

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

4

5 Ingo Weinberg, Enno Bahlmann\*, Tim Eckhardt, Walter Michaelis, and Richard Seifert

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

7 Bundesstraße 55, 20146 Hamburg, Germany

8 \*corresponding author: enno.bahlmann@zmaw.de

9 phone: +49-40-42838-5167

10 fax: +49-40-42838-6347

11

12 **Abstract**

13 Here we report fluxes of chloromethane (CH<sub>3</sub>Cl), bromomethane (CH<sub>3</sub>Br), iodomethane  
14 (CH<sub>3</sub>I), and bromoform (CHBr<sub>3</sub>) from two sampling campaigns (summer and spring) in the  
15 seagrass dominated subtropical lagoon Ria Formosa, Portugal. Dynamic flux chamber  
16 measurements were performed when seagrass patches were either air-exposed or submerged.  
17 Overall, we observed highly variable fluxes from the seagrass meadows and attributed them  
18 to diurnal cycles, tidal effects, and the variety of possible sources and sinks in the seagrass  
19 meadows. Highest emissions with up to 130 nmol m<sup>-2</sup> h<sup>-1</sup> for CH<sub>3</sub>Br were observed during  
20 tidal changes from air exposure to submergence and conversely. Furthermore, during the  
21 spring campaign, the emissions of halocarbons were significantly elevated during tidal  
22 inundation as compared to air exposure.

23 Accompanying water sampling during both campaigns revealed elevated concentrations of  
24 CH<sub>3</sub>Cl and CH<sub>3</sub>Br indicating productive sources within the lagoon. Stable carbon isotopes of  
25 halocarbons from the air and water phase along with source signatures were used to allocate  
26 the distinctive sources and sinks in the lagoon. Results suggest CH<sub>3</sub>Cl rather originating from  
27 seagrass meadows and water column than from salt marshes. Aqueous and atmospheric  
28 CH<sub>3</sub>Br was substantially enriched in <sup>13</sup>C in comparison to source signatures for seagrass

1 meadows and salt marshes. This suggests a significant contribution from the water phase on  
2 the atmospheric CH<sub>3</sub>Br in the lagoon.

3 A rough global upscaling yields annual productions from seagrass meadows of 2.3-4.5 Gg yr<sup>-1</sup>  
4 <sup>1</sup>, 0.5-1.0 Gg yr<sup>-1</sup>, 0.6-1.2 Gg yr<sup>-1</sup>, and 1.9-3.7 Gg yr<sup>-1</sup> for CH<sub>3</sub>Cl, CH<sub>3</sub>Br, CH<sub>3</sub>I, and CHBr<sub>3</sub>  
5 respectively. This suggests a minor contribution from seagrass meadows to the global  
6 production of CH<sub>3</sub>Cl and CH<sub>3</sub>Br with about 0.1 % and 0.7 %, respectively. In comparison to  
7 the known marine sources for CH<sub>3</sub>I and CHBr<sub>3</sub>, seagrass meadows are rather small sources.

8

## 9 **1 Introduction**

10 The halocarbons chloromethane (CH<sub>3</sub>Cl), bromomethane (CH<sub>3</sub>Br), iodomethane (CH<sub>3</sub>I), and  
11 bromoform (CHBr<sub>3</sub>) are prominent precursors of reactive halogens which affect the oxidative  
12 capacity of the atmosphere and initiate stratospheric ozone destruction (Saiz-Lopez and von  
13 Glasow, 2012 and references therein). Therefore, during the last decades, the sources and  
14 sinks of these trace gases have been intensively studied.

15 For CH<sub>3</sub>Cl, recent atmospheric budget calculations suggest that the known sinks can be  
16 balanced by large emissions from tropical terrestrial sources (Saito and Yokouchi, 2008; Xiao  
17 et al., 2010). Nevertheless, these calculations still incorporate large uncertainties. The  
18 atmospheric budget of CH<sub>3</sub>Br remains still unbalanced, with the known sinks exceeding  
19 known sources by about 30% (Yvon-Lewis et al., 2009). The current emission estimates for  
20 CH<sub>3</sub>I and CHBr<sub>3</sub> are assigned with even larger uncertainties (Bell et al., 2002; Quack and  
21 Wallace, 2003).

22 Stable carbon isotopes of halocarbons have been applied to further elucidate their sources and  
23 sinks by using individual source signatures (Keppler et al., 2005). While this was primarily  
24 done for CH<sub>3</sub>Cl, first isotopic source signatures of naturally-produced CH<sub>3</sub>Br were recently  
25 reported (Bill et al., 2002; Weinberg et al., 2013). Moreover, the biogeochemical cycling of  
26 halocarbons underlies various transformation processes which can be studied by the stable  
27 carbon isotope approach in addition to flux and/or concentration measurements.

28 Coastal zones are reported as being important source regions of halocarbons. In these salt  
29 water affected systems, halocarbon producers comprise phytoplankton (Scarratt and Moore,  
30 1998), macroalgae (Gschwend et al., 1985), salt marshes (Rhew et al., 2000), and mangroves  
31 (Manley et al., 2007).

1 With a net primary production of  $1211 \text{ g C m}^{-2} \text{ yr}^{-1}$ , seagrass meadows are one of the most  
2 productive ecosystems with a similar global abundance as mangroves and salt marshes  
3 (Duarte et al., 2005). They cover huge areas of the intertidal and subtidal zone in temperate  
4 and subtropical/tropical regions. Thus, they may represent an additional source for  
5 halocarbons to the atmosphere which is not yet sufficiently studied. Seagrass meadows are  
6 highly diverse ecosystems with respect to potential halocarbon producers. Along with the  
7 seagrass itself, they comprise epiphytes such as microalgae and diatoms, and sediment  
8 reassembling microphytobenthos and bacteria communities. All these constituents of the  
9 benthic community have been reported to produce halocarbons (Amachi et al., 2001; Blei et  
10 al., 2010; Manley et al., 2006; Moore et al., 1996; Rhew et al., 2002; Tokarczyk and Moore,  
11 1994; Urhahn, 2003). While first evidence for the release of halocarbons from seagrass was  
12 obtained by incubation experiments (Urhahn 2003), we could recently confirm this production  
13 potential in a field study of a temperate seagrass meadow in Northern Germany (Weinberg et  
14 al., 2013).

15 In order to refine these results, we conducted two field campaigns in the subtropical lagoon  
16 Ria Formosa, Portugal in 2011 and 2012. Here we report the results of these campaigns  
17 comprising dynamic flux chamber measurements for halocarbons over seagrass meadows  
18 during air exposure and tidal inundation. Using the flux and isotopic data, we present first  
19 insights into the environmental controls of halocarbon dynamics within this ecosystem.

20

## 21 **2 Materials and methods**

### 22 **2.1 Sampling site**

23 The Ria Formosa, covering an area of  $84 \text{ km}^2$ , is a mesotidal lagoon at the South-eastern coast  
24 of the Algarve, Portugal (Fig. 1). It is separated from the Atlantic Ocean by a series of barrier  
25 islands and two peninsulas. About 80% of the lagoon is intertidal with a semi-diurnal tidal  
26 regime and tidal ranges between 1.3 m during neap tides and 3.5 m during spring tides  
27 (Cabaço et al., 2012). Due to negligible inflow of fresh water and high exchange of water  
28 with the open Atlantic during each tidal cycle, the salinity within the lagoon is 35 to 36 PSU  
29 year round, except for periods of heavy rainfalls. About a quarter of the intertidal area ( $13.04$   
30  $\text{ km}^2$ ) is covered by dense stands of *Zostera noltii* Hornem (Guimarães et al., 2012). Further,  
31 but much less abundant, seagrass species in the lagoon are *Zostera Marina* L. and *Cymodocea*

1 *nodosa* (*Ucria*) *Ascherson* which are mainly located in shallow parts of the subtidal areas  
2 (Santos et al., 2004). About 30% of the lagoon's area is covered with salt marsh communities  
3 (Rui Santos, pers. comm.).

## 4 **2.2 Sampling**

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

15 During the two campaigns we used different dynamic flux chamber systems. During the 2011  
16 campaign, we measured the halocarbon fluxes during air exposure using a quartz-glass  
17 chamber (0.1m<sup>2</sup> surface area, 7 L enclosure volume) as described in Weinberg et al. (2013)  
18 with some adjustments. For this study a permanent backup flow (3± 0.2 L min<sup>-1</sup>) through the  
19 flux chamber during sampling and the change of cryotrap was applied to ensure sufficient  
20 mixing. Further, to overcome analytical problems with the high humidity in the sampled air,  
21 the water content was reduced using a condenser (-15°C). Briefly, the quartz-glass flux  
22 chamber was placed on the seagrass patch and sealed with surrounding sediment. Two  
23 sampling systems were operated simultaneously measuring inlet and outlet air of the flux  
24 chamber (flow rate 1± 0.2 L min<sup>-1</sup>). Prior to sampling, the flux chamber was flushed for about  
25 10 min ensuring sufficient equilibration of compounds in the chamber air.

26 During the 2012 campaign, we used a dynamic flux chamber system (0.037 m<sup>2</sup> bottom  
27 surface area, 8 L enclosure volume) suitable for flux measurements during both periods of air  
28 exposure and tidal immersion. The properties and setup of this dynamic chamber system is  
29 described in detail elsewhere (Bahlmann et al., 2014). Since this system acts as an ordinary  
30 purge and trap system, the extraction efficiencies were simulated using halocarbon  
31 equilibrated artificial seawater. While the results from these tests revealed that

1 monohalomethanes were almost completely extracted ( $\geq 90\%$ ), the purge efficiencies for  
2  $\text{CHBr}_3$  were only 33%. Thus the reported  $\text{CHBr}_3$  fluxes determined from seagrass meadows  
3 using the submersible chamber system represent an under-estimate.

4 Based on the sampling system for the determination of stable carbon isotopes of halocarbons  
5 (Bahlmann et al., 2011), we modified the cryogenic trapping system for the measurements of  
6 halocarbon mixing ratios, in order to establish a better temporal resolution by reducing the  
7 analysis time. This results in a final air volume of  $28 \pm 5$  L of air at the inlet and the outlet of  
8 the chambers, respectively. The specifications along with the results from test surveys are  
9 given in the Supplementary Materials.

10 The seagrass species sampled was exclusively *Z. Noltii*. The seagrass patches sampled had an  
11 area coverage of  $>95\%$  and were free of visible epiphytes such as macroalgae. In this low to  
12 medium intertidal region the epiphytes of *Z. Noltii* are almost exclusively diatoms whose  
13 contribution ranges from 0.5 to 4% of the total seagrass biomass (Cabaço et al., 2009). We  
14 further determined the fluxes from an adjacent bare sediment spot during the 2011 campaign.  
15 On 2 August 2011, these chamber-based measurements were complemented by atmospheric  
16 sampling at a nearby beach (Praia de Faro, upwind site) about 3 km distant from the lagoon  
17 during the summer campaign 2011 (Fig. 1). At this time the wind direction was south-  
18 westerly reflecting background air from the coastal ocean.

19 Discrete water samples for the determination of dissolved halocarbons concentration and  
20 isotopic composition at high tide were taken during both campaigns. The samples were taken  
21 directly above the studied seagrass meadow using Duran glass bottles (1-2 L volume). Air and  
22 sediment intrusions during water sampling were avoided. The water depth was between 0.3 m  
23 and 1 m. On April 24<sup>th</sup> 2012, a transect cruise through the middle and western part of the  
24 lagoon was conducted during rising waters (Fig. 1). The water samples were taken from a  
25 water depth of 1 m. Dissolved halocarbons were extracted from seawater using a purge and  
26 trap system. Seawater was purged with helium 5.0 (purge flow  $1\text{L min}^{-1}$ ) for 30 minutes.  
27 After water vapour reduction of the purge gas, the compounds were enriched on cryotrap  
28 (submerged in a dry shipper). The shape of the cryotrap used here was the same as those for  
29 flux chamber and atmospheric samples. The water samples were usually processed within 30  
30 minutes after sampling. Samples from the transect cruise were stored in the dark at  $4^\circ\text{C}$  and  
31 analyzed within eight hours. Purge efficiencies of monohalomethanes from lagoon water were  
32  $\geq 95\%$  (1 L and 2 L samples). However, the less volatile  $\text{CHBr}_3$  was only extracted with 50%

1 (1 L samples) and 30% (2 L samples). Therefore, the results of water concentration were  
2 corrected for the respective purge efficiency for this compound.

