were actually higher in spring than in summer due to higher water concentrations.

Comparing the data obtained from air-exposed sites during the two campaigns, the fluxes in summer were strongly enhanced by factors of 16 (CH_3Cl and CH_3Br), 2 (CH_3I), and 5 ($CHBr_3$) indicating that halocarbon fluxes increase from beginning of the growing season (spring) to the period where seagrass reproductive status is the highest (summer). This might correspond to the results from salt marshes where elevated fluxes for monohalomethanes where observed during the short flowering period (Manley et al., 2006). The differences of ambient conditions between the campaigns with lower air temperatures and cloudy sky in spring may have contributed to the differences in the emission patterns of halocarbons. That temperature is one of the emission controlling factors was reported from temperate salt marshes (Blei et al., 2010). Moreover, the halocarbon fluxes showed a distinct diurnal cycle during summer but not during spring. This suggests either a less productive benthic community or much stronger degradation processes during spring. The latter point is rather unlikely since the temperatures were distinctively lower and thus degradation processes are tentatively slower.

Overall, these differences observed in periods of air exposure between spring and summer might suggest a certain seasonality in seagrass meadows. However, further studies covering the entire seasoning are necessary to fully unravel the annual halocarbon emissions from seagrass meadows.

4.3 Halocarbons sources in the lagoon: an isotopic perspective

The results from the atmospheric sampling of Praia de Faro air (upwind) and lagoon air revealed certain difference regarding the mixing ratios and isotopic composition of CH_3Cl and CH_3Br (Tables 1 and 4). We observed elevated concentrations in the lagoon for both compounds, whereby the higher concentrations were accompanied with shifts towards isotopically light CH_3Cl but heavy CH_3Br. Beside the studied seagrass meadows other sources, in particular wide-abundant salt marshes, may have substantially contributed to the elevated mixing ratios. Assuming atmospheric stable conditions with negligible sinks in the atmosphere, the difference of air mixing ratios and $\delta^{13}C$ values between upwind air and lagoon air should reflect the isotopic source signature within the lagoon. Therefore, as a first approach, an isotope mass balance was used by integrating mean data from both sampling sites (Tables 1 and 4). The resulting source signatures within the lagoon are -49‰ for CH_3Cl and -16‰ for CH_3Br.

Isotopic source signatures of CH_3Cl from seagrass meadows during incubations (air exposure) in the Ria Formosa were -51±6‰ (summer) and -56±2‰ (spring). During the summer campaign, CH_3Cl emissions from the salt marsh plant *Spartina maritima* were determined with $\delta^{13}C$ values of -66 and -72‰. These values are in good agreement with those of Bill et al. (2002) from a Californian salt marsh (-69 to -71‰, daytime values). Unfortunately, we do not have isotopic data for the inundated periods from seagrass meadows, but the $\delta^{13}C$ values of CH_3Cl in the water phase (-42±2‰) come close to those measured in the atmosphere. An abiotic production mechanism has been reported for CH_3Cl from senescent plant material (Hamilton et al., 2003). While we cannot generally exclude additional CH_3Cl generation via this pathway, the isotopic data obtained in the Ria Formosa do not mirror strongly ^{13}C depleted values ($\delta^{13}C$ of -135±12‰, Keppler et al., 2004) as expected for compounds built by this production mechanism. Overall, this rather indicates a stronger imprint of the seagrass meadows and/or water column on the atmospheric CH_3Cl than from salt marshes or abiotic processes.

With $\delta^{13}C$ values of -42±17‰ the source signature of CH_3Br from seagrass meadows tend to be more depleted in ^{13}C compared with the calculated source signature from the atmospheric samples. It should be noted that the $\delta^{13}C$ values for this compound were more depleted in ^{13}C during periods of increased emission (-55‰) than during low emissions (-28‰). This shift can most likely be explained by simultaneous microbial degradation processes in the

~~sediments~~at the sediment surfaces ~~which occurred simultaneously~~. This corroborates our observations from Northern Germany with subsequent recalculation of a sedimentary sink function from accompanying sediment measurements (Weinberg et al., 2013). Reported source signatures of CH_3Br from salt marshes range from -59 to -65‰ (day time values, Bill et al., 2002). Our own measurements in the Ria Formosa indicate similar $\delta^{13}C$ values (-65‰) or even more depleted ones (unpublished data). In any case, neither source signatures from seagrass meadows nor salt marshes seem to match the overall source signature estimated from the atmospheric samples. Therefore, it is most likely that the atmospheric CH_3Br is strongly influenced by CH_3Br emissions from the surface waters ($\delta^{13}C$ values in water phase (summer): -23±3‰). Even during periods of low tide the water remains in the deep channels which may be sufficient to have an impact on the local atmosphere. Thus, despite the sources in the lagoon presumably producing isotopically light CH_3Br, $\delta^{13}C$ values in the atmosphere strongly reflect decomposed CH_3Br whose residual fraction is actually enriched in ^{13}C. Accordingly, aqueous CH_3Br appears to become rapidly degraded by biotic/abiotic processes such as hydrolysis, transhalogenation, and microbial degradation with strong isotopic fractionation (King and Saltzman, 1997; Miller et al. 2004). These decomposition mechanisms are temperature dependent with increasing destruction with increasing seawater temperature. This is most likely the reason why the $\delta^{13}C$ values in the lagoon waters in summer are more enriched in ^{13}C compared with ~~those~~ those from the spring campaign.

To the best of our knowledge, this is the first report of $\delta^{13}C$ values of CH_3I in the water phase. As shown by the water samples from the transect cruise, the sources in the lagoon may produce isotopic light CH_3I. Given this, CH_3I seems to some extent to follow the $\delta^{13}C$ values of CH_3Cl. These sources may be biotic by e.g. phytoplankton, seagrass meadows, or bacteria. On the other hand, Moore and Zafirou (1994) reported a photochemical source for CH_3I by radical recombination of iodine with seawater dissolved organic matter. Due to the lack of isotopic source signatures and fractionation factors for production (and consumption), it is difficult to draw conclusions from the data.

The $\delta^{13}C$ values of $CHBr_3$ were more depleted in ^{13}C from the lagoon inlet towards the parts deeper inside. This suggests a different combination of sources in water masses coming from the Atlantic. Moreover, this potential variation of source contribution can be further assumed by the certain change between summer and spring where e.g. macroalgae are more abundant in the latter period (Anibal et al., 2007). Already reported source signatures of phytoplankton,

macroalgae, and seagrass meadows cover the range of -10‰ to -23‰ (Auer et al., 2006; Weinberg et al., 2013), thus demonstrating certain differences in their isotopic fingerprint. Actually we cannot exclude that degradation might also have an effect on the $\delta^{13}C$ values determined in lagoon waters. As for CH_3I there is still need for further research on the $CHBr_3$ cycling utilizing stable carbon isotopes.

4.4 Magnitude of fluxes and comparison to other coastal measurements and first estimate of global source strength

The areal based fluxes of CH_3Cl, CH_3Br, and CH_3I from seagrass meadows in comparison to emission data of other coastal sources are presented in Fig. 3. In comparison to the emissions from a temperate seagrass meadow in late summer in Northern Germany (Weinberg et al., 2013), fluxes were elevated in the subtropical lagoon in summer during air exposure. This was more pronounced for CH_3Br (factor 33) than for CH_3Cl (factor 2), CH_3I (factor 2), and $CHBr_3$ (factor 5). In contrast, fluxes from air-exposed seagrass meadows recorded during spring are comparable to those determined in Northern Germany. Thus, the difference between fluxes from temperate and subtropical regions is less pronounced as reported for salt marshes with emissions from subtropical regions exceeding those from temperate regions by up to two orders of magnitude for CH_3Cl and CH_3Br (Blei et al. 2010; Cox et al., 2004; Dimmer et al., 2001; Drewer et al., 2006; Manley et al., 2006; Rhew and Mazéas, 2010; Rhew et al., 2000, 2014; Valtanen et al., 2009). Beside this regional (climatic) difference several authors attributed this to a highly species dependent emission potential.

Average emissions of CH_3Cl from the air-exposed seagrass meadows in summer are in the same range than those determined in temperate salt marshes (Blei et al. 2010; Cox et al., 2004; Dimmer et al., 2001; Drewer et al., 2006; Valtanen et al., 2009). In contrast, subtropical counterparts of these macrophytes are distinctively stronger emitters of this compound by at least one order of magnitude (Manley et al., 2006; Rhew and Mazéas, 2010; Rhew et al., 2000, 2014). Greenhouse grown mangroves produce significantly more CH_3Cl than seagrass meadows revealing a higher emission potential for these plants species on per area basis (Manley et al., 2007).

Fluxes of CH_3Br from subtropical seagrass meadows during air exposure exceed those of temperate macroalgae from Mace Head, Ireland (Carpenter et al., 2000) and temperate salt marshes (Blei et al. 2010; Cox et al., 2004; Dimmer et al., 2001; Drewer et al., 2006; Valtanen

1 et al., 2009). However, the CH_3Br fluxes from seagrass meadows are distinctively lower than

2 those of subtropical salt marsh plants (Manley et al., 2006; Rhew and Mazéas, 2010; Rhew et

3 al., 2000). Mangroves seem to have a similar emission potential as seagrass meadows

4 (Manley et al., 2007).

5 For CH_3I, seagrass meadows are a minor source in comparison to the high release of

6 macroalgae in subtropical areas (Leedham et al. 2013). Except for salt marshes from

7 Tasmania (Cox et al., 2004), plant-related communities such as mangroves (Manley et al.,

8 2007) and salt marshes (Dimmer et al., 2001) are more pronounced emission sources of this

9 compound. The same holds true for $CHBr_3$, where macroalgae communities from temperate

10 and subtropical/tropical regions dominate the emissions of polyhalomethanes on a per area

11 basis (e.g. Carpenter et al., 2000; Gschwend et al., 1985; Leedham et al., 2013).

