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Atmospheric Measurement Techniques Discussions

Interactive comment on "Airborne multi-axis DOAS measurements of atmospheric trace gases on CARIBIC long-distance flights" *by* B. Dix et al.

B. Dix et al.

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Dear referee # 1, thank you for taking the time to review our paper and for your helpful comments.

The focus of this paper is indeed on the technical side, but we followed this reviewer's remarks on the presentation of our first results and added more information in the results section. Detailed below are our answers to all comments.

1 Specific comments

Comment 1.1: Page 271, lines 6-16: Are fibre bundles with fibres of 210μm diameter (later changed to 150μm diameter fibres, p.275, l.7) a good choice for illuminating a slit of 50 μm width? Maybe there is a possibility for improvements here?

Answer 1.1: Either fibre diameter is sufficient to illuminate the slit width and height (200

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μm with 6 fibers of 150 μm diameter each giving a column height at the entrance slit of $>$900 μm), since for scattered ambient radiation measurements losses at the slit are not critical. Fibers with 150 μm diameter are an improvement over 210 μm, since they are more flexible and will break less easily.

Comment 1.2: Page 272, lines 20-21: This sentence is misleading as the resolution (FWHM) is not determined by the pixel number of the CCD, but by the combination of spectrometer entrance slit width, the dispersion of the grating and pixel size. Maybe a sentence like this would be more accurate, e.g.: "The whole system provides a spectral resolution of0.7 nm (FWHM)."

Answer 1.2: We agree. We changed page 272, lines 20-21 to read: The detector itself consists of a linear CCD array with 2048 pixels (SONY ILX511) and the whole system provides a spectral resolution of 0.7 nm (FWHM).

Comment 1.3: Page 276, line 16: The numbers given for the standard deviations of the fit residual reveal remaining systematic features. For purely statistical deviations, sigma should reduce much more between the 30s and the 450s case (by a factor of sqrt15). Some remaining systematic fraction is a common issue for DOAS retrievals. So this should be reformulated or an additional sentence included, as it now sounds as if hardly any systematic deviations remain. E.g.: "As sigma is not as much reduced as expected for purely statistical errors, some systematic deviations in the residuals remain." By the way, this is also a good reason, why the authors' choice is adequate to use the 30s spectra for the following analysis.

Answer 1.3: We agree with the reviewer. Note that on page 276, line 15, it was already stated (in best cases): "the fit residuals were mostly unstructured." To stress that point further we added more information as suggested on page 276, line 17, after "for a time resolution of 7.5min (15 co-added spectra).": The observed reduction is not as much as expected for purely statistical errors, indicating that some systematic deviations in the residuals remain.

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Comment 1.4: Page 276, lines 24-29 and Caption of Fig. 6: Please state more clearly which spectrum was used as background reference spectrum. The caption gives the altitude and SZA, but where was this taken, e.g. over polluted or clear region? How was this determined? This is important when judging the absolute values, because the result is a column difference with respect to the background spectrum.

Answer 1.4: We added the following information on page 276, line 25, after "... shown in Figs. 6 and 7.)." Reference spectra were always taken from clean regions, which were determined by choosing periods of minima in DOAS NO2 and HCHO data and in in-situ measured NO/NOy and CO.

We also added in Figure captions 6 and 7 "over a clean region" in the sentences on the reference spectrum. In Figure caption 8 we added "over a clean region at 05:40 UTC"

Comment 1.5: Page 277, lines 4-21: The observed peaks in the dSCD of HONO, NO2, HCHO are attributed to enhanced values while the simultaneous peaks in O3 and O4 are attributed to light path elongation. This finding is not obvious and needs to be properly justified as this cannot be seen in the data and information provided. The comparison with the in-situ data is surely of importance and supports the authors' interpretation, but cannot suffice as explanation for this discrimination.

Answer 1.5: We believe that p. 277, lines 7-11, describing the aircraft travelling inside a deep convective cloud, sufficiently supports the fact that the DOAS dSCDs measured inside this cloud are generally affected by multiple scattering. Since O4 has a rather (time-) constant vertical profile that is only pressure/temperature dependent, the strong peak in O4 columns inside the cloud can only be explained by light path elongation due to multiple scattering.