### 3 **2.3 Measurement and quantification**

4 The measurement procedure is described in detail in the Supplementary Materials. Briefly,  
5 compounds adsorbed on the cryotrap, were thermally desorbed and transferred to Peltier-  
6 cooled adsorption tubes. The analytes were further desorbed from the adsorption tubes and  
7 refocused cryogenically before injection to the GC-MS system. Air and water samples were  
8 measured on-site at Ramalhete research station using a GC-MS system (6890N/5975B,  
9 Agilent, Germany) equipped with a CP-PorabondQ column (25 m, 0.25  $\mu\text{m}$  i.d., Varian,  
10 Germany). The GC-MS was operated in the electron impact mode. Identification of  
11 compounds was executed by retention times and respective mass spectra. Aliquots of gas  
12 standard (Scott EPA TO 15/17, 65 compounds, 1 ppm each in nitrogen, Sigma Aldrich,  
13 Germany) containing  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{Br}$ , and  $\text{CHBr}_3$  were applied to quantify the target  
14 compounds. During onsite measurements,  $\text{CH}_3\text{I}$  was quantified using the response factor  
15 against  $\text{CH}_3\text{Br}$ . The response factor was determined prior to the campaign. Equivalent  
16 amounts of  $\text{CH}_3\text{I}$  and  $\text{CH}_3\text{Br}$  from single gas standards were analysed together for the  
17 response factor calculation. The analytical limit of detection was 0.3 ppt ( $\text{pmol mol}^{-1}$ ) for the  
18 halocarbons. The accuracy of the entire sampling method (sampling, sample treatment,  
19 measurement) was derived from test samples in triplicates. The deviation between the  
20 individual samples for  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{Br}$ ,  $\text{CH}_3\text{I}$ , and  $\text{CHBr}_3$  was 5.4%, 6.3%, 15.4% and 6.7%,  
21 respectively. A series of procedural blanks (cryotrap and adsorption tubes) were taken during  
22 the sampling campaigns. The occasionally detected blanks of  $\text{CH}_3\text{Cl}$  and  $\text{CH}_3\text{Br}$  from these  
23 determinations were  $\leq 3\%$  to the “real” samples taken from the seagrass meadows during  
24 sampling campaigns. Therefore, the halocarbon fluxes were not blank corrected.

25 Air and water samples for determining the isotopic composition of halocarbons were  
26 transferred to adsorption tubes and stored at  $-80^\circ\text{C}$  until measurements. The analysis was  
27 conducted using the GC-MS-IRMS system at our home laboratory (Bahlmann et al., 2011).  
28 Additional transport and storage blanks were processed which revealed no contamination for  
29 all halocarbons studied.

30

## 1 2.4 Calculations

2 The fluxes were determined with dynamic flux chambers. The chamber is positioned on the a  
3 sampling spot and flushed continuously with ambient air. The mixing ratios of compounds at  
4 the inlet and outlet air are then measured. The difference of mixing ratios of compounds  
5 between inlet and outlet air along with the flushing rate and the surface area are used for the  
6 flux calculation ( $F_{Net}$ ,  $\text{nmol m}^{-2} \text{h}^{-1}$ ):

$$7 \quad F_{Net} = \frac{Q \times (C_{out} - C_{in})}{A \times V \times 1000} \quad (1)$$

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

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

$$17 \quad F = k_w \times (C_w - C_a \times H^{-1}) \quad (2)$$

18 where  $k_w$  is the gas exchange velocity ( $\text{m h}^{-1}$ ),  $C_w$  and  $C_a$  the water concentration and air  
19 concentration ( $\text{pmol L}^{-1}$ ), respectively, and  $H$  the dimensionless and temperature dependent  
20 Henry's law constant taken from Moore (2000) for  $\text{CH}_3\text{Cl}$ , Elliott and Rowland (1993) for  
21  $\text{CH}_3\text{Br}$  and  $\text{CH}_3\text{I}$ , and Moore et al. (1995) for  $\text{CHBr}_3$ . Several approximations emerged to  
22 estimate the relationship between the gas exchange velocity  $k$  and the wind speed  $u$  for open  
23 and coastal oceans (e.g. Nightingale et al., 2000; Wanninkhof, 1992). These estimations rely  
24 on assumptions that trace gas exchange is based on wind-driven turbulence. This is not  
25 applicable in shallow estuarine and riverine systems where the sea-air gas exchange is  
26 additionally driven by wind-independent currents and the bottom turbulence and thus water  
27 depth and current velocities further play a major role (Raymond and Cole, 2001). Studying  
28 the sea-air exchange in the Ria Formosa, these additional factors have to be considered in  
29 addition to wind driven outgassing. Therefore, we used the parameterization of  $k_w$  with the

1 assumption that wind speed and water current driven turbulence are additive (Borges et al.,  
2 2004):

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

4 where  $w$  is the water current ( $\text{cm s}^{-1}$ ),  $h$  the water depth (m) and  $u$  the wind speed ( $\text{m s}^{-1}$ ). For  
5 the calculations of the sea-air flux in the lagoon, a mean water depth of 1.5m (Tett et al.,  
6 2003) and a mean water current of  $24 \text{ cm s}^{-1}$  (Durham, 2000) was used. The Schmidt number  
7 ( $Sc$ ) expresses the ratio of transfer coefficients of the kinematic viscosity of water and gas  
8 diffusivity of interest. The gas exchange velocity  $k_w$  for each gas was then normalized to a  
9 Schmidt number of 660, assuming a proportionality to  $Sc^{-0.5}$  (Borges et al., 2004). The  
10 individual Schmidt numbers were obtained from Tait (1995) for  $\text{CH}_3\text{Cl}$ , De Bruyn and  
11 Saltzman (1997) for  $\text{CH}_3\text{Br}$  and  $\text{CH}_3\text{I}$ , and Quack and Wallace (2003) for  $\text{CHBr}_3$ .

12

### 13 **3 Results**

#### 14 **3.1 Halocarbons in the atmosphere and lagoon water**

15 The air mixing ratios in the lagoon were adopted from the inlets of the flux chambers at 1 m  
16 above ground during both campaigns. The results of these measurements and those of the  
17 upwind site outside the lagoon (Praia de Faro) are presented in Table 1. In summer, elevated  
18 air mixing ratios of the monohalomethanes were observed during periods of easterly winds  
19 when air masses at the sampling site had presumably passed over major parts of the lagoon.  
20 These mixing ratios reached up to 1490 ppt for  $\text{CH}_3\text{Cl}$ , 61 ppt for  $\text{CH}_3\text{Br}$ , and 11 ppt for  $\text{CH}_3\text{I}$   
21 reflecting a potent source in this system. The mixing ratios at the upwind site (Praia de Faro)  
22 were distinctively lower with mean values of 613 ppt ( $\text{CH}_3\text{Cl}$ ), 13 ppt ( $\text{CH}_3\text{Br}$ ), 1 ppt ( $\text{CH}_3\text{I}$ ),  
23 and 8 ppt ( $\text{CHBr}_3$ ) further indicating a source inside the lagoon. In spring 2012, the mean air  
24 mixing ratios in the lagoon were significantly lower than during summer with 654 ppt for  
25  $\text{CH}_3\text{Cl}$ , 12 ppt for  $\text{CH}_3\text{Br}$ , 1 ppt for  $\text{CH}_3\text{I}$ , and 2 ppt for  $\text{CHBr}_3$ .

26 Discrete water samples were taken above the studied seagrass meadow during tidal inundation  
27 (summer  $n=9$ ; spring  $n=10$ ). The results are presented in Table 1. In summer, concentrations  
28 ranged from 158 to 301  $\text{pmol L}^{-1}$  ( $\text{CH}_3\text{Cl}$ ), 5 to 11  $\text{pmol L}^{-1}$  ( $\text{CH}_3\text{Br}$ ), 4 to 18  $\text{pmol L}^{-1}$  ( $\text{CH}_3\text{I}$ ),  
29 and 67 to 194  $\text{pmol L}^{-1}$  ( $\text{CHBr}_3$ ). During the spring campaign, the water concentrations were



1 101 to 267 pmol L<sup>-1</sup> for CH<sub>3</sub>Cl, 6 to 28 pmol L<sup>-1</sup> for CH<sub>3</sub>Br, 2 to 16 pmol L<sup>-1</sup> for CH<sub>3</sub>I, and 39  
2 to 133 pmol L<sup>-1</sup> for CHBr<sub>3</sub>.

3 The results obtained from samples of the transect cruise covered in 2012 (Fig. 1) are given in  
4 Table 2. We observed an about two-fold increase of concentration for CH<sub>3</sub>Cl (from 121 to  
5 241 pmol L<sup>-1</sup>) and CHBr<sub>3</sub> (from 26 to 55 pmol L<sup>-1</sup>) between position 1 (Faro-Olhão inlet) and  
6 position 2 (near to the seagrass meadows studied). The increase was less pronounced for  
7 CH<sub>3</sub>Br (5 to 7 pmol L<sup>-1</sup>) and not notable for CH<sub>3</sub>I. The seawater at positions 6 and 7, the  
8 nearest to the Ancão inlet, revealed rather low concentrations for all compounds. We further  
9 observed rising concentrations for all halocarbons along positions 3, 4, and 5 with increasing  
10 distance to the Ancão inlet. They increased from 96 to 180 pmol L<sup>-1</sup> for CH<sub>3</sub>Cl, from 9 to 19  
11 pmol L<sup>-1</sup> for CH<sub>3</sub>Br, 2 to 14 pmol L<sup>-1</sup> for CH<sub>3</sub>I, and 21 to 95 pmol L<sup>-1</sup> for CHBr<sub>3</sub>.

### 12 **3.2 Fluxes from seagrass meadows, sediment, and sea-air exchange**

13 The mean fluxes and ranges of CH<sub>3</sub>Cl, CH<sub>3</sub>Br, CH<sub>3</sub>I, and CHBr<sub>3</sub> from seagrass meadows,  
14 sediment, and from sea-air exchange calculations obtained from the two sampling campaigns  
15 are given in Table 3.

16 During the summer campaign (air exposure), we observed highly variable emission and  
17 deposition fluxes ranging from -49 to 74 nmol m<sup>-2</sup> h<sup>-1</sup> and -5.7 to 130 nmol m<sup>-2</sup> h<sup>-1</sup> for CH<sub>3</sub>Cl  
18 and CH<sub>3</sub>Br, respectively. The variability was less pronounced for CH<sub>3</sub>I (0.5 to 2.8 nmol m<sup>-2</sup> h<sup>-1</sup>)  
19 and CHBr<sub>3</sub> (-0.6 to 5.7 nmol m<sup>-2</sup> h<sup>-1</sup>) where predominantly emissions were measured.  
20 Strongly elevated fluxes up to 130 nmol m<sup>-2</sup> h<sup>-1</sup> for CH<sub>3</sub>Br were recorded in conjunction with  
21 tidal change from air exposure to inundation and conversely. These high fluxes were  
22 substantiated by a concurrent enhanced atmospheric mixing ratios ranging from 23 ppt to 118  
23 ppt (campaign median 14 ppt). Omitting these compound-specific tidal phenomena, the fluxes  
24 of CH<sub>3</sub>Cl and CH<sub>3</sub>Br were positively correlated (R<sup>2</sup> 0.55, p< 0.05). There were no significant  
25 correlations between CH<sub>3</sub>I and CHBr<sub>3</sub> and the other investigated halocarbons. Due to the  
26 inherent high variability of the fluxes, halocarbon fluxes were poorly correlated with solar  
27 radiation (R<sup>2</sup> ≤ 0.20).

28 The flux chamber measurements over the sediment during air exposure revealed  
29 predominantly emissions of all four halocarbons (n=5). These fluxes were 3.6±4.3 nmol m<sup>-2</sup> h<sup>-1</sup>  
30 (CH<sub>3</sub>Cl), 0.6±0.5 nmol m<sup>-2</sup> h<sup>-1</sup> (CH<sub>3</sub>Br), 0.3±0.2 nmol m<sup>-2</sup> h<sup>-1</sup> (CH<sub>3</sub>I), and 0.8±1.0 nmol m<sup>-2</sup>  
31 h<sup>-1</sup> (CHBr<sub>3</sub>). Except for CH<sub>3</sub>I, the halocarbon fluxes were statistically significant different

1 from zero (Mann-Whitney-U test;  $p < 0.05$ ). Hence, the bare sediment may contribute to the  
2 overall emissions above the seagrass by about 10 to 20% for  $\text{CH}_3\text{Cl}$  and  $\text{CH}_3\text{Br}$ , and 45% for  
3  $\text{CHBr}_3$ .

