1   # Large methyl halide emissions from south Texas salt marshes

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10

11   **Abstract**

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

23

24   **1   Introduction**

25   As atmospheric burdens of anthropogenic halocarbons decrease because of the Montreal
26   Protocol, the relative importance of methyl halides for stratospheric ozone destruction
27   increases. Methyl chloride (CH_3Cl) and methyl bromide (CH_3Br) are now the most abundant
28   long-lived organochlorine and organobromine compounds, respectively (Montzka and
29   Reimann, 2011). The atmospheric budgets of CH_3Cl and CH_3Br have large uncertainties

30   arising from the fact that they have a multitude of major anthropogenic (e.g., biomass burning,

31   fumigation use of CH_3Br, chemical feedstock use of CH_3Cl) and natural sources (e.g., oceans,

32   terrestrial ecosystems), some of which are poorly characterized. In our current understanding

33   of the CH_3Br budget, sinks outweigh the sources by about 30-35 Gg yr^{-1}, or roughly 20-25%

34   of the total annual flux (Montzka and Reimann, 2011). This large "missing source" for CH_3Br

35   is present in both pre-phaseout (1996-98) and current (2008) budgets and appears to be both

36   natural and terrestrial in origin (Yvon-Lewis et al., 2009).   The CH_3Cl budget may be

37   balanced with a very large low-latitude terrestrial source (Xiao et al., 2010), and a few *in situ*

38   studies of subtropical (Yokouchi et al., 2002; Yokouchi et al., 2007) and tropical forests (Blei

39   et al., 2010a; Saito et al., 2008) tentatively support this.

40   Coastal salt marshes have also been identified as globally significant sources of CH_3Cl

41   and CH_3Br, with emissions associated with halophytic vascular plants. However, measured

42   emissions show dramatic geographic variability, with large emissions from southern

43   California (Manley et al., 2006; Rhew et al., 2002; Rhew et al., 2000) and much smaller

44   emissions from higher latitude sites in Tasmania, Australia (Cox et al., 2004), Scotland (Blei

45   et al., 2010b; Drewer et al., 2006) and northern California (Rhew and Mazéas, 2010).

46   Measurements from lower latitude salt marshes have not yet been reported. In this study, we

47   characterize the magnitude and seasonality of CH_3Cl and CH_3Br emissions from subtropical

48   salt marshes in southern Texas. Obtaining a wider latitudinal range of measurements from

49   coastal salt marshes is essential to constrain their role in the global budget of methyl halides.

50

51   **2   Site Description**

52   Five field outings were conducted between April 2006 and November 2009 at several salt

53   marsh and coastal habitats on barrier islands in south Texas, USA off the Gulf of Mexico

54   (**Table 1**). Sites were all located between 27 to 28° N and 97° to 98° W. All sites had sandy

55   soils with elevations estimated at less than a meter above mean sea level. A total of 62 flux

56   measurements were made at 24 individual sites from three different tidally influenced

57   ecosystems.

58   The first field outing (TX1: April 28, 2006) took place on the southwestern shore of San

59   Jose Island (27° 52'N, 97° 03' W), a sandy barrier island north of the city of Port Aransas.

60   The goal of this initial outing was to survey emissions from predominant salt marsh plant

61 species of the region: *Borrichia frutescens* (sea ox-eye daisy), *Avicennia germinans* (black

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

63 The second field outing (TX2: May 16-18, 2008) occurred at three different locations:

64 San Jose Island (see TX1, two *B. maritima* sites, both slightly inundated during sampling),

65 Mustang Island beach (27° 46'N, 97° 6'W, six beached seaweed sites), and the Mollie Beattie

66 Habitat Community on the back bay of Mustang Island (27° 38'N, 97° 12'W, one *B. maritima*

67 site). The goal of this second outing was to determine the daytime range of fluxes from the

68 three *B. maritima* sites; to measure emissions from pelagic seaweed (*Sargassum* spp.)

69 deposited on the Gulf-side beach at different stages of decomposition; and to determine the

70 simultaneous gross consumption and production rates of methyl halides at all of these sites

71 using a stable isotope tracer technique.

