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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Atmospheric histories and emissions of chlorofluorocarbons CFC-13($CClF_3$), CFC-114 ($C_2Cl_2F_4$), and CFC-115 (C_2ClF_5)" *by* Martin K. Vollmer et al.

Anonymous Referee #2

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This is an impressive, comprehensive, thought-provoking, and very useful paper that describes the full atmospheric histories over eight decades for three CFCs that are present in the atmosphere at much lower concentrations than the primary CFCs. It documents continued emissions and, surprisingly, notable increases in global emissions of CFC-115 that are rightfully indicated as being difficult to explain given the global production phase-out for CFCs. New sources for emissions of these gases are identify and, using inverse analyses of high-frequency atmosphere data, continuing emissions of CFC-114 and -115 from East Asia (China) are inferred in amounts that account for a large portion of the ongoing global emissions.

The only substantive issue I have with the manuscript relates to two conclusions that I'm not convinced are defensible, given our uncertain knowledge of lifetimes. Once these are reconsidered, I think the paper is ready to publish.

Those issues: 1) on cumulative emission vs production comparisons (abstract and text), it seems necessary to express the influence of uncertain lifetimes on the differences argued for here for CFC-114. I pretty sure the lifetime uncertainty and hence uncertainty on derived global emissions is much larger than 10%, implying that one can't reliably conclude that there is a 10% discrepancy here or, by implication, evidence for significant unreported production. The authors might also consider if a discussion of bank magnitudes instead of cumulative emissions provides more insight (discussed below). 2) the assertion that emissions of CFC-114 and CFC-13 have increased in recent years. It is not at all clear from the figures of mole fraction rate of change or derived global emissions that the authors are correct in stating that emissions of these gases have actually increased in recent years beyond the variability and uncertainty envelope of recent years.

While that abstract states that CFC-115 impurity in HFC-125 production cannot account for all of the ongoing CFC-115 emission, consider also stating that it isn't likely that this impurity source, given an average impurity content of10e-3 to 10e-4 in HFC-125, is the cause of the identified CFC-115 emission increase in recent years (at least this is what I conclude looking at the numbers).

Consider mentioning 500-yr GWPs, given that this is the timeframe for atmospheric destruction for these gases so is certainly relevant... Along those lines, consider mentioning how CFC-115 impurities affect the 500-yr GWP of HFC-125 use (small effect it seems, on average).

Discussion of bank sizes relative to the current emission rate as a fraction of peak emissions. CFC-12 recently has been $\sim$10%, CFC-11 is higher... It mostly comes down to the size of banks and release rates from those banks.

The authors have done a good job of discussing the issue of CFC-114 and CFC-114a being measured as one chemical in this work and in most previous studies. The text is still confusing in places, however, as CFC-114 is used to indicate the sum of both and just the one isomer in studies in which separation was accomplished (in caption of Figure 5, to name one spot; in discussion of lifetime too, are lifetimes stated for 114 or is it 114+114a here? To clarify this I'd suggest not using CFC-114 to mean CFC-114 + CFC-114a; consider CFC-114* or CFC-114s (where s=sym as in Supplement) or something else to refer to the sum. I presume the presence of 114a with 114 relates to unavoidable co-production during synthesis and an inability to separate these isomers before sales, so that the presence of both in perhaps changing source ratios relates to different production pathways. I didn't see this mentioned, or missed it if it was.

Reconsider the discussion of banks and "cumulative emissions", as these seem different ways to express the outcome of essentially similar analyses. Yet it is difficult to ascertain the differences from the previous analyses (e.g., p. 9, line 28-31, bank determinations for 2016 are indicated to be v. small for 114 and 115 based on AFEAS emission histories and an analysis by Daniel and Velders (2007), that presumably considered atmospheric measurements in some way) and what the authors find here, which is expressed as "cumulative emissions" rather than an implied bank magnitude. This is relevant for 114, in particular, given the quite different history derived here compared to what has been considered in the past. I'm guessing that the new results suggest a negative bank for CFC-114 recently and a minimal bank for CFC-115 (i.e., <1 year's worth of emission). Typically, having an estimate of bank size is useful to consider for understanding current emission rates, and availing yourself of this would seem a useful addition. In the case of 114 and 115 it seems clear that any emission from banks are less likely to be the source of these ongoing emissions, since bank sizes estimated here are negligible (albeit their magnitude is not precisely known owing to lifetime uncertainty).

What I find very curious is the peak emission derived for CFC-114 the 1970s (the first

peak). This peak may generate the apparent negative bank today (assuming lifetimes are accurate). While a discussion is included to suggest it is a robust result, no discussion of its plausibility is presented. Given that this history is very different than the production-derived emission history, if it is accurate does it suggest emissions from a process unrelated to reported production (byproduct emission)? Does the timing correspond to other chlorinated & fluorinated ethane production histories, such as CFC-113? HCFC-142b had unusually high concentrations in the early CCAA recordâĂŤis the timing of that similar or not? Is it possible that the CFC114&114a sum is causing trouble here (the Supplement indicates that the error created could be an offset in time), given that the true ratio is not known before 1975?

Figure 3. I don't understand why the "zero growth" line is included in the figure. This line has little meaning other than to indicate steady-state, which isn't emphasized in paper, and it's clearly evident which side of steady state emissions are on currently, given one look at Figure 4. It seems to me the important reference line to retain here is the one indicating growth for zero emission–this other line I find distracting.

Figure 4 caption: the term "pollution filtered" isn't entirely clear. I presume you mean background atmospheric concentrations? Consider a different term.

p. 2, line 2. Consider additions and changes: "larger than would be expected from zero emissions **given currently estimated lifetimes**". Also, "unaltered" is ambiguous meaning here. I think you mean "constant" or "unchanging".

p. 3, line 35. This isn't true apriori. Be sure to comment on the lifetime difference for 114a and 114 to make clear to the reader if it is an important factor in affecting changes in the relative atmospheric abundance of these gases. p. 17, line 30, was the same lifetime used in Laube et al? Seems important to consider before discussing potential differences.

p S18, line 11 (Supplement text) don't forget to add the missing value here.

Regarding firn results, I didn't see the detection limit for instrumentation mentioned in the text or supplement, but would be useful to add.

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