

**Comment on “Evaluation of ambient ammonia measurements from a research aircraft using a closed-path QC-TILDAS spectrometer operated with active continuous passivation” by Da Pan, Xuehui Guo, and Mark Zondlo**

The manuscript assesses the performance of a closed-path, airborne-based ammonia instrument (Aerodyne Res. Inc.) by demonstrating the performance of active passivation under flight conditions. Ammonia is incredibly challenging to measure anywhere (with any technique) due to the significant adsorption/desorption effects on instrument/inlet surfaces, particularly on an airborne-based platform where temperatures, humidities, and ambient ammonia concentrations can vary dramatically. The authors show greatly improved performance when using the passivated versus unpassivated flows for sampling large NH<sub>3</sub> concentrations (10s-100s ppbv NH<sub>3</sub>) from farms and biomass burning plume. The documentation of the instrument performance versus flight maneuvers was particularly valuable. This manuscript represents a large advance in airborne-based ammonia measurements, and the authors’ experiences on using passivant additions in addition to /in lieu of frequent cleaning are important for future implementation of closed-path ammonia instruments in specific but also ammonia sampling more generally (laboratory experiments, calibrations, etc.). However, there remain some areas that require greater clarification to put the research in the proper context.

**1. The response times, and applicability, to smaller NH<sub>3</sub> variations should be discussed (and backgrounds relevant to very low free tropospheric values, <ppbv). The detection limit needs better justification.**

In this study, the step change of NH<sub>3</sub> was created by turning off the calibration gas. The change is around 85 – 115 ppbv. This variation is uncommon for sites away from source regions. At high NH<sub>3</sub> concentrations and large variations, NH<sub>3</sub> observations may be less impacted by surface interaction because a “clean” sampling line only has a finite number of adsorption sites which could be quickly fill up under this condition. This effect has been reported by Ellis et al.(1), and it may explain why passivation did not help to increase the response time of the instrument. At low NH<sub>3</sub> concentrations, a greater fraction of NH<sub>3</sub> molecules may interact with the inner surface.

Roscioli et al. showed that  $t_{90}$  of a similar instrument was 12 sec for a step change of 3 ppbv (from 0 to 3 ppbv) without passivation (2). When 4 ppmv passivant was applied,  $t_{90}$  decreased to 2 sec for the same step change. The instrument can be considered clean since it was flushed with NH<sub>3</sub>-free and low NH<sub>3</sub> gases. Therefore, even a “clean” closed-path instrument may not be capable for high-frequency (>1 Hz) field application with small NH<sub>3</sub> variations without passivation, and passivant additions may still not work for fast operation (> 1 Hz) under clean conditions. The authors should discuss in more details about the applicability and effectiveness of passivation to field applications with relatively low NH<sub>3</sub> concentrations (e.g. flux measurements in rural area and airborne observations away from sources).

Fig. 10: Because of the nature of the very large concentrations measured, it is hard to discern just how well the instrument/technique can observe cleaner, free tropospheric ammonia levels after seeing large plumes. For example, while the correlation is impressive in Fig. 10 and shows the value of this overall approach, with a several second response time for NH<sub>3</sub>, the “peaks” and “valleys” may still be attenuated to some extent. It would be helpful to show a plot against a true 1 Hz tracer correlation instead of two instruments with 2-3 second response times.