72 The third, fourth and fifth outings (TX3, TX4 and TX5) were all at the Mollie Beattie

73 habitat (see TX2 above), on the fringe of a small saltwater pond, which was tidally connected

74 with saline groundwater (**Text S1**). The purpose of these outings was to capture the full

75 diurnal (24 hour) range of fluxes from a pair of *B. maritima* sites located within 20 meters of

76 each other. These diurnal studies were conducted at three different times of the year: the early

77 growing season (TX3: March 7-8, 2009), the peak growing season (TX4: July 19-20, 2009),

78 and the end of the growing system (TX5: November 6-7, 2009). TX5 occurred after a period

79 of heavy rain, and many of the *B. maritima* leaves were shed on the ground. Also, between 1

80 a.m. and 11 a.m. during TX5, both sites were tidally inundated, with the shorter vegetation

81 site mostly underwater during the 7:30 and 10:30 a.m. samplings.

82 Four vegetation-free control experiments were conducted: two beach sites after the

83 removal of *Sargassum* (TX2), one salt marsh site with bare soil (TX4) and one salt marsh site

84 inundated with 30 cm of tidal water (TX5).

85

3 Methods

87 Gas fluxes were measured with static flux chambers consisting of two components: a

88 collar (61L, 0.264 m^2 footprint) placed in the wet sand > 2 cm depth and an insulated chamber

89 lid (127 L) with a ¼" stainless steel sample line used to withdraw air samples and two internal

90 fans to mix the chamber air. All-aluminum chambers were used to limit reactivity with

91 methyl halides, and dark chambers have been shown to yield similar methyl halide fluxes as

92   light chambers in other salt marshes (Rhew and Mazéas, 2010). To initiate the enclosure

93   period, the lid was placed into the water-filled channel on the rim of the base. Enclosure

94   times were 30 minutes or less (30, 22-28, 20, 16 and 16 minutes for TX1-5, respectively), and

95   three air samples were withdrawn from the chamber at equal time intervals. Samples were

96   collected into previously evacuated 1 L electropolished stainless steel canisters

97   (LabCommerce, San Jose, CA, USA) or 3 L fused silica lined canisters (Restek, Bellefonte,

98   PA, USA). While sampling, a vent line was opened to equilibrate air pressure between inside

99   and outside the chamber. In addition, ambient air samples were collected several times

100   throughout each field campaign.

101   Air temperature (inside chamber and ambient air) and soil temperature (5 cm and 10 cm

102   depth) were monitored with thermocouples (Omega Engineering Inc., Stamford, CT) during

103   the first three outings and with stainless steel thermocouple data loggers (iButtons, Maxim

104   Inc., Sunnyvale, CA, USA) for the last two outings. Soil moisture at 0-5 cm depth

105   (ThetaProbe soil moisture sensor, Delta-T Devices, Cambridge, UK) and air pressure were

106   monitored for each chamber experiment. For TX2-5, above-ground plant biomass was

107   harvested, rinsed and drained before fresh weight was determined. Plants were then dried

108   overnight at 65° C to determine the dry weight. Meteorological data including PAR, air

109   pressure and air temperature were also measured at the Mission-Aransas National Estuarine

110   Research Reserve monitoring station at the East Copano Bay, TX, USA

111   (http://lighthouse.tamucc.edu/MissionAransas/HomePage).

112   Air samples were measured for halocarbons (CH_3Br, CH_3Cl and $CHCl_3$) by gas

113   chromatography-mass spectrometry (GC/MS, Agilent 6890N/5973). Details regarding the

114   inlet system, chromatography, gas standards and calibration procedures are described

115   elsewhere (Rhew, 2011). Concentration trends were calculated using a linear regression of

116   the chamber air concentration versus time, with goodness of fit assessed both by R^2 and the

117   standard error on the slope. For the *B. maritima* sites, for example, R^2 values averaged 0.997

118   for CH_3Cl and 0.995 for CH_3Br. Net fluxes were calculated by multiplying this slope with the

119   moles of air in the chamber, divided by the enclosed surface area; net flux errors were

