

## ***Interactive comment on “Global emissions of HFC-143a (CH<sub>3</sub>CF<sub>3</sub>) and HFC-32 (CH<sub>2</sub>F<sub>2</sub>) from in situ and air archive atmospheric observations” by S. O’Doherty et al.***

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Received and published: 17 June 2014

I congratulate the authors to this work, which reports global trends and emissions of two rapidly increasing greenhouse gases from a high frequency observational network. In that it addresses very relevant Scientific questions within the scope of ACP. It also presents a wealth of novel data and reaches substantial conclusions, which are sufficiently supported by the high quality data. I consider the scientific methods valid but not clearly outlined in all cases. Another weakness is the inclusion and especially the lack of comparison to other published mixing ratio time series of these two gases.

C3764

The text has been modified and the scientific methods outlined more clearly thanks to many of the specific comments received from Reviewer 2.

At the time of preparing the first manuscript there were no other published mixing ratio time series available with the exception of Culbertson et al., for HFC-143a. The Culbertson time series (represented as annual means) generally covered a period of time where the mixing ratio was very low and before the rapid rate of growth started. In the case of CAPE MEARES the mixing ration only changed from 0.2-0.6 between 1978-1990, this type of small change is difficult to show in Figure 1. The time series for for Point Barrow and Palmer Station were also very short (4-5 data points). For this reason it was decided that very little useful information could be illustrated on the mole fraction time series plot, shown in Figure 1.

Until recently, we were unaware of the HFC-143a data presented in Miller et al., 2012, it would be useful to include these data in a comparison plot, however, we do not think these data have been archived for general access.

We are unaware of any other published time series of HFC-32.

The same is partly true for the emissions. The overall presentation is mostly well structured, clear, and concise. Finally I suggest including a link to the online archive of the actual underlying high frequency data, at least in the supplementary material. More specific comments can be found below.

We thank reviewer 2 for his overall positive assessment. A link to the AGAGE website and CDIAC database has been added to the supplementary information.

P3, I7: As of which year?

In 2012, this year is mentioned throughout the abstract (L9, 12, 16), so I do not really want to mention it again.

P3, I20-22: I suggest adding “mainly” as there are some other uses.

C3765

We agree, “mainly” will be added.

P4, I10: The lifetime of HFC-23 is much longer than 50 years.

Changed the text, “HFCs are partially fluorinated hydrocarbons that have atmospheric lifetimes in the range of 1-50 years (with the exception of HFC-23 and HFC-236fa which have lifetimes of 222 and 242 years, respectively). . .”

P4, I15: These GWPs are only high on average.

“Most HFCs currently used have relatively long atmospheric lifetimes (e.g., HFC-134a, with a lifetime of about 13 years) and GWPs in excess of 1000, and are sometimes referred to as high-GWP HFCs” [Velders et al., 2014].

P5, I4: If that second period starts on 1 January 2013, why hasn't it entered into force yet?

Even though Parties have accepted the Doha amendment, the amendment will not enter into force until at least 75% have sent in an instrument of acceptance. A total of 144 instruments of acceptance are required for the entry into force of the amendment. This has not yet happened.

See [https://unfccc.int/kyoto\\_protocol/doha\\_amendment/items/7362.php](https://unfccc.int/kyoto_protocol/doha_amendment/items/7362.php) for a more detailed description of the procedure.

P5, I9-12: It might be worth referencing at least some of the non-AGAGE publications “assessing the accuracy of globally and regionally aggregated reductions or increases in emissions of individual greenhouse gases...”. Especially since the term “greenhouse gases” includes studies on CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O.

Reviewer 1 also commented on this issue. We agree with both reviewers, and a broader range of publications is now referenced (see below).

The use of “greenhouse gases” in the original text was too general, of course I agree fully that there is a wealth of excellent studies reporting CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O, however,

C3766

I would like to remain focused on the halogenated GHGs, and have changed the text to clarify this: now include “individual halogenated greenhouse gases...”

Fang, Xuekun, BR Miller, and SS Su. 2014. “Historical Emissions of HFC-23 (CHF<sub>3</sub>) in China and Projections upon Policy Options by 2050.” *Environmental Science & Technology* 23. doi:doi.org/10.1021/es404995f. <http://pubs.acs.org/doi/abs/10.1021/es404995f>.

