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

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

9 University of Hamburg, Institute for Biogeochemistry and Marine Chemistry,
10 Bundesstraße 55, 20146 Hamburg, Germany

11 *corresponding author: enno.bahlmann@zmaw.de

12 phone: +49-40-42838-5167

13 fax: +49-40-42838-6347

14

15 **Abstract**

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

26 Accompanying water sampling during both campaigns revealed elevated concentrations of
27 CH_3Cl and CH_3Br indicating productive sources within the lagoon. Stable carbon isotopes of

1 halocarbons from the air and water phase along with source signatures were used to allocate
2 the distinctive sources and sinks in the lagoon. Results suggest CH_3Cl rather originating from
3 seagrass meadows and water column than from salt marshes. Aqueous and atmospheric
4 CH_3Br was substantially enriched in ^{13}C in comparison to source signatures for seagrass
5 meadows and salt marshes. This suggests a significant contribution from the water phase on
6 the atmospheric CH_3Br in the lagoon.

7 A rough global upscaling yields annual productions from seagrass meadows of 2.3-4.5 Gg yr^{-1}
8 ^{13}C , 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
9 respectively. This suggests a minor contribution from seagrass meadows to the global
10 production of CH_3Cl and CH_3Br with about 0.1 % and 0.7 %, respectively. In comparison to
11 the known marine sources for CH_3I and CHBr_3 , seagrass meadows are rather small sources.

12

13 1 Introduction

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

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

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

1 Coastal zones are reported as being important source regions of halocarbons. In these salt
2 water affected systems, halocarbon producers comprise phytoplankton (Scarratt and Moore,
3 1998), macroalgae (Gschwend et al., 1985), salt marshes (Rhew et al., 2000), and mangroves
4 (Manley et al., 2007).

5 With a net primary production of $1211 \text{ g C m}^{-2} \text{ yr}^{-1}$, seagrass meadows are one of the most
6 productive ecosystems with a similar global abundance as mangroves and salt marshes
7 (Duarte et al., 2005). They cover huge areas of the intertidal and subtidal zone in temperate
8 and subtropical/tropical regions. Thus, they may represent an additional source for
9 halocarbons to the atmosphere which is not yet sufficiently studied. Seagrass meadows are
10 highly diverse ecosystems with respect to potential halocarbon producers. Along with the
11 seagrass itself, they comprise epiphytes such as microalgae and diatoms, and sediment
12 reassembling microphytobenthos and bacteria communities. All these constituents of the
13 benthic community have been reported to produce halocarbons (Amachi et al., 2001; Blei et
14 al., 2010; Manley et al., 2006; Moore et al., 1996; Rhew et al., 2002; Tokarczyk and Moore,
15 1994; Urhahn, 2003). While first evidence for the release of halocarbons from seagrass was
16 obtained by incubation experiments (Urhahn 2003), we could recently confirm this production
17 potential in a field study of a temperate seagrass meadow in Northern Germany (Weinberg et
18 al., 2013).

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

24

25 **2 Materials and methods**

26 **2.1 Sampling site**

27 The Ria Formosa, covering an area of 84 km^2 , is a mesotidal lagoon at the South-eastern coast
28 of the Algarve, Portugal (Fig. 1). It is separated from the Atlantic Ocean by a series of barrier
29 islands and two peninsulas. About 80% of the lagoon is intertidal with a semi-diurnal tidal
30 regime and tidal ranges between 1.3 m during neap tides and 3.5 m during spring tides
31 (Cabaço et al., 2012). Due to negligible inflow of fresh water and high exchange of water

1 with the open Atlantic during each tidal cycle, the salinity within the lagoon is 35 to 36 PSU
2 year round, except for periods of heavy rainfalls. About a quarter of the intertidal area (13.04
3 km²) is covered by dense stands of *Zostera noltii Hornem* (Guimarães et al., 2012). Further,
4 but much less abundant, seagrass species in the lagoon are *Zostera Marina L.* and *Cymodocea*
5 *nodososa (Ucria) Ascherson* which are mainly located in shallow parts of the subtidal areas
6 (Santos et al., 2004). About 30% of the lagoon's area is covered with salt marsh communities
7 (Rui Santos, pers. comm.).

8 **2.2 Sampling**

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

19 During the two campaigns we used different dynamic flux chamber systems. During the 2011
20 campaign, we measured the halocarbon fluxes during air exposure using a quartz-glass
21 chamber (0.1m² surface area, 7 L enclosure volume) as described in Weinberg et al. (2013)
22 with some adjustments. For this study a permanent backup flow (3± 0.2 L min⁻¹) through the
23 flux chamber during sampling and the change of cryotrap was applied to ensure sufficient
24 mixing. Further, to overcome analytical problems with the high humidity in the sampled air,
25 the water content was reduced using a condenser (-15°C). Briefly, the quartz-glass flux
26 chamber was placed on the seagrass patch and sealed with surrounding sediment. Two
27 sampling systems were operated simultaneously measuring inlet and outlet air of the flux
28 chamber (flow rate 1± 0.2 L min⁻¹). Prior to sampling, the flux chamber was flushed for about
29 10 min ensuring sufficient equilibration of compounds in the chamber air.

30 During the 2012 campaign, we used a dynamic flux chamber system (0.037 m² bottom
31 surface area, 8 L enclosure volume) suitable for flux measurements during both periods of air

1 exposure and tidal immersion. The properties and setup of this dynamic chamber system is
2 described in detail elsewhere (Bahlmann et al., 2014). Since this system acts as an ordinary
3 purge and trap system, the extraction efficiencies were simulated using halocarbon
4 equilibrated artificial seawater. While the results from these tests revealed that
5 monohalomethanes were almost completely extracted ($\geq 90\%$), the purge efficiencies for
6 CHBr_3 were only 33%. Thus the reported CHBr_3 fluxes determined from seagrass meadows
7 using the submergible chamber system represent an under-estimate.

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

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

23 Discrete water samples for the determination of dissolved halocarbons concentration and
24 isotopic composition at high tide were taken during both campaigns. The samples were taken
25 directly above the studied seagrass meadow using Duran glass bottles (1-2 L volume). Air and
26 sediment intrusions during water sampling were avoided. The water depth was between 0.3 m
27 and 1 m. On April 24th 2012, a transect cruise through the middle and western part of the
28 lagoon was conducted during rising waters (Fig. 1). The water samples were taken from a
29 water depth of 1 m. Dissolved halocarbons were extracted from seawater using a purge and
30 trap system. Seawater was purged with helium 5.0 (purge flow 1L min^{-1}) for 30 minutes.
31 After water vapour reduction of the purge gas, the compounds were enriched on cryotrap
32 (submerged in a dry shipper). The shape of the cryotrap used here was the same as those for

1 flux chamber and atmospheric samples. The water samples were usually processed within 30
2 minutes after sampling. Samples from the transect cruise were stored in the dark at 4°C and
3 analyzed within eight hours. Purge efficiencies of monohalomethanes from lagoon water were
4 $\geq 95\%$ (1 L and 2 L samples). However, the less volatile CHBr₃ was only extracted with 50%
5 (1 L samples) and 30% (2 L samples). Therefore, the results of water concentration were
6 corrected for the respective purge efficiency for this compound.

