Large methyl halide emissions from south Texas salt marshes
R.C. Rhew, M.E. Whelan, and D.-H. Min
bg-2014-233 Submitted on 24 Apr 2014

RESPONSE TO REVIEWER #1

We appreciate the thoughtful and supportive review by Reviewer #1, who summarized the key findings and context of the manuscript concisely. We address first the general critique provided by Reviewer #1 regarding the limitations to the dataset, and then we address the 4 more specific comments below.

The reviewer notes that the number of field site visits were limited (the 62 flux measurements were from five field outings) and spread out over a period of several years. We acknowledge that higher frequency sampling over a shorter period of time would have provided a more continuous and complete picture of the seasonal trends in emissions. The sampling strategy in this study was a balance between addressing specific scientific questions and working within logistical constraints. The goals of the sampling strategy were at first to provide a survey of emissions from dominant plants and macroalgae, and then to characterize the diurnal cycle of emissions from the dominant emitting plant (*Batis maritima*). The key logistical constraint was that this project did not have any dedicated funding associated with it, and the field outings were undertaken when the collaborators could generate enough resources and time to conduct the measurements. The field site was nearly 3000 km away from the laboratory where the air samples were measured.

We ruefully acknowledge the tardiness in the preparation of this manuscript, when the last set of field measurements were undertaken over 4 years ago. In the intervening time, though, it became clearer how this work fit in the context of the rest of the literature on terrestrial methyl halide emissions, and we hope this discussion enhances its value.

Specific comments:

(1) Section 3: It is stated that the temperature inside the enclosures were measured but results are discussed in terms of outside ambient temperature. Would it not be appropriate to examine relationships with the actual temperature experienced within the enclosure?

Emission rates actually are compared with chamber air temperature, not ambient temperature (see captions in Figures 1 and S1). An omission in our text is likely the source of this confusion. We have now changed 'air temperature' to 'chamber air temperature' in the second paragraph of the discussion.

(2) P9457, L17 and P9458, L16: In the Discussion it is stated that molar ratio between CH_3Cl and CH_3Br emissions is ~15 on average, whilst in section 4.3 it is stated that the molar ratio is roughly 40 during the day and 20 at night. The statements in the two sections do not appear to be consistent with each other.

The linear regression of CH_3Cl vs CH_3Br fluxes has a slope of 15, but that allows a non-zero y-intercept. This slope would be greater if forced through zero (i.e., a weighted average of the ratios). Because the purpose of the linear regression was to show correlation, we removed the non-essential slope value from the text. We agree that it was unclear.

(3) P9459, L10-13: Two sentences seem to repeat here. The end of the first sentence indicates that the CH_3Cl:CH_3Br molar flux ratio is lower at higher latitude salt marshes, and the next sentence says the same thing. Please reword appropriately.

We have removed the redundant '(higher latitudes)' from the second sentence.

(4)Technical: P9459, L12: The in-text citation here should read Blei et al. (2010b). P9463, L13: The University of Texas MSI contribution number is missing.

These revisions will be incorporated. The MSI contribution # (1681) is added.

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RESPONSE TO REVIEWER #2
We appreciated the detailed comments and positive review by Reviewer #2. Responses to specific comments appear below.

1. The authors suggest that depletion of bromine and chlorine in Batis maritima could explain the diurnal changes in methyl bromide to methyl chloride emission ratios from this plant species. It seems reasonable that this will only have a significant effect on emission ratios if the amount of emitted bromine and chlorine makes up a large proportion of these stores. This should be testable to some extent: The authors could, if they have the resources and equipment, measure the chlorine and bromine content of Batis maritima tissues or as an easier way they can use literature values. The chlorine and bromine content values for Salicornia europea published in Blei et al. 2010b seem suitable, but the authors should look also for other sources as well.

We thank the reviewer for this excellent idea. Because we no longer have the plant samples to conduct halide concentration measurements, we used halide content values from the literature, as the reviewer suggested. The most relevant values were those from *Batis maritima* by Manley *et al*. 2006, but it should be noted that similarly high values were found in other succulent salt marsh plants, including *Salicornia virginica* in southern California (240 mg g^{-1} for Cl^- and 3700 ug g^{-1} for Br^-, Manley et al., 2006) and *Salicornia europea* in Scotland (192 ug g^{-1} for Cl^{-1} and 782 ug g^{-1} for Br^-, Blei et al., 2010b). In the discussion, we replaced "However such diurnal variations in plant biochemistry have not yet been measured" with the following:

However, the amount of chloride and bromide that is volatilized daily via methyl halide emission is not large enough to substantially change the overall Cl^- and Br^- content in plant tissue. In this study, the biomass normalized diel emission rates of CH_3Cl and CH_3Br were 1.25 ± 0.40 µmol $gdwt^{-1}$ d^{-1} and 0.062 ± 0.014 µmol $gdwt^{-1}$ d^{-1}, respectively (n=9 sites). If we assume that the *B. maritima* tissue halide contents are similar to those measured in southern California *B. maritima* plants (210 mg g^{-1} for Cl- and 2900 ug g^{-1} for Br- (Manley et al., 2006)), then we estimate that roughly 0.02% of Cl and 0.2% Br in the leaf tissue is removed daily via methyl halide emissions. Thus, to impact halide availability, there would need to be a small segregated subset of 'active' halides at the enzyme site. If this 'active' halide pool was 0.5% of the overall tissue content, then the methyl halide emissions could reduce that pool by 4% for Cl and 34% for Br daily. This would lead to an increased CH_3Cl to CH_3Br emission ratio, until the halide levels were replenished. A subset of 'active' halides in the cytoplasm of plant cells is implied by Ni and Hager (1998, 1999), who proposed that the function of halide methyltransferase is to dispose of excess chloride to regulate internal concentrations. "

2. One sticking point in the methodology is the relative small number of measurements. As the diurnal studies were carried out only on two locations three times over the course of a year there is a good chance that other influences such as changes in the influence of salt water vs rainwater, unusual cold and anything else could easily skew any findings in regards to annual emission patterns.

This study included 62 flux measurements from 24 individual sites from 3 coastal ecosystems. Additional measurements would have been desirable, but logistical issues limited the sampling frequency (see response to referee #1). It is indeed very possible that uncommon weather or tidal patterns could skew the emissions and hence interpretation of results. We note that the meteorological conditions for first four outings (TX1-4) were not climatically unusual (http://lighthouse.tamucc.edu/MissionAransas/HomePage). In the winter outing (TX5), when emission rates were already low, tidally inundation of the sites during the latter half of the measurement period clearly suppressed emission rates. This was noted in the Results section. We explicitly stated our assumptions in the extrapolations, and we now have added the following statement to the discussion: "Sampling over the full

range of environmental conditions at this field site would provide a more accurate representation of the annual flux."

While we entirely agree that more sampling would have provided a more accurate assessment of emissions, we also believe that the fundamental observation of very large methyl halide emissions from these Texas salt marshes was validated, with repeatedly high emission rates being observed (Figure 2), especially in comparison with literature values (Figure 3).

3. The level of uncertainty of methyl bromide fluxes presented in Figure 2 is very large compared to the measured changes in these fluxes. Either the statistics you present with the error bars is overly conservative or the information extracted from these measurements has little meaning. It seems difficult to have confidence in a cosine function if a straight line would fit these data just as well (when taking the uncertainty range into account).

In Figure 2, there is only one flux measurements has large enough error bars to be visible, and that error bar (from TX1) is not meant to be representative of the other sites. We added to the methods a description of the flux errors: "Net flux errors are calculated by propagating the error associated with estimating the number of moles of air in the chamber with the standard error on the slope of the linear regression of the concentration change versus time". And in Figure 2 caption: "Error bars that are smaller than the symbols are not shown."

4. Enclosure times of 16 to 30 minutes seem quite long. From previous experience I know that the concentration build-up inside the chamber can heavily skew the flux data to appear lower than they really are. This would be even more of a concern at such high emission levels. Could you outline (either in the publication or as an answer for the referee's benefit) how you derived the fluxes at time "0"?

Concentration dependent feedback effects include include first-order (or pseudo first order) consumption rates, chamber leakage, and reduction of diffusion from the leaves. These effects would manifest themselves through a nonlinear concentration trend in the chamber concentrations, something we would observe in the three air measurements taken over the enclosure period. To address potential feedback effects, we approached this issue in two ways.

First, we calculated the R^2 of the linear regression for all of our plots. For the *Batis maritima* sites, the fits were highly linear, with R^2 values averaging 0.997 for CH_3Cl and 0.995 for CH_3Br. At this point, we should note that all *B. maritima* enclosures were actually 16-22 minutes, except for one (during TX1), which was 30 minutes long. Not surprisingly, the TX1 site had by far the poorest fit (R^2 = 0.958 for CH_3Br) and spurred the 27-47% reduction in enclosure time thereafter. All the flux measurements with 28 or 30 minute enclosures were at lower emitting sites with different plants or macroalgae enclosed.

