

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

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11

12 **Abstract**

13 Here we report fluxes of chloromethane (CH₃Cl), bromomethane (CH₃Br), iodomethane
14 (CH₃I), and bromoform (CHBr₃) 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⁻² h⁻¹ for CH₃Br 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 CH₃Cl and CH₃Br 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 CH₃Cl rather originating from
27 seagrass meadows and water column than from salt marshes. Aqueous and atmospheric
28 CH₃Br was substantially enriched in ¹³C 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 CH₃Br in the lagoon.

3 A rough global upscaling yields annual productions from seagrass meadows of 2.3-4.5 Gg yr⁻¹
4 ¹, 0.5-1.0 Gg yr⁻¹, 0.6-1.2 Gg yr⁻¹, and 1.9-3.7 Gg yr⁻¹ for CH₃Cl, CH₃Br, CH₃I, and CHBr₃
5 respectively. This suggests a minor contribution from seagrass meadows to the global
6 production of CH₃Cl and CH₃Br with about 0.1 % and 0.7 %, respectively. In comparison to
7 the known marine sources for CH₃I and CHBr₃, seagrass meadows are rather small sources.

8

9 **1 Introduction**

10 The halocarbons chloromethane (CH₃Cl), bromomethane (CH₃Br), iodomethane (CH₃I), and
11 bromoform (CHBr₃) 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 CH₃Cl, 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 CH₃Br 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 CH₃I and CHBr₃ are assigned with even larger uncertainties (Bell et al., 2002 and reference
21 therein; Quack and Wallace, 2003 and references therein).

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 and references therein).
24 While this was primarily done for CH₃Cl, first isotopic source signatures of naturally-
25 produced CH₃Br were recently reported (Bill et al., 2002; Weinberg et al., 2013). Moreover,
26 the biogeochemical cycling of halocarbons underlies various transformation processes which
27 can be studied by the stable carbon isotope approach in addition to flux and/or concentration
28 measurements.

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

1 1998), macroalgae (Gschwend et al., 1985), salt marshes (Rhew et al., 2000), and mangroves
2 (Manley et al., 2007).

3 With a net primary production of $\sim 1200 \text{ g C m}^{-2} \text{ yr}^{-1}$ seagrass meadows are one of the most
4 productive ecosystems with a similar global abundance as mangroves and salt marshes
5 (Duarte et al., 2005). They cover huge areas of the intertidal and subtidal zone in temperate
6 and subtropical/tropical regions. Thus, they may represent an additional source for
7 halocarbons to the atmosphere which is not yet sufficiently studied. Seagrass meadows are
8 highly diverse ecosystems with respect to potential halocarbon producers. Along with the
9 seagrass itself, they comprise epiphytes such as microalgae and diatoms, and sediment
10 reassembling microphytobenthos and bacteria communities. All these constituents of the
11 benthic community have been generally reported to produce halocarbons (Amachi et al.,
12 2001; Blei et al., 2010; Manley et al., 2006; Moore et al., 1996; Rhew et al., 2002; Tokarczyk
13 and Moore, 1994; Urhahn, 2003). While first evidence for the release of halocarbons from
14 seagrass was obtained by incubation experiments (Urhahn 2003), we could recently confirm
15 this production potential in a field study of a temperate seagrass meadow in Northern
16 Germany (Weinberg et al., 2013).

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

27

28 **2 Materials and methods**

29 **2.1 Sampling site**

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

1 series of barrier islands and two peninsulas. About 80% of the lagoon is intertidal with a
2 semi-diurnal tidal regime and tidal ranges between 1.3 m during neap tides and 3.5 m during
3 spring tides (Cabaço et al., 2012). Due to negligible inflow of fresh water and high exchange
4 of water with the open Atlantic during each tidal cycle, the salinity within the lagoon is 35 to
5 36 PSU year round, except for periods of heavy rainfalls. About one-fourth of the intertidal
6 area (13.04 km²) is covered by dense stands of *Zostera noltii* Hornem (Guimarães et al., 2012;
7 Rui Santos, pers. comm.) Further, but much less abundant, seagrass species in the lagoon are
8 *Zostera Marina* L. and *Cymodocea nodosa* (Ucria) Ascherson which are mainly located in
9 shallow parts of the subtidal areas (Santos et al., 2004). About 30% of the lagoon's area is
10 covered with salt marsh communities (Rui Santos, pers. comm.).

11 **2.2 Sampling**

12 We conducted two sampling campaigns in the western part of the lagoon at the Ramalhete
13 research station (Centre of Marine Sciences (CCMAR), Universidade do Algarve) in the
14 vicinity of Faro (37.0°N, 7.6 W) (Fig. 1). The sampling was carried out from July 23rd –
15 August 7th 2011 and April 17th – April 28th 2012 coinciding with the beginning (2012
16 campaign) and peak (2011 campaign) of the seagrass reproductive season. Ambient air
17 temperatures were distinctively different between both campaigns ranging from 21 to 27°C
18 (mean 24°C) with almost entirely clear weather in summer and 13 to 23°C (mean 17°C) in
19 spring with frequent strong cloud cover. Mean water temperatures were 25.9°C (summer) and
20 17.5°C (spring). The prevailing wind direction during both campaigns was West to South-
21 West to with rather low average wind speeds of 4 m s⁻¹ during summer and 5 m s⁻¹ during
22 spring.

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

1 chamber (flow rate $1 \pm 0.2 \text{ L min}^{-1}$). Prior to sampling, the flux chamber was flushed for about
2 10 min ensuring sufficient equilibration of compounds in the chamber air.

3 During the 2012 campaign, we used a dynamic flux chamber system (0.037 m^2 bottom
4 surface area, 8 L enclosure volume) suitable for flux measurements during both periods of air
5 exposure and tidal immersion. The properties and setup of this dynamic chamber system is in
6 detail described elsewhere (Bahlmann et al., 2014). Since this system acts as an ordinary
7 purge and trap system, the extraction efficiencies were simulated using halocarbon
8 equilibrated artificial seawater. While the results from these tests revealed that
9 monohalomethanes were almost completely extracted ($\geq 90\%$), the purge efficiencies for
10 CHBr_3 were only 33%. Thus the reported CHBr_3 fluxes determined from seagrass meadows
11 using the submergible chamber system represent rather an under-estimate.