7 **2.3 Measurement and quantification**

8 The measurement procedure is described in detail in the [Supplementary Materials](#)
9 [Supplemental Material](#). Briefly, compounds adsorbed on the cryotrap, were
10 thermally desorbed and transferred to Peltier-cooled adsorption tubes. The analytes were
11 further desorbed from the adsorption tubes and refocused cryogenically before injection to the
12 GC-MS system. Air and water samples were measured on-site at Ramalhete research station
13 using a GC-MS system (6890N/5975B, Agilent, Germany) equipped with a CP-PorabondQ
14 column (25 m, 0.25 μm i.d., Varian, Germany). The GC-MS was operated in the electron
15 impact mode. Identification of compounds was executed by retention times and respective
16 mass spectra. Aliquots of gas standard (Scott EPA TO 15/17, 65 compounds, 1 ppm each in
17 nitrogen, Sigma Aldrich, Germany) containing CH₃Cl, CH₃Br, and CHBr₃ were applied to
18 quantify the target compounds. During onsite measurements, CH₃I was quantified using the
19 response factor against CH₃Br. The response factor was determined prior to the campaign.
20 Equivalent amounts of CH₃I and CH₃Br from single gas standards were analysed together for
21 the response factor calculation. The analytical limit of detection was 0.3 ppt ([pmol mol⁻¹](#)) for
22 the halocarbons. The accuracy of the entire sampling method (sampling, sample treatment,
23 measurement) was derived from test samples in triplicates. The deviation between the
24 individual samples for CH₃Cl, CH₃Br, CH₃I, and CHBr₃ was 5.4%, 6.3%, 15.4% and 6.7%,
25 respectively. A series of procedural blanks (cryotrap and adsorption tubes) were taken during
26 the sampling campaigns. The occasionally detected blanks of CH₃Cl and CH₃Br from these
27 determinations were $\leq 3\%$ to the “real” samples taken from the seagrass meadows during
28 sampling campaigns. Therefore, the halocarbon fluxes were not blank corrected.
29 Air and water samples for determining the isotopic composition of halocarbons were
30 transferred to adsorption tubes and stored at -80°C until measurements. The analysis was
31 conducted using the GC-MS-IRMS system at our home laboratory (Bahlmann et al., 2011).

1 Additional transport and storage blanks were processed which revealed no contamination for
2 all halocarbons studied.

3

4 **2.4 Calculations**

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

10
$$F_{Net} = \frac{Q \times (C_{out} - C_{in})}{A \times V \times 1000} \quad (1)$$

11 Here, Q is the flushing rate of air through the chamber (L h⁻¹), C_{out} and C_{in} are the mixing
12 ratios of target compounds (~~pmol mol⁻¹ ppt~~) at the outlet and the inlet of the flux chamber. A is
13 the enclosed surface area of the flux chamber (m²) and V is the molar volume (L) at 1013.25
14 mbar and 298.15 K.

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

20
$$F = k_w \times (C_w - C_a \times H^{-1}) \quad (2)$$

21 where k_w is the gas exchange velocity (m h⁻¹), C_w and C_a the water concentration and air
22 concentration (pmol L⁻¹), respectively, and H the dimensionless and temperature dependent
23 Henry's law constant taken from Moore (2000) for CH₃Cl, Elliott and Rowland (1993) for
24 CH₃Br and CH₃I, and Moore et al. (1995) for CHBr₃. Several approximations emerged to
25 estimate the relationship between the gas exchange velocity k and the wind speed u for open
26 and coastal oceans (e.g. Nightingale et al., 2000; Wanninkhof, 1992). These estimations rely
27 on assumptions that trace gas exchange is based on wind-driven turbulence. This is not
28 applicable in shallow estuarine and riverine systems where the sea-air gas exchange is
29 additionally driven by wind-independent currents and the bottom turbulence and thus water

1 depth and current velocities further play a major role (Raymond and Cole, 2001). Studying
2 the sea-air exchange in the Ria Formosa, these additional factors have to be considered in
3 addition to wind driven outgassing. Therefore, we used the parameterization of k_w with the
4 assumption that wind speed and water current driven turbulence are additive (Borges et al.,
5 2004):

6
$$k_w = 1.0 + 1.719 \times w^{0.5} \times h^{-0.5} + 2.58 \times u \quad (3)$$

7 where w is the water current (cm s^{-1}), h the water depth (m) and u the wind speed (m s^{-1}). For
8 the calculations of the sea-air flux in the lagoon, a mean water depth of 1.5m (Tett et al.,
9 2003) and a mean water current of 24 cm s^{-1} (Durham, 2000) was used. The Schmidt number
10 (Sc) expresses the ratio of transfer coefficients of the kinematic viscosity of water and gas
11 diffusivity of interest. The gas exchange velocity k_w for each gas was then normalized to a
12 Schmidt number of 660, assuming a proportionality to $Sc^{-0.5}$ (Borges et al., 2004). The
13 individual Schmidt numbers were obtained from Tait (1995) for CH_3Cl , De Bruyn and
14 Saltzman (1997) for CH_3Br and CH_3I , and Quack and Wallace (2003) for CHBr_3 .

15

16 **3 Results**

17 **3.1 Halocarbons in the atmosphere and lagoon water**

18 The air mixing ratios in the lagoon were adopted from the inlets of the flux chambers at 1 m
19 above ground during both campaigns. The results of these measurements and those of the
20 upwind site outside the lagoon (Praia de Faro) are presented in Table 1. In summer, elevated
21 air mixing ratios of the monohalomethanes were observed during periods of easterly winds
22 when air masses at the sampling site had presumably passed over major parts of the lagoon.
23 These mixing ratios reached up to 1490 ppt for CH_3Cl , 61 ppt for CH_3Br , and 11 ppt for CH_3I
24 reflecting a potent source in this system. The mixing ratios at the upwind site (Praia de Faro)
25 were distinctively lower with mean values of 613 ppt (CH_3Cl), 13 ppt (CH_3Br), 1 ppt (CH_3I),
26 and 8 ppt (CHBr_3) further indicating a source inside the lagoon. In spring 2012, the mean air
27 mixing ratios in the lagoon were significantly lower than during summer with 654 ppt for
28 CH_3Cl , 12 ppt for CH_3Br , 1 ppt for CH_3I , and 2 ppt for CHBr_3 .

29 Discrete water samples were taken above the studied seagrass meadow during tidal inundation
30 (summer n=9; spring n=10). The results are presented in Table 1. In summer, concentrations

1 ranged from 158 to 301 pmol L⁻¹ (CH₃Cl), 5 to 11 pmol L⁻¹ (CH₃Br), 4 to 18 pmol L⁻¹ (CH₃I),
2 and 67 to 194 pmol L⁻¹ (CHBr₃). During the spring campaign, the water concentrations were
3 101 to 267 pmol L⁻¹ for CH₃Cl, 6 to 28 pmol L⁻¹ for CH₃Br, 2 to 16 pmol L⁻¹ for CH₃I, and 39
4 to 133 pmol L⁻¹ for CHBr₃.

5 The results obtained from samples of the transect cruise covered in 2012 (Fig. 1) are given in
6 Table 2. We observed an about two-fold increase of concentration for CH₃Cl (from 121 to
7 241 pmol L⁻¹) and CHBr₃ (from 26 to 55 pmol L⁻¹) between position 1 (Faro-Olhão inlet) and
8 position 2 (near to the seagrass meadows studied). The increase was less pronounced for
9 CH₃Br (5 to 7 pmol L⁻¹) and not notable for CH₃I. The seawater at positions 6 and 7, the
10 nearest to the Ancão inlet, revealed rather low concentrations for all compounds. We further
11 observed rising concentrations for all halocarbons along positions 3, 4, and 5 with increasing
12 distance to the Ancão inlet. They increased from 96 to 180 pmol L⁻¹ for CH₃Cl, from 9 to 19
13 pmol L⁻¹ for CH₃Br, 2 to 14 pmol L⁻¹ for CH₃I, and 21 to 95 pmol L⁻¹ for CHBr₃.

