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

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1 Design of cryotraps used for air and seawater samples (Purge and trap)

The analytic procedure is based on the method of Bahlmann et al. (2011) for the isotopic determination of trace gases with some adjustments. We changed the design of the cryotraps in order to establish a better temporal resolution by reducing the sample preparation/analysis time. The self-made cryotraps were ¼” siltek capillary (40 cm) connected to a stainless steel capillary (60 cm) and were bowed forming a U-shape. This allows the cryotrap being easily submersed in the dry shipper (Voyageur 12, Air Liquide, Germany) as cooling source during sampling. The cryotraps were filled with Tenax TA (20-35 mesh, 5 cm, Grace, Deerfield, USA) at the lower end of ¼” capillary and fixed with silanized glass wool at the top and bottom of the packing material. The inlet and outlet were capped with Swagelok fittings and endcaps allowing rapid connection and closure before/after sampling and measurements.

2 Measurement of air and seawater samples

The instrumental set up is shown in Fig. S1. After sampling (air sampling or purge&trap of water samples), the samples were thermally desorbed from the cryotrap (310°C) under a flow of high-purity helium (50 mL min^{-1}, 99.999%, Linde, Germany) for 15 min (red lines/arrows). The analytes were re-trapped on peltier-cooled sampling tubes (Bahlmann et al., 2011) at -15°C using a Valco eight port valve (VICI, Valco instruments, Houston, USA). After sample transfer, the valco valve was switched and analytes were thermally desorbed (330°C) from the adsorbent tubes in counter-flow direction (He, 30 mL min^{-1}), here indicated as green lines/arrows. During the desorption (20 min), the analytes were then refocused on a cryotrap (quartz capillary, 60 cm, 0.32 i.d.) submerged in liquid nitrogen. The refocusing of analytes and injection into the GC-MS system proceeds using a second eight port valco valve. After retrapping, the valve is switched and compounds are sent to the GC-MS system in counterflow direction (black (dotted) lines/arrows) under ambient temperature. Due to high water amounts in air and water samples, the water was removed by two Nafion dryers (in silica gel), each after thermal desorption from the cryotraps and the adsorbent tubes.

The GC-MS (6890N/5975B, Agilent, Waldbronn, Germany) was equipped with a CP-PorabondQ column (25 m, 0.25 µm i.d., Varian). The flowrate was set to 3°mL. The oven temperature program was as follows: 40 °C, hold 4 min; 12° C min^{-1} to 200°C, hold 2 min, 8° C min^{-1} to 240°C; 30° C min^{-1} to 280°C, hold 5 min. The MS was operated in the electron impact mode at 70 eV. Temperatures of quadrupole, source, and transfer line were 150°C, 230°C, and 250°C. Acquisition was executed in full scan mode (33-300 u). Target analytes were identified by their retention times and respective mass spectra and quantified using their major mass fragments. Quantification of CH_3Cl, CH_3Br, and $CHBr_3$ of air and water samples was done by using aliquots of Scott EPA TO 15/17 gas standard (1 ppm in nitrogen, Sigma Aldrich, Germany). During on-site measurements, CH_3I was quantified by using the response factor against CH_3Br. Prior to the campaign, equivalent amounts of CH_3I and CH_3Br from single gas standards were analysed together for the response factor calculation.

The trapping and desorption efficiency (recovery rates) of the cryotraps was tested (n=4). 2 mL of Scott EPA TO 15/17 gas standard (1 ppm in nitrogen) and 20 µL CH_3I (100 ppm nitrogen) was injected to the cryotraps submerged in the dry shipper using a stream of helium. Simulating "real" air sampling, helium was stream was set to 1L min^{-1} for 30 min (resulting in 30 L). The whole sample treatment procedure was applied as described above. The mean recovery rates of a suite of halocarbons were 96% ranging from 93± 4% (CH_3Br) and 93± 10% (CCl_4) to 100± 4% for $CHBr_3$. Individual recovery rates are displayed in Fig. S2.