The discrimination between the assumed enhanced concentrations of HONO, NO2, and HCHO inside the cloud versus the assumption that the O3 dSCDs peak is caused by multiple scattering is based on the following considerations:

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1) O3 dSCDs measured in the nadir viewing direction are dominated by the stratospheric ozone signal and are hardly sensitive to tropospheric O3 or to moderate changes in the tropospheric mixing ratio unless there are extensive light path enhancements. In-situ O3 levels of about 60/65 ppb at the time of the reference spectrum (05:40 UTC) are in the same order of magnitude as within the cloud (05:55 UTC) (A. Zahn, personal communication, CARIBIC data base). The AMF for this cloud scenario (assuming multiple scattering, see below on how this was calculated) is a factor 4-5 higher than the nadir AMF for a pure Rayleigh atmosphere. Converting the O3 dSCD inside the cloud into a mixing ratio yields about 55 ppb, which is consistent with in-situ measurements. To measure the same dSCD without multiple scattering effects would require an O3 mixing ratio of about 300 ppb below the aircraft, which is inconsistent with in-situ data and which is too high to be found in the troposphere. Therefore changes in the O3 concentration cannot be excluded, but it is much more likely that the peak in the O3 dSCDs is mainly caused by multiple scattering effects inside the cloud.

2) A change of the stratospheric dSCD contribution of O3 (and NO2) is negligible, as between 05:40 and 06:00 UTC the SZA changes merely from 13.5° to 16.9°. Furthermore the stratospheric O3 (and NO2) concentration(s) are unlikely to change strongly over a distance of 300 km with a mainly easterly heading.

3) In contrast to O3, in-situ NO is below detection limit at 05:40 UTC and peaks inside the cloud (H. Ziereis, personal communication, CARIBIC data base). Since the deep convective cloud is part of a clearly distinct different air mass as described on page 277, lines 13-17, and characterized by a peak in NO, it is assumed that higher concentrations of NO2 and also HONO (as a product of NO and OH) are only present inside this air mass. Whether this is also true for HCHO is not clear at this point.

We changed p. 277, line 11 to: In this case the measured dSCDs are very likely enhanced by multiple scattering inside the cloud as suggested by the peak in O4 column values.

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We changed p. 277, line 13 to: The deep convective cloud is characterized by the presence of elevated columns of HONO, NO2, HCHO and O3.

We changed p. 277, line 18 to: Generally, O3 dSCDs measured in the nadir viewing direction are dominated by the stratospheric ozone signal and are hardly sensitive to tropospheric O3 unless there are extensive light path enhancements. In-situ measured O3 is in the same order of magnitude inside the cloud as where the reference spectrum is taken (at 05:40 UTC) and the corresponding change of the stratospheric contribution is negligible. It is therefore assumed that the peak in the O3 dSCDs is mainly caused by multiple scattering effects inside the cloud. In-situ NO, in contrast, is below detection limit at 05:40 UTC (H. Ziereis, personal communication, CARIBIC data base) and peaks inside the cloud, giving reason to assume that the NO2 and HONO dSCD peaks and possibly also the HCHO peak are caused by an increased concentration in this specific air mass.

Comment 1.6: How was the light path enhancement calculated, what are the assumptions? Why is the influence different for the different trace gases? Here, also the answer to the previous question on the background spectrum is interesting as the dSCD of HONO within the cloud shows positive values up to 3x10E15 molec/cm2. and falls to negative values of -2x10E15 molec/cm2. Does this imply that quite a large amount of HONO is also present in the background spectrum? I understand from Tab. 2 that the detection limit for these data is at 2.5x10E15 molec/cm2. It would be interesting to see the fit quality (chi square) in addition to the trace gases in the time series.

