

## ***Interactive comment on “Perfluorocarbons in the global atmosphere: tetrafluoromethane, hexafluoroethane, and octafluoropropane” by J. Mühle et al.***

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**Please note that we provide our replies in bold after each comment from J. Marks (received and published: 1 April 2010).**

This paper offers an important improvement in understanding of the current picture of global emissions trends for  $\text{CF}_4$ ,  $\text{C}_2\text{F}_6$  and  $\text{C}_3\text{F}_8$ .

**We thank the commentator for the positive assessment of our analytical and modeling work.**

However, the authors discussions on apportioning emissions among emissions

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sources is entirely conjectural and detracts from the main subject of the paper, global emission trends. I recommend eliminating that discussion or revising to present a more balanced view of the lack of availability of verifiable bottoms up emissions data, both on national and sectoral bases.

**We understand the sensitive nature of source apportioning of global perfluorocarbon (PFC) emissions and acknowledge the continuing, long-term effort of the International Aluminium Institute (IAI) to identify and reduce PFC emissions. We now also point out that the report of the World Semiconductor Council (WSC) on the voluntary perfluorocompound emission reductions program of the semiconductor manufacturers contains only very limited information. The discussions in the manuscript are valuable as they demonstrate that the sum of available PFC bottom-up emission estimates from the aluminum and semiconductor/electronics industries is significantly lower than global emissions inferred from our atmospheric measurements, and that this emission gap has been increasing. We point out in the revised manuscript that the missing  $\text{CF}_4$  emissions likely stem from the primary aluminum *and/or* the semiconductor/electronics industry. We have made changes to the revised manuscript to point out the shortcomings of the various inventories more clearly and to avoid any bias in the discussion.**

Specific comments follow:

p6489 lines 8-12 - This statement erroneously reports that the "detailed apportioning is difficult due to large uncertainties.....factors from aluminum production." In fact apportioning is impossible, because there is no viable methodology to apportion emissions among all the sources of PFC emissions.

**It is well known that the majority of modern  $\text{CF}_4$  and  $\text{C}_2\text{F}_6$  emissions before the use of these compounds in the semiconductor/electronics industry were from primary aluminum (Al) production. For later periods scientists have tried to ap-**

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portion observed global emissions based on assumptions about the timely evolution of emission factors from Al production and data from the EDGAR emission database about emissions from semiconductor/electronics manufacture. We believe that the Al industry and especially the semiconductor/electronics industry have the necessary information to provide a better appointment of these two main PFC sources.

The methodology presented later in the paper of linear (I suppose) extrapolation of admittedly unreliable EDGAR data from 2005 to assign emissions to aluminum production is not justifiable.

**The intention of this paper is not to assign CF<sub>4</sub> emissions to Al production, but to point out that the sum of Al production related CF<sub>4</sub> emissions (estimated from the IAI Anode Effect surveys) and semiconductor/electronics production related CF<sub>4</sub> emissions (EDGAR emission database) is significantly lower than global CF<sub>4</sub> emissions (inferred from our AGAGE atmospheric measurements), and that the gap has been increasing to ~6 Gg/yr CF<sub>4</sub> in 2005, a year for which EDGAR data are available. In simple terms, available bottom-up estimate do not explain global emissions. We have clarified this in Section 5.1 and correspondingly in Section 5.3.**

p6490 line 10 - The EDGARv4 database lacks transparency in its methodology and clearly contains serious flaws in some of the emissions data for aluminum production for countries that are major producers where we have good PFC measurement data as well as good International Aluminium Institute (IAI) data for anode effect performance and for production levels.

**In the revised manuscript we stress more clearly that the EDGAR database does not provide all details necessary to understand how the PFC emission estimates are calculated or apportioned. We also point out in the conclusion section that it would be highly desirable if IAI, WSC, global PFC suppliers, and EDGAR were**

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**to work together on improving estimates of CF<sub>4</sub> and C<sub>2</sub>F<sub>6</sub> emissions.**

If the EDGAR v4 data for semiconductors/electronics is of similar quality to that for PFCs from aluminum the authors have a base problem – and, the authors indicate that they made extrapolations from this poor base to reach some of the conclusions reported in Section 5.3.

