Response to Interactive Short Comment SC1 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

We thank the Zondlo group for their extremely thoughtful and constructive feedback. This discussion exemplifies the value of this particular forum. Please find the commenters suggestions highlighted in bold font below followed by our reply in plain text.

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_3 concentrations (10s-100s ppbv NH_3) 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_3 variations should be discussed (and backgrounds relevant to very low free tropospheric values, <ppbv). The detection limit needs better justification.

Thank you for these comments. See our responses below each specific comment/suggestion related to these topics.

In this study, the step change of NH_3 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_3 concentrations and large variations, NH_3 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_3 concentrations, a greater fraction of NH_3 molecules may interact with the inner surface.

We agree that a limitation of these experiments is a lack of tests with lower mixing ratios of NH_3, which could affect the applicability of these results to some specific applications, namely the remote free troposphere. As the commenters point out, the effect of decreasing instrument response time with increasing step change concentration has already been extensively characterized by Ellis et al. Therefore, the main goal of this paper is to further the works of Ellis et al. (2010) and Roscioli et al. (2016) by characterizing the effects of passivant addition on instrument time response in flight. For this discussion we also note that the results of Ellis et al. were reproducible in our own experiments when time profiles were generated with various levels of step change concentrations. One of which included a step change from ambient levels of NH_3 (e.g., between 5 and 12 ppbv) to zero, which was generated by switching on the overflow injection of NH_3-free air at the inlet tip after a period of sampling near homogeneous levels of ambient NH_3 for several minutes. All the same, we agree with the commenters that the text should be amended to clarify that these results may be most applicable to near source sampling because the instrument utilized for these experiments was optimized for sampling large and rapid gradients of NH_3 in smoke.

In response to this and the next comment, we have added the following text to Section 4.4:

"All the same, further measurements are recommended for assessing sampling biases that could arise during field measurements of low mixing ratios of NH_3 in clean environments following long periods of exposure to near source level concentrations. The potential for an adsorption-related "memory effect" of NH_3 (e.g., Williams et al., 1992) on the sampling surfaces following long-term exposure to high concentrations of NH_3 is discussed in following sections."

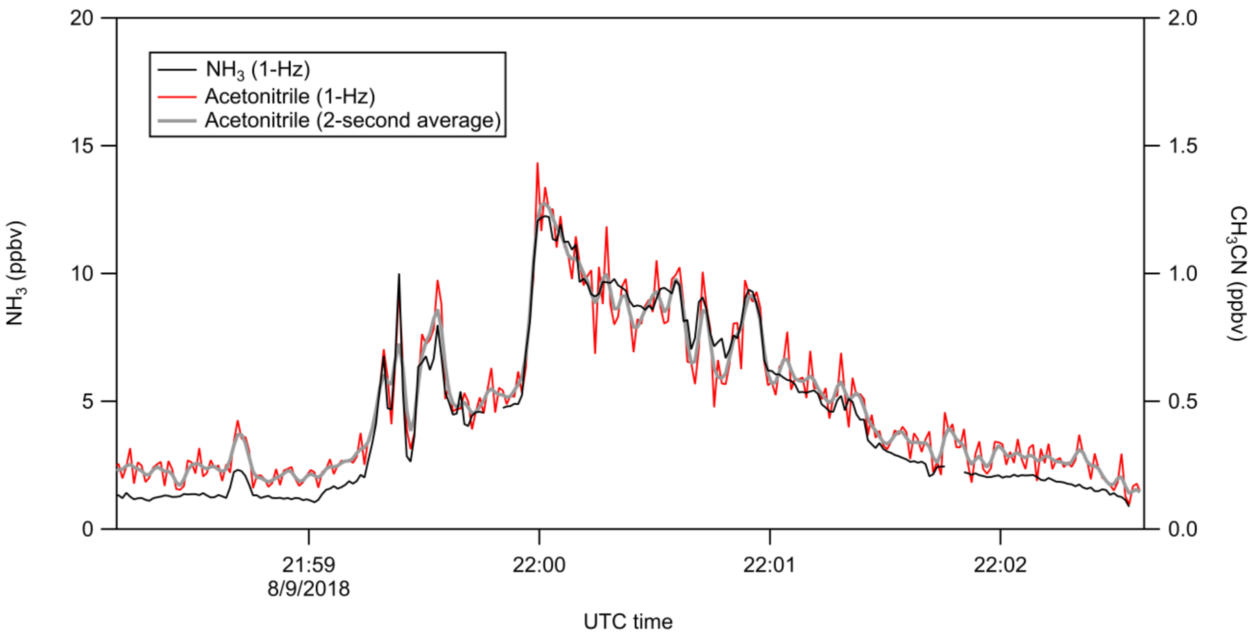
And we added this text to Section 5.1.1:
"In this study, the instrument response is rigorously tested with a single step change of NH_3 created by turning off a 50 ppbv calibration gas mixture. We note that such large variations in NH_3 mixing ratio may not been full applicable to field measurements in unpolluted regions away from concentrated sources of NH_3. As described by Ellis et al. (2010), large gradients in NH_3 may be less impacted by surface interactions because "clean" sampling surfaces only have a finite number of adsorption sites that could be quickly filled under high NH_3 conditions. At lower NH_3 concentrations, a greater fraction of NH_3 molecules may interact with the inner surfaces. This could explain why passivation did not help to increase the response time of the instrument."