4 During the 2012 spring campaign the halocarbon fluxes from seagrass meadows were  
5 determined during both, periods of air exposure and periods of tidal immersion. Furthermore,  
6 the measurements were complemented by other trace gases including hydrocarbons and  
7 sulphur containing compounds (Bahlmann et al., 2014). As in the summer campaign, the  
8 seagrass meadows were a net source for all halocarbons studied, but on a lower level. The  
9 individual ranges of air exposure measurements were  $-30$  to  $69 \text{ nmol m}^{-2} \text{ h}^{-1}$  ( $\text{CH}_3\text{Cl}$ ),  $-0.8$  to  
10  $3.9 \text{ nmol m}^{-2} \text{ h}^{-1}$  ( $\text{CH}_3\text{Br}$ ),  $-0.6$  to  $2.6 \text{ nmol m}^{-2} \text{ h}^{-1}$  ( $\text{CH}_3\text{I}$ ), and  $-0.5$  to  $1.3 \text{ nmol m}^{-2} \text{ h}^{-1}$   
11 ( $\text{CHBr}_3$ ). On average, the seagrass meadows were a net source also under submerged  
12 conditions ranging from  $-58$  to  $100 \text{ nmol m}^{-2} \text{ h}^{-1}$  for  $\text{CH}_3\text{Cl}$ ,  $-1.6$  to  $8.3 \text{ nmol m}^{-2} \text{ h}^{-1}$  for  
13  $\text{CH}_3\text{Br}$ ,  $0.1$  to  $8.0 \text{ nmol m}^{-2} \text{ h}^{-1}$  for  $\text{CH}_3\text{I}$ , and  $-0.4$  to  $10.6 \text{ nmol m}^{-2} \text{ h}^{-1}$  for  $\text{CHBr}_3$ . Due to the  
14 low purge efficiency of  $\text{CHBr}_3$  during high tide measurements, the fluxes determined with the  
15 submergible chamber are underestimated for this compound. Despite this high variability in  
16 production/decomposition during air exposure and inundation, the monohalomethanes were  
17 significantly correlated to each other ( $R^2 \geq 0.50$ ). These correlations were enhanced compared  
18 to those found when the seagrass meadows were air-exposed ( $R^2 \geq 0.50$ ). In this case, only  
19  $\text{CH}_3\text{I}$  and  $\text{CH}_3\text{Br}$  were significantly correlated ( $R^2 0.51$ ).  $\text{CHBr}_3$  was only slightly correlated  
20 to the monohalomethanes.

21 While deposition fluxes of  $\text{CH}_3\text{Cl}$  and  $\text{CH}_3\text{Br}$  of air-exposed seagrass meadows occurred  
22 predominantly during periods of low irradiance in summer, no obvious relation to the time of  
23 day and/or solar radiation was observed during spring when deposition fluxes were frequently  
24 detected. For  $\text{CH}_3\text{I}$  and  $\text{CHBr}_3$ , uptake was only occasionally observed and situations of  
25 emission clearly dominated.

26 As in the summer campaign, we observed some remarkable tidal effects on halocarbon fluxes  
27 during the spring campaign. Firstly, the highest fluxes of all halocarbons were measured when  
28 the lagoon water was just reaching the sampling site. Occasionally this was also observed  
29 from air exposure to tidal inundation, although less pronounced. However, these short-timed  
30 effects were not as strong as during the summer campaign. Secondly, at tidal maximum we  
31 observed deposition fluxes for  $\text{CH}_3\text{Cl}$  and  $\text{CH}_3\text{Br}$  and deposition fluxes or very weak

1 emissions for CH<sub>3</sub>I and CHBr<sub>3</sub>. Before and after this period, emission fluxes during incoming  
2 tide and ebb flow dominated.

3 The lagoon water was a net source for all investigated halocarbons to the atmosphere during  
4 both campaigns. In summer, the flux ranges were 13-45 nmol m<sup>-2</sup> h<sup>-1</sup> (CH<sub>3</sub>Cl), 0.6-1.7 nmol  
5 m<sup>-2</sup> h<sup>-1</sup> (CH<sub>3</sub>Br), 0.5-3.2 nmol m<sup>-2</sup> h<sup>-1</sup> (CH<sub>3</sub>I), and 1.0-8.0 nmol m<sup>-2</sup> h<sup>-1</sup> (CHBr<sub>3</sub>). The  
6 respective fluxes in spring were 3.5-32 (CH<sub>3</sub>Cl), 0.5-4.1 (CH<sub>3</sub>Br), 0.3-3.7 (CH<sub>3</sub>I), 3.8-24  
7 (CHBr<sub>3</sub>).

### 8 **3.3 Stable carbon isotopes of halocarbons**

9 Stable carbon isotope ratios of halocarbons were determined for selected samples of both  
10 campaigns (Table 4). Isotopic source signatures from seagrass meadows for CH<sub>3</sub>Cl and  
11 CH<sub>3</sub>Br were calculated using a coupled isotope and mass balance without integration of a  
12 possible sink function (Weinberg et al., 2013).

13 In 2011, the difference in atmospheric mixing ratios of CH<sub>3</sub>Cl and CH<sub>3</sub>Br between within the  
14 lagoon and the upwind position (Praia de Faro) was accompanied by a shift of δ<sup>13</sup>C values.  
15 More <sup>13</sup>C depleted values were found for CH<sub>3</sub>Cl in the lagoon (-42±2‰) compared to the  
16 upwind position (-39±0.4‰). In contrast, the δ<sup>13</sup>C values of CH<sub>3</sub>Br were significantly  
17 enriched in <sup>13</sup>C by about 10‰ inside the lagoon (-29±5‰) as compared to the upwind site (-  
18 38±3). These δ<sup>13</sup>C values found in air samples in the lagoon roughly correspond to the δ<sup>13</sup>C  
19 values of CH<sub>3</sub>Cl (-43±3‰) and CH<sub>3</sub>Br (-23±3‰) found in samples of lagoon waters.

20 Atmospheric CH<sub>3</sub>Cl and CH<sub>3</sub>Br were on average more enriched in <sup>13</sup>C in spring than in  
21 summer by 4 and 6‰, respectively. While the δ<sup>13</sup>C values of CH<sub>3</sub>Cl in the lagoon water were  
22 quite similar between both periods of the year, those of CH<sub>3</sub>Br were on average more depleted  
23 in <sup>13</sup>C during spring suggesting certain changes in production/decomposition processes. The  
24 isotopic composition of CH<sub>3</sub>I in lagoon water was quite similar between summer (-39± 9‰)  
25 and spring (mean -37±7‰). As for CH<sub>3</sub>Br, the δ<sup>13</sup>C values of CHBr<sub>3</sub> were more enriched in  
26 <sup>13</sup>C in summer when compared with those of the spring campaign.

27 The difference in concentration along the transect cruise was accompanied by variations in the  
28 carbon isotopic composition of all compounds (Table 1, Figure 2). The most <sup>13</sup>C depleted  
29 values of CH<sub>3</sub>Cl, CH<sub>3</sub>Br, and CH<sub>3</sub>I were detected at the position furthest from the inlet.  
30 Interestingly, CHBr<sub>3</sub> showed the opposite trend with more <sup>13</sup>C enriched values in the lagoon  
31 (-25.8‰ vs. ~ -18‰).

1 Using the fluxes and  $\delta^{13}\text{C}$  values from the inlet and outlet of the flux chamber, we were able  
2 to calculate the source signatures of seagrass covered areas. The resulting source signatures of  
3  $\text{CH}_3\text{Cl}$  from seagrass meadows were similar during both campaigns ( $-51\pm 6\%$  and  $-56\pm 2\%$ ,  
4 respectively) and independent from the strength of emission. For  $\text{CH}_3\text{Br}$ , we observed most  
5 depleted  $\delta^{13}\text{C}$  values of  $-53\%$  and  $-58\%$  at increased emission fluxes in summer, but values  
6 of  $-26\%$  and  $-29\%$  during periods of low emission. This corroborates the findings of  
7 isotopically heavy  $\text{CH}_3\text{Br}$  produced within the seagrass meadows ( $-29\%$ ) in spring 2012  
8 when all samples analysed for the isotopic composition were taken at situations of low  
9 emission.

10

## 11 **4 Discussion**

### 12 **4.1 Dissolved halocarbons**

13 A comparison of halocarbon concentrations in the lagoon water to other measurements of the  
14 coastal Atlantic found in the literature is displayed in Table 5. The lagoon waters appeared to  
15 be highly enhanced in  $\text{CH}_3\text{Cl}$ . Except one early study of Tait et al. (1994), our measurements  
16 gave the most elevated concentrations for this compound. Enhanced concentrations in the  
17 lagoon waters were also found for  $\text{CH}_3\text{Br}$ . Given the mean concentrations from other coastal  
18 Atlantic studies (Baker et al., 1999; Carpenter et al., 2000; Hu et al., 2010), we recorded  
19 higher concentration by a factor of 2 to 3 at our sampling site. The average water  
20 concentrations in the lagoon of  $\text{CH}_3\text{I}$  were in the same range as reported from other parts of  
21 the Atlantic (Moore and Groszko 1999; Zhou et al., 2005). However, especially those regions  
22 where macroalgae are the dominating source organisms possess higher maximum values  
23 (Bravo-Lineares and Mudge, 2009; Jones et al., 2009). This is even more pronounced for  
24  $\text{CHBr}_3$ , for which the seawater concentration within or in the vicinity of macroalgae beds are  
25 strongly elevated (Bravo-Lineares and Mudge, 2009; Carpenter et al., 2000; Jones et al.,  
26 2009). The area occupied by the prevalent macroalgae species *Enteromorpha spp.* and *Ulva*  
27 *spp.* in the Ria Formosa is estimated to be  $2.5 \text{ km}^2$  (Duarte et al., 2008), considerably below  
28 that of other abundant sources such as seagrass meadows. We cannot exclude that  
29 phytoplankton contributes significantly to the water concentration of halocarbons, but the  
30 predominantly low chlorophyll a concentrations ( $3.06 \mu\text{g L}^{-1}$  from long-term measurements,  
31 Brito et al., 2012) and low water volumes seem to limit the impact from this source.

1 Despite the short residence time of the lagoon water masses of which 50-75% is exchanged  
2 during one tidal cycle (Brito et al., 2010), the transect cruise along the main channels revealed  
3 a successive enrichment of halocarbon concentration in the water with increasing distance  
4 from the main inlets (Fig. 1 and Table 2). Therefore, the net halocarbon production in the  
5 lagoon appears to clearly exceed that outside the lagoon. This is supported by the distinctively  
6 increased air mixing ratios of halocarbons in the lagoon as compared to the upwind site  
7 (Table 1).

8 Overall, the lagoon seems to comprise highly potent halocarbon sources in the water column  
9 for  $\text{CH}_3\text{Cl}$  and  $\text{CH}_3\text{Br}$  but not for  $\text{CH}_3\text{I}$  and  $\text{CHBr}_3$ .

## 10 **4.2 Flux pattern from seagrass meadows**

11 The halocarbon fluxes from seagrass meadows were characterized by a high variability with  
12 deposition and emission fluxes occurring at all sampling spots. The same was observed within  
13 other studies investigating halocarbon fluxes in coastal environments (e.g. Blei et al., 2010;  
14 Manley et al., 2006; Rhew et al., 2000). Halocarbon dynamics in coastal systems where  
15 multiple sources and sinks interact are complex, and it should be noted that the fluxes  
16 discussed here refer to the entire benthic community constituting the seagrass meadows. Thus,  
17 some variability may relate to the activity of distinct source organisms which may be  
18 stimulated by different environmental factors. To gain insights into the common  
19 environmental controls for this ecosystem we discuss the following factors i) diurnal  
20 variations ii) tidal effects and iii) seasonal dependence.

