Atmospheric Measurement Techniques Discussions

Atmos. Meas. Tech. Discuss., author comment AC1
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Reply on RC1

Tatiana Macé et al.

Author comment on "Air pollution monitoring: development of ammonia (NH_3) dynamic reference gas mixtures at nanomoles per mole levels to improve the lack of traceability of measurements" by Tatiana Macé et al., Atmos. Meas. Tech. Discuss., https://doi.org/10.5194/amt-2022-6-AC1, 2022

We would like to thank the referee for reading our paper and for their comments.

Pg 1 line 17 : why choosing an amount fraction range between 1-400 nmol/mol ? It could be interesting to argue this choice in order to know the limits of this method development.

- Because this amount fraction range covers the NH3 amount fractions measured in ambient air (immissions) by the monitoring networks
- The draft has been modified in this way

Pg 2 line 33 (+abstract) : Need reference for effect on human health ? Which guidelines ? In fact NH3 at ambient levels have mostly effect on ecosystems. Direct effect on human health occurs at higher concentration (for instance in livestock buildings).

- Referee is right.
- We have modified the sentence as follows: “Measuring ammonia (NH3) in ambient air is a sensitive and priority topic because of its harmful effects on ecosystems at these low amount fractions (0 to 400 nmol/mol).”

Pg 2 line 37 : « In 2016, estimations suggested 4.2 million premature deaths worldwide caused by suspended particles (WMO, 2018). » not exactly à 4.2 million premature deaths worldwide caused by ambient air pollution and 2.5 million for PM2.5 exposure.

- According to our reference WMO (2018): "Ambient (outdoor) air pollution in both cities and rural areas was estimated to cause 4.2 million premature deaths worldwide per year in 2016; this mortality is due to exposure to fine particulate matter of 2.5 microns or less in diameter (PM2.5), which cause cardiovascular and respiratory disease, and cancer".
- In order to correct our figures accordingly, we would appreciate if the referee can provide the reference stating that 2.5 million premature deaths worldwide are cause by PM2.5 exposure.

Pg 2 line 42 : 60 % ? àprecise on which spatial scale?

- We have modified the draft as follows:
- “The latter accounts for about 60 % of the total NH3 global emissions based on grids models 2° x 2.5° or 2° x 3.0° “

Pg 2 line 46 : « continuously increased » à precise since when?

- We have modified the draft as follows:
- "Despite the management strategies adopted by EU, NH3 emissions have continuously increased since 1990."

Pg 3 line 72 : passive sampling isn't the only « indirect method » à add active sampling via denuder or on-line gas-liquid interaction systems (like MARGA, AIRMONIA, etc.) + ref to « Bobrutzki, Kristina & Braban, Christine & Famulari, Daniela & Jones, Stephanie & Blackall, T. & Smith, Thomas & Blom, M. & Coe, H. & Gallagher, Martin & Ghalaieny, M. & McGillen, M. & Percival, C. & Whitehead, James & Ellis, R. & Murphy, J. & Mohacsi, A. & Junninen, H. & Pogany, A. & Rantanen, Sami & Nemitz, Eiko. (2009). Field inter-comparison of eleven atmospheric ammonia measurement techniques. Atmospheric Measurement Techniques Discussions. 2. 1783-1835. 10.5194/amtd-2-1783-2009. » / For passive sampling, add reference to EN 17346 :2021 « Ambient air - Standard method for the determination of the concentration of ammonia using diffusive samplers » and to « Braban, Christine F.; de Bree, Frans; Crunaire, Sabine; Fröhlich, Marina; Fromage-Mariette, Anne; Goelen, Eddy; Hafkenscheid, Theo; Hangartner, Markus; van Hoek, Caroline; Martin, Nicholas A.; Michen, Benjamin; Noordijk, Erik; Stoll, Jean-Marc; Twigg, Marsailidh M.; Tang, Y. Sim; Cowan, Nicholas; Poskitt, Janet. 2018 Literature review on the performance of diffusive samplers for the measurement of ammonia in ambient air and emissions to air. Edinburgh, Centre for Ecology & Hydrology, 85pp. ».