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_3-free and low NH_3 gases. Therefore, even a "clean" closed-path instrument may not be capable for high-frequency (>1 Hz) field application with small NH_3 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_3 concentrations (e.g. flux measurements in rural area and airborne observations away from sources).

We greatly appreciate your comments with respect to the comparison of time responses that we collected with those reported by Roscioli et al. (2016). While we frame the results of the time response tests so that they can be directly compared to the works of Ellis et al. (2010) and Roscioli et al. (2016), we believe that it is difficult to compare the level of cleanliness of two different instrument systems. In this particular case, it may not be fair to say that our "clean" (aka. pristine, out-of-the-box, never-used-in-the-field) instrument is the same level of cleanliness as the copiously flushed, yet previously deployed instrument used by Roscioli et al. We are fortunate to know the history of both instruments, and surmise that the QC-TILDAS utilized by Roscioli et al. (2016) more closely resembles an instrument with a mid-level of cleanliness (similar to what we define as a "typical" operating condition) rather than the pristine, out-of-the-box condition that we referred to as "clean" in this work. This is because the instrument utilized by Roscioli et al. was a dual channel QC-TILDAS optimized to measure NH_3 as well as HNO_3 (aka. two well-known sticky molecules). Prior to lab tests, the instrument was deployed aboard the NSF/NCAR C-130 research aircraft in the 2014 FRAPPE field campaign where it had been exposed to near source levels of NH_3 and urban emissions in the Colorado Front Range. Further, during the lab tests, the dual channel instrument was used to test several strong bases as passivant agents for NH_3 and several strong acids as passivant agents for HNO_3. In our experience with contamination and cleaning of sampling surfaces, we found that the instrument flow path could only be truly cleaned by replacing tubing and inlet components where possible and by performing several cycles of ethanol/water rinse followed by week-long periods of flushing the sample flow path with NH_3-free air. The dual channel instrument was solely flushed with NH_3-free air prior to lab experiments, but sampling surfaces were not systematically cleaned and replaced. For these reasons, we categorize the instrument used by Roscioli et al. as an instrument operating under a middle level or cleanliness, like our "typical" operating condition. We also point out that Roscioli et al. (2016) found that the NH_3 time response of the instrument continually improved with increasing passivation concentration, presumably with an eventual lower limit somewhere at or above the volumetric flush time. Therefore, the degree to which one wants to achieve >1 Hz sensitivity can be determined by the amount of passivant added to the sampling system. In the case of the flights discussed here, we made a compromise between passivant use and time response in order to achieve a reasonable temporal response while not using an excessive amount of passivant. All the same, we agree with the commenters that further discussion is warranted about the applicability and effectiveness of active continuous passivation to field applications with relatively low NH_3 concentrations, such as flux measurements in rural areas and measurements away from sources. We now include this statement in Sect. 4 and reiterate this point in Sect. 5. See the text pasted in response to comment above.

<u>Fig. 10:</u> **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_3, 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.**

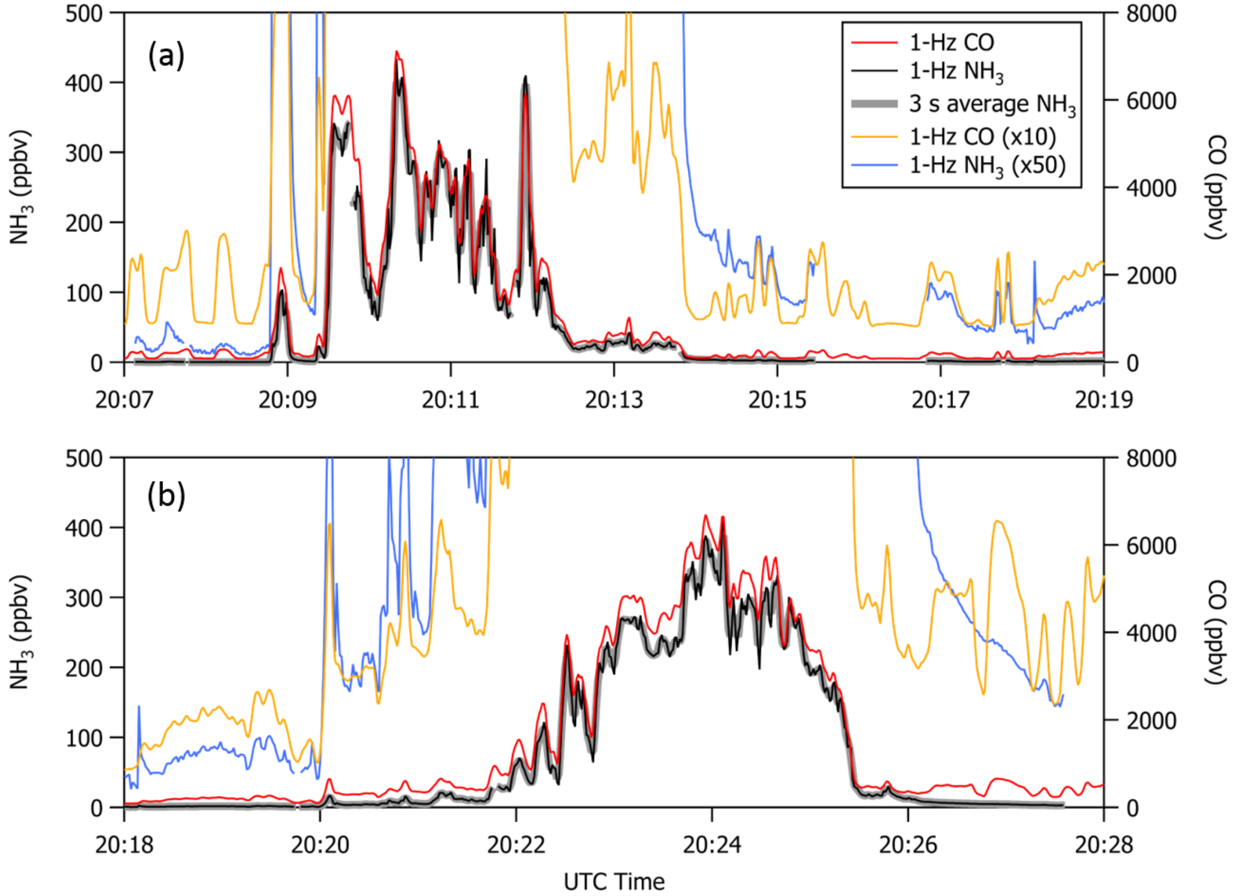
We agree with the commenters suggestion of trying to compare with a true 1 Hz tracer. We have identified acetonitrile, measured with the PTR-ToF-MS, as a better 1-Hz tracer that is well correlated with NH_3 in smoke. Unfortunately, we do not have measurements from the PTR-ToF-MS during RF15 when the aircraft performed transects of the S. Sugarloaf fire and the NH_3 instrument was systematically operated with and without passivant in flight through smoke. Instead, we use measurements of acetonitrile from the Bear Trap Fire (RF09) conducted on 09 August 2018 to perform a similar linear regression comparison of fine structure features as that described earlier in Sect. 5.2.2. Briefly, we conducted linear regression analysis of scatter plots of NH_3 versus CH_3CN incrementally averaged from 1 to 5 seconds until linear regression resulted in a maximum R^2 value. We found the best fits resulted from regressions of measured NH_3 with the 1-Hz reported and 2-second averaged CH_3CN ($R^2 > 0.97$ and within 0.001 of each other). A timeseries of NH_3 and CH_3CN from an example plume transect of the Bear Trap Fire in RF09 is included here for discussion with the commenters and mentioned briefly in the text, but since we cannot produce the same figure for RF15 when the NH_3 instrument was systematically tested with and without passivant, we feel that adding this as a figure to the paper does not add much to the discussion. We also note that there is little hysteresis in the recovery of background ratios of NH_3 to CH_3CN following the plume transect in RF09.