**There are two main conclusions in Sections 5.3 and 5.1 which are both independent of an extrapolation of EDGAR data beyond 2005.**

**First, from 1990 to 1992, when PFC emissions from China were likely small, there was an emission gap of  $\sim 3.7 \pm 1.1$  Gg/yr between Al production related CF<sub>4</sub> emissions (IAI) and global emissions (AGAGE). This *could* indicate that emissions from the IAI Anode Effect surveys are inherently underestimated as might be explained by fundamental problems with the application of IPCC methodologies *and/or* that emissions from the semiconductor/electronics industry were actually significant and much higher than estimated by EDGAR. We added the information that Maltais et al. (2010) recently discovered significant PFC emissions during the startup of reduction cells which may not be accounted for by IPCC methodology.**

**Second, the sum of Al production related CF<sub>4</sub> emissions (IAI) and semiconductor/electronics production related CF<sub>4</sub> emissions (EDGAR) is significantly lower than the global CF<sub>4</sub> emissions (AGAGE) and the gap has increased to ~6 Gg/yr in 2005. This gap can both be explained by underreporting of PFC emissions from Al production (IAI), especially from China which has become a major Al producer, *and/or* underestimation of PFC emission from the semiconductor/electronics industry (EDGAR). We clarified Section 5.1 and correspondingly Section 5.3.**

I have unsuccessfully made efforts to make contact with the owners of the EDGAR database and engage them in their methodology.

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**As pointed out above and added to the conclusion, it would be highly desirable if IAI, WSC, global PFC suppliers, and EDGAR were to work together on improving the estimates of CF<sub>4</sub> and C<sub>2</sub>F<sub>6</sub> emissions.**

p6507 starting line 4 "A recent IAI... - Statement is not factual correct. I recommend the following language. "PFC measurements made at Chinese smelters in 2008 as part of the Asia Pacific Partnership for Clean Energy and Climate and seven additional measurements reported by the Chinese producer CHALCO found a median emission factor for the measured Chinese PFPB smelters of 0.7 tons CO<sub>2</sub>-e per ton aluminum produced compared with median performance of 0.27 tons CO<sub>2</sub>-e per ton aluminum from IAI PFPB survey participants."

**We thank the commentator for the clarification and have made corresponding changes.**

p6508 lines 6 - 11 - While I also hear of reports of technology upgrades in some electronics/semiconductor operations in some parts of the world, typically Annex 1 countries and those countries where reporting is more transparent, there is no data of which I am aware that shows a global reduction in the semiconductor/electronics industry's emissions. As has already been noted the agreement with EDGAR v4 has very little significance.

**According to the WSC, semiconductor manufacturers in Europe, Japan, US, Korea, China, and Taiwan pursue a voluntary perfluorocompound emission reduction program, and indexed perfluorocompound emissions have increased from 1995 to 2001 by ~60% and then decreased slightly below 1995 values from 2001 to 2008 ([http://www.sia-online.org/galleries/Publications/2009\\_WSC\\_Joint\\_Statement.pdf](http://www.sia-online.org/galleries/Publications/2009_WSC_Joint_Statement.pdf)). However, the report lists only relative emissions, does not explain how they were measured, estimated, and/or verified, and gives no information how the emissions of specific perfluorocarbons such as CF<sub>4</sub> or C<sub>2</sub>F<sub>6</sub> have evolved. The use of the**

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**phrase perfluorocompounds instead of perfluorocarbons suggests that SF<sub>6</sub> and NF<sub>3</sub> may be included in the sum which would further complicate the interpretation of WSC data. Furthermore, we point out that the EDGAR emission database does not provide all details necessary to understand how PFC emissions from the semiconductor/electronics industry and from AI production are estimated. We now point out these caveats more clearly in Section 5.1 and have added corresponding statements to the Summary and Conclusions section.**

p6508 starting line 11 through 15 - I don't understand the point being made here. Can this be restated to add clarity?

If the point being made is that there is some serendipitous congruence between IAI reported emissions and the total Annex 1 UNFCCC emissions then the statement is irrelevant.

