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Large methyl halide emissions from south Texas salt marshes

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Abstract

Coastal salt marshes are natural sources of methyl chloride (CH_3Cl) and methyl bromide (CH_3Br) to the atmosphere, but measured emission rates vary widely by geography. Here we report large methyl halide fluxes from subtropical salt marshes of south Texas. Sites with the halophytic plant, *Batis maritima*, emitted methyl halides at rates that are orders of magnitude greater than sites containing other vascular plants or macroalgae. *B. maritima* emissions were generally highest at midday; however, diurnal variability was more pronounced for CH_3Br than CH_3Cl , and surprisingly high nighttime CH_3Cl fluxes were observed in July. Seasonal and intra-site variability were large, even taking into account biomass differences. Overall, these subtropical salt marsh sites show much higher emission rates than temperate salt marshes at similar times of the year, supporting the contention that low-latitude salt marshes are significant sources of CH_3Cl and CH_3Br .

1 Introduction

As atmospheric burdens of anthropogenic halocarbons decrease because of the Montreal Protocol, the relative importance of methyl halides for stratospheric ozone destruction increases. Methyl chloride (CH_3Cl) and methyl bromide (CH_3Br) are now the most abundant long-lived organochlorine and organobromine compounds, respectively (Montzka and Reimann, 2011). The atmospheric budgets of CH_3Cl and CH_3Br have large uncertainties arising from the fact that they have a multitude of major anthropogenic (e.g., biomass burning, fumigation use of CH_3Br , chemical feedstock use of CH_3Cl) and natural sources (e.g., oceans, terrestrial ecosystems), some of which are poorly characterized. In our current understanding of the CH_3Br budget, sinks outweigh the sources by about $30\text{--}35\text{ Ggyr}^{-1}$, or roughly $20\text{--}25\%$ of the total annual flux (Montzka and Reimann, 2011). This large “missing source” for CH_3Br is present in both pre-phaseout (1996–98) and current (2008) budgets and appears to be both

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natural and terrestrial in origin (Yvon-Lewis et al., 2009). The CH₃Cl budget may be balanced with a very large low-latitude terrestrial source (Xiao et al., 2010), and a few in situ studies of subtropical (Yokouchi et al., 2002, 2007) and tropical forests (Blei et al., 2010a; Saito et al., 2008) tentatively support this.

Coastal salt marshes have also been identified as globally significant sources of CH₃Cl and CH₃Br, with emissions associated with halophytic vascular plants. However, measured emissions show dramatic geographic variability, with large emissions from southern California (Manley et al., 2006; Rhew et al., 2002, 2000) and much smaller emissions from higher latitude sites in Tasmania, Australia (Cox et al., 2004), Scotland (Blei et al., 2010b; Drewer et al., 2006) and northern California (Rhew and Mazéas, 2010). Measurements from lower latitude salt marshes have not yet been reported. In this study, we characterize the magnitude and seasonality of CH₃Cl and CH₃Br emissions from subtropical salt marshes in southern Texas. Obtaining a wider latitudinal range of measurements from coastal salt marshes is essential to constrain their role in the global budget of methyl halides.

2 Site description

Five field outings were conducted between April 2006 and November 2009 at several salt marsh and coastal habitats on barrier islands in south Texas, USA off the Gulf of Mexico (Table 1). Sites were all located between 27 to 28° N and 97 to 98° W. All sites had sandy soils with elevations estimated at less than a meter above mean sea level. A total of 62 flux measurements were made at 24 individual sites from three different tidally influenced ecosystems.

The first field outing (TX1: 28 April 2006) took place on the southwestern shore of San Jose Island (27°52' N, 97°03' W), a sandy barrier island north of the city of Port Aransas. The goal of this initial outing was to survey emissions from predominant salt marsh plant species of the region: *Borrichia frutescens* (sea ox-eye daisy), *Avicennia*

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germinans (black mangrove), *Monanthochloe littoralis* (shoregrass) and *Batis maritima* (maritime saltwort).