12 Based on the sampling system for the determination of stable carbon isotopes of halocarbons
13 Bahlmann et al. (2011), we modified the cryogenic trapping system for the measurements of
14 halocarbon mixing ratios, in order to establish a better temporal resolution by reducing the
15 analysis time. This results in a final air volume $28 \pm 5 \text{ L}$ of air at the inlet and the outlet of the
16 chambers, respectively. The specifications along with the results from test surveys are given
17 in the supplementary.

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

27 Discrete water samples for the determination of dissolved halocarbons concentration and
28 isotopic composition at high tide were taken during both campaigns. The samples were taken
29 directly above the studied seagrass meadow using Duran glass bottles (1-2 L volume). Air and
30 sediment intrusions during water sampling were avoided. The water depth was between 0.3 m
31 and 1 m. On April 24th 2012, a transect cruise through the middle and western part of the
32 lagoon was conducted during rising waters (Fig. 1). The water samples were taken from a

1 water depth of 1 m. Dissolved halocarbons were extracted from seawater using a purge and
2 trap system. Seawater was purged with helium 5.0 (purge flow 1L min⁻¹) for 30 minutes.
3 After water vapour reduction of the purge gas, the compounds were enriched on cryotrap
4 (submerged in a dry shipper). The shape of the cryotrap used here was the same as those for
5 flux chamber and atmospheric samples. The water samples were usually processed within 30
6 minutes after sampling. Samples from the transect cruise were stored in the dark at 4°C and
7 analyzed within eight hours. Purge efficiencies of monohalomethanes from lagoon water were
8 ≥95% (1 L and 2 L samples). However, the less volatile CHBr₃ was only extracted with 50%
9 (1 L samples) and 30% (2 L samples). Therefore, the results of water concentration were
10 corrected for the respective purge efficiency for this compound.

11 **2.3 Measurement and quantification**

12 The measurement procedure is described in detail in the supplementary. Briefly, compounds
13 enriched on the cryotrap, were thermally desorbed and transferred to Peltier-cooled
14 adsorption tubes. The analytes were further desorbed from the adsorption tubes and refocused
15 cryogenically before injection to the GC-MS system. Air and water samples were measured
16 onsite at Ramalhete research station using a GC-MS system (6890N/5975B, Agilent,
17 Germany) equipped with a CP-PorabondQ column (25 m, 0.25 μm i.d., Varian, Germany).
18 The GC-MS was operated in the electron impact mode. Identification of compounds was
19 executed by retention times and respective mass spectra. Aliquots of gas standard (Scott EPA
20 TO 15/17, 65 compounds, 1 ppm each in nitrogen, Sigma Aldrich, Germany) containing
21 CH₃Cl, CH₃Br, and CHBr₃ were applied to quantify the target compounds. During onsite
22 measurements, CH₃I was quantified using the response factor against CH₃Br. The analytical
23 limit of detection was 0.3 ppt for the halocarbons. The accuracy of the entire sampling
24 method (sampling, sample treatment, measurement) was derived from test samples in
25 triplicates. The deviation between the individual samples for CH₃Cl, CH₃Br, CH₃I, and
26 CHBr₃ was 5.4%, 6.3%, 15.4% and 6.7%, respectively. A series of procedural blanks
27 (cryotrap and adsorption tubes) were taken during the sampling campaigns. The occasionally
28 detected blanks of CH₃Cl and CH₃Br from these determinations were ≤3% to the “real”
29 samples taken from the seagrass meadows during sampling campaigns. Therefore, the
30 halocarbon fluxes were not blank corrected.

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

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

4

5 **2.4 Calculations**

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

$$11 \quad F_{Net} = \frac{Q \times (C_{out} - C_{in})}{A \times V \times 1000} \quad (1)$$

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

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

$$21 \quad F = k_w \times (C_w - C_a \times H^{-1}) \quad (2)$$

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

1 additionally driven by wind-independent currents and the bottom turbulence and thus water
2 depth and current velocities further play a major role (Raymond and Cole, 2001). Studying
3 the sea-air exchange in the Ria Formosa, these additional factors have to be considered in
4 addition to wind driven outgassing. Therefore, we used the parameterization of k_w with the
5 assumption that wind speed and water current driven turbulence are additive (Borges et al.,
6 2004):

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

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

16

17 **3 Results**

18 **3.1 Halocarbons in the atmosphere and lagoon water**

19 The air mixing ratios in the lagoon were adopted from the inlets of the flux chambers at 1 m
20 above ground during both campaigns. The results of these measurements and those of the
21 upwind site outside the lagoon (Praia de Faro) are presented in Table 1. In summer, the mean
22 air mixing ratios were 828 ppt for CH_3Cl , 22 ppt for CH_3Br , 3 ppt for CH_3I , and 15 ppt for
23 CHBr_3 . Elevated air mixing ratios of the monohalomethanes were observed during periods of
24 easterly winds when air masses at the sampling site had presumably passed over major parts
25 of the lagoon. These mixing ratios reached up to 1490 ppt for CH_3Cl , 61 ppt for CH_3Br , and
26 11 ppt for CH_3I reflecting a potent source in this system. The mixing ratios at the upwind site
27 (Praia de Faro) were distinctively lower with mean values of 613 ppt (CH_3Cl), 13 ppt
28 (CH_3Br), 1 ppt (CH_3I), and 8 ppt (CHBr_3) further indicating a source inside the lagoon. In
29 spring 2012, the mean air mixing ratios in the lagoon were significantly lower than during
30 summer with 654 ppt for CH_3Cl , 12 ppt for CH_3Br , 1 ppt for CH_3I , and 2 ppt for CHBr_3 .

1 Discrete water samples were taken above the studied seagrass meadow during tidal inundation
2 (summer n=9; spring n=10). The results are presented in Table 1. In summer, concentrations
3 ranged from 160 to 300 pmol L⁻¹ (CH₃Cl), 5 to 11 pmol L⁻¹ (CH₃Br), 4 to 18 pmol L⁻¹ (CH₃I),
4 and 67 to 190 pmol L⁻¹ (CHBr₃). During the spring campaign, the water concentrations were
5 100 to 270 pmol L⁻¹ for CH₃Cl, 6 to 28 pmol L⁻¹ for CH₃Br, 2 to 16 pmol L⁻¹ for CH₃I, and 39
6 to 130 pmol L⁻¹ for CHBr₃.