We assert that the NH_3 observations are well correlated with the 1-Hz reported CH_3CN data as well as the 2-second average of CH_3CN in the discussion by adding the following text to the end of Sect. 5.2.2: "Since the time response of the CO measurement was limited by its sample flow rate and inlet configuration, we also compare NH_3 to acetonitrile (CH_3CN) measured by the PTR-ToF-MS. CH_3CN is well correlated with NH_3 in smoke, and may be more representative of a true 1-Hz tracer owing to operation of the instrument inlet at a flow rate of ~15 SLPM. However, there are no measurements from the PTR-ToF-MS during RF15, the research flight during which the NH_3 instrument was systematically tested with and without passivant. Instead, we use measurements of CH_3CN from the Bear Trap Fire (RF09) conducted on 09 August 2018 to perform a similar linear regression analysis of fine structure features of measured NH_3 versus CH_3CN, with CH_3CN incrementally averaged up to 5 seconds. We find the best fits result from linear regressions of measured NH_3 with the 1-Hz reported and 2-second averaged CH_3CN (R^2 is > 0.97 and within 0.001 of each other)."

There are also some differences between the start and end of the plumes in Fig. 10 in terms of the NH_3/CO ratio. As one progresses in the plume, the NH_3/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_3/CO level isn't the same, either.

We recognize that there could be differences in the NH_3/CO ratio between the start and end of the plumes in Fig. 10. Indeed, differences in background mixing ratios of NH_3 compared to CO before and after the first transect of the S. Sugarloaf fire are apparent when the NH_3 and CO signals in Fig. 10 are magnified by a factor of 50 and 10, respectively. To highlight this difference, we have amended the time series in Fig. 10 as follows:



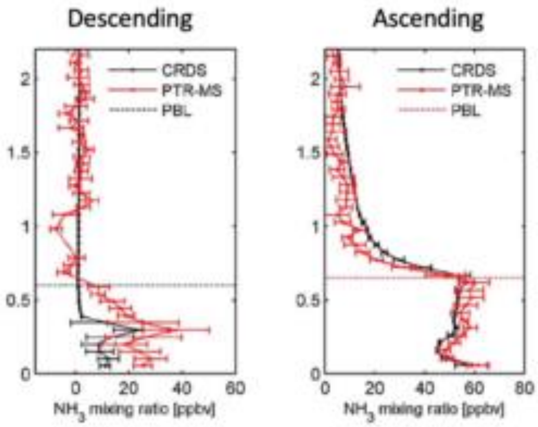
Updated caption for Fig. 10:

Time series of 1-Hz NH_3 (black lines) and CO (red lines) measured during a crosswind transect of the smoke plume from the South Sugarloaf Fire (RF15) on 26 August 2018. The transects represent nearly identical passes through the smoke plume with the only perturbation of the NH_3 instrument being operated (a) with passivant and (b) without passivant. Changes in fine structure features of NH_3 have the strongest R^2 correlation with CO when the NH_3 measurements are averaged to 3 s. A x50 magnified view of 1-Hz NH_3 (blue lines) and x10 magnified view of CO (orange lines) shows differences in background levels of NH_3 compared to CO before and after each plume transect.

