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Long-term CH₃Br and CH₃Cl flux measurements in temperate salt marshes,
E. Blei et al.

Authors' responses to full review comments

We thank both reviewers for their time and effort spent in the *Biogeosciences* review process.

Reviewer #2 has recommended publication of the manuscript with no further revisions specified.

Our responses to the comments posted by Reviewer #1, identified as Prof. Rhew, are given below, including description of where we have modified our paper. For clarity, we incorporate within our responses Prof. Rhew's original comments in italics and indented. Prof. Rhew's document also included a number of opening paragraphs of contextual 'General comments' for which no specific response is required – other than our thanks for these positive introductory remarks – and which we therefore do not repeat here.

As Prof. Rhew mentions in his comments, there has been simultaneous submission of our manuscript to *Biogeosciences* detailing extensive new measurements of methyl halide net fluxes at two salt marshes in Scotland with submission by Prof. Rhew to *Geophysical Research Letters* of a manuscript of new measurements by his group of methyl halide fluxes at salt marshes in northern California. Neither group were aware in advance of the other's impending submissions. Together these two papers significantly increase the number of salt marsh sites at which methyl halide fluxes have been quantified and consequently substantially increase the database of the ranges in flux values at different types of salt marsh. We now take this revision opportunity to incorporate a number of citations to Prof. Rhew's manuscript which is now fully published in *GRL* (Rhew and Mazéas, 2010).

II. Specific Comments

1. Methodological issue. Net fluxes are derived using only one chamber air sample, collected at time $t=10$ minutes, extracted from the chamber and stored in a 1L Tedlar bag. The concentration of the chamber at $t=0$ is assumed to be represented by an ambient air sample. It is difficult to assess the uncertainties generated by using one chamber air sample rather than the more typical 2-4 samples for a flux measurement. Aside from the 'flux linearity' issue discussed in the paper, having only one sample makes it difficult to identify a corrupted flux measurement (or to explain an outlier), owing to chamber or bag leakage or contamination. One possibility is to monitor other gases in the air sample. Potential biases that could underestimate or overestimate the flux are described below.

Response: Whilst it is accepted that taking only one sample on each occasion from each enclosure prevents statistical identification of a potential outlier, our experience from making several hundred flux measurements at these and other sites is that individual flux values can vary hugely both spatially across adjacent sampling locations and temporally between different samplings during a year. Our approach is therefore to focus on gathering very large datasets where the impact of a corrupted (or artefactual) outlier on calculated overall mean flux is minimal. In other words we focus on characterisation of the 'average' net annual flux of a particular ecosystem site as a whole through increased sampling of the whole ecosystem (in space and time) rather than through increased measurement of an individual enclosure. From a practical perspective, making consecutive withdrawals of headspace air from a single

enclosure introduces its own uncertainties through the need to account for the ingress of incoming air of different concentration from the headspace after each withdrawal. For the above reasons we did not routinely take consecutive samples from an enclosure, although we did conduct ‘flux linearity’ experiments – as described in the manuscript and below.

1a. Section 3.1.4 discusses the issue of flux linearity but is sparse on details. Why was that study inconclusive? How did the factor of 2.1 – 2.5 larger potential flux come about? Was it because the chamber concentrations level off with time? If so, is it because of chamber leakage or gross consumption competing with gross production?

Response: The factor range 2.1-2.5 that Prof. Rhew quotes above is in fact an error which we identified whilst our original manuscript was undergoing its initial behind-the-scenes ‘technical’ review and which we were able to correct for publication of the on-line *Discussions* version. The published *Discussions* paper contains the correct numerical factor of 1.5 in this section 3.1.4. We apologise for this initial error. Perhaps Prof. Rhew based his full review on the first submitted manuscript sent only to the reviewers rather than the on-line published version (the latter also had a few other minor changes following requests during this initial review).