7 The results obtained from samples of the transect cruise covered in 2012 (Fig. 1) are given in
8 Table 2. We observed an about two-fold increase of concentration for CH₃Cl (from 121 to
9 241 pmol L⁻¹) and CHBr₃ (from 26 to 55 pmol L⁻¹) between position 1 (Faro-Olhão inlet) and
10 position 2 (near to the seagrass meadows studied). The increase was less pronounced for
11 CH₃Br (5 to 7 pmol L⁻¹) and not notable for CH₃I. The seawater at positions 6 and 7, the
12 nearest to the Ancão inlet, revealed rather low concentrations for all compounds. We further
13 observed rising concentrations for all halocarbons along positions 3, 4, and 5 with increasing
14 distance to the Ancão inlet. They increased from 96 to 180 pmol L⁻¹ for CH₃Cl, from 9 to 19
15 pmol L⁻¹ for CH₃Br, 2 to 14 pmol L⁻¹ for CH₃I, and 21 to 95 pmol L⁻¹ for CHBr₃. The
16 difference in concentration along the transect was accompanied by variations in the carbon
17 isotopic composition of all compounds. The most ¹³C depleted values of CH₃Cl, CH₃Br, and
18 CH₃I were detected at the position furthest from the inlet. Interestingly, CHBr₃ showed the
19 opposite trend with more ¹³C enriched values in the lagoon (-25.8‰ vs. ~ -18‰).

20 **3.2 Fluxes from seagrass meadows, sediment, and sea-air exchange**

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

24 During the summer campaign (air exposure), we observed highly variable emission and
25 deposition fluxes ranging from -49 to 74 nmol m⁻² h⁻¹ and -5.7 to 130 nmol m⁻² h⁻¹ for CH₃Cl
26 and CH₃Br, respectively. The variability was less pronounced for CH₃I (0.5 to 2.8 nmol m⁻² h⁻¹)
27 and CHBr₃ (-0.6 to 5.7 nmol m⁻² h⁻¹) where predominantly emissions were measured.
28 Strongly elevated fluxes up to 130 nmol m⁻² h⁻¹ for CH₃Br were recorded in conjunction with
29 tidal change from air exposure to inundation and conversely. These high fluxes were
30 substantiated by a concurrent enhanced atmospheric mixing ratios ranging from 23 ppt to 120
31 ppt (campaign median 14 ppt). Omitting these compound-specific tidal phenomena, the fluxes

1 of CH₃Cl and CH₃Br were positively correlated to each other (R^2 0.55, $p < 0.05$). However,
2 CH₃I and CHBr₃ fluxes correlated neither with each other nor with any of the other
3 investigated halocarbons. Due to the inherent high variability of the fluxes, a direct
4 comparison of halocarbon fluxes with solar radiation revealed a rather low correlation ($R^2 \leq$
5 0.20).

6 The flux chamber measurements over the sediment during air exposure revealed
7 predominantly emissions of all four halocarbons ($n=5$). These fluxes were $3.6 \pm 4.3 \text{ nmol m}^{-2} \text{ h}^{-1}$
8 ¹ (CH₃Cl), $0.6 \pm 0.5 \text{ nmol m}^{-2} \text{ h}^{-1}$ (CH₃Br), $0.2 \pm 0.2 \text{ nmol m}^{-2} \text{ h}^{-1}$ (CH₃I), and $0.8 \pm 1.0 \text{ nmol m}^{-2}$
9 h^{-1} (CHBr₃). Hence, the bare sediment may contribute to the overall emissions above the
10 seagrass by about 10 to 20% for the monohalomethanes and 45% for CHBr₃.

11 During the 2012 spring campaign the halocarbon fluxes from seagrass meadows were
12 determined during both periods of air exposure and periods of tidal immersion. Furthermore,
13 the measurements were complemented by other trace gases including hydrocarbons and
14 sulphur containing compounds. High-time resolution CO₂ and methane flux measurements
15 were further conducted to gain insights in the biogeochemistry and tidal controls in this
16 system. These measurements along with other trace gases are reported in more detail in
17 Bahlmann et al. (2014). As in the summer campaign, the seagrass meadows were a net source
18 for all halocarbons studied, but on a lower level. The individual ranges of air exposure
19 measurements were -30 to 69 nmol m⁻² h⁻¹ (CH₃Cl), -0.8 to 3.9 nmol m⁻² h⁻¹ (CH₃Br), -0.6 to
20 2.6 nmol m⁻² h⁻¹ (CH₃I), and -0.5 to 1.3 nmol m⁻² h⁻¹ (CHBr₃). On average, the seagrass
21 meadows were a net source also under submerged conditions ranging from -58 to 100 nmol
22 m⁻² h⁻¹ for CH₃Cl, -1.6 to 8.3 nmol m⁻² h⁻¹ for CH₃Br, 0.1 to 8.0 nmol m⁻² h⁻¹ for CH₃I, and -
23 0.4 to 10.6 nmol m⁻² h⁻¹ for CHBr₃. Due to the low purge efficiency of CHBr₃ during high tide
24 measurements, the fluxes determined with the submergible chamber are underestimated for
25 this compound. Despite this high variability in production/decomposition during air exposure
26 and inundation, the monohalomethanes were significantly correlated to each other ($R^2 \geq 0.50$).
27 These correlations were enhanced compared to those found when the seagrass meadows were
28 air-exposed ($R^2 \geq 0.50$). In this case, only CH₃I and CH₃Br were significantly correlated (R^2
29 0.51). CHBr₃ was only slightly correlated to the monohalomethanes.

30 While deposition fluxes of CH₃Cl and CH₃Br of air-exposed seagrass meadows occurred
31 predominantly during periods of low irradiance in summer, no obvious relation to the time of
32 day and/or solar radiation was observed during spring when deposition fluxes were frequently

1 detected. For CH₃I and CHBr₃, uptake was only occasionally observed and situations of
2 emission clearly dominated.

3 As in the summer campaign, we observed some remarkable tidal effects on halocarbon fluxes
4 during the spring campaign. Firstly, the highest fluxes of all halocarbons were measured when
5 the lagoon water was just reaching the sampling site. Occasionally this was also observed
6 from air exposure to tidal inundation, although less pronounced. However, these short-timed
7 effects were not as strong as during the summer campaign. Secondly, we observed deposition
8 fluxes for CH₃Cl and CH₃Br at tidal maximum. Though uptake was not always observed for
9 CH₃I and CHBr₃, their emissions turned out to decline in any case. Before and after this
10 period emission fluxes during incoming tide and ebb flow dominated.