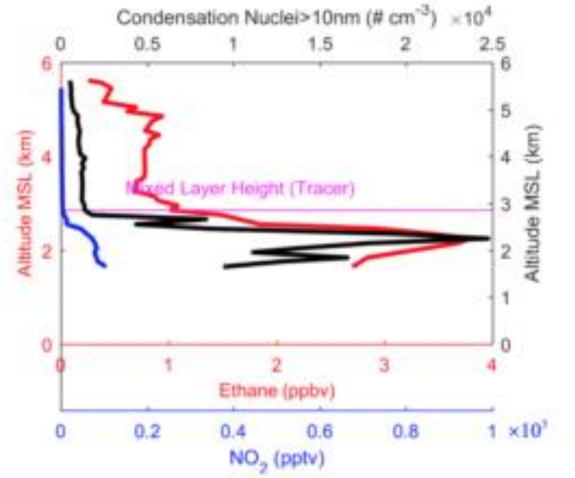
[As context for this discussion, we note that the instrument inlet was overblown with NH_3-free air for the duration of a 2-hour pre-flight exercise prior to take off. Following take-off, the instrument sampled a maximum of 5 ppbv NH_3 during ascent out of Boise and was then exposed to < 1 ppbv NH_3 for 1-hour during transit to the S. Sugarloaf fire.]

As the commenters suggest, there could be several causes for the differences in NH_3/CO ratio observed before and after the plume transect in Fig. 10. One reason could be physical differences in plume chemistry, mixing, or background composition. Another could be "memory effects" in the sample plumbing due to retention of NH_3 adsorbed to sampling surfaces following exposure to NH_3 mixing ratios in excess of 400 ppbv (Williams, et al., 1992). The observation could also reflect some combination of both. While distinct differences in background are apparent in Fig. 10, we note that differences in background before and after the plume were not always observed during WE-CAN research flights (e.g., RF07 conducted on 06 August 2018 described in the next section of this response). Since the root of the differences are not immediately obvious and because differences seem to vary among the WE-CAN research flights, we now also include a response time for the signal recovery shown in Fig. 10 assuming the worst-case scenario that the differences in background are solely attributed to memory effects on the sampling surfaces. In this worst case, the time for the NH_3 measurement following the plume transect to recover to near background mixing ratio levels observed prior to the plume transect (e.g., 1 ppbv) is roughly 250 s. This time frame most closely resembles $t_{99,obs}$ for the “typical” operating condition when operated with or without passivant. To highlight the commenter’s points, we have amended Sect. 5.2.2 with the following text: “Differences in background mixing ratios of NH_3 and CO measured before and after the first transect of the smoke plume from the S. Sugarloaf fire are apparent in the magnified timeseries for each in Fig. 10. The differences in NH_3/CO ratio observed at 20:14 UTC and 20:25 UTC following in-smoke measurements of NH_3 that exceeded 400 ppbv could have resulted from physical differences in plume chemistry, mixing or background composition on either side of the plume, adsorption-related memory effects in the sample plumbing due to retention of NH_3 molecules adsorbed to the sampling surfaces (Williams et al., 1992), or a combination of both. Since the root of the differences are difficult to distinguish and may vary among the WE-CAN research flights, we utilized these differences to characterize the instrument time response given the worst-case scenario that the differences in background observed in Fig. 10 are solely attributed to memory effects on the sampling surfaces. In this worst case, the response time for the NH_3 measurement following the plume transect to recover to near background mixing ratio levels observed prior to the plume transect (e.g., 1 ppbv) is roughly 250 s. The time frame most closely resembles $t_{99,obs}$ for the “typical” condition when the instrument is operated with or without passivant. This recovery time and “typical” cleanliness condition are within our expectations for the instrument during this research flight (RF15) since the instrument had routinely been used to sample near source concentrations of NH_3 in smoke during several prior consecutive research flights without refreshing the sampling surfaces between flights.”