120   calculated by propagating the errors of each of these components. For consistency, all fluxes

121   are reported in units of $\mu mol \ m^{-2} \ d^{-1}$ unless otherwise indicated, with negative values

122   representing consumption rates and positive values representing production rates. Also, a

123   stable isotope tracer technique was applied in the TX2 outing to separate the net flux into the

124 gross production and gross consumption components (**Text S2**). All times are reported as

125 U.S. Central Standard Time (CST= GMT – 6 hours).

126

127 **4   Results**

128 **4.1 TX1: April 2006**

129   Of the various vegetation sites sampled during TX1, the largest emissions by far were

130 from the *B. maritima* site (triangles in **Fig. 1**), which emitted 580 ± 30 µmol m^{-2} d^{-1} CH$_3$Cl

131 and 30 ± 12 µmol m^{-2} d^{-1} CH$_3$Br. As a comparison, the largest reported emissions observed

132 from a salt marsh previously were 570 and 42 µmol m^{-2} d^{-1}, respectively (Rhew et al., 2002;

133 Manley et al., 2006). The *A. germinans* site showed emissions <0.5% of the *B. maritima* site,

134 while the two *B. frutescens* sites and the *M. littoralis* site showed small to insignificant net

135 emissions of CH$_3$Cl (<0.3 µmol m^{-2} d^{-1}) and CH$_3$Br (<0.012 µmol m^{-2} d^{-1}).

136

137 **4.2 TX2: May 2008**

138   In TX2, the three *B. maritima* sites showed large net emissions of methyl halides,

139 comparable to TX1. Emission rates increased throughout the day (8:50 a.m. to 2:20 p.m.

140 CST), although the sampling period was too short to fully assess diurnal trends. One site had

141 a maximum flux of 620 ± 20 µmol m^{-2} d^{-1} CH$_3$Cl and 39 ± 2 µmol m^{-2} d^{-1} CH$_3$Br, which at

142 that point represented the largest CH$_3$Cl and second largest CH$_3$Br emission rate per unit area

143 from a natural source yet observed.

144   The three freshly deposited *Sargassum* sites at the Gulf coast beach showed net

145 emissions that were 3 orders of magnitude smaller that the *B. maritima* sites (**Fig. 1** and **Table**

146 **1**). Three other sites of *Sargassum* that were visibly at a more advanced stage of

147 decomposition and desiccation showed similar net emissions. When two of the *Sargassum*

148 sites were cleared of seaweed and measured as control experiments on a bare sand surface, net

149 emissions were an order of magnitude smaller still. Gross consumption rates measured with

150 stable isotope tracers were negligibly small (**Text S2**).

151

152 **4.3 TX3, TX4 and TX5: March, July and November 2009**

153   The next three outings each captured the diurnal variability of CH$_3$Cl and CH$_3$Br fluxes

154 over a 24 hour period from a pair of *B. maritima* dominated sites (**Fig. 2**). The day/night

155 differences in emissions were much more pronounced for CH$_3$Br than for CH$_3$Cl. For CH$_3$Br,

156 the maximum daytime averages were 2.3 times greater than the nighttime averages (n=6

157 sites), whereas the difference for CH_3Cl was 1.3 times. The molar ratio of CH_3Cl to CH_3Br

158 fluxes also showed a day to night difference (**Fig. 2**), shifting from roughly 40:1 at night to

159 20:1 during the daytime.

160   Surprisingly, the maximum observed CH_3Cl emission flux in July (630 ± 10 µmol m^{-2} d^{-1})

161 occurred in the middle of the night (1 a.m. CST). In fact, this represented the highest

162 observed emission rate from all the outings, comparable to the highest flux from TX2. The

163 lowest emissions were observed during November (TX5) during the morning at one site when

164 the vegetation was almost entirely submerged by high tide. The other site also was

165 submerged at the time, but had slightly more vegetation above the surface of the water.