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

16 **3.3 Stable carbon isotopes of halocarbons**

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

21 In 2011, the difference in atmospheric mixing ratios of CH₃Cl and CH₃Br between within the
22 lagoon and the upwind position (Praia de Faro) was accompanied by a shift of δ¹³C values.
23 More ¹³C depleted values were found for CH₃Cl in the lagoon (-42±2‰) compared to the
24 upwind position (-39±0.4‰). In contrast, the δ¹³C values of CH₃Br were significantly
25 enriched in ¹³C by about 10‰ inside the lagoon (-29±5‰) as compared to the upwind site (-
26 38±3). These δ¹³C values found in air samples in the lagoon roughly correspond to the δ¹³C
27 values of CH₃Cl (-43±3‰) and CH₃Br (-23±3‰) found in samples of lagoon waters.

28 Atmospheric CH₃Cl and CH₃Br were on average more enriched in ¹³C in spring than in
29 summer by 4 and 6‰, respectively. While the δ¹³C values of CH₃Cl in the lagoon water were
30 quite similar between both periods of the year, those of CH₃Br were on average more depleted
31 in ¹³C during spring suggesting certain changes in production/decomposition processes. The

1 isotopic composition of CH₃I in lagoon water was quite similar between summer (-39± 9‰)
2 and spring (mean -37±7‰). As for CH₃Br, the δ¹³C values of CHBr₃ were more enriched in
3 ¹³C in summer when compared with those of the spring campaign.

4 Using the fluxes and δ¹³C values from the inlet and outlet of the flux chamber we were able to
5 calculate the source signatures of seagrass covered areas. The resulting source signatures of
6 CH₃Cl from seagrass meadows were, with -51±6‰ and -56±2‰, similar between both
7 campaigns and independent from the strength of emission. For CH₃Br, we observed most
8 depleted δ¹³C values of -53‰ and -58‰ at increased emission fluxes in summer, but values
9 of -26‰ and -29‰ during periods of low emission. This corroborates the findings of
10 isotopically heavy CH₃Br produced within the seagrass meadows (-29‰) in spring 2012
11 when all samples analysed for the isotopic composition were taken at situations of low
12 emission.

13

14 **4 Discussion**

15 **4.1 Dissolved halocarbons**

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

1 phytoplankton contributes significantly to the water concentration of halocarbons, but the
2 predominantly low chlorophyll a concentrations ($3.1 \mu\text{g L}^{-1}$ from long-term measurements,
3 Brito et al., 2012) and low water volumes seem to limit the impact from this source.

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

11 Overall, the lagoon seems to comprise highly potent halocarbon sources into the water
12 column for CH_3Cl and CH_3Br rather than for CH_3I and CHBr_3 .

13 **4.2 Flux pattern from seagrass meadows**

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

24 i) Diurnal variations. The correlation analysis with solar radiation resulted in only a weak
25 association with the magnitude of fluxes. However, after grouping by daytime, our data
26 provide some indication for a diurnal pattern (Fig. 2). For CH_3Cl , there was the most obvious
27 relationship between time of day and actual emissions. Highest emissions were observed
28 during day periods with increased sunlight (midday and afternoon). In contrast, deposition
29 fluxes were exclusively recorded during periods of low radiation and nighttimes. The same
30 was also observed for CH_3Br . However, highest mean emissions of this compound seemed to
31 be shifted towards the afternoon. CH_3I was constantly emitted from the seagrass covered spot

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

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

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

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

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

1 believed that the production of trace gases during low tide exceeds that during inundation. For
2 halocarbons this was suggested for example by Carpenter et al. (1999) and Jones et al. (2009)
3 from atmospheric measurements over intertidal macroalgae beds in Mace Head, Ireland.
4 Nevertheless, in accordance with our results from halocarbon measurements we also observed
5 higher primary productivity by increased CO₂ uptake during submerged conditions
6 (Bahlmann et al., 2014). Therefore, the higher productivity may reflect higher enzymatic
7 activity (e.g. methyltransferases) within the organisms of the seagrass community, by which
8 monohalomethanes are presumably formed. Furthermore, the correlation analysis revealed a
9 different behaviour of halocarbons between the two tidal states with stronger correlations
10 between monohalomethanes during tidal inundation than air exposure. Obviously the change
11 in environmental conditions was accompanied with a shift in the halocarbon production-
12 decomposition pattern of the benthic community and/or different source organisms were
13 stimulated.

14 An interesting outcome of both campaigns is the observation of strongly elevated halocarbon
15 fluxes during tidal change from air exposure to submergence and reversely (Table 3).
16 Continuous high-time resolution CO₂ and methane flux measurements performed in spring
17 2012 (Bahlmann et al., 2014) principally support this observation. At the particular moment
18 when the water reached the sampling site, we observed a distinct peak flux of methane and
19 CO₂. This may be evidence for processes in the sediments attributable to changes in
20 hydrodynamic pressures resulting in the release of trace gases trapped in sedimentary pore
21 spaces (Bahlmann et al., 2014). On the other hand, these most likely sedimentary driven
22 emission processes can hardly explain our observation of enhanced emissions also when the
23 water was leaving the sampling site. Perhaps these emission increases relate to physiological
24 stress reaction of the benthic community to the short-timed changing environmental
25 conditions at the transition from inundation to air-exposure.

26 The remarkable deposition flux of CH₃Cl and CH₃Br during the maximum water level (Table
27 3) was accompanied by highest emissions of other trace gases such as methanethiol and
28 hydrogen sulfide as discussed by Bahlmann et al. (2014). These compounds are effective
29 nucleophiles which could have contributed to the degradation of halocarbons as described in
30 Barbash and Reinhard (1989). This suggests a significantly different biogeochemistry during
31 this period compared with incoming tide and ebb flow. Although we actually have no proof
32 for an existence of light dependence under these submerged conditions, it is however possible

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

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

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

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

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

1 4.3 Halocarbons sources in the lagoon: an isotopic perspective

2 The results from the atmospheric sampling of Praia de Faro air (upwind) and lagoon air
3 revealed certain difference regarding the mixing ratios and isotopic composition of CH₃Cl and
4 CH₃Br (Tables 1 and 4). We observed elevated concentrations in the lagoon for both
5 compounds, whereby the higher concentrations were accompanied with shifts towards
6 isotopically light CH₃Cl but heavy CH₃Br. Beside the studied seagrass meadows other
7 sources, in particular wide-abundant salt marshes, may have substantially contributed to the
8 elevated mixing ratios. Assuming atmospheric stable conditions with negligible sinks in the
9 atmosphere, the difference of air mixing ratios and $\delta^{13}\text{C}$ values between upwind air and
10 lagoon air should reflect the isotopic source signature within the lagoon. Therefore, as a first
11 approach, an isotope mass balance was used by integrating mean data from both sampling
12 sites (Tables 1 and 4). The resulting source signatures within the lagoon are -49‰ for CH₃Cl
13 and -16‰ for CH₃Br.

