Stability of Halocarbons in Whole Air Samples
Response to Referee #1

We thank referee#1 for the thorough reading of our manuscript, in particular for spotting the mismatch between the discussed compounds and compounds shown in Figure 3. All suggested changes and raised questions were carefully considered when revising the manuscript and we address them point by point in the following.

Main comments:

- *Figure 3. There seems to be some confusion regarding which species are presented. Panel B shows results for dichloromethane, whereas the text talks about tetrachloroethene (P6 L30, P7 L3). I'm assuming this is simply a mix-up, but it makes the entire section rather difficult to understand.*

   Tetrachloroethene was mentioned in the text erroneously as the substance shown is dichloromethane. We have corrected this.

- *With regards to Figure 3, it is also not clear to me as to why the dichloromethane/CFC-12 ratio of the 'orange' sample is higher than the other two samples filled with the exact same ratio of standard/synthetic gas. I suspect that all three are within the measurement uncertainty. In which case it might be good to find some way of showing the error bars which are currently omitted.*

   We have modified the figures for the revision of the manuscript now including daily values of the measurement precision for each individual day of measurement.

- *While there were several very interesting results presented, I did not feel that the authors provided much in the way of reasoning for a number of their findings. For instance, why did bromomethane and chloromethane increase in the cylinders over the length of the short-term (and long-term) storage tests? Presumably due to production as a result of the decomposition of more complex chlorinated compounds? The same can be said of H-1301, which would appear to be a strange result. I would not expect to see complex chemical mechanisms in this sort of paper, but it would be useful to have some brief discussion of these points.*
We think that the current experiments do not provide sufficient information to speculate about the mechanisms of the observed changes and this is beyond the scope of the experiment series. We have, however, seen growth of chloromethane and chloromethane in newly welded cylinders of identical shape to the ones used inside HIRES. In addition, we have seen both compounds to be unstable in a high-pressure stainless steel gas bottle, though on longer time periods of the order of months to years. The result for H-1301 is indeed strange and we will look into this further with new cylinders in future experiments with and without the multiposition valves.

- *I think the title needs to be revised. At current, it suggests that the storage tests were conducted on samples collected in the UTLS, while in fact they were conducted using samples prepared in the laboratory.*

  We agree and have modified the title which now reads: "*Stability of Halocarbons in Whole Air Samples Collected in Stainless Steel Canisters* "

- *P1 L1. 'Halogenated halocarbons of' should be changed to 'halocarbons in'.*
  Changed to: `Measurements of halogenated trace gases in ambient air …`

- *P1 L17. The sentence needs extending. Suggest 'growth was observed during storage for some compounds,…'*
  The sentence is modified and now reads: "`Also growth was observed during storage for some species, namely for HFC-152a, HFC-23, and Halon-1301.`"

- *P1 L21. Delete 'the' before stratospheric.*
  Done.

- *P2 L7. Remove comma after 'both'.*
- *P2 L24. Remove comma after 'both'.*
  Changed.

- *P2 L26. 'Flask' should be plural.*
  Done.

- *P2 L33. Start of sentence does not read correctly. Suggest replacing 'got' with 'has been'.*
  Changed.

- *P4 L26. 'Details' should be singular.*
  Changed.

- *P5 L4. There should be a space between 'Figure' and '2'.*
  Modified.

- *P5 L6. This sentence doesn't quite make sense. I think it's supposed to read 'bellows pumps, in this set-up the samples are pressurized…'.*
  The sentence was changed to: "`Contrary to the set-up in flight, when the HIRES cylinders are filled with ambient air pressurized by the metal bellows pumps, in this set-up they are pressurized directly from high pressure gas cylinders.`"

- *P5 L15. Purely out of curiosity – how many samples can be obtained from a single whole air sample at a flow rate of 100/150 ml/min? It might be good to include this figure at some point in the text.*

If the samples were exclusively for analysis in our lab, we could obtain 3 enrichments of 1 l from a 4.5bar cylinder (which is 3.5bar above ambient; at pressures below 0.5 bar above ambient the flow rate starts to decrease significantly and we found that measurements with very low enrichment flows are not reliable). From samples from our ground site program we usually do 2 enrichments for quality assurance. This cannot be done with HIRES samples because the air needs to be saved for other analyses. We prefer to not discuss this in the manuscript as it is unrelated to the question of compound stability.

