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## Interactive comment on "HFC-23 (CHF<sub>3</sub>) emission trend response to HCFC-22 (CHCIF<sub>2</sub>) production and recent HFC-23 emission abatement measures" by B. R. Miller et al.

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We thank Anonymous Referee #1 for the positive remarks and for comments that we believe have lead to the improvement of the manuscript doi:10.5194/acpd-10-13179-2010.

Please note that, based on a comparison of various manuscript versions, we assume that Referee #1 refers to page and line numbers from the initial submission version of our manuscript (file name "Miller\_et\_al\_HFC23\_manuscript\_v\_100412.pdf"), which does not include changes in content subsequently requested by the editor but made prior to publishing the web version on ACPD. We will therefore provide the online ver-

C5548

sion page and line numbers for reader clarity.

Minor points: 1. P3-4: Why is Montzka et al. (2009) not mentioned in the introduction? That paper addresses the same subject as this one and should be mentioned early in the paper.

Author response: Montzka et al. (2009) present observations of recent atmospheric abundance increases in HCFCs. They attribute these increases to exponential increases in developing country production. This conclusion is relevant to our discussion of rapid growth of HCFC-22 production in the developing world, and we therefore include the following sentences within the Introduction:

"Montzka et al. (2009) reported accelerated growth in the atmospheric abundance of HCFC-22 during 2006-2007, relative to that of 2003-2004. This growth coincided with exponential growth in developing countries' production and consumption of the three most abundant HCFCs."

There is more subject overlap between the current manuscript and Montzka et al. (2010), which discusses HFC-23 emissions. We do mention the HFC-23 incineration estimates for the CDM projects given by this reference within the Introduction, on web page 13183, lines 14-16, (initial submission version page 3, line 32 – page 4 and lines 1-2). However, Referee #1's request has pointed out the need to describe, as an overview within the Introduction, the HFC-23 emissions work of all the previous studies (in addition to the detailed comparisons already offered later in the manuscript). We therefore include the following paragraph within the Introduction:

"The first published time series of the atmospheric abundance of HFC-23 was given by Oram et al. (1998) and was based on analyses of subsamples of archived air from the Southern Hemisphere by gas chromatography/mass spectrometric detector (GC/MSD). They compared these observations with abundances derived from a 2-D global model to estimate global emissions of HFC-23. Subsequently, Culbertson et al. (2004) published a Northern Hemisphere time series based on GC/MSD analysis

of archived air samples, and used a one-box model to estimate global emissions of HFC-23. Most recently, Montzka et al. (2010) used GC/MSD analyses of Antarctic firn air and surface samples to estimate global emissions of HFC-23. The relationships between these previously published emission estimates and those derived in this paper are described in the Results section. The present paper extends HFC-23 atmospheric observations through 2009 and, in combination with an independent bottom-up analysis, improves upon the two latter studies by providing the temporal resolution that resolves several policy-relevant issues regarding source strength attribution and/or the efficacy of recent abatement measures, and additionally provides a foundation for anticipating future emission trends."

2. P5, L22-24: This sentence is too technical and not understandable by most readers. Rephrase or delete.

Author response: Web pg. 13185, lines 19-20, read:

"HFC-23 was quantified using target mass over charge (m/z) ratio 51 with qualifier m/z 69 to verify chromatographic separation from potential interferences."

We have reworded this statement for greater clarity and informational content to now read:

"MSD response to HFC-23 in samples was quantified using target mass over charge (m/z) ratio 51, which is the second most abundant ion in the mass spectrum of HFC-23. This ion fragment is not in common with PFC-116 (C2F6), which nearly co-elutes with HFC-23 on the separation column. The response of ion m/z 69, which is common to both PFC-116 and HFC-23, was also monitored as a qualifier ion to aid in identifying this and other potential chromatographic separation interferences."

3. P7, L1: "remarkably" seems an odd word to use here, since you want to (and do) convince the reader (me) that that the time of analysis does not affect the results.

Author response: We are pleased that Referee #1 finds our evidence to support stor-

C5550

age stability of HFC-23 in the archive tanks to be convincing. In such comparisons, there is the potential for any one of a number of analytical variables to cause a significant discrepancy between independent measurements, especially over long time spans. That this potential was not manifested to a significant degree in measurements made by us and by UEA leads us to observe a level of agreement that is indeed "remarkably close".

4. P7, L30: An uncertainty of 5% for 1995-2008 seems very small. What is this based on?

Author response: The uncertainty of 5% that we assign to the UNEP HCFC-22 production data is indeed a relatively small value. Note that, in this study, only the developing countries' production component of the UNEP data is actually used in the bottom-up history construction. The dominant producer in the developing countries is assumed to have the output of its facilities coordinated by the ministry, resulting in a relatively well-known production quantity, hence the small assigned uncertainty. To use a larger uncertainty estimate would have the affect of increasing the overlap of top-down vs. bottom-up history uncertainties, where we already have contiguous overlap for the period of interest.

5. P8, L12-14: "during 1990-1993". The lower panel of Fig. 3 shows that the data from McCulloch is also used for 1994-2005. Please clarify.

Author response: The caption of Fig. 3 has been modified to more clearly state that the data adopted for this study are designated by the red and blue solid lines. Also, the line widths of these red and blue solid lines have been increased as well, to aid visualization and distinguish between the different datasets and the adopted composite data used in this study.