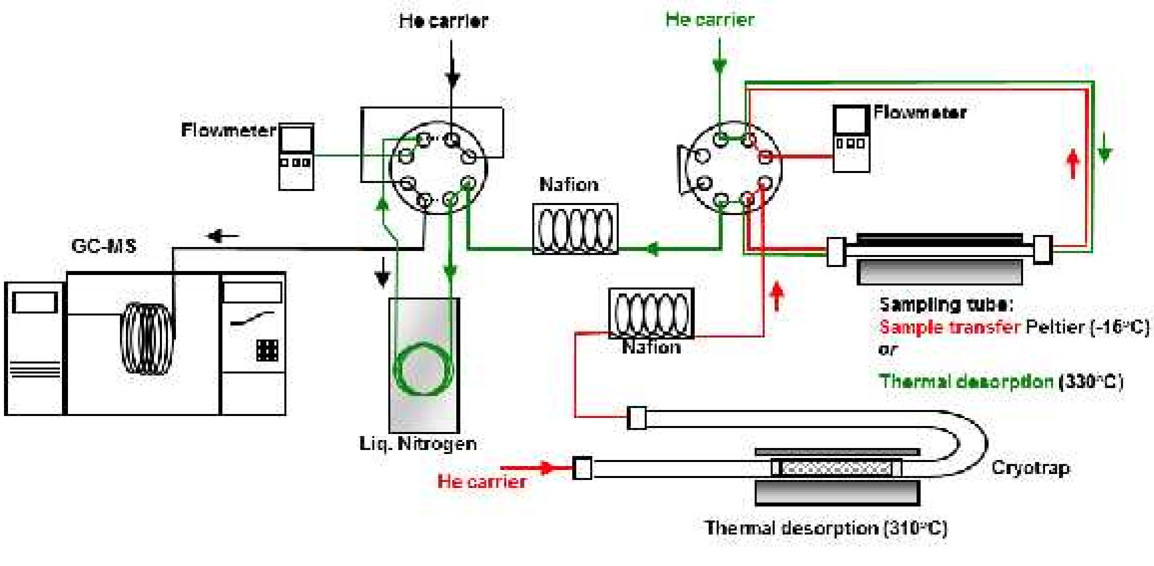


Fig. S1: Scheme of the analytical system for the determination of halocarbons from air and water samples.

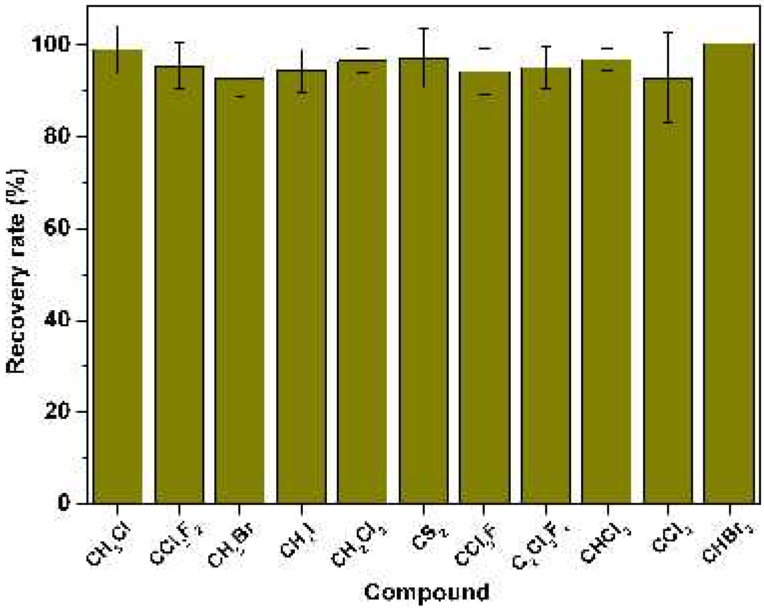
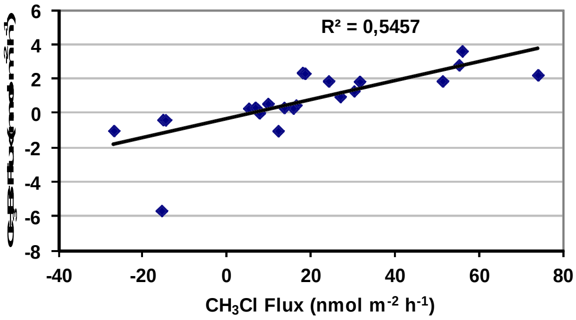
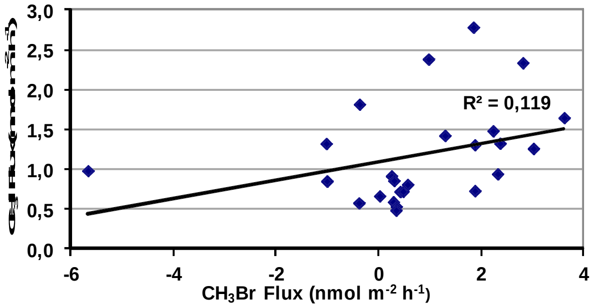


