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

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Abstract

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

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

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

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

1 Introduction

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

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

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

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

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

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

2 Materials and methods

2.1 Sampling site

The Ria Formosa, covering an ~~surface~~ area of 84 km^2, is a mesotidal lagoon at the South-eastern coast of the Algarve, Portugal (Fig. 1). It is separated from the Atlantic Ocean by a series of barrier islands and two peninsulas. About 80% of the lagoon is intertidal with a semi-diurnal tidal regime and tidal ranges between 1.3 m during neap tides and 3.5 m during spring tides (Cabaço et al., 2012). Due to negligible inflow of fresh water and high exchange of water with the open Atlantic during each tidal cycle, the salinity within the lagoon is 35 to 36 PSU year round, except for periods of heavy rainfalls. About ~~one-fourth~~a quarter of the intertidal area (13.04 km²) is covered by dense stands of *Zostera noltii Hornem* (Guimarães et al., 2012).~~; Rui Santos, pers. comm.)~~ Further, but much less abundant, seagrass species in the lagoon are *Zostera Marina L.* and *Cymodocea nodosa (Ucria) Ascherson* which are mainly located in shallow parts of the subtidal areas (Santos et al., 2004). About 30% of the lagoon's area is covered with salt marsh communities (Rui Santos, pers. comm.).

2.2 Sampling

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

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

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

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

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

Discrete water samples for the determination of dissolved halocarbons concentration and isotopic composition at high tide were taken during both campaigns. The samples were taken directly above the studied seagrass meadow using Duran glass bottles (1-2 L volume). Air and sediment intrusions during water sampling were avoided. The water depth was between 0.3 m and 1 m. On April 24th 2012, a transect cruise through the middle and western part of the lagoon was conducted during rising waters (Fig. 1). The water samples were taken from a water depth of 1 m. Dissolved halocarbons were extracted from seawater using a purge and trap system. Seawater was purged with helium 5.0 (purge flow 1L min^{-1}) for 30 minutes. After water vapour reduction of the purge gas, the compounds were enriched on cryotraps (submerged in a dry shipper). The shape of the cryotraps used here was the same as those for flux chamber and atmospheric samples. The water samples were usually processed within 30 minutes after sampling. Samples from the transect cruise were stored in the dark at 4°C and analyzed within eight hours. Purge efficiencies of monohalomethanes from lagoon water were ≥95% (1 L and 2 L samples). However, the less volatile $CHBr_3$ was only extracted with 50% (1 L samples) and 30% (2 L samples). Therefore, the results of water concentration were corrected for the respective purge efficiency for this compound.

2.3 Measurement and quantification

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

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

2.4 Calculations

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

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

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

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

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

where k_w is the gas exchange velocity (m h^{-1}), C_w and C_a the water concentration and air concentration (pmol L^{-1}), respectively, and H the dimensionless and temperature dependent Henry's law constant taken from Moore (2000) for CH_3Cl, Elliott and Rowland (1993) for CH_3Br and CH_3I, and Moore et al. (1995) for $CHBr_3$. Several approximations emerged to estimate the relationship between the gas exchange velocity k and the wind speed u for open and coastal oceans (e.g. Nightingale et al., 2000; Wanninkhof, 1992). These estimations rely on assumptions that trace gas exchange is based on wind-driven turbulence. This is not applicable in shallow estuarine and riverine systems where the sea-air gas exchange is additionally driven by wind-independent currents and the bottom turbulence and thus water depth and current velocities further play a major role (Raymond and Cole, 2001). Studying the sea-air exchange in the Ria Formosa, these additional factors have to be considered in addition to wind driven outgassing. Therefore, we used the parameterization of k_w with the assumption that wind speed and water current driven turbulence are additive (Borges et al., 2004):

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

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

3 Results

3.1 Halocarbons in the atmosphere and lagoon water

The air mixing ratios in the lagoon were adopted from the inlets of the flux chambers at 1 m above ground during both campaigns. The results of these measurements and those of the upwind site outside the lagoon (Praia de Faro) are presented in Table 1. In summer, ~~the mean air mixing ratios were 828 ppt for CH_3Cl, 22 ppt for CH_3Br, 3 ppt for CH_3I, and 15 ppt for $CHBr_3$. E~~elevated air mixing ratios of the monohalomethanes were observed during periods of easterly winds when air masses at the sampling site had presumably passed over major parts of the lagoon. These mixing ratios reached up to 1490 ppt for CH_3Cl, 61 ppt for CH_3Br, and 11 ppt for CH_3I reflecting a potent source in this system. The mixing ratios at the upwind site (Praia de Faro) were distinctively lower with mean values of 613 ppt (CH_3Cl), 13 ppt

(CH_3Br), 1 ppt (CH_3I), and 8 ppt ($CHBr_3$) further indicating a source inside the lagoon. In spring 2012, the mean air mixing ratios in the lagoon were significantly lower than during summer with 654 ppt for CH_3Cl, 12 ppt for CH_3Br, 1 ppt for CH_3I, and 2 ppt for $CHBr_3$.