Second, we quantified the error on the flux, using the standard error on the slope of the linear regression. We propagated this error with the chamber volume error (which itself is propagated from errors in chamber depth, air temperature, and air pressure during the sampling period) to determine the overall net flux error. As noted above, these errors are very small relative to the observed fluxes of *Batis maritima*, except for the one TX1 measurement.

In the revised manuscript, we add this detail in the text instead of only citing the reference:
"Concentration trends were calculated using a linear regression of the chamber air concentration versus time, with goodness of fit assessed both by R^2 and the standard error on the slope. For the *Batis maritima* sites, for example, R^2 values averaged 0.997 for CH_3Cl and 0.995 for CH_3Br. Net fluxes were calculated by multiplying this slope with the moles of air in the chamber, divided by the enclosed surface area; net flux errors were calculated by propagating the errors of each of these components."

5. In the first paragraph on page 9459 the authors discuss the possible effect of local leaf temperatures on emission rates in transparent chambers. It would be helpful to know what the leaf temperatures of naturally insolated Batis

maritima vegetation growing outside of a chamber is. Afterall this would be the natural state of a plant and would be valuable information for possible modelling efforts.

We agree that it would be helpful and interesting to know the leaf temperatures of naturally insolated *Batis maritima*. We have not determined a standardized method to do so, given the range of insolation within a single patch of vegetation. This is something to consider for future studies, especially those conducted at the leaf level. We change the word "regulating" to "modulating" here.

6. Without wanting to go into a discussion on the merits of transparent vs opaque chambers I would like to query how the authors on page 9462 suggest that higher photosynthetic rates might lead to higher concentrations of secondary metabolites. With little doubt higher insolation will generally lead to higher biomass yields and therefore have an indirect positive effect on emissions. However, the data published here are from dark chambers which cannot prove or disprove that secondary metabolites derived from photosynthesis might not directly affect emissions as there is no photosynthesis in opaque chambers.

We think it is valid to question the assumption that higher photosynthetic rates might lead to higher concentrations of secondary metabolites, which would then be available for metabolism during dark periods. We do not have direct evidence of this, so we edit the statement to emphasize the indirect effect (one that the reviewer also notes):

"greater photosynthesis rates lead to greater biomass, with associated increases in relevant secondary metabolites and enzymes"

ADDITIONAL CORRECTIONS MADE DURING PROOFS STAGE

Text
Page 6, Line 13: Please change "(triangles in Fig. 1)" to "(Fig. 1)"

References:
Pg 14, Line 31: "Plos One" should be "PLoS ONE"
Pg 14, Line 31: missing doi: 10.1371/journal.pone.0043542
Pg 15, Line 6, missing doi: 10.1029/2010GL044341
Pg 15, Line 16: missing doi: 10.1016/j.atmosenv.2013.02.048
Pg 15, Line 19: The 'E' should not be capitalized in the doi: "10.1021/es800411j"

Table 1:
3rd line where it says "San Jose Island fresh dry": The terms "fresh" and "dry" refer to fresh and dry biomass and do not belong here. These terms should go under the two Batis biomass columns, underneath each "kg m-2" label.

Page 6, line 22: "2.20" should be "2:20" (colon instead of period)
Page 8, line 17: a comma is needed between "air temperature" and "surface soil temperature".

Large methyl halide emissions from south Texas salt marshes

R. C. Rhew[1], M. E. Whelan[1,*], and D.-H. Min[2]

[1]{University of California at Berkeley, Dept of Geography, Berkeley, CA 94720, USA}

[2]{The University of Texas at Austin, Marine Science Institute, Port Aransas, TX 78373, USA}

[*]{now at: University of California, Merced, Sierra Nevada Research Institute, Merced, CA, 95343, USA}

Correspondence to: R. C. Rhew (rrhew@berkeley.edu)

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 30-35 Gg yr^{-1}, or roughly 20-25% 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 natural and terrestrial in origin (Yvon-Lewis et al., 2009). The CH_3Cl 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; Yokouchi et al., 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 CH_3Cl and CH_3Br, 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; Rhew et al., 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 CH_3Cl and CH_3Br 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: April 28, 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 germinans* (black mangrove), *Monanthochloe littoralis* (shoregrass) and *Batis maritima* (maritime saltwort).

