Atmos. Chem. Phys. Discuss., 13, C9025–C9030, 2013
www.atmos-chem-phys-discuss.net/13/C9025/2013/

Atmospheric Chemistry and Physics Discussions
Open Access

ACPD
13, C9025–C9030, 2013

Interactive Comment

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

Anonymous Referee #1

Received and published: 9 December 2013

In their paper "CARIBIC DOAS observations of nitrous acid and formaldehyde in a large convective cloud", the authors report on CARIBIC DOAS observations of enhanced NO2, HONO, and HCHO in a convective cloud. Similar observations have already been reported by Dix et al. (2008), but in this case, the impact of pollution could be excluded. Using radiative transfer calculations, the properties of the cloud are estimated and the DOAS slant columns converted to cloud averaged mixing ratios. These values are then compared to first order estimates and CABA box-model simulations, and the conclusion is drawn that HCHO (or its precursors) must have originated from the boundary layer while NOx is probably from lightning. According to the model runs, the observed HONO concentrations can only be explained by a combination of both, HCHO and NOx. Finally, a range of plausible NOx emission rates per flash is

Full Screen / Esc
Printer-friendly Version
Interactive Discussion
Discussion Paper

estimated which is at the lower end of current literature values.

The manuscript reports on interesting measurements of HONO in a convective cloud, and clearly extends on the Dix et al. paper in that the situation is clearer as pollution impacts can be excluded. The comparison with model results provides some insight into the chemistry under these conditions and the emission and updraught fluxes involved. The topic matches the scope of ACP and I therefore recommend publication after consideration of the points made below.

Major points

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

1. 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:

    (a) 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.

    (b) 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?

    (c) Why is the HONO peak in nadir direction so much broader than the peaks for O4, NO2, 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.

ACPD

13, C9025–C9030, 2013

2. The radiative transfer calculations needed for the conversion from differential slant columns to mixing ratios are not well constrained by the O4 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 O4 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.

3. The *in situ* NO measurements are highly variable at flight altitude. As the authors correctly point out, they cannot be directly compared to the NO2 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.

4. The estimation of NOx 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.

ACPD
13, C9025–C9030, 2013

5. 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.

Minor points

- Please check for acronyms (CPC, OPC, ARINC, . . .) and introduce them.
- p 24346, l 18, reach up to 10 => reaches up to 10
- p 24346, l 22, getting lost => being removed
- p 24347, l 22, mainly given by => mainly by
- p 24347, 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)
- p 24347, l 16, A more general . . . - is this announcement really needed here?
- 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?
- 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.

ACPD
13, C9025–C9030, 2013

- 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.

- 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 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 NO2, the assumed amount of absorber in the background spectrum appears to be relevant for the results so please state it.

- p 24357, l15: in side => inside

- p 24357, l27: test artificial => test on artificial

- 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.

- p 24358, l11: estimate influence => estimate the influence

- p 24357, l26: derives => results

- p 24360, l14: transport time of – something missing here?

- p 24361, l6: insitu => in situ

- p 24361, l8: factor three => factor of three

ACPD

13, C9025–C9030, 2013

- p 24361, l19: .. we showed ... - not sure this was showed, it was rather just stated (and probably is correct).
- p 24364, l23: found too weak => found to be too weak
- p 24367, l17: NO emission => NO emissions
- p 24369, l13: emieeion => emission
- p 24369, l18: .. which offered a rare opportunity. – for what?
- A1 – this appendix is to a large extent also contained in the main text – is this an editing error?
- p 24372, l27: thres-hold => threshold
- Table 2: please include the slant column values later used in the analysis
- Table 3: - what are the ranges given? Looking at Figure 2, the range in NO seems to be much larger than stated here
- Table 5: therefore NO => therefore no
- 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.
- Figure 2: overview in => Overview of
- Figure 3: why is a different time period shown than in Fig. 2?
- Figure 3: back ground => background

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

ACPD

13, C9025–C9030, 2013

Interactive Comment