

Interactive comment on “Analysis of non-methane hydrocarbons in air samples collected aboard the CARIBIC passenger aircraft” by A. K. Baker et al.

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The authors would like to thank the reviewers for their thorough reading of the manuscript and their thoughtful and constructive comments. Their input is greatly appreciated and helps us to improve the quality of the manuscript.

Below we respond to the comments of the reviewers.

Response to Referee #1

Comment: “...mention the type of valves used to seal the glass sampling flasks and the type of tanks used for the working and primary standards.”

C1020

Response: The sampling flasks are sealed using the multi-position Valco valves at the inlet and outlet ports. All standards are house in aluminum cylinders; working standard cylinders are 5L cylinders supplied by Scott Marrin, the primary standard cylinder is 10L and manufactured by Air Products (supplied by the NPL). This information has been added to the manuscript in the section describing the calibration standards.

Comment: “...it would be helpful to see more of their data and a comparison to existing airborne data. Are the data archived and accessible?”

Response: To avoid detracting from results discussed in data publications currently in preparation we have refrained from making a comparison to other airborne data. CARIBIC NMHC (and other) data are archived internally and are available upon request through either the project webpage or directly contacting us; a note to this effect has been made in the acknowledgements section, and the website address has been added to the introduction.

Comment: In regards to figures: Figure 1. This figure may need to be a large to accommodate larger font sizes. Figure 2. Again the font sizes are quite small. Figure 3. It appears the C8 hydrocarbon i-octane is out of sequence. Figure 4. The fonts are much too small and some of the colors much to faint.

Response: The figures have been reformatted so that they are easier to read. Regarding Figure 2, the order of the compounds was chosen as it represents the order of their retention times. This information has been added to the figure description.

Comment: Did you see any correlation of your co-eluting peak with specific humidity of the sample that was collected?

Response: This is an interesting question, although when looking at the data there appears to be no correlation between the areas of the co-eluting peaks and the water content of the samples. One note on the co-eluting peaks: some peaks have been qualitatively identified as OVOCs (e.g. acetone), however, quantification has been

C1021

found to be unlikely to achieve.

Comment: Some explanation might be appropriate as to why you switched from stainless steel canisters to glass canisters and why you went from an MS detector to an FID.

Response:

Stainless steel vs. glass canisters: At the time of the decision to build the new sampling system in 2003 there was not much information available on the behavior of glass canisters. Although deploying glass canisters on an aircraft is more challenging (e.g. increased weight, fragility), we preferred glass for the measurements of CO₂ concentration and isotopes (see Assanov et al., 2009, and references therein). Additionally, we had hoped that we might be able to analyze some additional compounds, such as acetone and alkyl nitrates, which were proved not to be feasible with stainless steel canisters. We found that acetone analysis is most likely not feasible, but analysis for alkyl nitrates is possible.

MSD vs. FID: The major advantage of the FID is the predictability of its response to hydrocarbons and other organic compounds. The nearly constant carbon atom response for all hydrocarbons provides a powerful tool for apparatus performance checks such as determination of the losses of C₂ hydrocarbons by insufficiently low cryotrapping temperatures or of the losses of heavier hydrocarbons on a drying agent or in the tubing (Slemr et al., 2004). The predictable C atom response also enables the quantification of compounds which are identified but not present in the calibration mixture. We considered these FID properties to be more important than the somewhat higher MS sensitivity to some hydrocarbons. The MS power of identification is less important if similar air samples are always analyzed for the same set of target compounds by an almost standardized procedure.

Response to Referee #2

C1022

Comments: Why were glass cylinders chosen which are not stable for alkenes, sacrificing ~50% of the potential NMHC data? Is it possible to deactivate those cylinders? Have tests been performed to evaluate if ozone is stored in the cylinders, possibly reacting with alkenes?;

Page 2380, line 14: Why were glass cylinders chosen over stainless steel cylinders? Stainless steel cylinders are typically used for non-methane hydrocarbons and previous work have shown that it is possible to condition them so that alkenes remain stable;

Page 2381, lines 21-25: Are all glass cylinders problematic or only certain ones? Is it possible to deactivate them with water vapor?

Response: The choice to use glass canisters has been discussed in our response to reviewer #1. We have not applied the usual passivation by adding water primarily to prevent water-mediated isotope exchange reactions that could negatively affect the analysis of CO₂ isotopic composition. Tests on storage of ozone have not been made. We have observed alkene artifacts in all glass canisters, which is in agreement with observations by Pollmann et al. (2008) who showed that alkene artifacts are a general property of glass canisters.

The loss of data by not reporting the alkene concentrations is likely to be much smaller than the 50% quoted by reviewer #2. Based on an already large fraction of n-heptane and n-hexane measurements below detection limit one would expect an even larger fraction of measurements with alkenes below detection limit. Only samples influenced by convective activity might contain measurable alkene concentrations and those represent only a small fraction of total CARIBIC samples.

