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Comment on amt-2022-107

Anonymous Referee #2

Referee comment on "In-situ measurements of NH_3: instrument performance and applicability" by Marsailidh M. Twigg et al., Atmos. Meas. Tech. Discuss., https://doi.org/10.5194/amt-2022-107-RC2, 2022

GENERAL COMMENTS

The manuscript presented by Twigg et al. represents an important study towards improving the quality of in-situ ammonia (NH3) measurements. Significant challenges still exist in obtaining accurate and precise NH3 measurements, specifically in field observations where a large range of ambient conditions impact the performance of instrumentation. So far, there have been only a limited number of studies comparing different NH3 measurement methodologies under field conditions.

The authors present a comparison of 13 online instruments, spanning over the most important measurement techniques, and 1 type of passive samplers, making it to my knowledge the broadest NH3 intercomparison study conducted up to date. The authors use different statistical methods to compare the instruments determining their precision and accuracy. The comparison of closed-path systems with the open-path miniDOAS as well as employing some instruments of the same type with different inlet systems, allows the authors to investigate dampening effects caused by inlet tubing surfaces. Finally, the authors also give advice on what future measurement setup should consider such as regular calibrations (which were missing in this study).

The setup of the study, analysis of data and presentation of results was performed with great care, considering the major challenges of each instrument. Given the importance and uniqueness of the study, I suggest it to be published in AMT after addressing the comments below. The major parts where the manuscript in my view needs improvement is (1) the determination of the residence time and (2) the description of inlet tubing effects and the derivation of time constants.

SPECIFIC COMMENTS

P. 1, L. 35: The CEN EN 17346 reference protocol for passive sampling is from the year 2020, therefore, I suggest to write "first developed in the 1990s" or similar.

P. 2, L. 13/14: Other studies, which investigate ammonia emissions on PM2.5 formation on a global scale include Gu et al. (2021) and Pozzer et al. (2017)

P. 4, L. 19 ff (2.2. Instrumentation): I suggest to give similar details in the instrument description (where possible). Sometimes performance indicators (like detection limits) are given. 2.2.7 is the only section where the instrument operators are named. Providing wavenumbers for the spectroscopic techniques in 2.2.4 and 2.2.5 would be beneficial.

P. 4, L. 23: Do you mean ½" OD? In Table 2, the tubing diameter is given as 9 mm, which is less than ½". In Table 2, I suggest to specify that the value represents the inner diameter.

P. 4, L. 24 ff & Table 2: When calculating the residence time from the flow rate and tubing dimensions, the pressure drop along the tubing and respective volume flow increase needs to be taken into account. Looking at some of the values in Table 2, is seems a constant volume flow was used for the calculation, is that correct? If so, values would need to be adjusted for the pressure drop, which would lead to faster residence times (assuming that given flow rates are at STP).

The residence time of the manifold (+inlet) is given as 1.8 s, however, in Table 2 both add up to 1.62 s. Is that correct? In Table 2, it should be specified if flow rate was at STP or different temp/pressure conditions.

P. 13, L. 13: I suggest to state the sampling interval (of the 282 ppb) to be clear that this is based on the original sampling interval and not on the 1 hr resolution (as in Table S1).

P. 17, Figure 6 caption: NH3 mixing ratios is the median value (as reported above)? If so, it should be clarified.

P. 17, L. 21 ff: The response time due to inlet effects was determined by low pass filtering the respective instrument time series to match the unattenuated miniDOAS time series.

While this approach seems sound, the retrieved response times seem very high (e-folding time ranging to more than 2 hrs). Another way to determine the response time is by investigating the exponential decay/rise during calibrations (when zero or span is applied). From Figure 13 a) the OGS (i.e. Picarro #2), seems to have a much lower e-folding time. E.g. the 63% (1-1/e) increase at the step change from 0 to 10 ppb (which would represent ambient conditions) seem to be reached within 1 min as opposed to the 49.5 min with the method used here.

The dampening effects of ammonia in inlet systems is better described by a double exponential function with a fast time constant that represents the air exchange in the inlet tubing and a slower time constant that describes the adsorption and desorption effects (Ellis et al., 2010). E.g. Moravek et al. (2019) showed the evolution of the dampening over time using the double exponential function.

Even if a single exponential decay/increase is used (-> the low pass filtering method yields a single time constant), the authors should include the time constant values from the calibration measurements, also as comparison with other studies. Also, it should be explained why the time constants of both methods (i.e. low pass filtering and visual fitting to miniDOAS time series) would be so different.

P. 18, L. 10-12: Why was it discounted or what is your underlying hypothesis regarding the influence of a turbulent flow regime? I would have thought the opposite: if laminar flow conditions are increasing the dampening (due to segregation along the tubing cross section), this would explain why the Picarro #1 does not perform as well as the Picarro #2 (a similar statement is expressed by the surface/volume ratio).

P. 21, Figure 8: The y-axis offsets from the linear regressions are used to describe the accuracy (i.e. over- or underestimation) of the respective instruments at low mixing ratios. However, the offset may also result in uncertainties in the linear fit (lowest ensemble median mixing ratios are just under 2 ppb). Was this taken into account?

P. 32, L. 24 ff: The authors use the results of the linear regression between instruments to described the precision. While the R2 value is influenced by the instruments' precisions, the slope would rather indicate the accuracy of an instrument in comparison to the ensemble median. I suggest to make clear that the precision only refers to the R2 value and not the slope.

P. 34, L. 25 ff: Next to the tubing material, contamination of the tubing surface over time can influence the time response significantly (e.g. Moravek et al., 2019). Although the experiment was probably not long enough for it to have a major influence, this point may be included in the discussion.

P. 34, L. 34 ff: Next to avoiding condensation, inlet line heating was shown to improve the time response in previous studies (e.g. Ellis et al., 2010). This should be mentioned here as well.

P. 35, L. 13 ff: Ideally, the humidity in the zero air would match the ambient air humidity levels. One way to produce zero air is by removing NH3 from ambient air through a heating catalyst (without a drying cartridge or similar). Assuming that the water vapor is conserved, the zero air would then have similar humidity levels than the ambient air. Next to its influence on spectroscopy, humidity levels can also affect the adsorption/desorption processes in the inlet line. Therefore, having humidified zero air (at least to some degree) would be a beneficial for all instruments with an inlet line.

TECHNICAL COMMENTS

P. 7, Table 2: Typo in "AiRRmonia #1" & "Operated with a filter" -> "No"

P. 7, L. 14: "are sampled" instead of "is sampled"

P. 7, L. 15: do you mean "through which air is drawn and …"?

P. 7, L. 27: ("Erisman, 2001)"

P. 22, L. 7: Insert space before "ppb".

P. 25, Figure 10: "a)" and "b)" missing

P. 33, L. 13: Move comma to at the end of subclause (after parentheses in L. 14).

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