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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Consistent simulation of bromine chemistry from the marine boundary layer to the stratosphere – Part 2: Bromocarbons" *by* A. Kerkweg et al.

Anonymous Referee #3

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This is a fairly interesting model study of bromine from bromocarbons. It represents a follow up to the Warwick et al. study performed with a different model. The present study draws upon many aspects of the previous work and makes extensive comparisons to existing measurements. Given the sensitivity of atmospheric Br burdens to transport and loss time-scales and the importance of Br to both tropospheric and stratospheric chemistry, analyses of these compounds by multiple models seems quite appropriate.

Some issues for consideration by the authors: Conclusions regarding a longer CH3Br lifetime are not supported (abstract, conclusion, p. 9492). CH3Br emissions are said to

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be derived from observed surface concentrations and a modeling approach TNUDGE, which is not qualitatively described in the paper thus making it difficult to assess its robustness. The observed surface concentrations used to constrain emissions are minimal: AGAGE surface concentrations are available from 2 sites only–these are assumed to be representative of all longitudes and are extrapolated to all latitudes (other, more widely distributed and published data is not considered). A significant flux in the CH3Br budget is related to oceanic production and loss–no mention of how the ocean is handled with respect to CH3Br is considered, yet a careful study of the CH3Br lifetime would include detailed consideration of this process. If oceanic loss is ignored in a simple assessment of CH3Br lifetime, the CH3Br lifetime becomes greater than 1 yr. Given these shortcomings, I conclude that this estimate of lifetime does not represent an advancement in our understanding of this important quantity.

The lifetimes quoted in WMO (2006) are explicitly stated to be local lifetimes (Table 2-1 in WMO report), i.e., calculated for a specific OH and light flux. The actual lifetime you calculate in your model is dependent upon the emission distribution you use. Hence, it isnot appropriate to suggest that the CHBr3 loss included in your model is larger than suggested by lifetime quoted in the WMO report (p. 9484, lines 20-30). You would need to calculate a local loss given the OH rate constant and photolysis parameters for equivalently averaged time and space to address the issue you hope to. (Text to qualify of the WMO lifetime in this regard in your Table 2 seems necessary too.)

CH3Br emissions are time-dependent, given the changes in industrial production that have been reported since 1998. While some accounting for this fact is included in the manuscript, it would be clearer if in Figures 17-23 years of the campaign were explicitly indicated in the caption. Also, it isn't explicitly stated that emissions were derived based on observations in the year 2000 alone, is this true?

The section on 'Bromocarbons as sources of reactive bromine' is interesting, but I can't see how the entries in Table 3 are consistent with Figure 24 regarding the rate of Br radicals from CH3Br and CHBr3. A fairly similar area above the tropopause looks to be

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shaded non-purple for both compounds (CH3Br max is even larger than CHBr3), and yet the rate of Br production from CHBr3 is stated in Table 3 as being 2.5 times higher than from CH3Br...? Furthermore, it seems that the graphical projection is drawn as a function of latitude, which potentially under-represents tropical latitudes. You might recheck the calculation and explain it, the averaging or summing, and weighting more fully.

Also in this section, some imprecise/unsupported text: Line 20-25, p. 9493: "Stratospheric bromine chemistry becomes important above..." with respect to ozone chemistry or something else? Furthermore, does most of the Br from CHBr3 formed in the lower stratosphere reach the upper stratosphere or not? Line 23-26, p. 9494: The sentence "In the stratosphere the photolysis of halons contributes substantially to the Br production' is not supported by any figures or discussion. On what basis is this conclusion drawn?

Can the accuracy of the Br production rates calculated here be assessed to any degree by the total Br mixing ratios they would imply? Mixing ratios of inorganic Br are not given, but might further confirm, if they were calculated to be above 25 ppt, for example, that the contribution of CHBr3 is likely overestimated here. This is one reason for the substantial interest in these compounds, no doubt. The authors have a tool to address this important issue, and for some reason don't follow through.

Following up on this, the text in the conclusion regarding CH3Br (lines 18-20) should include the point that the contribution to stratospheric Br calculated here is also likely overestimated.

Finally, I'm not sure all the multi-paneled figures are necessary. Furthermore, they don't readily convey how any discrepancy or agreement varies with region or season (e.g., line 19, p. 9491). Some summarizing of these differences might be useful. Perhaps plotting flight tracks on modeled distributions would be helpful too.

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