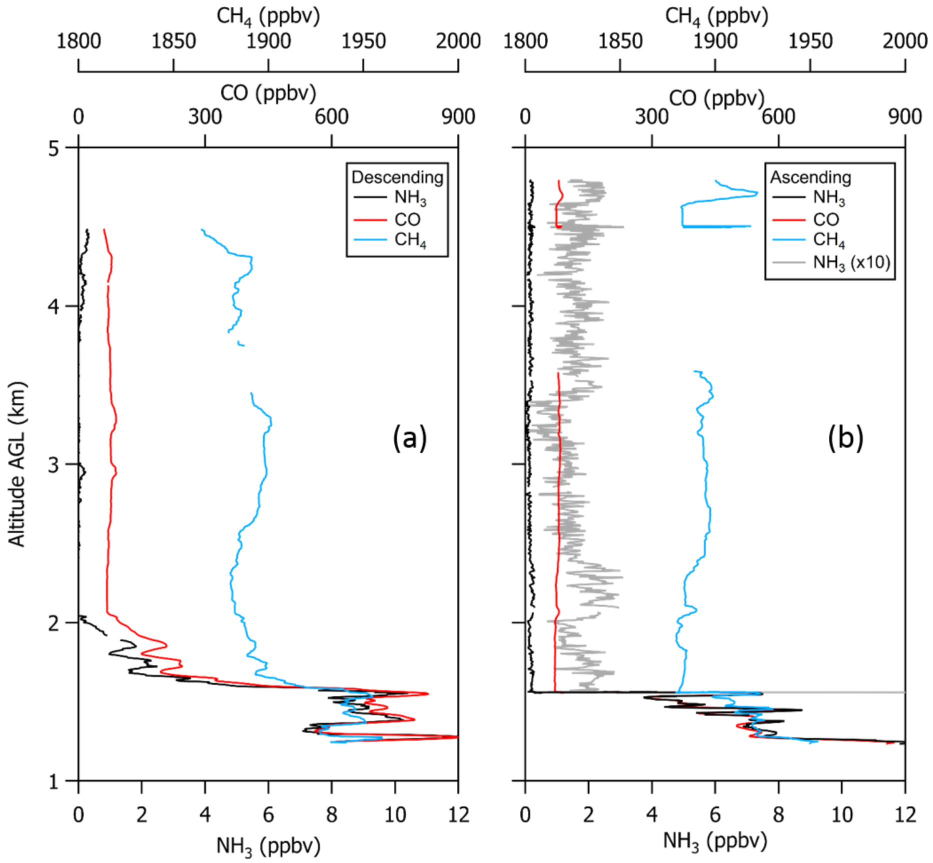
Related to this overall point, on the large y-scale axis (500 ppbv NH_3) in Fig. 10, while the concentration looks to be “close” to zero, in reality on this scale it could be numerous ppbv NH_3. Even if the instrument response time is nominally on the order of a few seconds, going from 400 ppbv NH3 to sub ppbv NH_3 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 NH3 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_3 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_3 to nominally sub-ppbv NH_3 at high altitude could still be an issue even with this approach. Also attached on the right is a profile of NO_2, 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_3 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.



(Sun et al., 2015)



We agree that comparing vertical profiles from an ascent and descent is a great suggestion. While we do not have extensive enough vertical information from the test flights near Greeley, we do have a spiral over the California Central Valley about 60 miles southeast of Sacramento during WE-CAN research flight RF07 conducted on 06 Aug 2018. The spiral aimed to sample aged smoke in the Central Valley, and thus consisted of a descent followed by a spiraling ascent spanning between 4.5 km and 1.2 km AGL. As such, the observations (shown below) likely reflect a combination of aged smoke and agricultural emissions. Changes in NH_3 are consistent with changes observed for other tracers. While it may appear that there is some hysteresis in NH_3 compared to CO and CH_4 around 1.5 km as the aircraft ascends through the mixed layer, a closer look (e.g., NH_3 magnified x10 in the figure below) shows that NH_3 mixing ratios immediately drop to ≤ 200 pptv. To put these observations into context of the ”memory effect” discussion above, it should be noted that the maximum NH_3 mixing ratio prior to ascent during the spiral in RF07 was < 15 ppbv compared to the background measured in RF15 following a smoke plume transect where NH_3 was > 400 ppbv. A systematic analysis of the WE-CAN research flights for physical differences in plume chemistry, mixing, background composition, and hysteresis with plume concentration are beyond the scope of this work, but several of these topics are forthcoming in WE-CAN publications. Therefore, we include the discussion of a worst-case scenario of hysteresis in the manuscript, and only provide the following plots of vertical profiles for discussion with the commenters.