The second field outing (TX2: 16–18 May 2008) occurred at three different locations: San Jose Island (see TX1, two *B. maritima* sites, both slightly inundated during sampling), Mustang Island beach (27°46' N, 97°6' W, six beached seaweed sites), and the Mollie Beattie Habitat Community on the back bay of Mustang Island (27°38' N, 97°12' W, one *B. maritima* site). The goal of this second outing was to determine the daytime range of fluxes from the three *B. maritima* sites; to measure emissions from pelagic seaweed (*Sargassum* spp.) deposited on the Gulf-side beach at different stages of decomposition; and to determine the simultaneous gross consumption and production rates of methyl halides at all of these sites using a stable isotope tracer technique.

The third, fourth and fifth outings (TX3, TX4 and TX5) were all at the Mollie Beattie habitat (see TX2 above), on the fringe of a small saltwater pond, which was tidally connected with saline groundwater (Text S1). The purpose of these outings was to capture the full diurnal (24 h) range of fluxes from a pair of *B. maritima* sites located within 20 m of each other. These diurnal studies were conducted at three different times of the year: the early growing season (TX3: 7–8 March 2009), the peak growing season (TX4: 19–20 July 2009), and the end of the growing system (TX5: 6–7 November 2009). TX5 occurred after a period of heavy rain, and many of the *B. maritima* leaves were shed on the ground. Also, between 1 a.m. and 11 a.m. during TX5, both sites were tidally inundated, with the shorter vegetation site mostly underwater during the 7:30 and 10.30 a.m. samplings.

Four vegetation-free control experiments were conducted: two beach sites after the removal of *Sargassum* (TX2), one salt marsh site with bare soil (TX4) and one salt marsh site inundated with 30 cm of tidal water (TX5).

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3 Methods

Gas fluxes were measured with static flux chambers consisting of two components: a collar (61 L, 0.264 m² footprint) placed in the wet sand > 2 cm depth and an insulated chamber lid (127 L) with a 1/4" stainless steel sample line used to withdraw air samples and two internal fans to mix the chamber air. All-aluminum chambers were used to limit reactivity with methyl halides, and dark chambers have been shown to yield similar methyl halide fluxes as light chambers in other salt marshes (Rhew and Mazéas, 2010). To initiate the enclosure period, the lid was placed into the water-filled channel on the rim of the base. Enclosure times were 30 min or less (30, 22–28, 20, 16 and 16 min for TX1–5, respectively), and three air samples were withdrawn from the chamber at equal time intervals. Samples were collected into previously evacuated 1 L electropolished stainless steel canisters (LabCommerce, San Jose, CA, USA) or 3 L fused silica lined canisters (Restek, Bellefonte, PA, USA). While sampling, a vent line was opened to equilibrate air pressure between inside and outside the chamber. In addition, ambient air samples were collected several times throughout each field campaign.

Air temperature (inside chamber and ambient air) and soil temperature (5 cm and 10 cm depth) were monitored with thermocouples (Omega Engineering Inc., Stamford, CT) during the first three outings and with stainless steel thermocouple data loggers (iButtons, Maxim Inc., Sunnyvale, CA, USA) for the last two outings. Soil moisture at 0–5 cm depth (ThetaProbe soil moisture sensor, Delta-T Devices, Cambridge, UK) and air pressure were monitored for each chamber experiment. For TX2–5, above-ground plant biomass was harvested, rinsed and drained before fresh weight was determined. Plants were then dried overnight at 65 °C to determine the dry weight. Meteorological data including PAR, air pressure and air temperature were also measured at the Mission-Aransas National Estuarine Research Reserve monitoring station at the East Copano Bay, TX, USA (<http://lighthouse.tamucc.edu/MissionAransas/HomePage>).

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Air samples were measured for halocarbons (CH_3Br , CH_3Cl and CHCl_3) by gas chromatography-mass spectrometry (GC/MS, Agilent 6890N/5973). Details regarding the inlet system, chromatography, gas standards, calibration procedures, and flux calculation methods are described elsewhere (Rhew, 2011). For consistency, all fluxes are reported in units of $\mu\text{mol m}^{-2} \text{d}^{-1}$ unless otherwise indicated, with negative values representing consumption rates and positive values representing production rates. Also, a stable isotope tracer technique was applied in the TX2 outing to separate the net flux into the gross production and gross consumption components (Text S2). All times are reported as US Central Standard Time (CST= GMT – 6 h).