The second field outing (TX2: May 16-18, 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 hour) range of fluxes from a pair of *B. maritima* sites located within 20 meters of each other. These diurnal studies were conducted at three different times of the year: the early growing season (TX3: March 7-8, 2009), the peak growing season (TX4: July 19-20, 2009), and the end of the growing system (TX5: November 6-7, 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).

3 Methods

Gas fluxes were measured with static flux chambers consisting of two components: a collar (61L, 0.264 m^2 footprint) placed in the wet sand > 2 cm depth and an insulated chamber lid (127 L) with a ¼" 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 minutes or less (30, 22-28, 20, 16 and 16 minutes 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).

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 and calibration procedures are described elsewhere (Rhew, 2011). Concentration trends were calculated using a linear regression of the chamber air concentration versus time, with goodness of fit assessed both by R^2 and the standard error on the slope. For the *B. maritima* sites, for example, R^2 values averaged 0.997 for CH_3Cl and 0.995 for CH_3Br. Net fluxes were calculated by multiplying this slope with the moles of air in the chamber, divided by the enclosed surface area; net flux errors were calculated by propagating the errors of each of these components. For consistency, all fluxes are reported in units of μmol m^{-2} 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

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gross production and gross consumption components (**Text S2**). All times are reported as U.S. Central Standard Time (CST= GMT – 6 hours).

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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 (triangles in **Fig. 1**), which emitted 580 ± 30 µmol m^{-2} d^{-1} CH_3Cl and 30 ± 12 µmol m^{-2} d^{-1} CH_3Br. As a comparison, the largest reported emissions observed from a salt marsh previously were 570 and 42 µmol m^{-2} 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 µmol m^{-2} d^{-1}) and CH_3Br (<0.012 µmol m^{-2} 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 ± 20 µmol m^{-2} d^{-1} CH_3Cl and 39 ± 2 µmol m^{-2} d^{-1} CH_3Br, which at that point represented the largest CH_3Cl and second largest CH_3Br 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 that 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 CH_3Cl and CH_3Br fluxes over a 24 hour period from a pair of *B. maritima* dominated sites (**Fig. 2**). The day/night differences in emissions were much more pronounced for CH_3Br than for CH_3Cl. For CH_3Br, the maximum daytime averages were 2.3 times greater than the nighttime averages (n=6

sites), whereas the difference for CH_3Cl was 1.3 times. The molar ratio of CH_3Cl to CH_3Br 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 CH_3Cl emission flux in July (630 ± 10 µmol m^{-2} 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 ± 130 µmol m^{-2} d^{-1} for CH_3Cl and 22 ± 5 µmol m^{-2} d^{-1} for CH_3Br. March emissions 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 ± 11% (or -20 ± 50 µmol m^{-2} d^{-1}) for CH_3Cl and 5 ± 22% (or 1 ± 2 µmol m^{-2} 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 roughly 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 (R^2=0.78). These fluxes also showed moderate correlations with chamber air temperature, surface soil temperature and biomass (R^2 = 0.40 to 0.53, **Figs. S1**

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192 **and S2**). Within individual outings, however, these environmental factors were poor
193 predictors. For example, large flux differences were observed between two adjacent sites
194 with similar biomass (e.g., TX4 and TX5) and could even show a slightly negative
195 relationship (e.g., TX3). CH_3Cl and CH_3Br showed no correlation with net fluxes of
196 chloroform and carbonyl sulfide (Whelan et al., 2013) that were measured simultaneously
197 (**Figs. S1 and S2**).

198 The very large nighttime emissions in July when temperatures were also high suggest that
199 temperature is a more proximate control on emission rates than insolation. This is consistent
200 with studies in southern California (Rhew et al., 2002) and Scotland (Blei et al., 2010b), but
201 contrasts with earlier studies in Scotland (Drewer et al., 2006) and Ireland (Dimmer et al.,
202 2001). At another salt marsh site in southern California, Manley et al. (2002) found that *B.*
203 *maritima* emissions were less correlated with either temperature or insolation compared to
204 other plants. We suggest that for studies that use transparent chambers, the effect of
205 insolation and temperature may be difficult to separate without monitoring leaf temperatures
206 directly or actively modulating the temperature in the chamber. This does not discount the
207 importance of insolation, which regulates seasonal changes in temperature and biomass.