**We have rewritten the section. We would like to point out that we find it is surprising that Annex I UNFCCC CF<sub>4</sub> emissions from AI and non-AI production agree so well with global AI production related CF<sub>4</sub> emissions estimated from the IAI reports (Annex I and non-Annex I AI production). This would require Annex I non-AI based CF<sub>4</sub> emissions to be large and comparable to non-Annex I AI production CF<sub>4</sub> emissions.**

p6510 line 4 - "Probably due" - Having been the source of the analysis I can say definitely the change is "definitely" due to the updates from the 2006 IPCC revisions.

The reason why the results for 2000, 2004 and 2005 remain very similar is that the technology mix has been rapidly changing to be predominated by the most modern point feed prebake technology and the IPCC 2006 methodology was essentially unchanged for the PFPB technology.

**We thank the commentator for the explanations and have made corresponding changes.**

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p6511 lines 4 - 6 - I recognize the interest in drawing comparisons to prior data; however, this comparison seems a shaky thing to do since the EDGAR v4 data base methodology is uncertain and the data contained within it is suspect. Extrapolations, particularly linear extrapolations are not meaningful. While the authors do not report details I assume it is a linear extrapolation. With the growth in the semiconductor/electronics industries some exponential method would likely be more appropriate. However, I question the EDGAR v4 2005 baseline veracity and extrapolated results would be even less viable.

**As detailed above for Section 5.1 the two main conclusions in Sections 5.1 and 5.3 are independent from an extrapolation of EDGAR data beyond 2005.**

**First, from 1990 to 1992, when PFC emissions from China were likely small, there was an emission gap of ~19 million tonnes CO<sub>2</sub>-equivalent emissions/yr between AI production related CF<sub>4</sub> and C<sub>2</sub>F<sub>6</sub> emissions (IAI) and global emissions (AGAGE). This *could* indicate that emissions from the IAI Anode Survey reports are inherently underestimated as might be explained by fundamental problems with the application of IPCC methodologies *and/or* that emissions from the semiconductor/electronics industry are significant and much larger than estimated in EDGAR. We also like to point out that Maltais et al. (2010) recently discovered significant PFC emissions during the startup of reduction cells which may not be accounted for by IPCC methodology.**

**Second, the CO<sub>2</sub>-equivalent sum of CF<sub>4</sub> and C<sub>2</sub>F<sub>6</sub> emissions related to AI production (IAI) and semiconductor production (EDGAR) is significantly lower than the CO<sub>2</sub>-equivalent sum of global CF<sub>4</sub> and C<sub>2</sub>F<sub>6</sub> emissions (AGAGE) and the gap has increased to ~42 million tonnes CO<sub>2</sub>-e in 2005. This gap can both be explained by under-reporting of PFC emissions from AI production (IAI), especially from China, which has become a major AI producer, *and/or* underestimation of PFC emission from the semiconductor/electronics industry (EDGAR). We have clarified Section 5.3 (and Section 5.1) to reflect this more clearly.**

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p6511 lines 9 - 10 - It is a biased argument to point to aluminum CF<sub>4</sub> as the reason for the gap mentioned here. To invoke the EDGAR v4 Database which is based on non-transparent methodology and which the authors contend contains circular data arguments to then conclude that "this indicates an inherent underestimation of CF<sub>4</sub> emissions by the IAI Anode Effect survey" is totally unwarranted. There is no mention at all here that an equally valid explanation is the surge over the same time period in production of semiconductor materials and flat screen displays which result in large quantities of PFC emissions. There is, unfortunately, no similar industry report of global emissions of PFCs produced by the semiconductor/electronics industry to the report that the IAI produces.

**As mentioned above we have clarified the section. Assuming that PFC emissions from China were likely small in the early 1990s, the observed emission gap from 1990 to 1992 *could* either explained by an inherent underestimation of CF<sub>4</sub> emissions in the IAI Anode Effect survey as might be explained by fundamental problems with the application of IPCC methodologies *and/or* by an underestimation of semiconductor/electronics manufacture emissions in EDGAR v4. We now also point out that the WSC report contains only limited information and that the EDGAR database does not report all details to understand how the PFC emissions have been calculated and apportioned. We also point out in the revised paper that Maltais et al. (2010) discovered significant PFC emissions during the startup of reduction cells which may not be accounted for by IPCC methodology.**

p6512 lines 6-7 - The parenthetical expression is only notationally correct in that the C<sub>2</sub>F<sub>6</sub> emissions are over 10% of the CF<sub>4</sub> emissions, an order of magnitude higher than the C<sub>3</sub>F<sub>8</sub> ratio to CF<sub>4</sub> estimated from Harnisch's work.

