



Determination of fluxes and isotopic composition of halocarbons from seagrass meadows using a dynamic flux chamber



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HIGHLIGHTS

- Seagrass meadows are a source for halocarbons to the atmosphere.
- Dynamic flux chambers are suitable to study stable carbon isotopes of halocarbons.
- A coupled isotope and mass balance was applied to gain source-related isotopic data.
- Accounting for production and degradation processes improve isotopic data.
- First source-related isotopic data of CH₃I is reported.

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ABSTRACT

Halocarbons are important vectors of reactive halogens to the atmosphere, where the latter participate in several chemical key processes. Many efforts have been made to quantify their sources and sinks. However, those are still designated to large uncertainties. In contrast to other coastal habitats such as salt marshes and kelp communities, seagrass meadows have so far not been investigated with regard to trace gases. In order to study seagrass meadows as a potential source for halocarbons to the atmosphere, we conducted dynamic flux chamber measurements at a coastal site in List/Sylt, Northern Germany. Emissions of halocarbons from seagrass meadows into the atmosphere were found for chloromethane (CH₃Cl), bromomethane (CH₃Br), iodomethane (CH₃I), and bromoform (CHBr₃) being the main compounds, while the sediment seems to be a net sink for CH₃Cl and CH₃Br. Stable carbon isotopes of halocarbons were determined using a newly developed comprehensive coupled isotope and mass balance for dynamic flux chambers. Mean stable carbon isotope compositions of the emitted halocarbons were −50‰ (CH₃Cl), −52‰ (CH₃Br), −63‰ (CH₃I) and −14‰ (CHBr₃).

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1. Introduction

Halocarbons, such as chloromethane (CH₃Cl), bromomethane (CH₃Br), and bromoform (CHBr₃) are precursors of reactive halogens, which contribute to the destruction of stratospheric ozone (Crutzen and Gidel, 1983; Solomon et al., 1994; Sturges et al., 2000; Wofsy et al., 1975), and, in the case of iodomethane (CH₃I), also to the formation of aerosols in the marine boundary layer (Carpenter, 2003). Known natural sources of halocarbons include salt marshes (Manley et al., 2006; Rhew et al., 2000), oceans (Butler et al., 2007; Quack et al., 2007), algae (Gschwend et al., 1985), fungi (Watling and Harper, 1998), and terrestrial plants (Saini et al., 1995; Saito and Yokouchi., 2006). However, there are still large uncertainties

concerning their atmospheric budgets. This particularly holds true for CH₃Br, whose known sinks exceed the known sources by more than 20% (Yvon-Lewis et al., 2009). Though recent modelling and field studies suggest that the atmospheric budget of CH₃Cl can be nominally closed by large emissions from tropical forests (Gebhardt et al., 2008; Saito and Yokouchi, 2008; Xiao et al., 2010), the strength of its known distinct sources are assigned with large uncertainties (Keppler et al., 2005; WMO, 2011). Furthermore, the role of coastal zones as sources for short-lived CH₃I and CHBr₃ remain scarcely resolved (Butler et al., 2007).

Incubation experiments have shown the ability of seagrasses to form a variety of halocarbons (Urhahn, 2003), and thus indicate that seagrass meadows might be a source of these compounds. Moreover, seagrass meadows cover a significant portion of global coastal zones with estimates of about 300,000 km² (Duarte et al., 2005).

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Stable carbon isotopes of halocarbons have been applied to elucidate their sources and sinks (Bahlmann et al., 2011; Bill et al., 2002b, 2004; Harper et al., 2003; Keppler et al., 2004; Miller et al., 2001, 2004). This holds especially true for CH₃Cl which has a typical tropospheric background concentration of about 550 ppt (WMO, 2011). The reported $\delta^{13}\text{C}$ -values of CH₃Cl from different sources cover a broad range of about 100‰ making them a useful tool to infer the sources and sinks of this compound (Keppler et al., 2005). Integrating isotopic data on source signatures and isotopic fractionations associated with degradation processes, atmospheric isotope and mass balances of CH₃Cl and CH₃Br were proposed (Keppler et al., 2005; McCauley et al., 1999; Saito and Yokouchi, 2008). However, still limited isotopic field data are available for CH₃Br (Bill et al., 2002b, 2004) as well as CH₃I and CHBr₃, yet (Auer et al., 2006; Bahlmann et al., 2011). This is particularly due to their low atmospheric mixing ratios with tropospheric background concentrations usually in the lower ppt range making the determination of the stable isotope ratios of these halocarbons a challenging task. Most recently, Bahlmann et al. (2011) developed a sampling method which allows determining the stable carbon isotopes of such low-concentrated compounds.

The objectives of this study were i) to provide first flux measurements of halocarbons from a temperate seagrass meadow ii) to improve the isotopic datasets for CH₃Cl and CH₃Br as well as to generate first source-related isotope field data of low concentrated CH₃I and CHBr₃ and iii) to develop a comprehensive coupled isotope and mass balance for a dynamic flux chamber system which includes source and sink terms.

