

Interactive comment on “Southern hemispheric halon trends and global halon emissions, 1978–2011” by M. J. Newland et al.

M. J. Newland et al.

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Thank you for taking the time to read and comment on our manuscript. This has helped to improve the quality and clarity of the paper.

Comment:

It isn't very clear to me if the entire CGAA sample record was re-analyzed or if some of the results were taken from Fraser et al., 1999. It would be good if you could clarify this.

Author response:

Replaced “The GasPro/Autospec Premier combination has also been used to reanal-

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yse selected samples from before 2006...” With “The current GasPro/Autospec-Premier combination has also been used to reanalyse selected samples (21) collected prior to 2005...”

This point is hopefully also clarified by the inclusion of the actual measurements in the supplementary information, as requested, which specify whether the analysis was made using the AI-PLOT column or the GasPro column.

Comment:

Part of the confusion is the unclear distinction between ‘measurement dates’ and ‘samples dates’. If you could be more specific about that throughout this paragraph, that might help a lot. E.g. l. 5 p. 29293, ‘Up until 2006, the ...’. Does this mean samples collected up to 2006, or does this mean that analysis date 2006?

Author response:

Replaced “Up until 2006, the Cape Grim samples were analysed using an Agilent 5890 gas chromatograph...” With “All Cape Grim samples collected between 1978 and the end of 2004 (94 samples) were analysed using an Agilent 5890 gas chromatograph...”

Comment:

Here it suggests that this year refers to when measurements were made (of the flasks), but that leaves unclear if this is coincident with the sample collections. It becomes more confusing later (l. 15) where then it is mentioned the ‘to reanalyse selected samples from before 2006’. Do you mean ‘selected samples collected before 2006’ or, ‘selected samples, which had been analysed before 2006’?

Author response:

Replaced “The GasPro/Autospec Premier combination has also been used to reanalyse selected samples from before 2006” With “The current GasPro/Autospec-Premier combination has also been used to reanalyse selected samples (21) collected prior to

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2005. . .”

Comment:

Is the assumption correct that the switch to the updated GC-MS and the switch to the Agilent GasPro column occurred at the same time? Would this mean that the individual effects of these two rather major changes could not be investigated (as the changes were simultaneous)?

Author response:

The changes did not occur simultaneously, the new AutoSpec came first and then the column change, but unfortunately no Cape Grim samples were analysed for the halons during the intervening period. However the good comparability of the record with the original setup and the new setup means that this is not a problem.

Comment:

‘During the 1978–2005 period, several different alumina-PLOT columns were used ...’ This suggests that you already started measuring these samples in 1978, but this is hard to believe. Comparison of the ‘seven samples’. Is it correct, that these selected samples were analyzed on a Chrompack PLOT column, then on an Agilent PLOT column, and later on an Agilent GasPro column (with the Autospec MS), so three times analyzed? If so, which two sets do we exactly see in the suppl figs? In that sense, the caption to the figs in the suppl. material could be a bit more detailed. You mention ‘seven’ samples, but it looks like more than seven samples on these plots.

Author response:

The plots in the supplementary material have been redone, as suggested by the reviewer later on, hopefully this clarifies the comparison.

Comment:

l. 27: suggest to replace ‘..H-2402 data which was ...’ by ‘... H-2402 samples, which
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were ...’ if this is what you’d like to say.

Author response:

‘was’ replaced by ‘were’

Comment:

Are the mean precisions 1 or 2 sigma, and how were they determined (through repeated Cape Grim sample analysis or perhaps differently)?

Author response:

The mean precisions are the mean of the precisions of all of the Cape Grim measurements for each halon. The precisions for each measurement are calculated as the absolute uncertainty divided by the measured mixing ratio. The uncertainty of each measurement is calculated as the 1-sigma standard deviation of the combined analytic and calibration uncertainties.

Comment:

Calibrations: Please state the accuracies for the NOAA-2006 scales for H-1301 and H-1211. Please do the same for H-1202 and H-2402 and explain what defines the UEA scale, how the primary material was prepared etc, how many primary standards etc, or refer to potential publications that may detail this. Is it correct that for each compound, so far (since Fraser et al., 1999) there has been one single UEA calibration scale, and that the UEA calibration scale was never revised since (except that for H-1301 and H-1211 the UEA scale is not used anymore in this paper)? Is the description in Fraser et al., 1999 still accurate?

Author response:

The accuracies are now stated, “The uncertainties for the NOAA-2006 gravimetric scale are estimated as 1% for H-1211 and 2% for H-1301 (Brad Hall, personal communication), those of the UEA volumetric scale are estimated as 4% for both H-2402 and

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H-1202 (Fraser et al., 1999)”

The standard preparation details are the same as in Fraser et al., this hopefully clarifies this, “H-1202 and H-2402 are presented on the UEA volumetric scale (see Fraser et al., 1999 for details of standard preparation).”

