

Interactive comment on “Replacing the AMOR by the miniDOAS in the ammonia monitoring network in the Netherlands” by A. J. C. Stijn Berkhout et al.

A. J. C. Stijn Berkhout et al.

stijn.berkhout@rivm.nl

Received and published: 25 July 2017

(comment from referee)

As I have a long lasting collaboration with the authors regarding the further development of MiniDOAS system to measure ambient NH₃ concentrations this is not an “official” review. I congratulate the Dutch authorities that they had the courage to replace the well- established AMOR systems (a wet-chemistry based point monitor) with the newly developed MiniDOAS systems (even though this seems more driven by financial then scientific reasons). To avoid inlet systems and wet chemistry analytic systems is a major advantage for ambient NH₃ measurements. The older systems all show varying smoothing behavior that hardly can be quantified and corrected. The new DOAS sys-

Printer-friendly version

Discussion paper



tems do provide real-time 1 minute values if there is no fog (or tractors or elephants) in the path. The replacement of the AMOR system occurred over a 15-month period with overlapping measurements on 6 stations. This allows an excellent comparison and an evaluation of the continuity that is crucial for a monitoring network. I see still two critical issues in the NH₃ concentration evaluation of MiniDOAS measurements: a) Accuracy of the sensitivity (i.e. the span of the calibration) b) Accuracy of the offset (related to the number density of NH₃ molecules on the reference path) To a) To determine the NH₃ calibration spectrum the authors used a short flow cell cuvette in the path flushed with a 300ppm gas concentration from a certified standard. As NH₃ is a very sticky compound it is not a very safe assumption that equilibrium is reached. I propose to analyse the time course of the measured DOAS concentration from the beginning and to monitor the concentration after the cell with an independent approach. Our own investigations show that (for our setup) equilibrium is reached only after at least one hour.

(author's response)

We allow the system to reach a steady state for 30 minutes, we then take data during 1 hour. We find that after 11 minutes the concentration is within 2% of the average concentration measured during the hour of actual data-taking. After 25 minutes, it is within 0.5%. Note that the concentration in the gas bottle is known with 2% accuracy, according to the gas manufacturer. The difference between our set-up and yours may arise from a larger flow, shorter tubing, et cetera. We insert the following sentence in the manuscript (page 7, line 8):

(author's change in manuscript)

We find that, after 25 minutes, the concentration in the cell is within 0.5% of the final concentration. We therefore allow the system 30 minutes to reach this steady state, then we collect spectra during 1 hour.

(comment from referee)

Printer-friendly version

Discussion paper



To b) The first step in the evaluation of the recorded spectra is the division by a reference spectra, both corrected by the dark current. In an ideal world, the reference spectra would be taken on the same conditions as the standard measurements but without any absorbing gas. The evaluated concentration then corresponds to the difference between the mean concentration on the path and the concentration of the reference spectra. Consequently, negative concentrations are physically possible and should be reported as such.

(author's response)

We do find negative concentrations and we do report them. In the entire dataset of 53908 hourly values (see also the supplement), 163 or 0.30% were negative. Averaging of the data leads to fewer negative values, as can be expected; we found no negative values in the daily or monthly averages.

(comment from referee)

It would be worthwhile to establish a clean air facility that allows to measure over normally used path length with concentrations well below the detection limit (e.g. 0.05 ppb for NH₃). Practically this is not yet possible and ways around this described by the authors and as by Sintermann et al. (AMT 2016) must be taken. Doing so accuracy better than 0.5 ppb can hardly be reached. Monitoring networks that aim at real-time value accessible over the web, will have difficulties with this issue and demand always positive values. This easily puts a scientifically not justifiable boundary conditions on DOAS measurements.

(author's response)

As outlined above, we do report negative concentrations.

(comment from referee)

The 15 month intercomparison on six stations is a very interesting data set that allows a deep insight into the performance of NH₃ monitoring systems that cannot be gained by

Printer-friendly version

Discussion paper



the different intercomparison exercises that has been published up to now (see e.g. von Bobruzki et al., Atmos.Meas. Tech., 3, 91–112, 2010,; Milford et al., Biogeosciences, 6, 819-834, 2009). The overall correspondence between the two systems based on the ensemble of monthly means is remarkably well. But going into details, doubts on this well behaving come up. In principle going to shorter integration intervals should not change the overall picture, but should increase the scatter. The used regression (least orthogonal distance fit) could be misleading as the high DOAS concentrations that are smoothed by the AMOR systems are kind of outliers. I guess that using a robust approach (e.g. “pbreg” or “deming” in the R-world) would give comparable slopes and offset for all three time resolutions.

(author’s response)

Thank you for the suggestion. We compared the effect of a robust regression (Winsorizing the differences at 2 standard deviations) to the least orthogonal distance fit. This confirms your expectation, the slopes of the regressions of the shorter timescale fits reduce (closer to 1) and the intercepts increase (closer to 0). These results are not elaborated in the paper because the comparison of hourly values is physically rather meaningless due to the memory effects observed in the AMOR.

(comment from referee)

In case I analyze the six stations separately I see persistent offset and slopes clearly different from 0 resp. 1 over several months, pointing of systematic drifts either in the AMOR and/or MiniDOAS systems. I do propose to analyse separately the time periods between service intervals of the AMOR systems as these actions constitutes a kind of reset of these instruments that might cause a change in the response function. The same should be done, in case a DOAS component is changed (lamp, reflector, etc).

(author’s response)

We performed the inverse analysis: we looked whether events in the dataset correlated

Printer-friendly version

Discussion paper



with AMOR service events. We found no such correlation. The analyses you propose come with difficulties. The AMOR systems were serviced every six weeks. Because intercomparison between AMOR and DOAS on short timescales are not feasible, this six-week period is too short to do meaningful comparisons. The miniDOAS systems, on the other hand, were exchanged only once or twice during the campaign. This makes intercomparisons difficult as well, especially when an exchange took place close to the beginning or end of the campaign period. Such an analysis could be the scope of a follow-up paper, once the miniDOAS systems have been running for 5 or 10 years.

(comment from referee)

As the DOAS systems are new we must learn about their long-term behavior and be open of surprises that might affect the performance. The presented dataset is an excellent playground. The DOAS technique also has the great advantage that concentration evaluation can be repeated in case new knowledge is available.

(author's response)

We wholeheartedly agree. This concentration re-evaluation is possible because the unprocessed spectra are stored. We would like to add a line summarising your comment to the outlook section in the manuscript (page 17, line 3):

(author's change in manuscript)

It should be noted that the miniDOAS instruments store the unprocessed spectra, averaged over 1 minute intervals. This means that reanalysis of the data, taking into account the latest insights, is always possible.

Interactive comment on Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2016-348, 2017.

Printer-friendly version

Discussion paper