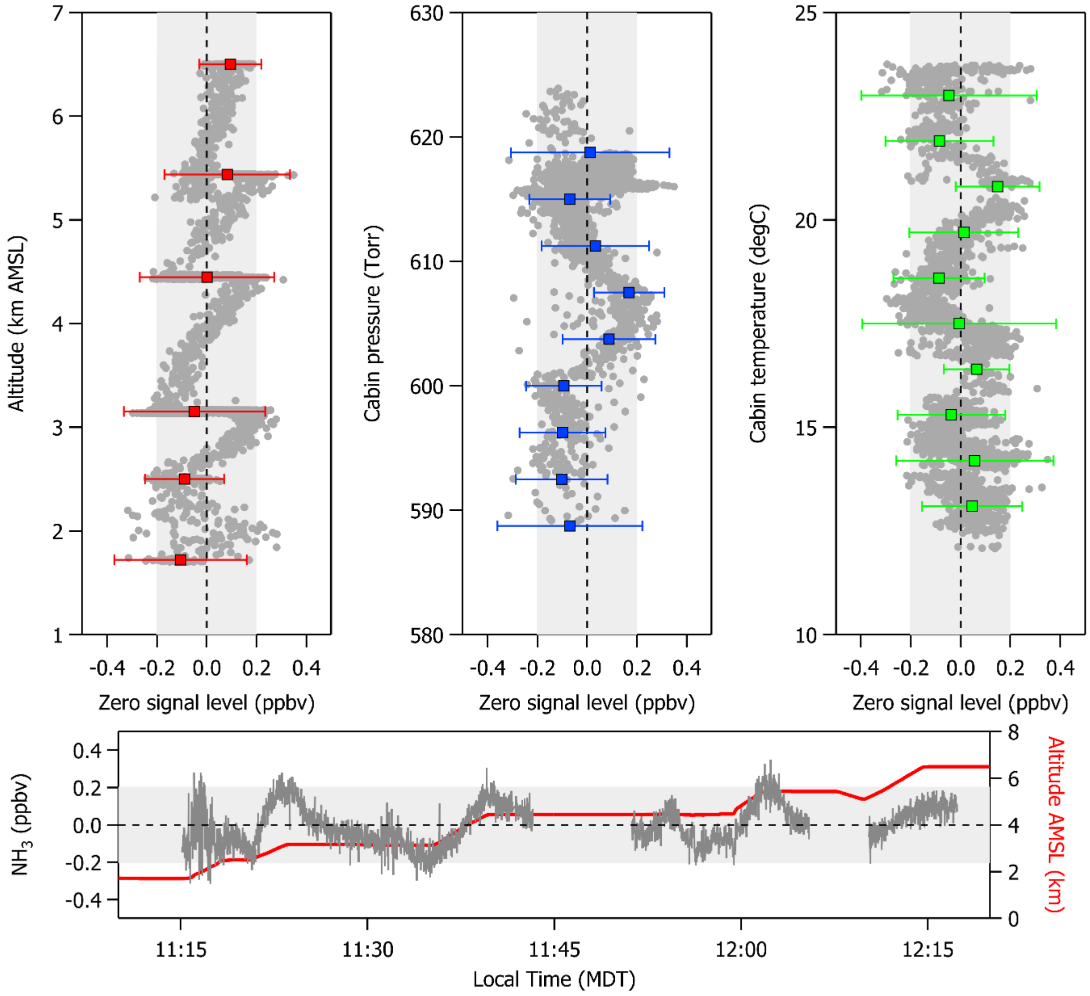


<u>Figure 3:</u> It is hard to see on Fig. 3a, but the constant altitude segments seem to show quite a bit of variability in the background, say, from -0.2 to +0.2 ppbv NH$_3$ within an altitude level for a given 1 Hz measurement. This calls to question as well the accuracy of anything < 0.5 ppbv, given 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$_3$ 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$_3$ 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.

The symbols and error bars in Fig. 3 represent the mean and 3σ standard deviation of the mean measured zero level during constant altitude legs. Here, we purposefully depict the 3σ standard deviation to illustrate the range of variability with respect to 3 times the Allan deviation, which we defined as the instrument's limit of detection. However, it is true that the zero signal level in Fig. 3 spans ±200 pptv around zero, or 400 pptv total. While we continue to report 3 times the precision as determined from the Allan variance since this is how the detection limit for similar instruments is reported in the literature, we have added the following to Sect. 4.1: "We note that the true detection limit of the instrument in flight may be better represented by the full range of variability about the mean zero signal level from the observations in Fig. 3 (e.g., an instrument detection limit of 400 pptv)." We have also added this information to the abstract.

Ascent profiles were typically performed at ~1000 ft/min. The 50 pptv sensitivity reported in Fig 4 and Sect. 4.2 is specific to turbulence and turns. To further clarify the variations in NH_3 zero signal level with altitude in Fig. 3, accelerations at the onset of an ascent at 1000 ft/min were measured to be 0.4 g for the up-down motion, 0.1 g for the side-side motion, and 0.07 g in the fore-aft motion. Given the accelerations during ascent and the slopes of the measured motion sensitivities (in units of ppbv/g) determined from Fig. 4., it is reasonable to expect as much as 400 ppt of variability from motion sensitivity. Sect. 4.1 and 4.2 have been updated with the following text to clarify the observations during ascent between constant altitude legs in Fig. 3: “It should also be noted that large accelerations in the up-down and fore-aft dimensions are also significant at the onset of vertical ascent. Accelerations measured in the up-down and fore-aft motions at the onset of a 1000 ft/min vertical ascent were measured to be 0.4 g and 0.08 g, respectively. Given the slopes above, these accelerations correspond to a maximum change in NH_3 zero signal level of 400 pptv during ascent, which is consistent with the variability in zero signal level observed in Fig. 3 when ascending between constant altitude legs.”

We have also added a time series of the vertical ascent profile while overblowing the inlet tip with NH_3-free air to the bottom of Fig. 3, as shown here.



Updated caption for Fig. 3:

In-flight variations in zero signal level (in units of ppbv of NH_3) with respect to changes in (a) altitude, (b) cabin pressure, and (c) cabin temperature. A time series (d) illustrates the effects of motion sensitivity on the zero signal level as the aircraft initiates an ascent and then levels off at a constant altitude. Gray symbols and lines represent the

1 s average of all of the 10-Hz data points collected in flight while overblowing the inlet tip with NH_3-free air; the red line in the time series is altitude AMSL. Colored symbols and error bars in the vertical profiles represent the average NH_3 zero signal and 3σ standard deviation for each constant altitude level, 5 Torr increments in cabin pressure, and 2˚C increments in cabin temperature. Variations are largely within ±200 pptv (denoted by the light gray shaded areas).

For further context, we have also added the following detail to Sect. 4.2: "For these experiments, the instrument inlet was continuously overflowed with NH_3-free air for the duration of a 3-hour pre-flight exercise prior to take off. Overflowing the inlet was purposefully done to keep the instrument system free of contaminants (e.g., exhaust from other aircraft and ground-based support equipment) prior to sampling in flight."

We added similar info to Sect. 5.2.2: "It should also be noted that during WE-CAN, the NH_3 instrument was typically zeroed between crosswind transects of a wildfire smoke plume when in background air and either just prior to or during turns. The instrument was zeroed every 10-20 mins during transits from Boise to the wildfires sampled with the frequency of zeros depending on the transit time. Zeros measured during WE-CAN research flights were typically collected for a period of 1 to 2 minutes, a duration much greater than the instrument response time, to ensure that zeros were measured well within 90% of the final zero signal level. Prior to each research flight, the NH_3 instrument was overflowed with NH_3-free air for the duration of a 2-hour pre-flight exercise."

