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Atmospheric Measurement Techniques Discussions

Interactive comment on "Greenhouse gas analysis of air samples collected onboard the CARIBIC passenger aircraft" *by* T. J. Schuck et al.

Anonymous Referee #1

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This manuscript discusses the collection procedure and GC analysis of whole air samples collected on an aircraft as part of the CARIBIC program. The samples are analyzed for the following four important greenhouse gases: CO2, CH4, N2O, and SF6. There is only limited information available on the vertical distributions of trace gases in the atmosphere. Thus, the results provided by the CARIBIC program have the potential to make valuable contributions to our understanding of the global distributions of trace gases and climate change.

However, the manuscript needs to be significantly revised before it will be acceptable for publication. The quality of the writing is extremely poor, and there are numerous grammatical errors throughout the entire text. I strongly recommend having the Editor and/or someone proficient in speaking and writing English thoroughly edit the entire

manuscript before resubmission to ensure that the writing is clear and concise. Furthermore, there are issues with the interpretation of some results which should be addressed. In the following commentary, I provide some recommendations for areas to focus on and questions that need to be addressed. Additionally, some specific examples of grammatical errors and sentences that need to be revised are noted. However, this list is not complete. There are too many improperly written sentences and grammar mistakes throughout the entire manuscript to list here.

General Comments I think this work has the potential to make important contributions to our understanding of the atmosphere. The quality of the data appears to be fine. However, it is difficult to follow the reasoning and some of the points being made by the authors because of the inappropriate phrasing and incorrect wording and grammar. This makes it very hard for the reader to fully grasp and appreciate the potential significance of the scientific results.

âĂć Grammatical errors. - Commas should be used before and after phrases that interrupt the flow of the sentence. Example: P919, L15-17: Replace "The sampling points are evenly distributed over the expected flight time and depending on the flight route samples are taken every 30 to 60 min." with "The sampling points are evenly distributed over the expected flight time, and depending on the flight route, samples are taken every 30 to 60 min." - An adverb clause (ex. a time clause) at the beginning of a sentence (i.e., before, after, during, when) needs to be followed with a comma. Example: P918, L26: The sentence should read "After 300s of flushing, the outlet valve is switched to the next position." - Do not have paragraphs that are one sentence unless you are trying to make a strong or high impact point. - There are a lot of improperly and awkwardly written sentences!

âĂć The phrases "good agreement" and "very good agreement" are used several times. These statements are qualitative and vague. How is "good" defined? âĂć The phrases 'greenhouse gas analysis' and 'greenhouse gases' are significantly overused. It makes the text very wordy. Just say gas or trace gas.

âĂć Abbreviations should be defined the first time they are used. P916, L7- define UT/LS P917, L16 replace "...CH4, CO2, N2O, and SF6..." with "methane (CH4), carbon dioxide (CO2), nitrous oxide (N2O), and sulfur hexafluoride (SF6)" P919, L20: define CO

âĂć Several obvious statements are given. For example: P932, L24: "If sampling in pollution plumes frequently happened, a considerable number of samples should contain high amounts of CO2..."

P933, L13: "With a longer sampling time the probability of sampling air from pollution plumes would increase but the sample would contain a mixture of plume air and background air."

âĂć Units should be used consistently. Examples: in section 2, the lengths of time for specific events (i.e., flushing, sampling) are given in seconds and minutes- 0.5 minutes and 30 seconds are the same. Also, psi was used on P920, L27, but mbar was used earlier.

Specific Comments Abstract Combine into one paragraph and revise. L1- "Atmosphere" is capitalized, but it is not capitalized in line 23.

Introduction The introduction is very wordy and unorganized. It needs to be written much more clearly and concisely. Additional references need to be included.

P917: The second paragraph of the introduction should be moved to section 2 because it discusses methods/experimental information. Currently, this paragraph interrupts the flow of the text because it is between two paragraphs focused on the scientific importance of aircraft data.

The significance and potential applications of this data set are briefly mentioned. However, the importance of the specific results obtained from the CARIBIC aircraft samples are not discussed in the broader context of global or lower stratospheric distributions in the subsequent sections.

P917, L1: delete "immediate" L2: rephrase "long-term regular surveying" L4: replace "spend" with "spent" L7: replace "it is deployed" with "the instrument package has been deployed..." L12: delete "tropical" L13-14: revise sentence

L18: Replace "For the entire CARIBIC experiment the greenhouse gas measurements are relevant for the interpretation of data because they contain information about influence of..." with "These measurements are relevant because they contain information about the biosphere (CO2, CH4, N2O), stratospheric processes (CH4, N2O), and emission sources (SF6) (ADD REFERENCE(s))"

Section 2 Air Sampling Procedure This section can be significantly shorter. It may be sufficient to just reference Brenninkmeijer et al. (2007).