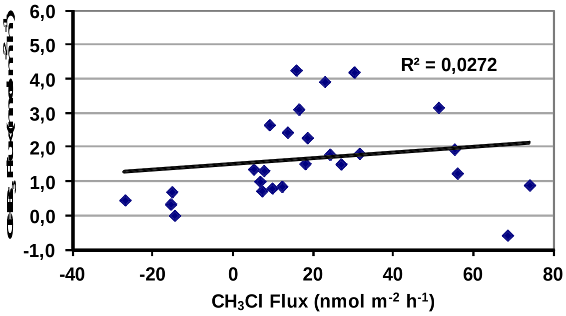
Fig. S2: Mean recovery rates and their absolute standard deviations of halocarbons from recovery experiments (n=4).

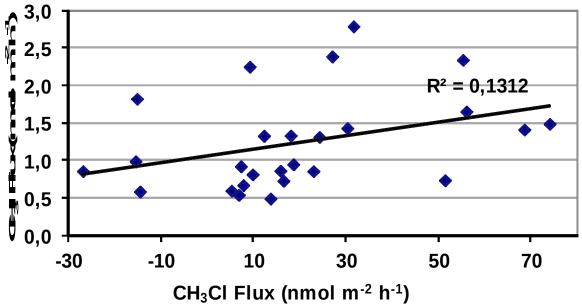
3 Correlation scatter plots of halocarbon fluxes from seagrass meadows

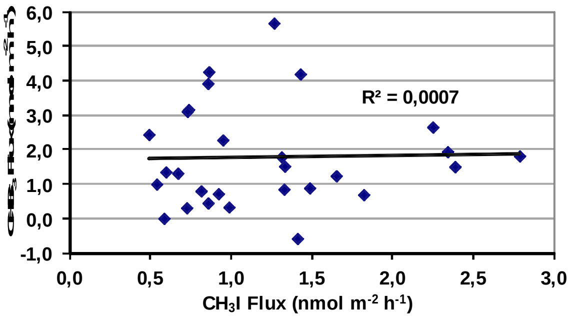
Correlation scatter plots of halocarbon fluxes from seagrass meadows during the summer campaign in 2011. Data refers to measurements obtained from air-exposed seagrass meadows.