4 Results

4.1 TX1: April 2006

Of the various vegetation sites sampled during TX1, the largest emissions by far were from the *B. maritima* site (Fig. 1), which emitted $580 \pm 30 \mu\text{mol m}^{-2} \text{d}^{-1} \text{CH}_3\text{Cl}$ and $30 \pm 12 \mu\text{mol m}^{-2} \text{d}^{-1} \text{CH}_3\text{Br}$. As a comparison, the largest reported emissions observed from a salt marsh previously were 570 and $42 \mu\text{mol m}^{-2} \text{d}^{-1}$, respectively (Rhew et al., 2002; Manley et al., 2006). The *A. germinans* site showed emissions < 0.5% of the *B. maritima* site, while the two *B. frutescens* sites and the *M. littoralis* site showed small to insignificant net emissions of CH_3Cl ($< 0.3 \mu\text{mol m}^{-2} \text{d}^{-1}$) and CH_3Br ($< 0.012 \mu\text{mol m}^{-2} \text{d}^{-1}$).

4.2 TX2: May 2008

In TX2, the three *B. maritima* sites showed large net emissions of methyl halides, comparable to TX1. Emission rates increased throughout the day (8:50 a.m. to 2:20 p.m. CST), although the sampling period was too short to fully assess diurnal trends. One site had a maximum flux of $620 \pm 20 \mu\text{mol m}^{-2} \text{d}^{-1} \text{CH}_3\text{Cl}$ and $39 \pm 2 \mu\text{mol m}^{-2} \text{d}^{-1}$

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CH₃Br, which at that point represented the largest CH₃Cl and second largest CH₃Br emission rate per unit area from a natural source yet observed.

The three freshly deposited *Sargassum* sites at the Gulf coast beach showed net emissions that were 3 orders of magnitude smaller than the *B. maritima* sites (Fig. 1 and Table 1). Three other sites of *Sargassum* that were visibly at a more advanced stage of decomposition and desiccation showed similar net emissions. When two of the *Sargassum* sites were cleared of seaweed and measured as control experiments on a bare sand surface, net emissions were an order of magnitude smaller still. Gross consumption rates measured with stable isotope tracers were negligibly small (Text S2).

4.3 TX3, TX4 and TX5: March, July and November 2009

The next three outings each captured the diurnal variability of CH₃Cl and CH₃Br fluxes over a 24 h period from a pair of *B. maritima* dominated sites (Fig. 2). The day/night differences in emissions were much more pronounced for CH₃Br than for CH₃Cl. For CH₃Br, the maximum daytime averages were 2.3 times greater than the nighttime averages ($n = 6$ sites), whereas the difference for CH₃Cl was 1.3 times. The molar ratio of CH₃Cl to CH₃Br fluxes also showed a day to night difference (Fig. 2), shifting from roughly 40 : 1 at night to 20 : 1 during the daytime.

Surprisingly, the maximum observed CH₃Cl emission flux in July ($630 \pm 10 \mu\text{mol m}^{-2} \text{d}^{-1}$) occurred in the middle of the night (1 a.m. CST). In fact, this represented the highest observed emission rate from all the outings, comparable to the highest flux from TX2. The lowest emissions were observed during November (TX5) during the morning at one site when the vegetation was almost entirely submerged by high tide. The other site also was submerged at the time, but had slightly more vegetation above the surface of the water.

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 (Fig. 2, Text S3). Of these three outings, the largest average diel emissions were in July (TX4) at $455 \pm 130 \mu\text{mol m}^{-2} \text{d}^{-1}$ for CH₃Cl and $22 \pm 5 \mu\text{mol m}^{-2} \text{d}^{-1}$ for CH₃Br. March emis-

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sions were roughly half of those, and November emissions were slightly lower than March (Table 1, Fig. 3). Even though nighttime measurements were not used in the model, the difference between the modeled to measured nighttime values was only $-4 \pm 11\%$ (or $-20 \pm 50 \mu\text{mol m}^{-2} \text{d}^{-1}$) for CH_3Cl and $5 \pm 22\%$ (or $1 \pm 2 \mu\text{mol m}^{-2} \text{d}^{-1}$) for CH_3Br . Thus the model was applied to the May (TX2) sites as well (Table 1).