12 Many uncertainties arise from a limited number of emission data to estimate the global

13 relevance of seagrass meadows. Those may be high variation in space and time, high

14 heterogeneity of seagrass meadows, species dependent emission potential, and errors

15 regarding the global seagrass abundance. Therefore, the scale-up of our data gives only a first

16 rough approximation; it was undertaken as follows. Since we did not measure a full annual

17 cycle, we assumed that seagrass measurements during the summer campaign represent

18 emissions from the reproductive season (May - September). The remaining period of the year

19 (October - April) was calculated with emission data from the spring campaign. The emission

20 data were weighted to tidal states using 8 hours and 16 hours per day as durations when

21 seagrass meadows are air-exposed or submerged, respectively. Due to the lack of flood tide

22 emission data in summer, we used those derived from the sea-air exchange. The resulting

23 average annual emissions from seagrass meadows of 150 µmol m^{-2} yr^{-1} (CH_3Cl), 18 µmol m^{-2}

24 yr^{-1} (CH_3Br), 14 µmol m^{-2} yr^{-1} (CH_3I), and 25 µmol m^{-2} yr^{-1} ($CHBr_3$) were scaled-up with the

25 current estimates of a global seagrass area ranging from $0.3x10^{12}$ m^2 (Duarte et al., 2005) to

26 $0.6x10^{12}$ m^2 (Charpy-Roubaud and Sournia, 1990).

27 The tentative estimate yields annual emissions of 2.3-4.5 Gg yr^{-1} for CH_3Cl, 0.5-1.0 Gg yr^{-1}

28 for CH_3Br, 0.6-1.2 Gg yr^{-1} for CH_3I, and 1.9-3.7 Gg yr^{-1} for $CHBr_3$. Based on the recent global

29 budget calculations (Xiao et al., 2010; Montzka and Reimann, 2011), these ranges are

30 equivalent to 0.06-0.11% and 0.45-0.89%, for CH_3Cl and CH_3Br, respectively. Seagrass

31 meadows would therefore cover a portion of 1.4-2.8% of the missing sources for CH_3Br

32 reported in the most recent WMO report (36.1 Gg yr^{-1}; Montzka and Reimann, 2011). Given

1 the emissions from oceanic sources (e.g. Butler et al., 2007; Quack and Wallace, 2003 and

2 references therein), CH_3I and $CHBr_3$ emissions from seagrass meadows are rather

3 insignificant on a global scale.

4

5   Conclusions

6 We presented the first detailed study of halocarbon fluxes from seagrass meadows. The data

7 were obtained from a subtropical mesotidal lagoon in southern Portugal. During air exposure,

8 fluxes of CH_3Cl and CH_3Br were highly variable with increasing fluxes at midday and

9 afternoon while deposition fluxes were predominantly observed in periods of low radiation

10 and at nighttimes. Diurnal fluctuations were less obvious for CH_3I and $CHBr_3$, though their

11 emission maxima were also shifted to the afternoon. Generally, diurnal variations and

12 emission rates were minor in spring than in summer, suggesting a certain seasonal

13 dependence. This is supported by distinctively lower atmospheric mixing ratios in spring.

14 Distinct emission peaks occurred in the certain moments when lagoon waters were just

15 arriving or leaving the sampling site. Moreover, a comparison between chamber

16 measurements during air exposure and tidal inundation revealed elevated emission rates

17 during flooding. Overall, seagrass meadows are highly diverse regarding their potential

18 halocarbon sources which might be responsible for the observed high variations of emission

19 fluxes. For example, we could show that the sediments were also able to emit halocarbons,

20 though in low quantities on per area basis.

21 The results from a transect cruise along the mid and western part of the lagoon clearly

22 revealed a significant halocarbon production within lagoon waters. This finding corresponds

23 to high halocarbon concentrations in the lagoon water above submerged seagrass meadows.

24 This was especially pronounced for CH_3Cl exhibiting the highest water concentration as

25 compared to other measurements from Atlantic waters. However, CH_3I and $CHBr_3$ water

26 concentrations were well below those reported from macroalgae-dominated coastlines.

27 To obtain further information on sources and sinks in the lagoon, stable carbon isotopes of

28 halocarbons from the air and water phase along with source signatures were studied. Results

29 suggest that CH_3Cl more originates from the water column and/or seagrass meadows than

30 from adjacent salt marshes or abiotic formation processes. Atmospheric and aqueous CH_3Br

31 in the lagoon was substantially enriched in ^{13}C pointing towards degradation processes and re-

emission into the atmosphere. Furthermore, we presented isotopic data of CH_3I and $CHBr_3$ from the water phase.

Monohalomethane emissions from seagrass meadows fall in-between those from temperate salt marshes and mangroves. For $CHBr_3$, seagrass-based emissions are distinctively below those of macroalgae. 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 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.

Future studies should focus on emission from seagrass-based systems from different regions in order to refine the global relevance. Likewise, since magnitudes of fluxes are often species-dependent, budgets calculations will certainly benefit from a more detailed view on different seagrass species. Furthermore, while this study focused on halocarbon dynamics from seagrass meadows on the level of the benthic community, it is worthwhile to identify the specific sources in these ecosystems. The sediments being capable of acting as both a sink and a source, should be further studied. Though our results suggest sediments being a weak producer on a per area basis which corroborates other studies from e.g. salt marshes (Manley et al., 2006), they may have a significant impact in view of their high area coverage in coastal zones exceeding by far all other macrophytic systems (see Duarte et al., 2005).

6   Acknowledgements

References

Amachi, S., Kamagata, Y., Kanagawa, T., and Muramatsu, Y.: Bacteria mediate methylation of iodine in marine and terrestrial environments, Appl. Environ. Microb., 67, 2718-2722, doi: 10.1128/aem.67.6.2718-2722.2001, 2001.

Anibal, J., Rocha, C., and Sprung, M.: Mudflat surface morphology as a structuring agent of algae and associated macroepifauna communities: A case study in the Ria Formosa, J. Sea Res., 57, 36-46, doi: 10.1016/j.seares.2006.07.002, 2007.

Auer, N. R., Manzke, B. U., and Schulz-Bull, D. E.: Development of a purge and trap continuous flow system for the stable carbon isotope analysis of volatile halogenated organic compounds in water, J. Chromatogr. A, 1131, 24-36, doi: 10.1016/j.chroma.2006.07.043, 2006.

Bahlmann, E., Weinberg, I., Seifert, R., Tubbesing, C., and Michaelis, W.: A high volume sampling system for isotope determination of volatile halocarbons and hydrocarbons, Atmos. Meas. Tech., 4, 2073-2086, doi: 10.5194/amt-4-2073-2011, 2011.

Bahlmann, E., Weinberg, I., Eckhardt, T., Michaelis, W., Santos, R., and Seifert, R.: Tidal controls on trace gas dynamics in a subtropical seagrass meadows in the Ria Formosa (Portugal), 2014, submitted to Biogeosciences.

Baker, J. M., Reeves, C. E., Nightingale, P. D., Penkett, S. A., Gibb, S. W., and Hatton, A. D.: Biological production of methyl bromide in the coastal waters of the North Sea and open ocean of the northeast Atlantic, Mar. Chem., 64, 267-285, doi: 10.1016/s0304-4203(98)00077-2, 1999.

Barbash, J. E. and Reinhard, M.: Reactivity of sulfur nucleophiles toward halogenated organic compounds in natural waters, in: Biogenic Sulfur in the Environment, edited by: Saltzman, E. and Cooper, W. J., American Chemical Society, Washington D.C., 101–137, 1989.

Bell, N., Hsu, L., Jacob, D. J., Schultz, M. G., Blake, D. R., Butler, J. H., King, D. B., Lobert, J. M., and Maier-Reimer, E.: Methyl iodide: Atmospheric budget and use as a tracer of marine convection in global models, J. Geophys. Res-Atmos., doi: 107, 4340, 10.1029/2001jd001151, 2002.

Bill, M., Rhew, R. C., Weiss, R. F., and Goldstein, A. H.: Carbon isotope ratios of methyl bromide and methyl chloride emitted from a coastal salt marsh, Geophys. Res. Lett., 29, doi: 104510.1029/2001gl012946, 2002.

Blei, E., Heal, M. R., and Heal, K. V.: Long-term CH3Br and CH3Cl flux measurements in temperate salt marshes, Biogeosciences, 7, 3657-3668, doi: 10.5194/bg-7-3657-2010, 2010.

Borges, A. V., Vanderborght, J. P., Schiettecatte, L. S., Gazeau, F., Ferron-Smith, S., Delille, B., and Frankignoulle, M.: Variability of the gas transfer velocity of CO2 in a macrotidal estuary (the Scheldt), Estuaries, 27, 593-603, doi: 10.1007/bf02907647, 2004.

Bravo-Linares, C. M., and Mudge, S. M.: Temporal trends and identification of the sources of volatile organic compounds in coastal seawater, J. Environ. Monitor, 11, 628-641, doi: 10.1039/b814260m, 2009.

Brito, A., Newton, A., Tett, P., and Fernandes, T. F.: Sediment and water nutrients and microalgae in a coastal shallow lagoon, Ria Formosa (Portugal): Implications for the Water Framework Directive, J. Environ. Monitor, 12, 318-328, doi: 10.1039/b909429f, 2010.

Brito, A. C., Quental, T., Coutinho, T. P., Branco, M. A. C., Falcao, M., Newton, A., Icely, J., and Moita, T.: Phytoplankton dynamics in southern Portuguese coastal lagoons during a discontinuous period of 40 years: An overview, Estuar. Coast. Shelf S., 110, 147-156, doi: 10.1016/j.ecss.2012.04.014, 2012.

Butler, J. H., King, D. B., Lobert, J. M., Montzka, S. A., Yvon-Lewis, S. A., Hall, B. D., Warwick, N. J., Mondeel, D. J., Aydin, M., and Elkins, J. W.: Oceanic distributions and emissions of short-lived halocarbons, Global Biogeochem. Cy., 21, GB1023, doi: 10.1029/2006gb002732, 2007.

