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Supplement of

Large methyl halide emissions from south Texas salt marshes

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Supplementary Materials

S1 Groundwater measurements

In July (TX4), groundwater levels were monitored from a ~0.6 m × ~0.6 m square excavated to ~1 m depth. Groundwater properties were measured with a YSI 6600-V2 multi-parameter sonde at an adjacent location. The sonde was equipped with a flow cell and a peristaltic pump, which drew the groundwater from 60-100 cm depth through a stainless steel tube and elastic hose. In this outing, the groundwater table was measured at ~60 cm depth, changing with the tidal cycle with a substantial time lag compared to that of the bays. The groundwater at the *Batis maritima* sites was high in salinity (S > 58-66), slightly low in pH (~7.1) and nearly anoxic (O_2 < 0.3 mg/L). The intersected *B. maritima* roots were observed to reach near the boundary of the groundwater table.

S2 Stable isotope tracer technique

During the TX2 outing, a stable isotope tracer technique was applied to separate the net flux into the gross production and gross consumption components (Rhew et al., 2003; von Fischer and Hedin, 2002). Briefly, this technique involved injecting ^{13}C isotope tracers and the inert CFC-113 into the chamber headspace immediately after enclosure to yield initial concentrations of ~130 ppt ^{13}CH$_3$Br, 1500 ppt ^{13}CH$_3$Cl and 1500 ppt CFC-113. By monitoring the trends in ^{13}C-labeled methyl halides simultaneously with the ^{12}C methyl halides, it is possible to separate the net flux into the gross production and consumption components. Loss of the inert tracer F-113 was used to assess the advective and diffusive loss of the added compounds, while excess loss rates represented biological and chemical consumption. Changes in ^{12}CH$_3$X and ^{13}CH$_3$X concentrations were used to numerically determine best fitted values for the production rate 'P', uptake rate constant 'k'(min^{-1}) and initial chamber air concentrations. Full details of this method are described elsewhere (Rhew, 2011).

The stable isotope tracer technique revealed that for the beach sites, with and without *Sargassum*, gross consumption rates were very small: 13 ± 19 nmol m^{-2} d^{-1} for CH$_3$Cl and 1.0 ± 0.6 nmol m^{-2} d^{-1} for CH$_3$Br (note the smaller units of nmol instead of μmol). Gross consumption rates for the *B. maritima* sites were not observable because the very large production rates overwhelmed the isotope spike of ^{13}CH$_3$Br and ^{13}CH$_3$Cl. For example, if the gross consumption rates measured at the *Sargassum* sites were representative of *B. maritima* sites, then the gross production rates would be 30000 times the gross consumption rates (and production of ^{13}C methyl halides would be 300 times their consumption). Hence, the stable isotope tracer method was not used in subsequent outings, and we treated the net fluxes of methyl halides at *B. maritima* sites as representative of gross production.

S3 Calculating an integrated daily flux

To derive an integrated daily flux, the fluxes at each site were modeled by a cosine function during daylight hours, with steady emissions assumed at night (Rhew et al., 2002). A least-squares fit was applied to the measurements using the function below:

$$\theta = a + b\left(1 + \cos\frac{t\pi}{d/2}\right)$$ (Eq. S1)