14 **3.2 Fluxes from seagrass meadows, sediment, and sea-air exchange**

15 The mean fluxes and ranges of CH₃Cl, CH₃Br, CH₃I, and CHBr₃ from seagrass meadows,
16 sediment, and from sea-air exchange calculations obtained from the two sampling campaigns
17 are given in Table 3.

18 During the summer campaign (air exposure), we observed highly variable emission and
19 deposition fluxes ranging from -49 to 74 nmol m⁻² h⁻¹ and -5.7 to 130 nmol m⁻² h⁻¹ for CH₃Cl
20 and CH₃Br, respectively. The variability was less pronounced for CH₃I (0.5 to 2.8 nmol m⁻² h⁻¹)
21 and CHBr₃ (-0.6 to 5.7 nmol m⁻² h⁻¹) where predominantly emissions were measured.
22 Strongly elevated fluxes up to 130 nmol m⁻² h⁻¹ for CH₃Br were recorded in conjunction with
23 tidal change from air exposure to inundation and conversely. These high fluxes were
24 substantiated by a concurrent enhanced atmospheric mixing ratios ranging from 23 ppt to 118
25 ppt (campaign median 14 ppt). Omitting these compound-specific tidal phenomena, the fluxes
26 of CH₃Cl and CH₃Br were positively correlated (R^2 0.55, $p < 0.05$). There were no significant
27 correlations between CH₃I and CHBr₃ and the other investigated halocarbons. Due to the
28 inherent high variability of the fluxes, halocarbon fluxes were poorly correlated with solar
29 radiation ($R^2 \leq 0.20$).

30 The flux chamber measurements over the sediment during air exposure revealed
31 predominantly emissions of all four halocarbons (n=5). These fluxes were 3.6 ± 4.3 nmol m⁻² h⁻¹

1 1 (CH₃Cl), 0.6±0.5 nmol m⁻² h⁻¹ (CH₃Br), 0.3±0.2 nmol m⁻² h⁻¹ (CH₃I), and 0.8±1.0 nmol m⁻² h⁻¹ (CHBr₃). Except for CH₃I, the halocarbon fluxes were statistically significant different from zero (Mann-Whitney-U test; p <0.05). Hence, the bare sediment may contribute to the overall emissions above the seagrass by about 10 to 20% for CH₃Cl and CH₃Br, and 45% for CHBr₃.

6 During the 2012 spring campaign the halocarbon fluxes from seagrass meadows were
7 determined during both, periods of air exposure and periods of tidal immersion. Furthermore,
8 the measurements were complemented by other trace gases including hydrocarbons and
9 sulphur containing compounds (Bahlmann et al., 2014). As in the summer campaign, the
10 seagrass meadows were a net source for all halocarbons studied, but on a lower level. The
11 individual ranges of air exposure measurements were -30 to 69 nmol m⁻² h⁻¹ (CH₃Cl), -0.8 to
12 3.9 nmol m⁻² h⁻¹ (CH₃Br), -0.6 to 2.6 nmol m⁻² h⁻¹ (CH₃I), and -0.5 to 1.3 nmol m⁻² h⁻¹
13 (CHBr₃). On average, the seagrass meadows were a net source also under submerged
14 conditions ranging from -58 to 100 nmol m⁻² h⁻¹ for CH₃Cl, -1.6 to 8.3 nmol m⁻² h⁻¹ for
15 CH₃Br, 0.1 to 8.0 nmol m⁻² h⁻¹ for CH₃I, and -0.4 to 10.6 nmol m⁻² h⁻¹ for CHBr₃. Due to the
16 low purge efficiency of CHBr₃ during high tide measurements, the fluxes determined with the
17 submergible chamber are underestimated for this compound. Despite this high variability in
18 production/decomposition during air exposure and inundation, the monohalomethanes were
19 significantly correlated to each other ($R^2 \geq 0.50$). These correlations were enhanced compared
20 to those found when the seagrass meadows were air-exposed ($R^2 \geq 0.50$). In this case, only
21 CH₃I and CH₃Br were significantly correlated ($R^2 = 0.51$). CHBr₃ was only slightly correlated
22 to the monohalomethanes.

23 While deposition fluxes of CH₃Cl and CH₃Br of air-exposed seagrass meadows occurred
24 predominantly during periods of low irradiance in summer, no obvious relation to the time of
25 day and/or solar radiation was observed during spring when deposition fluxes were frequently
26 detected. For CH₃I and CHBr₃, uptake was only occasionally observed and situations of
27 emission clearly dominated.

28 As in the summer campaign, we observed some remarkable tidal effects on halocarbon fluxes
29 during the spring campaign. Firstly, the highest fluxes of all halocarbons were measured when
30 the lagoon water was just reaching the sampling site. Occasionally this was also observed
31 from air exposure to tidal inundation, although less pronounced. However, these short-timed
32 effects were not as strong as during the summer campaign. Secondly, at tidal maximum we

1 observed deposition fluxes for CH₃Cl and CH₃Br and deposition fluxes or very weak
2 emissions for CH₃I and CHBr₃. Before and after this period, emission fluxes during incoming
3 tide and ebb flow dominated.

4 The lagoon water was a net source for all investigated halocarbons to the atmosphere during
5 both campaigns. In summer, the flux ranges were 13-45 nmol m⁻² h⁻¹ (CH₃Cl), 0.6-1.7 nmol
6 m⁻² h⁻¹ (CH₃Br), 0.5-3.2 nmol m⁻² h⁻¹ (CH₃I), and 1.0-8.0 nmol m⁻² h⁻¹ (CHBr₃). The
7 respective fluxes in spring were 3.5-32 (CH₃Cl), 0.5-4.1 (CH₃Br), 0.3-3.7 (CH₃I), 3.8-24
8 (CHBr₃).

9 **3.3 Stable carbon isotopes of halocarbons**

10 Stable carbon isotope ratios of halocarbons were determined for selected samples of both
11 campaigns (Table 4). Isotopic source signatures from seagrass meadows for CH₃Cl and
12 CH₃Br were calculated using a coupled isotope and mass balance without integration of a
13 possible sink function (Weinberg et al., 2013).

14 In 2011, the difference in atmospheric mixing ratios of CH₃Cl and CH₃Br between within the
15 lagoon and the upwind position (Praia de Faro) was accompanied by a shift of $\delta^{13}\text{C}$ values.
16 More ^{13}C depleted values were found for CH₃Cl in the lagoon (-42±2‰) compared to the
17 upwind position (-39±0.4‰). In contrast, the $\delta^{13}\text{C}$ values of CH₃Br were significantly
18 enriched in ^{13}C by about 10‰ inside the lagoon (-29±5‰) as compared to the upwind site (-
19 38±3). These $\delta^{13}\text{C}$ values found in air samples in the lagoon roughly correspond to the $\delta^{13}\text{C}$
20 values of CH₃Cl (-43±3‰) and CH₃Br (-23±3‰) found in samples of lagoon waters.

21 Atmospheric CH₃Cl and CH₃Br were on average more enriched in ^{13}C in spring than in
22 summer by 4 and 6‰, respectively. While the $\delta^{13}\text{C}$ values of CH₃Cl in the lagoon water were
23 quite similar between both periods of the year, those of CH₃Br were on average more depleted
24 in ^{13}C during spring suggesting certain changes in production/decomposition processes. The
25 isotopic composition of CH₃I in lagoon water was quite similar between summer (-39± 9‰)
26 and spring (mean -37±7‰). As for CH₃Br, the $\delta^{13}\text{C}$ values of CHBr₃ were more enriched in
27 ^{13}C in summer when compared with those of the spring campaign.