Comments: Test results whether the drying agent Mg(ClO₄)₂ influences C₅ and higher NMHC need to be more clearly presented to assess the possibility that Mg(ClO₄)₂ contributes to the depressed carbon response factors shown in Figure 3 for i-octane to o-xylene;

C1023

Page 2382, lines 17-28 and page 2383, lines 1-5: Is the approach to regenerate the $\text{Mg}(\text{ClO}_4)_2$ new? Would this also work for wet tropospheric samples? Other groups have reported loss of isoprene and C7–C9 hydrocarbons on $\text{Mg}(\text{ClO}_4)_2$. Could this contribute to the depressed carbon response factors shown in Figure 3 for i-octane to o-xylene? The authors only show good agreement for C2–C4 hydrocarbons with and without $\text{Mg}(\text{ClO}_4)_2$, but do not detail the results for C5 and higher hydrocarbons in samples without interference. Are carbon responses also depressed or are they as for C2–C4 NMHC in samples without interference when $\text{Mg}(\text{ClO}_4)_2$ is not used?

Response: The section discussing the influence of drying and not drying has been rewritten to be more clear and to provide more detail regarding the results. The procedure used is based on the findings of Rudolph et al. (1986), who determined that heating the $\text{Mg}(\text{ClO}_4)_2$ cartridge to at least 60C suppresses the losses of higher hydrocarbons. Measurements of the primary standard both with and without drying of the sample show no significant differences between the PCRFs determined for individual compounds under either condition. For the working (whole air) standards the same result is observed for the C2-C4 NMHC, however, for NMHC having larger carbon numbers this is not possible to assess, as these peaks are influenced by interference with co-eluting species. For some CARIBIC samples it was possible to determine peak area for the pentanes, hexane and toluene, and these were below 5% difference with the dried measurements. As the vast majority of samples do not contain n-heptane, i- and n-octane, ethylbenzene, and the xylenes at levels above the detection limit, it has not been possible to determine the influence of $\text{Mg}(\text{ClO}_4)_2$ on these compounds. Ultimately, from our work with the primary standards, $\text{Mg}(\text{ClO}_4)_2$ does not appear to be causing the reduction in PCRFs for NMHC with $C > 7$, however, we cannot discount the possibility of an influence, as we are unable to conclusively determine the same for whole air standards or samples.

Comments: Similarly, tests should be performed to assess whether the strong adsorbent Carboxpack BHT (which was chosen despite the relatively low temperatures)

C1024

possibly contributes to the depressed carbon response factors shown in Figure 3 for i-octane to o-xylene;

Page 2383, lines 6-9: At -130_C is it necessary to use the relatively strong adsorbent Carboxpack BHT? During NOMHICE (Apel et al., JGR, 108, D9, 4300, doi:10.1029/2002JD002936, 2003) it was observed that solid adsorbents often lead to poor agreement with the reference laboratory. Have tests been performed to exclude artifacts from the adsorbent, e.g. the depressed carbon response factors shown in Figure 3?

Response: The use of Carboxpack BHT is based on work by Matuska et al. (1986). Carboxtrap BHT is, with 10 m²/g, a rather weak adsorbent and we found it not to be responsible for the depressed carbon atom response. The procedure with Carboxpack BHT has been successfully used in on-line analyzers for long-term NMHC measurements at Izaña and Zugspitze. In addition to the inter-comparison described in this paper, the technique was also inter-compared with the GC/MS technique described by Mühle et al. (2002) and comparable results were found by Randa (2007).

Comment: In addition to the general discussion of the CARIBIC NMHC dataset in chapter 3 and 4 the authors could improve the impact of their article by evaluating the quality of their dataset similar e.g. to Parrish et al., J. Geophys. Res., 103(D17), 22339-22359, 1998.

Response: We evaluated the plausibility of the CARIBIC data according to the criteria recommended by Parrish et al. (1998) and found no inconsistencies for alkanes and aromatic compounds (Randa, 2007). The investigation of the plausibility of the alkene data did not make sense as we knew that they are produced in the canisters. As the paper is already long enough we omitted the discussion of these investigations.

Comment: Page 2380, line 21: Which filter is used (type, materials, manufacturer)? Could it contaminate or alter the sample?

Response: The filter type has been included in the manuscript (Swagelok 2 μ m sintered

C1025

stainless steel particle filter). While no tests have been conducted to test specifically from contamination by the filter, stainless steel construction is generally regarded as not having an influence on sample composition (as evidenced by its frequent use in sampling flask construction).

Comments: Page 2380, line 24: Are the glass flasks pre-evacuated? This could improve flushing;

Page 2380, line 25: What is the exact flush volume? 30 times?

Response: The canisters are not pre-evacuated and prior to the start of the flushing/sampling procedure contain the remaining air from the preceding sampling. The actual flush volume has been noted in the manuscript and is dependent on outside pressure. At typical sampling pressures this corresponds to about 10 times (see Schuck et al., 2009). As almost all of CARIBIC samples range from clean background to slightly polluted air crossover contamination is minimized. The justification of evacuation has, to the best of our knowledge, not been investigated, and we preferred flushing to establish an equilibrium between the walls and the sample.

