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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.

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We thank referee1 for the detailed comment on our manuscript.

All suggestions concerning structuring of paragraphs, language and wording have been considered during the preparation of the revised version. The re-submitted manuscript has been proof-read by a native English speaker. Additional references have been included, mainly in the introduction and in Section 4.

In the following, we would like to address individually the important points that were raised in the comment, that were not related to language issues or the structure of the text.

General remarks

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.

Section 2 was changed accordingly and minutes are used as time unit. The unit psi quoted from P920,L27 in section 3 has been changed to bar. However, in section 3 the columns measures are still given in non-metric units (inch and feet) because these units are the more commonly used ones in this context, e.g. by manufacturers.

Section 2 Air Sampling Procedure

This section can be significantly shorter. It may be sufficient to just reference Brenninkmeijer et al. (2007).

Brenninkmeijer et al. (2007) is a general description of the new CARIBIC system, briefly describing each device. It gives an overview of the sampling procedure, but it does not mention details such as for example information relevant for the integration of continuously measured data. Therefore, the manuscript describes both, the instrument and the sampling method, in detail.

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

We refrained from including such a figure, since a schematic of the 14 glass flasks connected to two 16-position valves would take up too much space.

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.

The event sampling had been projected in Brenninkmeijer et al. (2007). This is the reason why it is mentioned here. This remark was not meant to imply that there is anything wrong with the 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.

This has been made more clear now earlier in the text.

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?

The cylinders are flushed with outside air a second time for 300 seconds. A corresponding explanation has been added to the text.

Section 3 Characterization of the greenhouse gas GC system

P921, L14: What does the (5.0) after N_2 refer to?

The number refers to the purity to the gas. This expression has been changed to "N_2 (quality 5.0)"

Sections 3.1-3.3

P927: The authors indicate that the precision of SF_6 was lower than CO_2, CH_4, and N_2O, that there was a systematic offset in the ambient mixing ratios between measurements made at Mainz and Jena, and that the error in SF_6 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 SF_6 results presented in this manuscript by assuming the ECD response is linear. Can the "systematic error" (P927, L23) be quantified? How accurate are the SF_6 mixing ratios provided in this work?

In April 2009 we got three new standards extending the range of SF_6 mixing ratios covered from 3.82–4.78 ppt to 3.82–8.66. First measurements including the new standards allow for much better results of the SF_6 measurements. From the new calibration runs we concluded that still a linear approximation of the ECD response is the best description (based on chi square). While for the other three gases no major changes to the calibration scale are to be expected, for SF_6 we get a preliminary correction of

about 0.1 ppt. Applying the new, preliminary scale to the comparison with Jena the absolute mean difference is 0.04ppt (was 0.11ppt, standard deviation of the mean difference is 0.04 ppt, absolute error of our measurement is 0.04–0.08 ppt) Concluding, the special discussion of the SF_6 offset was omitted in the revised manuscript. All data shown were adopted to the new scale.

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 SF_6 mixing ratios. N_2O is also detected with an ECD. Is the response to N_2O linear or non-linear?

This paragraph has been revised and shortened. Based on the chi-square of a least-square fit, it was found that a linear response best describes the detector. This holds for N_2O and SF_6.

P928 and Figure 4: Mixing ratios of CO_2 in the whole air samples appear to agree with the in situ instrument. Are there any advantages to using the CO_2 data from whole air samples compared to the higher frequency in situ measurements?

In general, there are no advantages using the CO_2 data from the samples. Given the high time resolution of the IR-instrument the continuous data of course provides much more information, especially if looking at a single flight, not at monthly means. However, looking at the complete CARIBIC CO_2 data set, the data from the whole air sample analysis covers a much longer period of time, i.e. more flights. Therefore, the analysis of longer time series, such as shown in section 4.1., is currently not yet possible with the data from the in situ instrument. the main purpose of the manuscript if the presentation of the greenhouse gas analysis as part of the project and the CO_2 measurements are an essential part of it. In addition to this analysis, up to 50 NMHCs and halocarbons are measured. For the interpretation of these data the CO_2 from the samples, i.e. from exactly the same air is preferable.

