

Review of “Measurement report: Enhanced photochemical formation of formic and isocyanic acids in urban region aloft: insights from tower-based online gradient measurements”

General Comments

In this manuscript the authors present interesting measurements of a variety of VOCs along the vertical gradient of a very tall tower in Beijing, China. They focus on measurements of formic acid and isocyanic acid and attempt to explain how photochemical processes could be contributing to the variation in measured vertical gradients. I think this is an interesting set of measurements and worth publication. I left some comments that hopefully can improve the presentation and communication of the results.

Specific Comments

(Introduction) A reference that is missing that I think is relevant is Alwe, et al. (2019).¹ The authors of that study took measurements of formic acid eddy-covariance fluxes and vertical gradients in a forest and is one of the few studies of vertical gradient measurements of formic acid.

(Line 78-81) I believe that the 1 ppb number comes from Roberts, et al. (2011) and is based off a calculation where the concentration of NCO⁻ ions were measured from cells *in vitro* that had undergone carbamylation and based on the Henry's law constant of HNCO the 1 ppb threshold for potential health impacts was derived. The Fulgham, et al. 2020 study did not establish any threshold for acceptable levels of ambient HNCO so I recommend the authors remove the citations for the two studies associated with this statement. They could instead cite Roberts, et al. (2011).

(Line 151) What was the pore size and diameter of the filters?

(Line 169-188) The information related to the Figaero in this paragraph is confusing. If the authors are doing 4-min interval switching between the different sampling heights how does that impact the Figaero measurements? Were these measurements done the whole campaign? Did the authors just stop on one location for an hour and sample particles? I looked briefly ahead to see where Figaero measurements were discussed, but it's not clear. If these measurements aren't discussed can they be removed from this section?

(Line 204) I think this refers to “high” mass spectral peak resolution, not time.

(Line 210) Did the trace gas instrumentation have trouble maintaining adequate sample pressure when sampling through those long lines with the high flowrates?

(Line 250-252) HNCO is not an inorganic acid, it is an organic acid. The justification provided by the authors here is not valid. The authors should instead simply state that tubing delays are not discussed for HNCO.

(Figure 1) Can the authors include a vertical line in the plot that intersects with the formic acid trace to graphically show the determined delay time of 23 s?

(Line 273) I might be unfamiliar with this Taylor dispersion calculation. How is this calculation different from a plug-flow residence time calculation? For 13 SLPM, 0.37” inner diameter tube, and 400 m I calculated a plug-flow residence time of 129 s. Why is the Taylor dispersion number so low? Can the authors explain how to reconcile my plug-flow residence time calculation with their measured delay time of 29 s?

(Line 273 or Section 2.1) Can the authors report plug-flow residence times for the different lengths of tubing?

(Line 292-303) Could the authors decrease the influence of the long tailing by having a bypass pump that passivated the long lines while they were not being sampled?

(Section 3.1) I felt maybe this section could be condensed considerably. The main points are that the authors didn't observe any major impacts on tubing length when measuring HNCO and they were able to constrain tubing delay effects for HCOOH at the 400 m tubing length. I don't understand the calculation that was performed for Figure S3 and I don't understand what the authors are trying to convey with it. What is the significance of the $\Delta t = 14$ h for HCOOH? Is this saying that it takes 14 hours before the 400 m tubing is passivated?

(Figure 3) The authors conclude that HNCO does not experience the same tubing effects that HCOOH does. Is it useful to show the plot for HNCO then? Panel d in Figure 2 does not seem to imply a linear relationship and thus these data are confusing to show. Figure 3a is also only referred to briefly and it's not clear what the physical meaning of the slope is for the fit of δHCOOH and ΔHCOOH . I think the authors try and explain this analysis some in Lines 317-319, but I'm still not very clear on what specific information this analysis is providing. I'm not sure why the R^2 is shown in Figure 3 either, but after looking at it I wonder why the 200 m length tubing seems to be an outlier in this pattern.

(Line 353-361) Since the source of formic acid here is considered to originate from photochemistry, would it be more interesting to compare median formic acid mixing ratios measured between 10:00 and 15:00 between the two measurement heights? I wonder if a lot of variability is being introduced into the averages because HCOOH is normally high during the day and low at night. That comparison may show an even more compelling difference between the 5 m and 320 m heights.

(Figure 5) Figure 5 is a little confusing because CICs are shown in panel f but Figures 6-9 are discussed in the text before CICs are introduced on Line 466.

(Line 408) I find the "growth rate" terminology unusual. It immediately makes me think of new particle formation. Would the authors consider rephrasing "growth rate" to "enhancement rate" or "gradient"?