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208 The average CH_3Cl:CH_3Br molar flux ratio of 22 ± 9 is slightly greater than southern and
209 northern California salt marsh averages (7-17) (Manley et al., 2006; Rhew et al., 2002; Rhew
210 and Mazéas, 2010) and is much higher than the ratios of 2 to 4 reported from higher latitude
211 salt marshes (Blei et al., 2010b; Cox et al., 2004; Dimmer et al., 2001). This is consistent
212 with the observation of Blei et al. (2010b) that the salt marshes from more temperate climates
213 generally have lower emission ratios. However, this is not a consequence of higher
214 temperatures leading to higher ratios. At the Texas *B. maritima* sites, molar ratios did not
215 dramatically shift with the seasons, and the molar ratios of emissions were higher at night
216 (~40) and lower during the day (~20), opposite of the temperature trends (**Fig. 2**).

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217 This diurnal trend in ratios is clearly related to the much larger diurnal variation in CH_3Br
218 flux compared to CH_3Cl flux, as illustrated by the pronounced midday CH_3Br peak in this
219 study (**Fig. 2).** Interestingly, this same trend in molar ratios was also observed in a San Diego
220 salt marsh (Rhew et al., 2002), where it mirrored a diurnal shift in the carbon isotopic ratio
221 ($\delta^{13}C$) of CH_3Cl and CH_3Br. In that study, carbon isotopic signatures were heavier at night (-
222 50‰ CH_3Cl and -10 ‰ CH_3Br) compared to daytime (-70‰ CH_3Cl and -60‰ CH_3Br), with
223 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 CH_3Cl uptake over CH_3Br 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 CH_3Cl to CH_3Br 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 ($\delta^{13}C$ 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 CH_3Cl:CH_3Br 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 CH_3Cl than CH_3Br, 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 $\delta^{13}C$ 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 $\delta^{13}C$ 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 $\delta^{13}C$ (Keppler et al., 2004).

The other half of this hypothesis involves 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, the amount of chloride and bromide that is volatilized daily via methyl halide emission is not large enough to substantially change the overall Cl^- and Br^- content in plant tissue. In this study, the biomass normalized diel emission rates of CH_3Cl and CH_3Br were 1.25 ± 0.40 μmol $gdwt^{-1}$ d^{-1} and 0.062 ± 0.014 μmol $gdwt^{-1}$ d^{-1}, respectively (n=9 sites). If we assume that the *B. maritima* tissue halide contents are similar to those measured in southern California *B. maritima* plants (210 mg g^{-1} for Cl- and 2900 μg g^{-1} for Br- (Manley et al., 2006)), then we estimate that roughly 0.02% of Cl and 2% Br in the leaf tissue is removed daily via methyl halide emissions. Thus, to impact halide availability, there would need to be a small segregated subset of 'active' halides at the enzyme site. If this 'active' halide pool was 0.5% of the overall tissue content, then the methyl halide emissions could reduce that pool by 4% for Cl and 34% for Br daily. This would lead to an increased CH_3Cl to CH_3Br emission ratio, until the halide levels were replenished. A subset of 'active' halides in the cytoplasm of plant cells is implied by Ni and Hager (1998, 1999), who proposed that the function of halide methyltransferase is to dispose of excess chloride to regulate internal concentrations.

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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 mmol m^{-2} yr^{-1} for CH_3Cl and 4.7 mmol m^{-2} 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 mmol m^{-2} yr^{-1} for CH_3Cl and 2.4 mmol m^{-2} yr^{-1} for CH_3Br) (Manley et al., 2006). Sampling over the full range of environmental conditions would help refine these estimates of the annual flux.

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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 0.47-0.84 mmol m^{-2} 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 0.2-0.7 mmol m^{-2} 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 mmol m^{-2} yr^{-1} for CH_3Cl and 0.03 mmol m^{-2} 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).

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, with associated increases in relevant secondary metabolites and enzymes). *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 CH_3Cl and 3-9 Gg CH_3Br 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 CH_3Cl and CH_3Br will require further measurements at low latitude salt marsh sites.