Section 4

More references were added, mainly to section 4.1. and section 4.3.. Section 4.1. and 4.2 were re-arranged, and the discussion of the seasonal cycle of CO_2 has been moved to section 4.1. The comparison with other studies has been extended. The discussion of the example flights is now also more detailed, including more references and discussing all four gases in similar amounts.

The comment mentions that the largest part of the discussion concentrates on CO_2. The main intention of the manuscript is the technical description of the CARIBIC sampling system and the greenhouse gas analysis, and certainly the discussion of the complete data set is beyond its scope. Therefore, it was necessary to restrict the discussion to only few examples. The time series of CO_2 was chosen because of several studies carried out by the JAL collaboration. These studies are based on the analysis of CO_2 data from flask samples (and very recently also on continuous measurements) collected aboard commercial aircraft but concentrate on more southern latitudes (e.g. Matsueda02, Matsueda08, Machida08). It was mentioned in the comment our results were not adequately put into context with other measurements. The discussion of comparable measurements was thus extended in the revised manuscript.

CO_2 is of the four measured components the one that we can measure with the highest precision. Therefore, it is best suited to investigate the question of how representative the samples are for background air in section 4.2. In Section 4.3 of the revised manuscript we tried to give equal room in the discussion to all four gases.

L27: How is the "large error" of a3 determined? We use a standard software package (IGOR-Pro) for curve fitting that is based on the Levenberg-Marquardt nonlinear least squares optimization. The errors of the fit parameters are taken from the resulting error matrix. The software uses the ODRPACK95 package for orthogonal distance regression which is used in our analysis for all line fitting.

L20: Couldn't the absence of a latitudinal gradient also be because samples weren't collected south of 14oN (L2)?

This is most likely the reason and we have tried to make this more clear. Unfortunately, most publications we are aware of discuss the latitude range 30N-30S. A publication from February 2009 we had not been aware of when submitting the manuscript for the first time (Miyazaki et al., 2009) does discuss the latitudinal variations also at more northern latitudes. The discussion of the latitudinal variations has been extended in the revised manuscript, now also referring to this recent study.

Section 4.3

P933, L20: Indent first paragraph

The indentation of paragraphs is part of the manuscript formatting done by the journal editorial team. This is beyond our control as authors.

What specific PV values designate tropospheric and stratospheric air? What PV values are "high" and which are "low"?

Numbers have been added to the text. We considered values of PV > 3.5 PVU to indicate stratospheric air while values of PV $<$ 1.5 PVU were considered to indicate purely tropospheric air.

L9: "SF_6 is only emitted from anthropogenic sources" ADD REFERENCE(S)

An additional reference (Maiss and Brenninkmeijer 1998) has been added, but not directly after this sentence but after the next sentence, in addition to the already included references (Maiss and Levin 1994),(Gloor et al. 2007).

L15: "A positive correlation between CH_4 and CO_2 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 CO_2 mixing ratios in winter. Factors other than photosynthesis influence the mixing ratios of CO_2 in the atmosphere. For example, emissions of CO_2 occur all year.

This section has been rephrased. It was not intended to make a general statement

about the correlation between CH_4 and CO in the northern mid-latitudes. In contrast, the intention of this paragraph was only to describe what is observed in the CARIBIC data set which is presented here for the first time.

P934, L28-P935, L1: How do the authors know what caused the CH_4 to increase?

This statement has been rephrased to make clear that only from our measurements we can't know this. Increased emissions and enhanced transport can't be concluded from our measurements but are a possible explanation for the observed increase. References have been added.

Figures

Figure 2: 3.9 min should be 2.4 min

The axis labeling is correct in the figure ,but was unfortunately wrong in the figure caption.

The axis labeling of Figure 4 and the bottom axis of figure 5 were modified according to the suggestions

Figure 7: Caption and text say the monthly median is used, but the x-axis label says monthly mean.

The labeling of the bottom axis was not correct. In agreement with the discussion in the text, the deviations from the monthly median are shown. The axis labeling has been corrected.

Interactive comment on Atmos. Meas. Tech. Discuss., 2, 915, 2009.