21 i) Diurnal variations. The correlation analysis with solar radiation resulted in only a weak  
22 association with the magnitude of fluxes. However, after grouping by daytime, our data  
23 provide some indication for a diurnal pattern (Fig. 2). For  $\text{CH}_3\text{Cl}$ , there was the most obvious  
24 relationship between time of day and actual emissions. Highest emissions were observed  
25 during day periods with increased sunlight (midday and afternoon). In contrast, deposition  
26 fluxes were exclusively recorded during periods of low radiation and nighttimes. The same  
27 was also observed for  $\text{CH}_3\text{Br}$ . However, highest mean emissions of this compound seemed to  
28 be shifted towards the afternoon.  $\text{CH}_3\text{I}$  was constantly emitted from the seagrass covered spot  
29 revealing a weak diurnal dependence. The emissions did not cease during periods of low  
30 irradiance and darkness. Nevertheless, elevated mean emissions were observed in the

1 afternoon. Except one occasion,  $\text{CHBr}_3$  was emitted throughout the sampling periods. Mean  
2 emissions were higher around midday and afternoon as during night.

3 Several studies from salt marshes reported a diurnal trend of halocarbon emissions initiated  
4 by irradiance (Dimmer et al., 2001; Rhew et al., 2000, 2002; Drewer et al., 2006). The flux  
5 data of halocarbons from the summer campaign with elevated fluxes during midday and  
6 afternoon suggest a similar pattern also in seagrass meadows. However, this was more  
7 obvious for  $\text{CH}_3\text{Cl}$  and  $\text{CH}_3\text{Br}$  than for  $\text{CH}_3\text{I}$  and  $\text{CHBr}_3$ . The lower production of  $\text{CH}_3\text{I}$   
8 during the time of highest light intensity cannot fully be explained. Blei et al. (2010) reported  
9 that the main environmental association in salt marsh emissions of  $\text{CH}_3\text{Cl}$  and  $\text{CH}_3\text{Br}$  was  
10 with ambient temperature rather than light. However, during the summer campaign,  
11 temperature variations (day/night) were too low to explain the observed emission/deposition  
12 pattern of  $\text{CH}_3\text{Cl}$  and  $\text{CH}_3\text{Br}$ .

13 It is known that coastal sediments can act as a sink for  $\text{CH}_3\text{Cl}$  and  $\text{CH}_3\text{Br}$  mainly due to  
14 microbial degradation (Miller et al., 2004; Oremland et al. 1994). This would support our  
15 findings of the deposition fluxes during night times where production above the sediment is  
16 presumably lower than during daytime (summer campaign). While, in general, the deposition  
17 fluxes of  $\text{CH}_3\text{Cl}$  and  $\text{CH}_3\text{Br}$  occurred more frequently during the spring campaign, they did  
18 not exhibit a day-night-relationship. Moreover, the dependence of light intensity on the  
19 magnitude of emission fluxes of halocarbons seemed to have a minor effect during this period  
20 of the year.

21 ii) Tidal effects. During the spring campaign, mean fluxes derived from submerged seagrass  
22 meadows were elevated by factors of 17 ( $\text{CH}_3\text{Cl}$ ), 5 ( $\text{CH}_3\text{Br}$ ), 3 ( $\text{CH}_3\text{I}$ ), and 8 ( $\text{CHBr}_3$ ) when  
23 compared to the average fluxes during air exposure. This clearly higher production of  
24 halocarbons under submerged conditions was quite unexpected, as in general it is believed  
25 that the production of trace gases during low tide exceeds that during inundation. For  
26 halocarbons this was suggested for example by Carpenter et al. (1999) and Jones et al. (2009)  
27 from atmospheric measurements over intertidal macroalgae beds in Mace Head, Ireland.  
28 Nevertheless, in accordance with our results from halocarbon measurements we also observed  
29 higher primary productivity by increased  $\text{CO}_2$  uptake during submerged conditions  
30 (Bahlmann et al., 2014). Therefore, the higher productivity may reflect higher enzymatic  
31 activity (e.g. methyltransferases) within the organisms of the seagrass community, by which  
32 monohalomethanes are presumably formed. Furthermore, the correlation analysis revealed a

1 different behaviour of halocarbons between the two tidal states with stronger correlations  
2 between monohalomethanes during tidal inundation than air exposure. Obviously the change  
3 in environmental conditions was accompanied with a shift in the halocarbon production-  
4 decomposition pattern of the benthic community and/or different source organisms were  
5 stimulated.

6 An interesting outcome of both campaigns is the observation of strongly elevated halocarbon  
7 fluxes during tidal change from air exposure to submergence and reversely (Table 3).  
8 Continuous high-time resolution CO<sub>2</sub> and methane flux measurements performed in spring  
9 2012 (Bahlmann et al., 2014) principally support this observation. At the particular moment  
10 when the water reached the sampling site, we observed a distinct peak flux of methane and  
11 CO<sub>2</sub>. This may be evidence for processes in the sediments attributable to changes in  
12 hydrodynamic pressures resulting in the release of trace gases trapped in sedimentary pore  
13 spaces (Bahlmann et al., 2014). The remarkable deposition flux of CH<sub>3</sub>Cl and CH<sub>3</sub>Br during  
14 the maximum water level (Table 3) was accompanied by highest emissions of other trace  
15 gases such as methanethiol and hydrogen sulfide as discussed by Bahlmann et al. (2014).  
16 These compounds are effective nucleophiles which could have contributed to the degradation  
17 of halocarbons as described in Barbash and Reinhard (1989). This suggests a significantly  
18 different biogeochemistry during this period compared with tide and ebb flow.

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

21 iii) Seasonal dependence. There are considerable differences between the results from spring  
22 and summer campaign. We observed elevated mixing ratios for all halocarbons in ambient air  
23 as well as higher water concentrations for CH<sub>3</sub>Cl, CH<sub>3</sub>I, and CHBr<sub>3</sub> compounds in summer  
24 (Table 1). This observed signal of general increased halocarbon production in the lagoon  
25 during summer might be attenuated by enhanced degradation in the water phase and  
26 sediments at higher temperatures. Nevertheless, given the calculated sea-air flux there is only  
27 little evidence for a pronounced seasonal relationship in halocarbon volatilisation to the  
28 atmosphere from the lagoon water. While the fluxes of CH<sub>3</sub>Cl appeared to be enhanced in  
29 summer, those of CH<sub>3</sub>Br and CH<sub>3</sub>I seemed to be quite similar between spring and summer.  
30 CHBr<sub>3</sub> emissions were actually higher in spring than in summer due to higher water  
31 concentrations. Comparing the data obtained from air-exposed sites during the two  
32 campaigns, the fluxes in summer were strongly enhanced by factors of 16 (CH<sub>3</sub>Cl and

1 CH<sub>3</sub>Br), 2 (CH<sub>3</sub>I), and 5 (CHBr<sub>3</sub>). Moreover, the halocarbon fluxes showed a distinct diurnal  
2 cycle during summer but not during spring. The differences of ambient conditions between  
3 the campaigns with lower air temperatures and lower solar radiation in spring may have  
4 contributed to the differences in the emission patterns of halocarbons. That these  
5 environmental conditions can substantially influence the magnitude of fluxes was reported  
6 from other ecosystems such as salt marshes (Blei et al., 2010; Manley et al., 2006). However,  
7 further studies covering the entire season are necessary to fully unravel the annual  
8 halocarbon emissions from seagrass meadows.

### 9 **4.3 Halocarbons sources in the lagoon: an isotopic perspective**

10 The results from the atmospheric sampling of Praia de Faro air (upwind) and lagoon air  
11 revealed differences regarding the mixing ratios and  $\delta^{13}\text{C}$  values of CH<sub>3</sub>Cl and CH<sub>3</sub>Br (Tables  
12 1 and 4). We observed elevated concentrations in the lagoon for both compounds, whereby  
13 the higher concentrations were accompanied with shifts towards isotopically light CH<sub>3</sub>Cl but  
14 heavy CH<sub>3</sub>Br. Sources other than the studied seagrass meadows, for example the abundant  
15 salt marshes, may have contributed substantially to the elevated mixing ratios. Assuming  
16 atmospheric stable conditions with negligible sinks in the atmosphere, the difference of air  
17 mixing ratios and  $\delta^{13}\text{C}$  values between upwind air and lagoon air should reflect the isotopic  
18 source signature within the lagoon. Therefore, as a first approach, an isotope mass balance  
19 was used by integrating mean data from both sampling sites (Tables 1 and 4). The resulting  
20 source signatures within the lagoon are -49‰ for CH<sub>3</sub>Cl and -16‰ for CH<sub>3</sub>Br.

21 Isotopic source signatures of CH<sub>3</sub>Cl from seagrass meadows during chamber incubations (air  
22 exposure) in the Ria Formosa were  $-51\pm 6\text{‰}$  (summer) and  $-56\pm 2\text{‰}$  (spring). During the  
23 summer campaign, CH<sub>3</sub>Cl emissions from the salt marsh plant *Spartina maritima* were  
24 determined with  $\delta^{13}\text{C}$  values of -66 and -72‰. These values are in good agreement with those  
25 of Bill et al. (2002) from a Californian salt marsh (-69 to -71‰, daytime values).  
26 Unfortunately, we do not have isotopic data for the inundated periods from seagrass  
27 meadows, but the  $\delta^{13}\text{C}$  values of CH<sub>3</sub>Cl in the water phase ( $-42\pm 2\text{‰}$ ) come close to those  
28 measured in the atmosphere. An abiotic production mechanism has been reported for CH<sub>3</sub>Cl  
29 from senescent plant material (Hamilton et al., 2003). While we cannot generally exclude  
30 additional CH<sub>3</sub>Cl generation via this pathway, the isotopic data obtained in the Ria Formosa  
31 do not mirror strongly <sup>13</sup>C depleted values ( $\delta^{13}\text{C}$  of  $-135\pm 12\text{‰}$ , Keppler et al., 2004) as  
32 expected for compounds from this production mechanism. Overall, this rather indicates a



1 stronger imprint of the seagrass meadows and/or water column on the atmospheric CH<sub>3</sub>Cl  
2 than from salt marshes or abiotic processes.

3 With  $\delta^{13}\text{C}$  values of  $-42 \pm 17\text{‰}$  the source signature of CH<sub>3</sub>Br from seagrass meadows tend to  
4 be more depleted in <sup>13</sup>C compared with the calculated source signature from the atmospheric  
5 samples. It should be noted that the  $\delta^{13}\text{C}$  values for this compound were more depleted in <sup>13</sup>C  
6 during periods of increased emission ( $-55\text{‰}$ ) than during low emissions ( $-28\text{‰}$ ). This shift  
7 can most likely be explained by degradation processes in the sediments which occurred  
8 simultaneously. This corroborates our observations from Northern Germany with subsequent  
9 recalculation of a sedimentary sink function from accompanying sediment measurements  
10 (Weinberg et al., 2013). Reported source signatures of CH<sub>3</sub>Br from salt marshes range from -  
11 59 to  $-65\text{‰}$  (day time values, Bill et al., 2002). Our own measurements in the Ria Formosa  
12 indicate similar  $\delta^{13}\text{C}$  values ( $-65\text{‰}$ ) or even more depleted ones (unpublished data). In any  
13 case, neither source signatures from seagrass meadows nor salt marshes seem to match the  
14 overall source signature estimated from the atmospheric samples. Therefore, it is most likely  
15 that the atmospheric CH<sub>3</sub>Br is strongly influenced by CH<sub>3</sub>Br emissions from the surface  
16 waters ( $\delta^{13}\text{C}$  values in water phase (summer):  $-23 \pm 3\text{‰}$ ). Even during periods of low tide the  
17 water remains in the deep channels which may be sufficient to have an impact on the local  
18 atmosphere. Thus, despite the sources in the lagoon presumably producing isotopically light  
19 CH<sub>3</sub>Br,  $\delta^{13}\text{C}$  values in the atmosphere strongly reflect decomposed CH<sub>3</sub>Br whose residual  
20 fraction is actually enriched in <sup>13</sup>C. Accordingly, aqueous CH<sub>3</sub>Br appears to become rapidly  
21 degraded by biotic/abiotic processes such as hydrolysis, transhalogenation, and microbial  
22 degradation with strong isotopic fractionation (King and Saltzman, 1997; Miller et al., 2004).  
23 These decomposition mechanisms are temperature dependent with increasing destruction with  
24 increasing seawater temperature (King and Saltzman, 1997). This is most likely the reason  
25 why the  $\delta^{13}\text{C}$  values in the lagoon waters in summer are more enriched in <sup>13</sup>C compared with  
26 those those from the spring campaign.