166   To derive an integrated daily flux, the fluxes at each site were modeled by a cosine

167 function during daylight hours, with steady emissions assumed at night (**Fig. 2**, **Text S3**). Of

168 these three outings, the largest average diel emissions were in July (TX4) at 455 ± 130 µmol

169 m^{-2} d^{-1} for CH_3Cl and 22 ± 5 µmol m^{-2} d^{-1} for CH_3Br. March emissions were roughly half of

170 those, and November emissions were slightly lower than March (**Table 1, Fig. 3**). Even

171 though nighttime measurements were not used in the model, the difference between the

172 modeled to measured nighttime values was only $-4 \pm 11\%$ (or -20 ± 50 µmol m^{-2} d^{-1}) for

173 CH_3Cl and $5 \pm 22\%$ (or 1 ± 2 µmol m^{-2} d^{-1}) for CH_3Br. Thus the model was applied to the

174 May (TX2) sites as well (**Table 1**).

175

176 **5   Discussion**

177   The predominance of *B. maritima* emissions over emissions from other measured plant

178 and macroalgal species is similar to observations from southern California salt marshes,

179 where *B. maritima* was one of the two largest emitters of methyl halides (Manley et al., 2006;

180 Rhew et al., 2002). However, *B. maritima* sites from Texas generally showed much larger

181 diel averaged emissions of CH_3Cl and CH_3Br than those from southern California, especially

182 outside the peak summer growing season (**Fig. 3**). Even normalized by biomass, emission

183 rates from Texas sites were roughly ten times larger than Newport Bay California sites

184 (monthly averages) (Manley et al., 2006).

185   The production of CH_3Cl and CH_3Br at *B. maritima* sites are related, as illustrated by a

186 strong linear correlation ($R^2=0.78$). These fluxes also showed moderate correlations with

187 chamber air temperature, surface soil temperature and biomass ($R^2 = 0.40$ to 0.53, **Figs. S1**

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

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

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

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

220   Two hypotheses were proposed to explain these diurnal trends of ratios and isotopic

221   signatures (Bill et al., 2002; Rhew et al., 2002): 1) biogenic production dominates during the

222   day, while soil consumption becomes more significant at night; and 2) two different

223   production mechanisms with different isotopic signatures and ratios of production occur

224   simultaneously.

225   The first hypothesis could explain the lower overall net emission rates and heavier

226   isotopic signatures at night (since consumption favors lighter isotopes (Miller et al., 2001)),

227   but this study and others (Rhew and Mazéas, 2010) suggest that gross consumption is trivial

228   in salt marshes compared to *B. maritima* production rates, even at night (**Text S2**). Also,

229   gross consumption generally favors CH_3Cl uptake over CH_3Br by a molar factor of 30 to 40

230   (Rhew, 2011; Rhew and Mazéas, 2010), such that if nighttime consumption is important, the

231   net emission ratio of CH_3Cl to CH_3Br should decrease at night, not increase.

232   The second hypothesis is supported by having two known production mechanisms of

233   methyl halides from *B. maritima*: the enzymatically mediated methylation of halides (Ni and

234   Hager, 1999; Wuosmaa and Hager, 1990) and an abiotic reaction between plant pectin and

235   halides (Hamilton et al., 2003; Wishkerman et al., 2008). Because the abiotic mechanism

236   yields a very light isotopic signature ($\delta^{13}C$ of -78‰ for *B. maritima*) (Keppler et al., 2004), a

237   large abiotic increase during the daytime relative to enzymatic production could explain the

238   isotopic shift.   However, the $CH_3Cl:CH_3Br$ molar ratio of production for the abiotic

239   mechanism is also larger (45 to 58) (Wishkerman et al., 2008) than the predicted enzymatic

240   production (20 to 1) (Rhew et al., 2002), which would yield a larger diurnal shift for CH_3Cl

241   than CH_3Br, which is not observed.

242   An alternative hypothesis involves both a diurnal shift in the isotope signature of the

243   carbon substrate used to produce methyl halides combined with a shift in methylation ratios of

244   the halides.   If production is predominantly biological, a diurnal shift in the $\delta^{13}C$ signature of

245   the methyl donor (*S*-adenosyl-L-methionine) (Ni and Hager, 1999) and/or higher isotopic

246   fractionation rates during the daytime could yield the observed isotopic signal. It is also

247   possible that the abiotic production mechanism produces lighter $\delta^{13}C$ methyl halides at higher

248   temperatures, but the carbon source for abiotic production comes from structural components

249   of a plant that are not necessarily expected to have diurnal variation in $\delta^{13}C$ (Keppler et al.,

250   2004).

