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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 2 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.

Comment of anonymous referee #2 and responses

Comments of referee 2: This manuscript presents a high quality data set of measurements of radiatively important trace gases over a period of one year. The data has

been collected in globally important source region where in addition very little data has been published previously on these compounds. In addition the manuscript is well structured and – with the exception of some minor language problems – appropriately written. For these reasons I believe this to be a potentially very valuable contribution to the literature. There are, however, a number of problems mainly connected to the data analysis and interpretation that should be addressed first. The most important issue is the estimation of emissions in section 3.4. I agree with referee 1 that using carbon monoxide as the reference tracer here is highly questionable for several reasons. Firstly, the estimate of the Chinese emission inventory of CO is based on a single study (rather than the several cited) and a growth rate of 3.4% both of which is not explained or justified. Secondly, although showing a wind rose, the authors do not show or discuss any variations in wind speed or trajectory calculations. Without this information it is very hard to assess the actual source regions. Even if air masses arrive from SW they might well have been influenced by other sources in S or SE Asia, maybe even South Korea or Japan. The air mass origins in 2010 and 2011 are not necessarily similar to those presented in Vollmer et al., 2009. Moreover, it is very likely that for the halocarbons high concentration events are dominated by sources in or close to Beijing and thus not necessarily representative for all of China. On the other hand the CO part of these correlations could well be influenced by a variety of sources not all of which are halocarbon sources (e.g. biomass burning). Again, considering trajectories could help here. It would be very recommendable to show these correlations against CO to corroborate such a crucial part of this manuscript. In case of considerable scatter a revision of the estimated uncertainties might be advisable. Currently these emission estimates are in my opinion not comparable to Chinese emission estimates from other studies.

Response: Some of the concerns raised here were already raised by the first referee and we will only briefly repeat these replies here. First of all, we will include an additional sub-section on the tracer ratio method in the manuscript that will highlight some of the details and limitations of the method.

In the following we give some direct replies to the concerns raised here: Firstly, the Chinese CO emission for 2006 and a growth rate of 3.4%/yr used in this study were taken from the recent publication of Zhang et al. (2009). For a discussion of the CO emission uncertainties see reply to referee 1. As suggested by referee 2 and already outlined in the reply to referee 1 we will include "footprint" calculations in the revised manuscript. The total footprint for "above background" CO conditions shows that the influence of emissions outside China onto the measurements at SDZ was rather limited during the period of interest. While we agree that the site often receives direct pollution plumes originating from the Beijing area, the footprint still shows relatively large sensitivities beyond Beijing and also towards the south-east. Furthermore, emissions often accumulate and mix within the North China Plain before they are transported towards SDZ. Therefore, we expect SDZ to be representative not only of emissions from the Beijing area but more generally of the North-East of China. As pointed out in the reply to referee 1, total CO emissions and population in the areas "covered" by the station's footprint comprise about 50% and 45% of the Chinese total, respectively. Biomass burning emissions of CO in China make up less than 1 percent of anthropogenic emissions in China (see reply to referee 1) and, therefore, were neglected in our study.

As suggested by the referee we will include regression plots of HFCs/PFCs versus CO in the revised manuscript. These, indicate that the assumption of emission collocation is better justified for some of the compounds than for others. This is reflected by the Pearson regression coefficient of the compounds, but also by the estimated uncertainty of the tracer ratio. Since the latter is also used for the final emission estimate, we feel that the uncertainties of the tracer ratio method that arise from violations of the collocation assumptions are adequately addressed in our results.

Comments of referee 2: P3, l2: How do you define "large"? The GWPs of these compounds have a considerable range.

Response: We accept referee's suggestions and have revised line2 in section 1 to:

"Hydrofluorocarbons (HFCs) and perfluorocarbons (PFCs) are greenhouse gases with global-warming potentials (GWPs) ranging from 140 to 11'700 (IPCC, 2007) and they are included in the Kyoto Protocol."

Comments of referee 2: P3, l9: Only HFCs

Response: Revised.

Comments of referee 2: P3, l15: Should be "HFC and PFC measurements". Similar problems with plural can be found throughout the whole manuscript.

Response: Revised.

Comments of referee 2: P4, l18: 10 metres is hardly a "tall tower".

Response: This was a miss-understanding/language error, we wanted to say that the tower is 10 m in height, and not that it is a 'tall' tower. Revised as "The sample inlet was installed at 8 m on a 10 m tower".