14 Isotopic source signatures of CH₃Cl from seagrass meadows during incubations (air exposure)
15 in the Ria Formosa were $-51 \pm 6\text{‰}$ (summer) and $-56 \pm 2\text{‰}$ (spring). During the summer
16 campaign, CH₃Cl emissions from the salt marsh plant *Spartina maritima* were determined
17 with $\delta^{13}\text{C}$ values of -66 and -72‰. These values are in good agreement with those of Bill et
18 al. (2002) from a Californian salt marsh (-69 to -71‰, daytime values). Unfortunately, we do
19 not have isotopic data for the inundated periods from seagrass meadows, but the $\delta^{13}\text{C}$ values
20 of CH₃Cl in the water phase ($-42 \pm 2\text{‰}$) come close to those measured in the atmosphere. An
21 abiotic production mechanism has been reported for CH₃Cl from senescent plant material
22 (Hamilton et al., 2003). While we cannot generally exclude additional CH₃Cl generation via
23 this pathway, the isotopic data obtained in the Ria Formosa do not mirror strongly ¹³C
24 depleted values ($\delta^{13}\text{C}$ of $-135 \pm 12\text{‰}$, Keppler et al., 2004) as expected for compounds built by
25 this production mechanism. Overall, this rather indicates a stronger imprint of the seagrass
26 meadows and/or water column on the atmospheric CH₃Cl than from salt marshes or abiotic
27 processes.

28 With $\delta^{13}\text{C}$ values of $-42 \pm 17\text{‰}$ the source signature of CH₃Br from seagrass meadows tend to
29 be more depleted in ¹³C compared with the calculated source signature from the atmospheric
30 samples. It should be noted that the $\delta^{13}\text{C}$ values for this compound were more depleted in ¹³C
31 during periods of increased emission (-55‰) than during low emissions (-28‰). This shift
32 can most likely be explained by simultaneous microbial degradation processes at the sediment

1 surfaces. This corroborates our observations from Northern Germany with subsequent
2 recalculation of a sedimentary sink function from accompanying sediment measurements
3 (Weinberg et al., 2013). Reported source signatures of CH₃Br from salt marshes range from -
4 59 to -65‰ (day time values, Bill et al., 2002). Our own measurements in the Ria Formosa
5 indicate similar δ¹³C values (-65‰) or even more depleted ones (unpublished data). In any
6 case, neither source signatures from seagrass meadows nor salt marshes seem to match the
7 overall source signature estimated from the atmospheric samples. Therefore, it is most likely
8 that the atmospheric CH₃Br is strongly influenced by CH₃Br emissions from the surface
9 waters (δ¹³C values in water phase (summer): -23±3‰). Even during periods of low tide the
10 water remains in the deep channels which may be sufficient to have an impact on the local
11 atmosphere. Thus, despite the sources in the lagoon presumably producing isotopically light
12 CH₃Br, δ¹³C values in the atmosphere strongly reflect decomposed CH₃Br whose residual
13 fraction is actually enriched in ¹³C. Accordingly, aqueous CH₃Br appears to become rapidly
14 degraded by biotic/abiotic processes such as hydrolysis, transhalogenation, and microbial
15 degradation with strong isotopic fractionation (King and Saltzman, 1997; Miller et al. 2004).
16 These decomposition mechanisms are temperature dependent with increasing destruction with
17 increasing seawater temperature. This is most likely the reason why the δ¹³C values in the
18 lagoon waters in summer are more enriched in ¹³C compared with those those from the spring
19 campaign.

20 To the best of our knowledge, this is the first report of δ¹³C values of CH₃I in the water phase.
21 As shown by the water samples from the transect cruise, the sources in the lagoon may
22 produce isotopic light CH₃I. Given this, CH₃I seems to some extent to follow the δ¹³C values
23 of CH₃Cl. These sources may be biotic by e.g. phytoplankton, seagrass meadows, or bacteria.
24 On the other hand, Moore and Zafirou (1994) reported a photochemical source for CH₃I by
25 radical recombination of iodine with seawater dissolved organic matter. Due to the lack of
26 isotopic source signatures and fractionation factors for production (and consumption), it is
27 difficult to draw conclusions from the data.

28 The δ¹³C values of CHBr₃ were more depleted in ¹³C from the lagoon inlet towards the parts
29 deeper inside. This suggests a different combination of sources in water masses coming from
30 the Atlantic. Moreover, this potential variation of source contribution can be further assumed
31 by the certain change between summer and spring where e.g. macroalgae are more abundant
32 in the latter period (Anibal et al., 2007). Already reported source signatures of phytoplankton,

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

6 **4.4 Magnitude of fluxes and comparison to other coastal measurements and** 7 **first estimate of global source strength**

8 The areal based fluxes of CH_3Cl , CH_3Br , and CH_3I from seagrass meadows in comparison to
9 emission data of other coastal sources are presented in Fig. 3. In comparison to the emissions
10 from a temperate seagrass meadow in late summer in Northern Germany (Weinberg et al.,
11 2013), fluxes were elevated in the subtropical lagoon in summer during air exposure. This
12 was more pronounced for CH_3Br (factor 33) than for CH_3Cl (factor 2), CH_3I (factor 2), and
13 CHBr_3 (factor 5). In contrast, fluxes from air-exposed seagrass meadows recorded during
14 spring are comparable to those determined in Northern Germany. Thus, the difference
15 between fluxes from temperate and subtropical regions is less pronounced as reported for salt
16 marshes with emissions from subtropical regions exceeding those from temperate regions by
17 up to two orders of magnitude for CH_3Cl and CH_3Br (Blei et al. 2010; Cox et al., 2004;
18 Dimmer et al., 2001; Drewer et al., 2006; Manley et al., 2006; Rhew and Mazéas, 2010; Rhew
19 et al., 2000, 2014; Valtanen et al., 2009). Beside this regional (climatic) difference several
20 authors attributed this to a highly species dependent emission potential.