Cabaço, S., Machás, R., and Santos, R.: Individual and population plasticity of the seagrass Zostera noltii along a vertical intertidal gradient, Estuar. Coast. Shelf S., 82, 301-308, doi: http://dx.doi.org/10.1016/j.ecss.2009.01.020, 2009.

Cabaço, S., Santos, R., and Sprung, M.: Population dynamics and production of the seagrass Zostera noltii in colonizing versus established meadows, Marine Ecology, 33, 280-289, doi: 10.1111/j.1439-0485.2011.00494.x, 2012.

Carpenter, L. J., Sturges, W. T., Penkett, S. A., Liss, P. S., Alicke, B., Hebestreit, K., and Platt, U.: Short-lived alkyl iodides and bromides at Mace Head, Ireland: Links to biogenic sources and halogen oxide production, J. Geophys. Res-Atmos., 104, 1679-1689, doi: 10.1029/98jd02746, 1999.

Carpenter, L. J., Malin, G., Liss, P. S., and Küpper, F. C.: Novel biogenic iodine-containing trihalomethanes and other short-lived halocarbons in the coastal east Atlantic, Global Biogeochem. Cy., 14, 1191-1204, doi: 10.1029/2000gb001257, 2000.

Carpenter, L. J., Jones, C. E., Dunk, R. M., Hornsby, K. E., and Woeltjen, J.: Air-sea fluxes of biogenic bromine from the tropical and North Atlantic Ocean, Atmos. Chem. Phys., 9, 1805-1816, doi: 1805-1816,10.5194/acp-9-1805-2009, 2009.

Charpy-Roubaud, C., and Sournia, A.: The comparative estimation of phytoplanktonic microphytobenthic and macrophytobenthic primary production in the oceans, Marine Microbial Food Webs, 4, 31-58, 1990.

Cox, M. L., Fraser, P. J., Sturrock, G. A., Siems, S. T., and Porter, L. W.: Terrestrial sources and sinks of halomethanes near Cape Grim, Tasmania, Atmos. Environ., 38, 3839-3852, doi: 10.1016/j.atmosenv.2004.03.050, 2004.

DeBruyn, W. J., and Saltzman, E. S.: The solubility of methyl bromide in pure water, 35 parts per thousand sodium chloride and seawater, Mar. Chem., 56, 51-57, doi: 10.1016/s0304-4203(96)00089-8, 1997.

Dimmer, C. H., Simmonds, P. G., Nickless, G., and Bassford, M. R.: Biogenic fluxes of halomethanes from Irish peatland ecosystems, Atmos. Environ., 35, 321-330, doi: 10.1016/s1352-2310(00)00151-5, 2001.

Drewer, J., Heal, M. R., Heal, K. V., and Smith, K. A.: Temporal and spatial variation in methyl bromide flux from a salt marsh, Geophys. Res. Lett., 33, L16808, doi: 10.1029/2006gl026814, 2006.

Duarte, C. M., Middelburg, J. J., and Caraco, N.: Major role of marine vegetation on the oceanic carbon cycle, Biogeosciences, 2, 1-8, doi:10.5194/bg-2-1-2005, 2005.

Duarte, P., Azevedo, B., Guerreiro, M., Ribeiro, C., Bandeira, R., Pereira, A., Falcao, M., Serpa, D., and Reia, J.: Biogeochemical modelling of Ria Formosa (South Portugal), Hydrobiologia, 611, 115-132, doi: 10.1007/s10750-008-9464-3, 2008.

Durham, L.: A Kinematic Study of the Ancão Basin in the Ria Formosa Lagoon, Algarve, MSc thesis, School of Ocean Sciences, University of Wales, Bangor, 2000.

Elliott, S., and Rowland, F. S.: Nucleophilic-substitution rates and solubilities for methyl halides in seawater, Geophys. Res. Lett., 20, 1043-1046, doi: 10.1029/93gl01081, 1993.

Gschwend, P. M., Macfarlane, J. K., and Newman, K. A.: Volatile Halogenated Organic Compounds Released to Seawater from Temperate Marine Macroalgae, Science, 227, 1033-1035, doi: 10.1126/science.227.4690.1033, 1985.

Guimarães, M. H. M. E., Cunha, A. H., Nzinga, R. L., and Marques, J. F.: The distribution of seagrass (Zostera noltii) in the Ria Formosa lagoon system and the implications of clam farming on its conservation, Journal for Nature Conservation, 20, 30-40, doi: 10.1016/j.jnc.2011.07.005, 2012.

Hamilton, J. T. G., McRoberts, W. C., Keppler, F., Kalin, R. M., and Harper, D. B.: Chloride methylation by plant pectin: An efficient environmentally significant process, Science, 301, 206-209, doi: 10.1126/science.1085036, 2003.

Hu, L., Yvon-Lewis, S. A., Liu, Y., Salisbury, J. E., and O'Hern, J. E.: Coastal emissions of methyl bromide and methyl chloride along the eastern Gulf of Mexico and the east coast of the United States, Global Biogeochem. Cy., 24, GB1007, doi: 10.1029/2009gb003514, 2010.

Jones, C. E., Hornsby, K. E., Dunk, R. M., Leigh, R. J., and Carpenter, L. J.: Coastal measurements of short-lived reactive iodocarbons and bromocarbons at Roscoff, Brittany during the RHaMBLe campaign, Atmos. Chem. Phys., 9, 8757-8769, doi: 10.5194/acp-9-8757-2009, 2009.

Keppler, F., Kalin, R. M., Harper, D. B., McRoberts, W. C., and Hamilton, J. T. G.: Carbon isotope anomaly in the major plant C1 pool and its global biogeochemical implications, Biogeosciences, 1, 123-131, doi: 10.5194/bg-1-123-2004, 2004.

Keppler, F., Harper, D. B., Rockmann, T., Moore, R. M., and Hamilton, J. T. G.: New insight into the atmospheric chloromethane budget gained using stable carbon isotope ratios, Atmos. Chem. Phys., 5, 2403-2411, doi: 10.5194/acp-5-2403-2005, 2005.

King, D. B., and Saltzman, E. S.: Removal of methyl bromide in coastal seawater: Chemical and biological rates, J. Geophys. Res.-Oceans, 102, 18715-18721, doi: 10.1029/97jc01214, 1997.

1 Leedham, E. C., Hughes, C., Keng, F. S. L., Phang, S. M., Malin, G., and Sturges, W. T.: Emission of
2 atmospherically significant halocarbons by naturally occurring and farmed tropical macroalgae, Biogeosciences,
3 10, 3615-3633, doi: 10.5194/bg-10-3615-2013, 2013.

4

5 MacDonald, S., and Moore, R. M.: Seasonal and spatial variations in methyl chloride in NW Atlantic waters, J.
6 Geophys. Res.-Oceans, 112, C05028, doi: 10.1029/2006jc003812, 2007.

7

8 Manley, S. L., Wang, N.-Y., Walser, M. L., and Cicerone, R. J.: Coastal salt marshes as global methyl halide
9 sources from determinations of intrinsic production by marsh plants, Global Biogeochem. Cy., 20, GB3015, doi:
10 10.1029/2005gb002578, 2006.

11

12 Manley, S. L., Wang, N.-Y., Walser, M. L., and Cicerone, R. J.: Methyl halide emissions from greenhouse-
13 grown mangroves, Geophys. Res. Lett., 34, L01806, doi: 10.1029/2006gl027777, 2007.

14

15 Miller, L. G., Warner, K. L., Baesman, S. M., Oremland, R. S., McDonald, I. R., Radajewski, S., and Murrell, J.
16 C.: Degradation of methyl bromide and methyl chloride in soil microcosms: Use of stable C isotope fractionation
17 and stable isotope probing to identify reactions and the responsible microorganisms, Geochim. Cosmochim. Ac.,
18 68, 3271-3283, doi: 10.1016/j.gca.2003.11.028, 2004.

19

20 Montzka, S. A., and Reimann, S. et al.: Ozone-depleting substances and related chemicals, in: Scientific
21 Assessment of Ozone Depletion: 2010, Global Ozone Research and Monitoring Project – Report No. 52,
22 Geneva, Switzerland, 2011.

23

24 Moore, R. M.: The solubility of a suite of low molecular weight organochlorine compounds in seawater and
25 implications for estimating the marine source of methyl chloride to the atmosphere, Chemosphere - Global
26 Change Science, 2, 95-99, doi: http://dx.doi.org/10.1016/S1465-9972(99)00045-8, 2000.

27

28 Moore, R. M., and Groszko, W.: Methyl iodide distribution in the ocean and fluxes to the atmosphere, J.
29 Geophys. Res.-Oceans, 104, 11163-11171, doi: 10.1029/1998jc900073, 1999.

30

31 Moore, R. M., and Zafiriou, O. C.: Photochemical production of methyl iodide in seawater, J. Geophys. Res.-
32 Atmos., 99, 16415-16420, doi: 10.1029/94jd00786, 1994.

33

34 Moore, R. M., Geen, C. E., and Tait, V. K.: Determination of Henry's Law constants for a suite of naturally
35 occurring halogenated methanes in seawater, Chemosphere, 30, 1183-1191, doi: http://dx.doi.org/10.1016/0045-
36 6535(95)00009-W, 1995.

37

38 Moore, R. M., Webb, M., Tokarczyk, R., and Wever, R.: Bromoperoxidase and iodoperoxidase enzymes and
39 production of halogenated methanes in marine diatom cultures, J. Geophys. Res.-Oceans, 101, 20899-20908,
40 doi: 10.1029/96jc01248, 1996.