Comments of referee 2: P4, l24-25: No precision, accuracy or reference given.

Response: We have added precision of CO measurement and revised lines 24-25 of section 2.2 as "and with a measurement precision <10 ppb (parts per billion, 10-9, molar)".

Comments of referee 2: P5, l1-2: This sentence is irrelevant unless some of these measurements are used in the manuscript.

Response: We will remove the sentence mentioned in the revised manuscript.

Comments of referee 2: P5, l5: What does "closely tied" mean? Also, references should be given for the calibration scales. Have all of them been reported in the literature before? If not, information is needed on their accuracy and how they were defined.

Response: Our results are linked directly to AGAGE. These scales except for PFC-318

have been reported before. Here we add one more reference describing the scales of PFCs. PFC-318 results from SIO-10-p scales were removed from this study as the calibration scale is preliminary. So, we have revised the sentence as follows: "Our measurements are linked to the Advanced Global Atmospheric Gases Experiment (AGAGE) (Prinn et al., 2000; Mühle et al., 2010)".

Comments of referee 2: P5, l17: Ruckstuhl et al., 2010 has only reached the discussion stage in AMTD so far. The reviewers have requested some changes to this manuscript. It would be good to specify the exact method and criteria used here.

Response: As mentioned in the reply to referee 1, the statistical method as presented by Ruckstuhl et al. (2010) was not criticized for itself, but rather for its comparison with other background filters. The revised version of Ruckstuhl et al. is currently resubmitted to AMT but no changes to the method were required. Therefore, we don't think it necessary to repeat details of the method here. However, we will add the required settings used for our baseline estimation in the revised manuscript.

Comments of referee 2: P5, l22-24: Not only the mixing ratio difference is of interest here but also the changes relative to background mixing ratios, which are much larger for some of the PFCs. Also, Fig. 2 does not support the interpretation of pollution events being "rare" for any of the compounds.

Response: Here we want to emphasize that the mixing ratio differences reveal the emissions. The pollution events for PFCs are less compared to HFCs, so that lines 22-24 of section 3.1 were revised to: "The mean mixing ratio difference between pollution and background can be attributed to recent emissions. Of all compounds measured, HFC-134a has the greatest mixing ratio difference between pollution and background. Compared to HFCs, pollution events for the PFCs are less frequent and smaller in size, with the exception of CF4."

Comments of referee 2: P6, l8: Uncertainties should be given to demonstrate that these mixing ratios are indeed "consistent" with each other. It would also be recom-

mendable to compare growth rates.

Response: We agree with the referee and will add uncertainties of background mixing ratios in Table 2 in the revised manuscript.

Comments of referee 2: P 6, l24: How was this estimate carried out exactly?

Response: As suggested by the first referee, the estimate was updated by recent data from WMO Ozone Assessment report in the revised manuscript.

Comments of referee 2: P6, l27-28: Only when assuming that the growth rate has not changed since then. Also "growth rate" should be used throughout the manuscript.

Response: We have replaced "growing rate" with "growth rate" throughout the manuscript. We agree with the referee and have revised line 22 to line 28 of section 3.2 to: "However, there is no recent report on HFC-32 NH background levels. Global background mixing ratios are reported as 2.7 ppt for 2008 (WMO Ozone Assessment report 2011 see Montzka et al., 2011). Assuming that the growth rate remained the same as of 2008 (0.6 ppt/yr) , the global background mixing ratios from May 2010 to May 2011 are calculated as 4.2 ppt which are smaller than our study at SDZ. The difference (1.7 ppt) might be due to the difference between NH and SH, or bigger growth rate of HFC-32 since 2008."

Comments of referee 2: P7, l3-4: All other compounds? Also, why were different approaches used for different compounds?

Response: For HFC-23, HFC-152a, and 3 PFCs, annual mean growths are obtained from monthly mixing ratio means difference between May 2010 and May 2011 because the linear cure fitting for them were with poor R. We will mention this in the revised manuscript.

Comments of referee 2: P7, l5-9: Again it would be interesting to see the relative changes. Also, the use of small words such as "the" and "by" is incorrect in various places.