The duration of an enclosure is a balance between keeping it short in order to limit any influence of enclosure on natural processes but long enough to permit small fluxes to be quantified above analytical limit of detection. Based on experience from many measurements we use 10 min as an enclosure duration. The assigned uncertainty increases for quantifying smaller analyte and flux values, i.e. for the shortest enclosure durations (and for small net fluxes per se) which means that the confidence intervals for extrapolation to zero enclosure increase, and in some individual experiments results in no significant difference in derived flux with extrapolation from 10 min to zero enclosure time. This is the reason for our original statement that results from this experiment were inconclusive. We have now modified the text in this section (3.1.4) to provide some more detail on these experiments and to be more explicit about the source of this uncertainty.

1b. Section 3.2 second paragraph: What type of storage experiment was conducted? A statement was made (pg 8) that storing background air and chamber air samples under similar conditions would minimize uncertainties. This would not necessarily be true if the bags leaked in outside air, which would in most cases reduce the methyl halide concentrations of chamber air samples but may not significantly change those of ambient air samples. The result would be a reduced flux than expected. Further assurances about sample integrity would be welcome here.

Response: Extensive storage experiments have been conducted by our group using bags of methyl halide standard (up to 500 pptv) made of different material (Tedlar, Teflon, Cali-5-bond) stored for up to 4 weeks under different regimes of temperature (fridge, ambient, +40°C) and light (ambient, dark). We observed that Tedlar bags were most reliable, with no loss of sample integrity discernible over a week or so (except at elevated storage temperature) within assigned analytical uncertainties. Filled sample bags were at slight excess pressure to ambient, so those that subsequently leaked showed signs of deflation and were discarded from analysis, whilst ingress of outside air was unlikely. An additional couple of sentences providing some of the above detail has been added to the second paragraph of section 3.2 of the revised manuscript.

1c. On the other hand, using an ambient air sample as t=0 might underestimate fluxes, as the concentrations immediately above the salt marsh surface may be expected to be higher than ambient (depending on where or when the ambient sample is taken). Some information should be

given about how many/frequently ambient air samples are taken over the course of the day of measurements, and whether concentrations so measured are similar to background Northern Hemisphere concentrations. If only one ambient sample is taken, it is possible that some of the spatial coherence in fluxes observed between sites might be partly due to a shared anomalous $t=0$ value. Because of missing details, one wonders about the nature of outlier fluxes, especially for CH_3Cl . In figure 1a, the CH_3Cl net flux goes to zero for one measurement in the middle of the growing season - did that site really have no net flux, or was there a quantifiable uncertainty that exceeded the magnitude of the measured flux? The visual (but not statistical) relationship between CH_3Cl and PAR is strongly influenced by this one point.

Response: We are aware of potential issues surrounding where, and how many, ambient air samples to take. In this work, two samples of ‘background’ ambient air were taken from 1.5 m height above the ground at two different places on each occasion that enclosure samples were collected at each salt marsh. For the diurnal studies, a background sample was collected concurrently with each of the enclosure time points. Background samples therefore apply to contemporaneous air above the respective salt marshes, not to ambient air at a location completely distinct from the salt marshes. As with other issues already discussed here, there is a balance between sampling and analysis to characterise rigorously the flux at a single enclosure at a single time, and sampling and analysis to characterise the variation in fluxes across a greater number of sampling enclosures and a greater number of sampling time points. Additional detail has now been added to the penultimate paragraph of section 3.1 and to section 3.1.1.

Flux values of zero in our presentation signify that the derived net flux magnitude (emission or uptake) was less than the quantified limit of detection for a net flux for that set of measurements. As described in the text, the LOD was set at the flux for which the difference in concentration between enclosure and background samples equalled twice the assigned uncertainty in concentration of the background sample. Thus the CH_3Cl net flux at Heckie’s Hole salt marsh on 12th August 2008 identified in the comment was less than the LOD assigned through analysis of uncertainty for that set of measurements. Conventions vary as to how to express a value that is <LOD, ranging from setting it to the LOD value, to half the LOD value, or to zero. We chose the latter.