41

42 Nightingale, P. D., Malin, G., Law, C. S., Watson, A. J., Liss, P. S., Liddicoat, M. I., Boutin, J., and Upstill-
43 Goddard, R. C.: In situ evaluation of air-sea gas exchange parameterizations using novel conservative and
44 volatile tracers, Global Biogeochem. Cy., 14, 373-387, doi: 10.1029/1999gb900091, 2000.

45

46 Oremland, R. S., Miller, L. G., and Strohmaier, F. E.: Degradation of Methyl Bromide in Anaerobic Sediments,
47 Environ. Sci. Technol., 28, 514-520, doi: 10.1021/es00052a026, 1994.

Quack, B., and Wallace, D. W. R.: Air-sea flux of bromoform: Controls, rates, and implications, Global Biogeochem. Cy., 17, 1023, doi: 10.1029/2002gb001890, 2003.

Raymond, P. A., and Cole, J. J.: Gas exchange in rivers and estuaries: Choosing a gas transfer velocity, Estuaries, 24, 312-317, doi: 10.2307/1352954, 2001.

Rhew, R., and Mazeas, O.: Gross production exceeds gross consumption of methyl halides in northern California salt marshes, Geophys. Res. Lett., 37, L18813, doi: 10.1029/2010gl044341, 2010.

Rhew, R. C., Miller, B. R., and Weiss, R. F.: Natural methyl bromide and methyl chloride emissions from coastal salt marshes, Nature, 403, 292-295, doi: 10.1038/35002043, 2000.

Rhew, R. C., Miller, B. R., Bill, M., Goldstein, A. H., and Weiss, R. F.: Environmental and biological controls on methyl halide emissions from southern California coastal salt marshes, Biogeochemistry, 60, 141-161, doi: 10.1023/a:1019812006560, 2002.

Rhew, R. C., Whelan, M. E., and Min D.H.: Large methyl halide emissions from south Texas salt marshes, Biogeosciences Discuss., 11, 9451-9470,doi: doi:10.5194/bgd-11-9451-2014, 2014.

Saito, T., and Yokouchi, Y.: Stable carbon isotope ratio of methyl chloride emitted from glasshouse-grown tropical plants and its implication for the global methyl chloride budget, Geophys. Res. Lett., 35, L08807, doi: 10.1029/2007gl032736, 2008.

Saiz-Lopez, A., and von Glasow, R.: Reactive halogen chemistry in the troposphere, Chem. Soc. Rev., 41, 6448-6472, doi: 10.1039/c2cs35208g, 2012.

Santos, R., Silva, J., Alexandre, A., Navarro, N., Barron, C., and Duarte, C. M.: Ecosystem metabolism and carbon fluxes of a tidally-dominated coastal lagoon, Estuaries, 27, 977-985, doi: 10.1007/bf02803424, 2004.

Scarratt, M. G., and Moore, R. M.: Production of methyl bromide and methyl chloride in laboratory cultures of marine phytoplankton II, Mar. Chem., 59, 311-320, doi: 10.1016/s0304-4203(97)00092-3, 1998.

Tait, V. K. D. U.: An investigation of the oceanic source of methyl chloride, Dalhousie University, Halifax, N.S., 1995.

Tait, V. K., Moore, R. M., and Tokarczyk, R.: Measurements of methyl-chloride in the Northwest Atlantic, J. of Geophys. Res.-Oceans, 99, 7821-7833, doi: 10.1029/93jc03582, 1994.

Tett, P., Gilpin, L., Svendsen, H., Erlandsson, C. P., Larsson, U., Kratzer, S., Fouilland, E., Janzen, C., Lee, J. Y., Grenz, C., Newton, A., Ferreira, J. G., Fernandes, T., and Scory, S.: Eutrophication and some European waters of restricted exchange, Cont. Shelf Res., 23, 1635-1671, doi: 10.1016/j.csr.2003.06.013, 2003.

Tokarczyk, R., and Moore, R. M.: Production of volatile organohalogens by phytoplankton cultures, Geophys. Res. Lett., 21, 285-288, doi: 10.1029/94gl00009, 1994.

Urhahn, T.: Leichtflüchtige ECD-aktive Verbindungen in der marinen Grundschicht (MBL) des Atlantischen Ozeans : Vorkommen , Quellen und Verteilung, Department of Analytical Chemistry and Environmental Chemistry, University of Ulm, Ulm, Germany, 2003.

Valtanen, A., Solloch, S., Hartikainen, H., and Michaelis: Emissions of volatile halogenated compounds from a meadow in a coastal area of the Baltic Sea, Boreal Environment Research, 6095, 1-17, 2009.

Wanninkhof, R.: Relationship between wind speed and gas exchange over the ocean, J. Geophys. Res.-Oceans, 97, 7373-7382, doi: 10.1029/92jc00188, 1992.

Weinberg, I., Bahlmann, E., Michaelis, W., and Seifert, R.: Determination of fluxes and isotopic composition of halocarbons from seagrass meadows using a dynamic flux chamber, Atmos. Environ., 73, 34-40, doi: http://dx.doi.org/10.1016/j.atmosenv.2013.03.006, 2013.

Xiao, X., Prinn, R. G., Fraser, P. J., Simmonds, P. G., Weiss, R. F., O'Doherty, S., Miller, B. R., Salameh, P. K., Harth, C. M., Krummel, P. B., Porter, L. W., Muehle, J., Greally, B. R., Cunnold, D., Wang, R., Montzka, S. A., Elkins, J. W., Dutton, G. S., Thompson, T. M., Butler, J. H., Hall, B. D., Reimann, S., Vollmer, M. K., Stordal, F., Lunder, C., Maione, M., Arduini, J., and Yokouchi, Y.: Optimal estimation of the surface fluxes of methyl chloride using a 3-D global chemical transport model, Atmos. Chem. Phys., 10, 5515-5533, doi: 10.5194/acp-10-5515-2010, 2010.

Yvon-Lewis, S. A., Saltzman, E. S., and Montzka, S. A.: Recent trends in atmospheric methyl bromide: analysis of post-Montreal Protocol variability, Atmos. Chem. Phys., 9, 5963-5974, 10.5194/acp-9-5963-2009, 2009.

Zhou, Y., Varner, R. K., Russo, R. S., Wingenter, O. W., Haase, K. B., Talbot, R., and Sive, B. C.: Coastal water source of short-lived halocarbons in New England, J. Geophys. Res.-Atmos., 110, D21302, doi: 10.1029/2004jd005603, 2005.

1 Table 1: Summary of air mixing ratios and water concentrations of halocarbons in the Ria
2 Formosa and at the background site (Praia de Faro) for the sampling campaigns in summer
3 2011 and spring 2012. Values are given as means (bold) and ranges (in parentheses). Samples
4 from the Ria Formosa are data from the inlet of the flux chambers with a sampling height of 1
5 m above ground (summer: n=36; Praia de Faro: n=5; spring n=47). Given water
6 concentrations refer to n=8 (summer) and n=10 (spring).

7

	Air mixing ratio Ria Formosa (ppt)	Air mixing ratio Praia de Faro (ppt)	Water concentration Ria Formosa (pmol L^{-1})
summer 2011			
CH$_3$Cl	**828** (50~~03~~-1490)	**613** (498-685)	**220** (1~~6~~058-30~~0~~1)
CH$_3$Br	**22** (8-118)	**13** (9-19)	**8** (5-11)
CH$_3$I	**3** (2-11)	**1** (0.8-2)	**12** (4-18)
CHBr$_3$	**15**(6-31)	**8** (6-9)	**102** (67 -19~~0~~4)
spring 2012			
CH$_3$Cl	**654** (48~~0~~4-98~~0~~76)	-	**166** (10~~0~~1-27~~0~~67)
CH$_3$Br	**12** (4-40)	-	**10** (6-28)
CH$_3$I	**1** (0.4-4.8)	-	**7** (2-16)
CHBr$_3$	**2** (0.4-10)	-	**62** (39 - 13~~0~~3)

8
9

Table 2: Water concentration (pmol L^{-1}) and stable carbon isotope ratios of halocarbons (‰) obtained from a two-hours transect cruise on 24th April 2012 (see Fig. 1 for sampling positions).

Sample	Time (CET)	CH$_3$Cl pmol L^{-1}	‰	CH$_3$Br pmol L^{-1}	‰	CH$_3$I pmol L^{-1}	‰	CHBr$_3$ pmol L^{-1}	‰
1	15:09	121	-40.9	5	-25.6	5	-20.0	26	-25.8
2	15:50	241	-42.3	7	-21.2	5	-31.1	55	-18.3
3	15:58	96	-	9	-	2	-	21	-
4	16:10	106	-	11	-	5	-	31	-
5	16:21	180	-44.3	19	-35.9	14	-44.5	95	-18.9
6	16:46	72	-	5	-	3	-	18	-
7	16:50	82	-	4	-	5	-	14	-

Table 3: Mean net fluxes (bold) and ranges (parentheses) of halocarbons from flux chamber experiments seagrass meadows and sediments as well as those from sea-air exchange calculations. Data were obtained during the summer 2011 and spring 2012 campaigns in the Ria Formosa.

	n	CH_3Cl nmol m^{-2} h^{-1}	CH_3Br nmol m^{-2} h^{-1}	CH_3I nmol m^{-2} h^{-1}	$CHBr_3$ nmol m^{-2} h^{-1}
Summer 2011					
air exposure	28	**15.6** (-49 - 74)	**6.5** (-5.7 - 130)	**1.2** (0.5 - 2.8)	**1.8** (-0.6 - 5.7)
air exposure (sediment)	5	**3.6** (-1.9 - 8.1)	**0.6** (-0.2 - 1.1)	**0.2** (0.1 - 0.6)	**0.8** (-0.3 - 1.9)
Sea-air exchange	8	**29.8** (13 - 45)	**1.3** (0.6 - 1.7)	**2.2** (0.5 - 3.2)	**4.7** (1.0 - 8.0)
Spring 2012					
air exposure	17	**1.0** (-30 - 69)	**0.4** (-0.8 - 3.9)	**0.6** (-0.6 - 2.6)	**0.4** (-0.5 - 1.3)
tidal inundation	18	**16.6** (-58 - 100)	**1.8** (-1.6 - 8.3)	**1.9** (0.1 - 8.0)	**3.0** (-0.4 - 11)
tidal change	5	**40.1** (-14- 100)	**2.7** (0.1 - 8.3)	**3.3** (0.1 - 8.0)	**2.9** (0.2 - 11)
incoming tide	6	**11.4** (-15 - 37)	**1.8** (0.2 - 3.3)	**1.6** (0.1 - 2.9)	**2.8** (0.2 - 5.1)
tidal maximum	2	-18, -58	-0.5, -1.6	0.1, 0.1	0.5, -0.1
ebb flow	5	**21.3** (-14 - 46)	**2.1** (0.1 - 4.4)	**1.5** (0.2 - 3.0)	**4.5** (-0.4 - 8.6)
Sea-air exchange	10	**15.2** (3.5 - 32)	**1.4** (0.5 - 4.1)	**1.3** (0.3 - 3.7)	**8.3** (3.8 - 24)

45

Table 4: Compilation of stable carbon isotope values of halocarbons (‰) from the two sampling campaigns. Source signatures of seagrass meadows were calculated using a coupled mass and isotope balance (Weinberg et al., 2013).