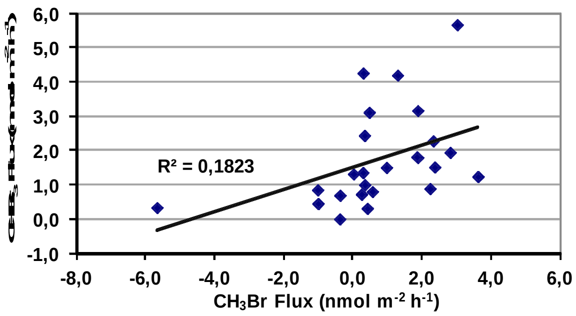




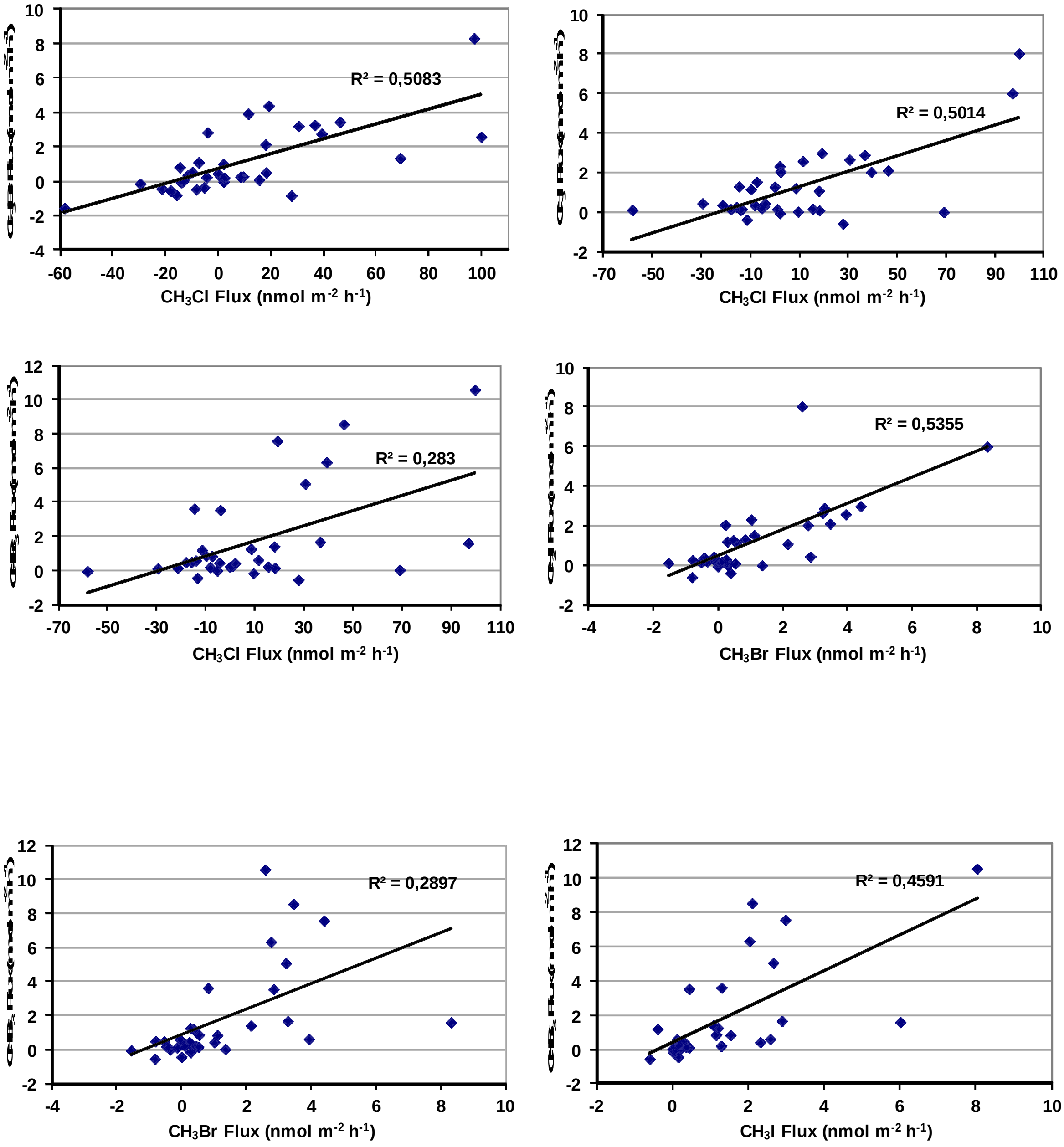




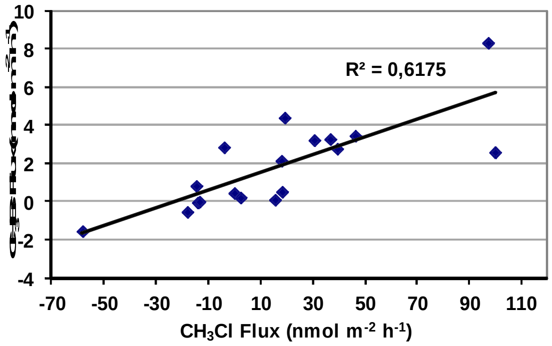


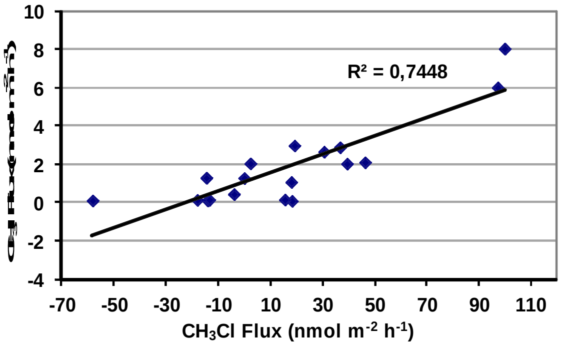


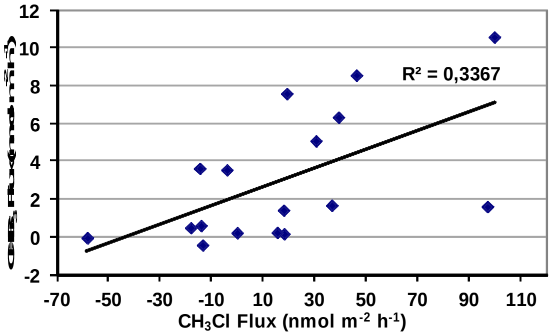
Correlation scatter plots of halocarbon fluxes from seagrass meadows during the spring campaign in 2012. Data refers to