2. To extrapolate or not to extrapolate The paper points out the large uncertainty associated with scaling up fluxes from a single geographic location, implicitly criticizing initial scale-ups from studies in southern California. And then the authors proceed to do the same thing, scaling up from the results from Scotland to the globe. It is a recurring criticism that global extrapolations from a single field study are fraught with uncertainty, but even this paper acknowledges that scaling up is a useful tool to assess the potential importance of a particular process or ecosystem (pg 15). Where this manuscript oversteps is to suggest, in several places, that the present study provides a more accurate representation for the global salt marsh source of CH_3Br and CH_3Cl .

This and the following paragraphs of ‘specific comments’ from Prof. Rhew all relate to the issue of global scale up (or not) of point measurements. We make a general response here, with further comments as required under later paragraphs.

We are sorry that Prof. Rhew has interpreted that we were singling out his (and co-workers’) global scale up of measurements from salt marshes in southern California for criticism. At the time of their publication, those were the only measurements of fluxes at salt marshes available anywhere, so no criticism of the use of these data to produce a scale up estimate at that time can be warranted or should be inferred. However, since the publication of those data other flux measurements have now been published from other salt marshes. Our intention was thus to

emphasise the point that measurements from different salt marshes are different and that therefore, trivially, a global scale up using a different point measurement gives a different global estimate. This message is aimed at researchers (probably those who are not conducting field measurements of methyl halides themselves), who may apply more sophisticated methods for determining global budgets of these two gases, to take note that the salt marsh global emission estimate included in the last two WMO assessments, which is based only on the southern California data, may need revising downwards (at least based on data as currently available). We were not intending to imply that our scale up value was correct, but to point out that with the benefit of subsequent measurements from other more temperate climate salt marshes (including the very recently-published measurements from the northern California salt marshes (Rhew and Mazéas, 2010)) a picture is emerging of generally lower emissions from salt marshes in these cooler climates. In the conclusion to our paper we used the qualifying phrase “temperate salt marshes” four times to emphasise that our conclusions were not to be interpreted as referring to all salt marshes globally. (A problem here may be in what is meant by “temperate” so we have now modified the text in the conclusion – see further response below.)

We explicitly acknowledged in our paper our acceptance that scale up from single localities is flawed, a criticism directed equally as much at our own work, with the following text “This study therefore confirms again the very distinct flux magnitudes of methyl halides from salt marshes in these two climates, highlighting the pitfalls of large scale extrapolation from a single example of an ecosystem” (p 6314 of discussion paper). In the revised manuscript we have deleted the part of this sentence containing “pitfalls” – see further response below.

However, we accept that there was a tendency for the presentation in our paper to imply that our scale up estimate is ‘more’ correct, whereas we should have explicitly stated that the true global salt marsh emission likely lies somewhere between that estimated from extrapolation of the southern California and Scotland measurements, a point Prof. Rhew also makes in his later comments below.

To address these concerns we have made a number of modifications to our text as described in more detail below.

Specifically, there are 3 paragraphs that should be rephrased slightly.

2a. pg3. abstract: “A tentative scale-up indicates that salt marshes account for 0.5-5.4% and 0.05-0.46% respectively of total global production of these two gases, in line with previous findings from this and other research groups, but consistently lower than past scale-up estimates from California salt marshes”. The adverb ‘consistently’ (besides referring here to the single scale up) suggests that the 3 studies of 3 marshes in Ireland, Scotland, Tasmania) are more representative of coastal salt marshes globally than the 3 studies of 3 salt marshes (Newport Bay, San Dieguito Lagoon, Mission Bay Marsh) in southern California. There really is not enough information to make this suggestion, and for reasons outlined below, this suggestion may actually not be correct.

Response: The abstract has been modified and re-ordered in a number of ways, including the following:

- The sentence originally containing the word “consistently” now reads: “The fluxes from this work are similar to findings from this and other research groups for salt marshes in cooler, higher latitude climates, but lower than values from salt marshes in the Mediterranean climate of southern California.”

