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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Changing trends and emissions of hydrochlorofluorocarbons and their hydrofluorocarbon replacements" *by* Peter G. Simmonds et al.

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Responses to Referees We thank both referees for their diligence in reviewing our paper and the very constructive and substantive comments which have improved the paper.

REFEREE #2

Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-977-RC1, 2017 Interactive comment on "Changing trends and emissions of hydrochlorofluorocarbons and their hydrofluorocarbon replacements" by Peter G. Simmonds et al. Anonymous Referee #2 Received and published: 12 January 2017

This manuscript provides updates on measurements of HCFCs and HFCs from a global sampling network that provide a global picture of the transition being made as a result of the Montreal Protocol. Results are provided and discussed in terms of atmospheric changes and inferred emission rates. Comparisons are made to emissions derived previously on a mass basis and are considered also on the basis of CO2-equivalent emissions for individual gases and for classes of gases. The paper presents high-quality measurement data that add to our understanding of recent atmospheric changes stemming from the Montreal Protocol. I found some sections in need of additional consideration before publication in ACP would be appropriate.

On uncertainties: It's not clear that the change derived for aggregate HCFC emissions from 2010 to 2015 is accurately characterized as a decrease given the substantial overlap in the stated uncertainties. The two different estimates are 483 +/- 70 and 444 +/- 75 (this decrease is mentioned in multiple places in the text). Same point can be made for the 1.4% difference in cumulative emissions over the two five-year periods (lines 553-559). This needs more careful consideration and an accurate description. The "increase" in aggregate HFC emission values also need considering, as there is substantial overlap there too. I also find it surprising that the uncertainties on global values provided in Figure 1 and 2 aren't dependent on mole fraction or the number of sampling stations used to derive the values (2 sites in early years with the ADS and more sites recently with the updated Medusa instruments). Why isn't this observed? Were the early measurements from two sites much more precise?

We have modified the relevant sentences to say: "We find that this change has coincided with a stabilisation, or moderate reduction, in global emissions of the four HCFCs. . . . . ." and- "Aggregating the four HCFCs we observe that there is an equal contribution of 3.9 Gt CO2-e over the two 5-yr periods, implying a stabilization of the cumulative emissions."

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the values (2 sites in early years with the ADS and more sites recently with the updated Medusa instruments). Why isn't this observed? Were the early measurements from two sites much more precise?

There is a small decrease in the relative uncertainty in the global mole fraction as the number of stations increases (e.g. for HFC-134a the uncertainty in the global mole fraction is 2.3% in 1995, dropping to around 1.5% in 2014). However, in our inversion the terms involving global mole fractions are strongly constrained using only two stations, so the difference is not dramatic when the number of stations is increased. This is most likely because the inversion sees that the model provides a constraint on the latitudinal gradient, and therefore information on the mole fraction in any box can be propagated through to a global average (it is important to note that our global averages are from the model into which data haves been assimilated, rather than a purely "data" driven average). It is possible that our global mole fraction estimates are somewhat over-confident, because, in this inversion, we have not accounted for the potential systematic model errors that would confound this propagation of information around the globe (e.g. if there were errors in the inter-hemispheric exchange rate, then global estimates based on Mace Head alone would also be erroneous). However, we would argue that, for this paper, these factors are relatively minor, and such uncertainties would not change the outcomes. In future, our inverse modelling framework will be modified to more fully account for potential systematic model errors, but it would require significant further work (note also that almost no existing inverse modelling schemes account for such uncertainties).

On implications for compliance with the Montreal Protocol: The text in the abstract (lines 29-33) and on lines 584-595 can be read to suggest that usage of HCFC has increased after 2013 despite the global cap on production and consumption. Text on lines 589-591 suggests developing country emissions have increased in spite of the 2013 cap on production. These seem to be fairly significant statements with important implications but no evidence is supplied to back them up. I don't doubt that HCFC

emissions and use increased prior to 2013 in developing countries, but what evidence suggests that use and emissions increased after 2013 from these countries?

There must be some confusion here as the text does not say what the referee is suggesting. Supplementary material shows how emissions in any year are not equal to consumption and production in that year. The substances are emitted from equipment that uses them, either during operation or when the equipment is eventually scrapped. Thus an increase in emissions is not indicative of a change in production or consumption and, over a period of several years, it is possible that emissions will exceed consumption significantly. As for the Article 5 emissions, it's this paper that's drawing the conclusion. The increase in emissions (that are mainly from China) are consistent with the projections beyond 2013 in Wan et al., (2009), Li et al., (2011), Fang et al., (2012) and Carpenter & Reimann et al. (2014).

On comparisons with emission estimates presented previously: Emission estimates for many gases and many sources (Figure 3). It's great to see the authors provide emission estimates from previous work for comparison of derived magnitudes and trends. Although I'm not sure it is surprising that CO2-e emissions of HCFC-22 are larger than the four HFCs, has this not been obvious from earlier work and WMO assessments? Regarding figure 3, it would be more useful for the reader if it were clear which results were derived independently from the AGAGE data (from different observations and model), which were derived independently from the AGAGE 12-box model but with AGAGE data, and which were derived from inventories (e.g., what are Velders et al., results derived from?).

We agree that this is not particularly surprising and "surprising" has been removed from the text. We have addressed the issue of which datasets and models are used by adding the following text in Section 4.2.1.1. "It should be noted that Montzka used a 3-box model and NOAA data, while Saikawa and Xiang used independent 3-D atmospheric chemistry-transport models with NOAA and AGAGE+NOAA data, respectively." Velders results are compiled from inventory sources but also take into account atmo-

spheric observations.