21 Average emissions of CH_3Cl from the air-exposed seagrass meadows in summer are in the
22 same range than those determined in temperate salt marshes (Blei et al. 2010; Cox et al.,
23 2004; Dimmer et al., 2001; Drewer et al., 2006; Valtanen et al., 2009). In contrast, subtropical
24 counterparts of these macrophytes are distinctively stronger emitters of this compound by at
25 least one order of magnitude (Manley et al., 2006; Rhew and Mazéas, 2010; Rhew et al.,
26 2000, 2014). Greenhouse grown mangroves produce significantly more CH_3Cl than seagrass
27 meadows revealing a higher emission potential for these plants species on per area basis
28 (Manley et al., 2007).

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

1 et al., 2009). However, the CH₃Br fluxes from seagrass meadows are distinctively lower than
2 those of subtropical salt marsh plants (Manley et al., 2006; Rhew and Mazéas, 2010; Rhew et
3 al., 2000). Mangroves seem to have a similar emission potential as seagrass meadows
4 (Manley et al., 2007).

5 For CH₃I, seagrass meadows are a minor source in comparison to the high release of
6 macroalgae in subtropical areas (Leedham et al. 2013). Except for salt marshes from
7 Tasmania (Cox et al., 2004), plant-related communities such as mangroves (Manley et al.,
8 2007) and salt marshes (Dimmer et al., 2001) are more pronounced emission sources of this
9 compound. The same holds true for CHBr₃, where macroalgae communities from temperate
10 and subtropical/tropical regions dominate the emissions of polyhalomethanes on a per area
11 basis (e.g. Carpenter et al., 2000; Gschwend et al., 1985; Leedham et al., 2013).

12 Many uncertainties arise from a limited number of emission data to estimate the global
13 relevance of seagrass meadows. Those may be high variation in space and time, high
14 heterogeneity of seagrass meadows, species dependent emission potential, and errors
15 regarding the global seagrass abundance. Therefore, the scale-up of our data gives only a first
16 rough approximation; it was undertaken as follows. Since we did not measure a full annual
17 cycle, we assumed that seagrass measurements during the summer campaign represent
18 emissions from the reproductive season (May - September). The remaining period of the year
19 (October - April) was calculated with emission data from the spring campaign. The emission
20 data were weighted to tidal states using 8 hours and 16 hours per day as durations when
21 seagrass meadows are air-exposed or submerged, respectively. Due to the lack of flood tide
22 emission data in summer, we used those derived from the sea-air exchange. The resulting
23 average annual emissions from seagrass meadows of 150 μmol m⁻² yr⁻¹ (CH₃Cl), 18 μmol m⁻²
24 yr⁻¹ (CH₃Br), 14 μmol m⁻² yr⁻¹ (CH₃I), and 25 μmol m⁻² yr⁻¹ (CHBr₃) were scaled-up with the
25 current estimates of a global seagrass area ranging from 0.3x10¹² m² (Duarte et al., 2005) to
26 0.6x10¹² m² (Charpy-Roubaud and Sournia, 1990).

27 The tentative estimate yields annual emissions of 2.3-4.5 Gg yr⁻¹ for CH₃Cl, 0.5-1.0 Gg yr⁻¹
28 for CH₃Br, 0.6-1.2 Gg yr⁻¹ for CH₃I, and 1.9-3.7 Gg yr⁻¹ for CHBr₃. Based on the recent global
29 budget calculations (Xiao et al., 2010; Montzka and Reimann, 2011), these ranges are
30 equivalent to 0.06-0.11% and 0.45-0.89%, for CH₃Cl and CH₃Br, respectively. Seagrass
31 meadows would therefore cover a portion of 1.4-2.8% of the missing sources for CH₃Br
32 reported in the most recent WMO report (36.1 Gg yr⁻¹; Montzka and Reimann, 2011). Given

1 the emissions from oceanic sources (e.g. Butler et al., 2007; Quack and Wallace, 2003 and
2 references therein), CH₃I and CHBr₃ emissions from seagrass meadows are rather
3 insignificant on a global scale.

4

5 **5 Conclusions**

6 We presented the first detailed study of halocarbon fluxes from seagrass meadows. The data
7 were obtained from a subtropical mesotidal lagoon in southern Portugal. During air exposure,
8 fluxes of CH₃Cl and CH₃Br were highly variable with increasing fluxes at midday and
9 afternoon while deposition fluxes were predominantly observed in periods of low radiation
10 and at nighttimes. Diurnal fluctuations were less obvious for CH₃I and CHBr₃, though their
11 emission maxima were also shifted to the afternoon. Generally, diurnal variations and
12 emission rates were minor in spring than in summer, suggesting a certain seasonal
13 dependence. This is supported by distinctively lower atmospheric mixing ratios in spring.
14 Distinct emission peaks occurred in the certain moments when lagoon waters were just
15 arriving or leaving the sampling site. Moreover, a comparison between chamber
16 measurements during air exposure and tidal inundation revealed elevated emission rates
17 during flooding. Overall, seagrass meadows are highly diverse regarding their potential
18 halocarbon sources which might be responsible for the observed high variations of emission
19 fluxes. For example, we could show that the sediments were also able to emit halocarbons,
20 though in low quantities on per area basis.

21 The results from a transect cruise along the mid and western part of the lagoon clearly
22 revealed a significant halocarbon production within lagoon waters. This finding corresponds
23 to high halocarbon concentrations in the lagoon water above submerged seagrass meadows.
24 This was especially pronounced for CH₃Cl exhibiting the highest water concentration as
25 compared to other measurements from Atlantic waters. However, CH₃I and CHBr₃ water
26 concentrations were well below those reported from macroalgae-dominated coastlines.

27 To obtain further information on sources and sinks in the lagoon, stable carbon isotopes of
28 halocarbons from the air and water phase along with source signatures were studied. Results
29 suggest that CH₃Cl more originates from the water column and/or seagrass meadows than
30 from adjacent salt marshes or abiotic formation processes. Atmospheric and aqueous CH₃Br
31 in the lagoon was substantially enriched in ¹³C pointing towards degradation processes and re-

1 emission into the atmosphere. Furthermore, we presented isotopic data of CH₃I and CHBr₃
2 from the water phase.

3 Monohalomethane emissions from seagrass meadows fall in-between those from temperate
4 salt marshes and mangroves. For CHBr₃, seagrass-based emissions are distinctively below
5 those of macroalgae. On a global scale, seagrass meadows are rather a minor source for
6 halocarbons but will have a certain imprint on the local and regional budgets. This holds in
7 particular true for subtropical coastlines where seagrass meadows belong to the most
8 abundant ecosystems. In these regions, where strong vertical motions occur, seagrass
9 meadows may be significant contributors to deliver halocarbons to the stratosphere.

