

## ***Interactive comment on “Atmospheric trends of the halon gases from polar firn air” by C. E. Reeves et al.***

**C. E. Reeves et al.**

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Response to Anonymous Referee #1

Below we respond (A) to each of the referees comments (R).

Firstly, we would like to thank the referee for their comments, which have helped us improve our manuscript.

R. General: This work represents a useful addition to our understanding of past atmospheric composition, especially regarding halons, which are potent ozone-depleting gases. It extends previous studies because lower mixing ratios were found in older air. This reduces the possibility of any significant natural contribution to halon amounts observed in today's atmosphere. The authors also use the results from the different

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hemispheres to provide constraints on emission distributions over time. Emphasis on inferred emissions tends to diminish the paper in some instances.

A. We are not entirely sure why the referee makes this final comment. Much of the purpose of the paper is to use the new firn data to determine the emissions of the halons. Not only does it allow us to extend previous studies because lower mixing ratios were found in older air as the referee points out, but for H-1202 and H-2402 it allows us to evaluate the latitudinal distribution of emissions since we provide the first long term record in the northern hemisphere.

R. Specific: I find the description of methodology confusing in the abstract, on p. 940, lines 10-15, and p. 942, lines 7-15. Why the emphasis on emissions here, which unnecessarily confuses and convolutes the issue? Wouldn't it be clearer and more accurate to state in each of these places specifically that atmospheric trends were derived fundamentally from archive air measurements in the SH, and these results were extended in time and space (across the globe and to earlier years) with a 2-D model calculation. These derived trends were used as input to a forward firn model, and the calculated depth profiles were compared to those measured. Along a similar vein, the fact that a measured depth profile can be reproduced with a calculated history and firn model shows that the history is consistent with the firn measurements. To suggest that the consistency "shows that the trends in global emissions are consistent with these firn measurements" is much more of a stretch, especially for H1202 (p. 945, lines 1-3).

A. We have tried to reword the abstract in light of the referees comments, but, as we say above, using the firn data to evaluate the emissions is an important part of the paper. Obviously we wish the methodology to be clear so we have reworded lines 8-14 of the abstract as follows: "A 2-D atmospheric model was run with emissions previously derived using archive air measurements from the southern hemisphere mid-latitudes to produce historical trends in atmospheric concentrations at the firn sites, which were then input into a firn diffusion model to produce concentration depth profiles for com-

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parison with the firn measurements. This comparison provides an evaluation of the model-derived atmospheric concentration histories in both hemispheres and thus an indirect evaluation of the emission rates and distributions used in the atmospheric model. Atmospheric concentration trends produced using global emissions previously determined from measurements at Cape Grim are found to be consistent with the firn data from the southern hemisphere.” We have also removed the first part of the sentence beginning on line 10 of page 940 as suggested by the other referee and trust that this removes the confusion referred to above. However, we are not sure what the referee finds confusing about p. 942, lines 7-15, so have left this unchanged. We have deleted the part of the sentence on page 945, lines 2-3, which the referee did not like.

R. On potential model transport scheme errors and uncertainties: Model tests on CFC-11, -12, or methyl chloroform don't test the validity of model-calculated photolysis rates at longer wavelengths, which are relevant to H1202. The model-inferred measurement differences in the NH are assumed to be entirely the result of emissions distributions though significant uncertainties in H1202 lifetime likely exist. How sensitive are your conclusions regarding emissions distributions of this halon, in particular, to the calculated photolysis rate of this gas? Would an increased photolysis rate of 20% negate your conclusion on the emission distribution of H1202, or is your conclusion robust? I think the authors would agree that the lifetime of H1202 has considerably more uncertainty than the other gases, hence some investigation into its influence on their conclusions seems warranted.

A. The referee makes a very good point here. The lifetime assumed for H1202 will affect the model-derived atmospheric concentrations. A model run was performed as suggested by the referee in which the photolysis rate of H1202 was increased by 20%. Although this reduces concentrations at NGRIP by up to about 10% (still much higher concentrations than implied by the firn data), it also reduces concentrations at Dome C such that the ratio between the concentrations at the two sites (NGRIP/Dome C) increases. One way to reduce this ratio would again be to shift the emissions to more

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southerly latitudes. However, decreasing the photolysis rates by 20% has the reverse effect of increasing concentrations, whilst reducing the concentration ratio. Although the model-derived atmospheric burden is then too high, the global emission rates could be reduced, since they were only after all derived using the model with the assumed photolysis rates. Thus it should be possible to adjust the photolysis rates and the global emission rates to give reasonable agreement at both sites without adjusting the latitudinal distribution of the emissions. So the question is how sensitive are model results and thus the conclusions to the photolysis rates? Decreasing the photolysis rates and increasing the emissions rates both by 20% reduces concentrations in 2001 at NGRIP by 9%, whilst only reducing those at Dome C by 1%. This change at NGRIP is still far less than the 30-50% required. To reflect this point the following text has been added to page 946, line 11. "Increasing the lifetime of H-1202 would decrease the IHG towards that implied by the firm data. Although this would increase the concentrations of H-1202, the global emission rates could be reduced since they were originally derived using the assumed lifetime. For example, decreasing the photolysis rates and increasing the emissions rates both by 20% reduces concentrations in 2001 at NGRIP by 9%, whilst only reducing those at Dome C by 1%. However, this change at NGRIP is still far less than the 30-50% required."