Also, a quick look at the Montzka et al., 2015 paper shows emissions derived and presented for HCFCs and HFCs for many years, not just 2012 (only 2012 results are plotted in this manuscript). This comes across as a bit misleading, but more importantly, the authors miss a significant opportunity to determine if the two measurement networks provide similar conclusions regarding the unusual inter-annual changes in emissions for these gases (particularly the uneven changes for HCFCs).

With regard to the Montska 2015 paper. We reported an emission for 2012, as this was the only data listed in the text of the paper and it would have been inaccurate to try and read values for other years off the figures. However, Dr Montzka has kindly supplied us with a table of data for the other years (including recent revisions) which we have now included in the appropriate figures in our paper. In addition, we have included in the Supplementary Material a section on a comparison of NOAA flask and AGAGE in situ HCFC and HFC measurements at common sites, which is summarised here as percentage differences (NOAA/AGAGE-1)*100: HCFC-22, -0.3$\pm$0.3%; HCFC-141b, -0.6$\pm$0.5%; and HCFC-142b, -2.6$\pm$0.5%.It is quite clear from this co-plot of the AGAGE and NOAA data that variations in the HCFCs trends are well matched. Modified text as follows:- “Montzka et al., (2015), using an independent sampling network, also provided emissions estimates for HCFCs-141b and -142b which are included in Figures 3 b,c and agree within the uncertainties of our estimates with similar fluctuations.”

Unusual insertions in the text:

(1) The first mention of HFC-23 is in the conclusion section. This seems out of place and, I’d suggest, inappropriate given that none of the information provided about HFC-23 is derived from data or analyses of observations presented in this manuscript and the points made aren’t closely relevant for this manuscript.

This text has been moved to the introduction. We consider that it is not inappropriate to mention the association of HCFC-22 and HFC-23 with the linkage to the Clean

Development Mechanism and the relevant references.

(2) The discussion of HFCs being released predominantly in blends seems out of place and unusual. This is a straightforward conclusion based on uses of these gases by industry and it is not clear how the atmospheric data add to this discussion. There is a related point made in the conclusion about results not agreeing with some from Montzka et al (2014?), but there is no indication given as to the reason for this difference. Is it because the derived emissions disagree or is it because more information was brought to the analysis in the present manuscript than was available previously that defines our knowledge?

It is far from "a straightforward conclusion based on the use of these gases by industry". The only data from industry that are available are the compositions of the blends. All information about quantities, both of blends and individual HFCs, is commercially confidential. Supplementary information shows clearly the conclusion that global emissions calculated from atmospheric measurements are consistent with releases of HFCs wholly in blends. This is an important conclusion and not one that could have been obtained otherwise. It is not that we disagree with Montzka et al, 2015. In our analysis of the changing blends in the Supplementary material we were simply unable to confirm this hypothesis.

Details: Citation seems important but is lacking on line 50.

Reference (AFEAS, 2016).has been added.

Lines 61-65. Have no HFC results been reported by NOAA since 2004?

Montzka et al., 2015 reference has been added.

Precisions are quoted on lines 151-154 as single numbers, but I would guess that they have changed over time with different instruments and as atmospheric mole fractions have increased from v small levels. Does typical = median?

We have replaced lines 151-154 as follow:- “The GC-MS-Medusa measurement preci-

sions for the four HCFCs and four HFCs are determined as the precisions of replicate measurements of the quaternary standards over twice the time interval as for sample-standard comparisons (Miller et al., 2008). Accordingly, they are upper-limit estimates of the precisions of the sample-standard comparisons. Typical daily precisions for each compound vary with abundance and individual instrument performance over time. Typical ranges for each compound measured between 2004 and 2016 are: for HCFC-22 (0.5 - 1.0 ppt); for -141b (0.05 - 0.1 ppt); for -142b; (0.05 - 0.1 ppt); for -124; (0.03 - 0.06 ppt); for HFC-134a (0.15 - 0.3 ppt), -125 (0.03 - 0.06 ppt), -143a (0.07 - 0.15 ppt) and -32 (0.04 - 0.2 ppt)."

Results and Discussion: How comparable are the model output mole fractions to the actual results? No indication of this is presented or mentioned.

We have included residual plots in the Supplementary Material which show the percentage difference between the model calculated mole fractions and the observed mole fractions.

Are growth rates quoted (line 237-238) based on some time interval, or just the measured change during 2015?

We have slightly modified this sentence but it does state in 2015. "The global mean mole fractions (pmol mol-1) observed in 2015, in descending order of abundance, are HFC-134a (83.3), HFC-125 (18.4), HFC-143a (17.7) and HFC-32 (10.5) with growth rates (pmol mol-1 yr-1 yr-1) for HFC-134a (5.6), HFC-125 (2.3), HFC-143a (1.5) and HFC-32 (1.6)."

Line 309, reconsider text. HCFC-141b growth rate isn't reported before 1998, so it doesn't seem accurate to suggest that emissions peaked in that year.

We apologies for this error. Our plots had been cut off at 1998, as this is the year in which the time series begin for several compounds. We have now extended these plots back to 1995, when in situ data began for some of these species. Figure 2 now shows

the first maximum in the growth rate of HFC-141b in 1998.

Consider units on increasing emission rates as per yr per yr.

Our Figures 3 and 4 refer just to emissions in Gg/yr.

Line 499 and 561-562. I believe this is correct only if you refer to relative rates of increase.

Text has been changed to reflect that rates are relative.

Line 565. "emissions of HCFC-22 represent 79% of the global cumulative HCFC burden: : :" doesn't make sense. Is the percentage relating to mole fractions or emissions? Please read text carefully it says "emissions"

WMO reports are appropriately cited by lead coauthor names; consider doing that as recommended in the reports.

WMO reports. We have altered the WMO references to reflect the Lead authors.

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