Atmos. Chem. Phys. Discuss., 13, C11773–C11790, 2014
www.atmos-chem-phys-discuss.net/13/C11773/2014/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "CARIBIC DOAS observations of nitrous acid and formaldehyde in a large convective cloud" *by* K.-P. Heue et al.

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Received and published: 31 January 2014

We thank the referees for their detailed and knowledgeable reviews.

1 General comments of Referee 1

In spite of the overall interesting topic and study, I have several rather general concerns:

The HONO slant columns which are the very basis of the study are in my opinion not as clear and certain as is suggested in the paper. In fact, they have several obvious problems on which the authors should comment:

- The scatter in values is large but seems to be reduced within the cloud. I do not understand why that's the case for the nadir observations which should not see a large change in intensity between measurements above and within the cloud.

  The referee is right, the scatter is reduced in this period, and it is indeed caused by an increase in the intensity. The intensity in the nadir telescope increases when the aeroplane is above the cloud, there is no significant change when flying into the cloud. I do not plan to include the intensity plot in the paper as it contains not much information, but we will add a statement about the intensity.
  As the referee already pointed out, the HONO peak is wider than O_4 peak, which indicates, that HONO was observed before flying into the cloud. Whether this was inside the uppermost layer of the cloud or just above cannot be distinguished.

- There are offsets and variations in the HONO values outside the cloud which are of a similar order of magnitude as the values inside the cloud. Do the authors consider these background values (about 2 10^{15} molec cm^{-2} for the downward looking directions) as real or as artefacts?

  The background are not considered as real and are therefore subtracted for the calculations, some of the other variations outside show a large dependency on the wavelength interval, and are therefore not considered in the later discussion. A respective statement will be included.

- Why is the HONO peak in nadir direction so much broader than the peaks for O_4, NO_2, and HCHO? I cannot see a radiative transfer explanation for this but maybe the authors can explain it? To me this seems to be an important point as this figure suggests the presence of large HONO amounts above the cloud where the sensitivity of the measurements is much reduced in comparison to the data taken inside the cloud.

  We focus on this period in this study, because the HONO SCD is largest inside the cloud and because also some other trace gases show enhancements

when the plane is in the core of the cloud. Nevertheless the referee is absolutely right when pointing out that the HONO is already enhanced before flying into the cloud, whereas NO_2 and HCHO are not enhanced during this period. This might be caused by different altitude profiles of these three tracers. According to our general description of the chemical process in the introduction, we expect higher HONO values in the uppermost layer of the cloud or above the cloud. For NO_2 however, we expect the enhancements to be at lower altitudes due to the enhanced actinic flux at the cloud top. In the following we will try to estimate the HONO concentration in the topmost cloud layer and above the cloud up to the flight altitude. Let us assume that the cloud top is at 9 km, and that the observed HONO is localised in altitude range from 7 km to the flight altitude (11.6 km). Compared to the observations inside the cloud the enhancement in the HONO SCD is roughly half for nadir (1.5 10^{15} molec cm^{-2}). In combination with the simulated Box-AMF for the case the plane is above a cloud, the SCDs result in HONO mixing ratios up to 100 ppt. A respective estimate will be included in the paper.

- The radiative transfer calculations needed for the conversion from differential slant columns to mixing ratios are not well constrained by the O_4 column (as far as I understood, there is basically only one piece of information available as all three directions observe very similar radiation fields inside the cloud). In addition, there appears to be a problem with the reference measurement (why was no other measurement selected?). Also the situation inside the small cloud is quite special as the peaked form of the O_4 column (increasing until the middle of the cloud and then decreasing again) indicates that the light path is limited by the horizontal, not the vertical extent of the cloud. More fundamentally, there is no way to estimate the vertical profile within the cloud and as the authors point out, there is good reason to assume that it is not homogeneous. All these considerations lead me to the conclusion that the uncertainties of the mixing ratios derived

are large and therefore they are only of limited value for the modelling exercise.

Yes it is indeed a large problem that all instruments more or less see the same radiation field, and therefore the O_4 columns of all viewing directions increase simultaneously. This is the reason why we do not get a unique solution for the simulation but have a range of possible solutions of cloud top height and cloud extinctions. However, the range in the retrieved averaged mixing ratios is rather small ($<$10%), therefore we consider the simulation to be quite robust, with respect to this problem.
The "surface" of a real cloud is a very fractional structure, and we just don't know what it looks like. So I am not sure, how much of the observed increase inside the cloud is caused by horizontal extension of the light path inside the cloud. I tried to simulate the horizontal radiative transport inside the cloud, and got a stronger effect than expected, but I am still not sure if this information might be used to better constrain the conditions inside the cloud. Therefore no changes to the manuscript will be made, here.
The influence on the model simulation is answered together with the next general comment.