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.

We have updated the discussion about detection limit given the 400 pptv variability in Fig. 3. We have also added notes about sampling biases in accord with the responses above.

2. 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_3 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_3 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 biexponential decay model and discuss its validity.

After a step change, changes of the mixing ratio of NH_3 inside the instrument χ is caused by 1) the

difference of NH_3 mixing ratio between the gas currently inside the chamber and the newly introduced gas (χ_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; κ is the conductance of NH_3 between surface and air interface; χs 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_3 concentration inside the instrument. When there are no phase changes and chemical reactions, and the surface is not saturated by NH_3 or exhausted of NH_3 during the process, χs could be simplified as

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

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

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

For the step change described in this study, χ_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

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

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, χ will approach χs and the solution to the differential equations becomes significantly more complicated and is unlikely to follow biexponential 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.

τ_1 and τ_2 represents the combined effects of both gas exchange and air-surface exchange instead of representing the effects separately. Therefore, the statements about τ_1 and τ_2 from line 22 to line 24 on page 10 should be removed.

We greatly appreciate the time and effort by the commenters to provide us with a detailed surface-air exchange model for the bi-exponential decay. We would be happy to include your model in this paper or future papers if a peer-reviewed reference can be provided. However without that, we feel that derivations of this model are beyond the scope of this paper, and it seems more appropriate for the commenters to develop this model as the originators of these concepts. All the same, we agree that the bi-exponential fits do not always provide a perfect representation of the observations, which could indicate instances where the model fails to adequately describe the physical system. As suggested by the commenters, we now also include values for t_{90} and t_{99} in Table 1 that are directly determined from the observations in Fig. 5. The new parameters are denoted as $t_{90,obs}$ and $t_{99,obs}$. However, we also continue to frame the results using the existing bi-exponential decay model in the literature for the following reasons: 1) as a way to provide context for fitting the time response profiles, 2) for consistency with the approach utilized in the peer-reviewed literature for similar instruments (Zahniser et al., 1995; Ellis et al., 2010; Roscioli et al., 2016), and 3) for ease of comparison to prior assessments with similar instrumentation by Ellis et al. (2010) and Roscioli et al. (2016).

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 NH3 between the 90 − σ_{obs} percentile and the 90 + σ_{obs} percentile.

For comparison to the uncertainties derived from error propagation of the bi-exponential fit coefficients, we now also include an observation-based determination of the uncertainties for $t_{90.\text{obs}}$ and $t_{99,obs}$ in Sect. 4.3. These uncertainties reflect the Δt spread in times associated with the 90±1% and 99±1% signal recovery levels, where ±1% on the signal recovery level corresponds to ±0.5 ppbv for a 50 ppbv step change, which is within the instrument's limit of detection.

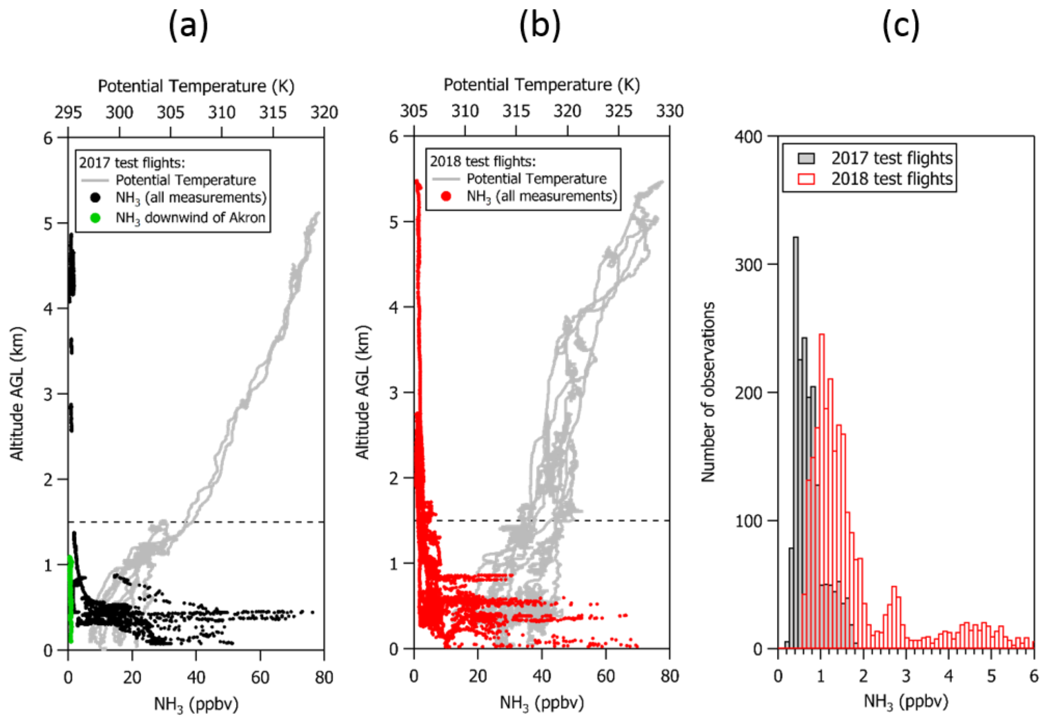
****

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 NH3 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?