Laube, J. C., P. Martinerie, E. Witrant, T. Blunier, J. Schwander, C. a. M. Brenninkmeijer, T. J. Schuck, et al. 2010. “Accelerating Growth of HFC-227ea (1,1,1,2,3,3,3-Heptafluoropropane) in the Atmosphere.” *Atmospheric Chemistry and Physics* 10 (13) (July 2): 5903–5910. doi:10.5194/acp-10-5903-2010. <http://www.atmos-chem-phys.net/10/5903/2010/>.

Miller, B. R., and L. J. M. Kuijpers. 2011. “Projecting Future HFC-23 Emissions.” *Atmospheric Chemistry and Physics* 11 (24) (August 16): 13259–13267. doi:10.5194/acp-11-13259-2011. <http://www.atmos-chem-phys-discuss.net/11/23081/2011/>.

Montzka, S. a., L. Kuijpers, M. O. Battle, M. Aydin, K. R. Verhulst, E. S. Saltzman, and D. W. Fahey. 2010. “Recent Increases in Global HFC-23 Emissions.” *Geophysical Research Letters* 37 (2) (January 29): n/a–n/a. doi:10.1029/2009GL041195. <http://doi.wiley.com/10.1029/2009GL041195>.

P5, I12-13: That is not quite true. Both HFC-143a and HFC-32 are included in Rigby et al. (2014, GRL). One of the main messages of their work is that “half of the world's HFC emissions were unaccounted for in 2011”.

We agree with the reviewers comment that the HFC emissions as a total have been explored, however, no detailed global emissions information relating to the individual compounds reported here have yet been published.

Text changed to:

“These techniques have recently been applied to global observations of HFCs in gen-

C3767

eral [Rigby et al., 2014] but not used to explore the individual estimates of HFC-143a and HFC-32”.

P6, 14-5: Including this information is a very good idea, but why is it listed very detailed in the introduction and not used anywhere else, e.g. to compare to AGAGE emission estimates in section 4.2? Also, why is the work of Li et al. (2011, EST, cited later) and Miller et al. (2012, JGR) not mentioned here (or compared later)?

When this manuscript was first started Li et al and Miller et al had not been published, the Culbertson data were included here to provide a history of the current measurements to date. This section has been updated to include references to Li et al and Miller et al.

The Culbertson emissions data have been added to the figures and discussed further.

P6, 112: This information is outdated. The SPARC Assessment (2013) recommends a lifetime of 51 years for HFC-143a.

We agree, and have updated the lifetime.

P6, 120 and p7, 18: Again, instead of citing outdated work, SPARC (2013) would be better here. This is especially puzzling since many of the authors of this work were also authors of the SPARC Assessment.

We agree, and have now cited SPARC (2013).

P8, 17-8: I agree that the calibration procedure is well established. But data specific to the calibrations of these two gases is missing here. What was the precision of the calibrations? How many dilutions were prepared? Which mixing ratio range was covered? Was linear response behaviour confirmed?

The reviewer raises some valid points about the calibration procedure. These points have been addressed in the following text and in the reply to the next question:

“The measurements at each AGAGE site are reported relative to the SIO-2007 gravi-  
C3768

metric calibration scale (as dry gas mole fractions in pmol mol<sup>-1</sup>). The SIO-2007 scale is based on five stable primary calibration standards in zero air with prepared values of 5-6 ppt, each containing ~20 torr water vapour. Repeated measurements indicated that the relative standard deviation of the scale was 0.56% (HFC-143a) and 0.49% (HFC-32). The estimated absolute accuracy of the calibration scale for both compounds is ~2-3%”.

P8, 117-18: Does that mean that the actual precision of the standards run at each individual instrument was not considered, including changes over time? Does it also mean that the precision was not dependent on the actual concentration in the standard? 0.10 ppt would mean >10 % for HFC-32 in 2003.

The text states that the typical precision was calculated at 0.10 ppt. Of course this value varies, and is dependent on a number of factors such as how well each instrument is running, and the mole fraction present in the current working standard. The text has been altered to add extra information and clarify the original statement:

“Working standards were prepared for each AGAGE station by compressing ambient air into 35L electropolished stainless steel canisters (Essex Cryogenics, Missouri, USA) using a modified oil-free compressor (SA-3, RIX California, USA). An exception to this was the Cape Grim station, where the working standards were filled using a cryogenic filling technique. Working standards were filled to 50-60 bar and had a working life of approximately two months. Such a rapid turnaround of working standards resulted in minimal sampling and detector non-linearity issues since the ambient mole fractions and working standard mole fractions were very similar. Measurement precision ( $1\sigma$ ) was determined as one standard deviation of the ratio of each standard response to the average of the closest in time preceding and subsequent standard responses. The typical daily precision for each standard varies with respect to mole fraction, at the 5-6 ppt level it was calculated to be 0.10 ppt. The daily precision value was used to estimate the precision of the in situ measurements. The analytical systems showed no sign of blanks and were determined to be linear over the 0.3-5 ppt

and 0.2-7 ppt range for HFC-143a and HFC-32 respectively”.