In Eq. S1, θ represents the flux (units of μmol m^{-2} d^{-1}); a and b are fitted constants, where a is the nighttime baseline flux and b is the amplitude; t is the time difference (in hours) from 1 p.m., which was between maximum PAR and air temperature; and d is the approximate daytime length. For these calculations, d is taken as 16 hours, and nighttime is $24 - d$ hours. Using Eq. S1, the averaged diel flux may be calculated as $a + bd/24$.
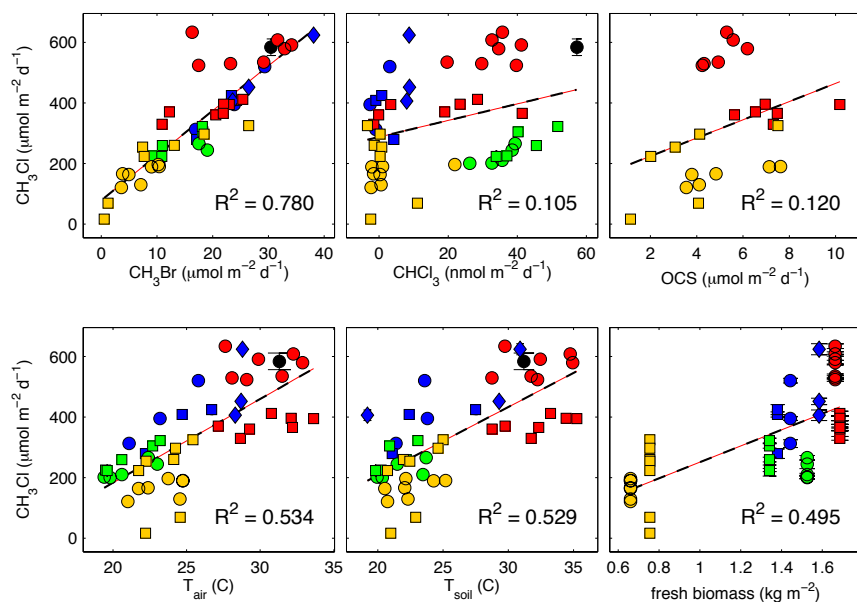
S4   Flux correlations

Figure S1. Net CH_3Cl flux correlations at *B. maritima* sites. Top row: net CH_3Cl flux versus net fluxes of CH_3Br, $CHCl_3$, and OCS. Bottom row: net CH_3Cl flux versus chamber air temperature, soil temperature (at 5 cm depth), and fresh weight biomass. The linear regression fit (dashed line) and coefficient of determination (R^2) are also shown. Colors represent the different outings, as in Figure 1: black = TX1 (April 2006), blue = TX2 (May 2008), green = TX3 (March 2009), red = TX4 (July 2009), and yellow = TX5 (November 2009). Different symbol shapes represent different sites within the outing.
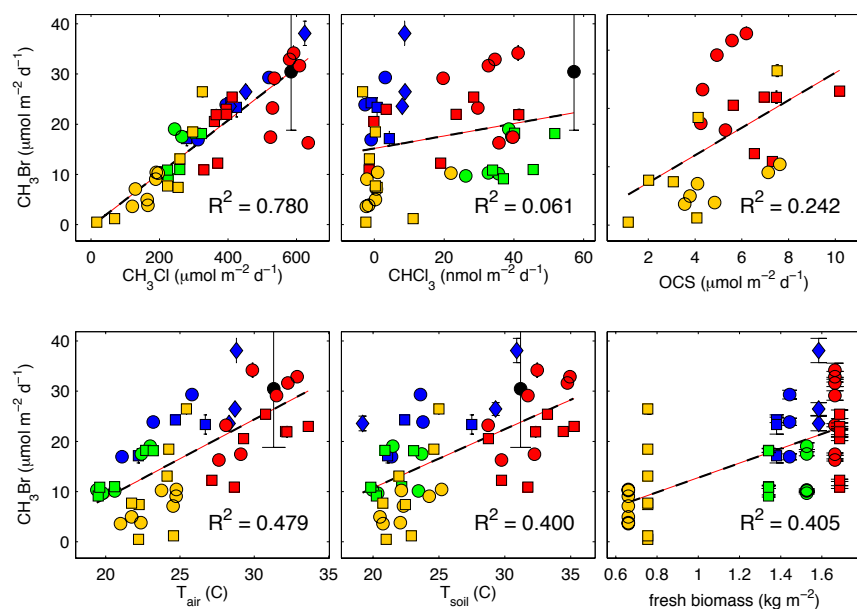

Figure S2. Net CH_3Br flux correlations at *B. maritima* sites. Top row: net CH_3Br flux versus net fluxes of CH_3Cl, $CHCl_3$, and OCS. Bottom row: net CH_3Br flux versus chamber air temperature, soil temperature (at 5 cm depth), and fresh weight biomass. See Figure S1 for the color and symbol coding.

S5 References for Supplementary Materials

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