	Atmosphere Ria Formosa (‰)	n	Atmosphere Praia de Faro (‰)	n	lagoon water (‰)	n	source signature seagrass meadow (‰)	n
summer 2011								
CH₃Cl	-42 ± 2	7	-39 ± 0.4	5	-43 ± 3	7	-51 ± 6	5
CH₃Br	-29 ± 5	7	-38 ± 3	5	-23 ± 3	7	-42 ± 17	4
CH₃I	-	-	-	-	-39 ± 9	7	-	-
CHBr₃	-	-	-	-	-13 ± 1	7	-	-
spring 2012								
CH₃Cl	-38 ± 1	3	-	-	-42 ± 1	5	-56 ± 2	3
CH₃Br	-23 ± 10	3	-	-	-33 ± 8	5	-26; -33	2
CH₃I	-	-	-	-	-37 ± 7	5	-	
CHBr₃	-	-	-	-	-18 ± 1	5	-	

1   Table 5: Mean concentrations (bold) and ranges (parentheses) of dissolved halocarbons (pmol

2   L^{-1}) from the subtropical lagoon Ria Formosa in summer 2011 (n=9) and spring 2012 (n=10)

3   in comparison to published data from coastal Atlantic waters.

location	CH_3Cl	CH_3Br	CH_3I	$CHBr_3$
Faro, Portugal (summer) [1]	**220** (16058 - 3001)	**8** (5-11)	**12** (4 - 18)	**102** (67 -19004)
Faro, Portugal (spring) [1]	**166** (1001 - 27067)	**10** (6 - 28)	**7** (2 - 16)	**62** (39 - 13003)
East Atlantic [2,#]	-	-	-	**68.3** (36.6 - 102.0)
Roscoff, France [3,#]	-	-	**12.9** (9.0 - 31.8)	**217.4** (1254.8 - 519.4)
Greenland, NW Atlantic [4]	104 - 260	-	0.2 - 16.1	-
Norfolk, UK [5]	-	**3.2** (1.7 - 8.7)	-	-
Menai Strait, UK [6,#]	-	-	**6.7** (0.0 - 80.0)	**214.2** (3.0 - 3588.4)
Mace Head, Ireland [7,#]	-	**3.7** (1.7 - 5.7)	**15.3** (10.9 - 19.2)	**388.0** (2221.8 - 554.3)
West Atlantic [8]	**88.4** (61.5 - 179.0)	**1.9** (0.8-5)	-	-
North West Atlantic [9]	**71.0** (55.0 - 106.0)	-	-	-
Nova Scotia, Canada [10]	-	-	4 - 6	-
Gulf of Maine, UK [11,#]	-	-	8 -18	40 - 1240

4   [1] this study; [2] Carpenter et al. (2009); [3] Jones et al. (2009); [4] Tait et al. (1994); [5] Baker et al. (1999); [6] Bravo-

5   Linares and Mudge (2009); [7] Carpenter et al. (2000); [8] Hu et al. (2010); [9] MacDonald and Moore (2007); [10]

6   Moore and Groszko (1999); [11] Zhou et al. (2005); [#] macroalgae dominated

7

1

2
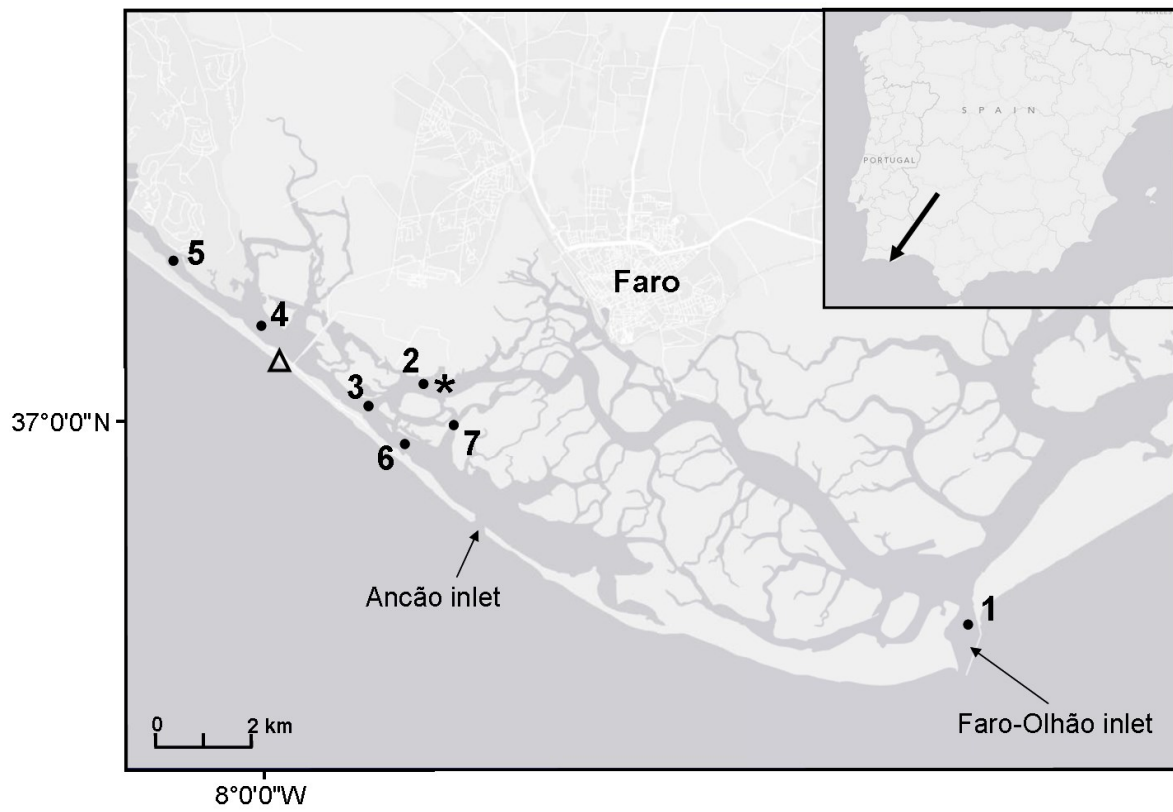
3 Fig. 1: Map of the lagoon Ria Formosa, Portugal. Asterisk: site of seagrass meadow studies;

4 triangle: sampling site on the Praia de Faro (upwind position). Dots with numbers represent

5 sampling points during the transect cruise.

6
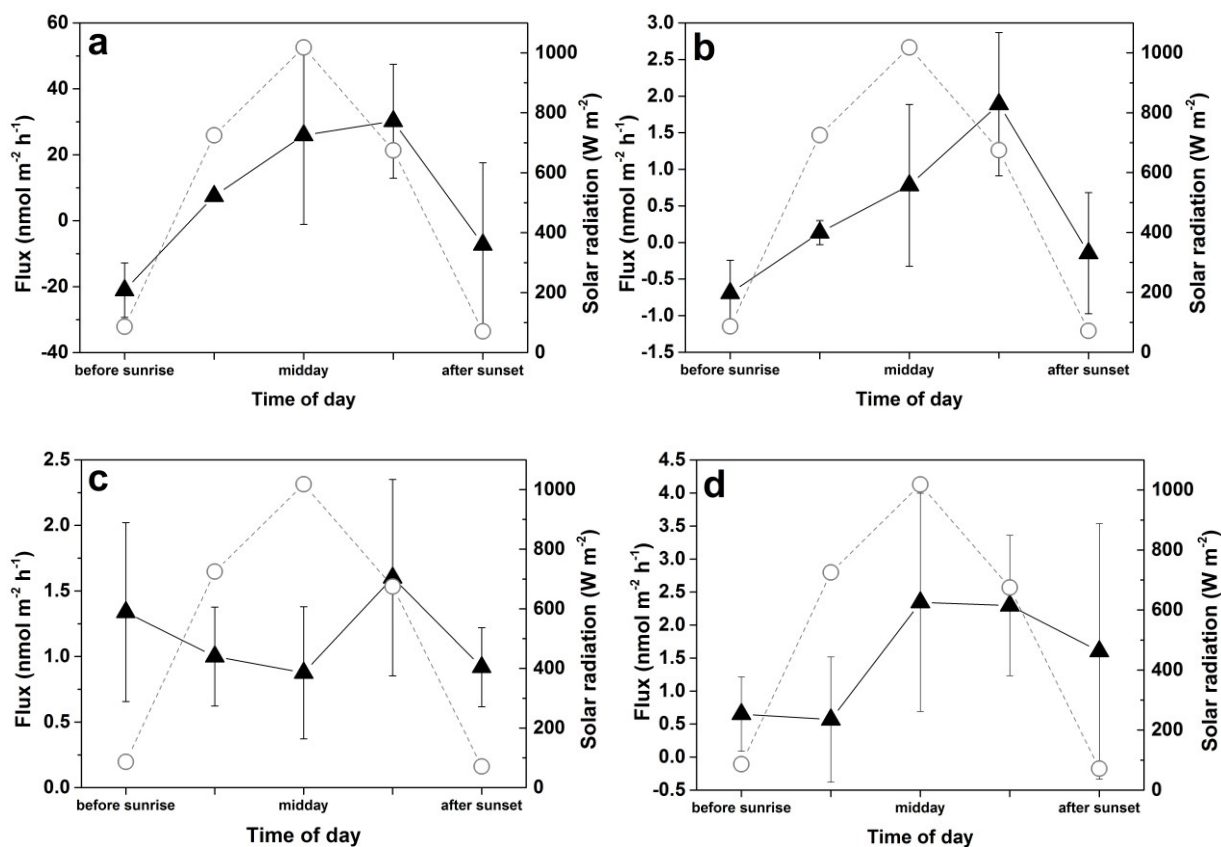
Fig. 2a-d: Diurnal variation of mean halocarbon fluxes (triangles) from seagrass meadows during periods of air exposure in summer 2011 (a: CH_3Cl, b: CH_3Br, c: CH_3I, d: $CHBr_3$). Error bars refer to standard deviations. Circles are solar radiation values. Note that the scales on y-axis are different for each compound.