Response: Here we have added a description of relative changes as follows: “Compared to their background mixing ratios, HFC-23, HFC-32, HFC-125, HFC-134a, HFC-152a, CF4, PFC-116, and PFC-218 increased by 2.9%, 24%, 16%, 6.2%, 11%, 0.5%, 1.2%, 1.8% per year, respectively. HFCs also show higher relative trends compared to PFCs, of which HFC-32 shows the biggest relative trend up to 24%/yr.”

Comments of referee 2: P7, l11: What are the criteria for “big differences”?

Response: As suggested by referee 1, we have removed the paragraph of the comparison of the yearly trends with previous studies.

Comments of referee 2: P7, l14-15: Which changes? And would they not also have the potential of greatly altering any emission estimates? Adding a reference might also be advisable here.

Response: Same answer as above.

Comments of referee 2: P7, l21: “year” instead of yr.

Response: We have replaced “yr” with ‘year”.

Comments of referee 2: P7, l22: Which measurements were carried out? These should also be added to section 2.2.

Response: In section 2.2, we have added a description as follows: “Horizontal surface wind data with a resolution of 1 h are obtained from the top of the same tower.”

Comments of referee 2: P7, l23: Was the wind data measured at the surface or at the air inlet at 10m?

Response: It is measured at the top of the 10m tower. This is now mentioned in the revised manuscript.

Comments of referee 2: P7, l27: Should be “previous studies”

Response: Revised.

Comments of referee 2: P8, l4 and Figure 4: What criteria are being used to identify “distinct emission sources”? It would also be good to put these anomalies loadings in context by comparing to other literature.

Response: For PFC-218, we saw few pollution events with enhanced concentration less than 0.7 ppt (see fig. 4 in the revised manuscript) and anomalies were within 0.01 ppt, thus reveals there are no distinct emissions for this compound. We do not find any literature report anomalies and loadings of HFCs and PFCs, so it hard to make comparisons.

Comments of referee 2: P9, l2: The variable “p” is not explained.

Response: P means the P-Value.

Comments of referee 2: P9, l10-11: Is this a repetition of l2-3 or are both “all measurements” and “enhanced mixing ratios” significantly correlated? If so, which correlation was used?

Response: Yes, here is a repetition of l2-3, and linear correlation was used.

Comments of referee 2: P9, l16: How is the 10% uncertainty justified?

Response: Here we have update the uncertainty of CO emission to 35% from Zhang et al. (2009) for 2006 and 36% for our extrapolated emissions in 2010/2011 (see reply to referee 1). We now use this uncertainty to estimate the HFC/PFC emissions from North-Eastern China and add an additional 10% uncertainty when we extrapolate to total Chinese emissions. The latter remains an educated guess. These uncertainties will be discussed in more detail in the revised manuscript.

Comments of referee 2: P9, l21-23: If the correlation is weak, then its scatter may well be used to infer a more realistic uncertainty range.

Response: As we will highlight in the extended sub-section describing the tracer ratio method, the uncertainty of the tracer ratio as estimated through weighted total least

square regression reflects the scatter in the data. This uncertainty is also included in the final emissions uncertainty estimate. However, the largest contributor to the final emission uncertainty remains the uncertainty of the underlying total CO emissions. This will be discussed in the revised manuscript in more detail.

Comments of referee 2: P10, l4-5: Which facts corroborate the hypothesis of previous projections overestimating growth rates?

Response: We have re-analyzed the emission estimate by two method of trace ratio method. For HFC-134a, the emission estimate may be questionable due to insignificant correlation between HFC-134a and CO and the results of the two methods differ a lot. So here we removed the comparison of HFC-134a emission between our study and previous projections.

Comments of referee 2: P10, l27: Should be “Our”.

Response: Revised.

Comments of referee 2: P11, l4: It would be good to be more quantitative here and to name the compounds again. Also, very little context is given in this section.

Response: We have named the compounds in line 4 as: “and positive trends were found for HFC-23, HFC-32, HFC-125, HFC-134a, HFC-152a, CF4, PFC-116, and PFC-218”.

Comments of referee 2: P16, Table 1: CO is missing.

Response: Because this paper is focused on HFCs and PFCs in-situ measurement, and CO data were only used for correlation analysis with HFCs and PFCs. So here we show the results of HFCs and PFCs without CO in table1.

Comments of referee 2: P18, Table 3: This comparison is questionable as very different times and time ranges are compiled.

Response: As mentioned before, we have removed table 3 and also the interpretations

with comparison of trends.

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