Atmos. Chem. Phys. Discuss., 12, C13039–C13048, 2013
www.atmos-chem-phys-discuss.net/12/C13039/2013/

Atmospheric Chemistry and Physics Discussions

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

M. J. Newland et al.

m.newland@uea.ac.uk

Received and published: 1 March 2013

We would like to thank the reviewer for their thorough review which has helped to improve the quality and clarity of our manuscript.

Referee comment:

I am not in favour of publishing the manuscript in ACP in its present form, as there are too many messages packed in this paper which are rather speculative, which could be resolved in a better way (assumptions about the source of H-1202 and estimations of banks, based on the application of a simple 2-D model and new lifetimes from a paper in ACPD).

Author response:

The basis of this paper is the extension of a set of well established measurements of halon concentrations and the derivation of global halon emissions based on previously published methods using a 2-D model. The estimation of the banks is simply calculated as the difference between the derived emissions and the production data reported by HTOC, and is a useful check for consistency. None of this is speculative. The results from this work however raise some interesting questions, for example the source of the H-1202. Furthermore the recent re-evaluation of the stratospheric lifetimes of, in particular, H-1211, which is now accepted for publication in ACP, also raises questions about the size of the bank. Answering these questions is beyond the scope of this paper, but we think it is worth some speculation in order to highlight areas of future research that may lead to answers to these questions.

As stated above we have now re-ordered the paper to separate the work that is based on established methods and reported data from that which is based on new lifetimes, to provide clearer distinction. Moreover, we have taken on much of the advice given by referee #1 (and referee #2) to reduce the speculation.

Referee comment:

P.29290 L.8: Mention that the increase of H-1301 is still on-going in 2011, in order to distinguish this finding from that made in chapter 1 of WMO (2011).

Author response:

Replaced “Mixing ratios of H-1211, H-2402 and H-1202 began to decline in the early to mid-2000s but those of H-1301 continue to increase throughout the record.” With “Mixing ratios of H-1211, H-2402 and H-1202 began to decline in the early to mid-2000s but those of H-1301 continue to increase up to mid-2011”

Referee comment:

P29292. L.12 Do authors mean stratospheric?

Author response:

ACPD

12, C13039–C13048, 2013

No. Unfortunately we can't comment on stratospheric bromine contribution (though it is obviously linked to tropospheric bromine) because the atmospheric model does not represent the whole of the stratosphere.

Referee comment:

P29293. L5ff Mention that these samples were measured at UEA. Or were some samples measured at Cape Grim/CSIRO?

Author response:

Replaced "Approximately 130 samples collected at Cape Grim, Tasmania (40.4°S, 144.4°E) have been analysed for the 4 major halons (1211, 1301, 2402, 1202)." With "Approximately 130 samples collected at Cape Grim, Tasmania (40.4°S, 144.4°E) have been analysed at UEA for the 4 major halons (1211, 1301, 2402, 1202)."

Referee comment:

P.29293 L: 26: It is mentioned that measurement before 1989 were excluded from the analysis. Why are then brown data points shown in Figure 1? Does that in essence mean that the analysis should only go back to 1989 (then the title needs to be changed)? Or do authors use numbers from a different source (e.g. Fraser et al. 1999)? Then this should be mentioned.

Author response:

The original measurements (made using a Chrompak Al-PLOT column) of H-1211 and H-2402 from samples collected prior to 1989 were excluded due to an apparent small unexplained non-linearity, as explained in Section 2.2 and in the supplement. However seven samples collected before 1994 (five of which were before 1989) were reanalysed for these two compounds using an Agilent Al-PLOT column. These do not show any detectable non-linearity and are presented for these two compounds prior to 1989. Also some samples (five for H-1301 and H-1211 and four for H-2402 and H-1202) from this period were reanalysed using the new setup (GasPro column and AutoSpec Premier),

ACPD

12, C13039–C13048, 2013

Interactive Comment

these measurements are also presented.

This was obviously unclear in the original paper since all reviewers have mentioned it. We have re-written Section 2.2 to hopefully be clearer and we have also included a full table of the measurements presented in the supplement detailing which system was used for each analysis.

Referee comment:

P. 29296 L6ff: I don't really see the point why the OH radical is included, as halons do practically not react with OH (or not to my knowledge).

Author response:

The authors agree with the reviewer's comment that the rate of reaction of halons is very slow. We have done model runs which suggest that the lifetime with respect to OH is at least 50 times greater than that with respect to photolysis for all of the halons. However we do emphasise in the introduction that the main loss of the halons is to photolysis and would like to leave the reference to OH in for the sake of completeness.