- *P6 L16. The mention of the presence of an air-conditioning unit in the laboratory is fitting given the nature of the gases studied. However, it would be more useful to quote the refrigerant blend used, e.g. R-410A. Very high levels of these gases in the laboratory environment might affect the analysis, if there are small leaks in the system.*

The air conditioning of the laboratory uses water, thus it can be excluded that the results are influenced. We have added the following statement in the revised version of the manuscript: "`The air conditioning uses water and is therefore not expected to adversely influence halocarbon analysis.`"

- *P7 Figure 3 caption. I'm confused by what the solid black line represents. From the caption 'The solid black line represents the value expected from direct measurements of the standard gas and the synthetic air.' Why is the black line a mix of the two gases? I would have thought it would be better if the black line was a direct measurement of the undiluted standard gas? Or is this to account for contamination in the synthetic air. Some additional description would be useful here.*

We look at ratios of all discussed compounds relative to CFC-12, and the black line does indeed represent that ratio for the undiluted standard gas. However, for those compounds which are present as contamination in the synthetic air, i. e. carbonyl sulfide, chloromethane, HFC-152a, and tetrachlorethene, this contamination has to be - and is – taken into account. We have removed that somewhat confusing statement here and refer to the explanation in section 2.3 instead.

- *P7 L9. Throughout the previous paragraph tetrachloroethene is referred to as 'C2Cl4', but here it is referred to be its full name. Suggest using C2Cl4 throughout.*

As noted above the figure shows dichloromethane while the text said tetrachlorethene (for which results are similar). This is corrected in the revised version of the manuscript.

- *P8 L2. Suggest replacing 'right' with 'immediately'.*

Changed to: "`already one day after pressurization`"

- *P8 L19. 'Is' should be 'are'.*

Changed to "`shown is the ratio`" as in the figure caption.

– *P9 Figure 4. Some more explanation of the light blue trend in panel b) is required.*

The corresponding paragraph now reads:
"*Some substances that were found to be stable during the one week short-term test decreased after longer storage times, for example dichloromethane shown in Figure 4(b). A similar behaviour was observed for trichloromethane (CHCl3), tetrachloromethane (CCl4), trichloroethene (C2HCl3), tetrachloroethene (C2Cl4), tribromomethane (CHBr3), and bromochloromethane (CH2BrCl). Measurements of these compounds should not be evaluated for the HIRES canisters if analysis takes place later than two weeks after sample collection as the long-term test indicates changes of mixing ratios start to occur after that period. In general, the decrease during long-term seems to be independent of the influence of ozone, although the gas mixture that shows the largest depletion (light blue dashed line, mostly cut off in Figure 4) did contain ozone. Ozone could not be monitored during the pressurization of the samples. It can therefore not be excluded that this gas mixture may have been exposed to a different amount of ozone than the one represented by the dashed brown line which could have caused the stronger depletion.*"

– *P9 Figure 4. There is no mention of HFC-152a (panel c) in the caption.*
This was added.

– *P9 L1. Why did HFC-152a increase over time?*
– *P9 L3. Why did H-1301 increase over time?*
Currently we do not have any explanation for this. As we speculate in the original manuscript, a possible source of fluourinated compounds could be valve sealing material as the seals of the Valco multiposition valves are made from PFTE and currently we cannot add any further reasoning on why these compounds grow.

We hope that further tests with new cylinders with and without this type of valves will shed some light on this growth. The result for Halon-1301 is indeed confusing. In an experiment performed with newly welded cylinders only using stainless steel parts (including the valves) we did not observed measurable changes of Halon-1301 over a storage period of 12 days. We will perform further experiments with and without the multiposition valves.

– *P11 Figure 5. Are the ozone measurements from multiple instruments? What is the difference between the diamonds and the red line? It looks like one is an in-situ instrument and the other based on the flasks – either way, it would be good to include this information in the Figure caption.*
The diamonds are the results of the fast in-situ measurement integrated of the sample period of the canister samples. This information is added to the figure caption which in the revised manuscript reads: "Time series of ozone (red), CFC-12 (yellow) and dichloromethane (blue) during a flight from Munich to Denver on 22 March 2018. Ozone high resolution data represented by the red line were

integrated over the sampling period of each whole air
sample (red diamonds)."

- *P13 Figure 6. It would be useful to include the R value somewhere on each individual plot.*
  R² values were added to the plots.

- *P13 Figure 6. There is some overlap of the colour bar with the underlying scatter plot.*
  This is on purpose to not interfere with axis labels.