Consider adding a figure or diagram of the cylinder sampling system.

What is the point of mentioning that event sampling hasn't been conducted yet? There is nothing wrong with the regular sampling of background air.

It is not clearly indicated anywhere that the cylinders are filled on the aircraft, but are analyzed in the lab. The first time this is implied is P919, L10. Please clarify.

P919, L22-24: After the first flight leg, how do you ensure that the cylinders are completely vented and do not contain air from previous flights still?

P918, L22: insert a comma after "Prior to pressurization, the sample cylinders...." P919, L14: Insert "and" before "it stops..." P920, L2: replace "de-installed" with "uninstalled" L4: delete "as well as for measurements of the"

Section 3 Characterization of the greenhouse gas GC system This section is wordy and difficult to follow. P920, L7: delete "greenhouse gas" L9: replace "electronic" with "electron" L12: delete "sampling". The GC system does not collect the sample. L16: delete "All valve switching is automated." because it is redundant. The first sentence in the paragraph stated that the system is automated. L19: synchronously and simultaneously have the same meaning. Please revise this sentence.

P921, L5: delete the sentence “Valve 5 controls the flow towards the FID.” because it is redundant (see P920, L21) L14: What does the (5.0) after N2 refer to? The sentence “The FID channel is equipped. . .. . .flow rate of 50 ml/min.” should be separated into two sentences.

L15-17: Revise to something such as: The FID temperature was 220oC, and the make-up gases were hydrogen (flow rate $\sim$ 80 ml/min) and synthetic air (flow rate $\sim$ 250 ml/min).

L23-24: delete “At an oven temperature of 50oC. . .” because it is redundant. It was stated two sentences earlier that the temperature was 50oC.

P922, L9-11: The sentence which begins as “Both, peak area and peak height. . .” is very confusing. Please rewrite it.

Move the last sentence of this section (“The typical precision. . .) to the preceding paragraph. For example, put it after the sentence describing how the precision is calculated (P921, L28).

Also, the measurement precision is mentioned at least three times (P922, P924, P925). One time is sufficient.

Sections 3.1-3.3 P922, L22-27: Revise to something such as: “. . ..It was used as the running standard until December 2007. Currently, SIL194 is used for that purpose. SIL194 and SIL195 were filled at the Schauinsland observatory in southern Germany (1205m a.s.l.) (Schmidt et al., 2003) in September 2005, and SIL196 was filled in November 2005. All working standards were prepared using Drierite (CaSO4) as the drying agent.”

P923, L3-4: Revise. How can the standards be analyzed “regularly” and “less frequently”? By deleting “regularly”, the purpose of this sentence (that these two working standards are not analyzed every month) will be maintained. Or rephrase to: “The running standard is calibrated against the NOAA standard the day before the monthly

analysis. A rotating schedule is used for the three running standards.”

P927: The authors indicate that the precision of SF6 was lower than CO2, CH4, and N2O, that there was a systematic offset in the ambient mixing ratios between measurements made at Mainz and Jena, and that the error in SF6 measurements will be evaluated in future studies when a standard is available containing a appropriate range of mixing ratios. It would be useful to estimate how much uncertainty is introduced into the SF6 results presented in this manuscript by assuming the ECD response is linear. Can the “systematic error” (P927, L23) be quantified? How accurate are the SF6 mixing ratios provided in this work?

As the authors mention, ECD responses are often non-linear, but it can’t be said that the response is “known to be non-linear” (P927, L23) if this hasn’t been verified by analyzing standards which contain the appropriate range of SF6 mixing ratios.

N2O is also detected with an ECD. Is the response to N2O linear or non-linear?

P927, L19: The standard is not analyzed simultaneously with the samples. Analysis of the running standard and a sample is alternated.

P928 and Figure 4: Mixing ratios of CO2 in the whole air samples appear to agree with the in situ instrument. Are there any advantages to using the CO2 data from whole air samples compared to the higher frequency in situ measurements?

Section 4 Results In this section, the time series, seasonal trends, and latitudinal distributions of trace gases are discussed. However, these results are not put in context with previous studies or with other studies conducted by the CARIBIC program. It would be helpful to the reader to explicitly state the connections between the CARIBIC results and the broader scientific issues mentioned in the introduction (i.e., relationship between the UT/LS measurements and the biosphere, source identification, the use of tracers to study transport processes).

References need to be added. In section 4.1, there are no references, and in section

4.2, there is only one reference (Matsueda et al., 2008). Again, without appropriately citing research which has already been conducted, the reader cannot make meaningful connections to their own work or to our current knowledge of atmospheric chemistry, and cannot identify which results are new, complementary, contradictory, or advance our scientific understanding.