27 To the best of our knowledge, this is the first report of  $\delta^{13}\text{C}$  values of CH<sub>3</sub>I in the water phase.  
28 As shown by the water samples from the transect cruise, the sources in the lagoon may  
29 produce isotopic light CH<sub>3</sub>I. Given this, CH<sub>3</sub>I seems to some extent to follow the  $\delta^{13}\text{C}$  values  
30 of CH<sub>3</sub>Cl. These sources may be biotic by e.g. phytoplankton, seagrass meadows, or bacteria.  
31 On the other hand, Moore and Zafirou (1994) reported a photochemical source for CH<sub>3</sub>I by  
32 radical recombination of iodine with seawater dissolved organic matter. Due to the lack of

1 isotopic source signatures and fractionation factors for production (and consumption), it is  
2 difficult to draw conclusions from the data.

3 The  $\delta^{13}\text{C}$  values of  $\text{CHBr}_3$  were more depleted in  $^{13}\text{C}$  from the lagoon inlet towards the parts  
4 deeper inside. This suggests a different combination of sources in water masses coming from  
5 the Atlantic. Moreover, this potential variation of source contribution can be further assumed  
6 by the certain change between summer and spring where e.g. macroalgae are more abundant  
7 in the latter period (Anibal et al., 2007). Already reported source signatures of phytoplankton,  
8 macroalgae, and seagrass meadows cover the range of -10‰ to -23‰ (Auer et al., 2006;  
9 Weinberg et al., 2013), thus demonstrating differences in their isotopic fingerprint. We cannot  
10 exclude that degradation might also have an effect on the  $\delta^{13}\text{C}$  values determined in lagoon  
11 waters. As for  $\text{CH}_3\text{I}$ , there is still need for further research on the  $\text{CHBr}_3$  cycling utilizing  
12 stable carbon isotopes.

#### 13 **4.4 Magnitude of fluxes and comparison to other coastal measurements and** 14 **first estimate of global source strength**

15 The areal based fluxes of  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{Br}$ , and  $\text{CH}_3\text{I}$  from seagrass meadows in comparison to  
16 emission data of other coastal sources are presented in Fig. 3. In comparison to the emissions  
17 from a temperate seagrass meadow in late summer in Northern Germany (Weinberg et al.,  
18 2013), fluxes were elevated in the subtropical lagoon in summer during air exposure. This  
19 was more pronounced for  $\text{CH}_3\text{Br}$  (factor 33) than for  $\text{CH}_3\text{Cl}$  (factor 2),  $\text{CH}_3\text{I}$  (factor 2), and  
20  $\text{CHBr}_3$  (factor 5). In contrast, fluxes from air-exposed seagrass meadows recorded during  
21 spring are comparable to those determined in Northern Germany. Thus, the difference  
22 between fluxes from temperate and subtropical regions is less pronounced than reported for  
23 salt marshes with emissions from subtropical regions exceeding those from temperate regions  
24 by up to two orders of magnitude for  $\text{CH}_3\text{Cl}$  and  $\text{CH}_3\text{Br}$  (Blei et al. 2010; Cox et al., 2004;  
25 Dimmer et al., 2001; Drewer et al., 2006; Manley et al., 2006; Rhew and Mazéas, 2010; Rhew  
26 et al., 2000, 2014; Valtanen et al., 2009). Beside this regional (climatic) difference several  
27 authors attributed this to a highly species dependent emission potential.

28 Average emissions of  $\text{CH}_3\text{Cl}$  from the air-exposed seagrass meadows in summer are in the  
29 same range than those determined in temperate salt marshes (Blei et al. 2010; Cox et al.,  
30 2004; Dimmer et al., 2001; Drewer et al., 2006; Valtanen et al., 2009). In contrast, subtropical  
31 counterparts of these macrophytes are distinctively stronger emitters of this compound by at

1 least one order of magnitude (Manley et al., 2006; Rhew and Mazéas, 2010; Rhew et al.,  
2 2000, 2014). Greenhouse grown mangroves produce significantly more CH<sub>3</sub>Cl than seagrass  
3 meadows revealing a higher emission potential for these plants species on a per area basis  
4 (Manley et al., 2007).

5 Fluxes of CH<sub>3</sub>Br from subtropical seagrass meadows during air exposure exceed those of  
6 temperate macroalgae from Mace Head, Ireland (Carpenter et al., 2000) and temperate salt  
7 marshes (Blei et al. 2010; Cox et al., 2004; Dimmer et al., 2001; Drewer et al., 2006; Valtanen  
8 et al., 2009). However, the CH<sub>3</sub>Br fluxes from seagrass meadows are distinctively lower than  
9 those of subtropical salt marsh plants (Manley et al., 2006; Rhew and Mazéas, 2010; Rhew et  
10 al., 2000). Mangroves seem to have a similar emission potential as seagrass meadows  
11 (Manley et al., 2007).

12 For CH<sub>3</sub>I, seagrass meadows are a minor source in comparison to the high release of  
13 macroalgae in subtropical areas (Leedham et al. 2013). Except for salt marshes from  
14 Tasmania (Cox et al., 2004), plant-related communities such as mangroves (Manley et al.,  
15 2007) and salt marshes (Dimmer et al., 2001) are more pronounced emission sources of this  
16 compound. The same holds true for CHBr<sub>3</sub>, where macroalgae communities from temperate  
17 and subtropical/tropical regions dominate the emissions of polyhalomethanes on a per area  
18 basis (e.g. Carpenter et al., 2000; Gschwend et al., 1985; Leedham et al., 2013).

19 Many uncertainties arise from a limited number of emission data to estimate the global  
20 relevance of seagrass meadows. Those may be high variation in space and time, high  
21 heterogeneity of seagrass meadows, species dependent emission potential, and errors  
22 regarding the global seagrass abundance. Therefore, the scale-up of our data gives only a first  
23 rough approximation; it was undertaken as follows. Since we did not measure a full annual  
24 cycle, we assumed that seagrass measurements during the summer campaign represent  
25 emissions from the reproductive season (May - September). The remaining period of the year  
26 (October - April) was calculated with emission data from the spring campaign. The emission  
27 data were weighted to tidal states using 8 hours and 16 hours per day as durations when  
28 seagrass meadows are air-exposed or submerged, respectively. Due to the lack of flood tide  
29 emission data in summer, we used those derived from the sea-air exchange. The resulting  
30 average annual emissions from seagrass meadows of 150 μmol m<sup>-2</sup> yr<sup>-1</sup> (CH<sub>3</sub>Cl), 18 μmol m<sup>-2</sup>  
31 yr<sup>-1</sup> (CH<sub>3</sub>Br), 14 μmol m<sup>-2</sup> yr<sup>-1</sup> (CH<sub>3</sub>I), and 25 μmol m<sup>-2</sup> yr<sup>-1</sup> (CHBr<sub>3</sub>) were scaled-up with the

1 current estimates of a global seagrass area ranging from  $0.3 \times 10^{12} \text{ m}^2$  (Duarte et al., 2005) to  
2  $0.6 \times 10^{12} \text{ m}^2$  (Charpy-Roubaud and Sournia, 1990).

3 The tentative estimate yields annual emissions of  $2.3\text{-}4.5 \text{ Gg yr}^{-1}$  for  $\text{CH}_3\text{Cl}$ ,  $0.5\text{-}1.0 \text{ Gg yr}^{-1}$   
4 for  $\text{CH}_3\text{Br}$ ,  $0.6\text{-}1.2 \text{ Gg yr}^{-1}$  for  $\text{CH}_3\text{I}$ , and  $1.9\text{-}3.7 \text{ Gg yr}^{-1}$  for  $\text{CHBr}_3$ . Based on the recent global  
5 budget calculations (Xiao et al., 2010; Montzka and Reimann, 2011), these ranges are  
6 equivalent to 0.06-0.11% and 0.45-0.89%, for  $\text{CH}_3\text{Cl}$  and  $\text{CH}_3\text{Br}$ , respectively. Seagrass  
7 meadows would therefore cover a portion of 1.4-2.8% of the missing sources for  $\text{CH}_3\text{Br}$   
8 reported in the most recent WMO report ( $36.1 \text{ Gg yr}^{-1}$ ; Montzka and Reimann, 2011). Given  
9 the emissions from oceanic sources (e.g. Butler et al., 2007; Quack and Wallace, 2003 and  
10 references therein),  $\text{CH}_3\text{I}$  and  $\text{CHBr}_3$  emissions from seagrass meadows are rather  
11 insignificant on a global scale.

12

## 13 **5 Conclusions**

14 Our data are the first to report detailed halocarbon fluxes from seagrass meadows. The fluxes  
15 of halocarbons were highly variable with increased fluxes when the seagrass meadows were  
16 submerged, and distinct emission peaks when lagoon waters were just arriving or leaving the  
17 sampling site. For  $\text{CH}_3\text{Cl}$  and  $\text{CH}_3\text{Br}$  we observed a diurnal dependence on the fluxes with  
18 increased emissions during midday/afternoon and deposition fluxes during periods of low  
19 radiation. Generally, diurnal variations (during air exposure), atmospheric mixing ratios, and  
20 emission rates of halocarbons were smaller in spring than in summer, suggesting a seasonal  
21 dependence. Our results indicate that on a global scale, seagrass meadows are a minor source  
22 of halocarbons, but that they will have an imprint on the local and regional budgets,  
23 particularly on subtropical coastlines, where seagrass meadows belong to the most abundant  
24 ecosystems.

25 Our stable carbon isotope results suggest that  $\text{CH}_3\text{Cl}$  originates predominantly from the water  
26 column and/or seagrass meadows, rather than from adjacent salt marshes or abiotic formation  
27 processes. Atmospheric and aqueous  $\text{CH}_3\text{Br}$  in the lagoon was substantially enriched in  $^{13}\text{C}$   
28 pointing towards degradation processes and re-emission into the atmosphere.

29 Future studies should focus on halocarbon emissions from seagrass-based systems from  
30 different regions in order to refine the global relevance. Since the magnitudes of fluxes are  
31 often species-dependent, budget calculations would benefit from a more detailed investigation

1 of fluxes from different seagrass species. More work is also required to identify other  
2 elements of these ecosystems, such as the sediments, which are capable of acting as both a  
3 sink and a source of halocarbons.

#### 4 **6 Acknowledgements**

5 The authors thank the German Federal Ministry of Education and Research (BMBF) for  
6 funding (grants 03F0611E and 03F0662E). The stay at the Ramalhete research station in Faro,  
7 Portugal was co-funded by ASSEMBLE EU FP7 research infrastructure project. Rui Santos,  
8 João Reis, and Bruno Fragoso (CCMAR, Universidade do Algarve) are greatly acknowledged  
9 for their extensive support during sampling site selection and sampling. Our technical staff  
10 members Sabine Beckmann and Ralf Lendt are thanked for their valuable help. We express  
11 gratitude to three anonymous reviewers and especially the associate editor Jens-Arne Subke  
12 for their comments and suggestions, which considerably improved the quality of the  
13 manuscript.