(Line 408) How were the "growth rates" calculated?

(Figure 8) Instead of the x-axis being "growth rate" could it just be normalized concentration like Figure 9?

(Line 466) Maybe the authors should just say boundary layer instead of mentioning the residual layer.

(Line 466) My intuition says that an atmospheric column integration calculation would be concentration times the assumed volume of the column (which should only vary as a function of boundary layer height). I'm having a hard time conceptualizing molecules cm^{-2} .

(Figure 5f) So does this mean that the total number of molecules throughout the boundary layer stay constant as a function of hour of day? Can the authors explain this more in the text? I'm not sure I connect how this calculation demonstrates how ground measurements are not capturing vertical distribution dynamics of HCOOH better than the gradient measurements shown in other figures.

(Line 543 and Figure 12) It's really interesting to see measurements of all the different amides as a function of height of the tower. On the other hand, the authors seem to be reaching further than the data suggest to explain small differences in concentrations with a complicated chemical mechanism that was

vaguely speculated around Line 100 in the introduction. It's okay if the authors can't explain where these chemicals come from. The measurements are fairly novel and interesting in and of themselves. A much more detailed chemical analysis is warranted to articulate chemical mechanisms responsible for HNCO production.

(Line 543) Did the amides experience any tubing effects?

(Line 564) Please replace all mentions of "growth rates" with more suitable terminology like suggested above.

(Line 574) Again, I don't really understand the utility of using the CIC calculation to critique ground level measurements. If the authors want to make the point that chemicals can be produced at higher altitudes and so using ground level measurements for modeling may not be adequate for answering some questions that would be reasonable.

(Conclusions) I'm confused about the authors conclusions regarding the tubing analysis. My understanding from the data is that formic acid experiences significant tubing effects from the long lines and HNCO did not. The authors didn't really provide any information on if they had to correct the data for tubing delays or best practices when measuring formic acid from really long lines. Did the authors have to correct HCOOH concentrations for the tubing effects?

Technical Corrections

(Line 72) HNCO is an organic acid.

(Line 98-102) Can the authors start this hypothesized mechanism with "We hypothesize.." or something like that to indicate that this potentially important mechanism is the authors thoughts?

(Line 93-105) The authors might consider removing this paragraph. There's three sentences of loose speculation in it and I think the important point could be summarized in a single sentence tacked on to the last sentence of the previous paragraph. Basically "vertical gradient measurements of HNCO can help elucidate potential formation sources and mechanisms".

(Line 106) Replace "mass spectrometer" with "mass spectrometry"

(Line 108-110) I would recommend removing this statement. In the following sentences the authors cite studies that provide evidence to the contrary. In 2013 a group from Cal-Tech put their CIMS instrument on top of a tower for measurements.

(Line 125) Remove "alkane" from PFA definition.

(Line 172) Replace "ionic" with "ion molecule reaction"

(Line 175) "MIR" should be "IMR"

(Line 179-181) Move this sentence to Line 170 in front of "A filter inlet for gases and aerosols..."

(Line 201) Replace "eliminated" with "corrected for"

(Line 366-369) Consider rewording...

"Photochemical formation of secondary pollutants was largely suppressed from July 13th to 30th due to weak solar radiation (characterized by small $j(\text{NO}_2)$ values) and precipitation."

(Figure 8) Instead of putting $X=1$ in the figure can the authors just write in the caption that a dotted line is shown for the normalized “growth rate” of 1?

(Line 436) Consider rephrasing to “Our results point to the likely importance of photochemistry as a source of formic acid that is enhanced with increasing height within the boundary layer.”

(Line 445) Consider citing Link, et al. (2021).²

(Line 470) I think the authors mean Figure 5f.

(Figure 12) Can the authors provide a description in the caption of what the patterning indicates for the bars?

(Barnes, et al. 2010 Reference) Should the journal abbreviation be ChemPhyChem?

References for Review

- (1) Alwe, H. D.; Millet, D. B.; Chen, X.; Raff, J. D.; Payne, Z. C.; Fledderman, K. Oxidation of volatile organic compounds as the major source of formic acid in a mixed forest canopy. *Geophysical research letters* **2019**, *46* (5), 2940-2948.
- (2) Link, M. F.; Brophy, P.; Fulgham, S. R.; Murschell, T.; Farmer, D. K. Isoprene versus Monoterpenes as Gas-Phase Organic Acid Precursors in the Atmosphere. *ACS Earth and Space Chemistry* **2021**, *5* (6), 1600-1612.