251   The other half of this hypothesis involves the Cl/Br ratios in the plant changing during the
252   day. Bromide is preferentially halogenated by both biotic and abiotic mechanisms relative to
253   their availability (Ni and Hager, 1998; Wishkerman et al., 2008) and may be replenished
254   during the day and depleted at night, perhaps in conjunction with transpiration rates.
255   However, the amount of chloride and bromide that is volatilized daily via methyl halide
256   emission is not large enough to substantially change the overall Cl^- and Br^- content in plant
257   tissue. In this study, the biomass normalized diel emission rates of CH_3Cl and CH_3Br were
258   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
259   assume that the *B. maritima* tissue halide contents are similar to those measured in southern
260   California *B. maritima* plants (210 mg g^{-1} for Cl- and 2900 μg g^{-1} for Br- (Manley et al.,
261   2006)), then we estimate that roughly 0.02% of Cl and 2% Br in the leaf tissue is removed
262   daily via methyl halide emissions. Thus, to impact halide availability, there would need to be
263   a small segregated subset of 'active' halides at the enzyme site. If this 'active' halide pool
264   was 0.5% of the overall tissue content, then the methyl halide emissions could reduce that
265   pool by 4% for Cl and 34% for Br daily. This would lead to an increased CH_3Cl to CH_3Br
266   emission ratio, until the halide levels were replenished. A subset of 'active' halides in the
267   cytoplasm of plant cells is implied by Ni and Hager (1998, 1999), who proposed that the
268   function of halide methyltransferase is to dispose of excess chloride to regulate internal
269   concentrations.

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

278   The surface area coverage of *B. maritima* in Texas salt marshes was not quantified for this
279   study. In Newport Bay, California, *B. maritima* covered 10% of the entire salt marsh area
280   (including barren areas) and 18% of the vegetated area (Manley et al., 2006). For the purpose
281   of comparison, we will assume that these Texas salt marshes have the same *B. maritima*
282   coverage and that the remaining 82-90% of salt marsh has negligible emission rates. Spatially

283 averaged emissions for the entire salt marsh are then estimated at 9-17 and 0.47-0.84 mmol m$^-$

284 ^{2} yr^{-1} for CH$_3$Cl and CH$_3$Br, respectively. These fluxes are slightly greater than those reported

285 from Newport Bay salt marshes (3-8 and 0.2-0.7 mmol m^{-2} yr^{-1} for CH$_3$Cl and CH$_3$Br,

286 respectively, with the range representing total area and only vegetated areas), which have

287 other large emissions associated with *Frankenia grandifolia* (Manley et al., 2006). However,

288 these rates are one to two orders of magnitude greater than annually averaged salt marsh

289 fluxes in Scotland (0.11 mmol m^{-2} yr^{-1} for CH$_3$Cl and 0.03 mmol m^{-2} yr^{-1} for CH$_3$Br) (Blei et

290 al., 2010b; Drewer et al., 2006). The Scotland salt marsh fluxes are similar in magnitude to

291 other high latitude salt marshes, including Tasmania, Australia (Cox et al., 2004) and northern

292 California (Rhew and Mazéas, 2010).

293 Collectively, these studies show that methyl halide emissions from coastal salt marshes

294 have a strong climatic dependence, with small emissions at higher latitudes and large

295 emissions at lower latitudes. This climatic dependence may be related to both temperature

296 (higher temperatures yield faster enzymatic and abiotic production rates of methyl halides)

297 and insolation (greater photosynthesis rates lead to greater biomass, with associated increases

298 in relevant secondary metabolites and enzymes). *B. maritima* alone may be responsible for

299 globally significant amounts of methyl halides, as it is an evergreen succulent shrub found

300 widely in tropical and subtropical salt marshes, brackish marshes and mangrove swamps

