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Atmospheric Chemistry and Physics Discussions

Interactive comment on "In-situ measurements of atmospheric hydrofluorocarbons (HFCs) and perfluorocarbons (PFCs) at the Shangdianzi regional background station, China" *by* B. Yao et al.

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We would like to thank referee 1 for the thorough review and the many useful comments and suggestions. We believe by addressing these, we can improve our manuscript. Below, we list the referees' comments individually followed by our answers.

Comments of anonymous referee #1 and response

Comments of referee 1: This is an interesting set of results from a region of the globe not well characterized for these compounds. The results appear to be of high quality,

given the consistency derived in the background atmosphere compared to other NH locations. The mixing ratio enhancements make sense with respect to input from regional sources, given the wind rose analysis. It is clear that this type of data will be invaluable for discerning the contributions of an important region of the global to atmospheric changes. Despite the very nice experimental work, however, I think the interpretations provided in this manuscript need improving before this paper is publishable.

Correlation in the observed mixing ratio enhancements above background for HFCs and PFCs relative to CO are used to derive Chinese emissions of halocarbons. The measured correlation slope can provide an estimate of halocarbon emission given an independent estimate for CO emissions. This approach has been used in the past by a number of investigators, but better descriptions about assumptions that are made and the accuracy of the information (e.g., CO emissions) are needed. Firstly, HFC emissions are derived as total Chinese emissions, and they are derived from a total Chinese CO emission based on a 2006 estimate and a growth rate for the intervening years of 3.4%/yr. What is this rate of increase in total Chinese CO emissions based upon? Multiple estimates of Chinese CO emissions estimates from the mid-2000s are given, yet no indication of their consistency or accuracy is presented. The authors assume an uncertainty of 10% on the total Chinese CO emissions, but no discussion is presented on how this number was derived. Secondly, issues of spatial scale are not considered. Are the measurements at Shiangdanzi representative of all of China? Or must some assumptions be made with regard to extrapolating the results from this site so as to be representative of emissions from all of China? What fraction of CO emissions from China is from industrialized regions (and/or processes) likely to be associated with emissions of HFCs? My guess is that this ratio is smaller than for more broadly industrialized nations where ratios to CO have been studied, and this may substantially influence these emission estimates and seems appropriate to consider. Thirdly, the description of the tracer ratio method needs some improvement, what is an "inherent relationship"? The tracer ratio method requires many important assumptions (source co-location, etc.) that aren't mentioned here. No indication of how background

mixing ratios of CO are derived. Was this also with the statistical method?

Response: We agree with the referee that the description of the tracer ratio method and especially the required assumptions and resulting limitations of the method were not adequately covered in our manuscript. We will revise the manuscript accordingly, adding an additional subsection in the methods section, giving more details on the actual method, but also highlighting the major restrictions. Due to a re-evaluation of the observation data and changes in the underlying uncertainties of CO emission, we also re-analyzed HFC/PFC emissions and will update the manuscript accordingly. As a reply to the more detailed referees concerns the following points will be addressed in the revised manuscript.

Both total Chinese CO emission for 2006 and an average growth rate of 3.4%/yr for the years 2001-2006 were taken from Zhang et al. (2009). An extrapolation of the growth rate for the years 2007 to 2011 seems reasonable considering the Chinese economic growth and technology improvements in these years. Zhang et al. (2009) compared their results with other bottom-up and top-down inventories (see their table 10). Their estimate for 2006 is at the upper-end of other bottom up estimates, but compares well with the top-down estimate of 170 Tg/yr by Tanimoto et al. (2008) for the year 2005. The latter estimate includes also emissions from biomass burning, which are not included in Zhang et al. (2009). However, according to the satellite derived GFED biomass burning inventory (http://www.globalfiredata.org/) CO emissions from biomass burning are only a minor contributor to total Chinese emissions (1.6 Tg/yr for 2010) and can be neglected in our considerations. Our previous assumption of an uncertainty of 10 % (1 sigma level) of the total Chinese CO emissions was too low. Zhang et al. (2009) actually give an uncertainty of 70 % (2 sigma level) for the total Chinese emissions. Considering the extrapolation of total Chinese emissions to 2010/2011, we revised our assumption of the total Chinese CO emission uncertainty and use a value of 36 % (1 sigma level) which results from the uncertainty of 35 % in 2006 and an uncertainty in the growth rate, which we conservatively assumed to be 100 % (1 sigma

level).