Comment:

My main concern is that I cannot reproduce your scale conversion from UEA to NOAA-2006, when I compare the results in Fraser et al., 99 (UEA scale) to the present ones (NOAA-2006), which presumably the fitted CGAA results in Table S1 are reported on (It would help to mention in the caption that these results are on NOAA-2006 for H-1301 and H-1211, and on UEA scale for the other two compounds).

Your statement on p. 29294 l. 10 ff is confusing. 'The ratios of the UEA volumetric scale, used in previous work, to the NOAA-2006 gravimetric scale is 1.13 for H-1211? Is it not the other way around? As is written now, I would think that mole fraction reported on UEA are higher than those reported on NOAA-2006. That is clearly not the case when comparing the data sets. It may be less confusing if rephrased to something like 'the conversion between the two scales is such that mole fractions, previously reported on UEA must be multiplied by 1.13 to convert to NOAA-2006.

But then comes the next confusion, e.g. take Fraser et al., 1996 values (2.0 ppt on UEA), and try to convert to the (fitted) new 1996 values of 2.45, that is clearly not a factor of 1.13 (or the reverse of it). This needs an explanation. The conversion also doesn't seem to be correct for H- 1301 although there it is a bit more difficult to compare the measured flask values and the yearly means from the fit. For H-2402, the results in Table S1 (present work) and Table 1 (Fraser et al.) are both on the UEA scale, and the measurements for samples younger than 1998, which are not affected by the small nonlinearity issue, should then identical within the measurement precisions of the two data sets. Is this correct? If not, could you comment on agreement/disagreement. Same for H-1202.

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Author response:

The calibrations section was written in a confusing way, the text now reads: “To convert from the UEA volumetric scales, used in previous work, to the NOAA-2006 gravimetric scales, H-1211 mixing ratios are multiplied by 1.19 and H-1301 mixing ratios are multiplied by 0.89. H-1202 and H-2402 are presented on the UEA volumetric scale as described in Fraser et al. (1999).”

I agree that measurements post 1998 should be the same as the Fraser et al., paper. However this refers to only one measurement and there is agreement for that one measurement.

Comment:

Is it possible that not all samples show in Fraser et al., Table 1 were re-analyzed. It looks like the current data set before about 1990 looks much more sparse, particularly for H-1301.

Author response:

For H-1301 and H-1202 all the original samples from the Fraser et al. paper are shown (but now on the adjusted NOAA-2006 calibration scale for H-1301). The symbols have been changed to solid black diamonds to make them easier to see in the inset panels. The distinction between the data from the two analysis setups (originally presented as brown circles and open black diamonds) has also now been removed since we consider it to be one consistent dataset. All UEA measurements are now shown as open black diamonds in the main panels and solid black diamonds in the insets.

Comment:

While I recognize the very valuable listing of yearly Cape Grim mixing ratios from fitted data (Table S1), it is really a pity that you do not publish your measurement results of the CGAA, and I'd like to encourage you to do so in an additional table (given that the samples were really re-analyzed, which is not becoming clear to me when reading the

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manuscript). Such a table would allow for a comparison with (yet unpublished) CGAA halon measurements by other groups.

Author response:

This has been done.

Comment:

Are the numbers reported in para 4 those listed in Table S2? If so, this should be mentioned. Some of these numbers (e.g. p. 29300 1.4 , 3.0 Gg), don't seem to match those in Tables S2. Also, the HTOC cumulative emissions for H-1301 1979–2009 seem to be 97 (not 99) Gg if you define 1979–2009 by subtracting the cumulative emission reported for the year 1979 from the year 2009.

Author response:

The numbers in the text of Section 4 now match those in Table S2.

The HTOC cumulative emissions should be 99 Gg. They were calculated by adding up each year's emissions as reported by HTOC. Subtracting the cumulative emission reported for the year 1979 from the year 2009 would give you the cumulative emissions of 1980 to 2009 inclusive.

Comment:

Reference Douglass et al., 2008 seems to be missing. The citation Montzka and Reimann (2011) is not consistent, see e.g Table 2 caption.

Author response:

Added Douglass reference and changed all references to Montzka and Reimann (2011).

Comment:

One last comment that might help improve the figures of the supplementary materi-
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als. Presuming that the purpose of the figs S1 to S4 is to demonstrate the degree of agreement/disagreement between various measurement techniques: Then it would be much more illustrative to not show GasPro vs AI-Plot but to display the difference GasPro–AI-Plot on the y-axis while keeping the AIPlot on the x-axis. This difference could be plotted in ppt or as percentage, or both. That would show much more details on potential variability. Also, it should be stated that the fits were forced through 0/0, if that is the case, and if the fitting routine has taken both delta-x and delta-y into account, or perhaps only delta-y.

Author response:

These plots have been re-done as suggested hopefully making the comparison between the measurements acquired using different techniques clearer.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 29289, 2012.