A well-mixed layer below roughly 1 km was initially assumed. There could be differences in the structure of the boundary layer for the different test flights, which could be due to the colder/wetter ambient conditions during the test flights in September 2017 compared to the warmer/drier conditions during test flights in July 2018. Unfortunately, we have very few parameters to compare from the test flights as the instrument payload was minimal in 2017 and not all instruments were fully operational/optimized at the time of the WE-CAN test flights in 2018. On the other hand, we reliably have potential temperature, which was collected during each flight as part of the aircraft's standard suite of measurements. Vertical profiles of potential temperature do indicate a planetary boundary layer height was primarily between 1 and 1.5 km for both the 2017 and 2018 test flights. Although, there could have been more than one mixed layer during the 2018 test flights. We have added the following text to Sect. 4.4: "All the same, further measurements are recommended for assessing sampling biases that could arise during field measurements of low mixing ratios of NH_3 in clean environments following long periods of exposure to near source level concentrations. The potential for a "memory effect" of NH_3 on the sampling surfaces following long-term exposure to high concentrations of NH_3 is discussed in following sections." We have also modified Fig. 6 to include potential temperature and a rough guideline for the boundary layer height.



Updated caption for Fig. 6:

Vertical profiles of NH_3 (in ppbv) and potential temperature (in K) from (a) the first and third test flight in 2017 and (b) the test flights in 2018 when the instrument was operated without passivant. NH_3 mixing ratios as high as 80 ppbv were observed in the mixed boundary layer during missed approaches at Greeley-Weld County Airport and over northeastern Colorado compared to average mixing ratios of ~0.8 ppbv near Akron, Colorado following several days of rain. (c) Histograms of the corresponding NH_3 measurements collected above 1.5 km AGL (dashed line) show that measurements were frequently larger than 200 ppt, especially measurements that were collected in the free troposphere.

Page 12, line 40-45: The authors should be aware that the relationship between water content and NH_3 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.

We appreciate the commenter's points. The Vaittinen et al. (2018) and Pogany et al. (2016) references have been added to Sect. 5.1.3 and we have amended the section with the following text: "We only measured two extreme relative humidity conditions for these tests, even though the relationship of surface interactions may be non-linear and vary greatly depending on the fraction of water vapor added as suggested by Pogany et al. (2016) and Vaittinen et al. (2018)."

And, "…a caveat of these tests is that the humidity levels tested here may not provide enough information to fully characterize the effects of passivant addition over the full range of dry to humid sampling conditions. Further characterization of the humidity dependence with and without passivant addition is recommended prior to future deployments of this instrument system (or similar QC-TILDAS instruments) in humid field environments."

Page 13, line 40-43: It is not clear what criteria the authors used to determine that the NH_3 transmission shows little difference between the non-passivant and with-passivant transects. (By the response time/maximum reading/amount of the NH_3 measured?)

The comparison is based on the amount of NH_3 measured by the detector. We have amended the text on Pg. 13 to clarify.

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

We have amended Fig. 6 to include vertical profiles of potential temperature, which was measured as part of the aircraft's standard suite of parameters during the test flights. We agree that this is a helpful addition because of the subtle differences in mixed layers between the 2017 and 2018 test flight cases described above.

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?

We greatly appreciate the commenters finding these typos. The smaller dots are meant to indicate smaller facilities in terms of head of cattle, and some of the beef and dairy animal operations are collocated. All the same, the original plot did have some defects in symbol outlines and layering that complicated its appearance. The plot, legend, and caption have been updated to clarify these differences.

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

We have added a Sect. 2.4 to describe the power, weight and space utilized by the instrument. The following text has been added in this new section. “The instrument system described above in the configuration that it was utilized aboard the C-130 aircraft requires the space of an entire NSF/NCAR G-V aircraft equipment rack (approximate dimensions 21.5” W x 28” D x 50” H). The equipment without the rack weighed approximately 150 kg and included a 30 kg uninterruptable power supply (UPS) and a 10 kg display laptop. The total power used by the instrument system was 1600 watts, with roughly one third of this total (600 watts) being dedicated to the main pumping system (Agilent, model Triscroll 600, 100 lbs installed). It is possible that the power, weight and space required for this instrument system can be reduced for future deployments by eliminating the UPS and display laptop. It may also be possible to reduce the size of the pump if different field applications allow for a lower sample flow rate to be used.”

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

Agreed. We have implemented these changes.

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

We agree that the application of the offset is misleading as currently written. Owing to the vibration applied to the laser objective, the noise guidelines were offset by -150 ppt to align with the observations. The observations were not adjusted. We have updated Sect. 4.1 and the figure caption to clarify.

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.

We have added (Pogany et al., 2016) and (Vaittinen et al., 2018) to Sect. 5.1.3 to aid in discussion of the limitations of the humidity tests performed with and without passivant addition in this work. We have also added mention of other materials used in the past as potential passivant coatings to Sect. 2.2.5 via addition of the (Pogany et al., 2016) and (Yokelson et al., 2003) references. This reads: “Prior studies have shown inlet coatings such as a halocarbon wax (Yokelson et al., 2003) and SilcoNert 2000 (Pogány et al., 2016) can prevent the adsorption of NH_3 and water vapor on instrument sampling surfaces. While current coating technology can provide relatively non-sticky surfaces, we note that in field environments, these surface treatments can quickly become overcoated with dust, salt, and other condensables, that ultimately compromise their non-stick properties. Continual re-application of a non-stick coating via the active continuous passivation method described here mitigates this issue.”