2. Experimental

2.1. Sampling

Sampling was conducted in an intertidal seagrass meadow at List/Sylt (55°1'N, 8°25'E), Northern Germany, from 26th August to 4th September 2010 which is rather end of the growing season (late summer/autumn). Ambient temperatures averaged 16 °C with partly strong cloud cover (181–617 W m⁻²). The sampled seagrass species were *Zostera marina* L. ($n = 5$) and *Zostera noltii* Hornem. ($n = 4$) which are the dominant species in the study region. The sampled seagrass patches were free of visible epiphytes, and residuals of macroalgae material were removed from the patches to avoid interferences. However, it should be noted that the flux measurements were carried out on the community and not on the species level. The canopy coverage of the two seagrass species were estimated to >80% (*Z. marina*) and 50–60% (*Z. noltii*). The leave biomass above ground enclosed by the chamber was about 16 g (dry weight) for *Z. Marina* and 11 g (dry weight) for *Z. Noltii*. Mixed beds of both species were avoided. Additional flux measurements were carried out above adjacent bare sediment patches ($n = 2$). The measurements were made during low tide by placing a semi-cylindrical flux chamber made of quartz glass (0.3 cm wall thickness) directly on the seagrass and bare sediment patches, respectively. Quartz was chosen as an appropriate material for the flux chamber because of its high transparency in the UV band and chemical inertness. The chamber had a headspace volume of 7 L and a bottom surface area of 0.1 m². Prior to sampling, it was sealed by surrounding muddy sands. For the simultaneous sampling of the chamber (outlet) and ambient air (inlet), two sampling systems were operated. During the experiments we observed a slight temperature increase between chamber and ambient air (≤ 5 °C). The sampling was performed as described by Bahlmann et al. (2011). Briefly, air was drawn through the sampling system using membrane pumps (KNF Neuberger N86 KNDC, Freiburg, Germany) at a flow of 1 L min⁻¹. The sampling durations were between 60 and

90 min resulting in an average air volume of 70 L per sample. Sampling times depended on the tidal conditions and were between 10 a.m. and 6 p.m. local time. The target compounds were enriched in cryotrap, submerged in a dry shipper filled with liquid nitrogen as cooling source. After sampling, the compounds were transferred to adsorption tubes, sealed and stored at –80 °C until analysis.

2.2. Measurements and quantification

The determination of the mixing ratios and the isotope composition of halocarbons from air samples is described in detail elsewhere (Bahlmann et al., 2011). Briefly, the compounds were thermally desorbed from the adsorption tubes, cryofocused and directed to a GC–MS (6890N/5975B, Agilent, Germany). After chromatographic pre-separation on a Gaspro column (Agilent, 30 m, 0.32 μm i.d.), about 20% of sample is directed to the MS for quantification of the target analytes. The remaining portion is externally fractionated into a target and a residual fraction. This fractionation procedure is to isolate the target compounds from the bulk of co-trapped compounds and hence to avoid peak overlapping during isotope ratio determination. Both fractions are then injected to a GC–MS–IRMS system (DSQ II, DeltaV IRMS, Thermo Finnigan, Germany) equipped with a CP–PorabondQ column (Varian, 25 m, 250 μm i.d.) in order to determine the stable carbon isotopes of the target compounds. The coupled MS was simultaneously operated to monitor the purity of the analytes. Quantification of CH₃Cl, CH₃Br, CH₃I and CHBr₃ was performed on the Agilent system used for pre-separation against a working standard (Scott EPA TO 15/17 Sigma–Aldrich, Germany). The analytical precision of the stable carbon isotope determination was $\pm 0.25\%$ for CH₃Cl, $\pm 1.8\%$ for CH₃Br, $\pm 2.2\%$ for CH₃I, and $\pm 2.7\%$ for CHBr₃ (Bahlmann et al., 2011).

3. Calculations

Halocarbon fluxes have often been determined using static chamber systems (Blei et al., 2010; Manley et al., 2006; Redeker and Kalin, 2011; Rhew et al., 2000). Here, we employed a dynamic flux chamber as dynamic chambers allow for larger sampling volumes and longer sampling times, which is a prerequisite for determining the carbon isotope ratios of the emitted halocarbons and/or the apparent kinetic isotope effects (KIEs) of the deposition fluxes. Dynamic flux chambers have been widely used in trace gas studies (Gao et al., 1997; Kim and Lindberg, 1995; Zhang et al., 2002), whereas net fluxes are commonly calculated according to

$$F_{\text{Net}} = \frac{Q_N \times (C_{\text{out}} - C_{\text{in}})}{A \times V_N \times 1000} \times 60 \quad (1)$$

where F_{Net} is the net flux [nmol m⁻² h⁻¹], Q_N is the flushing flow rate through the chamber [L min⁻¹, at 1013.25 mbar and 298.15 K], C_{out} and C_{in} are the air mixing ratios of target compounds [ppt] at the outlet and the inlet of the flux chamber, respectively, A is bottom surface area of the flux chamber [m²], and V_N [L] is the molar volume at 1013.25 mbar and 298.15 K. The number 60 results from the conversion from min⁻¹ to h⁻¹.

Moyes et al. (2010) and Powers et al. (2010) used a dynamic flux chamber to determine the fluxes and isotope ratios of CO₂ effluxes from soils. The authors proposed a mass weighted isotope balance to calculate the isotope ratios of the emitted CO₂ from the mixing and isotope ratios measured at the inlet and outlet, respectively. However, their approach does not account for simultaneous occurring emission and deposition fluxes between the plant soil

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