

Interactive comment on “Two instruments based on differential optical absorption spectroscopy (DOAS) to measure accurate ammonia concentrations in the atmosphere” by H. Volten et al.

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Reply to the comments of referee Arjan Hensen

We would like to thank the referee Arjan Hensen for his kind remarks and constructive comments that will help us to improve the paper. We will adapt the paper to answer his questions and comments the best we can.

We agree that it may be desirable to build a miniDOAS that fits in a box small enough

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to not disturb the wind field when used in an open frame tower. Up to now, when using the RIVM DOAS systems for a gradient method measurement, the instruments were housed in fairly large containers. This forced us to use only data collected when the wind was from a direction that was not disturbed by the containers, i.e. half the wind directions were discarded (see Wichink Kruit et al. 2010 (reference in the paper)). The miniDOAS itself is small enough, even now; finding a small weatherproof temperature-controlled cabinet remains to be done.

We will add a sentence about this subject to the end of Conclusions and Outlook, page 5054, line 25:

In particular for this application of the miniDOAS it will be highly desirable to design or procure a small, stable, weatherproof and temperature controlled housing that may be used in masts or on open frame towers.

Specific comments & questions.

Referee:

For the RIVM DOAS you mention that the CCD has a wavelength mapping of 0.0306 nm per pixel. For the zinc lamp locking method you mention locking within 0.0025 nm so you will not “see that with the CCD I guess? Is it a calculated lock accuracy or measured in another way?

Reply:

The observed line width of the zinc line at 213.84 nm is 0.10 nm (FWHM), i.e. wider than 0.0025 nm. The peak position of the line is determined by a quadratic polynomial fit, and this peak position is adjusted by a stepper motor with a resolution of 0.0010 nm (see Fig 5).

We will adjust the text on page 5043, lines 22-27 as follows:

The zinc lamp has a distinctive emission line at 213.84 nm with a narrow linewidth

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of 0.10 nm. Its light is projected onto the spectrograph, along with the light from the telescope. The peak position of the zinc emission line on the CCD pixels is determined at sub-pixel resolution with a quadratic polynomial fit. This position is checked every minute. If the position deviates by more than 0.0012 nm from the desired position, the grating angle is micro-adjusted by a stepper motor with a resolution of 0.0010 nm. As a result the wavelength mapping is locked onto the CCD with an accuracy of 0.0025 nm (see Fig. 5).

Referee:

Section 3.2: at pg 5045 in line 7 you mention you only use the range 200-230nm and “to avoid edge effects and noisy part of the spectrum” So you use 205-229nm. At 205 here is a nice absorption line for NH₃ and a smaller one for NO that you now use for about 50%. So is that indeed providing better results compared with using the whole line shape down to say 204 nm? Figure 8 does not look that noisy just left of the 205 line?

Reply:

The range from 205 to 229 nm has been determined experimentally to yield the best sigma values. Below 205 nm the UV lamp emits only very little light, Rayleigh scattering and the onset of the oxygen absorption lines (see Fig. 1) further weaken what little light there is, so below 205 nm the noise becomes relatively large. Note that the reference spectra shown in Fig. 8 were obtained with a path length of only 1 m, instead of with 100 m as the real concentration measurements were. Therefore, the light below 205 nm was not extinguished as much as for the real measurements. We hope that an enlarged Fig. 8 will show this more clearly.

We will amend the text on page 5057, lines 12-14 as follows:

We found experimentally that narrowing the wavelength range to 205-229 nm was optimal for avoiding edge effects caused by the moving averaging, and for eliminating

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parts of the spectrum that either are noisy (at the shorter wavelengths, due to Rayleigh extinction and the onset of oxygen absorption) or do not contain absorption features (at the longer wavelengths).

We will also provide an enlarged Fig. 8.

Referee:

If 200 to 230 nm is the range, why choose the 206 centre wavelength filter (not a 215 one) is that related to availability or to the spectral shape of I_0 ?

Reply:

Indeed, the centre wavelength of the filter is chosen at 206 because the lamp emits much more light in the range from 215 to 230 nm than in the range from 200 to 215 nm, while the strongest and most distinctive spectral features of ammonia are at shorter wavelengths.

We will change the text on page 5043, lines 1-6 as follows:

The light received by the telescope is focused by the secondary mirror and a folding mirror onto an optical fiber bundle with an narrow bandpass interference filter (Newport, G25-206-F, center wavelength 206nm, bandwidth 26 nm FWHM) placed in front of it. This interference filter is necessary to overcome problems caused by straylight in the spectrograph. Its center wavelength is optimal for the region of 200 to 215 nm, where the strongest and most distinctive spectral features of ammonia are located, but where the intensity of the xenon lamp is lowest. At 200 nm the intensity of the UV lamp is only about one hundredth of the intensity at 400 nm and beyond.

Referee:

In section 4 you describe that the lamp I_0 spectrum is specific for a lamp and that it will change over time. I_0 is measured at the start and “the changes over the life span are accounted for in the moving average“. Does this imply that the spectral shape stays

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the same but only the total intensity varies?

Reply:

The spectral changes in the lamp lo spectrum are broad band changes only, and therefore are accounted for in the moving average.

We will change the text on page 5046, lines 18-20 as follows:

The potential spectral changes during a lamp life span are broadband changes and are accounted for in the moving average that is used to estimate the broadband extinction.