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

20

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28

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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 (500-1490)	613 (498-685)	220 (160-300)
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 -190)
<i>spring 2012</i>			
CH ₃ Cl	654 (480-980)	-	166 (100-270)
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 - 130)

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	‰	pmol L ⁻¹	‰	pmol L ⁻¹	‰	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)	0.2 (0.1 - 0.6)	0.8 (-0.3 - 1.9)
Sea-air exchange	8	29.8 (13 - 45)	1.3 (0.6 - 1.7)	2.2 (0.5 - 3.2)	4.7 (1.0 - 8.0)
<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	-	-

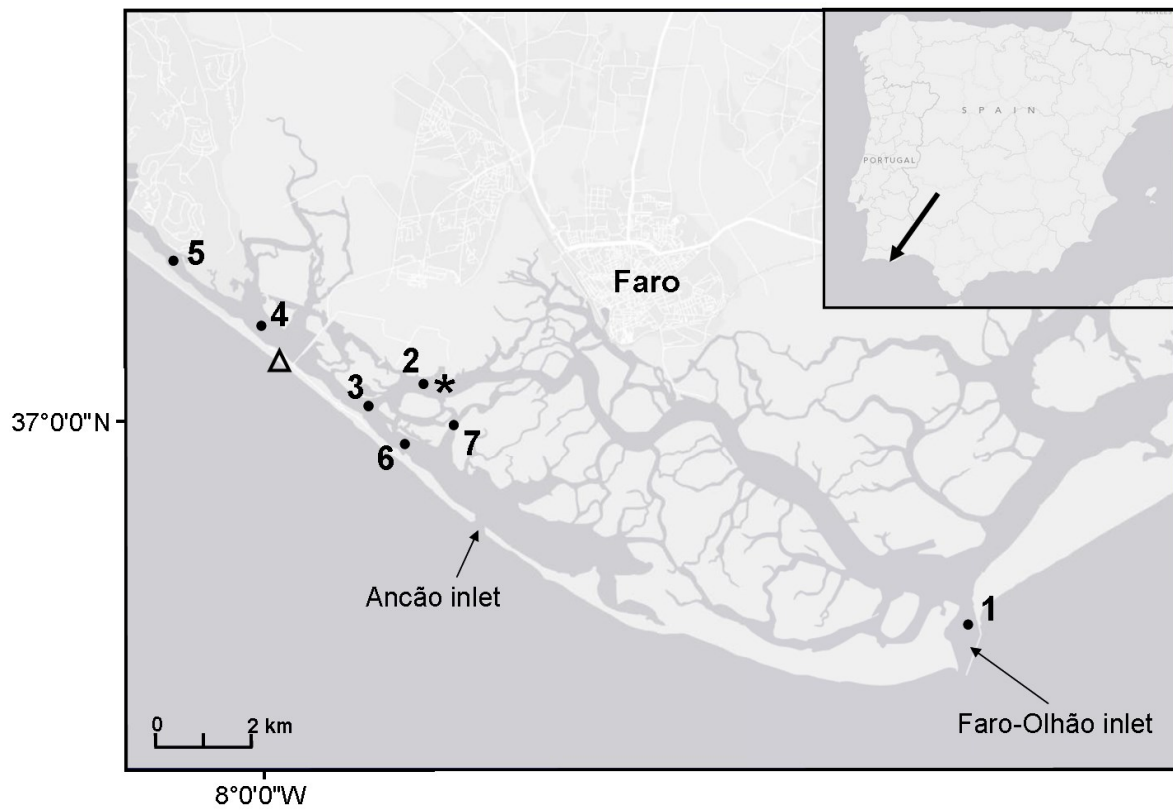
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5

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.

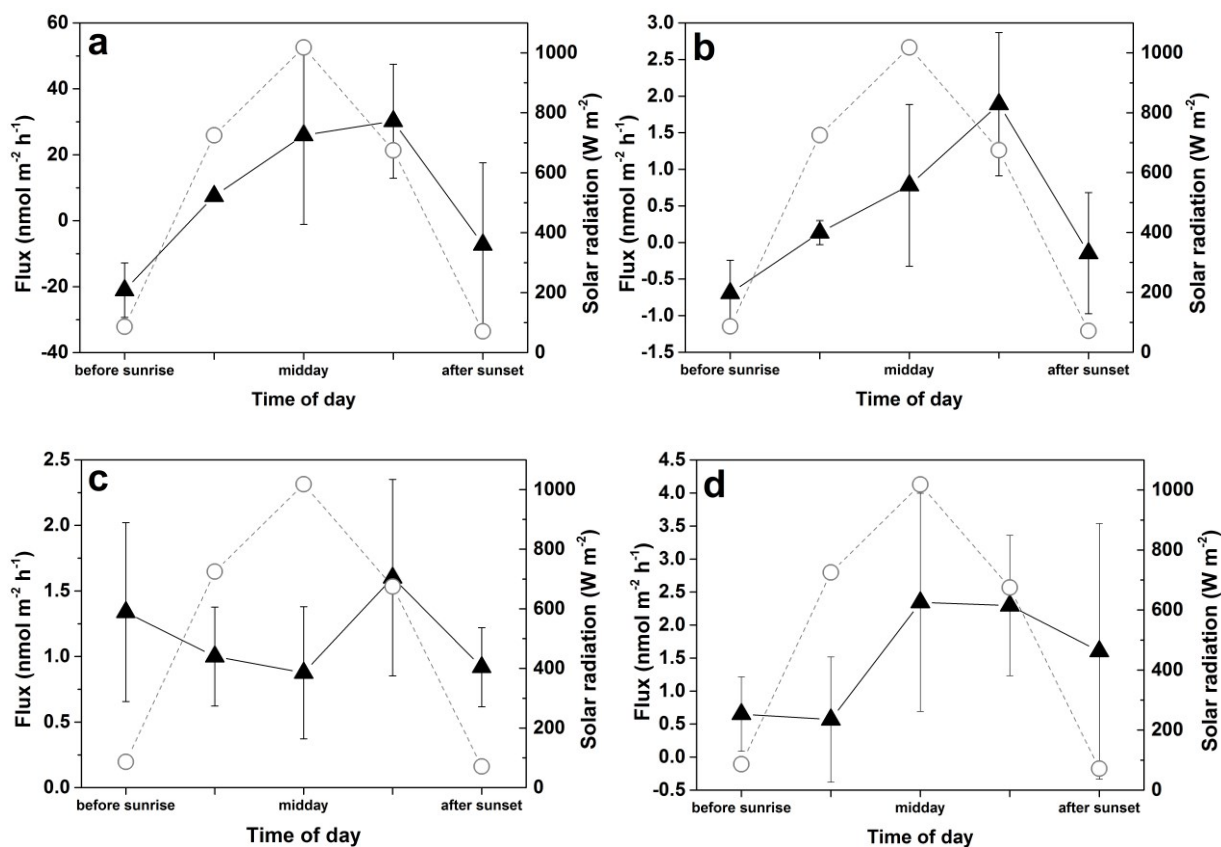
location	CH ₃ Cl	CH ₃ Br	CH ₃ I	CHBr ₃
Faro, Portugal (summer) ¹	220 (160 - 300)	8 (5-11)	12 (4 - 18)	102 (67 -190)
Faro, Portugal (spring) ¹	166 (100 - 270)	10 (6 - 28)	7 (2 - 16)	62 (39 - 130)
East Atlantic ^{2,#}	-	-	-	68.3 (36.6 - 102.0)
Roscoff, France ^{3,#}	-	-	12.9 (9.0 - 31.8)	217 (125 - 519)
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 (3.0 - 3588)
Mace Head, Ireland ^{7,#}	-	3.7 (1.7 - 5.7)	15.3 (10.9 - 19.2)	388 (222 - 554)
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
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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.