CH3Cl

Seagrass meadows
- Portugal (summer), air exposure[1]
- Portugal (spring), air exposure[1]
- Portugal (spring), inundation[1]
- Germany, air exposure[2]

Salt marshes
- temperate[3,4,5,7]
- subtropical[8,9,10] *downscaled by a factor of 10*

Mangroves
- greenhouse experiments[11]

Flux (nmol m^{-2} h^{-1})

CH3Br

Seagrass meadows
- Portugal (summer), air exposure[1]
- Portugal (spring), air exposure[1]
- Portugal (spring), inundation[1]
- Germany, air exposure[2]

Salt marshes
- temperate[3,4,5,6]
- subtropical[8,9,10]

Mangroves
- greenhouse experiments[11]

Macroalgae
- Ireland[12]

Flux (nmol m^{-2} h^{-1})

CH3I

Seagrass meadows
- Portugal (summer), air exposure[1]
- Portugal (spring), air exposure[1]
- Portugal (spring), indundation[1]
- Germany air exposure[2]

Salt marshes
- California, USA[9]
- Tasmania[4]
- Ireland[5]

Mangroves
- greenhouse experiments[11]

Macroalgae
- Malaysian coastline[13]

Flux (nmol m^{-2} h^{-1})

50

Fig. 3: Compilation of mean emissions (bold black vertical lines) and ranges from different sources in coastal environments for CH_3Cl (upper panel), CH_3Br (middle panel) and CH_3I (lower panel). Note the different scales. Published data adopted from: [1] this study; [2] Weinberg et al. (2013); [3] Blei et al. (2010); [4] Cox et al., (2004); [5] Dimmer et al. (2001); [6] Drewer et al. (2006); [7] Valtanen et al. (2009); [8] Rhew and Mazéas (2010); [9] Manley et al. (2006); [10] Rhew et al. (2000); [11] Manley et al. (2007); [12] Carpenter et al. (2000); [13] Leedham et al. (2013). Note that the data of CH_3Cl from subtropical salt marshes are downscaled by a factor of 10 for visualization reasons. Where multiple references were used, the individual study means were averaged and presented along with the resulting ranges. Thus, ranges of halocarbon fluxes in each single study are not covered. Studies reporting a strong species dependency in magnitude of fluxes were averaged over all species for simplicity reasons. Macroalgae emissions given in g fresh weight per hour were converted by using the species' fresh weights and spatial coverage in the coastal belt in Mace Head, Ireland for CH_3Br (Carpenter et al., 2000) and the Malaysian coastline for CH_3I (Leedham et al., 2013), respectively.

1 **Supplement to**

2 **A halocarbon survey from a seagrass dominated**

3 **subtropical lagoon, Ria Formosa (Portugal): Flux pattern**

4 **and isotopic composition**

5

6 Ingo Weinberg, Enno Bahlmann[*], Tim Eckhardt, Walter Michaelis, and Richard Seifert

7 University of Hamburg, Institute for Biogeochemistry and Marine Chemistry,

8 Bundesstraße 55, 20146 Hamburg, Germany

9 [*]corresponding author: enno.bahlmann@zmaw.de

10   phone: +49-40-42838-5167

11   fax: +49-40-42838-6347

12

13 **7 Design of cryotraps used for air and seawater samples (Purge and trap)**

14 The analytic procedure is based on the method of Bahlmann et al. (2011) for the isotopic

15 determination of trace gases with some adjustments. We changed the design of the cryotraps

16 in order to establish a better temporal resolution by reducing the sample preparation/analysis

17 time. The self-made cryotraps were ¼" siltek capillary (40 cm) connected to a stainless steel

18 capillary (60 cm) and were bowed forming a U-shape. This allows the cryotrap being easily

19 submersed in the dry shipper (Voyageur 12, Air Liquide, Germany) as cooling source during

20 sampling. The cryotraps were filled with Tenax TA (20-35 mesh, 5 cm, Grace, Deerfield,

21 USA) at the lower end of ¼" capillary and fixed with silanized glass wool at the top and

22 bottom of the packing material. The inlet and outlet were capped with Swagelok fittings and

23 endcaps allowing rapid connection and closure before/after sampling and measurements.

24

8 Measurement of air and seawater samples

The instrumental set up is shown in Fig. S1). After sampling (air sampling or purge&trap of water samples), the samples were thermally desorbed from the cryotrap (310°C) under a flow of high-purity helium (50 mL min^{-1}, 99.999%, Linde, Germany) for 15 min (red lines/arrows). The analytes were re-trapped on peltier-cooled sampling tubes (Bahlmann et al., 2011) at -15°C using a Valco eight port valve (VICI, Valco instruments, Houston, USA). After sample transfer, the valco valve was switched and analytes were thermally desorbed (330°C) from the adsorbent tubes in counter-flow direction (He, 30 mL min^{-1}), here indicated as green lines/arrows. During the desorption (20 min), the analytes were then refocused on a cryotrap (quartz capillary, 60 cm, 0.32 i.d.) submerged in liquid nitrogen. The refocusing of analytes and injection into the GC-MS system proceeds using a second eight port valco valve. After retrapping, the valve is switched and compounds are sent to the GC-MS system in counterflow direction (black (dotted) lines/arrows) under ambient temperature. Due to high water amounts in air and water samples, the water was removed by two Nafion dryers (in silica gel), each after thermal desorption from the cryotraps and the adsorbent tubes.

The GC-MS (6890N/5975B, Agilent, Waldbronn, Germany) was equipped with a CP-PorabondQ column (25 m, 0.25 µm i.d., Varian). The flowrate was set to 3°mL. The oven temperature program was as follows: 40 °C, hold 4 min; 12° C min^{-1} to 200°C, hold 2 min, 8° C min^{-1} to 240°C; 30° C min^{-1} to 280°C, hold 5 min. The MS was operated in the electron impact mode at 70 eV. Temperatures of quadrupole, source, and transfer line were 150°C, 230°C, and 250°C. Acquisition was executed in full scan mode (33-300 u). Target analytes were identified by their retention times and respective mass spectra and quantified using their major mass fragments. Quantification of air and water samples was done by using aliquots of Scott EPA TO 15/17 gas standard (1 ppm in nitrogen, Sigma Aldrich, Germany) and CH_3I gas standard (100 ppm in nitrogen, Air Liquide, Germany) injected to the GC-MS.

The trapping and desorption efficiency (recovery rates) of the cryotraps was tested (n=4). 2 mL of Scott EPA TO 15/17 gas standard (1 ppm in nitrogen) and 20 µL CH_3I (100 ppm nitrogen) was injected to the cryotraps submerged in the dry shipper using a stream of helium. Simulating "real" air sampling, helium was stream was set to 1L min^{-1} for 30 min (resulting in 30 L). The whole sample treatment procedure was applied as described above. The mean recovery rates of a suite of halocarbons were 96% ranging from 93± 4% (CH_3Br) and 93± 10% (CCl_4) to 100± 4% for $CHBr_3$. Individual recovery rates are displayed in Fig. S2.