measurements obtained from air-exposed and submerged seagrass meadows.

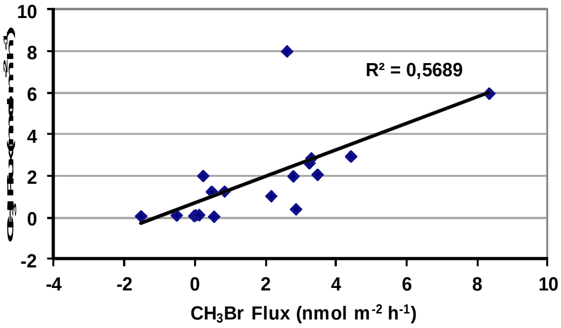


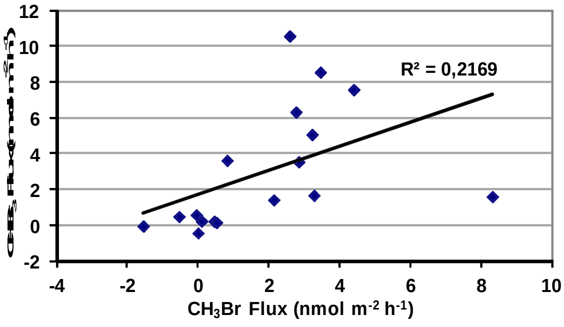
Correlation scatter plots of halocarbon fluxes from seagrass meadows during the spring campaign in 2012. Data refers to measurements obtained from submerged seagrass meadows, only.

