Atmospheric Measurement Techniques Discussions

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Comment on amt-2021-432

Anonymous Referee #1

Referee comment on "Comparison of airborne measurements of NO, NO2, HONO, NOy and CO during FIREX-AQ" by Ilann bourgeois et al., Atmos. Meas. Tech. Discuss., https://doi.org/10.5194/amt-2021-432-RC1, 2022

Review of Burgeois et al. "Comparison of airborne measurements of NO, NO_2, HONO, NO_y and CO during FIREX-AQ"

Thank you for giving me the opportunity to review this manuscript. I hope my input will be useful to the authors.

I appreciate this paper very much. The paper describes results from an intercomparison of different measurement techniques for what many would call "basic" photochemical tracers but the validity and precision of these tracer measurements are in fact critical for the success of any atmospheric chemistry mission.

This paper is a timely and very relevant contribution at a time during which measurement capabilities are expanding rapidly. It is well structured and clearly written using precise language. The scientific methods are sound. The content is entirely appropriate for publication in AMT. The reference list is appropriate. I recommend accepting the manuscript for publication after considering the following suggestions.

HONO:

I have a bit of a hard time wrapping my mind around the HONO comparison numbers and illustrations.

- How can the distribution of the factional errors be so tight around a value of 2 (Figure S1)? When plugging into the equation CES/CIMS values mentioned at various places in the manuscript (1.36, 1.8, 2.48 and 3.9) I calculate values for FE between 0.3 and 1.2. This should center the gaussian somewhere in the middle of that range and show a much broader distribution.
- Figure S4e shows that the CES measures anywhere from zero to 25 ppb while the CIMS measures between 0 and 3 ppb. How does this reconcile with the gaussian distribution shown in Figure 5 and the mean difference plots in figure S9?

This might require a bit more explanation than what is currently presented in the text.

While I can appreciate that the IMR temperature may have an influence on sensitivity I'd be curious to know why this would only affect HONO and not also other analytes. Other readers might be left wondering about this.

Was there an attempt made to correct the HONO values for IMR temperature, and how does the comparison look like then?

NOy:

For lack of a better word, I find the assessment of the NOy measurements somewhat sugarcoated. In my view there are too many uncertainties to make these measurements ultimately useful, at least for fire smoke research. The facts I gather are the following:

- Particulate nitrate makes up the largest fraction of total NOy in western wildfire smoke and a significant fraction in the eastern fires.
- The sampling efficiency of particulates is highly dependent on airspeed but the real airspeed at the inlet tip (and the dependency on type of aircraft, banking and attack angle, or install location on the aircraft) is unknown.
- Particulates used in the model described are assumed to be ammonium nitrate. The exact composition of the nitrates contained in fire smoke particulates is not known. There could be a significant fraction of organics, in particular nitroaromatics, but their volatilization behavior and conversion efficiency in the gold converter is unknown.
- In the best case of sampling efficiency, 25% of the nitrate could be unaccounted for. Looking at the graph in Figure 10a, that fraction could be more than 50% in the worst case.

I'd agree with the authors if you call this a devil's advocate assessment, but at the end of the day my impression is that NOy measurements and "oxidized nitrogen closure" calculations based on these measurements or their use as photochemical clocks, etc. still need to be taken with a (fairly large) grain of salt. Just like they had to in the past.

What would a comparison of plume dilution calculated using CO versus a similar calculation using NOy look like?

Minor suggestions:

Section 2 intro: Maybe a figure with a plumbing diagram of the manifolds described in the manuscript could be helpful

Section 2.2.1.: What was the conversion efficiency of the photolysis converter?

Line 134: Suggest replacing "minimal" with "least possible"

Line 169: NOy is missing in the list

Section 2.2.3.: What is the inlet material? What was is shared with?

Line 305: How can the addition of 1% flow of saturated nitrogen stabilize the I- / I-*H20 clusters to such a precise ratio?

Line 401: should be CH3NO2

Line 511: If this uncertainty is based only on the spread of the trajectory ensemble, does this mean that there is additional uncertainty arising from the plume rise time, calculated using a fixed vertical transport speed?

Line 575: I am not certain what the logic is behind putting some figures into the supplement and others into the main manuscript. Maybe this could be revisited.

Line 633: Could the positive artifact in the CL instrument be caused by thermal decomposition of peroxynitrate species inside the photolytic converter cell (which might be warmed by the heat output of the LEDs?)

Line 699: Suggest starting the paragraph with “The interpretation of literature….”

Line 733: If there is an obvious problem with the CIMS HONO measurements, why are these being used here?

Line 749: one or more ?

Line 757: see NOy discussion. How is this known?

Line 787: “…higher than…”

Line 936: see NOy discussion above

Conclusions point 6: Averaging data always results in less scatter. How useful really are instrument comparisons when averaging data spanning orders of magnitude?