Discrete water samples were taken above the studied seagrass meadow during tidal inundation (summer n=9; spring n=10). The results are presented in Table 1. In summer, concentrations ranged from 158 to 301 pmol L^{-1} (CH_3Cl), 5 to 11 pmol L^{-1} (CH_3Br), 4 to 18 pmol L^{-1} (CH_3I), and 67 to 194 pmol L^{-1} ($CHBr_3$). During the spring campaign, the water concentrations were 101 to 267 pmol L^{-1} for CH_3Cl, 6 to 28 pmol L^{-1} for CH_3Br, 2 to 16 pmol L^{-1} for CH_3I, and 39 to 133 pmol L^{-1} for $CHBr_3$.

The results obtained from samples of the transect cruise covered in 2012 (Fig. 1) are given in Table 2. We observed an about two-fold increase of concentration for CH_3Cl (from 121 to 241 pmol L^{-1}) and $CHBr_3$ (from 26 to 55 pmol L^{-1}) between position 1 (Faro-Olhão inlet) and position 2 (near to the seagrass meadows studied). The increase was less pronounced for CH_3Br (5 to 7 pmol L^{-1}) and not notable for CH_3I. The seawater at positions 6 and 7, the nearest to the Ancão inlet, revealed rather low concentrations for all compounds. We further observed rising concentrations for all halocarbons along positions 3, 4, and 5 with increasing distance to the Ancão inlet. They increased from 96 to 180 pmol L^{-1} for CH_3Cl, from 9 to 19 pmol L^{-1} for CH_3Br, 2 to 14 pmol L^{-1} for CH_3I, and 21 to 95 pmol L^{-1} for $CHBr_3$. ~~The difference in concentration along the transect was accompanied by variations in the carbon isotopic composition of all compounds. The most ^{13}C depleted values of CH_3Cl, CH_3Br, and CH_3I were detected at the position furthest from the inlet. Interestingly, $CHBr_3$ showed the opposite trend with more ^{13}C enriched values in the lagoon (-25.8‰ vs. ~ -18‰).~~

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

The mean fluxes and ranges of CH_3Cl, CH_3Br, CH_3I, and $CHBr_3$ from seagrass meadows, sediment, and from sea-air exchange calculations obtained from the two sampling campaigns are given in Table 3.

During the summer campaign (air exposure), we observed highly variable emission and deposition fluxes ranging from -49 to 74 nmol m^{-2} h^{-1} and -5.7 to 130 nmol m^{-2} h^{-1} for CH_3Cl and CH_3Br, respectively. The variability was less pronounced for CH_3I (0.5 to 2.8 nmol m^{-2} h^{-1}) and $CHBr_3$ (-0.6 to 5.7 nmol m^{-2} h^{-1}) where predominantly emissions were measured. Strongly elevated fluxes up to 130 nmol m^{-2} h^{-1} for CH_3Br were recorded in conjunction with tidal change from air exposure to inundation and conversely. These high fluxes were substantiated by a concurrent enhanced atmospheric mixing ratios ranging from 23 ppt to 118 ppt (campaign median 14 ppt). Omitting these compound-specific tidal phenomena, the fluxes of CH_3Cl and CH_3Br were positively correlated ~~to each other~~ (R^2 0.55, $p< 0.05$). There were no significant correlations between ~~However,~~ CH_3I and $CHBr_3$ ~~fluxes correlated neither with each other nor with any of~~and the other investigated halocarbons. Due to the inherent high variability of the fluxes, ~~a direct comparison of~~ halocarbon fluxes were poorly correlated with solar radiation ~~revealed a rather low correlation~~ ($R^2 \leq 0.20$).

The flux chamber measurements over the sediment during air exposure revealed predominantly emissions of all four halocarbons (n=5). These fluxes were 3.6±4.3 nmol m^{-2} h^{-1} (CH_3Cl), 0.6±0.5 nmol m^{-2} h^{-1} (CH_3Br), 0.3±0.2 nmol m^{-2} h^{-1} (CH_3I), and 0.8±1.0 nmol m^{-2} h^{-1} ($CHBr_3$). Except for CH_3I, 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 ~~the monohalomethanes~~CH_3Cl and CH_3Br, and 45% for $CHBr_3$.

During the 2012 spring campaign the halocarbon fluxes from seagrass meadows were determined during both, periods of air exposure and periods of tidal immersion. Furthermore, the measurements were complemented by other trace gases including hydrocarbons and sulphur containing compounds (Bahlmann et al., 2014). ~~High time resolution CO_2 and methane flux measurements were further conducted to gain insights in the biogeochemistry and tidal controls in this system. These measurements along with other trace gases are reported in more detail in Bahlmann et al. (2014).~~ As in the summer campaign, the seagrass meadows were a net source for all halocarbons studied, but on a lower level. The individual ranges of air exposure measurements were -30 to 69 nmol m^{-2} h^{-1} (CH_3Cl), -0.8 to 3.9 nmol m^{-2} h^{-1} (CH_3Br), -0.6 to 2.6 nmol m^{-2} h^{-1} (CH_3I), and -0.5 to 1.3 nmol m^{-2} h^{-1} ($CHBr_3$). On average, the seagrass meadows were a net source also under submerged conditions ranging from -58 to 100 nmol m^{-2} h^{-1} for CH_3Cl, -1.6 to 8.3 nmol m^{-2} h^{-1} for CH_3Br, 0.1 to 8.0 nmol m^{-2} h^{-1} for CH_3I, and -0.4 to 10.6 nmol m^{-2} h^{-1} for $CHBr_3$. Due to the low purge efficiency of $CHBr_3$ during high tide measurements, the fluxes determined with the submergible chamber are underestimated for this compound. Despite this high variability in production/decomposition during air exposure and inundation, the monohalomethanes were significantly correlated to each other ($R^2 \geq 0.50$). These correlations were enhanced compared to those found when the seagrass meadows were air-exposed ($R^2 \geq 0.50$). In this case, only CH_3I and CH_3Br were significantly correlated (R^2 0.51). $CHBr_3$ was only slightly correlated to the monohalomethanes.