- We have modified the draft as follows:
- "Examples of indirect methods are passive samplers (EN17346, 2020; Braban et al., 2018) or active sampling using denuders or on-line gas-liquid interactions systems (e.g. MARGA, AIRMONIA) (Bobrutzki et al., 2009) that are exposed to ambient air for a certain period of time."

Pg 2 line 73: Verify « spectrometry » à mass spectrometry? + add « conductimetry » ?

- We will try to add additional references

Pg 2 lines 76-78 : « these methods are often poorly characterized and they do not allow reliable measurements taking into account effective quality assurance and quality control procedures (QC/QA) (calibration, traceability, maximum allowed expanded uncertainty, etc.)» => not right for passive sampling because a standard exist!

- We have modified the draft as follows:
- "Since NH3 is not regulated in ambient air, these methods are often poorly characterized and they do not allow reliable and comparable measurements taking into account effective quality assurance and quality control procedures (QC/QA) (calibration, traceability, maximum allowed expanded uncertainty, etc.) even if some methods are based on established standard (ex: passive sampling in standard (EN 17346, 2020))."

Pg 4 lines 120-122 « The results obtained by METAS during the study showed a very good stability in the generation of NH3 with short response times, even at very low amount fractions. » => what is « good stability » ? « what is short response times » ? => add values / precise these terms.

- We have modified the draft as follows:
- "The results obtained by METAS during the study showed a very good stability (standard deviation better than 1.5%) in the generation of NH3 with short response times lower than 60 min, even at very low amount fractions."

Pg 5 line 137-138 : In order to know the robustness of the system it could be important to

specify the precision and the resolution of the balance and the temperature sensor

- We have modified the draft as follows:
- "The permeation rate of the tube is determined by measuring its mass loss over time using a microbalance with a resolution of 1 µg and a BORDA substitution method under controlled temperature conditions using a temperature sensor with a resolution of 0.01°C and a standard deviation of 0.05°C to guarantee the traceability to the SI."

Pg 5 figure 1 : The diagram seems simplistic and merits better specification of the constraints linked to this generation such as temperature and air flow control

- The referee is right.
- We will improve the diagram

Pg 5 line 149 : « 2M PROCESS » => precise country ?

- We have modified the draft as follows:
- "The reference generator was implemented by the French company 2M PROCESS on the specific request of LNE, based on a very close collaboration involving metrological, technical and software development skills."

Pg 6 line 159-162 and figure 2 : We know that oven temperature control is crucial for permeation. This paragraph does not indicate how this parameter is controlled. It would be interesting to add validation tests to measure the temperature in the oven, in order to control the absence of a gradient and cinetic between the heating element and the probe which allows control of the heating of the oven. The diagram could illustrate this significant addition to this development

- We have modified the draft by adding the following sentence:
- "The temperature is only a control value, but not an entry parameter for the determination of the permeation rate. After the weighing of the tube, it is replaced in the oven exactly at the same position; in this way, the influence of the temperature gradient has not to be taken into account."

Pg 7 line 181 : The normal molar volume : l_n/mol

- We won't change in the draft because we have indicated that the normal molar volume is at 273.15 K and at 1.013 bar

Pg 8 para. 4.2.4 : Takes up the remark made earlier. It seems important to be more detailed by test results the fact that you consider the correction accounting for the stability of the temperature in the oven as equal to zero

- Cf. the response to the remark made earlier (Pg 6 line 159-162 and figure 2)
- And modification of the draft in § 4.2.4 as follows: "The stability of the oven temperature is equal to 0.05 °C. Since the influence of temperature on the permeation rate of the tube is of the order of 8% per degree, considering a uniform law (Eq. (5)), the standard uncertainty was:…"

Pg 9 table 1 : This table seems useless since we find in figure 4 the graph. Can be just indicate the mean and the standard deviation on the evolution of the permeation rate over time.