Answer 1.6: A more detailed discussion on the HONO finding will be published elsewhere. For this publication we changed the first paragraph on page 278 as follows: Converting the HONO peak dSCD into a mixing ratio yields about 70 ppt HONO. This conversion was done in two steps: 1) In order to derive a proper AMF for the measurement inside the cloud, the above introduced radiative transfer model Tracy II was used to vary modelled cloud properties, until measured and modelled O4 SCDs agreed. The single scattering albedo was set to 0.99999 and the asymmetry param-

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eter g to 0.85, which are suitable values for most cloud scenarios. Initial cloud top heights (12-18 km) as well as cloud optical density (60) were taken from MODIS data (http://ladsweb.nascom.nasa.gov). The best agreement of O4 SCDs (within 5%) was achieved for a cloud with an optical density of 100, expanding from 2 km up to 14-15 km altitude, which are suitable values for a deep convective cloud near the Tropics. 2) Utilizing these best fitting cloud properties resulted in an AMF of about 8 for light path enhancements within the cloud.

Subsequently the above stated HONO mixing ratio was calculated, assuming a homogeneous trace gas distribution inside the cloud. To get a first estimate on the quality of this conversion, the peak O3 dSCD was also converted into a mixing ratio, yielding about 55 ppb, compared to 60 to 65 ppb measured in-situ (A. Zahn, personal communication, CARIBIC data base), which is within 15% and renders this method a reasonable approach.

The dSCD peaks for HONO, HCHO and O3 and NO2 seem comparable within error, and correlate with the extent of this specific air mass as seen by in-situ data. The O4 peak drops more sharply, which could be caused by a typical "T-shape" of the cloud: Once the aircraft has passed the cloud base, but is still within the cloud outflow, multiple scattering is effective for trace gases at flight altitude, but becomes less strong for O4, as this is most abundant at lower altitudes. The above discussed conversion of dSCDs into mixing ratios was only done for the peak dSCDs at 05:55 UTC, where the full vertical extent of the cloud can be assumed around the aircraft.

The question on the reference spectrum has been answered above already. Below the respective consequences on the HONO analysis are briefly discussed:

As stated in Table 2, a suitable detection limit for HONO is 2.5 E15 molec/cm^2 (for 30 s data). Data outside the cloud scatters randomly around zero (+/- 2 E15 molec/cm^2), indicating that there is very likely no HONO present. Data analyses with different references reproduced the HONO peak result within 10%, so that it can be safely assumed

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that there is no HONO present in the current reference spectrum. The one sigma residual noise for the HONO analysis, as measure for the fit quality, is in the order of 6E-4 from 05:40 UTC to 06:00 UTC and almost doubles thereafter (mainly caused by photon statistics), indicating that values after 06:05 are definitively below detection limit.

To keep Figures consistent, we'd prefer to keep Fig. 8 as slant column plot only.

Comment 1.7: Page 277, lines 23-27: If the enhanced HCHO values could be explained by "updraft of polluted air through deep convection" could this also be true for HONO?

Answer 1.7: The underlying assumptions for the observed HONO are sufficient amounts of OH and NO, which are attributed to lightning and steady state conditions inside the cloud. We added on page 277, line 27: Since HONO photolyzes quickly, it is highly unlikely that it had been transported to this height from a ground based pollution source.

Comment 1.8: Page 278, lines 1-8: I understand that the authors refer to a future publication for the detailed analysis of the HONO concentrations. Nevertheless, if the results are emphasized as new findings here, the procedure for the derivation needs to be clarified. I don't think this should inhibit further publication of a more detailed analysis. Which assumptions enter these radiative transfer calculations? Please mention the code that has been used here - probably the same mentioned only later in another case (cp. page 279, line 29 ff)? The radiative transfer in deep convective clouds is a complex procedure - does the comparison using the O4 values result in reasonable cloud properties?

Answer 1.8: We believe all of these questions are already addressed above.

Comment 1.9: Page 278, line 24: The enhanced values in NO2 and O3 are not as clearly to identify as it sounds in the text. In the O3 results, this is somewhat better visible than in NO2, especially when considering its dependency on the SZA due to

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stratospheric light path enhancement. Maybe this connection to the SZA should be mentioned in this place, as this might support the authors' interpretation which could be formulated somewhat more carefully.