While deposition fluxes of CH_3Cl and CH_3Br of air-exposed seagrass meadows occurred predominantly during periods of low irradiance in summer, no obvious relation to the time of day and/or solar radiation was observed during spring when deposition fluxes were frequently detected. For CH_3I and $CHBr_3$, uptake was only occasionally observed and situations of emission clearly dominated.

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

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

3.3 Stable carbon isotopes of halocarbons

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

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

38±3). These $\delta^{13}C$ values found in air samples in the lagoon roughly correspond to the $\delta^{13}C$ values of CH_3Cl (-43±3‰) and CH_3Br (-23±3‰) found in samples of lagoon waters.

Atmospheric CH_3Cl and CH_3Br were on average more enriched in ^{13}C in spring than in summer by 4 and 6‰, respectively. While the $\delta^{13}C$ values of CH_3Cl in the lagoon water were quite similar between both periods of the year, those of CH_3Br were on average more depleted in ^{13}C during spring suggesting certain changes in production/decomposition processes. The isotopic composition of CH_3I in lagoon water was quite similar between summer (-39± 9‰) and spring (mean -37±7‰). As for CH_3Br, the $\delta^{13}C$ values of $CHBr_3$ were more enriched in ^{13}C in summer when compared with those of the spring campaign.

The difference in concentration along the transect cruise was accompanied by variations in the carbon isotopic composition of all compounds (Table 1, Figure 2). The most ^{13}C depleted values of CH_3Cl, CH_3Br, and CH_3I were detected at the position furthest from the inlet. Interestingly, $CHBr_3$ showed the opposite trend with more ^{13}C enriched values in the lagoon (-25.8‰ vs. ~ -18‰).

Using the fluxes and $\delta^{13}C$ values from the inlet and outlet of the flux chamber, we were able to calculate the source signatures of seagrass covered areas. The resulting source signatures of CH_3Cl from seagrass meadows were~~, with -51±6‰ and -56±2‰,~~ similar ~~between~~ during both campaigns (-51±6‰ and -56±2‰, respectively) and independent from the strength of emission. For CH_3Br, we observed most depleted $\delta^{13}C$ values of -53‰ and -58‰ at increased emission fluxes in summer, but values of -26‰ and -29‰ during periods of low emission. This corroborates the findings of isotopically heavy CH_3Br produced within the seagrass meadows (-29‰) in spring 2012 when all samples analysed for the isotopic composition were taken at situations of low emission.

4 Discussion

4.1 Dissolved halocarbons

A comparison of halocarbon concentrations in the lagoon water to other measurements of the coastal Atlantic found in the literature is displayed in Table 5. The lagoon waters appeared to be highly enhanced in CH_3Cl. Except one early study of Tait et al. (1994), our measurements gave the most elevated concentrations for this compound. Enhanced concentrations in the lagoon waters were also found for CH_3Br. Given the mean concentrations from other coastal Atlantic studies (Baker et al., 1999; Carpenter et al., 2000; Hu et al., 2010), we recorded higher concentration by a factor of 2 to 3 at our sampling site. The average water concentrations in the lagoon of CH_3I were in the same range as reported from other parts of the Atlantic (Moore and Groszko 1999; Zhou et al., 2005). However, especially those regions where macroalgae are the dominating source organisms possess higher maximum values (Bravo-Lineares and Mudge, 2009; Jones et al., 2009). This is even more pronounced for $CHBr_3$, for which the seawater concentration within or in the vicinity of macroalgae beds are strongly elevated (Bravo-Lineares and Mudge, 2009; Carpenter et al., 2000; Jones et al., 2009). The area occupied by the prevalent macroalgae species *Enteromorpha spp.* and *Ulva spp.* in the Ria Formosa is estimated to be 2.5 km^2 (Duarte et al., 2008), considerably below that of other abundant sources such as seagrass meadows. We cannot exclude that phytoplankton contributes significantly to the water concentration of halocarbons, but the predominantly low chlorophyll a concentrations (3.06 µg L^{-1} from long-term measurements, Brito et al., 2012) and low water volumes seem to limit the impact from this source.

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

Overall, the lagoon seems to comprise highly potent halocarbon sources in~~to~~ the water column for CH_3Cl and CH_3Br ~~rather than~~but not for CH_3I and $CHBr_3$.

