Atmospheric Measurement Techniques Discussions

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Comment on amt-2022-244

Anonymous Referee #2

Referee comment on "Airborne flux measurements of ammonia over the southern Great Plains using chemical ionization mass spectrometry" by Siegfried Schobesberger et al., Atmos. Meas. Tech. Discuss., https://doi.org/10.5194/amt-2022-244-RC2, 2022

Schobesberger et al. demonstrate the first-time airborne deployment of the C6D6-CIMS to measure ammonia concentrations and ensemble average and wavelet eddy covariance fluxes over the Southern Great Plains. The novel setup seems outcompeting other approaches for fast and ultrasensitive NH3 measurements. The manuscript generally reads well and the method has potential to improve accuracy of inventory estimates and location of missing NH3 emission sources. Despite numerous strong and exciting aspects of the study, I also arrived at some relatively major comments mostly regarding missing details or lack of clarity which hopefully can be addressed in the revised version.

- Humidity dependence is a major issue that the authors seem to be aware of and they used a thoughtful approach of humidity dependent sensitivity correction based on pH2O in the IMR. However, given a typically strong flux of water vapor in the troposphere and if there is a humidity dependence, the question arises if the flux contribution may not come just from NH3 but from the high frequency fluctuation in the H2O loss? This issue is neither discussed nor quantified.
- A simultaneous comparison with other methods (e.g. Picarro NH_3) would have been more reassuring especially given the humidity issues and unexplained sensitivity drift before and after the flights.
- It is surprising why the zero measurement results in only 1-2 orders of magnitude signal decay (e.g. Figure 3). As the ambient concentrations may vary several orders of magnitude, it seems therefore uncertain if the instrument will be able to resolve variabilities spanning orders of magnitude within a short amount of time like it is a case when going in and out of the plume.
- NH3 concentrations (and fluxes due to flux divergence) in the PBL and free troposphere are expected to change with altitude. However, surprisingly the concentrations look suspiciously stable for some of the RFs (e.g., Fig 3, the flight on the left RF14 or RF15 which are plotted using a similar color shade). The lack of changes in NH3 concentrations across such a broad altitude range (1000-4200 m) looks somewhat odd and potential issues with instrumental background should be excluded.
- It is unclear how the data are normalized to primary ions and/or dimers. The NH3 signal does not only depend on the ambient NH3 concentration but also on the variability in the primary ion signal (C6D6 – not temperature controlled). The lack of

insight into factors behind the changes in sensitivity sounds like a missed opportunity which should not be left for other papers to investigate. The reader specifically wonders how stable primary ions were throughout research flights and if heating of the benzene reservoir could be beneficial in improving this stability.

- The setup looks very neat overall, but I wonder if it has been tested for changes in ambient pressure, especially that that no calibrations or targets were performed during the flight.
- It is great to see eddy covariance estimates for ammonia. However, the flux methodology shows great potential for improvement. The introduction does not give credit to all the progress achieved in the multiple airborne EC campaigns (e.g. CABERNET, CARAFE) that have compared FFT and wavelet fluxes. I like the IRQ footprint contribution, but it would be interesting to look at the ratio between FFT and wavelet fluxes for different RFs and shed light on flux uncertainties (see #8).
- It is unclear if the W2018 flux toolkit was blindly used or if the investigators were aware of factors affecting systematic and random errors and if the corrections for the systematic error have been made. Given the high altitude and short legs these errors are likely rather high. Because the paper is making quantified estimates, I would strongly recommend to include the calculation of those errors as well as flux specific detection limits (e.g., as 3 x s.d. of the covariance noise far away from the lag-time).
- Fig. S4, why was the lag time negative? Is it because the vertical wind data were not synchronized? What was the actual residence time?
- The cospectra , Fig S4, center row, are too short to evaluate LF losses. Could both FFT and wavelet co-spectra be shown for a relatively long flight leg? It would also be elegant to include in the methods how the data was filled, stitched, interpolated after removing zero air measurements.
- I really like the research making reflection on the safety of the reagent ion. Indeed, toluene could be a much safer alternative if it works similarly well for NH3. It would be useful to add how the exhaust was routed outside of the cabin or through a VOC trap to prevent exposure.

Technical

- Fig 7, the color of the outside-coi CWT line cannot be easily discerned from the full-scale CWT line.
- L29, L44, L371 10s can be confusing with 10 s, I suggest using “tens”.