9   Correlation scatter plots of halocarbon fluxes from seagrass meadows

Correlation scatter plots of halocarbon fluxes from seagrass meadows during the summer campaign in 2011. Data refers to measurements obtained from air-exposed seagrass meadows.
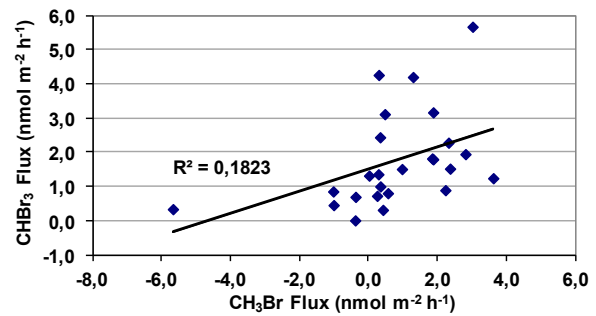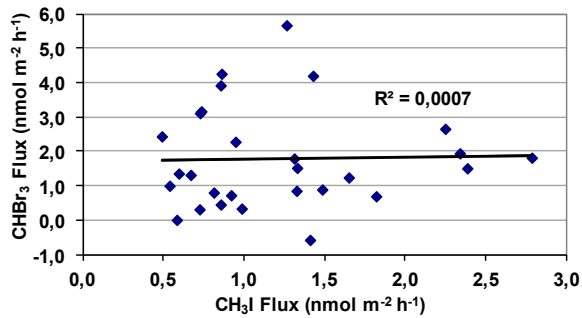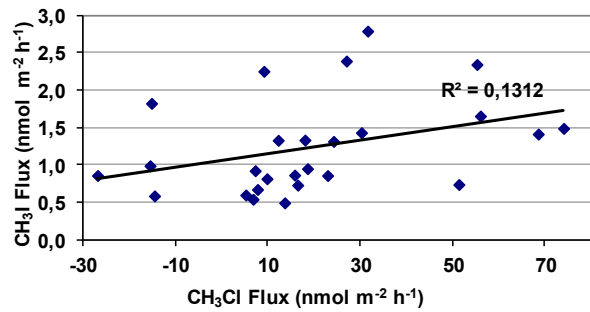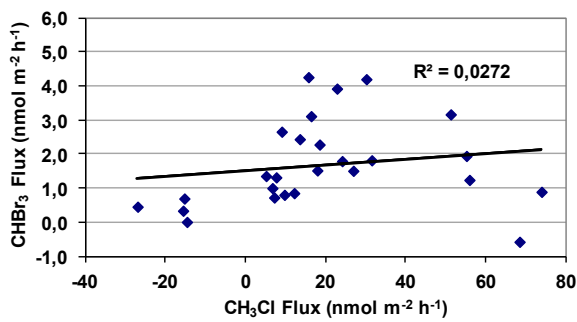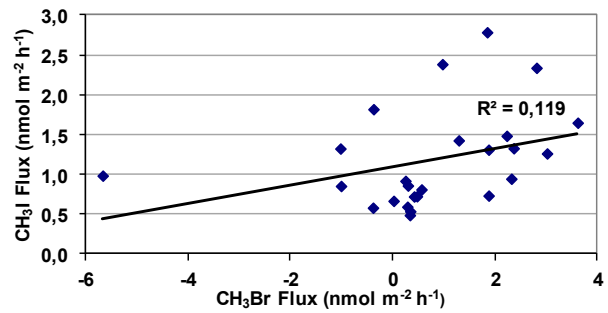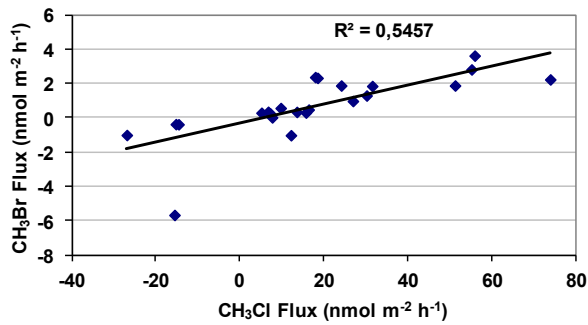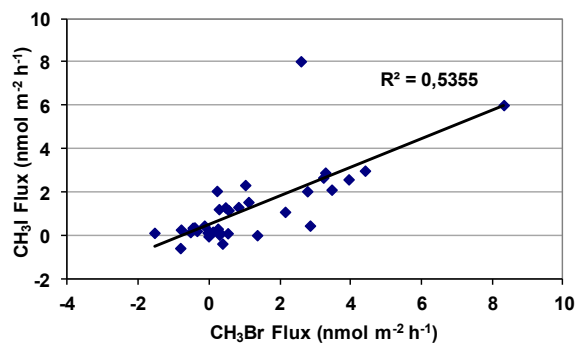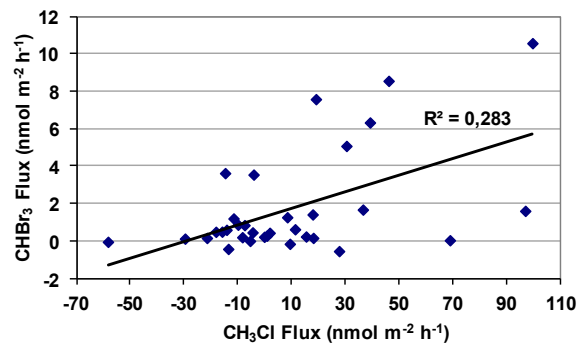
1 Correlation scatter plots of halocarbon fluxes from seagrass meadows during the spring

2 campaign in 2012. Data refers to measurements obtained from air-exposed and submerged
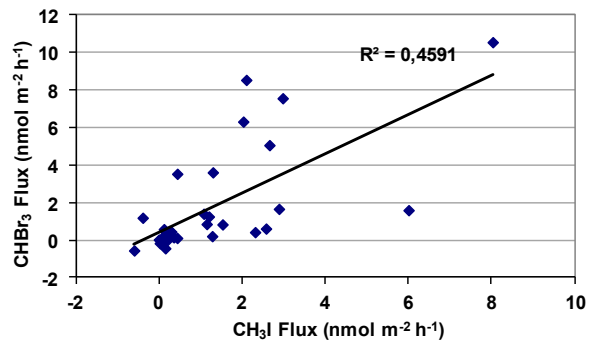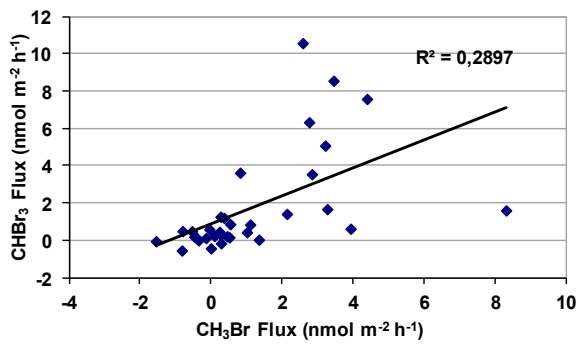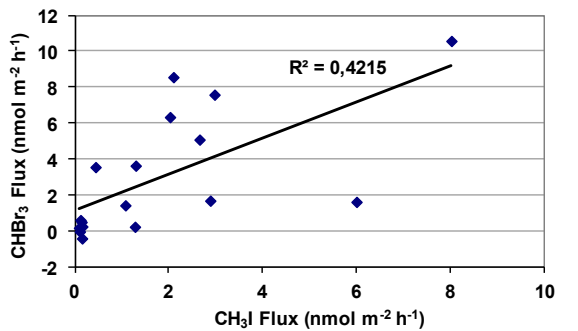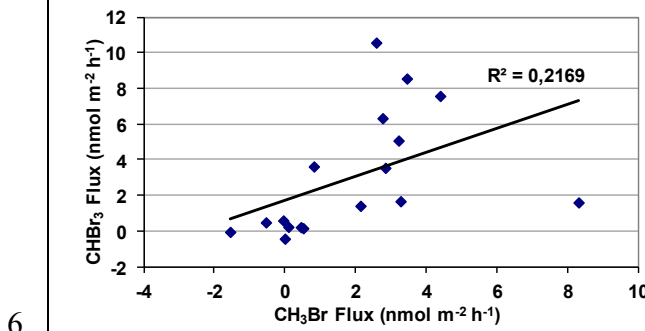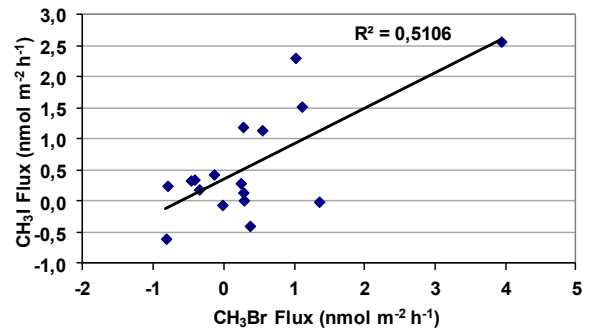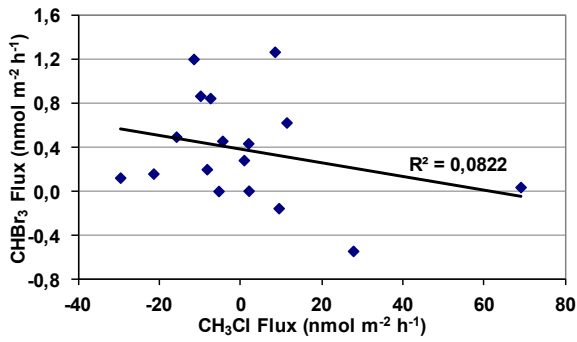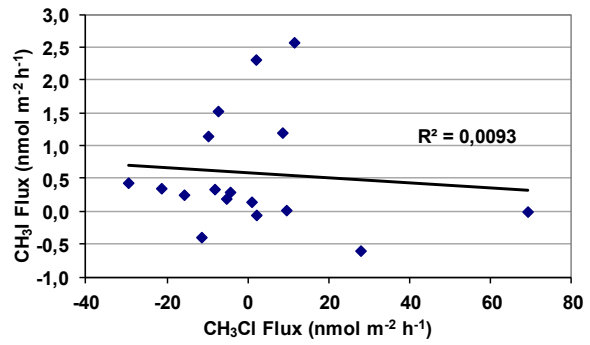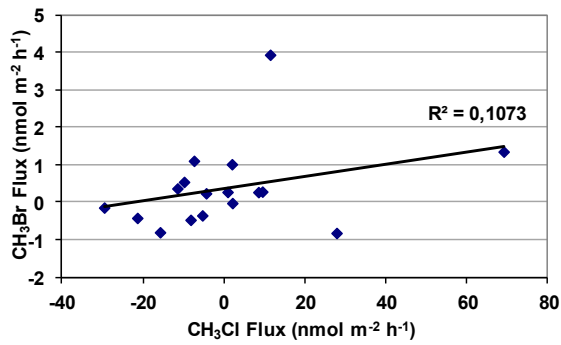
3 seagrass meadows.
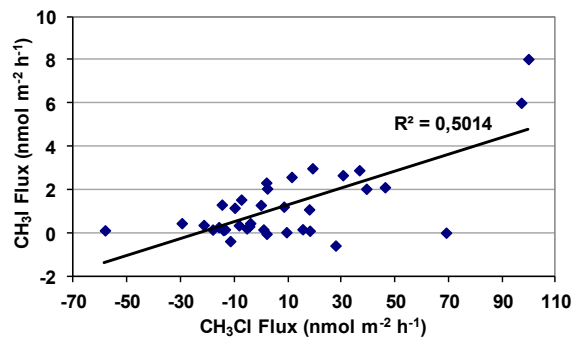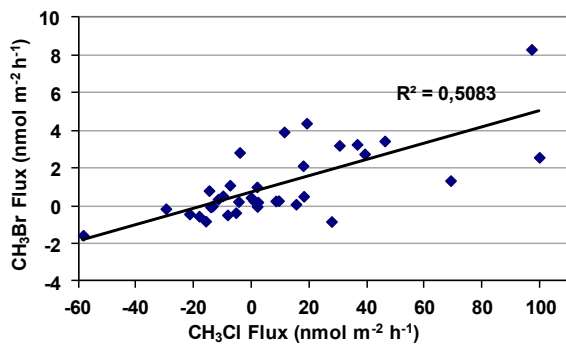
1 Correlation scatter plots of halocarbon fluxes from seagrass meadows during the spring

