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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Atmospheric abundance and global emissions of perfluorocarbons CF_4, C_2F_6 and C_3F_8 since 1900 inferred from ice core, firn, air archive and in situ measurements" *by* Cathy M. Trudinger et al.

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Author response to reviewer comments

We thank both reviewers for their helpful comments. In particular it was good to have feedback from an industry perspective. Reviewers Comments (RC), Authors' Response (AR) and Manuscript Changes (MC) are are follows:

Comments from Reviewer 1

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RC The term “anode events" (p. 2, line 10) used to describe the release of PFCs from aluminium production is incorrect. The correct and most widely used industry terminology is instead “anode effects", as is also described by the authors’ two references on this topic Holiday and Henry (1959) and Tabereaux (1994).

AR Thank you

MC “anode events" will be changed to “anode effects".

RC C3F8 emissions from aluminium smelting. While CF4 and C2F6 gases are commonly cited as PFC gases generated from aluminium smelters during anode effects, C3F8 is very seldom measured in industrial aluminium smelting studies, the only exceptions being Fraser et al, 2013 (as cited by the paper) and Li et al, 2012 (who detected C3F8 only in two out of five smelters surveyed, see References at end of review). Furthermore, the industry does not currently account for them (International Aluminium Institute, 2014, cited in paper), nor are they mentioned in the current 2006 IPCC Guidelines (2006, see References at end of review) for bottom up accounting of PFCs from aluminium smelters. **Can the authors comment on this in the paper, and/or provide more clarification of why this might be?** It could well be that C3F8 are at levels below common detection limits for industrial measurements.

AR The reviewer is probably right that the reason C3F8 emissions are not accounted for in aluminium industry reports or mentioned in the IPCC guidelines is that the levels are so low that that they would be below detection limits for many measurement systems.

MC We will include the following: “C_3F_8 has been detected at low levels in emissions from aluminium smelters (Fraser et al., 2013, Li et al., 2012). The aluminium industry does not currently account for C_3F_8 emissions (International Aluminium Institute, 2014) or include them in the current IPCC guidelines for bottom up accounting of PFC emissions from aluminium production (IPCC, 2006), but due to the low levels compared to

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the other PFCs (Fraser et al., 2013, Li et al., 2012) C_3F_8 is likely to be difficult to detect with the measurement systems used by the aluminium industry."

RC It may be helpful for authors to specify or discuss the setting of this date "T1" for each gas (if they differ for CF4, C2F6, C3F8); analysis of Figures 2-4 suggests T1 is approx. 1985.

AR T1 was 1985 for CF4 and C2F6, and 1988 for C3F8.

MC The value for T1 will be given, the reasons for their choice have already been given (5 years after the beginning of the E1 inversion).

RC Latitudinal distribution of emissions (Section 4.4) describes some differences in PFC emissions in northern and southern hemispheres, but there is no discussion or interpretation of how this relates to PFC generation geographically by aluminium, semiconductor or other industries. Is there any further comment/discussion/further interpretation that could be offered in this section?

AR Yes, we can make further comment, as follows:

MC We will add that the reduction in the 30-90N box is around 20% of the total emissions for both CF4 and C2F6, and the following: "We note that our inversion using the AGAGE 12-box model is not particularly well suited to this type of conclusion, and analysis with a model that has more accurate atmospheric transport, such as a 3-dimensional atmospheric transport model, would be required to obtain a robust result. However, a general equatorward shift of a proportion of the total emissions is consistent with the rapid rise of China into the aluminium market from the 1990s into the 2000s (IAI, 2009, 2014) at a lower latitude on average than previous emissions based in countries such as North America, Europe, Canada and Norway (a map of the location of many aluminium smelters is shown in Wong et al. (2015), with a significant number of Chinese smelters south of 30°N). The emergence of semiconductor emis-

sions in recent decades, with significant contributions of emissions from Asia, would also have caused an equatorward shift of a proportion of the emissions."

RC There is no mention in the paper of the possibility of another potential significant contribution of PFCs, particularly in the last 10 years, by the Rare Earth Industry (particularly in China) which uses very similar electrolysis technologies to aluminium smelting (with molten fluoride salts and carbon anodes), as described by Vogel (2015). This perhaps should be acknowledged within the paper.

AR We agree.

MC The possibility of emissions from the rare earth industry will be mentioned.

RC In sections 4.6 (recent years) and 5 (conclusions), there should be an emphasis that the need to work on reduction in PFCs needs to come from ALL anthropogenic sources and PFC generating industries, not just Aluminium, but also Semiconductor, HCFC/Fluorochemical production and potentially Rare Earth industries also.

AR We agree.

MC The need for all industries to focus on emissions reduction will be emphasised in sections 4.6 and 5.

RC Figures 1-4, Figure D1 - all these figures contain the acronym "NH" and "SH", which presumably refer to Northern Hemisphere and Southern Hemisphere, respectively, but are not introduced/explained anywhere in the body of text in the paper, nor in the Figure captions.

AR Sorry, this should have been explained.

MC NH and SH will be introduced.

RC In all of Figures 2-4, graphs B for the Greens function for CF4, C2F6 and C3F8 are fairly complex. Are these graphs relevant/important in explaining the method/results?

AR We believe that the b) panels in Figs 2-4 are an important part of the figures. The Greens functions are the link between individual firn or ice core measurements and the time histories of their mole fraction. They are a reminder that individual firn or ice core measurements represent a spread of ages, rather than discrete ages, and these curves show the width of these distributions at different depths and locations as well as showing the significant overlap of Green's functions over the 20th century. We do point to some individual curves in these panels on two occasions (page 11, line 25 and page 13, line 17).

MC We would like to retain the b) panels showing Greens functions. We will change the color for EDML so that it is easier to distinguish from NEEM when printed.