14

## 1 References

- 2 Amachi, S., Kamagata, Y., Kanagawa, T., and Muramatsu, Y.: Bacteria mediate methylation of iodine in marine  
3 and terrestrial environments, *Appl. Environ. Microb.*, 67, 2718-2722, doi: 10.1128/aem.67.6.2718-2722.2001,  
4 2001.
- 5
- 6 Anibal, J., Rocha, C., and Sprung, M.: Mudflat surface morphology as a structuring agent of algae and  
7 associated macroepifauna communities: A case study in the Ria Formosa, *J. Sea Res.*, 57, 36-46, doi:  
8 10.1016/j.seares.2006.07.002, 2007.
- 9
- 10 Auer, N. R., Manzke, B. U., and Schulz-Bull, D. E.: Development of a purge and trap continuous flow system  
11 for the stable carbon isotope analysis of volatile halogenated organic compounds in water, *J. Chromatogr. A*,  
12 1131, 24-36, doi: 10.1016/j.chroma.2006.07.043, 2006.
- 13
- 14 Bahlmann, E., Weinberg, I., Seifert, R., Tubbesing, C., and Michaelis, W.: A high volume sampling system for  
15 isotope determination of volatile halocarbons and hydrocarbons, *Atmos. Meas. Tech.*, 4, 2073-2086, doi:  
16 10.5194/amt-4-2073-2011, 2011.
- 17
- 18 Bahlmann, E., Weinberg, I., Lavrič, J. V., Eckhard, T., Michaelis, W., Santos, R., and Seifert, R.: Tidal controls  
19 on trace gas dynamics in a seagrass meadow of the Ria Formosa lagoon (southern Portugal), *Biogeosciences*  
20 *Discuss.*, 11, 10571-10603, 2014.
- 21
- 22 Baker, J. M., Reeves, C. E., Nightingale, P. D., Penkett, S. A., Gibb, S. W., and Hatton, A. D.: Biological  
23 production of methyl bromide in the coastal waters of the North Sea and open ocean of the northeast Atlantic,  
24 *Mar. Chem.*, 64, 267-285, doi: 10.1016/s0304-4203(98)00077-2, 1999.
- 25
- 26 Barbash, J. E. and Reinhard, M.: Reactivity of sulfur nucleophiles toward halogenated organic compounds in  
27 natural waters, in: *Biogenic Sulfur in the Environment*, edited by: Saltzman, E. and Cooper, W. J., American  
28 Chemical Society, Washington D.C., 101-137, 1989.
- 29
- 30 Bell, N., Hsu, L., Jacob, D. J., Schultz, M. G., Blake, D. R., Butler, J. H., King, D. B., Lobert, J. M., and Maier-  
31 Reimer, E.: Methyl iodide: Atmospheric budget and use as a tracer of marine convection in global models, *J.*  
32 *Geophys. Res-Atmos.*, doi: 107, 4340, 10.1029/2001jd001151, 2002.
- 33
- 34 Bill, M., Rhew, R. C., Weiss, R. F., and Goldstein, A. H.: Carbon isotope ratios of methyl bromide and methyl  
35 chloride emitted from a coastal salt marsh, *Geophys. Res. Lett.*, 29, doi: 104510.1029/2001gl012946, 2002.
- 36
- 37 Blei, E., Heal, M. R., and Heal, K. V.: Long-term CH<sub>3</sub>Br and CH<sub>3</sub>Cl flux measurements in temperate salt  
38 marshes, *Biogeosciences*, 7, 3657-3668, doi: 10.5194/bg-7-3657-2010, 2010.
- 39
- 40 Borges, A. V., Vanderborght, J. P., Schiettecatte, L. S., Gazeau, F., Ferron-Smith, S., Delille, B., and  
41 Frankignoulle, M.: Variability of the gas transfer velocity of CO<sub>2</sub> in a macrotidal estuary (the Scheldt),  
42 *Estuaries*, 27, 593-603, doi: 10.1007/bf02907647, 2004.
- 43
- 44 Bravo-Linares, C. M., and Mudge, S. M.: Temporal trends and identification of the sources of volatile organic  
45 compounds in coastal seawater, *J. Environ. Monitor*, 11, 628-641, doi: 10.1039/b814260m, 2009.

1  
2 Brito, A., Newton, A., Tett, P., and Fernandes, T. F.: Sediment and water nutrients and microalgae in a coastal  
3 shallow lagoon, Ria Formosa (Portugal): Implications for the Water Framework Directive, *J. Environ. Monitor*,  
4 12, 318-328, doi: 10.1039/b909429f, 2010.  
5  
6 Brito, A. C., Quental, T., Coutinho, T. P., Branco, M. A. C., Falcao, M., Newton, A., Icely, J., and Moita, T.:  
7 Phytoplankton dynamics in southern Portuguese coastal lagoons during a discontinuous period of 40 years: An  
8 overview, *Estuar. Coast. Shelf S.*, 110, 147-156, doi: 10.1016/j.ecss.2012.04.014, 2012.  
9  
10 Butler, J. H., King, D. B., Lobert, J. M., Montzka, S. A., Yvon-Lewis, S. A., Hall, B. D., Warwick, N. J.,  
11 Mondeel, D. J., Aydin, M., and Elkins, J. W.: Oceanic distributions and emissions of short-lived halocarbons,  
12 *Global Biogeochem. Cy.*, 21, GB1023, doi: 10.1029/2006gb002732, 2007.  
13  
14 Cabaço, S., Machás, R., and Santos, R.: Individual and population plasticity of the seagrass *Zostera noltii* along a  
15 vertical intertidal gradient, *Estuar. Coast. Shelf S.*, 82, 301-308, doi:  
16 <http://dx.doi.org/10.1016/j.ecss.2009.01.020>, 2009.  
17  
18 Cabaço, S., Santos, R., and Sprung, M.: Population dynamics and production of the seagrass *Zostera noltii* in  
19 colonizing versus established meadows, *Marine Ecology*, 33, 280-289, doi: 10.1111/j.1439-0485.2011.00494.x,  
20 2012.  
21  
22 Carpenter, L. J., Sturges, W. T., Penkett, S. A., Liss, P. S., Aliche, B., Hebestreit, K., and Platt, U.: Short-lived  
23 alkyl iodides and bromides at Mace Head, Ireland: Links to biogenic sources and halogen oxide production, *J.*  
24 *Geophys. Res-Atmos.*, 104, 1679-1689, doi: 10.1029/98jd02746, 1999.  
25  
26 Carpenter, L. J., Malin, G., Liss, P. S., and Küpper, F. C.: Novel biogenic iodine-containing trihalomethanes and  
27 other short-lived halocarbons in the coastal east Atlantic, *Global Biogeochem. Cy.*, 14, 1191-1204, doi:  
28 10.1029/2000gb001257, 2000.  
29  
30 Carpenter, L. J., Jones, C. E., Dunk, R. M., Hornsby, K. E., and Woeltjen, J.: Air-sea fluxes of biogenic bromine  
31 from the tropical and North Atlantic Ocean, *Atmos. Chem. Phys.*, 9, 1805-1816, doi: 1805-1816,10.5194/acp-9-  
32 1805-2009, 2009.  
33  
34 Charpy-Roubaud, C., and Sournia, A.: The comparative estimation of phytoplanktonic microphytobenthic and  
35 macrophytobenthic primary production in the oceans, *Marine Microbial Food Webs*, 4, 31-58, 1990.  
36  
37 Cox, M. L., Fraser, P. J., Sturrock, G. A., Siems, S. T., and Porter, L. W.: Terrestrial sources and sinks of  
38 halomethanes near Cape Grim, Tasmania, *Atmos. Environ.*, 38, 3839-3852, doi:  
39 10.1016/j.atmosenv.2004.03.050, 2004.  
40  
41 DeBruyn, W. J., and Saltzman, E. S.: The solubility of methyl bromide in pure water, 35 parts per thousand  
42 sodium chloride and seawater, *Mar. Chem.*, 56, 51-57, doi: 10.1016/s0304-4203(96)00089-8, 1997.  
43  
44 Dimmer, C. H., Simmonds, P. G., Nickless, G., and Bassford, M. R.: Biogenic fluxes of halomethanes from Irish  
45 peatland ecosystems, *Atmos. Environ.*, 35, 321-330, doi: 10.1016/s1352-2310(00)00151-5, 2001.  
46

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

3

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

6

7 Duarte, P., Azevedo, B., Guerreiro, M., Ribeiro, C., Bandeira, R., Pereira, A., Falcao, M., Serpa, D., and Reia, J.:  
8 Biogeochemical modelling of Ria Formosa (South Portugal), *Hydrobiologia*, 611, 115-132, doi:  
9 10.1007/s10750-008-9464-3, 2008.

10

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

13

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

16

17 Gschwend, P. M., Macfarlane, J. K., and Newman, K. A.: Volatile Halogenated Organic Compounds Released to  
18 Seawater from Temperate Marine Macroalgae, *Science*, 227, 1033-1035, doi: 10.1126/science.227.4690.1033,  
19 1985.

20

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

24

25 Hamilton, J. T. G., McRoberts, W. C., Keppler, F., Kalin, R. M., and Harper, D. B.: Chloride methylation by  
26 plant pectin: An efficient environmentally significant process, *Science*, 301, 206-209, doi:  
27 10.1126/science.1085036, 2003.

28

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

32

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

36

37 Keppler, F., Kalin, R. M., Harper, D. B., McRoberts, W. C., and Hamilton, J. T. G.: Carbon isotope anomaly in  
38 the major plant C1 pool and its global biogeochemical implications, *Biogeosciences*, 1, 123-131, doi:  
39 10.5194/bg-1-123-2004, 2004.

40

41 Keppler, F., Harper, D. B., Rockmann, T., Moore, R. M., and Hamilton, J. T. G.: New insight into the  
42 atmospheric chloromethane budget gained using stable carbon isotope ratios, *Atmos. Chem. Phys.*, 5, 2403-  
43 2411, doi: 10.5194/acp-5-2403-2005, 2005.

44

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



1  
2 Leedham, E. C., Hughes, C., Keng, F. S. L., Phang, S. M., Malin, G., and Sturges, W. T.: Emission of  
3 atmospherically significant halocarbons by naturally occurring and farmed tropical macroalgae, *Biogeosciences*,  
4 10, 3615-3633, doi: 10.5194/bg-10-3615-2013, 2013.  
5  
6 MacDonald, S., and Moore, R. M.: Seasonal and spatial variations in methyl chloride in NW Atlantic waters, *J.*  
7 *Geophys. Res.-Oceans*, 112, C05028, doi: 10.1029/2006jc003812, 2007.  
8  
9 Manley, S. L., Wang, N.-Y., Walser, M. L., and Cicerone, R. J.: Coastal salt marshes as global methyl halide  
10 sources from determinations of intrinsic production by marsh plants, *Global Biogeochem. Cy.*, 20, GB3015, doi:  
11 10.1029/2005gb002578, 2006.  
12  
13 Manley, S. L., Wang, N.-Y., Walser, M. L., and Cicerone, R. J.: Methyl halide emissions from greenhouse-  
14 grown mangroves, *Geophys. Res. Lett.*, 34, L01806, doi: 10.1029/2006gl027777, 2007.  
15  
16 Miller, L. G., Warner, K. L., Baesman, S. M., Oremland, R. S., McDonald, I. R., Radajewski, S., and Murrell, J.  
17 C.: Degradation of methyl bromide and methyl chloride in soil microcosms: Use of stable C isotope fractionation  
18 and stable isotope probing to identify reactions and the responsible microorganisms, *Geochim. Cosmochim. Ac.*,  
19 68, 3271-3283, doi: 10.1016/j.gca.2003.11.028, 2004.  
20  
21 Montzka, S. A., and Reimann, S. et al.: Ozone-depleting substances and related chemicals, in: *Scientific*  
22 *Assessment of Ozone Depletion: 2010, Global Ozone Research and Monitoring Project – Report No. 52,*  
23 *Geneva, Switzerland, 2011.*  
24  
25 Moore, R. M.: The solubility of a suite of low molecular weight organochlorine compounds in seawater and  
26 implications for estimating the marine source of methyl chloride to the atmosphere, *Chemosphere - Global*  
27 *Change Science*, 2, 95-99, doi: [http://dx.doi.org/10.1016/S1465-9972\(99\)00045-8](http://dx.doi.org/10.1016/S1465-9972(99)00045-8), 2000.  
28  
29 Moore, R. M., and Groszko, W.: Methyl iodide distribution in the ocean and fluxes to the atmosphere, *J.*  
30 *Geophys. Res.-Oceans*, 104, 11163-11171, doi: 10.1029/1998jc900073, 1999.  
31  
32 Moore, R. M., and Zafiriou, O. C.: Photochemical production of methyl iodide in seawater, *J. Geophys. Res.-*  
33 *Atmos.*, 99, 16415-16420, doi: 10.1029/94jd00786, 1994.  
34  
35 Moore, R. M., Geen, C. E., and Tait, V. K.: Determination of Henry's Law constants for a suite of naturally  
36 occurring halogenated methanes in seawater, *Chemosphere*, 30, 1183-1191, doi: [http://dx.doi.org/10.1016/0045-](http://dx.doi.org/10.1016/0045-6535(95)00009-W)  
37 [6535\(95\)00009-W](http://dx.doi.org/10.1016/0045-6535(95)00009-W), 1995.  
38  
39 Moore, R. M., Webb, M., Tokarczyk, R., and Wever, R.: Bromoperoxidase and iodoperoxidase enzymes and  
40 production of halogenated methanes in marine diatom cultures, *J. Geophys. Res.-Oceans*, 101, 20899-20908,  
41 doi: 10.1029/96jc01248, 1996.  
42  
43 Nightingale, P. D., Malin, G., Law, C. S., Watson, A. J., Liss, P. S., Liddicoat, M. I., Boutin, J., and Upstill-  
44 Goddard, R. C.: In situ evaluation of air-sea gas exchange parameterizations using novel conservative and  
45 volatile tracers, *Global Biogeochem. Cy.*, 14, 373-387, doi: 10.1029/1999gb900091, 2000.  
46

