Biogeosciences Discuss., 7, C3155–C3162, 2010
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Biogeosciences Discussions

Interactive comment on "Long-term CH_3Br and CH_3Cl flux measurements in temperate salt marshes" *by* E. Blei et al.

R. Rhew (Referee)

rrhew@berkeley.edu

Received and published: 6 October 2010

I. General comments

This manuscript presents a 2+ year time-series of net flux measurements at two coastal salt marshes in Scotland and explores the environmental and biological factors that influence these fluxes. CH3Br and CH3Cl are the most abundant natural sources of bromine and chlorine to the stratosphere, where they undergo photolysis and contribute to halogen-catalyzed stratospheric ozone depletion. A major motivation for this particular study is that coastal salt marshes appear to be globally significant sources of methyl halides, but different geographic regions show disparities in the magnitude and the drivers of their fluxes. Consequently, there is a large uncertainty about the magnitude of methyl halide emissions from salt marshes globally, with some studies

suggesting a large influence while others (including this one) suggesting a smaller role.

The present work builds on their research group's prior study (Drewer et al., 2006, "Temporal and spatial variation in methyl bromide flux from a salt marsh") in several important ways: this study includes CH3Cl along with CH3Br; this study is conducted at two different salt marshes instead of one; and the time series is twice as long (2 yrs vs 1 yr). It replicates and thereby confirms their earlier findings regarding salt marsh CH3Br fluxes in Scotland, including the range of net fluxes, the strong diurnal and seasonal variability, the prominent role of vegetation, and the modest correlations with chamber or air temperatures.

The authors' argument for higher frequency measurements is supported by the large variability of fluxes over the course of a season. The auxiliary studies on effect of sunlight, plant halide contents, and vegetation removal provide insights on the drivers of the fluxes as well as ideas for future methodological improvements. The study provides a valuable dataset that is presented clearly in tables and in elegant figures. The paper convincingly makes the case that salt marshes in Scotland emit CH3Br and CH3Cl at rates similar to coastal or salt marshes in Ireland, Tasmania, and Scotland (in an earlier year), but at rates lower than those observed in southern California.

The authors are aware that the submission of this paper coincided with the submission of a related paper by our own group (now published as: Rhew and Mazéas, Gross production exceeds gross consumption of methyl halides in northern California salt marshes, Geophysical Research Letters, 37, L18813, doi: 10.1029/2010GL044341 (2010)), and hence anonymity here is waived. Our work in northern California salt marshes focused on measuring gross fluxes of CH3Br and CH3Cl, and there were several points that deserved cross-referencing. First, the range of fluxes observed in northern California was similar to that found in Scotland (and lower than southern California), supporting some of their points but requiring that California marshes be now distinguished as either northern or southern. Second, plant species variability

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dominates the variability of observed fluxes. Third, a strong correlation exists between CH3Cl and CH3Br fluxes, although the flux ratio differs between sites.

Overall, this study represents a solid advancement in our understanding of salt marsh fluxes of CH3Br and CH3Cl. There are a couple important issues that I believe the authors should address though. The first is a methodological issue regarding their flux measurements, which introduces uncertainties that are not fully discussed. The second is the suggestion that this study provides a better estimate of the global salt marsh source after employing the same method that the authors criticize: extrapolating from a single geographic region/study. These issues are discussed immediately below, with more technical issues addressed in the 3rd section.

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.

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?

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

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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.

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 CH3Cl. In figure 1a, the CH3Cl 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 CH3Cl and PAR is strongly influenced by this one point.

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 CH3Br and CH3Cl.

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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.

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,

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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.

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?

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

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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.

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.

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

5. (3.2 GC Analysis): Phenomenex in "Torrance", not Torrence.

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

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.

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.

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. . ."

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.

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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.

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).

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.

Interactive comment on Biogeosciences Discuss., 7, 6295, 2010.