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Interactive comment on "Atmospheric bromoform at Mace Head, Ireland: Evidence for a peatland source" *by* L. J. Carpenter et al.

L. J. Carpenter et al.

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Atmospheric bromoform at Mace Head, Ireland: Seasonality and evidence for a peatland source, Carpenter et al.

Reply to Referees

Referee #1:

Specific comments:

p. 5937, l. 16. Yes, actually the reference is Biester et al. (2004). This has been added.

p. 5939. We have added "the Bristol data presented here were instead calibrated using contemporaneous York CHBr3 data collected at Mace Head, as described below" to the

text.

p. 5940, l. 9. The term “organic correlation” is a standard definition. The line of organic correlation minimizes errors in both the x and y directions and defines the best-fit straight line as the line that minimizes the sum of the areas of right triangles formed by horizontal and vertical lines extending from observations to the fitted line (Helsel and Hirsch, 1992, p. 276). In comparison, the line of ordinary least squares minimizes errors in the y direction only and defines the best-fit straight line as the line that minimizes the sum of the squares of the distances of the data points from the best-fit straight line (Helsel and Hirsch, 1992, p. 275). Thus, for data sets containing errors in both x and y directions, the line of organic correlation is the preferable statistical tool. Text has been added to page 5940 to further explain the term.

p. 5940, l. 22. We have added the figures for the relative standard deviations of the CHCl3 and CHBr3 atmospheric data, demonstrating the higher RSD’s for CHBr3. Although the lifetime of CHBr3 is indeed 2 weeks - it will still show higher natural variability than CHCl3 whose lifetime is ˜ 3-5 months. Thus, the fact that the York and Bristol measurements were not taken over the exact same time periods will introduce more scatter in the CHBr3 comparison than the CHCl3 comparison.

p. 5941, l. 10. Done.

p. 5941, l. 12. Done.

p. 5941, l. 21. We have shown an additional event to highlight the strong co-variance (also see replies to Referee 2).

p. 5942, eq. 1. We have added more discussion of the tracer-ratio technique.

p. 5942, l.12. Done.

p. 5943, l. 21-24. References have been added.

p. 5944, l.21. Relative standard deviation surely needs no explanation - it is a com-

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monly used and well-known statistical term.

p. 5945, l.12.This is a typo, the CHCl3/CHBr3 ratio should actually be DCHCl3 / DCHBr3 : this has been corrected.

p5945, l.12-14. The value of the molar ratio (now 2.5 rather than 1.9) is now mentioned earlier, in section 3.2. The value used to calculate the actual emission ratios (in g) is this molar ratio multiplied by the MWt ratio: this is now explained more clearly in section 2.4 (equation 2).

p. 5945, l. 13-14. The same ratio has been used because it is assumed that the data reflect both peatland and other wetland sources (i.e. conifer forests). Of course, we have no way of providing separate ratios for peatland and for wetland sources.

Figures Fig 3 (now Fig 4). Solid line has been improved. Fig 4 (now Fig 5). For only 2 or 3 data points, it is inevitable that deviation from the average in one year will lead to a large increase in the error bars. Fig 6b. This was a typo - in any case this Figure has now been changed and incorporated into Figure 6.

References. All references have been corrected.

Referee #2:

Specific comments:

1. Correlation between the York and AGAGE CHBr3 data: We chose a linear fit to correct the data because, not only does it give the best correlation between data sets (as judged from R2 values: polynomial and exponential fits were also performed, and gave slightly worse fits to the data), but has a better physical basis in reality, because of the mass spectrometer's inherently linear response. The precise reason for the non-zero intercept is not known; we agree that incomplete trapping is probably unlikely due to the low-volatility of bromoform, however in the text (pg 5940, ln 23) we refer to "incomplete trapping or recovery". We believe the latter is more likely - i.e. possibly retention in the trap because of insufficient desorption temperatures. The adsorbent mixture used in

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the AGAGE microtraps have a high surface area with a macro/micro and meso-porous bed not tailored to suit quantitative recovery of CHBr3 at the desorption temperature used (245◦C). The text on pg 5940 has been changed to “incomplete recovery”

2. See reply to Referee 1.

3. We agree with the reviewer that the correlation between the York and AGAGE CHBr3 data is not very good at high concentrations, and that this could lead to an underestimate of the delta-CHBr3 values user in the tracer-tracer correlations. We already highlighted this as a potential source of error on pg 5945, ln 5. However, even an error of 100% in the delta-CHBr3 values used would comprise only a small contribution to the uncertainties stated in our estimates of global peatland emissions, which span over 2 orders of magnitude. Therefore, we maintain that this upper limit of a factor of 2 in the delta-CHBr3 values is an acceptable level of error for this sort of estimate, and certainly would not change the overall conclusions of the paper. The absolute numbers for the maximum levels of CHBr3 observed at Mace Head should indeed be treated with some caution though, although the monthly averages reported are believed to be accurate.

4. Regarding the regression of the delta-CHBr3 versus delta-CHCl3, shown in original Fig 6b, we have re-analysed the data and only included those points which back trajectories (included as a new Figure (7)) show had no immediate coastal influence. These data points are now shown as different symbols on Figure 6; the difference in these ratios compared to the immediate coastally-influenced ratios is clear. Because only 3 data points are used, clearly it makes sense to take the mean of the ratios rather than use a regression, as suggested by the referee. The average value of these new, selected, ratios is 2.5, compared to the original value of 1.9 from the regression. This has reduced slightly our CHBr3 emissions estimates.

5. The reviewer asks whether for the land breeze-events, the variation in CHCl3 are correlated with the variation in CHBr3. Figure 5 (in the original manuscript - now Figure 3) originally showed just one example of this, but we have now inserted another exam-

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ple. Clearly CHCl3 and CHBr3 are well correlated in each event and also the decrease in O3 is clear. The correlations were as clear as this on every single event - the Figures below give yet more examples. The data taken together strongly suggest a common source. We have added text to pg 5944, ln 6, emphasising that the variation in CHCl3 correlated very well with the variations in CHBr3 and in O3 during every one of these events.

Figures inserted here - sent in pdf file to Editor

6. Finally, (1) the height of the near-surface boundary layer should only influence the magnitude of the events, not the ratio of CHCl3/CHBr3, and (2) by using the back-trajectories as an additional selection criteria (see point 4), we hope to indeed eliminate any coastal influence on the data.

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 5935, 2005.