- Text on extrapolation has been moved to the end of the abstract, and includes the additional statements: “Extrapolation based solely on data from this study...” and “...actual global contributions likely lie between these values and those derived from southern California.”

(Additional factual note: The upper values of the ranges of % contribution to global budgets that Prof. Rhew quotes in his commentary above are not the values in the published on-line version of our *Biogeosciences Discussion* paper. The values differ because of the error we identified in our original reporting of the ‘linearity’ experiments in section 3.1.4 (see our comment on this above). As a consequence of correcting this error, the upper values of global scale-up ranges reported in the abstract and the discussion were modified downwards in the published *Discussions* paper compared with the version originally submitted for the technical review and from which Prof. Rhew quotes.)

2b and 2c. pg 18: This suggestion reappears with a statement on pg 18: “This study therefore confirms again the very distinct flux magnitudes of methyl halides from salt marshes in these two climates, highlighting the pitfalls of large scale extrapolation from a single example of an ecosystem”. Here, the term ‘pitfalls’ suggests that extrapolating from a single study is logically flawed, but the authors then accept their own extrapolation as a closer version of the true global value, both in the abstract as well as in the conclusion: “However, temperate salt marshes are unlikely to be a large global source of either methyl halide, amounting to only a few percent of the total global annual CH₃Br production and an order of magnitude less for CH₃Cl. . .”. The critique of regional or global extrapolations (common to all bottom-up studies) needs to be more nuanced. To assert that extrapolations are flawed because they are based on limited data (and yield tentative results) is not a useful criticism. Extrapolations are, by definition, based on limited data and should be made using the full range of data available. A valid criticism, in my opinion, is when extrapolations are made that use only SOME of the available data, but that is what the present study does: it extrapolates from two high latitude salt marshes in Scotland to the globe, when several other publications already exist from different regions. If the authors wish to provide a better, albeit tentative, extrapolation, they should use all the data available to them. On the other hand, if the point is to illustrate differences between different studies, then there should be less emphasis that this particular study represents the true global value.

There are reasons to argue that the best estimate for the global salt marsh source lies in between the extrapolations reported in this study and those from southern California. First, one of the ‘consistently’ smaller emitting marsh sites in Ireland was actually not a salt marsh but rather a coastal marsh located 40m from the high tide line (Dimmer et al., 2001). While likely influenced by sea spray, the predominant plants studied were not salt marsh plants. Second, all three ‘consistent’ marshes were relatively high latitude salt marshes, at 56 N, 53 N and 41 S. Our recent study of two northern (38 N) California salt marshes also shows a similar range, although the focus of our study was on gross fluxes rather than a complete seasonal study, so likely did not capture the full range of fluxes. In contrast, the southern California studies were at 33-34 N. The lower latitudes appear to support both the predominant vegetation and climatic regimes to produce much larger fluxes. The case can now be made that none of these salt marshes are representative of salt marshes globally. I think a valid point that the authors make, one that could be emphasized as the main point, is that there appear to be differences between temperate salt marshes and Mediterranean climate salt marshes. Thus, a global extrapolation should account for the global distribution of salt marshes and the geographic differences in net fluxes. A few small modifications in the text should provide a more appropriately contextualized conclusion.

Response: The above are all reasoned and valid points and it is very helpful that Prof. Rhew has brought these into the open discussion forum of *Biogeosciences (Discussions)*. We wholly agree that the accumulated data, including Prof. Rhew’s recent new data which we cite in the revised manuscript, now indicate different flux magnitudes between cooler temperate and

Mediterranean climate salt marshes, and that a more nuanced scale up taking into account the areas of salt marshes in different climate regimes is the way forward. We have made a number of changes throughout the paper to emphasise these points, including the following:

- In the opening sentence of section 4.7 we emphasise that the described scale up utilises only the measurements obtained in this work.
- Later in section 4.7, when presenting the derived annual global emissions, we again emphasise that the values utilise only the measurements from this study.
- In the penultimate paragraph of section 4.7 we have deleted the sub-clause that referred to “pitfalls of...extrapolation...” and have inserted in its place the following text: “This work therefore confirms again the very distinct flux magnitudes of methyl halides from salt marshes in these two climates. It now seems clear that a more nuanced scale up needs to take account of these differences and that salt marsh contribution to global annual emissions of CH₃Cl and CH₃Br will lie somewhere between those estimated here and those estimated by Rhew et al. (2000) (and Manley et al. (2006)) and used in the WMO reports.”
- We have modified text in part of the conclusion to read: “It appears that salt marshes in cooler temperate climates are unlikely to be a large global source of either methyl halide, ..., compared with the contribution of higher emissions from salt marshes in warmer, Mediterranean-type climates.”

III. Technical comments

1. (Introduction, 3rd paragraph): “no conclusive data on both the size and drivers of methyl halide emissions” should be re-worded. How can any data conclusively achieve that goal?

Response: Sentence has been rewritten to state that “...data remain sparse...”

2. (Introduction, 3rd paragraph): The Drewer 2006 reference should appear after the mention of a previous monitoring project. Also, the location name “Heckie’s Hole” did not appear in the prior paper. Only on page 17 did I learn that Heckie’s Hole was the same site reported in the Drewer 2006 paper. It would be preferable to include this detail also in the introduction.

Response: The sentence has been rewritten to make clear that the east coast salt marsh is called Heckie’s Hole and is the one previously studied by Drewer et al. (2006).

3. (2. Site descriptions): Overall a good description, except the part about the two small steps that makes the vertical zonation of the marsh difficult to visualize. This sounds like there are at least 3 parts to the marsh (lower, middle, upper) rather than 2 parts.

Response: The text has been clarified to refer only to the first step that separates the lower salt marsh (which has the 3 distinct vegetation zones described) from the upper salt marsh. The second step originally cited in the description marks the transition from the upper salt marsh to non salt marsh land. It is not relevant information and has been removed.

4. (3.1 Field enclosures): What is the ‘wet area nearest to the mainland (collar pair H)’?

Response: The answer is provided in the following sentence in section 2, the site description: “The lower marsh contains at least three distinct topographical and vegetation zones starting from the sea with a flat, sparsely vegetated zone mainly comprising *Puccinellia maritima*, intermittent areas of hollows and hummocks covered by *Aster tripolium*, and a narrow zone nearest to the mainland which is covered by a mix of *Aster tripolium*, *Juncus gerardi*, *Plantago maritima*, *Puccinellia maritima* and *Triglochin maritima* and which is markedly

wetter than the other parts of the lower marsh.” To assist the reader we have also reworded the start of the third paragraph of section 3.1 to refer back to previous description: “At Hollands Farm in the lower marsh area a single collar was installed on a bare patch of sediment (collar E) and one collar pair each on the previously described flat area (collar pair G), on the hummocks (collar pair F) and in the narrow wetter zone nearest to the mainland (collar pair H) on the 30 and 31 May 2007.”

5. (3.2 GC Analysis): *Phenomenex in “Torrance”, not Torrence.*

Response: This has been corrected.

6. (3.2 GC Analysis): *end of second paragraph: “mitigated” rather than “minimised”.*

Response: Text has been changed as requested.

7. (4.1 Results): *I found this paragraph confusing. The mean CH₃Br fluxes at Heckie’s hole do not appear to be “in general larger than fluxes recorded at Holland’s Farm”. The overall average is slightly larger, but the more important point is stated later: that the CH₃Br fluxes at Holland’s farm have a much larger standard deviation.*

Response: The text has been changed to “...on average larger and less variable than...”

8. (4.1 Results): *The paragraphs would benefit from a more parallel structure. The first paragraph discusses the differences of CH₃Br fluxes between the two marshes, and I was expecting the second paragraph to do the same, but instead it shifts immediately to the influence of vegetation on fluxes. It would be useful to have a similar comparison of CH₃Cl fluxes between sites to contextualize the vegetation effects later noted.*

Response: The following additional sentence has been inserted to provide the comparison requested: “In contrast to CH₃Br, mean unweighted CH₃Cl fluxes recorded at Hollands Farm were up to a third larger than fluxes at Heckie's Hole, but again were spatially more variable.”