RC Figure 4A - The horizontal X-axis has a different range (0-120m) compared to Figures 2A and 3A. Suggest using the same X-axis scale of "0-250m" as Figures 2A and Fig 3A, for consistency and better comparison, unless there is a good reason not to.

AR Yes, the axis range can be changed for consistency.

MC Change the x-axis range for Fig 4A to 0-250m.

RC Figures 5 - For sensitivity studies, it is unclear to the reader that graphs A to C refer to CF4 emissions per year, but graph D refers to C2F6. Apart from the caption, the only identifier is on the Y-axis of of graphs A-C vs. D. Recommend addition of more obvious labels for "CF4" and "C2F6" to be placed in a corner of each graph, as is done in Figure 6.

AR We agree.

MC Labels will be added.

RC Figure 6 - recommend use of consistent/identical colour schemes as with earlier graphs in Figures 2A-B, 3A-B and 4A-B for ease of comparison; currently these differ.

AR We agree.

MC Colors of lines in Fig 6 will be changed to match Figures 2-4. We will also change the colors in Fig 5a to match the same color scheme for the sites in Figs 2-4.

RC Figure 8 - Particularly when the paper is printed in hard copy, it is difficult to differentiate between the lines for modelled InvE1 and InvE2 inversions vs. the 95% confidence interval lines for each model, since line thicknesses are similar. For clarity, recommend thicker lines for the model, and thinner lines (or dashed lines) for the 95% confidence interval.

AR We agree.

MC Thicker lines will be used for the model and thin dotted lines for the confidence intervals.

Comments from Reviewer 2

RC It's a minor point, but I do have a concern about the authors' use of the phrase 'late- Holocene, pre-industrial" in describing their measurement records. The Holocene era goes back about 10,000 years and "pre-industrial" is meant in IPCC and other documents to capture years before 1750. It's a leap of faith, albeit a small one, to say that what is observed around 1900 represents what the atmosphere looked like before 1750. I've seen papers that use 1800 to describe "pre-industrial", but never 1900, the years after which capture the domain of this study. They might want to prefer describing

their data set as a “20th century" or a “late 19th through 21st century" record to be more representative.

AR We do agree that the term ‘late-Holocene, pre-industrial’ could be confusing in the context of the PFCs. However, it seems that we haven’t made it clear enough in the paper that the CF_4 and C_2F_6 measurements from DE08 ice cover most of the 1800s as well as after 1900. The deepest DE08 ice sample contains air with mean ages of CF_4 and C_2F_6 of 1841 and 1837, respectively, and Green’s functions that extend back to the early 1800s. Their measured mole fraction is stable at 34.1 ± 0.3 ppt for CF_4 and below detection for C_2F_6, indicating stable levels through the 1800s. Although C_3F_8 was not measured in the ice, the earliest firn measurements with Green’s functions back to the early 1800s are below detection limits, and the very long lifetime of C_3F_8 implies that atmospheric levels between 1800-1900 would not have been significantly different.

MC We propose to change ‘1900’ in the title to ‘1800’, to emphasise the fact that the ice core measurements go back through the 19th century. In the abstract, instead of using the term ‘late-Holocene pre-industrial’, we will say ‘We show that 19th century atmospheric levels, before significant anthropogenic influence, were stable at ...’. Section 4.1 will be renamed to ‘Pre-anthropogenic levels’. We will begin this section with “Our oldest samples are from DE08, and contain air with CF_4 and C_2F_6 mean ages of 1841 and 1837, respectively, and Green’s functions extending to before 1810. The oldest EDML firn sample also has PFC Green’s functions extending back to before 1810. Our early measurements therefore tell us about PFCs from about 1800.” We will add later “The DE08 ice core measurements of CF_4 (purple symbols in Figure 2a) are constant with depth, indicating that CF_4 levels in the 19th century were stable. The low measurement must be an outlier rather than reflecting real atmospheric variations, due to the long lifetime of CF_4 and the fact that the Green’s functions of nearby measurements have significant overlap.”

RC My other concern is that, in testing the diffusivity of the various sites they only

used one data point for South Pole. Butler et al. (1999) published records of several gases in South Pole firn-air which suggested that independently derived (i.e, inventory driven) atmospheric histories were consistent with observed firn-air distributions. It would have been instructive to use those same depth profiles of, say, CFC-11 and CFC-12, to test the diffusivity throughout the South Pole firn profile for this study as well, even though they only had one data point from that study. Also, the Butler et al (2001) study referenced in this paper included an additional set of depth profiles of the same gases that could have been used in the same way. Finally, an archive of $\sim$10 large cylinders of firn air was collected for future analyses. If the one from 120 m could be measured for these perfluorocarbons, I would think that the others could have been as well.

AR Both the CSIRO and LGGE-GIPSA firn models use diffusivity profiles for South Pole that were calibrated using the firn measurements from many depths collected during the 2001 South Pole campaign and described by Butler et al. (2001) (different from the 1995 South Pole campaign described by Butler et al 1999). Calibration of the firn models was described in Trudinger et al. (2013) and Witrant et al (2012), but to avoid confusion we should point out here that the full profile of measurements was used, and not just a single point.

The cylinder from 120m that was analysed on the Medusa at CSIRO was not part of the sets of cyclinders mentioned by the reviewer. Instead it was filled specifically for measurement at CSIRO, but samples from other depths were not available due to a sample pump failure. PFC measurements from other depths at South Pole would be unlikely to add significant extra information to our analysis, because the Green's functions at South Pole are very wide, and we already have very good coverage from the other 7 sites included in the paper.

MC Clarify that although only one firn sample from South Pole 2001 was analysed in this study for the PFCs, measurements through the full depth profile were used to calibrate diffusivity in both firn models.

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