5 Discussion

The predominance of *B. maritima* emissions over emissions from other measured plant and macroalgal species is similar to observations from southern California salt marshes, where *B. maritima* was one of the two largest emitters of methyl halides (Manley et al., 2006; Rhew et al., 2002). However, *B. maritima* sites from Texas generally showed much larger diel averaged emissions of CH_3Cl and CH_3Br than those from southern California, especially outside the peak summer growing season (Fig. 3). Even normalized by biomass, emission rates from Texas sites were ten times larger than Newport Bay California sites (monthly averages) (Manley et al., 2006).

The production of CH_3Cl and CH_3Br at *B. maritima* sites are related, as illustrated by a strong linear correlation (average slope of 15, $R^2 = 0.78$). These fluxes also showed moderate correlations with air temperature, surface soil temperature and biomass ($R^2 = 0.40$ to 0.53 , Figs. S1 and S2). Within individual outings, however, these environmental factors were poor predictors. For example, large flux differences were observed between two adjacent sites with similar biomass (e.g., TX4 and TX5) and could even show a slightly negative relationship (e.g., TX3). CH_3Cl and CH_3Br showed no correlation with net fluxes of chloroform and carbonyl sulfide (Whelan et al., 2013) that were measured simultaneously (Figs. S1 and S2).

The very large nighttime emissions in July when temperatures were also high suggest that temperature is a more proximate control on emission rates than insolation. This is consistent with studies in southern California (Rhew et al., 2002) and Scotland (Blei et al., 2010b), but contrasts with earlier studies in Scotland (Drewer et al., 2006)

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and Ireland (Dimmer et al., 2001). At another salt marsh site in southern California, Manley et al. (2002) found that *B. maritima* emissions were less correlated with either temperature or insolation compared to other plants. We suggest that for studies that use transparent chambers, the effect of insolation and temperature may be difficult to separate without monitoring leaf temperatures directly or actively regulating the temperature in the chamber. This does not discount the importance of insolation, which regulates seasonal changes in temperature and biomass.

The average $\text{CH}_3\text{Cl} : \text{CH}_3\text{Br}$ molar flux ratio of 22 ± 9 is slightly greater than southern and northern California salt marsh averages (7–17) (Manley et al., 2006; Rhew et al., 2002; Rhew and Mazéas, 2010) and is much higher than the ratios of 2 to 4 reported from higher latitude salt marshes (Blei et al., 2010b; Cox et al., 2004; Dimmer et al., 2001). This is consistent with the observation of Blei et al. (2010) that the salt marshes from more temperate climates (higher latitudes) generally have lower emission ratios. However, this is not a consequence of higher temperatures leading to higher ratios. At the Texas *B. maritima* sites, molar ratios did not dramatically shift with the seasons, and the molar ratios of emissions were higher at night (~ 40) and lower during the day (~ 20), opposite of the temperature trends (Fig. 2).

This diurnal trend in ratios is clearly related to the much larger diurnal variation in CH_3Br flux compared to CH_3Cl flux, as illustrated by the pronounced midday CH_3Br peak in this study (Fig. 2). Interestingly, this same trend in molar ratios was also observed in a San Diego salt marsh (Rhew et al., 2002), where it mirrored a diurnal shift in the carbon isotopic ratio ($\delta^{13}\text{C}$) of CH_3Cl and CH_3Br . In that study, carbon isotopic signatures were heavier at night (-50‰ CH_3Cl and -10‰ CH_3Br) compared to daytime (-70‰ CH_3Cl and -60‰ CH_3Br), with the isotopic shift much more pronounced for CH_3Br than CH_3Cl (Bill et al., 2002).