301 ranging from northern Brazil (3°S) to South Carolina (33°N) (Lonard et al., 2011). A major

302 uncertainty involves the spatial distribution and global coverage of coastal wetlands, with 2.2-

303 40 Mha of tidal marsh and 13.8-15.2 Mha of mangroves (Pendleton et al., 2012). As an

304 illustrative exercise, if *B. maritima* or similarly emitting plants cover 10% of the surface area

305 of tidal marshes and mangroves, and if averaged emissions are as calculated here, then this

306 subset of salt marsh vegetation would contribute 30-90 Gg CH$_3$Cl and 3-9 Gg CH$_3$Br per

307 year. Deriving a more accurate global source strength will require a much broader geographic

308 distribution of measurements, along with better estimates of ecosystem surface areas and plant

309 distributions. Clarifying the importance of coastal salt marsh vegetation in the global budgets

310 of CH$_3$Cl and CH$_3$Br will require further measurements at low latitude salt marsh sites.

311

312 **6   Conclusion**

313 Large emissions of CH$_3$Cl and CH$_3$Br were observed from subtropical salt marshes

314 located on the Gulf coast of Texas. These large emissions were associated with *B. maritima*,

315 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 CH_3Cl and CH_3Br 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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416 **Table 1.** Field conditions and predominant vegetation at Texas coastal field sites