- The in situ NO measurements are highly variable at flight altitude. As the authors correctly point out, they cannot be directly compared to the NO_2 mixing ratios derived from the DOAS observations, and in fact, the ratio of the two is also not in agreement with expectation and the model. In my opinion, the same argument holds for the HCHO and HONO data, which are averaged over a large volume having varying temperatures, velocities, actinic fluxes, and lightning activity which all are bound to lead to variations in concentration. Nevertheless, the authors proceed to assume constant mixing ratios and apply them (in combination with the NO from flight altitude) in the box model calculations. I'm not sure how much sense that makes.

The box model simulations are used as a tool to explore what level of mixing

ratios of HONO, NO_2, and HCHO can be explained by known gas-phase chemistry. The simulations do not use DOAS observations as input. Simulation results are compared to DOAS observations to help with their interpretation and discussion. Some observations, notably VOCs, are only available at one sample point towards the exit of the cloud system. We used these values and medians from continuous observations within the cloud as a representative set of mixing ratios. However, we acknowledge, that these values are not co-located and the set thus somewhat arbitrary. To amend the situation, we will use an ensemble of model simulations. Results will be shown as ranges or shading in the new modelling diagrams.

- The estimation of NO_x emissions per lightning flash is based on many quite uncertain assumptions which the authors admit and document in Fig. 7. However, in the abstract and conclusions, the emission values derived appear to have no or rather small uncertainties. I think that needs to be revised.

  The uncertainties of the emission rates will be better quantified and included in the new abstract.

- I found the manuscript too long and unclear in several parts. I think it would benefit from strongly reducing the section on first order estimates. I would also suggest to rewrite both abstract and conclusions - the abstract contains a lot of information which should go into the introduction and could be shorter and more succinct. The conclusions on the other hand would in my opinion benefit if a short summary of what was done in the study would be included.

  Will be done

2 General comment referee 2

The article presents the summary of a very comprehensive effort to explain the observed chemical state inside the deep convective cloud, including radiative transfer and chemical simulations. However its conclusions stop short in explaining or at least trying to estimate potential global effects, e.g. the potential importance of deep convective systems on OH chemistry. While realizing that the article describes a case study, the fact that similar events have been observed before, though rarely, speaks in my opinion for a more general pattern that deserves attention. Section 1 introduces HONO and its relevance to OH production. Adding a short paragraph that places the examined case study in a broader context would make this paper well rounded and increase its significance towards a broader audience.

A respective paragraph will be added. We estimated $4.2{\cdot}10^9$ NO molec/flash, scaling this number up with the global flash rate of 46 flashes per second (Cecil, et al.,2014) results in an annual emission of 1.4 tg N/a. The HONO production depends of course on the updraught of HCHO, the net chemical HONO production was quantified and will be added as well. Also on a global scale, however, here we have to assume the HCHO updraught to be representative.
(Cecil, D.J., Buechler, D.E., Blakeslee, R.J., 2014. Gridded lightning climatology from TRMM-LIS and OTD: Dataset description. Atmospheric Research 135-136, 404-414.)

3 Minor points Referee 1

- p 24348, l 10, namely => in particular (is it correct that HONO is observed when flying over clouds (in contrast to within clouds)? This would be interesting as it would point at very large HONO levels in the upper part of the cloud)

  Yes and no, there are only very few cases when the aeroplane flew through large

clouds, on the other hand there are many cases when the plane flew over clouds (CTH≈9-11 km). They were quantified by a strong reduction in the observed O_4 SCD, similar to the described case before entering the cloud and in about half of them HONO was observed as well. However compared to the case study presented here the HONO SCDs are much smaller, and sometimes close to the detection limit. Nevertheless, as the estimate above shows, the HONO concentrations might be high (up to 100 ppt).

- p 24355, l 7, How can the cloud base be fixed using the video camera?

- p 24355, l 8, How was the 9 km derived?

  When we flew towards the cloud, a triangulation was made based on the video data. The centre of picture is at -13° and the vertical field of view is 36.4°. The time difference between the observation of the cloud edge in the centre and lower edge of the field of view is proportional to the distance considered in the triangulation. A similar calculation was already used in Heue et al 2011. The explanation will be improved.