Two hypotheses were proposed to explain these diurnal trends of ratios and isotopic signatures (Bill et al., 2002; Rhew et al., 2002): (1) biogenic production dominates during the day, while soil consumption becomes more significant at night; and (2) two

different production mechanisms with different isotopic signatures and ratios of production occur simultaneously.

The first hypothesis could explain the lower overall net emission rates and heavier isotopic signatures at night (since consumption favors lighter isotopes (Miller et al., 2001)), but this study and others (Rhew and Mazéas, 2010) suggest that gross consumption is trivial in salt marshes compared to *B. maritima* production rates, even at night (Text S2). Also, gross consumption generally favors CH₃Cl uptake over CH₃Br by a molar factor of 30 to 40 (Rhew, 2011; Rhew and Mazéas, 2010), such that if nighttime consumption is important, the net emission ratio of CH₃Cl to CH₃Br should decrease at night, not increase.

The second hypothesis is supported by having two known production mechanisms of methyl halides from *B. maritima*: the enzymatically mediated methylation of halides (Ni and Hager, 1999; Wuosmaa and Hager, 1990) and an abiotic reaction between plant pectin and halides (Hamilton et al., 2003; Wishkerman et al., 2008). Because the abiotic mechanism yields a very light isotopic signature ($\delta^{13}\text{C}$ of -78‰ for *B. maritima*) (Keppler et al., 2004), a large abiotic increase during the daytime relative to enzymatic production could explain the isotopic shift. However, the CH₃Cl : CH₃Br molar ratio of production for the abiotic mechanism is also larger (45 to 58) (Wishkerman et al., 2008) than the predicted enzymatic production (20 to 1) (Rhew et al., 2002), which would yield a larger diurnal shift for CH₃Cl than CH₃Br, which is not observed.

An alternative hypothesis involves both a diurnal shift in the isotope signature of the carbon substrate used to produce methyl halides combined with a shift in methylation ratios of the halides. If production is predominantly biological, a diurnal shift in the $\delta^{13}\text{C}$ signature of the methyl donor (*S*-adenosyl-L-methionine) (Ni and Hager, 1999) and/or higher isotopic fractionation rates during the daytime could yield the observed isotopic signal. It is also possible that the abiotic production mechanism produces lighter $\delta^{13}\text{C}$ methyl halides at higher temperatures, but the carbon source for abiotic production comes from structural components of a plant that are not necessarily expected to have diurnal variation in $\delta^{13}\text{C}$ (Keppler et al., 2004). The other half of this hypothesis in-

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volves the Cl/Br ratios in the plant changing during the day. Bromide is preferentially halogenated by both biotic and abiotic mechanisms relative to their availability (Ni and Hager, 1998; Wishkerman et al., 2008) and may be replenished during the day and depleted at night, perhaps in conjunction with transpiration rates. However, such diurnal variations in plant biochemistry have not yet been measured.

The Texas salt marsh fluxes measured over several months strongly suggest a seasonality of fluxes. Assuming that the seasonality can be characterized with a sinusoidal fit to the diel averaged data (Fig. 3) and that these measurements are temporally and spatially representative, we derive an estimated annual flux of $92 \text{ mmol m}^{-2} \text{ yr}^{-1}$ for CH_3Cl and $4.7 \text{ mmol m}^{-2} \text{ yr}^{-1}$ for CH_3Br . These annual values are 2 to 3 times larger than those estimated for the *B. maritima* sites in Upper Newport Bay ($28 \text{ mmol m}^{-2} \text{ yr}^{-1}$ for CH_3Cl and $2.4 \text{ mmol m}^{-2} \text{ yr}^{-1}$ for CH_3Br) (Manley et al., 2006).