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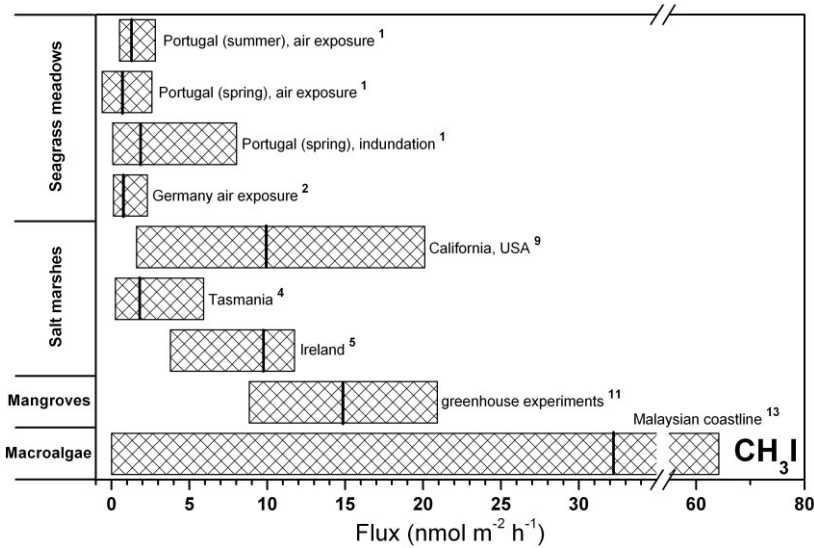
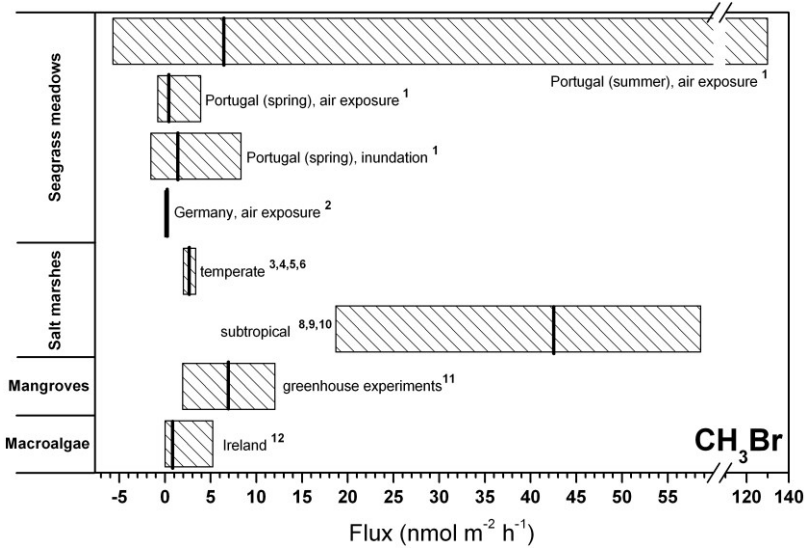
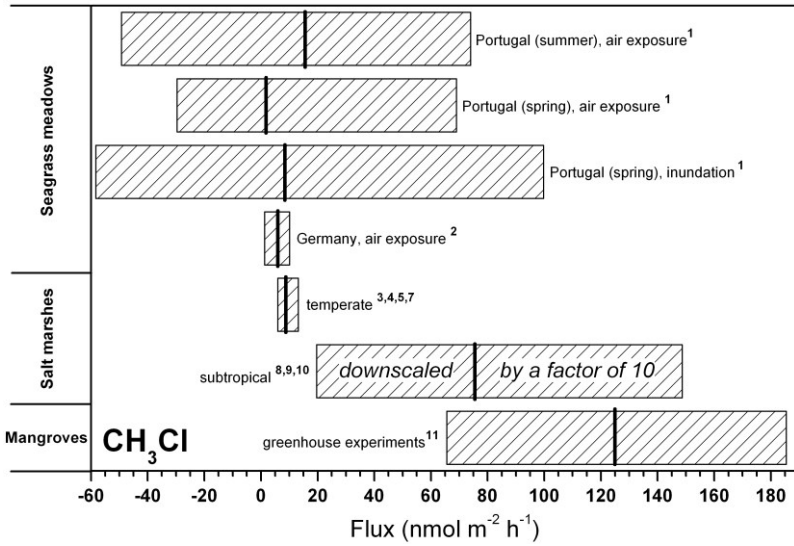
2 Fig. 2a-d: Diurnal variation of mean halocarbon fluxes (triangles) from seagrass meadows
 3 during periods of air exposure in summer 2011 (a: CH₃Cl, b: CH₃Br, c: CH₃I, d: CHBr₃).
 4 Error bars refer to standard deviations. Circles are solar radiation values. Note that the scales
 5 on y-axis are different 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.