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Discussions

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Interactive comment on "Atmospheric abundance and global emissions of perfluorocarbons CF$_4$, C$_2$F$_6$ and C$_3$F$_8$ since 1900 inferred from ice core, firn, air archive and in situ measurements" *by* Cathy M. Trudinger et al.

Anonymous Referee #1

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General Comments

This paper presents new findings on the generation of perfluorocarbon (PFC) gases – CF4, C2F6, C3F8 – across the time series from 1900 to 2014, derived from ice cores, firn, air archives and in-situ measurements. It clearly differentiates pre-industrial (pre-1900) natural background levels of these gases vs. post-1900 emission levels relating to anthropogenic sources, in particular from the primary aluminium smelting industry (up until the 1980's). The paper has a high level of scientific content and is very rigorous in detail, particularly in its (1) description of methodologies used, (2)

examination of assumptions and factors used in modelling of atmospheric PFCs over the time series, and (3) examination of the influence of the difference sources/sites of ice core, firn and air measurement data on the resulting model for PFC gases.

This review focuses more specifically on the results and discussions as they relate to the aluminium industry (as well as other anthropogenic sources of PFC gases), rather than on the specifics of atmospheric measurements and methodologies used. Some technical comments / suggestions are also offered.

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Specific Comments

With regards to technical feedback on the paper:

1) Modelled PFC emission factors for the aluminium industry prior to 1950's. Two comments:

a. As discussed in the paper's section 4.3 and references therein, the results presented on trends in PFC emission factors particularly before 1950 appear to be valid, and agree with the scale/magnitude of emission factors that might be expected prior to advancements made in aluminium smelting after 1948, which included modernized Soderberg technologies, controls for feeding of alumina to the process, etc (Oye et al, 1999 and Edwards, Frary & Jefferies, 1930, cited in paper) and the realization by the industry that anode effects (which generated PFC emissions) were undesirable from both an environmental and cost/process efficiency point of view (Oye et al, 1999).

b. The assumption that emission factor is technology dependent and that similar aluminium smelting technologies were applied widely to build the extreme capacity within the span of a year or two (during World War II) is logical and most likely the case.

2) Specific Peaks/Dips in PFC generation in 1940's and 2008-2009.

The peak in global PFC production in 1940's and the attribution to the demand for

aluminium (demand for aircraft) due to WWII agrees well. Similarly the dip in in CF4 and C2F6 generation around the period 2008-2009 also agrees well with the authors' attribution to the Global Financial Crises (GFC).

3) Terminology.

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 & Henry (1959) and Tabereaux (1994).

4) 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.

5) T1 limit for modelled PFC emission factors.

It is understood from the paper that PFC emission factors for the aluminium industry (kg PFC/t Al) are estimated only up to a specific date "T1" (referred to in pp. 7, 10), since beyond this date, PFC emissions from other anthropogenic sources/industries start to become significant. While this date is described in the text, it is not specified. 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.

6) 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?

7) PFCs from other industries – particularly from the Semiconductor industry is discussed to a certain extent in the paper, but much of the focus is on relating PFC emission factors and emission rates to aluminium smelting production, particularly up till 1980s. However, it is no longer the only major contributor to global PFCs after this period:

a. 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.

b. 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.

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Technical Corrections

Figures provided in this work are very detailed and help illustrate and support the results discussed in the paper, but in our opinion, some appear to be overly complex or difficult to read/interpret. Anything that can be done to simplify diagrams would be ben-

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eficial to readers. Some specific recommendations or suggestions to improve clarity might be as follows:

1) 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.

2) 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?

3) 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.

4) 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.

5) 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.

6) 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.

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References

Unless specified, all references in this review are those referred to by authors in the paper. Additional references cited in this review as follows:

1) IPCC (2006) 2006 IPCC Guidelines for National Greenhouse Gas Inventories, Prepared by the National Greenhouse Gas Inventories Programme, Eggleston H.S., Buendia L., Miwa K., Ngara T. and Tanabe K. (eds). Chapter 4 Metal Inventory Emissions, pp. 4.49-4.58, Published: IGES, Japan.

2) Li, W., Chen, X., Yang, J., Hu, C., Liu, Y., Li, D., & Guo, H. (2012). Latest results from PFC investigation in China. Paper presented at the TMS Light Metals, Orlando, FL, pp. 619-622.

3) Vogel, H. Friedrich, B. (2015), Development and Research Trends of the Neodymium Electrolysis – A Literature Review, Development and Research Trends of the Neodymium Electrolysis, Proceedings of EMC 2015.

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