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6 Conclusion

Large emissions of CH_3Cl and CH_3Br 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

331 southern California salt marshes. However, *B. maritima* emission rates in this study were 2 to
332 3 times larger than those reported from California, and spatially averaged emission rates from
333 Texas salt marshes were much larger overall than those reported from higher latitude salt
334 marsh sites. Diurnal trends in CH_3Cl and CH_3Br emission rates, along with their ratio of
335 emissions, were similar to those observed in southern California salt marshes. To derive a
336 better estimate of the global salt marsh contribution to the atmospheric budgets of the methyl
337 halides, more information is needed about the spatial extent, vegetation cover and methyl
338 halide emission rates from low latitude salt marsh sites.
339

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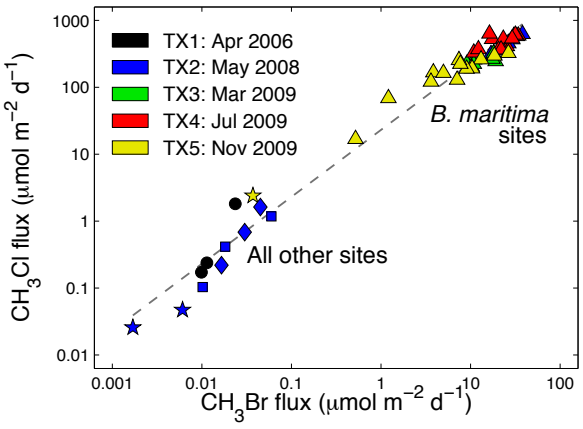
Table 1. Field conditions and predominant vegetation at Texas coastal field sites

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

* modeled diel flux (μmol m^{-2} d^{-1}) based on daytime measurements
† *Borrichia frutescens* and *Monanthochloe littoralis*
‡ soil surface covered with water for some or all measurements
§ vegetation H_2O estimated as 81.9% based on average of other outings



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

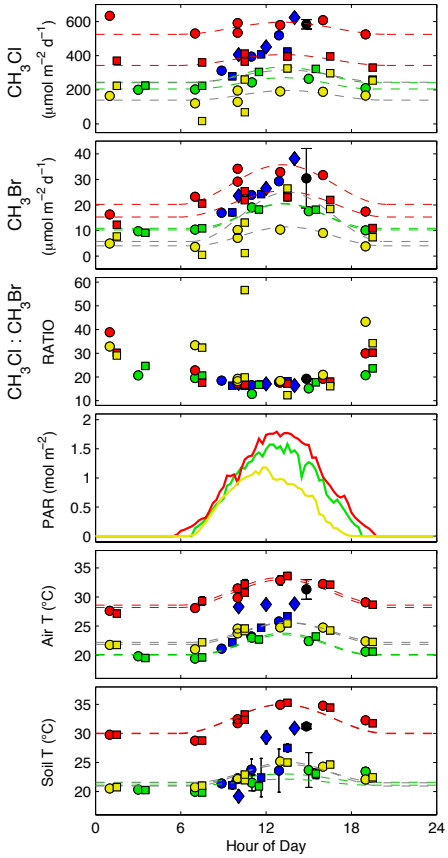

Figure 2. Net fluxes of CH_3Cl, net fluxes of CH_3Br, the CH_3Cl to CH_3Br flux ratio, photosynthetically active radiation (PAR), chamber air temperature and surface soil temperature at *B. maritima* sites versus time of day (Central Standard Time). Colors represent different outings, as in Fig. 1; different symbols (circles, squares, diamonds) represent different sites at the same outing. Error bars that are smaller than the symbols are not shown The dashed lines represents the model fit to TX3-5 (March, July, and November) results. PAR is a 15 minute interval measurement averaged over the two days of each field outing.

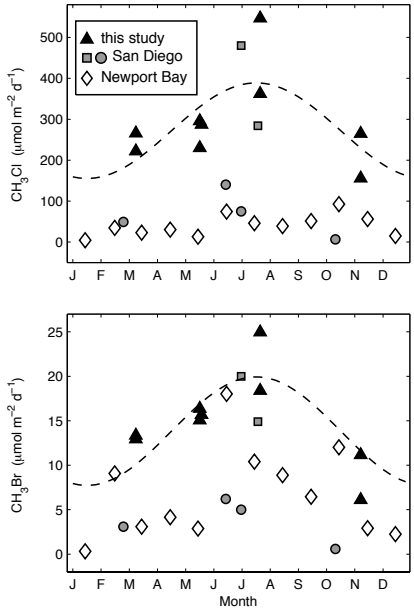

Figure 3. Comparison of *B. maritima* methyl halide emissions from three coastal salt marshes. This study (black triangles) shows diel averages. The San Diego, California sites show diel averages (gray squares) at two *B. maritima* sites and daytime fluxes (gray circles) at mixed *B. maritima /Salicornia bigelovii* sites [Rhew et al., 2000; Rhew et al., 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.