- p 24355, l 20, I think that applying this ad hoc factor is questionable, in particular for airborne measurements. I'm also not sure that it has been suggested in this Wagner et al. 2009 (wrong reference). I'd suggest not to apply the factor here.

  The referee is right. The correction factor was introduced in the other paper Wagner et al. 2009. We corrected that of course:
  Wagner, T. Deutschmann, T. and Platt, U. Determination of aerosol properties from MAX-DOAS observations of the Ring effect, Atmos. Meas. Tech. 2,495-512 doi: 10.5194/amt-2-495-2009, 2009.
  The exact origin of the correction factor is still under investigation; it was shown in several studies of scattered light DOAS measurement that the factor of 0.8 shows the best agreement between modelled and measured O_4 column densities. The observations in our studies are not sufficient to constrain the correction factor.

  Therefore, we applied a factor as often used for scattered light DOAS measurements. Because we knew about this drawback in our study, we also included the results for the light path and the mixing ratios without the correction factor.
  We do not think that additional changes of the manuscript are necessary.

- p 24357: I find the section describing the determination of average volume mixing ratios confusing and unclear. In particular, the selection and treatment of the background spectrum needs to become clearer.

  The choice of the background as well as the correction in the radiative transfer simulations will be clarified.

- p 24357, l5: I do not understand equation 2. To me, the BoxAMF is a vector, as are the partial vertical columns inside the cloud. Is this a shorthand scalar product? Why is the left side the differential slant column density?

  I am sorry for the confusion, the reason is that the BoxAMF is not defined for a fixed box, i.e. if you co-add the BoxAMF multiplied with the VCD for all boxes in the cloud, this sum equals another product of the VCD inside the cloud and one BoxAMF for the complete cloud:

$$
\begin{aligned}
dSCD &= SCD_{cloud} - SCD_{reference} \\
&= \sum_i (BoxAMF_{i,cloud} \cdot VCD_{i,cloud}) \\
&\quad - \sum_i (BoxAMF_{i,reference} \cdot VCD_{i,reference}) \\
&= MR \cdot \sum_i (BoxAMF_{i,cloud} \cdot VCD_{i,cloud}(air)) \\
&\quad - \sum_i (BoxAMF_{i,reference} \cdot VCD_{i,reference}) \\
&= MR \cdot BoxAMF_{cloud} \cdot VCD_{cloud}(air) - SCD_{reference}
\end{aligned}
$$

$$\Rightarrow$$
$$MR = \frac{dSCD + SCD_{reference}}{BoxAMF_{cloud} \cdot VCD_{cloud}(air)}$$

The product $BoxAMF_{cloud} \cdot VCD_{cloud}(air)$ represents the box air mass factor for the complete cloud multiplied with the vertical column density of air inside the cloud. The respective section and equation 2 will be clarified, and the background will be included.

- I do not understand the paragraph following this equation. I also have no clue what is done with the reference SCDs, what was assumed for HONO and HCHO, and how the correction factors were derived. My feeling is, that it would be much more straight forward to just include the offset in equation 2 instead of assuming a constant mixing ratio and then computing ratios of box AMFs. Judging from your numbers for NO_2, the assumed amount of absorber in the background spectrum appears to be relevant for the results so please state it.

  Based on the background measurements cited in Schumann and Huntrieser, the typical background NO_2 mixing ratio is 100 ppt or less. In cobination with our background AMF this results in an NO_2 SCD of 2.8 to 4.9$\cdot 10^{15}$ molec cm^{-2}, depending on the viewing direction, for 100 ppt NO_2. If we add this to the measured SCD, our retrieved mixing ratio increases by $\approx$50 ppt inside the cloud (assuming a constant mixing ratio). For HCHO the same calculations will be included. Based on a HCHO profile retrieved from the EMAC-model, the HCHO reference SCDs are in range of 4.3 to 9.3 $\cdot 10^{15}$ molec cm^{-2}, this adds roughly 60 ppt to the results. However, for HONO hardly any measurements in the free troposphere are available. Therefore we assumed the background to be negligible. The estimated background will be included in the corrected version.

- A1 - this appendix is to a large extent also contained in the main text - is this an editing error?

It is actually not an error, but just based on the fact, that the appendix was originally part of the manuscript and then shifted into an appendix and shortened in the manuscript. The respective paragraph in the manuscript will be changed.

4 Minor points Referee 2

- p.24346 ln.23: Is it "on top of high reaching clouds" or in(side) the upper parts of high reaching clouds?