The surface area coverage of *B. maritima* in Texas salt marshes was not quantified for this study. In Newport Bay, California, *B. maritima* covered 10% of the entire salt marsh area (including barren areas) and 18% of the vegetated area (Manley et al., 2006). For the purpose of comparison, we will assume that these Texas salt marshes have the same *B. maritima* coverage and that the remaining 82–90% of salt marsh has negligible emission rates. Spatially averaged emissions for the entire salt marsh are then estimated at 9–17 and $0.47\text{--}0.84 \text{ mmol m}^{-2} \text{ yr}^{-1}$ for CH_3Cl and CH_3Br , respectively. These fluxes are slightly greater than those reported from Newport Bay salt marshes (3–8 and $0.2\text{--}0.7 \text{ mmol m}^{-2} \text{ yr}^{-1}$ for CH_3Cl and CH_3Br , respectively, with the range representing total area and only vegetated areas), which have other large emissions associated with *Frankenia grandifolia* (Manley et al., 2006). However, these rates are one to two orders of magnitude greater than annually averaged salt marsh fluxes in Scotland ($0.11 \text{ mmol m}^{-2} \text{ yr}^{-1}$ for CH_3Cl and $0.03 \text{ mmol m}^{-2} \text{ yr}^{-1}$ for CH_3Br) (Blei et al., 2010b; Drewer et al., 2006). The Scotland salt marsh fluxes are similar in magnitude to other high latitude salt marshes, including Tasmania, Australia (Cox et al., 2004) and northern California (Rhew and Mazéas, 2010).

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Collectively, these studies show that methyl halide emissions from coastal salt marshes have a strong climatic dependence, with small emissions at higher latitudes and large emissions at lower latitudes. This climatic dependence may be related to both temperature (higher temperatures yield faster enzymatic and abiotic production rates of methyl halides) and insolation (greater photosynthesis rates lead to greater biomass and production of secondary metabolites used in methyl halide production). *B. maritima* alone may be responsible for globally significant amounts of methyl halides, as it is an evergreen succulent shrub found widely in tropical and subtropical salt marshes, brackish marshes and mangrove swamps ranging from northern Brazil (3° S) to South Carolina (33° N) (Lonard et al., 2011). A major uncertainty involves the spatial distribution and global coverage of coastal wetlands, with 2.2–40 Mha of tidal marsh and 13.8–15.2 Mha of mangroves (Pendleton et al., 2012). As an illustrative exercise, if *B. maritima* or similarly emitting plants cover 10 % of the surface area of tidal marshes and mangroves, and if averaged emissions are as calculated here, then this subset of salt marsh vegetation would contribute 30–90 Gg CH₃Cl and 3–9 Gg CH₃Br per year. Deriving a more accurate global source strength will require a much broader geographic distribution of measurements, along with better estimates of ecosystem surface areas and plant distributions. Clarifying the importance of coastal salt marsh vegetation in the global budgets of CH₃Cl and CH₃Br will require further measurements at low latitude salt marsh sites.

6 Conclusion

Large emissions of CH₃Cl and CH₃Br were observed from subtropical salt marshes located on the Gulf coast of Texas. These large emissions were associated with *B. maritima*, a widespread succulent salt marsh plant that was also observed to be a large emitter in southern California salt marshes. However, *B. maritima* emission rates in this study were 2 to 3 times larger than those reported from California, and spatially averaged emission rates from Texas salt marshes were much larger overall than those

reported from higher latitude salt marsh sites. Diurnal trends in CH₃Cl and CH₃Br emission rates, along with their ratio of emissions, were similar to those observed in southern California salt marshes. To derive a better estimate of the global salt marsh contribution to the atmospheric budgets of the methyl halides, more information is needed about the spatial extent, vegetation cover and methyl halide emission rates from low latitude salt marsh sites.

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Table 1. Field conditions and predominant vegetation at Texas coastal field sites.