| Outing/date: (dd/mm/yy) Enclosed species	Location	Net flux (μmol m^{-2} d^{-1}) CH$_3$Cl	CH$_3$Br	Modeled diel flux* CH$_3$Cl	CH$_3$Br	*Batis* biomass kg/m^2 fresh	kg/m^2 dry
TX1: 28/04/06	San Jose Island	n					
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$_2$O estimated as 81.9% based on average of other outings
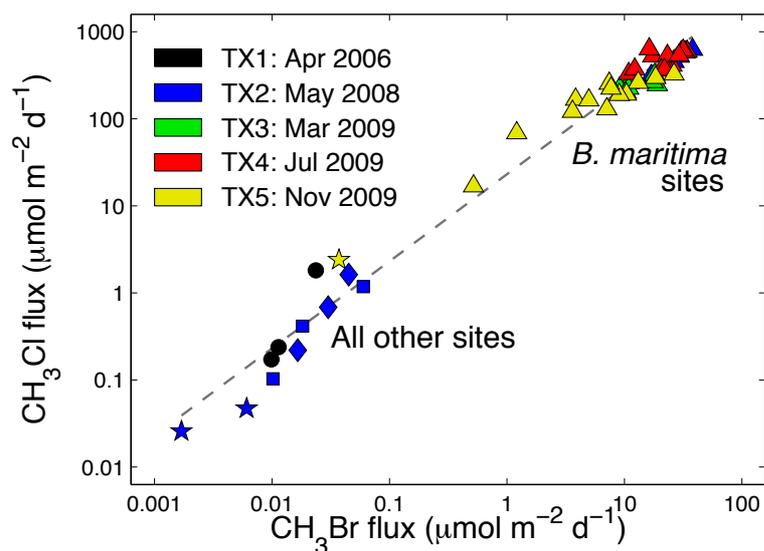
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449 **Figure 1.** Net fluxes of CH₃Cl and CH₃Br for all field sites in south Texas. Triangles = *B.*
450 *maritima*; squares = fresh *Sargassum*; diamonds = decaying *Sargassum*; circles = other
451 vegetation (*M. littoralis*, *A. germinans*, *B. frutescens*), stars= vegetation-free control. Note the
452 log-log scale. The gray dashed line shows the overall average 23:1 molar ratio. Two
453 chambers that had small negative fluxes are not included.
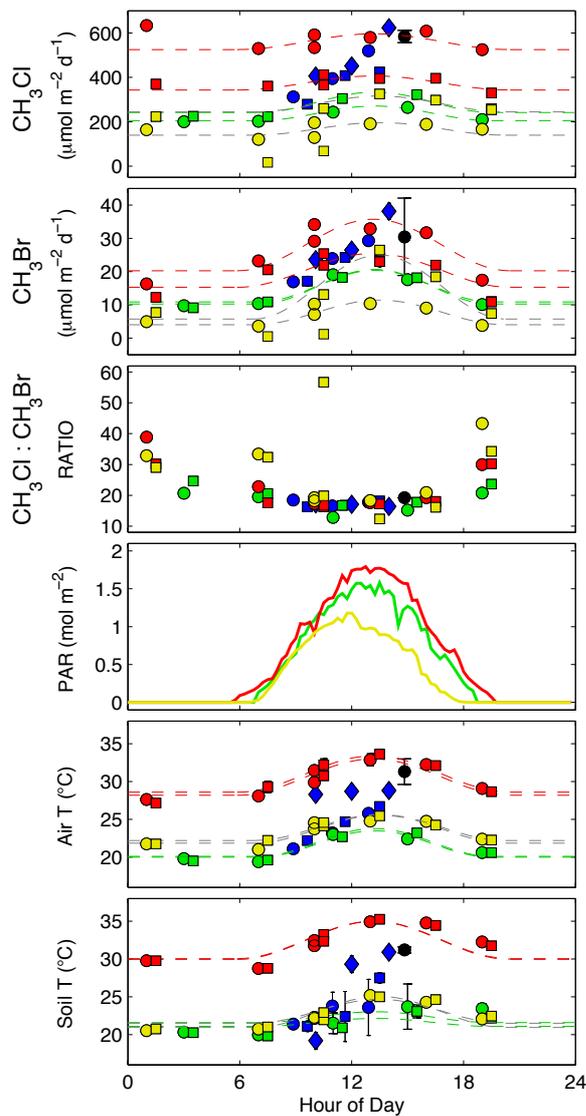
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455 **Figure 2.** Net fluxes of CH₃Cl, net fluxes of CH₃Br, the CH₃Cl to CH₃Br flux ratio,
456 photosynthetically active radiation (PAR), chamber air temperature and surface soil
457 temperature at *B. maritima* sites versus time of day (Central Standard Time). Colors represent
458 different outings, as in Fig. 1; different symbols (circles, squares, diamonds) represent
459 different sites at the same outing. Error bars that are smaller than the symbols are not shown
460 The dashed lines represents the model fit to TX3-5 (March, July, and November) results.
461 PAR is a 15 minute interval measurement averaged over the two days of each field outing.
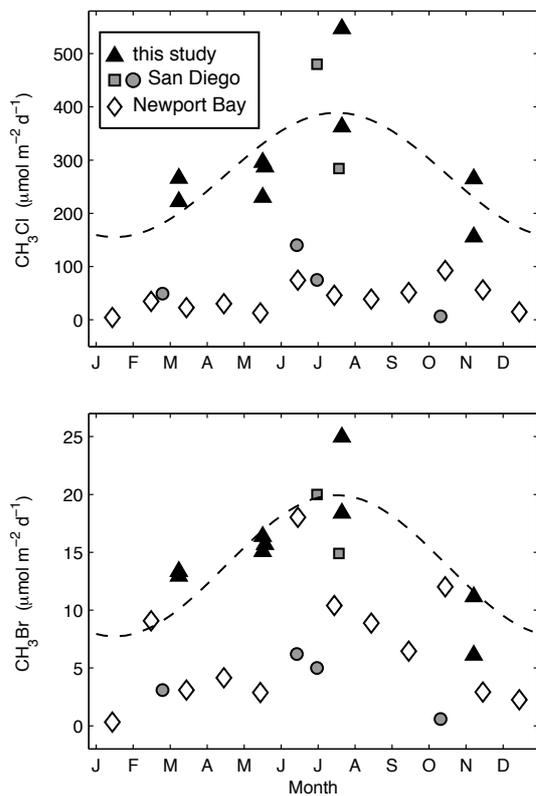
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Figure 3. Comparison of *B. maritima* methyl halide emissions from three coastal salt
marshes. This study (black triangles) shows diel averages. The San Diego, California sites
show diel averages (gray squares) at two *B. maritima* sites and daytime fluxes (gray circles) at
mixed *B. maritima /Salicornia bigelovii* sites [Rhew et al., 2000; 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.