  I am not sure whether this can be distinguished, the HONO production rate depends on the intensity (high intensity means low NO_2) and on the available precursors NO and OH. The intensity is enhanced in the uppermost cloud layer but also above the cloud. Therefore the HONO concentration profile should not show a strong gradient at the cloud top.

- p.24348, ln. 12ff: introduction of importance and use of O_4 is missing here.

  Will be added.

- p.24354, ln. 27ff: the choice of simulated cloud dimensions is not obvious to me - why not even smaller and save more modelling time?

  The cloud dimension is some kind of trade-off between saving time and not being influenced by the cloud edge, will be added to the manuscript. See comment above the edge effect of the cloud.

- p.24355, ln.3-4: Please explain focus on CE and CTH.

  In our radiative transfer model, the cloud is described by the dimension (width x length x height and altitude above ground) and the cloud extinction and the asymmetry factor. The length can be estimated based on the O_4 or water data; the width is expected not to be relevant for this simulation, unless it gets be too

small. But for the O_4 absorption, the two chosen parameters (CTH and CE) are most relevant, and we have less estimates for these two parameters, because the triangulation used for the top of the cloud before entering the cloud does not work for the cloud top, and the video camera data do not support enough information to estimate the cloud extinction parameter. Therefore it was straight forward to vary CTH and CE and look for the best agreement with measurement. For the verification of our model result additional information such as CTH from MODIS can be used.
Of course, it can also be done the other way round: one might first ignore the DOAS measurement and simulate the data for the cloud, based on ECMWF and satellite data, but I would not expect this to agree with measurements, therefore a least one parameter should be varied to adopt the simulation to the measurements. The respective section will be clarified.

- p.24370ff: Please change Appendix text so that it only contains additional information and remove copied text from the main sections.

  We will do it the other way round and shorten the manuscript in this point.

- p.24371, ln. 2: "model's uncertainty" - which uncertainty specifically?

  The statistical error of the Monte Carlo model as estimated by the polynomial fit. Included in the appendix.

- Proof reading by a native speaker would be a bonus.

5 Technical comments (referee 1 and referee 2)

- Please check for acronyms (CPC, OPC, ARINC, ...) and introduce them.

  ARINC stands for Aeronautical Radio Incorporated, which is a company in Annapolis, Maryland, USA. Moreover it is the name given to the common data bus

  system (www.arinc.com) used in the aviation industry. We will give some more information on the acronyms and add "data bus system" to ARINC, section 2.

- p.24344, ln. 4: "... 4 consecutive commercial airline flights operated by Lufthansa" instead of "Lufthansa flights".

  We do not agree with referee in this point, Lufthansa flights is clear and easy to understand. "Flights operated by Lufthansa" might be misunderstood as a flight you booked by any other "Star Alliance" partner and when you arrive at the airport it turns out this flight is "operated by Lufthansa."

- p 24346, l 18, reach up to 10 → reaches up to 10

- p.24346, ln.18: replace "... reach up to 10" with "it can be as high as 10"

  We choose the second Version.

- p.24346, ln.20: replace "...by a factor up to" with "by up a to factor of"

  done

- p 24346, l 22, getting lost → being removed

  done

- p 24347, l 22, mainly given by → mainly by

  done

- p.24348, ln.3: replace "...the second only" with "only the second"

  done

- p 24348, l 10, namely → in particular

  done

- p 24348, l 16, A more general ... - is this announcement really needed here?
- p.24348, ln.16 delete "the"

  We delete the complete announcement.
- p.24350, ln.24: "paths" instead of "path"

  done
- p.24355, ln:18: placement of (CTH and CE) confusing here

  If the dimensions of the polynomial are obvious, I can delete this statement. However several co-authors were a bit irritated, and found it much clearer if the dimensions are named. Therefore we prefer to leave it like this.
- p.24355, ln:26: replace "...cloud top height (CTH)" with "CTH".

  done
- p 24357, l15: in side → inside

  done
- p 24357, l27: test artificial → test on artificial
- p.24357, ln:27: "on artificial spectra"

  done
- p 24358, l5: This paragraph is misleading - the errors of the mixing ratios are of course not the same as those of the slant columns as the conversion introduces additional uncertainties.

  We will correct that: The error of slant column densities adds to the error of the mixing ratio.