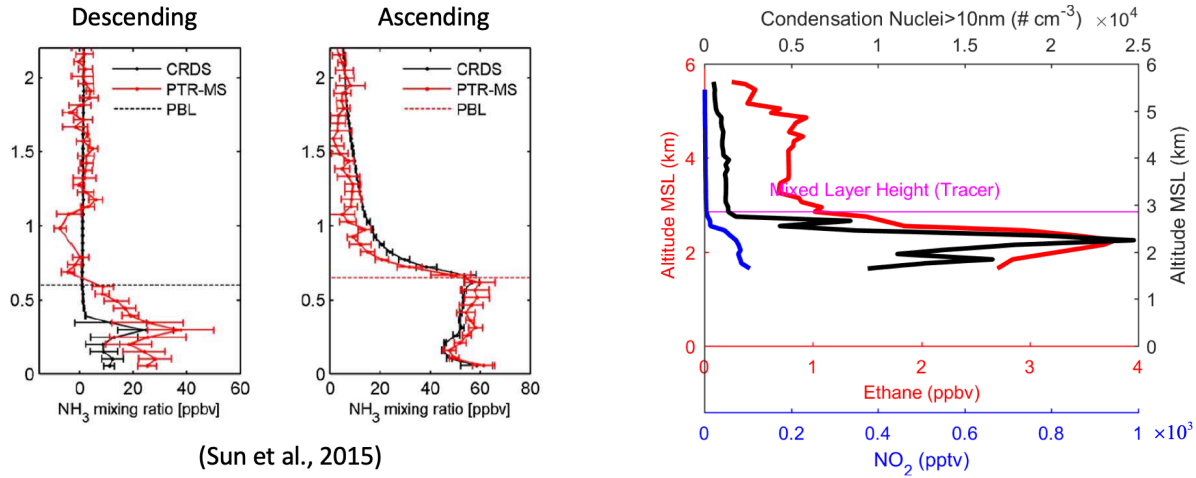
There are also some differences between the start and end of the plumes in Fig. 10 in terms of the NH<sub>3</sub>/CO ratio. As one progresses in the plume, the NH<sub>3</sub>/CO ratio seems to get higher, which would be consistent if the background is growing. Differences in plume chemistry across the transect may be a reason for this, too. However, outside the plume (start/end of timeseries), the NH<sub>3</sub>/CO level isn't the same, either.

Related to this overall point, on the large y-scale axis (500 ppbv NH<sub>3</sub>) in Fig. 10, while the concentration looks to be "close" to zero, in reality on this scale it could be numerous ppbv NH<sub>3</sub>. Even if the instrument response time is nominally on the order of a few seconds, going from 400 ppbv NH<sub>3</sub> to sub-ppbv NH<sub>3</sub> could take a long time and may result in biases in clean conditions in the free troposphere. It may be helpful to show a vertical profile of NH<sub>3</sub> in the ascent out of Greeley (where high agricultural emission concentrations exist) and compare it to another, short-lived boundary layer tracer that would be highly enhanced in the boundary layer vs. the free troposphere. On the left below, I show a vertical profile of NH<sub>3</sub> from the NASA DISCOVER-AQ California in the San Joaquin Valley (taken from Sun et al., 2015), where the importance of the authors' large improvement is clearly validated (needed), but where concerns of going very high NH<sub>3</sub> to nominally sub-ppbv NH<sub>3</sub> at high altitude could still be an issue even with this approach. Also attached on the right is a profile of NO<sub>2</sub>, ethane, and CN in the Greeley area from DISCOVER-AQ Colorado. I'm not sure if these are necessarily the best tracers per se from a quick look, but one can see very sharp gradients at the top of the boundary layer, and it would be illustrative to see how the shape of the NH<sub>3</sub> profile compares to other ~ short-lived tracers when ascending/descending across the mixed layer height. WE-CAN should have plenty of such measurements on the C-130 to compare.

Figure 3: It is hard to see on Fig. 3a, but the constant altitude segments seem to show quite a bit of variability in the background, say, from -0.2 to +0.2 ppbv NH<sub>3</sub> within an altitude level for a given 1 Hz measurement. This calls to question as well the accuracy of anything < 0.5 ppbv, given that the background is changing by 0.4 ppbv. What were the ascent rates/g's after each constant altitude leg? The 50 pptv NH<sub>3</sub> sensitivity to typical flight maneuvers mentioned in the text doesn't seem consistent with Fig. 3a. If most of the variability is due to the ascent portions (g-forces), then perhaps a 1 Hz timeseries of the constant leg would be helpful. Also, how "polluted" was NH<sub>3</sub> prior to overfilling the inlet for a zero for these flights upon takeoff in Broomfield? How often was it zeroed vs. sampling? 10% duty cycle? Entire flight? 50%? The wording wasn't clear in the text for this portion of the flight.