28 The difference in concentration along the transect cruise was accompanied by variations in the
29 carbon isotopic composition of all compounds (Table 1, Figure 2). The most ^{13}C depleted
30 values of CH₃Cl, CH₃Br, and CH₃I were detected at the position furthest from the inlet.

1 Interestingly, CHBr₃ showed the opposite trend with more ¹³C enriched values in the lagoon
2 (-25.8‰ vs. ~ -18‰).

3 Using the fluxes and $\delta^{13}\text{C}$ values from the inlet and outlet of the flux chamber, we were able
4 to calculate the source signatures of seagrass covered areas. The resulting source signatures of
5 CH₃Cl from seagrass meadows were similar during both campaigns (-51±6‰ and -56±2‰,
6 respectively) and independent from the strength of emission. For CH₃Br, we observed most
7 depleted $\delta^{13}\text{C}$ values of -53‰ and -58‰ at increased emission fluxes in summer, but values
8 of -26‰ and -29‰ during periods of low emission. This corroborates the findings of
9 isotopically heavy CH₃Br produced within the seagrass meadows (-29‰) in spring 2012
10 when all samples analysed for the isotopic composition were taken at situations of low
11 emission.

12

13 **4 Discussion**

14 **4.1 Dissolved halocarbons**

15 A comparison of halocarbon concentrations in the lagoon water to other measurements of the
16 coastal Atlantic found in the literature is displayed in Table 5. The lagoon waters appeared to
17 be highly enhanced in CH₃Cl. Except one early study of Tait et al. (1994), our measurements
18 gave the most elevated concentrations for this compound. Enhanced concentrations in the
19 lagoon waters were also found for CH₃Br. Given the mean concentrations from other coastal
20 Atlantic studies (Baker et al., 1999; Carpenter et al., 2000; Hu et al., 2010), we recorded
21 higher concentration by a factor of 2 to 3 at our sampling site. The average water
22 concentrations in the lagoon of CH₃I were in the same range as reported from other parts of
23 the Atlantic (Moore and Groszko 1999; Zhou et al., 2005). However, especially those regions
24 where macroalgae are the dominating source organisms possess higher maximum values
25 (Bravo-Lineares and Mudge, 2009; Jones et al., 2009). This is even more pronounced for
26 CHBr₃, for which the seawater concentration within or in the vicinity of macroalgae beds are
27 strongly elevated (Bravo-Lineares and Mudge, 2009; Carpenter et al., 2000; Jones et al.,
28 2009). The area occupied by the prevalent macroalgae species *Enteromorpha spp.* and *Ulva*
29 *spp.* in the Ria Formosa is estimated to be 2.5 km² (Duarte et al., 2008), considerably below
30 that of other abundant sources such as seagrass meadows. We cannot exclude that
31 phytoplankton contributes significantly to the water concentration of halocarbons, but the

1 predominantly low chlorophyll a concentrations ($3.06 \mu\text{g L}^{-1}$ from long-term measurements,
2 Brito et al., 2012) and low water volumes seem to limit the impact from this source.

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

10 Overall, the lagoon seems to comprise highly potent halocarbon sources in the water column
11 for CH_3Cl and CH_3Br but not for CH_3I and CHBr_3 .

12 **4.2 Flux pattern from seagrass meadows**

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

23 i) Diurnal variations. The correlation analysis with solar radiation resulted in only a weak
24 association with the magnitude of fluxes. However, after grouping by daytime, our data
25 provide some indication for a diurnal pattern (Fig. 2). For CH_3Cl , there was the most obvious
26 relationship between time of day and actual emissions. Highest emissions were observed
27 during day periods with increased sunlight (midday and afternoon). In contrast, deposition
28 fluxes were exclusively recorded during periods of low radiation and nighttimes. The same
29 was also observed for CH_3Br . However, highest mean emissions of this compound seemed to
30 be shifted towards the afternoon. CH_3I was constantly emitted from the seagrass covered spot
31 revealing a weak diurnal dependence. The emissions did not cease during periods of low

1 irradiance and darkness. Nevertheless, elevated mean emissions were observed in the
2 afternoon. Except one occasion, CHBr_3 was emitted throughout the sampling periods. Mean
3 emissions were higher around midday and afternoon as during night.

4 Several studies from salt marshes reported a diurnal trend of halocarbon emissions initiated
5 by irradiance (Dimmer et al., 2001; Rhew et al., 2000, 2002; Dreher et al., 2006). The flux
6 data of halocarbons from the summer campaign with elevated fluxes during midday and
7 afternoon suggest a similar pattern also in seagrass meadows. However, this was more
8 obvious for CH_3Cl and CH_3Br than for CH_3I and CHBr_3 . The lower production of CH_3I
9 during the time of highest light intensity cannot fully be explained. Blei et al. (2010) reported
10 that the main environmental association in salt marsh emissions of CH_3Cl and CH_3Br was
11 with ambient temperature rather than light. However, during the summer campaign,
12 temperature variations (day/night) were too low to explain the observed emission/deposition
13 pattern of CH_3Cl and CH_3Br .

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

22 ii) Tidal effects. During the spring campaign, mean fluxes derived from submerged seagrass
23 meadows were elevated by factors of 17 (CH_3Cl), 5 (CH_3Br), 3 (CH_3I), and 8 (CHBr_3) when
24 compared to the average fluxes during air exposure. This clearly higher production of
25 halocarbons under submerged conditions was quite unexpected, as in general it is believed
26 that the production of trace gases during low tide exceeds that during inundation. For
27 halocarbons this was suggested for example by Carpenter et al. (1999) and Jones et al. (2009)
28 from atmospheric measurements over intertidal macroalgae beds in Mace Head, Ireland.
29 Nevertheless, in accordance with our results from halocarbon measurements we also observed
30 higher primary productivity by increased CO_2 uptake during submerged conditions
31 (Bahlmann et al., 2014). Therefore, the higher productivity may reflect higher enzymatic
32 activity (e.g. methyltransferases) within the organisms of the seagrass community, by which

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

7 An interesting outcome of both campaigns is the observation of strongly elevated halocarbon
8 fluxes during tidal change from air exposure to submergence and reversely (Table 3).
9 Continuous high-time resolution CO₂ and methane flux measurements performed in spring
10 2012 (Bahlmann et al., 2014) principally support this observation. At the particular moment
11 when the water reached the sampling site, we observed a distinct peak flux of methane and
12 CO₂. This may be evidence for processes in the sediments attributable to changes in
13 hydrodynamic pressures resulting in the release of trace gases trapped in sedimentary pore
14 spaces (Bahlmann et al., 2014). The remarkable deposition flux of CH₃Cl and CH₃Br during
15 the maximum water level (Table 3) was accompanied by highest emissions of other trace
16 gases such as methanethiol and hydrogen sulfide as discussed by Bahlmann et al. (2014).
17 These compounds are effective nucleophiles which could have contributed to the degradation
18 of halocarbons as described in Barbash and Reinhard (1989). This suggests a significantly
19 different biogeochemistry during this period compared with tide and ebb flow.