The second concern regarding the representativeness of the measurements in Shangdianzi (SDZ) is twofold. On the one hand, the referee is concerned with the fact that the observed “above baseline” concentrations do not originate from emissions from the whole of China. We agree with the referee that this is a limitation of the presented results. However, the area influencing the observations at SDZ can be assessed by back-trajectory calculations. We performed additional source-receptor relationship (also called “footprint”) calculations using the Lagrangian particle dispersion model FLEXPART. Similar to the results presented by Vollmer et al. (2009), the site SDZ was sensitive to emissions from large areas of north-east Asia, actually representing about 50 % of the countries total CO emissions and about 45 % of the population. The contribution from other Asian countries was minor with the exception of Mongolia. However, no major emissions of HFCs and PFCs are expected from Mongolia. In contrast, the contribution from North and South Korea is rather limited and not considered a major factor influencing the tracer ratio calculation. A figure showing the site’s “footprint” for the period of investigation will be added to the manuscript. The relatively large fraction of emissions covered by the observations at SDZ actually increases our confidence in extrapolating the obtained tracer ratio to the whole country. However, to meet the concerns of the referee we will split the emission analysis for the revised manuscript in two parts. The first will give the emissions only for the area covered by the SDZ observations using the uncertainty of 36% as mentioned above. The second part will extrapolate the tracer ratio to the whole of China, but considering an additional uncertainty of 10 % due to possible variability in the emission ratio throughout the country which are not covered by the variability observed at SDZ. On the other hand, the question is raised how valid the assumption of collocated CO and HFC/PFC emissions is for China. The following considerations have to be taken into account. Depending on the usage of the HFC/PFC of concern, their emissions can be more related to industrial processes (solvents, blowing agents, electrolytic reduction), residential use (refrigerants) or traffic (mobile air conditioners). The fractions of CO emissions from in-

dustrial processes, residential use and traffic can vary strongly from country to country depending on the countries mix of primary energy sources and exhaust treatment technology. The EDGAR emission inventory V4.2 (http://edgar.jrc.ec.europa.eu/index.php), for example, gives very different residential fractions of CO emissions for different industrialized countries (2% USA, 10% Canada, 30% Germany, 21% Italy, 18% UK, 20% France) for which the tracer ratio method was already applied. From this perspective China (32%) does not seem to be a large exception. Possible problems for China might arise from the fact that development standards vary strongly from urban to rural areas. From the latter we may expect relatively large CO emissions from biofuel and coal burning in small inefficient furnaces and stoves but virtually no HFC/PFC emissions. While these concerns about collocation can never be fully ruled out, the method in our manuscript considers the uncertainties that arise from non-collocated sources by using the uncertainty of the obtained tracer ratio, which will reflect the spatiotemporal variability in the emission ratio.

The third issue raised by the referee is on the description of the tracer ratio method. As mentioned before, we will revise this section in the revised manuscript giving it more space in an additional sub-section within the methods. For the tracer ratio method, the background mixing ratios of CO were also derived by applying the statistical filter of robust local regression (Ruckstuhl et al., 2010), we will add a more detailed description of the filter in the methods section of the revised manuscript.

Comments of referee 1: Atmospheric increases based on the observations over a 1-year period are presented in the paper. No indication is given about the robustness of these trends or their uncertainty. I agree that communicating how the atmospheric composition changed in background air at this site is a useful thing to do, but some indication of the potential accuracy of derived trends is needed. A close inspection of Figure 2, for example, suggests that the application of the statistical filter to isolate the background data has the potential to bias the derived trends (e.g., would a slightly different statistical filtering give substantially different trends for some compounds?).

Furthermore, defining a metric related to annual changes is difficult to derive from only one year of data. A simple sinusoid has a non-zero slope and a correlation coefficient of 0.5. Consider quoting the May-to-May change for all gases at least, though a close look at Figure 2 suggests only a very small amount of data are available during May 2011. In the text the authors rightly suggest that these rates are quite uncertain, but this caveat needs to be expressed throughout (abstract in particular) the paper.

Response: (1) We agree with referee that the potential accuracy of derived trends is important, so we will add uncertainties of trends in the revised manuscript. (2) Concerning the application of the statistical filter it needs to be mentioned that the baseline is estimated from an iterative local regression that subsequently removes data outside a 3.5 sigma range from the baseline. This sigma is estimated as the standard deviation of the residuals of the fit below the mode. The filter does not take care of observations within the overlapping part of the frequency distribution (data that could either belong to the baseline distribution or the pollution distribution) and considers these to belong to the background. Hence, when estimating the background concentration from the data that was flagged background the estimated might be biased high. However, the baseline estimate itself is more robust because for the local regression fit robustness weights are used for data above the background, giving limited influence to points at the upper end of the 3.5 sigma range. For more details please refer to the method described in Ruckstuhl et al. (2010), which, although still in the discussion stage of AMT, was not criticized in general but rather for the comparison with other filter methods. (3) When calculating the yearly trends from the May-to-May change, we use the monthly average of May 2010 (May 6th to May 31st) and May 2011 (May 1st to May 31st). For the discussion of other sections, we use only one year of data (May 6th 2010 to May 5th 2011), so in Fig 2, we just show the data until May 5th 2011.

