

Interactive comment on “Stability of Halocarbons in Whole Air Samples from the Upper Troposphere and Lowermost Stratosphere” by Tanja J. Schuck et al.

Anonymous Referee #2

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General notes: The tests of the stability of samples inside the HIRES sampler are welcome (though they should have been performed much earlier).

General: This paper adds valuable information about the stability of halocarbons measured sampled by the CARIBIC project using the HIRES sampler in the UT/LS. It reveals problems for many species with respect to general stability and/or reactivity towards ozone. These tests are welcome, though they should have been performed much earlier. Similar tests for other analyzed species, such as hydrocarbons would be of value as well.

In addition to the tests with artificial air mixtures, the HIRES sampler should be tested

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under flight conditions. That is, several cylinders should be filled with the same UT/LS air and then analyzed over the course of days to weeks in the laboratory. Otherwise, the title should probably be changed to something like "Stability of Halocarbons in Simulated Air Samples from the Upper Troposphere and Lowermost Stratosphere". The authors have already some supporting evidence from actual flights; see CH₂Cl₂ in Figure 5, as well as Figures 6. This should be added to the discussion and table 1. Then the title could perhaps be retained.

Specific comments:

P. 3. Line 9: What kind of stainless steel is the sampler made out of? Is it electropolished? How was it welded?

P. 3. Line 13: How were the leak tests performed? Static with a gas? If so, using what gas at what pressure? Or is it evacuated? Why does the sampler contain either air from the previous flight or gas from the leak test? Also, have the authors considered to precondition the cylinders with moist air? This may have a positive impact on storage for several species (unless the water layer is removed quickly by the dry UT/LS air).

P. 3. Line 17: What final pressure is usually achieved after 20 s venting? In other words, what is the dilution factor? If tropospheric/laboratory air is still in the cylinders, more flushing is needed than if previous UT/LS samples are still in the cylinders.

P. 3. Line 18: Again, what is the final dilution? 0.2 to the 8? Is this dilution sufficient to flush out lower tropospheric/laboratory air?

P. 4. Line 1: The flushing/filling procedure should be explained in more details. Are the three flushing iterations in addition to the previous 8 times? Or are those the last three of the eight?

P. 4. Line 5: How much time does usually pass (min/max/mean) between sample taking in the airplane and analysis in the lab?

P. 4. Line 9: What is the effect of heating the Mg(ClO₄)₂ on the analytes?

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Section 2.2: There does not seem to be any focusing step involved, other than on the pre-column, which at 50 oC probably does not focus very much. How sharp/wide are the peaks of the most volatile peaks? Have the authors considered to add a micro-focusing trap?

P. 4. Line 29: Please identify the individual Scripps scales for each compound somewhere. Please keep in mind scale revisions.

P. 4. Line 30: What are the calibration scales for CO and O₃/how are their measurements calibrated?

Section 2.3: Does your Mg(ClO₄)₂ drying result in water vapor mixing ratios similar to those in the UT/LS? Please specify the dryness of the standard used for the experiments in comparison to UT/LS dryness. Keep in mind that the drier the samples, the more storage problems are likely to occur for certain halogenated compounds.

P. 5. Line 13: Were the HIRES cylinders flushed the same way as during flight? If not, how? What dilutions were achieved? Did you measure final water vapor in the HIRES cylinders?

P. 5. Line 15: Is one week the typical storage time for actual HIRES samples before halocarbon analysis? In the next sentence you indicate that storage time is usually much longer. Are your tests therefore representative of actual storage effects?

P. 6. Line 6: Have you considered to sample six cylinders at a time, thus increasing the volume and measuring an average storage effect rather than the storage effects in individual cylinders? If you had one rogue cylinder (which behaves much worse) could your tests identify it?

P. 6. Line 17: You cannot assume that synthetic air is free of halocarbons at the ppt level. I see that you have analyzed the zero air. Please rephrase the paragraph.

P. 6. Line 30ff: The text refers to C₂Cl₄, but figure 3b refers to CH₂Cl₂. Which one is it? Please check the correct chemical names/formulas throughout the text.

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P. 7. Line 7: Why are no error bars for the individual data points shown? Please add them.

P. 7. Line 8ff and Figure 3: Why is the spread of the measurements on day 1 (and day 8) so much larger than the gray shaded area?