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

22 iii) Seasonal dependence. There are considerable differences between the results from spring
23 and summer campaign. We observed elevated mixing ratios for all halocarbons in ambient air
24 as well as higher water concentrations for CH₃Cl, CH₃I, and CHBr₃ compounds in summer
25 (Table 1). This observed signal of general increased halocarbon production in the lagoon
26 during summer might be attenuated by enhanced degradation in the water phase and
27 sediments at higher temperatures. Nevertheless, given the calculated sea-air flux there is only
28 little evidence for a pronounced seasonal relationship in halocarbon volatilisation to the
29 atmosphere from the lagoon water. While the fluxes of CH₃Cl appeared to be enhanced in
30 summer, those of CH₃Br and CH₃I seemed to be quite similar between spring and summer.
31 CHBr₃ emissions were actually higher in spring than in summer due to higher water
32 concentrations. Comparing the data obtained from air-exposed sites during the two

1 campaigns, the fluxes in summer were strongly enhanced by factors of 16 (CH_3Cl and
2 CH_3Br), 2 (CH_3I), and 5 (CHBr_3). Moreover, the halocarbon fluxes showed a distinct diurnal
3 cycle during summer but not during spring. The differences of ambient conditions between
4 the campaigns with lower air temperatures and lower solar radiation in spring may have
5 contributed to the differences in the emission patterns of halocarbons. That these
6 environmental conditions can substantially influence the magnitude of fluxes was reported
7 from other ecosystems such as salt marshes (Blei et al., 2010; Manley et al., 2006). However,
8 further studies covering the entire season are necessary to fully unravel the annual
9 halocarbon emissions from seagrass meadows.

10 **4.3 Halocarbons sources in the lagoon: an isotopic perspective**

11 The results from the atmospheric sampling of Praia de Faro air (upwind) and lagoon air
12 revealed differences regarding the mixing ratios and $\delta^{13}\text{C}$ values of CH_3Cl and CH_3Br (Tables
13 1 and 4). We observed elevated concentrations in the lagoon for both compounds, whereby
14 the higher concentrations were accompanied with shifts towards isotopically light CH_3Cl but
15 heavy CH_3Br . Sources other than the studied seagrass meadows, for example the abundant
16 salt marshes, may have contributed substantially to the elevated mixing ratios. Apart from the
17 studied seagrass meadows other sources, in particular abundant salt marshes, may have
18 substantially contributed to the elevated mixing ratios. Assuming atmospheric stable
19 conditions with negligible sinks in the atmosphere, the difference of air mixing ratios and
20 $\delta^{13}\text{C}$ values between upwind air and lagoon air should reflect the isotopic source signature
21 within the lagoon. Therefore, as a first approach, an isotope mass balance was used by
22 integrating mean data from both sampling sites (Tables 1 and 4). The resulting source
23 signatures within the lagoon are $-49\text{\textperthousand}$ for CH_3Cl and $-16\text{\textperthousand}$ for CH_3Br .

24 Isotopic source signatures of CH_3Cl from seagrass meadows during chamber incubations (air
25 exposure) in the Ria Formosa were $-51\pm6\text{\textperthousand}$ (summer) and $-56\pm2\text{\textperthousand}$ (spring). During the
26 summer campaign, CH_3Cl emissions from the salt marsh plant *Spartina maritima* were
27 determined with $\delta^{13}\text{C}$ values of -66 and $-72\text{\textperthousand}$. These values are in good agreement with those
28 of Bill et al. (2002) from a Californian salt marsh (-69 to $-71\text{\textperthousand}$, daytime values).
29 Unfortunately, we do not have isotopic data for the inundated periods from seagrass
30 meadows, but the $\delta^{13}\text{C}$ values of CH_3Cl in the water phase ($-42\pm2\text{\textperthousand}$) come close to those
31 measured in the atmosphere. An abiotic production mechanism has been reported for CH_3Cl
32 from senescent plant material (Hamilton et al., 2003). While we cannot generally exclude

1 additional CH₃Cl generation via this pathway, the isotopic data obtained in the Ria Formosa
2 do not mirror strongly ¹³C depleted values ($\delta^{13}\text{C}$ of -135±12‰, Keppler et al., 2004) as
3 expected for compounds from this production mechanism. Overall, this rather indicates a
4 stronger imprint of the seagrass meadows and/or water column on the atmospheric CH₃Cl
5 than from salt marshes or abiotic processes.

6 With $\delta^{13}\text{C}$ values of -42±17‰ the source signature of CH₃Br from seagrass meadows tend to
7 be more depleted in ¹³C compared with the calculated source signature from the atmospheric
8 samples. It should be noted that the $\delta^{13}\text{C}$ values for this compound were more depleted in ¹³C
9 during periods of increased emission (-55‰) than during low emissions (-28‰). This shift
10 can most likely be explained by degradation processes in the sediments which occurred
11 simultaneously. This corroborates our observations from Northern Germany with subsequent
12 recalculation of a sedimentary sink function from accompanying sediment measurements
13 (Weinberg et al., 2013). Reported source signatures of CH₃Br from salt marshes range from -
14 59 to -65‰ (day time values, Bill et al., 2002). Our own measurements in the Ria Formosa
15 indicate similar $\delta^{13}\text{C}$ values (-65‰) or even more depleted ones (unpublished data). In any
16 case, neither source signatures from seagrass meadows nor salt marshes seem to match the
17 overall source signature estimated from the atmospheric samples. Therefore, it is most likely
18 that the atmospheric CH₃Br is strongly influenced by CH₃Br emissions from the surface
19 waters ($\delta^{13}\text{C}$ values in water phase (summer): -23±3‰). Even during periods of low tide the
20 water remains in the deep channels which may be sufficient to have an impact on the local
21 atmosphere. Thus, despite the sources in the lagoon presumably producing isotopically light
22 CH₃Br, $\delta^{13}\text{C}$ values in the atmosphere strongly reflect decomposed CH₃Br whose residual
23 fraction is actually enriched in ¹³C. Accordingly, aqueous CH₃Br appears to become rapidly
24 degraded by biotic/abiotic processes such as hydrolysis, transhalogenation, and microbial
25 degradation with strong isotopic fractionation (King and Saltzman, 1997; Miller et al., 2004).
26 These decomposition mechanisms are temperature dependent with increasing destruction with
27 increasing seawater temperature (King and Saltzman, 1997). This is most likely the reason
28 why the $\delta^{13}\text{C}$ values in the lagoon waters in summer are more enriched in ¹³C compared with
29 those from the spring campaign.

30 To the best of our knowledge, this is the first report of $\delta^{13}\text{C}$ values of CH₃I in the water phase.
31 As shown by the water samples from the transect cruise, the sources in the lagoon may
32 produce isotopic light CH₃I. Given this, CH₃I seems to some extent to follow the $\delta^{13}\text{C}$ values

1 of CH_3Cl . These sources may be biotic by e.g. phytoplankton, seagrass meadows, or bacteria.
2 On the other hand, Moore and Zafirou (1994) reported a photochemical source for CH_3I by
3 radical recombination of iodine with seawater dissolved organic matter. Due to the lack of
4 isotopic source signatures and fractionation factors for production (and consumption), it is
5 difficult to draw conclusions from the data.

6 The $\delta^{13}\text{C}$ values of CHBr_3 were more depleted in ^{13}C from the lagoon inlet towards the parts
7 deeper inside. This suggests a different combination of sources in water masses coming from
8 the Atlantic. Moreover, this potential variation of source contribution can be further assumed
9 by the certain change between summer and spring where e.g. macroalgae are more abundant
10 in the latter period (Anibal et al., 2007). Already reported source signatures of phytoplankton,
11 macroalgae, and seagrass meadows cover the range of $-10\text{\textperthousand}$ to $-23\text{\textperthousand}$ (Auer et al., 2006;
12 Weinberg et al., 2013), thus demonstrating differences in their isotopic fingerprint. We cannot
13 exclude that degradation might also have an effect on the $\delta^{13}\text{C}$ values determined in lagoon
14 waters. As for CH_3I , there is still need for further research on the CHBr_3 cycling utilizing
15 stable carbon isotopes.