Comments of referee 1: The comparison of trends among different studies (Table 3) is also problematic, as only one of the other results included in the table are for concurrent periods. What are we to take away from this comparison? That the measurements are

done well or that growth rates at Shiangdianzi are anomalous? I'd expect these growth rates would change over time, but this isn't considered. If kept, the trend comparisons would benefit from consideration of some more recent data (including updates to data originally published in Greally et al and other studies) that appear in Chapter 1 of WMO (2011, Table 1-15) Ozone Assessment report.

Response: As the referee mentioned, the growth rates would change over time, hence a comparison between studies covering different periods may be biased. We have therefore decided to remove the trend comparisons with other studies.

Comments of referee 1: Clarity issues: English usage is OK, but needs some improvement in a few places.

Response: We have now re-written some parts of the manuscript in an attempt to improve the language.

Comments of referee 1: Abstract lines 15-16, "small local contributions..."? Without a definition of the term "loadings" as it is used in the abstract, it seems likely to be misinterpreted.

Response: We have revised lines 15-16 in the abstract to: "North-easterly winds were associated with negative contributions to atmospheric HFC and PFC loadings (anomalies multiplied by the wind frequencies and by observation time), whereas south-westerly advection (urban sector) showed positive loadings."

Comments of referee 1: Minor issues: I'm a bit surprised that PFCs are mentioned as being substitutes for CFCs and HCFCs in the introduction. I hadn't consider them as such, especially for all three PFCs considered here despite the text in the introduction (Mulhe et al., do indicate C3F8 as being a refrigerant and perhaps some enhanced use a few years ago so maybe the comment is true for this gas only). Certainly they haven't taken the place of any significant fraction of CFC and HCFC past usage.

Response: We agree that only HFCs are the dominant replacements compounds for

CFCs and HFCFs. We have revised lines 9-10 in the introduction to: "HFCs are replacing chlorinated ozone-depleting gases such as chlorofluorocarbons (CFCs) and hydrofluorochlorocarbons (HCFCs)."

Comments of referee 1: p. 11155, lines 23-24, pollution events for PFC-318 occur fairly often and range from 2-3 times background levels, seemingly inconsistent with the text. Some clarification would be useful.

Response: Since the calibration scale of PFC-318 is still preliminary (SIO-2010-p), we have decided to remove the PFC-318 results from this paper.

Comments of referee 1: Section 3.2, para starting on line 14. It would be useful to indicate that these larger differences are expected as they are typically observed for all long-lived gases emitted in substantial quantities from human activities.

Response: We agree with the referee and have revised lines 14-16 in section 3.2 to: "There are differences for the background mixing ratios of HFCs and PFCs up to several ppt between SDZ and Cape Grim, especially for HFC-134a and HFC-152a. These larger differences are expected as they are typically observed for all long-lived gases emitted in substantial quantities from human activities."

Comments of referee 1: Section 3.2, para starting on line 19 and 23. These paragraphs might be reconsidered. The approach is not communicated clearly especially in the latter para... also, given the extrapolation required from 2004 data (with a trend apparently determined in that study from 1 year of data) it would seem the only appropriate conclusion is that mixing ratios of HFC-32 have increased since then. Updated HFC-32 data are included in the WMO (2011) report, Chapter 1.

Response: As mentioned before, we have decided to remove the PFC-318 results from this paper because the calibration scale of PFC-318 is preliminary (SIO-2010-p). For HFC-32, we appreciate the mentioning of the WMO 2011 report by the referee and we are now comparing our results with updated results from this report.

Comments of referee 1: Loadings section 3.3. Indicate if this analysis was performed on the full set of measurements, not just background or polluted results. The authors also might reconsider the definition of loadings provided (line 26, p. 11157), given that the unit used is ppt hr and not ppt/hr.

Response: Here we used the full set of measurements. As suggested by the referee, we have revised lines 26-27 in section 3.3 to: "Anomalies (differences between mixing ratios in each wind sector and their means) and loadings (anomalies multiplied by the wind frequencies and by observation time which is 8760h) were calculated based on the method described in the previous study (Zhang et al., 2010; Zhou et al., 2003, 2004). Both anomalies and loadings are performed on the full set of measurements."

Comments of referee 1: p. 1158, line 19, Palmer misspelled.

Response: We have made the correction in the manuscript.

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