bg-2014-233 Large methyl halide emissions from south Texas salt marshes
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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. Revised text added to the manuscript is illustrated in red font color.

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 370 ug g^{-1} for Br^-, Manley et al., 2006) and *Salicornia europea* in Scotland (192 mg 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 290 ug 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 5% of the overall tissue content, then the methyl halide emissions could reduce that pool by 0.4% 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, as 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 would help refine these estimates 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 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), which is why subsequent enclosure times for *B. maritima* were reduced by 27 to 47%. All of the other 28 or 30 minute enclosures were at lower emitting sites with different plants or macroalgae enclosed.

Second, we quantified the error on the flux by 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 total 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 *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."

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"