Table 2: I really appreciated the mass balance in Table 2/discussion (neat experiment!), though even here differences of ~ 10% of counting molecules still could mean significant backgrounds still exist relative to very clean conditions (though I recognize this mass balance counting is within the instrument uncertainty).

In summary of all of the above, taking 3 times the 1 Hz precision doesn't seem justified for the detection limit, nor an assessment of instrument accuracy at low concentrations. It seems the instrument is well-designed for fires/agriculture but future work is still needed for clean conditions after such large plumes (or more justification in the manuscript). This is particularly true when going from dirty to clean conditions, given the many sampling biases that still may exist for ammonia.



### 3. Validity of using bi-exponential decay model and meaning of the parameters should be addressed:

The bi-exponential decay model is essential to the discussion about instrument response time. The authors used the bi-exponential decay model to determine the response times of the instrument to associate gas exchange and the interaction of NH<sub>3</sub> molecules with sampling surfaces. The fit results were also used to extrapolate the 90% and 99% signal recovery times ( $t_{90}$  and  $t_{99}$ ). Therefore, it is necessary to address the validity of the bi-exponential decay model.

The bi-exponential decay model was first introduced to characterize response time of QC-TILDAS to NH<sub>3</sub> changes by Ellis et al.(1). However, the validity of the model was not discussed in the original work. Here, we propose to use the following a simplified surface-air exchange model to derive the bi-exponential decay model and discuss its validity.

After a step change, changes of the mixing ratio of NH<sub>3</sub> inside the instrument  $\chi$  is caused by 1) the difference of NH<sub>3</sub> mixing ratio between the gas currently inside the chamber and the newly introduced gas ( $\chi_0$ ); 2) adsorption or desorption to the inner surface of the instrument. These processes can be expressed as

$$\frac{d\chi}{dt} = \frac{Q}{V}(\chi_0 - \chi) + \kappa(\chi_s(t) - \chi)$$

where Q is the flow rate and V is the inner volume of the instrument;  $\kappa$  is the conductance of NH<sub>3</sub> between surface and air interface;  $\chi_s$  is the compensation point of the inner surface (adsorption occurs when  $\chi > \chi_s$ , desorption occurs when  $\chi < \chi_s$ ). The compensation point is a function of time and its variation depends on historical changes of NH<sub>3</sub> concentration inside the instrument. When there are no phase changes and chemical reactions, and the surface is not saturated by NH<sub>3</sub> or exhausted of NH<sub>3</sub> during the process,  $\chi_s$  could be simplified as

$$\frac{d\chi_s}{dt} = \kappa(\chi - \chi_s).$$

When the surface is clean such that  $\chi_s \ll \chi$ ,  $\chi_s$  equation can be approximated as

$$\frac{d\chi_s}{dt} = \kappa\chi.$$

For the step change described in this study,  $\chi_0=0$ . Combine all the equations, we have

$$\frac{d^2\chi}{dt^2} + \left(\frac{Q}{V} + \kappa\right) \frac{d\chi}{dt} = \kappa^2 \chi.$$

The general solution to the differential equation is

$$\begin{aligned} \chi &= A_1 \exp \left[ -\frac{1}{2} \left( \sqrt{\left(\frac{Q}{V}\right)^2 + 2\left(\frac{Q}{V}\right)\kappa + 5\kappa^2} + \left(\frac{Q}{V}\right) + \kappa \right) t \right] \\ &\quad + A_2 \exp \left[ \frac{1}{2} \left( \sqrt{\left(\frac{Q}{V}\right)^2 + 2\left(\frac{Q}{V}\right)\kappa + 5\kappa^2} - \left(\frac{Q}{V}\right) - \kappa \right) t \right] \\ &= A_1 \exp \left( -\frac{t}{\tau_1} \right) + A_2 \exp \left( -\frac{t}{\tau_2} \right) \end{aligned}$$

It can be seen from above derivation that the bi-exponential decay model approximates the universal solution of the differential equations, but it only works under certain conditions - the most important one is the relative cleanliness of the surface. After certain time,  $\chi$  will approach  $\chi_s$  and the solution to the differential equations becomes significantly more complicated and is unlikely to follow bi-exponential decay model. The authors should clarify the applicability of the bi-exponential decay model.