2 campaign in 2012. Data refers to measurements obtained from submerged seagrass meadows,

3 only.
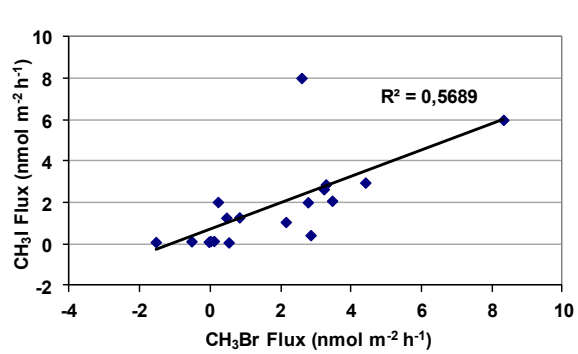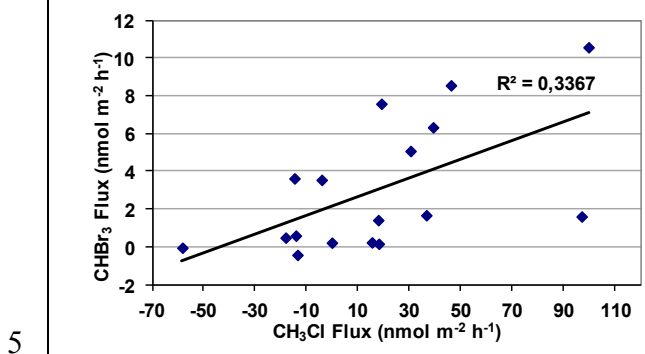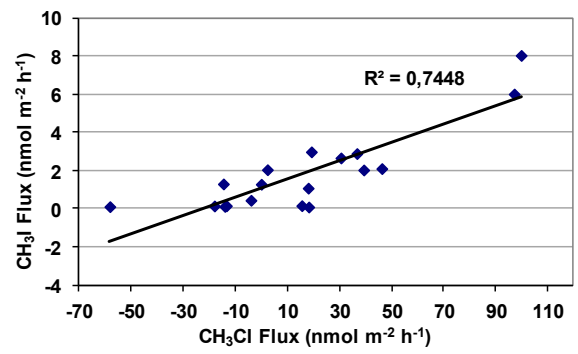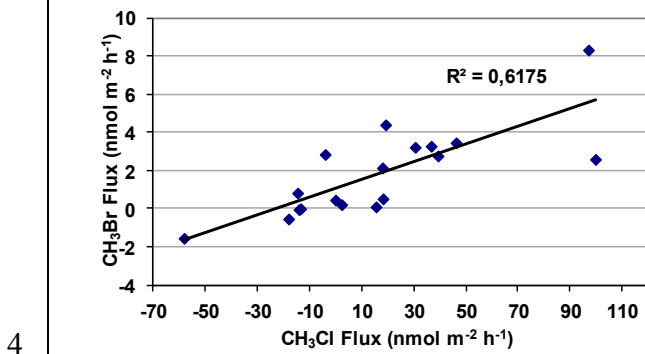
Correlation scatter plots of halocarbon fluxes from seagrass meadows during the spring campaign in 2012. Data refers to measurements obtained from air-exposed seagrass meadows, only.
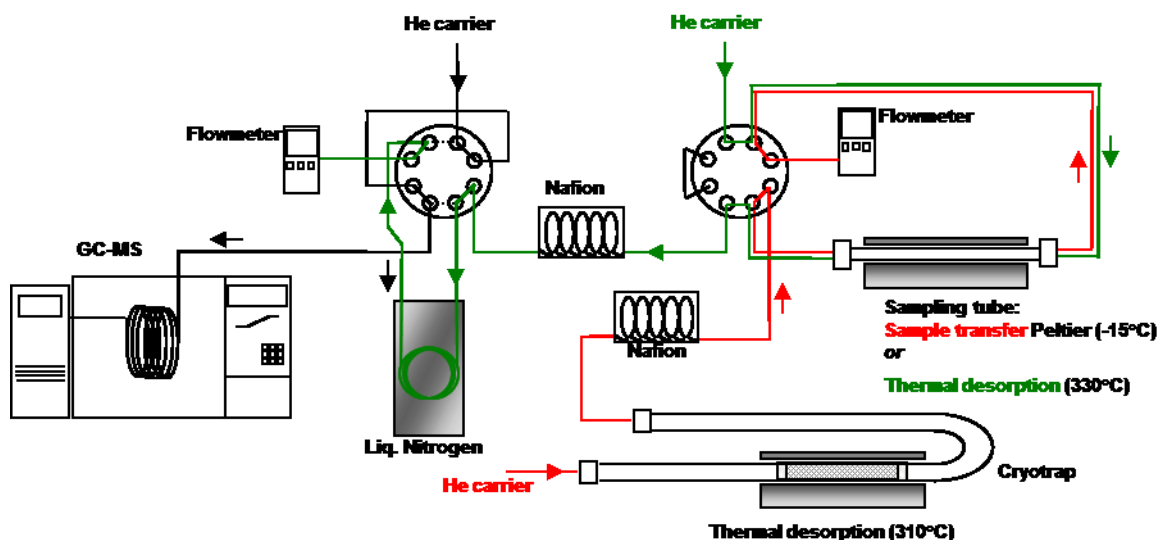
References
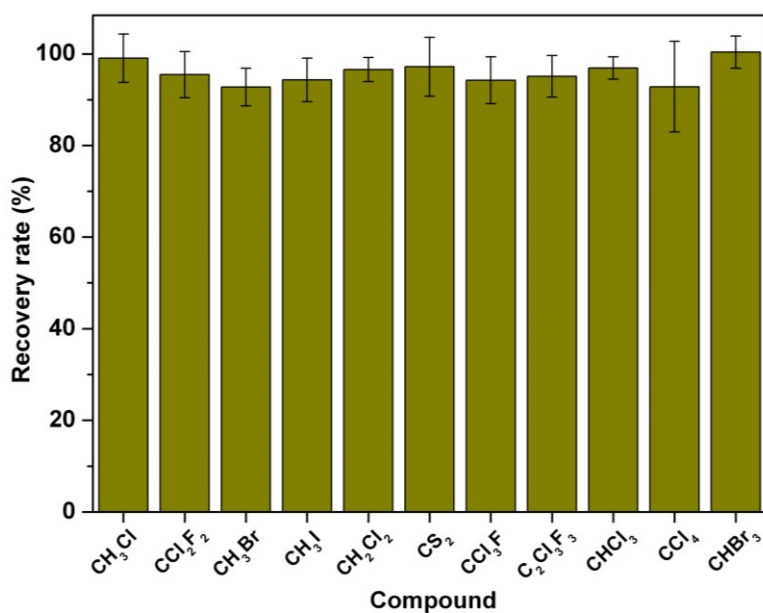
Bahlmann, E., Weinberg, I., Seifert, R., Tubbesing, C., and Michaelis, W.: A high volume sampling system for isotope determination of volatile halocarbons and hydrocarbons, Atmos. Meas. Tech., 4, 2073-2086, 10.5194/amt-4-2073-2011, 2011.

1

2

3
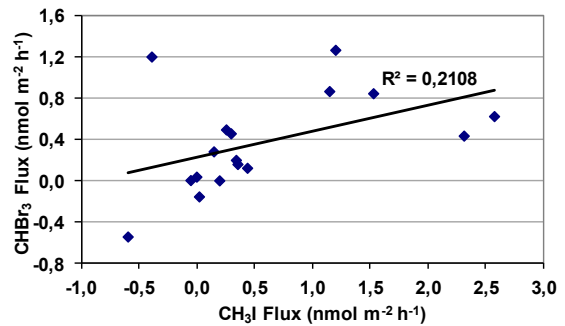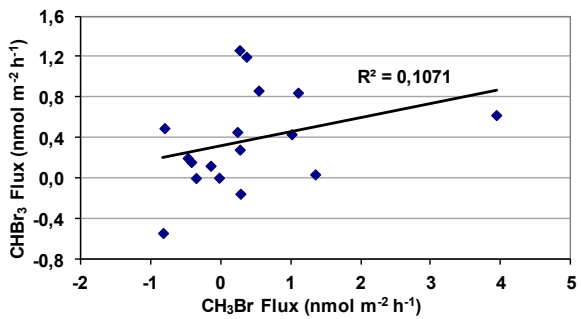
4 Fig. S1: Scheme of the analytical system for the determination of halocarbons from air and

5 water samples.

6

7

8 Fig. S2: Mean recovery rates and their absolute standard deviations of halocarbons from

9 recovery experiments (n=4).

10

11

1