4.2 Flux pattern from seagrass meadows

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

i) Diurnal variations. The correlation analysis with solar radiation resulted in only a weak association with the magnitude of fluxes. However, after grouping by daytime, our data provide some indication for a diurnal pattern (Fig. 2). For CH_3Cl, there was the most obvious relationship between time of day and actual emissions. Highest emissions were observed during day periods with increased sunlight (midday and afternoon). In contrast, deposition fluxes were exclusively recorded during periods of low radiation and nighttimes. The same was also observed for CH_3Br. However, highest mean emissions of this compound seemed to be shifted towards the afternoon. CH_3I was constantly emitted from the seagrass covered spot revealing a weak diurnal dependence. The emissions did not cease during periods of low irradiance and darkness. Nevertheless, elevated mean emissions were observed in the afternoon. Except one occasion, $CHBr_3$ was emitted throughout the sampling periods. Mean emissions were higher around midday and afternoon as during night.

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

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

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

ii) Tidal effects. During the spring campaign, mean fluxes derived from submerged seagrass meadows were ~~remarkably~~ elevated by factors of 17 (CH_3Cl), 5 (CH_3Br), 3 (CH_3I), and 8 ($CHBr_3$) when compared to the average fluxes during air exposure. This clearly higher production of halocarbons under submerged conditions was quite unexpected, as~~.~~ ~~In~~ in general it is believed that the production of trace gases during low tide exceeds that during inundation. For halocarbons this was suggested for example by Carpenter et al. (1999) and Jones et al. (2009) from atmospheric measurements over intertidal macroalgae beds in Mace Head, Ireland. Nevertheless, in accordance with our results from halocarbon measurements we also observed higher primary productivity by increased CO_2 uptake during submerged conditions (Bahlmann et al., 2014). Therefore, the higher productivity may reflect higher enzymatic activity (e.g. methyltransferases) within the organisms of the seagrass community, by which monohalomethanes are presumably formed. Furthermore, the correlation analysis revealed a different behaviour of halocarbons between the two tidal states with stronger correlations between monohalomethanes during tidal inundation than air exposure. Obviously the change in environmental conditions was accompanied with a shift in the halocarbon production-decomposition pattern of the benthic community and/or different source organisms were stimulated.

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

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

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

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

Comparing the data obtained from air-exposed sites during the two campaigns, the fluxes in summer were strongly enhanced by factors of 16 (CH_3Cl and CH_3Br), 2 (CH_3I), and 5 ($CHBr_3$). Moreover, the halocarbon fluxes showed a distinct diurnal cycle during summer but not during spring. The differences of ambient conditions between the campaigns with lower air temperatures and lower solar radiation in spring may have contributed to the differences in the emission patterns of halocarbons. That these environmental conditions can substantially influence the magnitude of fluxes was reported from other ecosystems such as salt marshes (Blei et al., 2010; Manley et al., 2006). indicating that halocarbon fluxes increase from beginning of the growing season (spring) to the period where seagrass reproductive status is the highest (summer). This might correspond to the results from salt marshes where elevated fluxes for monohalomethanes where observed during the short flowering period (Manley et al., 2006). The differences of ambient conditions between the campaigns with lower air temperatures and cloudy sky in spring may have contributed to the differences in the emission patterns of halocarbons. That temperature is one of the emission controlling factors was reported from temperate salt marshes (Blei et al., 2010). Moreover, the halocarbon fluxes showed a distinct diurnal cycle during summer but not during spring. This suggests either a less productive benthic community or much stronger degradation processes during spring. The latter point is rather unlikely since the temperatures were distinctively lower and thus degradation processes are tentatively slower. Overall, these differences observed in periods of air exposure between spring and summer might suggest a certain seasonality in seagrass meadows. However, further studies covering the entire seasoning are necessary to fully unravel the annual halocarbon emissions from seagrass meadows.

4.3 Halocarbons sources in the lagoon: an isotopic perspective

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

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

With $\delta^{13}C$ values of -42±17‰ the source signature of CH_3Br from seagrass meadows tend to be more depleted in ^{13}C compared with the calculated source signature from the atmospheric samples. It should be noted that the $\delta^{13}C$ values for this compound were more depleted in ^{13}C during periods of increased emission (-55‰) than during low emissions (-28‰). This shift can most likely be explained by degradation processes in the sediments which occurred simultaneously. This corroborates our observations from Northern Germany with subsequent recalculation of a sedimentary sink function from accompanying sediment measurements (Weinberg et al., 2013). Reported source signatures of CH_3Br from salt marshes range from -59 to -65‰ (day time values, Bill et al., 2002). Our own measurements in the Ria Formosa indicate similar $\delta^{13}C$ values (-65‰) or even more depleted ones (unpublished data). In any case, neither source signatures from seagrass meadows nor salt marshes seem to match the overall source signature estimated from the atmospheric samples. Therefore, it is most likely that the atmospheric CH_3Br is strongly influenced by CH_3Br emissions from the surface waters ($\delta^{13}C$ values in water phase (summer): -23±3‰). Even during periods of low tide the water remains in the deep channels which may be sufficient to have an impact on the local atmosphere. Thus, despite the sources in the lagoon presumably producing isotopically light CH_3Br, $\delta^{13}C$ values in the atmosphere strongly reflect decomposed CH_3Br whose residual fraction is actually enriched in ^{13}C. Accordingly, aqueous CH_3Br appears to become rapidly degraded by biotic/abiotic processes such as hydrolysis, transhalogenation, and microbial degradation with strong isotopic fractionation (King and Saltzman, 1997; Miller et al., 2004). These decomposition mechanisms are temperature dependent with increasing destruction with increasing seawater temperature (King and Saltzman, 1997). This is most likely the reason why the $\delta^{13}C$ values in the lagoon waters in summer are more enriched in ^{13}C compared with those those from the spring campaign.