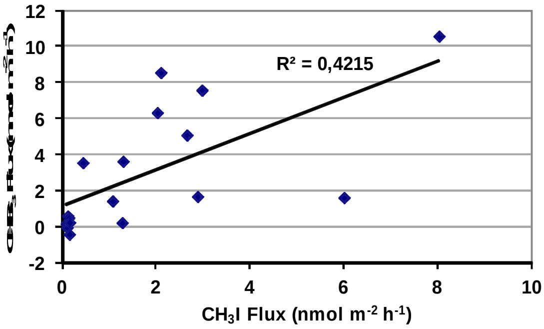




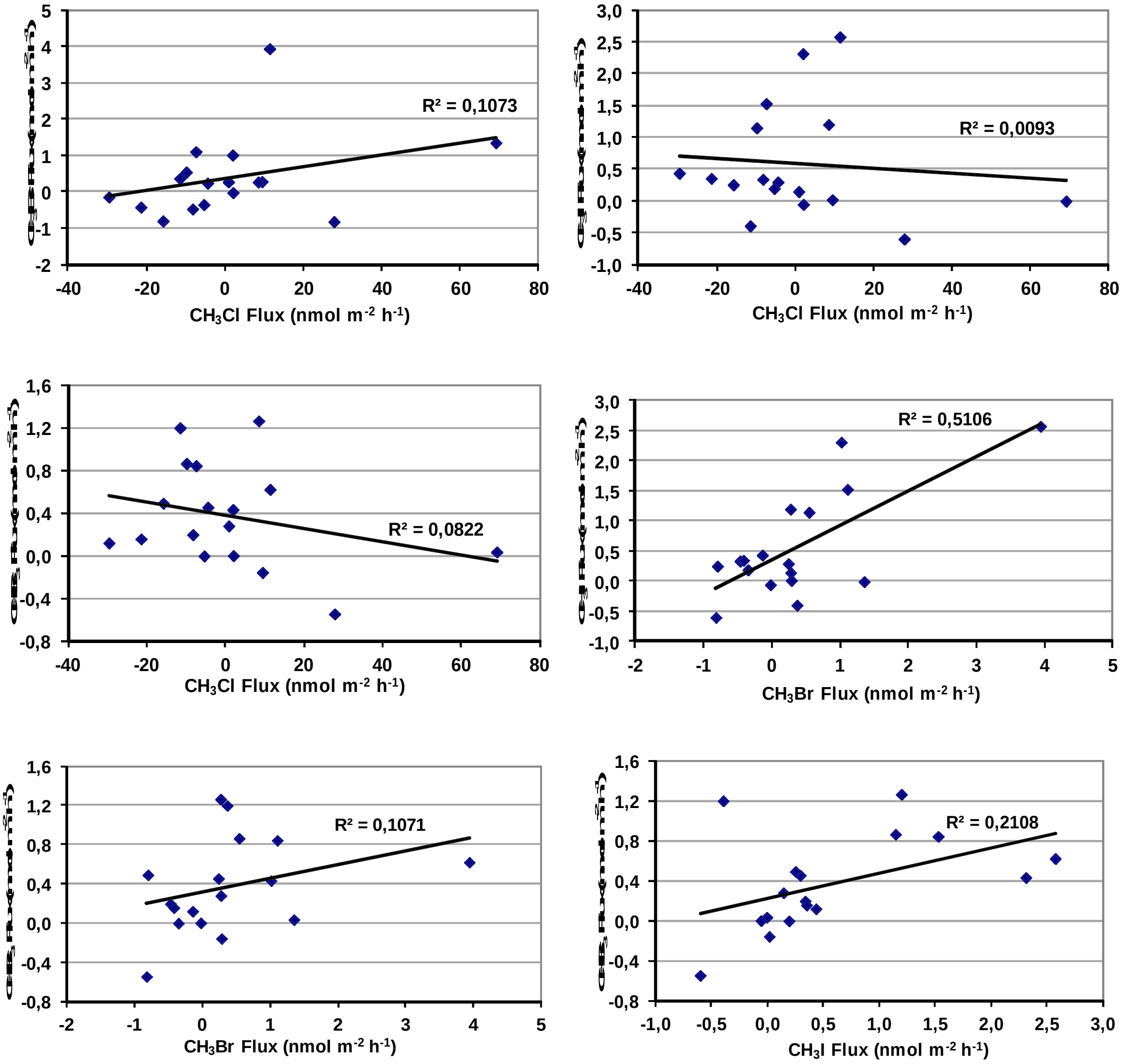








Correlation scatter plots of halocarbon fluxes from seagrass meadows during the spring campaign in 2012. Data refers to measurements obtained from air-exposed seagrass meadows, only.



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