The authors acknowledge that it is difficult to draw strong conclusions based on their CO2 data because of error in the polynomial fit and because only three years of data are currently available. However, the majority of the analysis is focused on CO2. Perhaps a similar amount of time should be devoted to presenting results for each gas, especially because a separate manuscript focused on CO2 is in preparation (P928, L27).

Specific questions to consider are: - How do your results compare with previously reported measurements made by other research programs and/or from different time periods or sampling locations? With ground-based measurements (i.e., NOAA-ESRL, AGAGE programs)? With satellites? - Does this aircraft data provide any novel results or information? - What are the implications of the shift in the CO2 seasonal cycle? - Has this shift been observed before?

A few possible references are: âĂć Hoor et al. (2004), Seasonality and extent of extratopical TST derived from in situ CO measurments during SPURT, Atmos. Chem. Phys., 4, 1427-1442, and references therein. âĂć Andrews et al. (1999), Empirical age spectra for the lower tropical stratosphere from in situ observations of CO2: Implications for stratospheric transport, J. Geophys. Res., 104(D21), 26581-26595. âĂć Gurk et al. (2008), Airborne in-situ measurements of vertical, seasonal, and latitudinal distributions of carbon dioxide over Europe, Atmos. Chem. Phys., 8, 6395-6403.

Figure 5: It is not clear whether the error bars are the standard deviation of all 28 samples or are the standard deviation of the mean. Replace the phrase 'standard deviation of one month's measurements' with either 'standard deviation of the mean'

or just 'standard deviation'. This phrase is used several times (ex. P929, L7; P931 L7; Figures 5 and 6 captions).

P929, L10: replace "devided" with "divided" L18: change "fitted" to "fit" L27: How is the "large error" of a3 determined? P930, L12: Why is the weakening of the seasonal cycle amplitude "expected"? L15-17: The first sentence in section 4.2 is confusing. Either rewrite or delete it. The standard deviation of what can't be calculated? "As during" is not correct English (also used on P932, L21). L19: remove "so-called"

P931, L13: change "fitted" to "fit L20: Couldn't the absence of a latitudinal gradient also be because samples weren't collected south of 14oN (L2)? L21-23, 28: There are several typos- insert space between timeseries and timeshift; replace "extend" with "extent." P932, L27: Insert a period between "higher" and "In". L28: replace pppm with ppm (also P933, L7) and "around" with "of"

Section 4.3 This section is wordy, and the explanations for certain observations need to be clarified. References need to be added to put the results in context.

P933, L20: Indent first paragraph What specific PV values designate tropospheric and stratospheric air? What PV values are "high" and which are "low"?

P934, L2-4: awkward sentence; revise to something such as: "Throughout all four flights, CH4, CO2, N2O, and SF6 were positively correlated in both the troposphere and stratosphere. The mixing ratios of all four gases were lower in the stratosphere."

L6-8: Revise to: "N2O mixing ratios show a strong gradient above the tropopause because it is stable and well mixed in the troposphere and photochemically destroyed in the stratosphere (Ko et al., 1991)."

L9: "SF6 is only emitted from anthropogenic sources" ADD REFERENCE(S)

L11-14: Revise. The way this sentence is worded implies that N2O and SF6 mixing ratios are lower because the tropopause is lower. That is not correct. The stratosphere was sampled more frequently because the tropopause was lower in winter. The N2O

and SF6 mixing ratios are lower because their sources are in the troposphere, and they are removed in the stratosphere.

L15: “A positive correlation between CH4 and CO2 is typically seen at northern mid-latitudes during CARIBIC flights in boreal winter.” ADD REFERENCE(S)

L17: Weaker photosynthetic activity is not the only explanation for lower CO2 mixing ratios in winter. Factors other than photosynthesis influence the mixing ratios of CO2 in the atmosphere. For example, emissions of CO2 occur all year. Please rephrase and clarify.

P934, L28-P935, L1: How do the authors know what caused the CH4 to increase? ADD REFERENCE(S)

The majority of this section is focused on CO2 and CH4 and gives rather vague descriptions for their seasonal and spatial trends. SF6 and N2O are tracers of tropospheric sources. So, what do the SF6 and N2O measurements indicate about the sources and variability of CO2 and CH4 observed in UT/LS?

Section 5 Summary and Conclusions P935, L10: insert “I” in “CARIBC” L22: replace “accross” with “across” P936, L1-9: Poorly written. Revise.

Figures There are several typos in the figure captions. Figure 1 last line: “throw” should be “through” Figure 2: 3.9 min should be 2.4 min Figure 3: Replace Mainz with MPIC in the x-axis title to be consistent with the y-axis and the caption. Figure 4: Add a space between “timeseries” and “wholeair” Figure 5: Every tick mark on the x-axis does not need to be labeled. Consider putting a label every 6 months. Figure 7: Caption and text say the monthly median is used, but the x-axis label says monthly mean.

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