

Interactive comment on “Atmospheric histories and emissions of chlorofluorocarbons CFC-13 (CClF₃), CFC-114 (C₂Cl₂F₄), and CFC-115 (C₂ClF₅)” by Martin K. Vollmer et al.

Reply to : Anonymous Referee #1

Received and published: 10 November 2017

This paper describes the atmospheric histories of CFC-13, CFC-114, and CFC-115; substances controlled under the Montreal Protocol on Substances that Deplete the Ozone Layer. The authors present atmospheric measurements and measurements of air archived in cylinders and firn, and use these to estimate historical emissions. They also investigate regional emissions using high-frequency measurements at a site in Korea.

The results are significant in that they represent the first comprehensive study of atmospheric CFC-13. The results also complement a recent study of CFC-114. The Vollmer et al study includes new information on possible sources of these gases, including emission as impurities in other gases used in refrigeration. This study provides constraints on current emissions of gases controlled under the Montreal Protocol, and recent (possibly unexpected) increases in emissions.

Reply: We thank the referee for his/her thorough comments and have provided some answers below, which we have incorporated into a revised manuscript that would be ready to distribute in case the editor decides to proceed to the next review step with this manuscript.

General Comments

This paper is comprehensive, well-written, and based on well-established methods. I do not have any objections to publication. The overall body of work and technical information available in the Supplement will be of interest to others in this field.

Specific Comments

Table 1: Why not include GWP from WMO 2014 (CFC-114, CFC-115)? Also, the lifetime of CFC-13 was reported as 640 yr in WMO 2006 and WMO 2011, but is not listed in Table 1.

Reply: These suggestions are now added to the table.

Table 2: How do you define a “hot spot”? It looks like there could be “hot spot” emissions of CFC-114 also in 2013.

Reply: We have used the term “hot spot” in a loosely way of describing an area with enhanced emissions. We have now removed the wording in one place in the text and described it a bit more in detail in Table 2. It is true that there are also areas of enhanced emissions for CFC-114 but these are by far not as pronounced as for CFC-115, and for CFC-114 we do not have corresponding factory locations at hand (as the HFC-125 factory locations we have for CFC-115).

Pg. 8, Line 2: You use the term “primary calibration scale”. Consider using “interim calibration scale” instead since you refer to the “interim” scale on line 10.

Reply: done, this makes it more clear.

Pg 9, Line 28: Add “(See Supplement)” after “Extrapolation of the AFEAS data, as in Daniel and Velders (2007)”

Reply: Done

Pg. 9, Line 33: I don't see emission scenarios from 1930-2100 in the 2006 Assessment Report. Do you mean atmospheric abundances from 1990-2040 (Fig 8-2) or 1955-2100 (Table 8-5)?

Reply: Emission scenarios were used to derive atmospheric abundances. To clarify this, we change the text to “*Some of these data were used in the Ozone Assessment Report 2006 to*”

produce emission scenarios for 1930--2100 on which the atmospheric abundances for the same period were based (Daniels and Velders, 2007)".

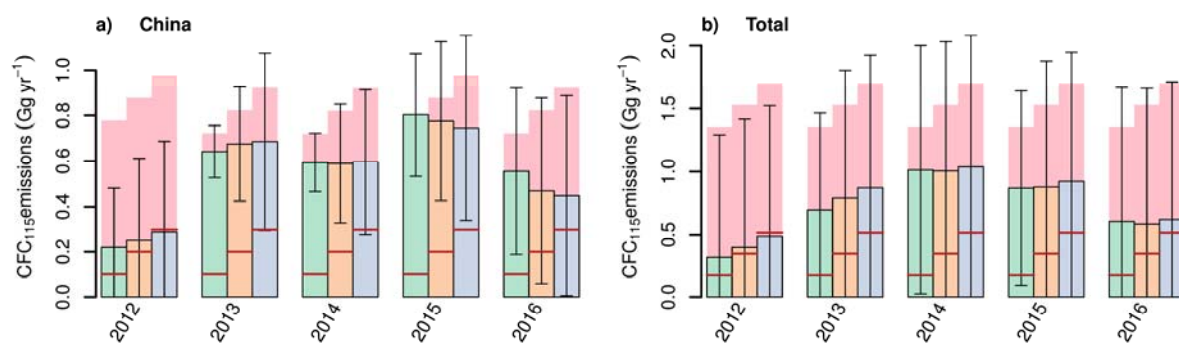
Pg 12, Line 11: What is meant by "regularization"? Do you simply mean "additional constraints"?

Reply: We have now removed that part and it now reads: "*The characteristics of these data necessitate the use of constraints on the inversion to avoid unrealistic oscillation in the reconstructed mole fractions or negative values of mole fraction or emissions.*" In the Supplement we have described the regularization for the coefficient alpha in more detail.

Pg 13, Line 14: Can you comment on the sensitivity of posterior emissions to the magnitude of the priors?

Reply: We analyzed the sensitivity of our inversion results towards the magnitude of our prior. For differences of the prior of +/- 50 % we don't get a strong response in the a-posteriori emissions. For some years the a-posteriori emissions remain practically independent of the prior, whereas for other years the differences resulting from different priors are well within the uncertainty estimates of the a-posteriori (see figure below). We added the following sentence to the revised manuscript (in the Supplement):

"The choice of the magnitude of the prior emission was tested by running additional sensitivity inversions with 50% higher and lower prior emissions. The influence on the a-posteriori emissions was small compared to the a-posteriori uncertainty estimate."