Referee comment:

P.29297 L 11: From the figure 1 it looks more like 3.75 ppt than 3.9, which would also be more in line with AGAGE and NOAA measurements.

Author response:

Replaced "The mixing ratio of H-1211 grew rapidly during the 1980s and 1990s from about 1.3 ppt (parts per trillion) in 1985 to a mean of 3.9 ppt in 1999..." With "The mixing ratio of H-1211 grew rapidly during the 1980s and 1990s from about 1.3 ppt (parts per trillion) in 1985 to a mean of 3.9 ppt at the end of 1999. . ."

Referee comment:

P.29297 L 13: be more specific: began to slowly decline in 2006.

ACPD

12, C13039–C13048, 2013

Author response:

Replaced “The mixing ratio began to level off after 1999 reaching a maximum of 4.2 ppt and concentrations at Cape Grim began to slowly decline. The mean mixing ratio in the first half of 2011 was 4.0 ppt.” With “The growth rate began to slow after 1999 and mixing ratios reached a maximum of 4.2 ppt in 2003 – 2005. Thereafter the concentrations at Cape Grim began to slowly decline to a mean mixing ratio in the first half of 2011 of 4.0 ppt.”

Referee comment:

P.29302L.17ff This hypothesis could be either easily tested by measuring a sample of H-1211 (as you suggest on page 13. Line 22, and I strongly suggest that you do this) or by asking HTOC (see below) what they think about this. If this is the case and H-1202 is contained to about 4% in H-1211 this would be a major finding of the paper.

Another reason could be that there is another source not connected directly with the usage of H-1211 and which also has stopped. Interestingly, I have found a safety data sheet for recycled H-1202 at a specialised company for fire protection in airplanes and for military applications.

http://www.walterkidde.net/Files/KiddeAeroSpace/Global/US-en/Recycled_Halon_1202_- _KA005_1107.pdf

A very good person to ask (or THE world expert in the field) is Dan Verdonik DANV@haifire.com, who is part of HTOC. I would strongly suggest that you ask him about this issue.

Author response:

As suggested by the reviewer we have contacted Dan Verdonik who tried to find any information on the contamination we propose. His response was, “Companies that purchase and recycle halon 1211 have never seen halon 1202 as a contaminant. I tried to get information from Asia, particularly China but was unable to. It is possible it

ACPD

12, C13039–C13048, 2013

is in China's halon 1211 but that would not explain the amounts before China had any halon 1211 production" He suggests that it could be used as a chemical feedstock in various processes.

We have followed up the referee's suggestion of looking at the Walter Kidde reports. Reports such as http://www.walterkidde.net/Files/KiddeAeroSpace/Global/US-en/TechnicalPaper.pdf suggest that H-1202 was originally more widely used by the military but later largely replaced by H-1301. The issue of its use as a fire extinguishant in military aircraft has also been mentioned in previous HTOC reports. The 1991 HTOC report (http://ozone.unep.org/teap/Reports/HTOC/HTOC91.pdf) suggests that the military's H-1202 was purchased from H-1211 producers, having been produced as a by-product of the H-1211 production. Another possibility for the decline in use of H-1202 could be the cessation of H-1211 production and hence there being no further source of H-1202.

The suggestion of obtaining and analysing an old halon fire extinguisher is a sensible one, but given the comments of Dan Verdonik (above) and the timeframe available, this has not been possible. Moreover, we do not believe that testing a single sample from one source would have provided sufficient proof. A far more extensive study would be required, including the analysis of extinguishers from a range of international suppliers, which we consider to be beyond the scope of this paper.

To address the referee's comments we have changed the discussion in section 7. Firstly, we have focussed on what our measurements and derived emissions can actually provide as constraints and the questions that they raise. Secondly, we have then put forward some suggestions of possible explanations that will require future investigations. By its nature, this latter part is still somewhat speculative, but we hope that it is now more robust, especially with the inclusion of the extra information discussed above.

Referee comment:

ACPD

12, C13039–C13048, 2013

P 29308. L22ff: Here authors are also advised to get in contact with HTOC. It just seems very speculative to have only 10 Gg of banks left. The purple line is actually from HTOC and tells something about the emissions from banks (bottom-up). So it would be a good thing to see by how much production has to be elevated with the new lifetimes so that the banks are again fitting to those estimated by HTOC.