P11, I5: Over what period was that rate of increase calculated?

We have now included an additional line explaining how the growth rate was calculated “The growth rate was calculated from the optimized model-derived global mean mole fractions. Monthly global growth rates were smoothed using a Kolmogorov–Zurbenko filter with a 0.7 year smoothing window and 4 filter passes, leading to an effective smoothing window of 1.4 years. The mean growth rate centered on July 2012 for HFC-143a was  $1.4 \pm 0.04$  ppt yr<sup>-1</sup>.”

P11, I5-12: So how do these numbers compare with Culbertson et al. (2000), Culbertson et al. (2004), and Greally et al. (2005)?

The numbers compare well with Greally et al. (2005), as he was using AGAGE data with the same calibration scale. There is an offset between the Culbertson data – most likely due to calibration differences.

P11, I12: This should be ppt/year.

The reviewer is correct – this was a typo and has been fixed.

P11, I26-27: While I agree, that it is important to cite other AGAGE papers and do not question their excellence: Again, this is not a very representative sample of the literature available on inter-hemispheric gradients of anthropogenic trace gases.

We agree – several further important references have been included:

Montzka, S. a., B. D. Hall, and J. W. Elkins. 2009. “Accelerated Increases Observed for Hydrochlorofluorocarbons since 2004 in the Global Atmosphere.” *Geophysical Research Letters* 36 (3) (February 5): L03804. doi:10.1029/2008GL036475. <http://doi.wiley.com/10.1029/2008GL036475>.

Montzka, S. a., L. Kuijpers, M. O. Battle, M. Aydin, K. R. Verhulst, E. S. Saltzman, and D. W. Fahey. 2010. “Recent Increases in Global HFC-23 Emissions.” *Geochimica et Cosmochimica Acta* 74 (12): C3770.

*Geophysical Research Letters* 37 (2) (January 29): n/a–n/a. doi:10.1029/2009GL041195. <http://doi.wiley.com/10.1029/2009GL041195>.

Laube, J C, P Martinerie, E Witrant, T Blunier, and J Schwander. 2010. “Rapid Growth of HFC-227ea” (March).

P12, I3-4: I don’t agree. Emissions might also shift within hemispheres as demonstrated by Montzka et al. (2009) for HCFCs.

The reviewer is correct; this interpretation was too simplistic and has been removed from the text.

P12, I3-18: Most of this discussion is on emissions. I suggest moving it to section 4.2. Also, why is the discussion on regional emissions limited to Australia and Asia?

The focus of this manuscript is to publish a global analysis, however, some inclusion of regional analyses are useful in highlighting the discrepancies between estimates derived from observations and estimates derived from National inventory accounting (or some such bottom up method). For example the Asian estimate of HFC-32 from Li et al., is greater than 100% of the global estimates derived from bottom up methods (UNFCCC and EDGAR). I think this is an interesting point to highlight.

P12, I20: I suggest deleting the FIRST “of”.

Agree – this was a typo and has been fixed.

P12, I23: This is inconsistent with Table 3 and the conclusions, both of which suggest that emissions only started in 1981.

We agree with the reviewer. The figures quoted in the text were incorrect and have now been corrected to be consistent with the information reported in Table 3 and the conclusions.

P13, I12: Citing a UN presentation is not a traceable (nor a peer-reviewed) reference and in my opinion inappropriate here.

This point was only brought up by reviewer 2. If the editor would like this reference removed I will do so.

P22, t2 and p29, f5: Why are the Culbertson and the Miller emissions not shown here?

The Culbertson emissions data have been added to the plot. The Miller estimate is a US estimate and adds no particular benefit to the plot. The Miller work is however, included in the modified discussion.

P25 - 28: Why is there no comparison to other published work in any of these figures (e.g. Culbertson et al. and Miller et al.)?

We have answered this question fully at the beginning of our replies.

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Interactive comment on Atmos. Chem. Phys. Discuss., 14, 6471, 2014.