6. P10, L24: Reference the SAR report here instead of AR4.

Author response: We thank Referee #1 for pointing out the more appropriate reference

for the 100-yr horizon GWP of HFC-23 used in UNFCCC conversions to tonnes CO2 equivalents. We have changed the reference from "Forster and Ramaswamy, 2007" to:

"Intergovernmental Panel on Climate Change (IPCC), Second Assessment Report, Climate Change 1995, The Science of Climate Change, edited by J. T. Houghton, L. G. Meira Filho, B. A. Callander, N. Harris, A. Kattenberg and K. Maskell, online available at: http://www.ipcc.ch/publications\_and\_data/publications\_and\_data\_reports.htm#1, 1996."

7. P11, L30-32: I think you underestimate the HFC-23 emissions by the assumption. Is it not likely that the facilities under CDM projects have a low HFC-23/HCFC 22 ratio that other facilities? Or do you want a conservative estimate of the HFC emissions (as mentioned in the next sentence). Please explain.

Author response: The referenced text states "...we assume that these CDM annual mean HFC-23/HCFC-22 co-production ratios [derived from the CDM monitoring reports] are representative of the mean from all developing countries producers." One might argue, as does Referee #1, that CDM projects would be expected to operate at lower co-production ratios than non-CDM plants in the developing world. Indeed, the time series of ratios for the CDM projects shown in Fig. 4 indicates a slight decrease in ratio, especially in comparing "historical" data, which were acquired when the plants received no CERs, with later data when they operated as approved projects. Should we assume that, prior to approval, these CDM projects were operating at ratios characteristic of the non-CDM plants? Perhaps, or alternatively there may be a "learning-curve" or startup characteristic to the temporal evolution of a plant's co-production ratio. Or perhaps the non-CDM plants, which are newer than the CDM project facilities, could have been designed to operate at more efficient ratios. We simply don't know. On the other hand, others have argued that there is a "perverse incentive" for CDM projects to operate at higher ratios, supposedly thereby increasing the subsidy attained through derived CERs, and that non-CDM plants will operate at lower ratios so as to increase the proportion of marketable HCFC-22 product. If this later expectation were true, then

C5552

by our calculations we would be overestimating the developing world HFC-23 production, and overestimating emissions from non-CDM facilities. At this time, we have no direct measure of this ratio in non-CDM plants to substantiate or refute either expectation. In view of these opposite expectations and scant evidence, we augment the discussion in the manuscript as follows:

"Based on a 2008 total HCFC-22 production of 256.0 Gg from the CDM monitoring reports and the UNEP 2008 developing countries total production of 501 Gg, we attribute  $\sim\!51\%$  of the total developing countries HCFC-22 production to the CDM projects. There are opposing viewpoints that suggest that CDM projects would have either higher or lower co-production ratios compared to non-CDM plants in the developing world. A discussion of this debate is outside the scope of this manuscript. In view of this non-resolved difference in expectations of relative co-production ratios, and considering the large sampling of developing countries facilities that the CDM projects represent, we make the simple assumption that these CDM annual mean HFC-23/HCFC-22 co-production ratios are representative of the mean from all developing countries producers."

Note that the sentence that follows the referenced text refers to what we deem to be a conservative uncertainty assigned to the CDM annual total quantities of non-released HFC-23, not to a "conservative estimate of the HFC emissions."

8. P12, L4-7: That fact that the data is needed as an a priori estimate seems less important that the fact that it is considered as a bottom-up emission history. I suggest to move the second sentence to the front.

Author response: We agree that the bottom-up history segment of the a priori certainly has strong relevance regarding emissions verification and is important to the conclusions of this paper. At the same time, the a priori is an important component in the inversion calculation that produces the top-down history. Both are critical to their respective end uses. Given that the bottom-up segment is derived from the a priori, we

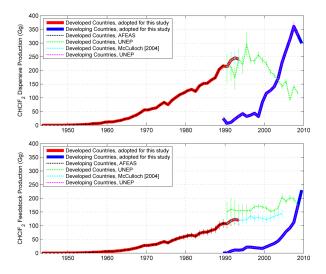
believe it logical to present the a priori first in the discussion, then designate the bottomup as a segment of the a priori that has a particularly useful level of uncertainty.

9. P35: Note that Figure 4 shows good on screen, but the printout shows black bars and lines on the graph.

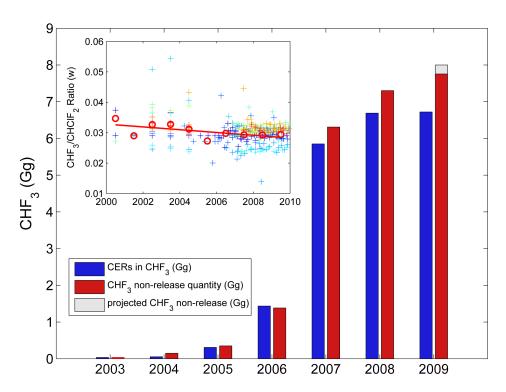
Author response: We thank Referee #1 for pointing out the difference in online vs. hardcopy appearance of Fig. 4. The bar graph has now been redrawn with lighter shades of blue and red for better hardcopy reproduction.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 13179, 2010.

C5554



**Fig. 1.** (Revised) Figure 3. Reported data for a) HCFC-22 (CHCIF2) production for dispersive uses and b) for feedstock use for developing and developed countries as compiled from various sources and were...



**Fig. 2.** (Revised) Figure 4. Annual amounts of HFC-23 (CHF3) involved in the Clean Development Mechanism (CDM) HFC-23 emission abatement projects. ...

C5556