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

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

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

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

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

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

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

Many uncertainties arise from a limited number of emission data to estimate the global relevance of seagrass meadows. Those may be high variation in space and time, high heterogeneity of seagrass meadows, species dependent emission potential, and errors regarding the global seagrass abundance. Therefore, the scale-up of our data gives only a first rough approximation; it was undertaken as follows. Since we did not measure a full annual cycle, we assumed that seagrass measurements during the summer campaign represent emissions from the reproductive season (May - September). The remaining period of the year (October - April) was calculated with emission data from the spring campaign. The emission data were weighted to tidal states using 8 hours and 16 hours per day as durations when seagrass meadows are air-exposed or submerged, respectively. Due to the lack of flood tide emission data in summer, we used those derived from the sea-air exchange. The resulting average annual emissions from seagrass meadows of 150 µmol m^{-2} yr^{-1} (CH_3Cl), 18 µmol m^{-2} yr^{-1} (CH_3Br), 14 µmol m^{-2} yr^{-1} (CH_3I), and 25 µmol m^{-2} yr^{-1} ($CHBr_3$) were scaled-up with the current estimates of a global seagrass area ranging from $0.3x10^{12}$ m^2 (Duarte et al., 2005) to $0.6x10^{12}$ m^2 (Charpy-Roubaud and Sournia, 1990).

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

5 Conclusions

We presented the first detailed study of halocarbon fluxes from seagrass meadows. The data were obtained from a subtropical mesotidal lagoon in southern Portugal. During air exposure, The fluxes of CH_3Cl and CH_3Brhalocarbons were highly variable with increasing increased fluxes at midday and afternoon while deposition fluxes were predominantly observed in periods of low radiation and at nighttimes.when the seagrass meadows were submerged. Distinct emission peaks occurred in the certain moments when lagoon waters were just arriving or leaving the sampling site. For CH_3Cl and CH_3Br we observed a diurnal dependence on the fluxes with increased emissions during midday/afternoon and deposition fluxes during periods of low radiation. Diurnal fluctuations were less obvious for CH_3I and $CHBr_3$, though their emission maxima were also shifted to the afternoon. Generally, diurnal variations (during air exposure), atmospheric mixing ratios, and emission rates of halocarbons were minor in spring than in summer, suggesting a seasonal dependence. This is supported by distinctively lower atmospheric mixing ratios in spring. Distinct emission peaks occurred in the certain moments when lagoon waters were just arriving or leaving the sampling site. Moreover, a comparison between chamber measurements during air exposure and tidal inundation revealed elevated emission rates during flooding. Overall, seagrass meadows are highly diverse regarding their potential halocarbon sources which might be responsible for the observed high variations of emission fluxes. For example, we could show that the sediments were also able to emit halocarbons, though in low quantities on per area basis.Monohalomethane emissions from seagrass meadows fall in-between those from temperate salt marshes and mangroves. For $CHBr_3$, seagrass-based emissions are distinctively below those of macroalgae. On a global scale, seagrass meadows are rather a minor source for halocarbons but will have an imprint on the local and regional budgets. This holds in particular true for subtropical coastlines where seagrass meadows belong to the most abundant ecosystems. In these regions, where strong vertical motions occur, seagrass meadows may be significant contributors to deliver halocarbons to the stratosphere.

Stable carbon isotopes of halocarbons were used to identify possible sources in the lagoon. The results from a transect cruise along the mid and western part of the lagoon clearly revealed a significant halocarbon production within lagoon waters. This finding corresponds to high halocarbon concentrations in the lagoon water above submerged seagrass meadows. This was especially pronounced for CH_3Cl exhibiting the highest water concentration as compared to other measurements from Atlantic waters. However, CH_3I and $CHBr_3$ water concentrations were well below those reported from macroalgae-dominated coastlines.

To obtain further information on sources and sinks in the lagoon, stable carbon isotopes of halocarbons from the air and water phase along with source signatures were studied. Results suggest that CH_3Cl more originates from the water column and/or seagrass meadows than from adjacent salt marshes or abiotic formation processes. Atmospheric and aqueous CH_3Br in the lagoon was substantially enriched in ^{13}C pointing towards degradation processes and re-emission into the atmosphere. Furthermore, we presented isotopic data of CH_3I and $CHBr_3$ from the water phase.