- The referee is right.
- The table was removed

Pg 13 line 300-304 : It could be interesting to indicate the references of the filter and its filtration efficiency in order to guarantee the residual amount fraction

- We added the reference of the filter, but not the filtration efficiency. In fact, what is important is to have the NH3 residual amount fraction after the air has passed through the filter
- Modification of the draft as follows: "Because the dilution gas was further purified by means of an Entegris filter (CE2500KF04R), the NH3 residual amount fraction was considered to be equal to 0.005 nmol/mol. The standard uncertainty was estimated following Eq. (11) (uniform law):…"

Pg 14 table 4 : Standardize the results of the weight column

- The referee is right.
- The value have been modified

Pg 14 para. 6.1 : Regarding the calibration what are the concentration levels and what were your results. The contribution of tables and graphs would make it possible to validate this calibration

- First point => we have modified the sentence as follows: "NH3 amount fractions between 0 and 400 nmol/mol were generated during 2 hours for each amount fraction level using the reference generator."
- Second point the referee is right because it's not clear. We have modified the draft as follows

"6 Characterization of the calibration method of NH_3 analyzers

We determined the repeatability, reproducibility and uncertainty budget of the calibration procedure in order to characterise it. For that purpose, the reference generator was permanently switched on during the characterization and the NH3 permeation tube was continuously flushed by a synthetic air flow at 100 ml/min…"

Pg 15 para. 6.2 : You indicate that this is a repeatability test. In the paragraph there is no indication how many times you have to repeat the different levels just that the standard deviations calculated over the last 30 minutes of génération for each of the 9 points. On reading it is more of a linearity test than repeatability

- As indicated in air quality european standards such as EN 14211, 14212, 14625 and 14626, we determine the repeatability only one time by calculating the standard deviation on the measurements after obtaining the stability.
- But we have modified the first sentence to be clearer as follows: "To evaluate the repeatability of the calibration method at different amount fractions, nine levels were generated in the range between 1 and 400 nmol/mol."

Pg 17 table 7 : Standardize the results of the Intercept column

- The referee is right.
- The value have been modified

Pg 17 line 382 $u^2(F)$ <> $u^2(xref)$

- The referee is right.
- The modification has been done

P19 line 430-433 : It could be interesting to apply a table identical to table 9 for your own

results in order to be able to compare the same things and this even if the concentrations are different from that of METAS

- The LNE's values are in the table 6

Pg 20 table 10 : indicate the units

- The values have no units.
- We have modified the draft as follows: "Table 9: Result comparison between LNE and METAS; b is the slope of the calibration functions (no units); Std is the standard deviation of the calibration slopes obtained by LNE between 15-27 May 2020 (no units); u(b) is the standard uncertainty of the slope determination (no units); U(b) is the expanded uncertainty of the slope determination and k its coverage factor (no units). En is the normalized deviation between LNE and METAS slopes (no units)."

Pg 20 para. 8 : You specify measurement levels between 1 and 400 nmol/mol. Except your graph presented in figure 6 only shows the results between 1 and 300 nmol/mol. What is the reason?

- To be clearer we have modified the draft as follows:
- "Figure 6 presents an example of the NH3 analyser calibration performed for the monitoring networks: it shows the recordings of the ammonia reference amount fractions and the amount fractions measured by the NH3 analyzer number 2244-AHDS2115 (G2103, Picarro Inc., CA, USA) over the range from 1 nmol/mol to 300 nmol/mol. The standard deviations over the last 30 minutes were calculated and given in Figure 6."

In addition, which analyzer did you use to perform this test presented in fig 6 and how do you explain the greater measurement dispersion when the concentration increases ?

- First point: The same analyser was used for the tests of figures 6 and 7 => we have modified the draft
- Second point: there is a greater measurement dispersion when the concentration increases in absolute, but the relative standard deviations are similar in the whole range. We have modified the draft by adding the sentence "The relative standard deviation of the analyser readings is always lower that 0.5%." in the legend of the figure 6.

Pg 22 figure 7 : What is the point of having so many figures concerning the regression line and R^2

- We need some clarifications for this comment
- We think that the referee speaks about the table 11. For us it' impotant to have this table, because it shows that the calibration can be very different from one to another NH3 analyzer of the same trademark and model up to an accuracy error of 4 %.