Answer 1.9: We changed page 278, line 24 as follows: Higher slant columns of O3 can be clearly identified and the effect is also slightly visible in the NO2 columns, as both trace gases exhibit maxima in the stratosphere. The "down welling" of the tropopause is caused by tropopause folding activity over the Andes, which is a common phenomenon in this region. Both, O3 and NO2 dSCDs are also affected by stratospheric light path enhancements caused by a change in SZA. The trace of the local SZA (Figure 9) indicates this effect on measured slant columns, which is again clearly visible in the O3 columns and less pronounced in the NO2 columns. Superimposed features as seen in the red and green boxes for O3 and NO2 are consequently due to other causes.

Comment 1.10: Page 280, line 18: The following sentence is not clear: "Retrieved concentrations are likely to be underestimated owing to horizontal inhomogeneities". Inhomogeneities of which parameter are referred to? If inhomogeneous trace gas concentrations are referred to, I wonder why underestimations are more likely than overestimations. Maybe inhomogeneities in surface elevation are addressed? In case of surface elevations in the area of the aircraft ascent and descent, the retrieved columns would have less vertical extent than assumed and therefore concentrations would be underestimated as suggested. Please add a few clarifying words here.

Answer 1.10: We changed page 280, lines 16-20 as follows: Instead of "Furthermore... " The total descent inside this boundary layer averaged over a 50 km distance to the airport. Therefore the retrieved aerosol profile as well as the retrieved concentrations are the product of averaging over locally varying aerosol and trace gas distributions. Sensitivity studies need to be conducted to provide further insight on the accuracy of this profile retrieval.

Comment 1.11: Page 280, line 23: Owing to the problems with the ś10ž directions that

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are openly discussed, maybe change the sentence to: "Most parts of the CARIBIC DOAS instrument performed reliably during the 30 flight operations." There is no question that the regular operation of this or a similar DOAS instrument in the presented manner is well feasible and represents a good opportunity for obtaining useful datasets. But a more cautious formulation would be more suitable here.

Answer 1.11: Agreed, we changed the sentence as suggested.

Comment 1.12: Page 281, line 9: I guess this statement is true for the nadir direction of the past data and might be also true for the ś10 ž directions in future.

Answer 1.12: Page 281, line 9 is changed to: The 30s time resolution is suitable for the analysis of most trace gases in the nadir viewing direction. It allows the resolution of unique events as shown by the detection of HONO in a deep convective cloud and will very likely also be suitable for the analysis of the other viewing directions in the future.

Comment 1.13: Page 282, lines 9-11: What sort of changes, which different system are the authors thinking of? If a larger system is considered, wouldn't this inhibit measurements during ascent and descent as stated on page 273, line 24? Is there a system that would fulfil all requirements?

Answer 1.13: We changed page 282, lines 9-11. Instead of "A change of the spectrograph-detector unit would improve the overall sensitivity of the CARIBIC DOAS instrument and..." into: "A more light efficient spectrograph-detector unit would improve current detection limits and could enable the detection of IO, glyoxal and water vapour. Such units that would still comply with weight and power requirements are by now commercially available (e.g. Ocean Optics QE65000)."

2 Technical remarks:

Comment 2.1: Page 267, line 24: The sequence of the references seems arbitrary, maybe this should be ordered either chronologically or by content.

Answer 2.1: This was changed to a chronological order.

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Comment 2.2: Page 270, line 13: "direction" instead of "directions" Page 271, line 11: Please remove the doubling of "the" Page 271, line 28: I guess the authors mean "feed-through" instead of "feed-trough" here... Page 272, line 3: ... and "trough" instead of "through" here. Figure 1: It is confusing that the "nadir" direction has actually 98° viewing angle and is plotted vertically in the picture. Therefore, the 98° in the caption appears like a typo which it is not. So I recommend a slant viewing angle in the picture and quotations around "nadir" (also in the text). Figure 6 and 7: Please add the units of the SCDs in the graphs.

Answer 2.2: All of the above were changed accordingly.

Comment 2.3: Figure 10: The abbreviation FRS for Fraunhofer reference spectrum has not been used before and has not been introduced. Please use the full term or specify FRS (e.g. on page 275, l.28).

Answer 2.3: FRS was changed to reference spectrum to be consistent with previous uses.

Interactive comment on Atmos. Meas. Tech. Discuss., 2, 265, 2009.