- p 24358, l11: estimate influence → estimate the influence
- p.24358, ln:11: "estimate the influence"

  done
- p.24358, ln:23: "leads" instead of "lead"

  done
- p.24358, ln.18: "ratio"

  I do not think it is correct to use the singular here, because the mixing ratios of three trace gases are listed: "the averaged mixing ratio is 33.3ppt HONO, 357ppt HCHO, and 155ppt NO_2." Is this correct?
- p 24358, l26: derives → results

  done
- p.24359, ln.21: replace "aware" with "cautious"

  done
- p.24360, ln.12: Sentence on wind speed is unclear; "the" instead of "The"
- p 24360, l14: transport time of - something missing here?

  Yes, somehow the transport time (37 minutes) was deleted. Corrected.
- p 24361, l6: insitu → in situ

  corrected
- p 24361, l8: factor three → factor of three

  corrected

- p 24361, l19: .. we showed ... - not sure this was showed, it was rather just stated (and probably is correct).

  Changed to: "In the previous section we explained that lightning is probably the dominant NOx source."

- p 24364, l23: found too weak → found to be too weak

- p.24364, ln.23: "is found to be too weak"

  done

- p.24365, ln.11: remove comma after "that"

  done

- p 24367, l17: NO emission → NO emissions

  done

- p 24369, l13: emieeion → emission

  done

- p 24369, l18: .. which offered a rare opportunity. - for what?

  Changed to: "Aircraft generally avoid strong convection and lightning which means that we have few data for such events."

- p 24372, l27: thres-hold → threshold

  done

- Table 2: please include the slant column values later used in the analysis

  done

- Table 3: - what are the ranges given? Looking at Figure 2, the range in NO seems to be much larger than stated here

  As mentioned earlier the in situ NO data are highly variable caused by the variations in time and space. The DOAS data on the other hand average over a large area and altitude range. Therefore for the in situ data the median values inside the cloud is used for further calculation, the range denotes the standard deviation from the median, it does not represent the whole range of measurements.

- Table 5: therefore NO → therefore no

  corrected

- Figure 1: Something is wrong with the Ring corrections shown - the right one is much smoother (and fits less well to the data) then the right one.

  The impression that the fit quality is different for the ring fit in the two wavelength regions might be caused by the fact that accidently different scales were used (-90 to -20 and -90 to -30) or by the resolution of the PDF - file. Therefore I scaled in on the ring fit and the fits look similar for both wavelength intervals. Here (Fig. 1 the same data as in the manuscript are shown. In the manuscript now the same scales are used for both fits. To show an additional figure of the ring fit does not seem to be necessary.

- Figure 2: overview in → Overview of

- p.24394, caption Fig.2: "Overview of" instead of "in"

  corrected

- Figure 3: why is a different time period shown than in Fig. 2?

  There was no reason to use different time periods here, maybe I changed one of them and forgot to change the other one as well. Time period adapted to the one used in figure 2.

- Figure 3: back ground → background corrected

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 24343, 2013.

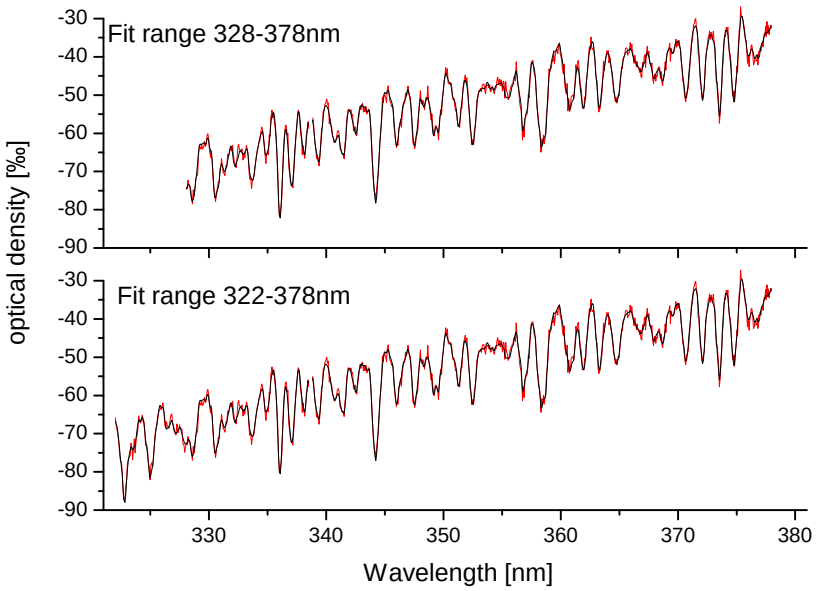

Fig. 1. Ring fit for the two different wavelength intervals (328-378 nm and 322-378nm)