Author response:

The purple line is from AGAGE, the black line is from HTOC. Even so, HTOC calculate the banks from the reported production of the halons minus their bottom-up estimate of emissions. Of these two values we believe the production to be more robust, as it is based on reported data, whereas the emissions come from algorithms of release rates. The reviewer's suggestion would only be valid if the banks estimated by HTOC were independent of their production data. The calculation of the small H-1211 bank comes from our top-down, observationally constrained, emission estimates and use of an alternative H-1211 lifetime. We explain the background for this alternative lifetime, much of which is based on a new, published, estimate of the stratospheric lifetime of H-1211. The reason for using this alternative lifetime is to demonstrate the implications of such a lifetime on estimates of the emissions and the banks. This is not speculative. However, such a small bank does seem odd and therefore suggests that there are still large uncertainties in the atmospheric budget of H-1211, which we think is an important point to make. The size of the H-1211 bank was something that we asked Dan Verdonik about, but we received no answer to that question.

Additional comments kindly provided by Referee #1 in response to a request via the editor:

As you see from below I am not against publishing these results but I would expect a little bit more of careful testing potential options rather than run into one direction – which potentially leads to revisions of the paper, if assumptions are wrong. Maybe authors can handle this by more careful writing, but I would also suggest that more

ACPD

12, C13039–C13048, 2013

Interactive Comment

careful checking of options should also be performed.

Author response:

We are very pleased to see that the referee is not against publishing these results. Although we have been unable to do any physical testing of options (as explained above) we have followed up the suggested HTOC contact. With the new information that we have gleaned and more careful writing we have moderated the discussion on potential options, putting less emphasis on one possible explanation, in particular for the source of the H-1202.

Referee comment:

Here are more specific suggestions for the two of the remaining issues:

1. It is a little bit a mix of information when authors speak of the fact that new data in the stratosphere and balloon flights have lead to a new estimate of global lifetimes (in the conclusion). If this would the case, then this new lifetime should be an exclusive issue of the Laube et al. paper. But to my understanding authors have used the Laube numbers and connected them within a 2D-model with information from the troposphere. Please be more specific about this. Author response:

The point is that we want to re-examine the lifetimes since, as stated in the paper, the lifetimes reported in the WMO report of 2010 are still those derived from a 1-D model by Burkholder et al. in 1991. There is different information available to us for each halon.

For H-1211 we have the new stratospheric lifetimes derived by Laube et al. (2012). We combine this with a tropospheric lifetime derived from the model to get a total atmospheric lifetime.

For H-1301 there is no loss in the troposphere and so the new stratospheric lifetime from Laube et al. (2012) is taken as the total lifetime. Although this is not work done in this paper we want to report it both for the sake of completeness but more because

ACPD

12, C13039–C13048, 2013

the effect of revised lifetimes for the halons is within the scope of the paper.

For H-2402 and H-1202 there are no newly reported stratospheric lifetimes but we have some data from balloon flights which we are able to use to constrain the model somewhat in derivation of stratospheric lifetimes (though this method is not ideal, hence why we consider the numbers from Laube et al. to be more accurate where available). These are then combined with tropospheric lifetimes from the model to give total lifetimes.

Where we previously referred to these as "new" atmospheric lifetimes, we now refer to them as "alternative" lifetimes. The main purpose was then to demonstrate how changes to the lifetime estimates, based largely on the Laube et al study, impact the top-down estimates of emissions.

Referee comment:

Furthermore, it would be good if authors could simply tell the reader what was the change in stratsopheric lifetimes the Laube et al. paper came up with and how this is rationalized. I know that the reader could read the other paper as well, but this is also an issue because them Laube et al.paper is still in revision as well.

Author response:

Laube et al is now published in ACP. However we have added a little more explanation of the relevant work

"The stratospheric steady state lifetimes of H-1211 and H-1301 have recently been re-evaluated by Laube et al. (2012b) based on tracer analysis using samples collected by the high altitude research aircraft, M55 Geophysica, and a range of balloon flights. Laube et al. (2012b) applied a relative method to calculate stratospheric lifetimes using CFC-11 as a reference tracer. For this method the stratospheric lifetime of CFC-11 must be known and Laube et al. (2012b) derived two sets of halon lifetimes relative to a CFC-11 lifetime of 45 years (as recommended in Montzka and Reimann, 2011) and

ACPD
12, C13039–C13048, 2013

of 60.1 years. . .."

Referee comment:

2. The proposed revision of the banks seems to be another issue where authors rather specifically pick one option. Another option would be that historic emission/production numbers are wrong. This could also be mentioned/worked out.

Author response:

It is absolutely true that the calculated value for the banks is dependent on the emission and production data used (as explained above). We do already mention in the discussion that errors in the production data could be one possible explanation. The uncertainties in the top-down emission estimates is what we are, in part, trying to address by looking at the effect of using different lifetimes to calculate these emissions.

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

ACPD

12, C13039–C13048, 2013