1 Oremland, R. S., Miller, L. G., and Strohmaier, F. E.: Degradation of Methyl Bromide in Anaerobic Sediments,  
2 Environ. Sci. Technol., 28, 514-520, doi: 10.1021/es00052a026, 1994.  
3  
4 Quack, B., and Wallace, D. W. R.: Air-sea flux of bromoform: Controls, rates, and implications, Global  
5 Biogeochem. Cy., 17, 1023, doi: 10.1029/2002gb001890, 2003.  
6  
7 Raymond, P. A., and Cole, J. J.: Gas exchange in rivers and estuaries: Choosing a gas transfer velocity,  
8 Estuaries, 24, 312-317, doi: 10.2307/1352954, 2001.  
9  
10 Rhew, R., and Mazeas, O.: Gross production exceeds gross consumption of methyl halides in northern California  
11 salt marshes, Geophys. Res. Lett., 37, L18813, doi: 10.1029/2010gl044341, 2010.  
12  
13 Rhew, R. C., Miller, B. R., and Weiss, R. F.: Natural methyl bromide and methyl chloride emissions from  
14 coastal salt marshes, Nature, 403, 292-295, doi: 10.1038/35002043, 2000.  
15  
16 Rhew, R. C., Miller, B. R., Bill, M., Goldstein, A. H., and Weiss, R. F.: Environmental and biological controls  
17 on methyl halide emissions from southern California coastal salt marshes, Biogeochemistry, 60, 141-161, doi:  
18 10.1023/a:1019812006560, 2002.  
19  
20 Rhew, R. C., Whelan, M. E., and Min D.H.: Large methyl halide emissions from south Texas salt marshes,  
21 Biogeosciences Discuss., 11, 9451-9470, doi: 10.5194/bgd-11-9451-2014, 2014.  
22  
23 Saito, T., and Yokouchi, Y.: Stable carbon isotope ratio of methyl chloride emitted from glasshouse-grown  
24 tropical plants and its implication for the global methyl chloride budget, Geophys. Res. Lett., 35, L08807, doi:  
25 10.1029/2007gl032736, 2008.  
26  
27 Saiz-Lopez, A., and von Glasow, R.: Reactive halogen chemistry in the troposphere, Chem. Soc. Rev., 41, 6448-  
28 6472, doi: 10.1039/c2cs35208g, 2012.  
29  
30 Santos, R., Silva, J., Alexandre, A., Navarro, N., Barron, C., and Duarte, C. M.: Ecosystem metabolism and  
31 carbon fluxes of a tidally-dominated coastal lagoon, Estuaries, 27, 977-985, doi: 10.1007/bf02803424, 2004.  
32  
33 Scarratt, M. G., and Moore, R. M.: Production of methyl bromide and methyl chloride in laboratory cultures of  
34 marine phytoplankton II, Mar. Chem., 59, 311-320, doi: 10.1016/s0304-4203(97)00092-3, 1998.  
35  
36 Tait, V. K. D. U.: An investigation of the oceanic source of methyl chloride, Dalhousie University, Halifax, N.S.,  
37 1995.  
38  
39 Tait, V. K., Moore, R. M., and Tokarczyk, R.: Measurements of methyl-chloride in the Northwest Atlantic, J. of  
40 Geophys. Res.-Oceans, 99, 7821-7833, doi: 10.1029/93jc03582, 1994.  
41  
42 Tett, P., Gilpin, L., Svendsen, H., Erlandsson, C. P., Larsson, U., Kratzer, S., Fouilland, E., Janzen, C., Lee, J.  
43 Y., Grenz, C., Newton, A., Ferreira, J. G., Fernandes, T., and Scory, S.: Eutrophication and some European  
44 waters of restricted exchange, Cont. Shelf Res., 23, 1635-1671, doi: 10.1016/j.csr.2003.06.013, 2003.  
45

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

3

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

7

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

10

11 Wanninkhof, R.: Relationship between wind speed and gas exchange over the ocean, *J. Geophys. Res.-Oceans*,  
12 97, 7373-7382, doi: 10.1029/92jc00188, 1992.

13

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

17

18 Xiao, X., Prinn, R. G., Fraser, P. J., Simmonds, P. G., Weiss, R. F., O'Doherty, S., Miller, B. R., Salameh, P. K.,  
19 Harth, C. M., Krummel, P. B., Porter, L. W., Muehle, J., Greally, B. R., Cunnold, D., Wang, R., Montzka, S. A.,  
20 Elkins, J. W., Dutton, G. S., Thompson, T. M., Butler, J. H., Hall, B. D., Reimann, S., Vollmer, M. K., Stordal,  
21 F., Lunder, C., Maione, M., Arduini, J., and Yokouchi, Y.: Optimal estimation of the surface fluxes of methyl  
22 chloride using a 3-D global chemical transport model, *Atmos. Chem. Phys.*, 10, 5515-5533, doi: 10.5194/acp-10-  
23 5515-2010, 2010.

24

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

27

28 Zhou, Y., Varner, R. K., Russo, R. S., Wingenter, O. W., Haase, K. B., Talbot, R., and Sive, B. C.: Coastal water  
29 source of short-lived halocarbons in New England, *J. Geophys. Res.-Atmos.*, 110, D21302, doi:  
30 10.1029/2004jd005603, 2005.

31

32

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

	<b>Air mixing ratio</b>	<b>Air mixing ratio</b>	<b>Water concentration</b>
	<b>Ria Formosa (ppt)</b>	<b>Praia de Faro (ppt)</b>	<b>Ria Formosa (pmol L<sup>-1</sup>)</b>
<i>summer 2011</i>			
<b>CH<sub>3</sub>Cl</b>	<b>828</b> (503-1490)	<b>613</b> (498-685)	<b>220</b> (158-301)
<b>CH<sub>3</sub>Br</b>	<b>22</b> (8-118)	<b>13</b> (9-19)	<b>8</b> (5-11)
<b>CH<sub>3</sub>I</b>	<b>3</b> (2-11)	<b>1</b> (0.8-2)	<b>12</b> (4-18)
<b>CHBr<sub>3</sub></b>	<b>15</b> (6-31)	<b>8</b> (6-9)	<b>102</b> (67 -194)
<i>spring 2012</i>			
<b>CH<sub>3</sub>Cl</b>	<b>654</b> (484-976)	-	<b>166</b> (101-267)
<b>CH<sub>3</sub>Br</b>	<b>12</b> (4-40)	-	<b>10</b> (6-28)
<b>CH<sub>3</sub>I</b>	<b>1</b> (0.4-4.8)	-	<b>7</b> (2-16)
<b>CHBr<sub>3</sub></b>	<b>2</b> (0.4-10)	-	<b>62</b> (39 - 133)

8

9

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

Sample	Time (CET)	CH <sub>3</sub> Cl		CH <sub>3</sub> Br		CH <sub>3</sub> I		CHBr <sub>3</sub>	
		pmol L <sup>-1</sup>	‰	pmol L <sup>-1</sup>	‰	pmol L <sup>-1</sup>	‰	pmol L <sup>-1</sup>	‰
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	-

4

5

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

	n	<b>CH<sub>3</sub>Cl</b> nmol m <sup>-2</sup> h <sup>-1</sup>	<b>CH<sub>3</sub>Br</b> nmol m <sup>-2</sup> h <sup>-1</sup>	<b>CH<sub>3</sub>I</b> nmol m <sup>-2</sup> h <sup>-1</sup>	<b>CHBr<sub>3</sub></b> nmol m <sup>-2</sup> h <sup>-1</sup>
<i>Summer 2011</i>					
<b>air exposure</b>	28	<b>15.6</b> (-49 - 74)	<b>6.5</b> (-5.7 - 130)	<b>1.2</b> (0.5 - 2.8)	<b>1.8</b> (-0.6 - 5.7)
<b>air exposure (sediment)</b>	5	<b>3.6</b> (-1.9 - 8.1)	<b>0.6</b> (-0.2 - 1.1)	<b>0.3</b> (0.1 - 0.6)	<b>0.8</b> (-0.3 - 1.9)
<b>Sea-air exchange</b>	8	<b>29.8</b> (13 - 45)	<b>1.3</b> (0.6 - 1.7)	<b>2.2</b> (0.5 - 3.2)	<b>4.7</b> (1.0 - 8.0)
<i>Spring 2012</i>					
<b>air exposure</b>	17	<b>1.0</b> (-30 - 69)	<b>0.4</b> (-0.8 - 3.9)	<b>0.6</b> (-0.6 - 2.6)	<b>0.4</b> (-0.5 - 1.3)
<b>tidal inundation</b>	18	<b>16.6</b> (-58 - 100)	<b>1.8</b> (-1.6 - 8.3)	<b>1.9</b> (0.1 - 8.0)	<b>3.0</b> (-0.4 - 11)
tidal change	5	<b>40.1</b> (-14 - 100)	<b>2.7</b> (0.1 - 8.3)	<b>3.3</b> (0.1 - 8.0)	<b>2.9</b> (0.2 - 11)
incoming tide	6	<b>11.4</b> (-15 - 37)	<b>1.8</b> (0.2 - 3.3)	<b>1.6</b> (0.1 - 2.9)	<b>2.8</b> (0.2 - 5.1)
tidal maximum	2	-18, -58	-0.5, -1.6	0.1, 0.1	0.5, -0.1
ebb flow	5	<b>21.3</b> (-14 - 46)	<b>2.1</b> (0.1 - 4.4)	<b>1.5</b> (0.2 - 3.0)	<b>4.5</b> (-0.4 - 8.6)
<b>Sea-air exchange</b>	10	<b>15.2</b> (3.5 - 32)	<b>1.4</b> (0.5 - 4.1)	<b>1.3</b> (0.3 - 3.7)	<b>8.3</b> (3.8 - 24)

5

6

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

	Atmosphere		Atmosphere		source signature			
	Ria Formosa (‰)	n	Praia de Faro (‰)	n	lagoon water (‰)	n	seagrass meadow (‰)	n
<i>summer 2011</i>								
<b>CH<sub>3</sub>Cl</b>	-42 ± 2	7	-39 ± 0.4	5	-43 ± 3	7	-51 ± 6	5
<b>CH<sub>3</sub>Br</b>	-29 ± 5	7	-38 ± 3	5	-23 ± 3	7	-42 ± 17	4
<b>CH<sub>3</sub>I</b>	-	-	-	-	-39 ± 9	7	-	-
<b>CHBr<sub>3</sub></b>	-	-	-	-	-13 ± 1	7	-	-
<i>spring 2012</i>								
<b>CH<sub>3</sub>Cl</b>	-38 ± 1	3	-	-	-42 ± 1	5	-56 ± 2	3
<b>CH<sub>3</sub>Br</b>	-23 ± 10	3	-	-	-33 ± 8	5	-26; -33	2
<b>CH<sub>3</sub>I</b>	-	-	-	-	-37 ± 7	5	-	-
<b>CHBr<sub>3</sub></b>	-	-	-	-	-18 ± 1	5	-	-