16 **4.4 Magnitude of fluxes and comparison to other coastal measurements and 17 first estimate of global source strength**

18 The areal based fluxes of CH_3Cl , CH_3Br , and CH_3I from seagrass meadows in comparison to
19 emission data of other coastal sources are presented in Fig. 3. In comparison to the emissions
20 from a temperate seagrass meadow in late summer in Northern Germany (Weinberg et al.,
21 2013), fluxes were elevated in the subtropical lagoon in summer during air exposure. This
22 was more pronounced for CH_3Br (factor 33) than for CH_3Cl (factor 2), CH_3I (factor 2), and
23 CHBr_3 (factor 5). In contrast, fluxes from air-exposed seagrass meadows recorded during
24 spring are comparable to those determined in Northern Germany. Thus, the difference
25 between fluxes from temperate and subtropical regions is less pronounced than reported for
26 salt marshes with emissions from subtropical regions exceeding those from temperate regions
27 by up to two orders of magnitude for CH_3Cl and CH_3Br (Blei et al. 2010; Cox et al., 2004;
28 Dimmer et al., 2001; Drewer et al., 2006; Manley et al., 2006; Rhew and Mazéas, 2010; Rhew
29 et al., 2000, 2014; Valtanen et al., 2009). Beside this regional (climatic) difference several
30 authors attributed this to a highly species dependent emission potential.

1 Average emissions of CH_3Cl from the air-exposed seagrass meadows in summer are in the
2 same range than those determined in temperate salt marshes (Blei et al. 2010; Cox et al.,
3 2004; Dimmer et al., 2001; Drewer et al., 2006; Valtanen et al., 2009). In contrast, subtropical
4 counterparts of these macrophytes are distinctively stronger emitters of this compound by at
5 least one order of magnitude (Manley et al., 2006; Rhew and Mazéas, 2010; Rhew et al.,
6 2000, 2014). Greenhouse grown mangroves produce significantly more CH_3Cl than seagrass
7 meadows revealing a higher emission potential for these plants species on a per area basis
8 (Manley et al., 2007).

9 Fluxes of CH_3Br from subtropical seagrass meadows during air exposure exceed those of
10 temperate macroalgae from Mace Head, Ireland (Carpenter et al., 2000) and temperate salt
11 marshes (Blei et al. 2010; Cox et al., 2004; Dimmer et al., 2001; Drewer et al., 2006; Valtanen
12 et al., 2009). However, the CH_3Br fluxes from seagrass meadows are distinctively lower than
13 those of subtropical salt marsh plants (Manley et al., 2006; Rhew and Mazéas, 2010; Rhew et
14 al., 2000). Mangroves seem to have a similar emission potential as seagrass meadows
15 (Manley et al., 2007).

16 For CH_3I , seagrass meadows are a minor source in comparison to the high release of
17 macroalgae in subtropical areas (Leedham et al. 2013). Except for salt marshes from
18 Tasmania (Cox et al., 2004), plant-related communities such as mangroves (Manley et al.,
19 2007) and salt marshes (Dimmer et al., 2001) are more pronounced emission sources of this
20 compound. The same holds true for CHBr_3 , where macroalgae communities from temperate
21 and subtropical/tropical regions dominate the emissions of polyhalomethanes on a per area
22 basis (e.g. Carpenter et al., 2000; Gschwend et al., 1985; Leedham et al., 2013).

23 Many uncertainties arise from a limited number of emission data to estimate the global
24 relevance of seagrass meadows. Those may be high variation in space and time, high
25 heterogeneity of seagrass meadows, species dependent emission potential, and errors
26 regarding the global seagrass abundance. Therefore, the scale-up of our data gives only a first
27 rough approximation; it was undertaken as follows. Since we did not measure a full annual
28 cycle, we assumed that seagrass measurements during the summer campaign represent
29 emissions from the reproductive season (May - September). The remaining period of the year
30 (October - April) was calculated with emission data from the spring campaign. The emission
31 data were weighted to tidal states using 8 hours and 16 hours per day as durations when
32 seagrass meadows are air-exposed or submerged, respectively. Due to the lack of flood tide

1 emission data in summer, we used those derived from the sea-air exchange. The resulting
2 average annual emissions from seagrass meadows of $150 \mu\text{mol m}^{-2} \text{yr}^{-1}$ (CH_3Cl), $18 \mu\text{mol m}^{-2}$
3 yr^{-1} (CH_3Br), $14 \mu\text{mol m}^{-2} \text{yr}^{-1}$ (CH_3I), and $25 \mu\text{mol m}^{-2} \text{yr}^{-1}$ (CHBr_3) were scaled-up with the
4 current estimates of a global seagrass area ranging from $0.3 \times 10^{12} \text{ m}^2$ (Duarte et al., 2005) to
5 $0.6 \times 10^{12} \text{ m}^2$ (Charpy-Roubaud and Sournia, 1990).

6 The tentative estimate yields annual emissions of $2.3\text{--}4.5 \text{ Gg yr}^{-1}$ for CH_3Cl , $0.5\text{--}1.0 \text{ Gg yr}^{-1}$
7 for CH_3Br , $0.6\text{--}1.2 \text{ Gg yr}^{-1}$ for CH_3I , and $1.9\text{--}3.7 \text{ Gg yr}^{-1}$ for CHBr_3 . Based on the recent global
8 budget calculations (Xiao et al., 2010; Montzka and Reimann, 2011), these ranges are
9 equivalent to $0.06\text{--}0.11\%$ and $0.45\text{--}0.89\%$, for CH_3Cl and CH_3Br , respectively. Seagrass
10 meadows would therefore cover a portion of $1.4\text{--}2.8\%$ of the missing sources for CH_3Br
11 reported in the most recent WMO report (36.1 Gg yr^{-1} ; Montzka and Reimann, 2011). Given
12 the emissions from oceanic sources (e.g. Butler et al., 2007; Quack and Wallace, 2003 and
13 references therein), CH_3I and CHBr_3 emissions from seagrass meadows are rather
14 insignificant on a global scale.

15

16 5 Conclusions

17 ~~We presented the first detailed study of halocarbon fluxes from seagrass meadows. The data~~
18 ~~were obtained from a subtropical mesotidal lagoon in southern Portugal. Our data are the first~~
19 ~~to report detailed halocarbon fluxes from seagrass meadows.~~ The fluxes of halocarbons were
20 highly variable with increased fluxes when the seagrass meadows were ~~submerged~~
21 ~~and distinct emission peaks when lagoon waters were just arriving or leaving the sampling~~
22 ~~site.~~ Distinct emission peaks occurred in the certain moments when lagoon waters were just
23 arriving or leaving the sampling site. For CH_3Cl and CH_3Br we observed a diurnal
24 dependence on the fluxes with increased emissions during midday/afternoon and deposition
25 fluxes during periods of low radiation. Generally, diurnal variations (during air exposure),
26 atmospheric mixing ratios, and emission rates of halocarbons were ~~minor~~
27 than in summer, suggesting a seasonal dependence. ~~Monohalomethane emissions from~~
28 ~~seagrass meadows fall in between those from temperate salt marshes and mangroves. For~~
29 ~~CHBr_3 , seagrass-based emissions are distinctively below those of macroalgae. On~~
30 ~~Our results indicate that on~~ a global scale, seagrass meadows are ~~rather~~ a minor source ~~for~~
31 ~~of~~ halocarbons, but ~~that they~~ will have an imprint on the local and regional budgets, ~~particularly on~~
32 ~~subtropical coastlines.~~ This holds in particular true for subtropical coastlines where seagrass

1 meadows belong to the most abundant ecosystems. ~~In these regions, where strong vertical~~
2 ~~motions occur, seagrass meadows may be significant contributors to deliver halocarbons to~~
3 ~~the stratosphere.~~