Monohalomethane emissions from seagrass meadows fall in-between those from temperate salt marshes and mangroves. For $CHBr_3$, seagrass-based emissions are distinctively below those of macroalgae. On a global scale, seagrass meadows are rather a minor source for

~~halocarbons but will have a certain imprint on the local and regional budgets. This holds in particular true for subtropical coastlines where seagrass meadows belong to the most abundant ecosystems. In these regions, where strong vertical motions occur, seagrass meadows may be significant contributors to deliver halocarbons to the stratosphere.~~

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

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

	Air mixing ratio Ria Formosa (ppt)	**Air mixing ratio Praia de Faro (ppt)**	**Water concentration Ria Formosa (pmol L^{-1})**
summer 2011			
CH_3Cl	**828** (503-1490)	**613** (498-685)	**220** (158-301)
CH_3Br	**22** (8-118)	**13** (9-19)	**8** (5-11)
CH_3I	**3** (2-11)	**1** (0.8-2)	**12** (4-18)
$CHBr_3$	**15**(6-31)	**8** (6-9)	**102** (67 -194)
spring 2012			
CH_3Cl	**654** (484-976)	-	**166** (101-267)
CH_3Br	**12** (4-40)	-	**10** (6-28)
CH_3I	**1** (0.4-4.8)	-	**7** (2-16)
$CHBr_3$	**2** (0.4-10)	-	**62** (39 - 133)

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

Sample	Time	CH_3Cl		CH_3Br		CH_3I		$CHBr_3$	
	(CET)	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	-

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

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

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

	Atmosphere Ria Formosa (‰)	**n**	**Atmosphere Praia de Faro (‰)**	**n**	**lagoon water (‰)**	**n**	**source signature seagrass meadow (‰)**	**n**
summer 2011								
CH_3Cl	-42 ± 2	7	-39 ± 0.4	5	-43 ± 3	7	-51 ± 6	5
CH_3Br	-29 ± 5	7	-38 ± 3	5	-23 ± 3	7	-42 ± 17	4
CH_3I	-	-	-	-	-39 ± 9	7	-	-
$CHBr_3$	-	-	-	-	-13 ± 1	7	-	-
spring 2012								
CH_3Cl	-38 ± 1	3	-	-	-42 ± 1	5	-56 ± 2	3
CH_3Br	-23 ± 10	3	-	-	-33 ± 8	5	-26; -33	2
CH_3I	-	-	-	-	-37 ± 7	5	-	
$CHBr_3$	-	-	-	-	-18 ± 1	5	-	

Table 5: Mean concentrations (bold) and ranges (parentheses) of dissolved halocarbons (pmol L^{-1}) from the subtropical lagoon Ria Formosa in summer 2011 (n=9) and spring 2012 (n=10) in comparison to published data from coastal Atlantic waters.

location	CH_3Cl	CH_3Br	CH_3I	$CHBr_3$
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

[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-Linares and Mudge (2009); [7] Carpenter et al. (2000); [8] Hu et al. (2010); [9] MacDonald and Moore (2007); [10] Moore and Groszko (1999); [11] Zhou et al. (2005); [#] macroalgae dominated

