

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

**Anonymous Referee #2**

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This paper presents a 2.5 year time-series of atmospheric bromoform measurements from the Mace Head site. It is one of the very few such available time series for this compound, and has considerable value due to this fact alone. A major issue is that this coastal site has a summer maximum in bromoform concentration whereas other available long-term time-series have winter maxima.

The long time-series is based mainly on a long time-series of uncalibrated bromoform measurements made by the AGAGE network. Concentrations are assigned based on correlation with contemporaneous measurements that were made with a calibrated but separate analysis system, albeit for a period of only about 10 days. This is a clever way to extract useful information.

Overall the paper argues that in addition to strong local sources from coastal macroalgae, there is a significant source of both  $\text{CHCl}_3$  and  $\text{CHBr}_3$  from peatlands. On the basis of tracer-tracer correlations, a very rough estimate of this peatland/wetland source strength is made and this is scaled up to the global scale.

Overall I think the paper contains useful data concerning the seasonal cycle and variability of bromoform that are worthy of publication. However I have a few criticisms, questions and suggestions that need to be addressed/considered prior to acceptance.

#### Specific Comments:

The basis for the paper is the “calibration” of the uncalibrated AGAGE measurements with quite a short measurement campaign using a calibrated technique. Whereas for chloroform, there is good agreement between the two techniques, there is some uncertainty for bromoform. In particular the correlation between York  $\text{CHBr}_3$  and AGAGE relative responses (Fig 1b) is not really so good, with almost a factor of 2 uncertainty at higher concentrations. I specifically question the choice of a linear fit to the correlation between these measurements. The residuals seem to be non-randomly distributed at high concentrations, and the non-zero intercept also has also to be explained. With respect to the explanation of the intercept: it is unclear to me why the AGAGE trapping would be incomplete for the low-volatility bromoform. In any case, the sense of the intercept seems to be that it is the AGAGE measurements that are higher at low concentrations.

Higher natural variability for  $\text{CHBr}_3$  could possibly explain the scatter, but this difference in variability between  $\text{CHCl}_3$  and  $\text{CHBr}_3$  is not quantified from the data set, even though this should have been possible. Figure 6 seems to suggest  $\text{CHCl}_3$  variability can be both higher and lower than  $\text{CHBr}_3$  variability.

Inspection of Figure 1b suggests to me that a non-linear regression might better explain the York-AGAGE correlation. Assuming correct calibration of the York data, then this might imply that the relative response of the AGAGE data for  $\text{CHBr}_3$  is non-linear. Is

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this possible? Use of a non-linear regression, perhaps even forced through the origin, might provide a much better fit and also a better representation of the highs and lows in the time-series. Presently, the linear fit seriously underestimates peak concentrations observed in the York data set. This might in turn alter the magnitude of the delta-CHBr3 values used for the tracer-tracer correlations in Figure 6.

Hence the calibration of the AGAGE time-series is potentially critical to the overall conclusions of the paper and needs some more critical discussion, justification and possibly revision.

In section 3.2, it is not clear to me if the regression of the delta-CHBr3 versus delta-CHCl3 that is shown in Figure 6b is, in fact, significant. Also, the stated  $r^2$  value in the text (0.17) seems to differ from that shown in Figure 6b (in my copy this looks like -0.3187 which seems an unlikely value for an  $r^2$ !). Also: given that the ratio is based on differences of CHBr3 and CHCl3 from a 'baseline' atmospheric value, it is unclear to me why a regression with a non-zero intercept was used to estimate the ratio of emissions. Would it not be simpler to simply calculate the individual "delta" ratio values for the individual events and average them, or take the median?

It occurs to me that perhaps the really important question is: for the land breeze events, are the variations in CHCl3 correlated with the variations in CHBr3? If so, then this might indeed suggest a common source for both compounds. If not, then the data may be telling us that there are separate sources for both (see below). In the manuscript at present, a common source seems to be assumed a priori, and an attempt is then made to calculate the emissions ratio.

In the discussion of the land-sea breeze events and ratios, a couple of further issues are not fully discussed: (1) might the height of the near-surface boundary layer be a factor that can affect the ratios? (2) Can it be absolutely ruled out, for the northeasterly trajectories, that the CHBr3 might still be "mixed-into" the air mass from a nearby coastal source whereas the CHCl3 comes predominantly from the peatlands? Are the

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trajectories truly devoid of possible coastal influence (see abstract).

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