4 ~~Our stable Stable-carbon isotope resultss of halocarbons were used to identify possible~~
5 ~~sources in the lagoon. Results suggest that CH₃Cl more originates predominantly~~ from the
6 water column and/or seagrass meadows, ~~rather~~ than from adjacent salt marshes or abiotic
7 formation processes. Atmospheric and aqueous CH₃Br in the lagoon was substantially
8 enriched in ¹³C pointing towards degradation processes and re-emission into the atmosphere.
9 ~~Furthermore, we presented isotopic data of CH₃I and CHBr₃ from the water phase.~~

10 Future studies should focus on halocarbon emissions from seagrass-based systems from
11 different regions in order to refine the global relevance. Likewise, s~~Since the~~ magnitudes of
12 fluxes are often species-dependent, budgets calculations ~~will certainly would~~ benefit from a
13 more detailed view investigation of fluxes from on different seagrass species. More work is
14 also required to identify other elements of these ecosystems, such as the sediments, which are
15 capable of acting as both a sink and a source of halocarbons. Furthermore, while this study
16 focused on halocarbon dynamics from seagrass meadows on the level of the benthic
17 community, it is worthwhile to identify the specific sources in these ecosystems. The
18 sediments being capable of acting as both a sink and a source, should be further studied.
19 Though our results suggest sediments being a weak producer on a per area basis which
20 corroborates other studies from e.g. salt marshes (Manley et al., 2006), they may have a
21 significant impact in view of their high area coverage in coastal zones exceeding by far all
22 other macrophytic systems (see Duarte et al., 2005).

23

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3

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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)
<i>summer 2011</i>			
CH ₃ Cl	828 (503-1490)	613 (498-685)	220 (158-301)
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 -194)
<i>spring 2012</i>			
CH ₃ Cl	654 (484-976)	-	166 (101-267)
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 - 133)

8

9

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

Sample	Time (CET)	CH ₃ Cl		CH ₃ Br		CH ₃ I		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	-

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	CH₃Cl nmol m ⁻² h ⁻¹	CH₃Br nmol m ⁻² h ⁻¹	CH₃I nmol m ⁻² h ⁻¹	CHBr₃ nmol m ⁻² h ⁻¹
<i>Summer 2011</i>					
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)	0.3 (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)
<i>Spring 2012</i>					
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)

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>								
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	-	-
<i>spring 2012</i>								
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	-	-

4

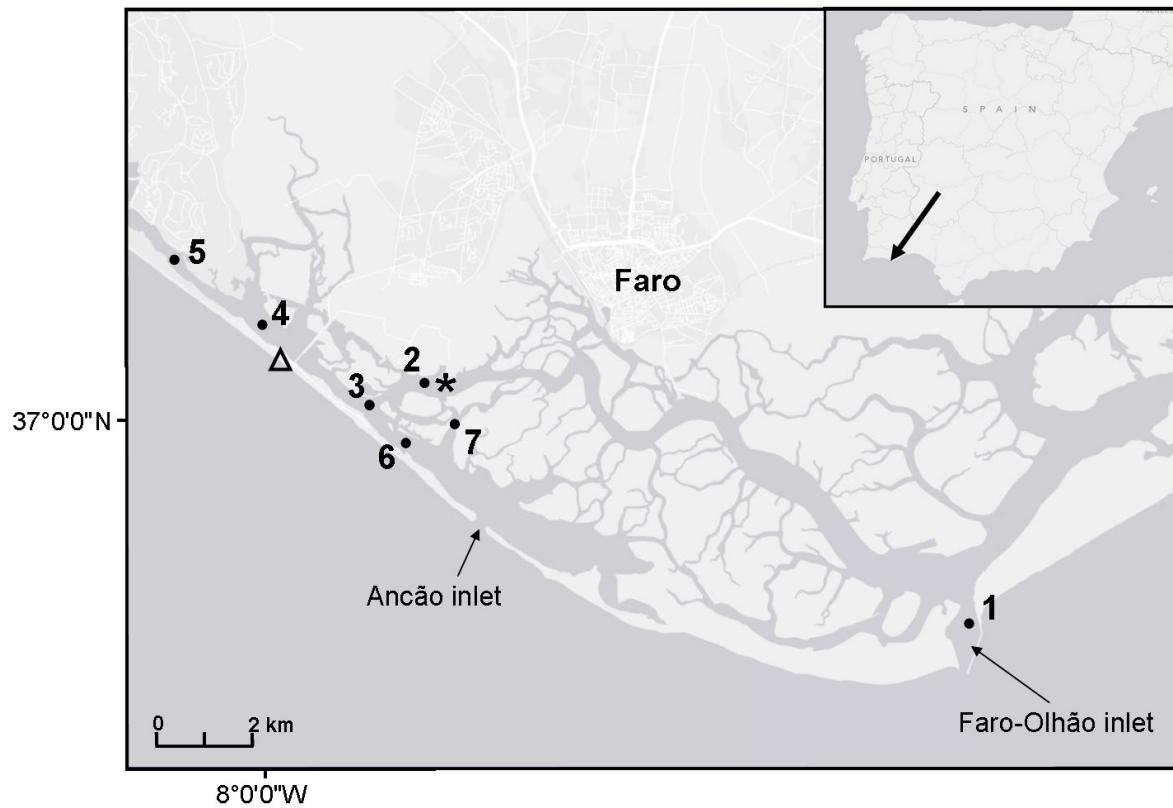
5

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.

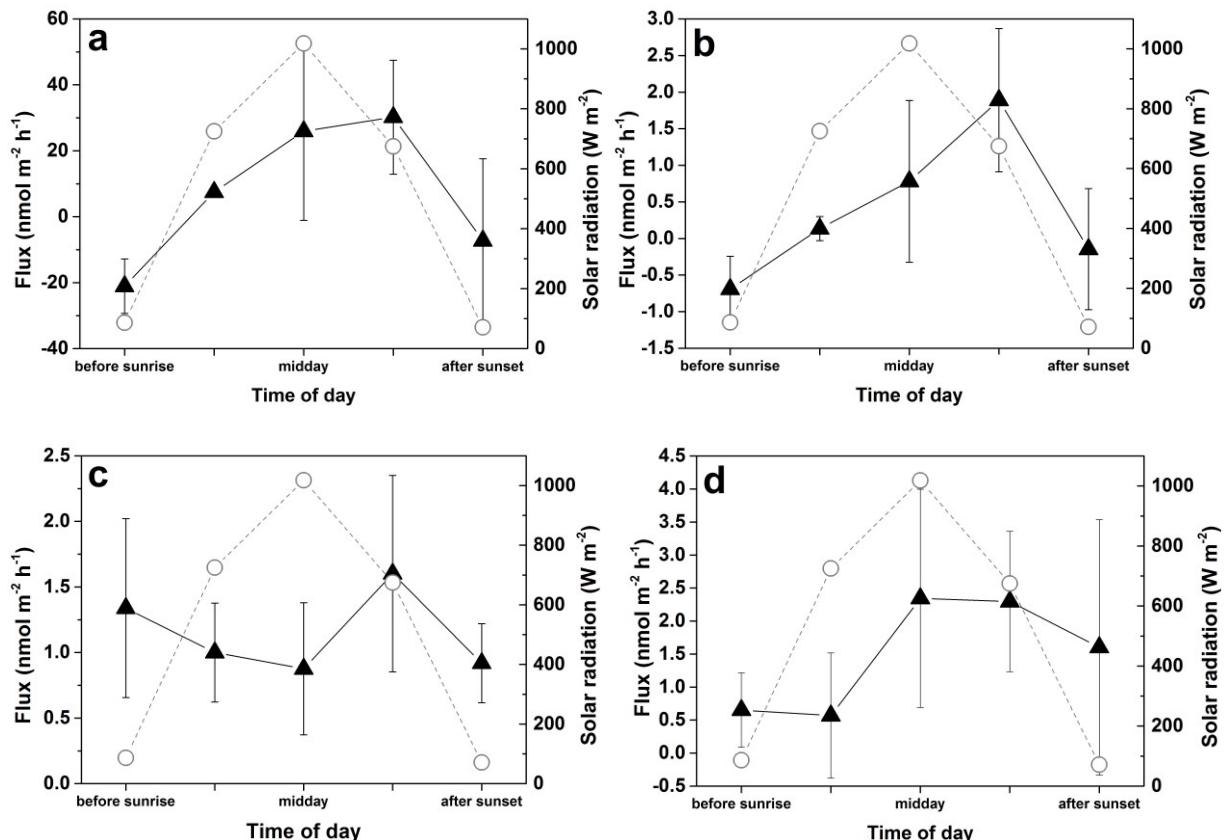
location	CH ₃ Cl	CH ₃ Br	CH ₃ I	CHBr ₃
Faro, Portugal (summer) ¹	220 (158 - 301)	8 (5-11)	12 (4 - 18)	102 (67 -194)
Faro, Portugal (spring) ¹	166 (101 - 267)	10 (6 - 28)	7 (2 - 16)	62 (39 - 133)
East Atlantic ^{2, #}	-	-	-	68.3 (36.6 - 102.0)
Roscoff, France ^{3, #}	-	-	12.9 (9.0 - 31.8)	217.4 (124.8 - 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 (221.8 - 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

