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Comment on acp-2021-857

Anonymous Referee #3

Referee comment on "Global emissions of perfluorocyclobutane (PFC-318, *c*-C_4F_8) resulting from the use of hydrochlorofluorocarbon-22 (HCFC-22) feedstock to produce polytetrafluoroethylene (PTFE) and related fluorochemicals" by Jens Mühle et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-857-RC3, 2021

General Comments:

This paper represents an important advance in our understanding of the sources of global perfluorocyclobutane emissions. These emissions matter. As discussed in this paper and in Mühle et al (2019), perfluorocyclobutane is a long-lived, potent synthetic GHG whose emissions are rapidly growing. Other data sources also indicate that perfluorocyclobutane emissions are significant. Data from the US Inventory of GHG Emissions and Sinks and from the USEPA Greenhouse Gas Reporting Program indicate that perfluorocyclobutane is the third most emitted perfluorocarbon in the US in GWP-weighted terms, behind perfluoromethane and perfluoroethane. Perfluorocyclobutane is also consistently among the top two or three most emitted fluorinated GHGs of any kind from US fluorochemical production in GWP-weighted terms.

The data and analysis presented in the paper make a compelling case that pyrolysis of HCFC-22 is the chief source of perfluorobutane emissions globally. This case begins with the detailed and richly sourced discussion of the pyrolysis process and the role of perfluorocyclobutane in it and proceeds through the author's calculations of global emissions of perfluorocyclobutane and discussion of HCFC-22 feedstock production in developed and developing countries. The authors' representation of the pyrolysis process and its generation of perfluorocyclobutane is consistent with discussions that this reviewer has had with US producers of HFP and TFE. Their analysis of UNEP and TEAP reports of HCFC-22 production for feedstock use, and the correlations between this production and perfluorocyclobutane emissions, is thorough and thoughtful. Their interpretation of these trends and relationships is persuasive but nuanced.

Specific Comments:

To put the inferred global c-C4F8 emissions into perspective, it would be helpful to

compare them briefly to inferred global emissions of other long-lived GHGs, such as SF6, CF4, and C2F6, both in unweighted and GWP-weighted terms.

On page 2, line 35, recommend deleting "regulated and" and "the Kyoto Protocol of," resulting in the following sentence: "Emissions of c-C4F8 from developed countries are reported under the United Nations Framework 35 Convention on Climate Change (UNFCCC)." The requirement to report emissions of c-C4F8 is what is relevant here, and it applies to countries that are signatories to the UNFCCC but not the Kyoto Protocol.

On page 2, line 58, the authors mention electrochemical fluorination (ECF) as a potential alternative means for manufacturing TFE and HFP that would generate less waste than the currently dominant method. This was surprising, because at least some types of ECF are known to generate large quantities of waste products. This reviewer is not familiar with the research cited by the authors in support of their suggestion to explore ECF as an alternative (Ebnesajjad and Mierdel), which may be based on more recent and refined types of ECF. I recommend qualifying the recommendation, perhaps by inserting "refined methods of" before "electrochemical fluorination" on line 58 and in other places where ECF is mentioned.

Figure 2 on page 6 contains a wealth of interesting data that is generally thoroughly discussed in the paper. Particularly fascinating was the analysis of using the 1996 through 2000 feedstock and emissions data to estimate an emission factor for developed countries, where the authors concluded that the current emission factor from developed countries was probably lower than the average from that period. However, there was a sharp divergence between c-C4F8 emissions and global feedstock production in 2009 that the authors did not mention. This is sufficiently striking that it is probably worth discussing briefly, even if the conclusion is that the cause of the divergence is not known. (The same is true of a smaller divergence in 2016.)

On page 8, the authors state "Current industry knowledge is that less than 2% of HCFC-22 FS produced is used in reactions that do not involve the TFP/HFP/c-C4F8 route," but they do not cite a source. A source should be cited for this statement because the correlation between HCFC-22 feedstock production and TFP/HFP/c-C4F8 production is fundamental to the method used by the authors to reach their conclusions.

Technical Corrections

Page 2, line 55: "TFE producer" is missing an "s."

Figure 2: The legend is missing an entry for the black diamonds, which appear to represent global inferred c-C4F8 emissions. In addition, the black diamonds appear to be offset from the other icons in the chart, perhaps because the values shown are from the

middle of the year. Whatever the reason for the offset, it should be explained.

Figure 3: The legend currently appears very close to the data, making it look as if the icons being explained in the legend are part of the data. Recommend either moving the legend or enclosing it in an outline so that the reader can distinguish between the legend and the data.