9. (4.2. Annual and diurnal flux variations): *The term “spatial homogeneity” suggests similar fluxes across space, but I believe you are looking for some other term, like “spatially coherent response to. . .”*

Response: The text has been changed as suggested.

10. (4.2.): *There is a possibly relevant reference in Moore, 2008, “A photochemical source of methyl chloride in saline waters”, Environmental Science & Technology, 42, 1933-1937.*

Response: We are aware of this publication but think there is insufficient link with this work to warrant its citation.

11. (4.3.): *The organization of these paragraphs are roughly: season > location > air temp /chamber temp/ soil temperatures/ PAR. May I suggest organizing this more clearly by environmental factor > location > season? It is difficult to compare the influence of, say, ambient air temperature, when one has to read across paragraphs.*

Response: Since submission of this manuscript we have revisited the analysis of the data underpinning the observations described in this section. As originally presented, the interpretation of the possible influences of the range of drivers under consideration was based solely on statistical significance of a very large number of bivariate correlations. This

approach is susceptible to multiple testing issues and does not utilise the dataset as a whole to examine the influence of multiple factors simultaneously. We have therefore undertaken more sophisticated general linear model statistical analysis (including Bonferroni corrections for multiple testing) to draw out more generalised interpretations of the influence of site, season, and possible environmental drivers. Consequently the material in this sub-section has now been rewritten somewhat, with general statistical findings more clearly highlighted by the addition of two small tables.

12. (4.6 last sentence; also last paragraph in 4.7): There are numerous enzyme studies showing preference of Br over Cl. It may not have to do with nucleophilic substitution reactions favoring Br over Cl, but rather the kinetics associated with the plant methyltransferases (i.e., bromine is a more favored substrate at the enzyme active site).

Response: In the original manuscript it is not stated that nucleophilic substitution reactions are occurring. What we state is the propensity of CH₃Br production over CH₃Cl production and that bromide/bromine is more nucleophilic than chlorine/chloride. It does not seem unreasonable that the greater nucleophilicity of bromide/bromine contributes to it being a more favoured substrate for methyl halide formation at the enzyme active site; however whether the molecular mechanism of the enzymatic (or other) reaction is substitution or not we do not know so do not state.

13. (4.7, step #7.) How is the average relative standard deviations of the daytime fluxes at that salt marsh estimated? Are they weighted by area, similar to fluxes? Perhaps some detail can be provided in step #2 about this.

Response: Final standard deviations were derived by multiplying the mean pooled standard deviations of unweighted raw flux data of all collars used for the scale up by the final value of the seasonally and spatially weighted fluxes. The word ‘unweighted’ has now been inserted in step #7 to clarify this. Although the RSD values used were not adjusted by spatial weighting the values derived should still give a reasonable measure of uncertainty.

Drewer, J., Heal, M. R., Heal, K. V., Smith, K. A., 2006. Temporal and spatial variation in methyl bromide emissions from a salt marsh. *Geophysical Research Letters* 33, L16808, doi:10.1029/2006GL026814.

Manley, S. L., Wang, N. Y., Walser, M. L., Cicerone, R. J., 2006. Coastal salt marshes as global methyl halide sources from determinations of intrinsic production by marsh plants. *Global Biogeochemical Cycles* 20, GB3015, doi:10.1029/2005GB002578.

Rhew, R., Mazéas, O., 2010. Gross production exceeds gross consumption of methyl halides in northern California salt marshes. *Geophysical Research Letters* 37, L18813, doi:10.1029/2010GL044341.

Rhew, R. C., Miller, B. R., Weiss, R. F., 2000. Natural methyl bromide and methyl chloride emissions from coastal salt marshes. *Nature* 403, 292-295.