4

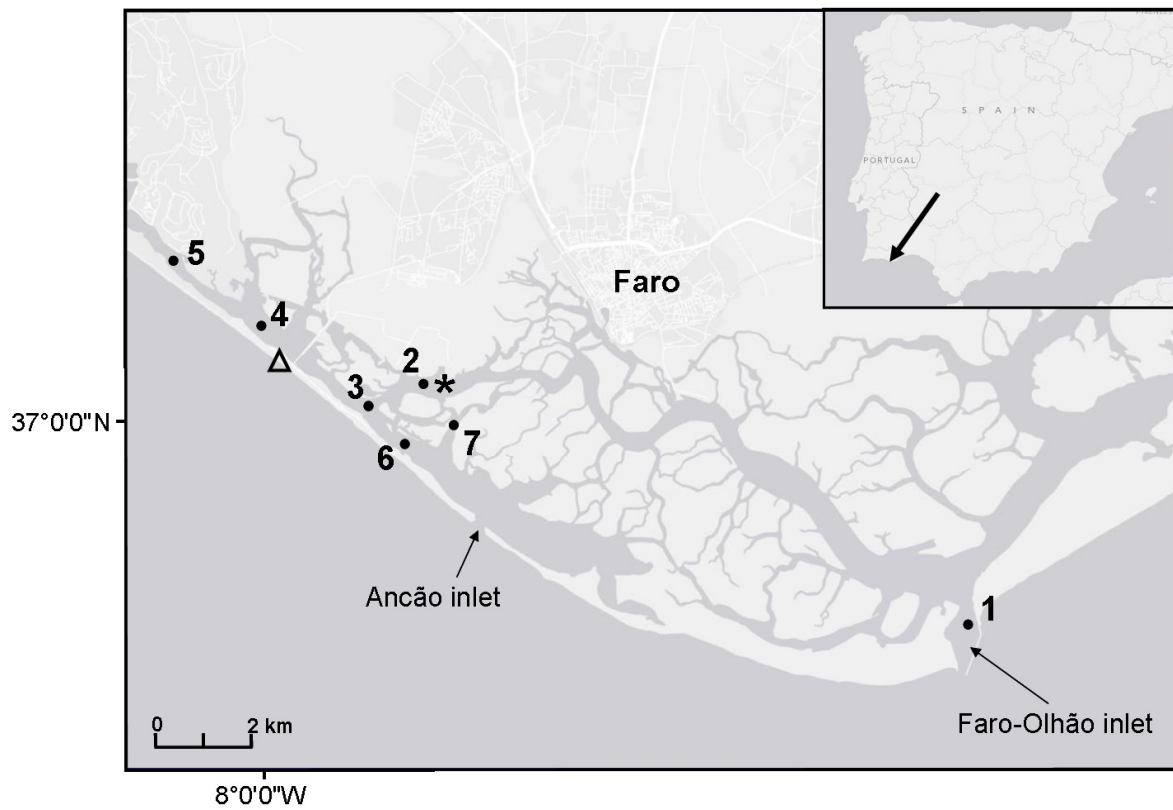
5

1 Table 5: Mean concentrations (bold) and ranges (parentheses) of dissolved halocarbons (pmol  
 2 L<sup>-1</sup>) 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 <sub>3</sub> Cl	CH <sub>3</sub> Br	CH <sub>3</sub> I	CHBr <sub>3</sub>
Faro, Portugal (summer) <sup>1</sup>	<b>220</b> (158 - 301)	<b>8</b> (5-11)	<b>12</b> (4 - 18)	<b>102</b> (67 -194)
Faro, Portugal (spring) <sup>1</sup>	<b>166</b> (101 - 267)	<b>10</b> (6 - 28)	<b>7</b> (2 - 16)	<b>62</b> (39 - 133)
East Atlantic <sup>2,#</sup>	-	-	-	<b>68.3</b> (36.6 - 102.0)
Roscoff, France <sup>3,#</sup>	-	-	<b>12.9</b> (9.0 - 31.8)	<b>217.4</b> (124.8 - 519.4)
Greenland, NW Atlantic <sup>4</sup>	104 - 260	-	0.2 - 16.1	-
Norfolk, UK <sup>5</sup>	-	<b>3.2</b> (1.7 - 8.7)	-	-
Menai Strait, UK <sup>6,#</sup>	-	-	<b>6.7</b> (0.0 - 80.0)	<b>214.2</b> (3.0 - 3588.4)
Mace Head, Ireland <sup>7,#</sup>	-	<b>3.7</b> (1.7 - 5.7)	<b>15.3</b> (10.9 - 19.2)	<b>388.0</b> (221.8 - 554.3)
West Atlantic <sup>8</sup>	<b>88.4</b> (61.5 - 179.0)	<b>1.9</b> (0.8-5)	-	-
North West Atlantic <sup>9</sup>	<b>71.0</b> (55.0 - 106.0)	-	-	-
Nova Scotia, Canada <sup>10</sup>	-	-	4 - 6	-
Gulf of Maine, UK <sup>11,#</sup>	-	-	8 -18	40 - 1240

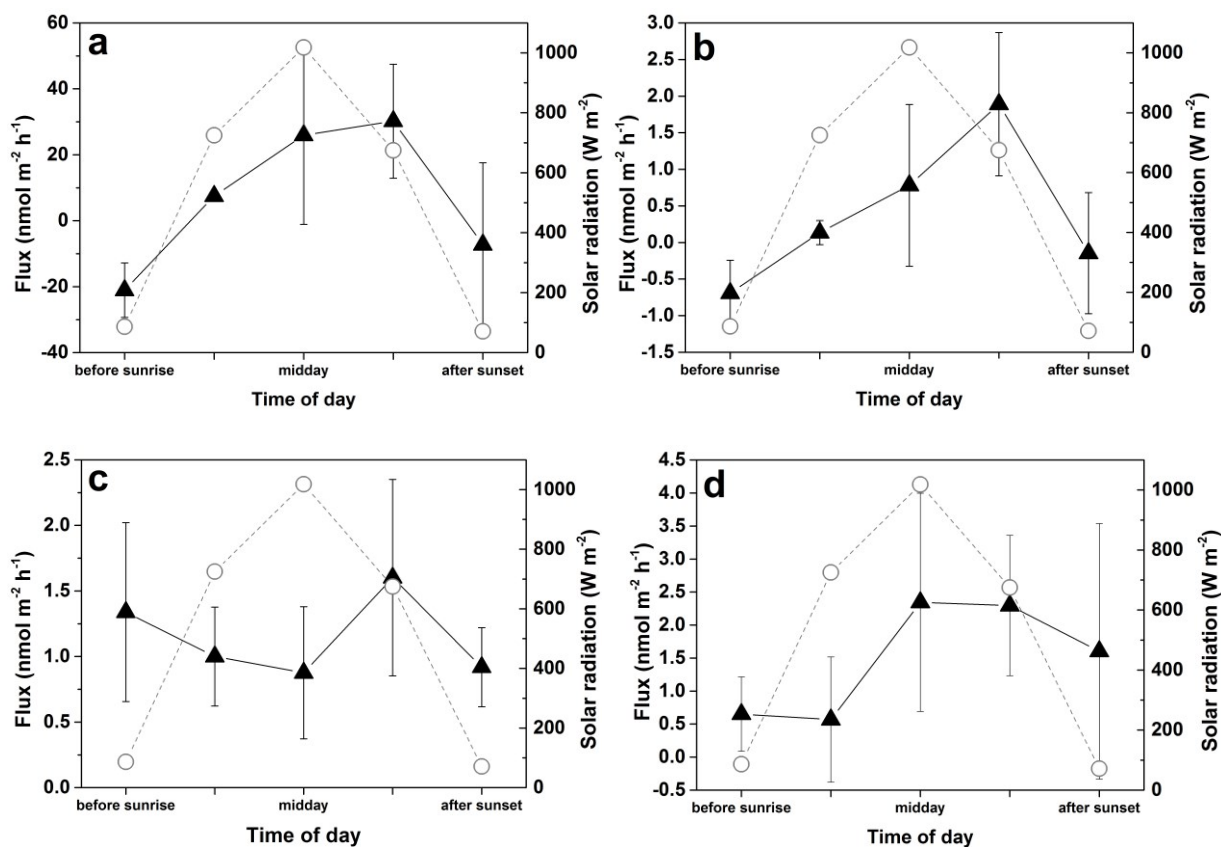
4 <sup>1</sup> this study; <sup>2</sup> Carpenter et al. (2009); <sup>3</sup> Jones et al. (2009); <sup>4</sup> Tait et al. (1994); <sup>5</sup> Baker et al. (1999); <sup>6</sup> Bravo-  
 5 Linares and Mudge (2009); <sup>7</sup> Carpenter et al. (2000); <sup>8</sup> Hu et al. (2010); <sup>9</sup> MacDonald and Moore (2007); <sup>10</sup>  
 6 Moore and Groszko (1999); <sup>11</sup> Zhou et al. (2005); # macroalgae dominated  
 7





1  
2  
3  
4  
5  
6

Fig. 1: Map of the lagoon Ria Formosa, Portugal. Asterisk: site of seagrass meadow studies; triangle: sampling site on the Praia de Faro (upwind position). Dots with numbers represent sampling points during the transect cruise.



1

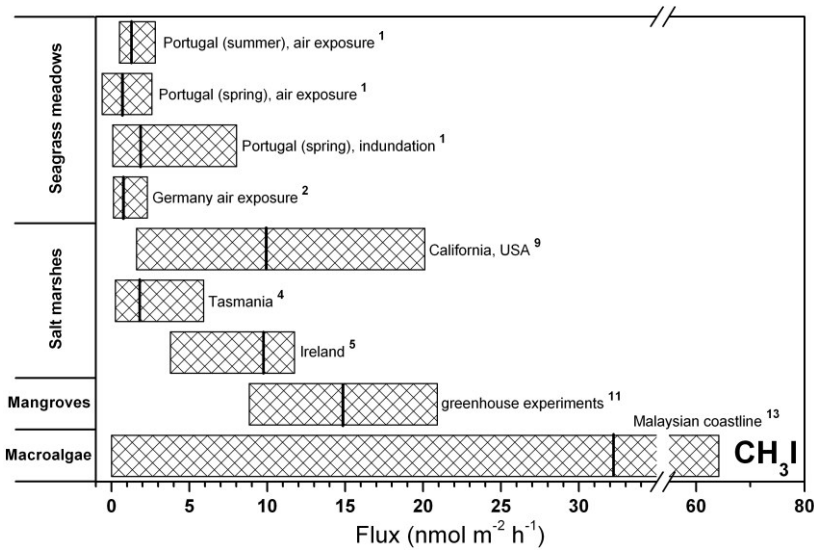
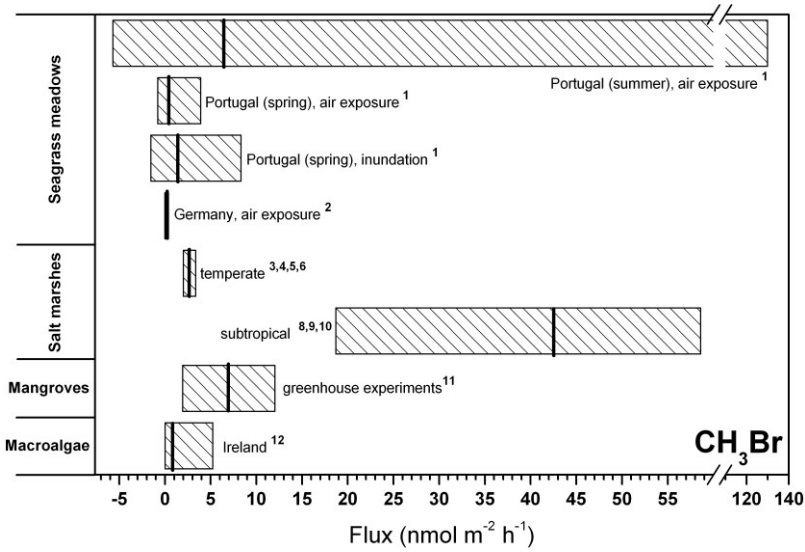
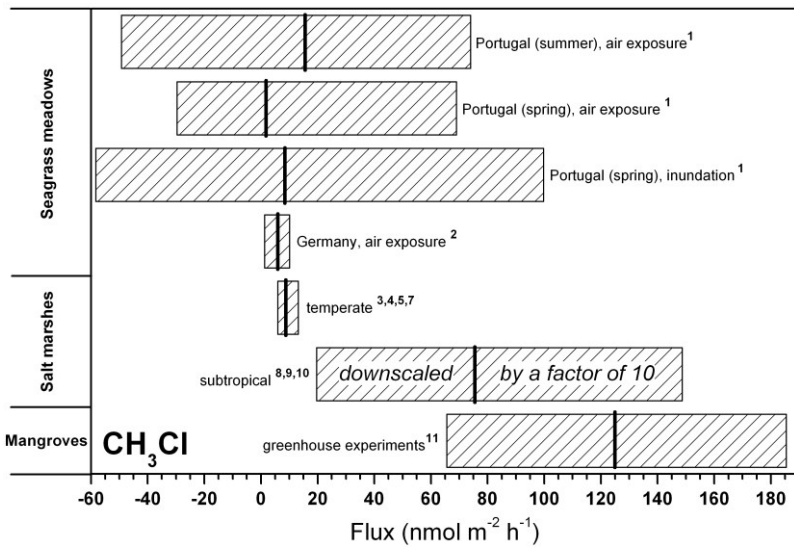
2 Fig. 2a-d: Diurnal variation of mean halocarbon fluxes (triangles) from seagrass meadows  
 3 during periods of air exposure in summer 2011 (a: CH<sub>3</sub>Cl, b: CH<sub>3</sub>Br, c: CH<sub>3</sub>I, d: CHBr<sub>3</sub>).  
 4 Error bars refer to standard deviations. Circles are solar radiation values. Note that the scales  
 5 on y-axis are different for each compound.

6

7

8

9



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