R. The authors should consider showing the updated atmospheric trends used in the forward firm model (else change the title to mention emissions), even if they are similar to those shown by Fraser et al (1999). How else are to we evaluate the extent to which the "firm measurements provide constraints on the atmospheric concentrations in both hemispheres" (argued as being made possible by this work in the abstract).

A. The atmospheric trends were updated by extending the model run from 1998 to 2001 to make use of the more recent data collected at Cape Grim since the Fraser et al (1999) paper. These observations from Cape Grim are part of another paper in preparation so we do not wish to show them here. We do, however, provide historical trends in atmospheric concentrations of total organic bromine from the halons for the

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two sites in Figure 6. After considering the referees comment, we do agree that the title of the paper does not reflect well the content of the paper so have changed it to “Trends of halon gases in polar firn air: Implications for their emission distributions”. Since the firn measurements are from both Arctic and Antarctic sites they do provide constraints on atmospheric concentrations in both hemispheres so we do not understand the comment made by the referee here. For H-1202 and H-2402, we provide the first long term record in the northern hemisphere, and it is this that allows us to show that there is problem with the modelled budget of H-1202 which can be solved by shifting the emissions further south.

R. Perhaps this would allow you to open the discussion and help the reader understand, for example, why the measured mixing ratio in the deepest Devon Island sample has a mixing ratio  $<0.001$  despite a CFC-12 mean age that encompasses years (1930-1977) in which H1202 emissions were non-zero.

A. Independent iterative firn-modelling of the H1202 trend (the technique of (Trudinger, Etheridge et al. 2002)) has been used to directly derive atmospheric concentration histories of the halons at North GRIP (this work is not shown in the paper in the interests of brevity and because it did not alter the overall findings). This modelling showed a NH atmospheric H1202 concentration of about 0.005 ppt in 1970; obviously increasing towards 1977 and less in earlier years (zero before about 1958). The CFC-12 age spectrum referred to in the paper is derived from a Green function calculation, as shown in (Sturges, Penkett et al. 2001) wherein the shape of such probability curves is illustrated for Devon Island. Let us say that the youngest ages (e.g. 1960 to 1977) account for as much as 20% of the age spectrum, and are represented by an atmospheric concentration of 0.005 ppt, and that the older air has a concentration of zero. The concentration in the firn air sample from this point would then be 0.001 ppt, i.e. right on the detection limit. It is also worth noting that the actual ages are dependent on the diffusivity of the particular gas and its local concentration gradient. In the case of H1202 it is less diffusive than CFC-12 and so the age range quoted for CFC-12

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will in any case be shifted a little older for H1202. Really one has to consider the firm model to interpret the reconstructions, rather than assign specific dates to a particular firm air sample or depth level. We do not feel that it is necessary to explain all of this for the purposes of this paper, but have added the following text to help clarify things “The spread of ages within each individual sample, however, particularly at the bottom of the firm, is very large (Sturges et al., 2001b). This age spectrum for CFC-12 is given to provide an indication of the spread of ages at depth in the firm. The mean ages for the halons will differ slightly from that of CFC-12 since (with the exception of H-1301) they have free air diffusivities less than that of CFC-12 (e.g. 21% less in the case of H-2402), and so will likely have slightly older mean ages than CFC-12 at the same depth. The firm model is required to obtain more accurate representations of the temporal trends of the molecules of interest.”

R. Technical items Text indicating “concentrations are zero” would be more accurately and appropriately stated (at least initially) as “mixing ratios were below detection (<0.001 ppt)”. I would think it useful to mention that this represents 2% of the modern day atmospheric abundance of H1202 and much less for the other halons.

A. We agree that technically it is not correct to state that the concentrations were zero. We have therefore altered the text accordingly. I.e. In the abstract we have now written “to be close to zero (i.e. below the detection limit of 0.001 ppt)” and in the results section “below detection limit (<0.001 ppt) at the base of the firm (Fig. 1), which represents 2% of the modern day atmospheric abundance of H-1202 and much less for the other halons.”

R. p. 941, lines 13-21. Calibration scales change over time, is there a time stamp on the intercomparisons that could be mentioned here (or AGAGE scale date)? Or is this information based upon the same intercalibration activities that were discussed in Fraser et al., 1999 (if so, reference)?

A. We have added the date when this information was received from Fraser.

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R. p. 944, line 15. Results from convective zones not included in plots-OK, but please indicate the depths excluded at the different sites (in text or figures caption).

A. We have now specified the depths excluded: “(above 10m for NGRIP and Dome C, and above 3 m for Devon Island)”.

R. Section 3.3 and Figure 6 caption would be better labeled as “Total organic bromine from halons” and “Historical trends &#711;E of organic bromine from halons at (a) &#711; E”

A. We have changed the Figure 6 caption to the following to account for the comments made by both referees: “Historical trends in atmospheric concentrations of total organic bromine from halons at (a) NGRIP, (b) Dome C (plotted as the sum of Br from the halons).”

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Interactive comment on Atmos. Chem. Phys. Discuss., 5, 937, 2005.

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