**We agree that the amounts of CF<sub>4</sub>, C<sub>2</sub>F<sub>6</sub>, and C<sub>3</sub>F<sub>8</sub> emitted during AI production are very different. However, the estimation of CF<sub>4</sub>, C<sub>2</sub>F<sub>6</sub> and C<sub>3</sub>F<sub>8</sub> emissions from AI production are similar in the sense that their emissions, in a first estimate, can be related to the mass of AI produced. We have clarified the parenthetical**

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**statement accordingly.**

p6512 line 26 - I am not aware of any specific literature reports of measurements of  $C_3F_8$  from aluminum production (the authors refer to an estimate from Harnish) that would support the proposal that it amounts to 0.48% (by mass) of the  $CF_4$  emissions. If  $C_3F_8$  were emitted from aluminum production in amounts equivalent to 0.48% of the  $CF_4$  emission rate and given the 0.7 t  $CO_2$ -eq/t Al in the 2009 IAI report of 2008 results and a weight ratio of 0.1 for ratio of  $C_2F_6/CF_4$  then the reported 0.0048 ratio of  $C_3F_8$  to  $CF_4$  would result in an increase of about 0.5% in  $CO_2$ -eq rather than 8%.

**Harnisch and colleagues estimate global  $C_3F_8$  emissions from Al production of  $\sim 0.1$  Gg/yr (Harnisch J., Die globalen atmosphärischen Haushalte der Spurengases Tetrafluormethan ( $CF_4$ ) und Hexafluorethan ( $C_2F_6$ ), Georg-August-University Göttingen, 1996; Harnisch, J., I. S. Wing, H. D. Jacoby, and R. G. Prinn, Primary Aluminum Production: Climate Policy, Emissions and Costs, Massachusetts Institute of Technology, 1998). This is similar to the emissions we estimate for the 1970s. Relating the 1970s 0.1 Gg/yr  $C_3F_8$  emission estimate to  $CF_4$  emissions from Al production would result in an emission ratio of 0.048% (by mass)  $C_3F_8/CF_4$ . We agree with the commentator that if this emission ratio were still valid in 2008 it could not explain current  $C_3F_8$  emissions of  $\sim 0.64$  Gg in 2008. We conclude that non-Al production related emissions are likely the dominant  $C_3F_8$  source. We have clarified and expanded the corresponding section.**

**However, we have verified that global total  $C_3F_8$   $CO_2$ -e emissions from all sources, not only from Al production, add  $\sim 0.5\%$  in the early 1970s,  $\sim 8\%$  in 2002 and 2003, and  $\sim 5\%$  in 2008 to the global total  $CO_2$ -e emissions of  $CF_4$  and  $C_2F_6$  (again from all sources). We have clarified the corresponding section and added the details given here.**

p6514 line 20 - I agree with the authors assertion here that it is impossible with our current knowledge to determine which is true; however, this statement is at clear odds

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with the statement in line 10 p 6511 where it is asserted "indicates an inherent underestimation of  $CF_4$  emissions by the IAI Anode Effect surveys as found in Sect. 5.2." There should be mention here of the absence of an international report of electronics/semiconductor/plasma screen PFC emissions. This statement should be added to the rationale emphasizing the need for more accurate emissions inventory.

**We now point out that the gap found for the 1990s when PFC emissions from China were likely small, *could* indicate an inherent underestimation of  $CF_4$  emissions by the IAI Anode Effect survey as might be explained by fundamental problems with the application of IPCC methodologies *and/or* that the semiconductor/electronics manufacture emissions in EDGAR v4 are underestimated. In the revised manuscript we point out that the report of the WSC on the voluntary per-fluorocompounds emission reduction program of the semiconductor industry contains only very limited information.**

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Interactive comment on Atmos. Chem. Phys. Discuss., 10, 6485, 2010.

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