Outing/date: (dd/mm/yy) Enclosed species	Location <i>n</i>	Net flux ($\mu\text{mol m}^{-2} \text{d}^{-1}$)		Modeled diel flux ¹		<i>Batis</i> biomass	
		CH_3Cl	CH_3Br	CH_3Cl	CH_3Br	kg m^{-2} fresh	kg m^{-2} dry
TX1: 28/04/06	San Jose Island						
<i>Batis maritima</i>	1	584 ± 27	30 ± 12	–	–	n.d.	n.d.
<i>Avicennia germinans</i>	1	1.8 ± 0.4	0.023 ± 0.010	–	–	–	–
<i>Various</i> ²	3	≤ 0.2	≤ 0.02	–	–	–	–
TX2: 16/05/08–18/05/08	San Jose Island, Mustang Island Beach and Mollie Beattie						
<i>B. maritima</i> (site A) ³	3	409 ± 115	23 ± 5	296	16	1.44	0.25
<i>B. maritima</i> (site B) ³	3	371 ± 80	22 ± 4	230	15	1.38	0.23
<i>Sargassum</i> (fresh)	3	0.56 ± 0.55	0.029 ± 0.027	–	–	–	–
<i>Sargassum</i> (decaying)	3	0.84 ± 0.72	0.030 ± 0.014	–	–	–	–
Sand (beach)	2	0.04 ± 0.02	0.004 ± 0.003	–	–	–	–
<i>B. maritima</i> (site C)	3	494 ± 115	29 ± 8	287	16	1.58	0.30
TX3: 07/03/09–08/03/09	Mollie Beattie						
<i>B. maritima</i> (site A)	5	220 ± 30	13 ± 5	222	13	1.52	0.28 ⁴
<i>B. maritima</i> (site B)	5	270 ± 40	13 ± 4	266	13	1.34	0.24 ⁴
TX4: 20/07/09–21/07/09	Mollie Beattie						
<i>B. maritima</i> (site A)	7	571 ± 43	27 ± 7	547	25	1.66	0.31
<i>B. maritima</i> (site B)	7	374 ± 28	20 ± 6	362	18	1.68	0.29
Sand (marsh)	1	–0.073 ± 0.061	0.004 ± 0.002	–	–	–	–
TX5: 06/11/09–07/11/09	Mollie Beattie						
<i>B. maritima</i> (site A) ³	7	165 ± 30	7.0 ± 2.9	156	6	0.66	0.13
<i>B. maritima</i> (site B) ³	7	207 ± 117	10.7 ± 9.4	265	11	0.75	0.13
Saltwater (marsh) ³	1	2.40 ± 0.07	0.037 ± 0.001	–	–	–	–

¹ Modeled diel flux ($\mu\text{mol m}^{-2} \text{d}^{-1}$) based on daytime measurements.

² *Borrhchia frutescens* and *Monanthonchloe littoralis*.

³ Soil surface covered with water for some or all measurements.

⁴ Vegetation H₂O estimated as 81.9% based on average of other outings.

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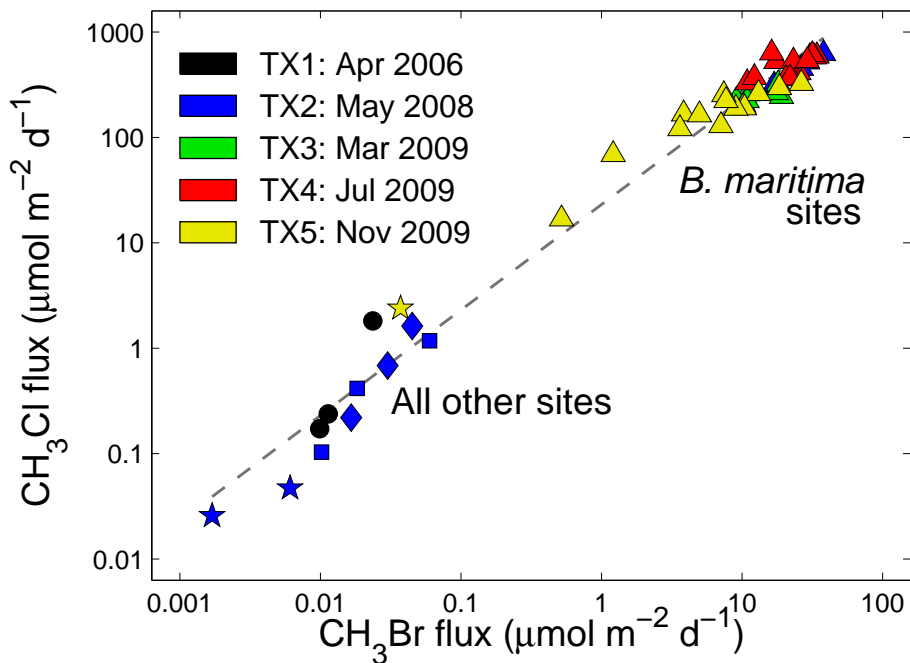