Pg. 15, Line 33: "more unexpected" than what?

Reply: This is indeed poorly phrased: We have now rephrased this part (also following some suggestions of another reviewer), and the text now reads: "*For all three CFCs we find persistent lingering emissions in the past decades. While the emissions for CFC-13 and CFC-114 have remained stable within uncertainties, those for CFC-115 have increased in recent years.*"

Pg. 17, Line 29: Suggest "projected by Velders and Daniel . . ." since 2016 emissions would have been a projection in 2014

Reply: Done

Pg. 18, Line 10: Do you mean that a "change" in the latitudinal gradient has not been detected? There is clearly a gradient (N-S).

Reply: This is indeed a wrong statement we have made. We suggest to change these sentences to: "*The observed latitudinal gradient in CFC-114 abundance suggests predominant NH emissions. Pollution events in the Asian region, as detected from our high-resolution in-situ measurements, and the absence thereof in other regions suggest that at least some of these emissions originate from Asia. Increased abundances of CFC-114a, compared to Cape Grim,*

from samples collected in Taiwan were reported on by Laube et al. (2016), partially supporting our findings.”

Pg 18, Line 19: Possibly re-phase. The use of “improvement/improved” in same sentence not entirely clear. Or refer to Supplement for model performance?

Reply: We agree and have revised the sentence. It now reads: *“The overall transport model performance and its improvement through the inversion (see Supplement) were considerably better as in the case of CFC-13, lending sufficient confidence in the inversion results.”*

Figure 2: I’m not sure how the blue line (SPO) adds to the story, being based on only one sample from the SPO firm. Since this paper does not focus heavily on firm results, it might be better to keep the SPO sample “point”, but delete the “line”.

Reply: We prefer to keep the line in there, leaving it out would make the reader wonder why it is not there. It also helps to put the SPO point into perspective.

Figure 6: Hard to tell the difference between orange and red lines.

Reply: Agreed, we have now changed the colors and hope that the two lines can now be distinguished more easily.

Figure S4: panels “b” and “c” look very similar. Perhaps draw a circle around green points in “c” to draw attention to what is different?

Reply: We agree, but we have decided to highlight the difference in a different way by changing colors and symbol sizes. We have now also modified the caption to clarify the purpose of this figure.

Pg S18, Line 11: Something still missing [Cathy to calculate this value]?

Reply: Thank you for spotting this, this is now fixed, it reads: *“The difference it makes to the CSIRO inversion, when we consider only zero mole fraction at 52 m DSSW20K, or with both the zero and non-zero value, is within the uncertainties in emissions.”*

Pg. 17, Line 4: Seems like a sentence is needed here to clarify that CFC-13 emissions were not reported by Fraser et al, 2013 (if that is what you are saying). I suggest: “CFC-13 was previously found in the emissions from aluminum plants (Penkett et al., 1981; Harnisch, 1997), but was not reported by Fraser et al (2013) from a similar study.” And then follow with: “On re-analysis of the Fraser et al samples, we found enhancements over background levels of 45 ppt – 130 ppt in the various smelter samples. “

Reply: In the Fraser et al. (2013) publication, CFC-13 emissions were reported as absent, which we discovered to be an erroneous statement. We have now rephrased this part, hoping that it is now clear that Fraser et al. (2013) reported zero CFC-13 emissions but that our re-analysis showed significant CFC-13 emissions.

Technical Corrections

Pg 7, Line 17: Add comma between “measurements” and “samples”

Reply: done

Pg 14, Line 5: delete “again”

Reply: done

Pg 15, line 11: Suggest: “Its growth rate then slowed during the mid-2000s to near zero, with . . .”

Reply: Changed according to the suggestion, but left the word “rate” out.

Pg 16, Line 3: Suggest substitute “removal rates” for “removal fluxes”

Reply: We prefer to keep the term “fluxes” as the term “rates” could here be confusing and e.g. mistaken for chemical reaction rates.

Pg. 18, Line 25: add “since 2010” after “steadily”

Reply: done

Pg. 19, Line 7: Suggest: “Large posterior emissions were detected for all analyzed years . . .”

Reply: We agree and changed the sentence accordingly.

Pg. 19, Line 13: I calculate a different number (0.63 kt) for the average Chinese emissions in the years 2013-2016 from values in Table 2 (0.68, 0.59, 0.78, 0.47).

Reply: This is an embarrassing mistake we made, it is now corrected --- thanks for spotting it.

Pg. 19, Line 13: Total Chinese emissions in 2012: (0.23±0.38 kt yr¹) does not match value shown in Table 2 for 2012.

Reply: Same as above, and we have now cross-checked other numbers as well to ensure that not more error of that kind are present.

Fig. 9 caption: change “derives from” to “was derived from”

Reply: We changed that phrase to: “... is the result from ...”

Fig. S4: “Laube et al 2017” should be “Laube et al 2016” (two places in figure, caption is correct)

Reply: Thank you for spotting this, it is now fixed.

Pg. S16, Line 8: Suggest replacing “emissions are rather faster” with “emissions occur earlier in the life-cycle”

Reply: We agree and have now changed to the suggested wording.

Pg. S17, Line 12: This sentence does not read well. “The very crude approach we have taken is still based on the above assumption of similarities to CFC-115 but are comparing production data, . . .”. Do you mean “ . . . but is based on a comparison of production data”?

Reply: Agreed. We changed the wording of several sentences in this paragraph to provide more clarity.