Comment: Page 2381, line 5: How is the sample pressure measured? Which pressure sensor is used (type, material, manufacture)? Could it contaminate or alter the sample?

Response: Sample pressure is measured using a SENSYM piezoresistive pressure sensor placed between the outlet of the pumping system and the inlet of the sampling unit.

Comment: Page 2381, line 12/13: Are the samples sent to Australia for further analysis?

Response: The Fraser et al., 1999 manuscript provides a detailed description of the analytical system used to measure halocarbons from CARIBIC samples, while the dissertation written by D. O'Sullivan (2007) provides a description of the results of these measurements.

C1026

Comment: Page 2382, lines 7-8 and Figure 1: It would be beneficial if the diagram of the analytical system were described more thoroughly, e.g. by showing more than one operating condition. Why are all valve ports in Figure 1 connected both by straight and bend connections? Only one is active. Which rotor materials are used?

Response: The explanation of the diagram was expanded in the text and the diagram itself was modified to make gas flows more clear. The curved and straight lines refer to A or B configurations of the valves; as these descriptions are only relevant in house, this has been modified in the figure to provide a more universally meaningful depiction.

Comment: Page 2384, lines 25-28: Which flow controllers are used (type, materials, manufacturer)? Could they contaminate or alter the standard gas stream? Are the flow controllers NIST traceable? Do they need temperature stabilization? Have other linearity tests been performed, such as sampling of increasingly larger volumes of ppt range ambient air?

Response: The flow controllers used are 100 sccm (N₂) mass flow controllers manufactured by MKS instruments and this has been added to the text. Linearity tests have been conducted using the primary standard where different volumes were trapped and the responses compared; these resulted in a linear response with volume, the results of which have been omitted from the manuscript in the interest of brevity.

Comment: Page 2385, lines 9-20: It is excellent that the carbon response factors up to C₆ are similar (with the known exception of acetylene). However, e.g. Plass-Düllmer et al., J. Chromat. A, 953, 175-197, 2002 have observed only marginally depressed carbon response factors up to C₈ hydrocarbons. Did the authors perform tests to exclude that the reduced carbon response from i-octane to o-xylene are an artifact of the analytical system, e.g. from the used relatively strong adsorbent or the used drying agent?

Response: Tests regarding the use of a drying agent and Carbopack BHT do not indicate an influence on the carbon response factors, however, in the case of the drying

C1027

agent, tests on whole air have had limited success for C5 and greater NMHC.

Comment: Page 2385, lines 24-26: What types of tanks are used and how were they filled?

Response: This has been addressed in the response to referee #1.

Comment: Page 2388, line 9: How were the back-trajectories calculated? Why 8-days?; Page 2388, line 14: How were the PV values calculated?

Response: Meteorological analysis of CARIBIC samples is conducted at KNMI and is based on ECMWF re-analyzed data, with trajectories calculated using the KNMI model TRAJKS. A brief description of these analyses has been added to the text along with the appropriate references [Scheele et al., 1996 and van Velthoven, 2009].

Comment: Page 2388, line 15: Citations for O3 and CO measurements?

Response: The appropriate citations have been added to the text in the section describing the collection of CARIBIC samples.

Comment: Page 2389, line 9: Strike out easily.

Response: After some discussion we have opted to keep this line in the manuscript.

Comment: Page 2389, line 18: insert "and reactivity towards the OH radical and ozone".

Response: We have made the recommended addition to the line, which now reads "This was more frequent in samples that exhibited stratospheric influence than in samples collected in the upper troposphere, and is a product of the longer transport times associated with troposphere-stratosphere exchange and reactivity towards the OH radical and ozone".

Comment: Page 2381, lines 26-27: Pollman et al., 2008 (not 2007)

Response: The reference has been amended to have the correct year.

C1028

References:

Assonov, S., Taylor, P., and Brenninkmeijer, C.A.M.: A system for high-quality CO₂ isotope analyses of air samples collected by the CARIBIC Airbus A340-600. *Rapid Commun. Mass Spectrom.* 23, 1347–1363, 2009.

Matuska, P., Koval, M., Seiler, W.: A high resolution GC-analysis method for determination of C₂-C₁₀ hydrocarbons in air samples, *J. High Resol. Chromatog. Chromatog. Commun.* 9, 577-583, 1986.

Mühle, J., Brenninkmeijer, C.A.M., Rhee, T.S., Slemr, F., Oram, D.E., Penkett, S.A., Zahn, A.: Biomass burning and fossil fuel signatures in the upper troposphere observed during a CARIBIC flight from Namibia to Germany, *Geophys. Res. Lett.* 29; No 19, 1910, doi:10.1029/2002GL015764, 2002.

Randa, B.: Development and application of a GC system for NMHC analyses of air samples from the CARIBIC aircraft project, Ph.D. Thesis, University of Mainz, 2007.

Rudolph, J., Johnen, F.J., Khedim, A.: Problems connected with the analysis of halocarbons and hydrocarbons in the non-urban atmosphere, *Int. J. Environ. Anal. Chem.* 27, 97-122, 1986.

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C1029