Figure 1. Net fluxes of CH_3Cl and CH_3Br for all field sites in south Texas. Triangles = *B. maritima*; squares = fresh *Sargassum*; diamonds = decaying *Sargassum*; circles = other vegetation (*M. littoralis*, *A. germinans*, *B. frutescens*), stars = vegetation-free control. Note the log-log scale. The gray dashed line shows the overall average 23 : 1 molar ratio. Two chambers that had small negative fluxes are not included.

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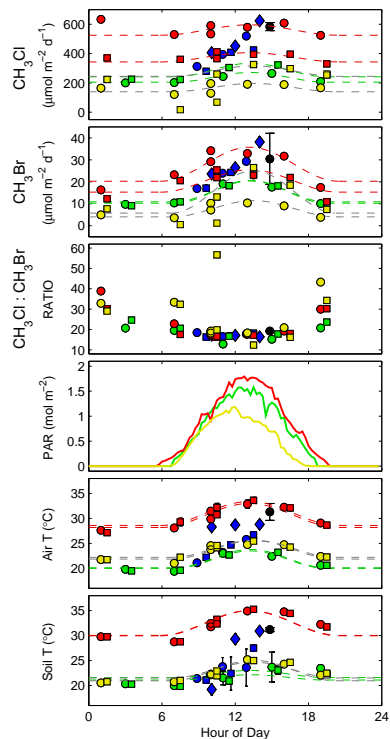


Figure 2. Net fluxes of CH_3Cl , net fluxes of CH_3Br , the CH_3Cl to CH_3Br flux ratio, photosynthetically active radiation (PAR), chamber air temperature and surface soil temperature at *B. maritima* sites vs. time of day (Central Standard Time). Colors represent different outings, as in Fig. 1; different symbols (circles, squares, diamonds) represent different sites at the same outing. The dashed lines represents the model fit to TX3–5 (March, July, and November) results. PAR is a 15 min interval measurement averaged over the two days of each field outing.

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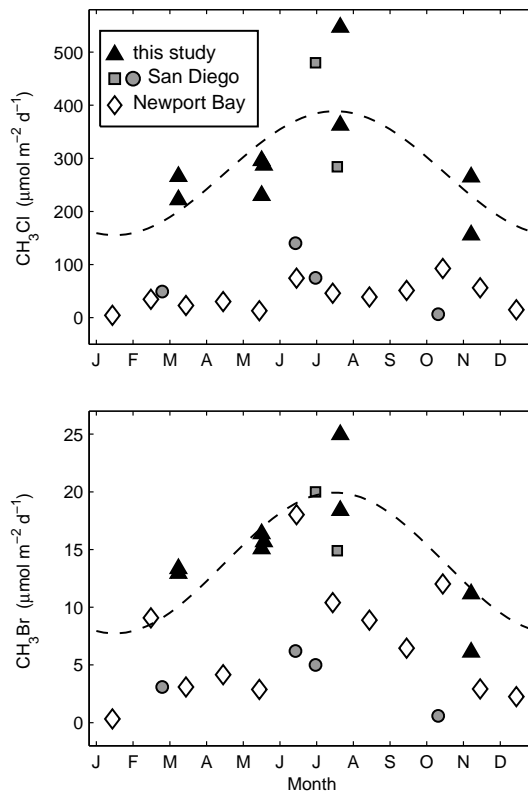


Figure 3. Comparison of *B. maritima* methyl halide emissions from three coastal salt marshes. This study (black triangles) shows diel averages. The San Diego, California sites show diel averages (gray squares) at two *B. maritima* sites and daytime fluxes (gray circles) at mixed *B. maritima*/*Salicornia bigelovii* sites (Rhew et al., 2000, 2002). The Upper Newport Bay, California sites (white diamonds) show daytime fluxes of monospecific *B. maritima* sites (Manley et al., 2006). The dashed line is a sinusoidal curve fit to the Texas data.