Referee:

In your conclusion and out look:

You provide 3 different (fair) reasons why the AMOR would over estimate the concentration levels. I guess there is no hypothesis available at all on how a DOAS could somehow underestimate the concentrations is there? Please comment.

Reply:

Indeed there is a possible reason for the DOAS to underestimate concentrations due to the calibration procedure followed. We now assume that over the 1 m path used during the zero and span measurements, we may neglect ambient concentrations. If the ambient concentration is however in the order of $50 \mu\text{g}/\text{m}^3$ (which in extreme cases may occur indoors), this will cause an offset in the zero concentration measurement of 1% (because it is attributed to a 100 m path later) of this concentration, i.e. $0.5 \mu\text{g}/\text{m}^3$. For the span measurements using concentrations which are equivalent to ambient concentrations of $200 \mu\text{g}/\text{m}^3$ the additional $0.50 \mu\text{g}/\text{m}^3$ falls within the error of the measurements. So in short, there is a possibility that the DOAS underestimates ammonia concentrations, but this cannot explain the discrepancies between the DOAS systems and the AMOR.

We will amend the text in two places:

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1. On page 5046, line 18 we will add:

Since for real concentration measurements the retroreflector is placed at a distance of 50 m, any gas that is present in the atmosphere will induce an error of 1% of its concentration during the lamp spectrum measurements. As those measurements are performed in a well ventilated room and ambient concentrations are expected to be low, we assume that this value may be neglected.

2. On page 5054, line 2: we will add:

Alternatively, the DOAS systems could underestimate the ammonia concentrations due to assumptions made during the calibration procedure. To determine zero and span values we use measurements over a 1 m path assuming that the ambient ammonia contributions over this path may be neglected. However, if the ambient concentration would be high, e.g. $50 \mu\text{g}/\text{m}^3$, this would cause an offset in the zero concentration, resulting in an underestimation of the measured ammonia concentration by $0.5 \mu\text{g}/\text{m}^3$. For the span measurements using concentrations which are equivalent to ambient concentrations of $200 \mu\text{g}/\text{m}^3$ this additional $0.50 \mu\text{g}/\text{m}^3$ falls within the error of the measurements. In short, this potential underestimation of the DOAS systems could explain only a small part of the discrepancy of $3.4 \mu\text{g}/\text{m}^3$.

Referee:

For gradient application you suggest to use two minidoas instruments at different heights. Will this be better than one instrument with a “flipping” mirror that selects either of two paths/heights? That might be economically attractive and avoid the problem of differences in drift in detector or lamps.

Reply:

Such a solution will indeed eliminate (almost) all differences between the paths that are due to instrumental differences (the retroreflectors are not the same, so the differences can never be fully eliminated). Whether it is more economical remains to be seen:

extra mirrors and moving optics come at a price, this may be close to the price tag of a second miniDOAS instrument. But our main reason for not pursuing a one instrument – two path is that we then no longer measure the two light paths synchronously. A two instrument solution, like the one we use now, is completely free from timing uncertainties. We find from test measurements of two instruments placed parallel at the same height, that already small differences in the time synchronization (of the order of a minute) reduce the correlation of the two instrument results considerably. Apparently, ammonia concentrations fluctuate a lot in the atmosphere.

Referee:

What about water vapor and density effects when using the open path setup for gradient measurements? Do you suggest extra measurements there?

Reply:

Unlike in the IR part of the spectrum, there are no water lines interfering with the ammonia lines in the UV. Water vapor therefore does not affect the (mini)DOAS measurements.

At the different measurements heights between 1 and 4 m for the gradient measurements, air density differences may be neglected.

We will add to the text on page 5041, line 26:

Ammonia also has lines in the IR part of the spectrum, but in this region strong water bands may interfere with the ammonia lines.

Referee:

You now use the 150 W lamp. Bigger lamps are available, could that enlighten research on NH₃ concentration levels even more?

Reply:

The relative absorption will not increase with the intensity of the lamp. A bigger lamp would mainly enable us to use a longer path length. However, in our current quest for a simple and inexpensive miniDOAS we try to reduce the path length rather than increasing it. We currently find that the quality of the measurements is not reduced significantly by using a smaller lamp and a shorter path length. We hope to say more on the subject in a next paper.

We will amend the text in the Conclusions and outlook on page 5054, line 15:

For this purpose we will study the possibilities of reducing the path length to the retroreflector from 50 m to around 10 m, and of using a smaller UV lamp producing less heat.

Technical suggestions:

Referee: P5040 I4 suggestion: “for 5 min average” instead of “Over 5 min average”

Reply: This will be changed as suggested.

Referee: P5041 I3 & 10 seem to tell the same thing twice.

Reply: We will remove line 10-11, The total extinction . . . specified light path.

Referee: P5045 I15: you did not mention sigma before this point so explain or refer.

Reply: We will add a reference to Eq.3 where sigma is defined.

Referee: P5050 I7 suggestion: annual instead of yearly

Reply: This will be changed as suggested in three places.

Referee: Figure 8: please enlarge (my eyes are getting older)

Reply: We will enlarge the figure in consultation with the editor to arrive at a figure that is best suited for the journal layout.

Referee: Figure 11: any clue for the low value at 75 ug/m³

Reply: We think it is simply a statistical outlier. The values plotted in the figure are quite

small, considering the relatively large concentrations of SO₂ applied.

Interactive comment on Atmos. Meas. Tech. Discuss., 4, 5037, 2011.

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