Given the validity of the bi-exponential decay model, it may be more reliable to derive  $t_{90}$  and  $t_{99}$  using observed time series directly if the measurements are not noisy.

$\tau_1$  and  $\tau_2$  represents the combined effects of both gas exchange and air-surface exchange instead of representing the effects separately. Therefore, the statements about  $\tau_1$  and  $\tau_2$  from line 22 to line 24 on page 10 should be removed.

### 3. Uncertainty of response time may not be representative:

The uncertainty of the response time is currently estimated using error propagation of the fitted results. However, given the exponential natural of the issue, parameters like  $t_{90}$  and  $t_{99}$  may have a skewed distribution (i.e. log-normal distribution) with a long tail. This behavior may not be correctly captured by error propagation method. If fitted results are used, Monte Carlo method should be used. If the real time series is used,  $t_{90}$  could be estimated as the standard deviation of time stamps of observations with  $\text{NH}_3$  between the  $90 - \sigma_{obs}$  percentile and the  $90 + \sigma_{obs}$  percentile.

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Summary: The authors have shown a marked improvement in the use of airborne-based ammonia measurements. In fact, these measurements are the most impressive and reliable to date in the literature and have set a new standard for all future campaigns (airborne and ground-based). The technique has applicability to Picarro and other closed-path sensors, as well as calibration methods for open-path sensors (which, indeed, have to be “closed” typically for calibration). However, there are still many gremlins for airborne ammonia, particularly with its enormous dynamic range in concentration

and adsorption issues, which get magnified for sub-ppbv NH<sub>3</sub> levels that are expected in the free (or at least upper) troposphere (Asian UT monsoon levels excepted, possibly). I hope the points above allow for some clarifications that strengthen the manuscript.

\*\*\*\*others\*\*\*\*

Page 11, line 4-10: The manuscript never mentions how the boundary layer height was determined. Was it known accurately in each case or simply assumed to be <1 km?

Page 12, line 40-45: The authors should be aware that the relationship between water content and NH<sub>3</sub> adsorption is not necessarily linear. The interaction mechanism varies significantly depending on the amount of water present. A previous study by Vaittinen et al., 2018, has demonstrated this. Therefore, the two scenarios (dry vs 80% humidified) tested here may not be representative enough to tell the whole story.

Page 13, line 40-43: It is not clear what criteria the authors used to determine that the NH<sub>3</sub> transmission shows little difference between the non-passivant and with-passivant transects. (By the response time/maximum reading/amount of the NH<sub>3</sub> measured?)

Figure 6a: It would be helpful to show the exact boundary layer height for this profile for better clarity.

Figure 8 (upper): I am confused by the brown circles/dots labeled as beef and dairy. Do the small dots indicate smaller facilities as compared to the large circles? The two circles on the upper and lower right presumably refer to dairy but there is a dot in the center of each circle. Does this mean the facilities have both dairy and beef?

The total power output of the system should be described, since power seemed to be an issue even on an aircraft.

Abstract: "Flight-ready" in the abstract seems redundant for the topic; also "custom" is mentioned three times in the first sentence.

For the Allan plot, what offset was applied and how much? As written, it is confusing.

SilcoNert 2000 has been shown to work very well for ammonia and water vapor adsorption – can the authors – Pogany et al., Meas. Sci. Tech., <https://iopscience.iop.org/article/10.1088/0957-0233/27/11/115012/meta>

## References

1. Ellis R, et al. (2010) Characterizing a quantum cascade tunable infrared laser differential absorption spectrometer (QC-TILDAS) for measurements of atmospheric ammonia. *Atmospheric Measurement Techniques* 3(2):397-406.
2. Roscioli J, Zahniser M, Nelson D, Herndon S, & Kolb C (2015) New Approaches to measuring sticky molecules: improvement of instrumental response times using active passivation. *The Journal of Physical Chemistry A* 120(9):1347-1357.
3. Sun, K. et al., JGR, 2015.