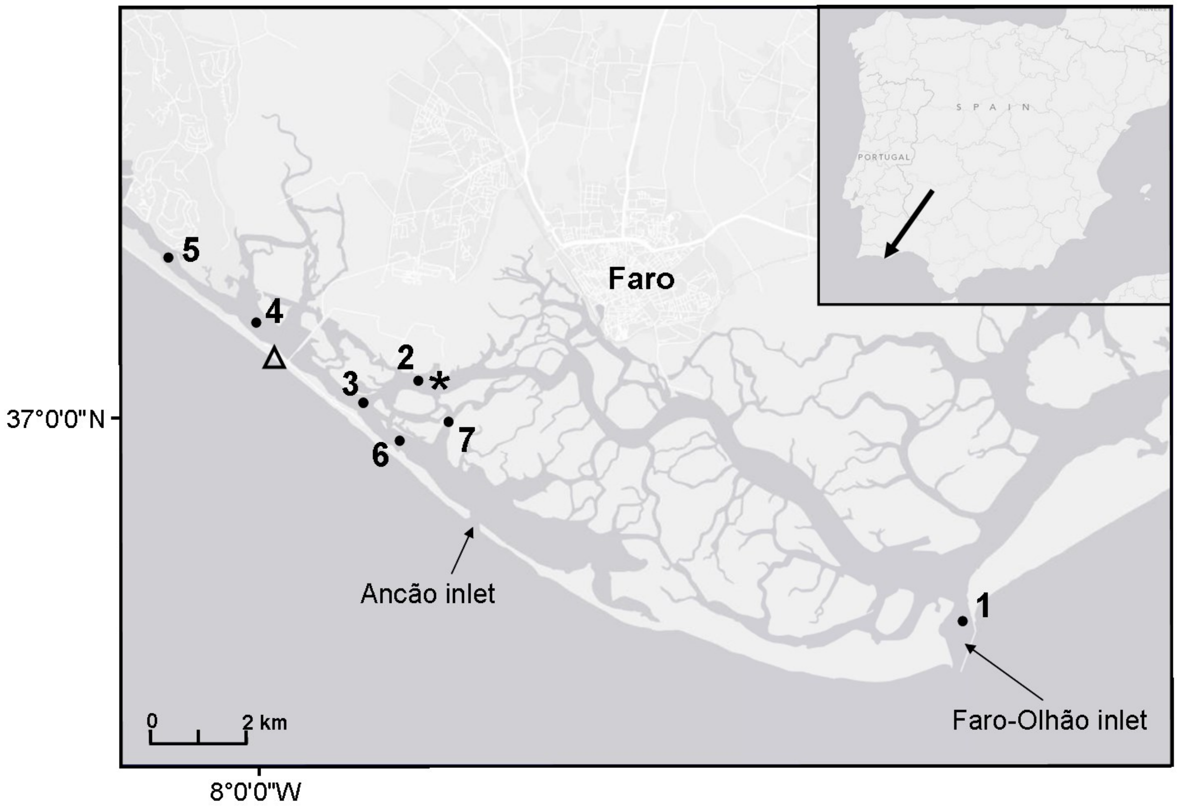


Fig. 1: Map of the lagoon Ria Formosa, Portugal. Asterisk: site of seagrass meadow studies; triangle: sampling site on the Praia de Faro (upwind position). Dots with numbers represent sampling points during the transect cruise.

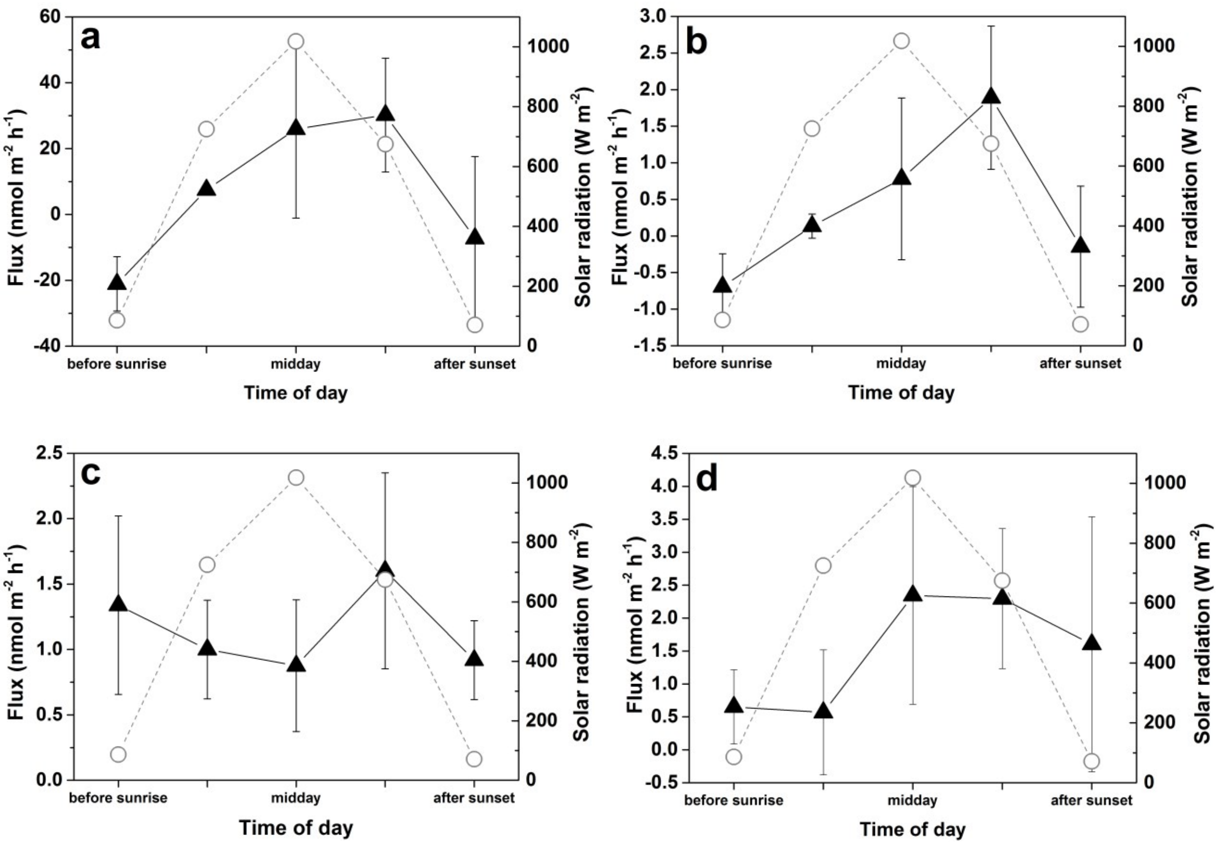
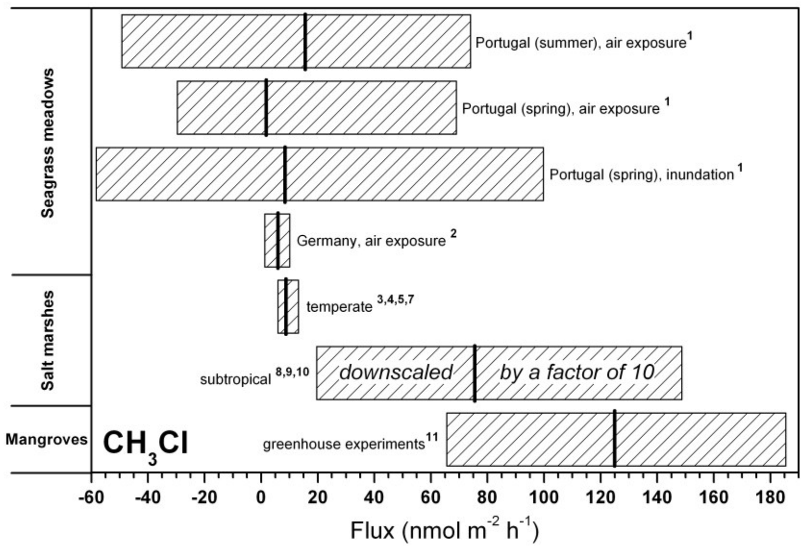
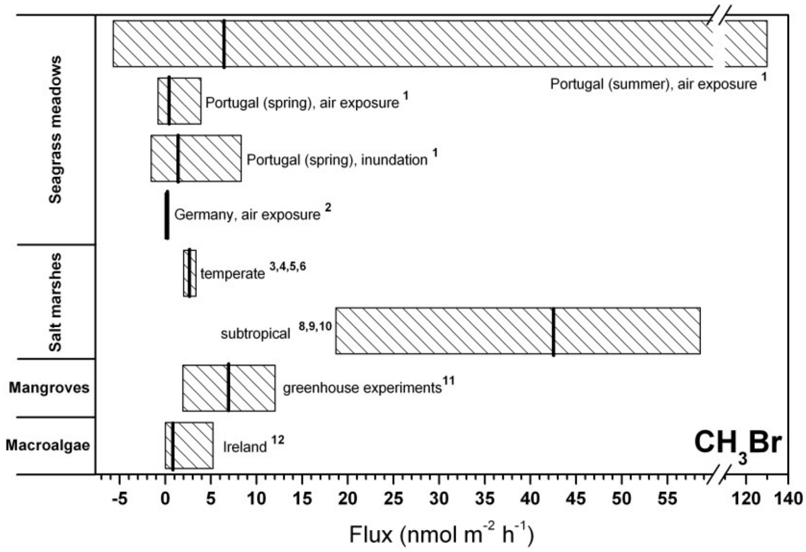