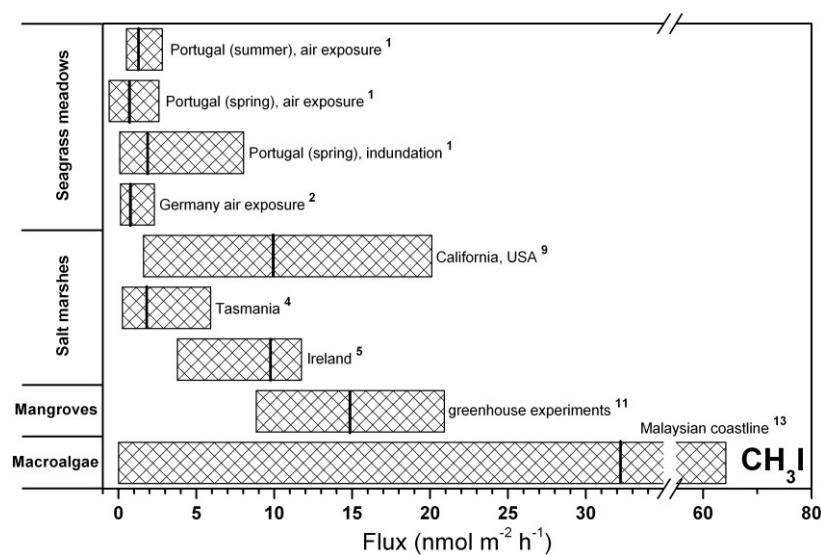
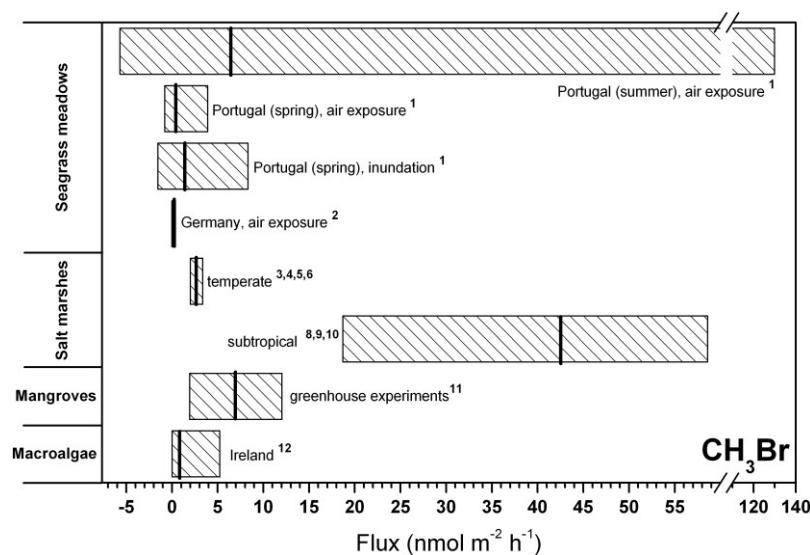
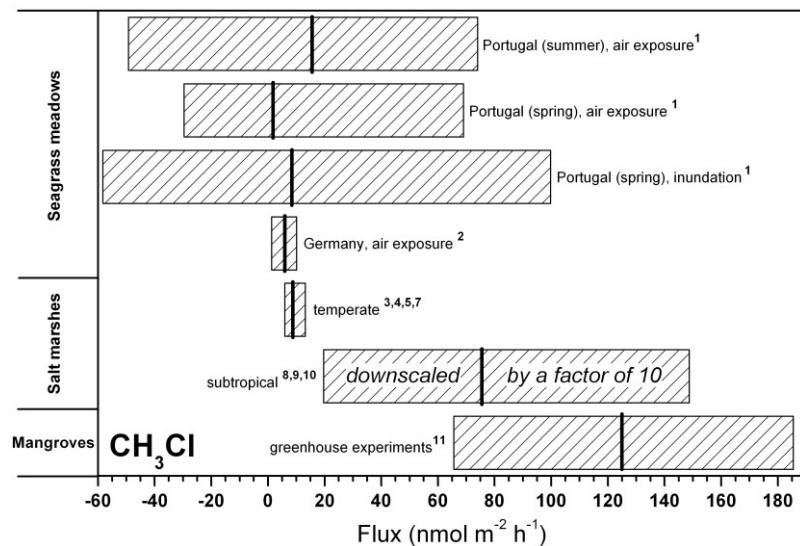


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3 Fig. 1: Map of the lagoon Ria Formosa, Portugal. Asterisk: site of seagrass meadow studies;
4 triangle: sampling site on the Praia de Faro (upwind position). Dots with numbers represent
5 sampling points during the transect cruise.
6



2 Fig. 2a-d: Diurnal variation of mean halocarbon fluxes (triangles) from seagrass meadows
3 during periods of air exposure in summer 2011 (a: CH₃Cl, b: CH₃Br, c: CH₃I, d: CHBr₃).
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.

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1 Fig. 3: Compilation of mean emissions (bold black vertical lines) and ranges from different
2 sources in coastal environments for CH₃Cl (upper panel), CH₃Br (middle panel) and CH₃I
3 (lower panel). Note the different scales. Published data adopted from: ¹ this study; ² Weinberg
4 et al. (2013); ³ Blei et al. (2010); ⁴ Cox et al., (2004); ⁵ Dimmer et al. (2001); ⁶ Drewer et al.
5 (2006); ⁷ Valtanen et al. (2009); ⁸ Rhew and Mazéas (2010); ⁹ Manley et al. (2006); ¹⁰ Rhew
6 et al. (2000); ¹¹ Manley et al. (2007); ¹² Carpenter et al. (2000); ¹³ Leedham et al. (2013). Note
7 that the data of CH₃Cl 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 CH₃Br (Carpenter et al., 2000) and the
14 Malaysian coastline for CH₃I (Leedham et al., 2013), respectively.