P. 8. Line 4ff: It seems straightforward that ozone reacts with any of the compounds containing double bonds, but I am very surprised that CH₂Cl₂ and CH₃CCl₃ (and CHBr₂Cl) were also depleted. CH₂Cl₂ for example is considered to be inert in organic chemistry. It is used as an inert solvent for ozonolysis of other compounds. Of course, we are talking about very different concentrations, but I just do not see how ozone reacts with CH₂Cl₂ or CH₃CCl₃. Do you have any explanation for this? Could you think of any other experimental problem for these compounds? CH₂Cl₂ for example, shows a very variable behavior in Figure 4. Have you repeated the storage tests to see if they are reproducible? The fact that CH₂Cl₂ is depleted in Figure 5 for all high-ozone periods is compelling, however. Do the other compounds which are affected by ozone also show this (consistently) during actual post-flight analysis? If so, please discuss and add another column to table 1.

P. 8. Line 12ff: It is known that CH₃Cl and CH₃Br may grow in stainless steel cylinders if they were not filled using particle filters. Whether this is due to sea salt or organic material or other compounds is unclear. Are the HIRES samples filled through a fine particulate filter?

P. 8. Line 4ff: Which of the observed effects in the ozone experiment do not agree with the long-term storage tests? In other words, could some of the "ozone" problems be general "storage" problems? If so, please discuss this.

Figure 3 and 4: Please add error bars. Figures for all compounds should be shown in the Supplement.

P. 8. Line 22: Please show error bars. Without error bars, the reader cannot put the

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scatter of the results into perspective.

P. 8. Line 22ff: "some scatter" is unscientific. Also, without error bars, the reader cannot evaluate your statement about 2 sigma agreement.

P. 8. Line 24ff: Do you have an explanation why the red and blue experiments are so different? The red, yellow, blue, and dashed brown experiments indicate stability of CH₂Cl₂, while the other experiments show problems. Is it possible that individual cylinders are worse than others? How would you test that? Please expand your discussion at the end of page 8.

P. 8. Line 28: How do you determine two weeks (rather than one week)?

P. 9. Line 4: What polymer materials are used inside the sampling and the analytical system? Is Viton used by any chance? This could explain HFC-23 increases.

Figure 5 and 6: Please add a discussion of evidence for the observed storage tests from actual flights to the discussion. Please add Figures 5 and 6 for all compounds to the Supplement.

Figure 5 and 6: Please add correlation lines and R² values (excluding the tropospheric outliers for CO) to Figures 5 and 6.

P. 12. Lines 6ff: I do not think that the discussion of correlations for an unstable compound is very informative.

P. 12. Line 30: I think this identifies a general weakness of CARIBIC. Can this be improved? Do the results from this paper have any implications for previously published results?

P. 15. Line 5ff: It is good to learn that a new sampler is being designed taking into account the lessons learned from this paper and that more rigorous tests will be performed.

Table 1: Can you exclude that the change of mixing ratios for drifting compounds is NOT

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caused by drift of the working standard itself? In other words, do you have evidence for stability of the working standard for all compounds over the relevant time scales?

Minor comments:

P. 1. Line 21: Strike out "the". It should say "responsible for stratospheric ozone depletion".

P. 1. Line 23: ".. as an entry point for chlorinated and brominated species into the stratosphere".

P. 2. Lines 1/2: The trace gas composition in the ... can be analyzed ... or using air sample collection ...".

P. 2. Line 10: Even CO₂ is not stable in all cylinders.

P. 2. Line 23: Flights take place over ...

P. 2. Lines 33ff: It has been regularly deployed since 2010 for post-flight measurements of greenhouse ...

P. 3. Line 1: Please add a few citations.

P. 3. Line 9: HIRES has been defined before.

P. 4. Line 16: What is 2 x 2 L reference volume? 4 L?

P. 4. Line 18: Please provide the supplier of the helium and the grade.

P. 4. Line 30: Strike out "in contrast".

P. 5. Line 5: This sentence is not quite right. Consider changing to "Contrary to ..., when the HIRES cylinders are filled with ambient air pressurized by ..., in this setup, the HIRES cylinders are ...".

P. 9. Line 3: "This also occurred for ...".

Table 1: The short-term column should be before the long-term column.

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Figure 1: The CAD drawing of the sampler is nice, but I would also (perhaps rather) like to a drawing of the flow path.

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