Fig. 2a-d: Diurnal variation of mean halocarbon fluxes (triangles) from seagrass meadows during periods of air exposure in summer 2011 (a: CH_3Cl, b: CH_3Br, c: CH_3I, d: $CHBr_3$). Error bars refer to standard deviations. Circles are solar radiation values. Note that the scales on y-axis are different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


Seagrass meadows
Salt marshes
Mangroves
CH3Cl
Portugal (summer), air exposure 1
Portugal (spring), air exposure 1
Portugal (spring), inundation 1
Germany, air exposure 2
temperate 3,4,5,7
subtropical 8,9,10
downscaled by a factor of 10
greenhouse experiments 11
-60 -40 -20 0 20 40 60 80 100 120 140 160 180
Flux (nmol m-2 h-1)


Seagrass meadows
Salt marshes
Mangroves
Macroalgae
Portugal (summer), air exposure 1
Portugal (spring), air exposure 1
Portugal (spring), inundation 1
Germany, air exposure 2
temperate 3,4,5,6
subtropical 8,9,10
greenhouse experiments 11
Ireland 12
CH3Br
-5 0 5 10 15 20 25 30 35 40 45 50 55 120 140
Flux (nmol m-2 h-1)

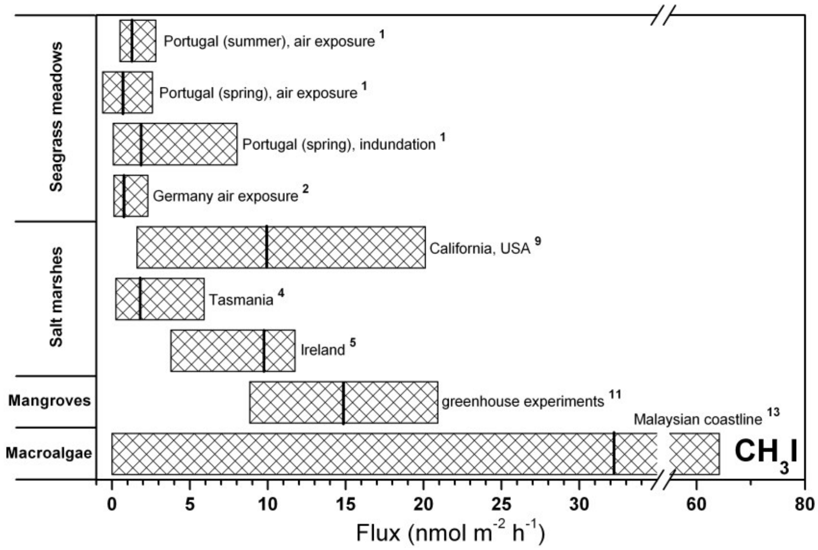

Seagrass meadows
Salt marshes
Mangroves
Macroalgae
Portugal (summer), air exposure 1
Portugal (spring), air exposure 1
Portugal (spring), indundation 1
Germany air exposure 2
California, USA 9
Tasmania 4
Ireland 5
greenhouse experiments 11
Malaysian coastline 13
CH3I
0 5 10 15 20 25 30 60 80
Flux (nmol m-2 h-1)

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