

Editor's comments on the paper amt-2017-30

"Spectroscopic real-time monitoring of NO₂ for city scale modelling" by Hundt et al.

General comments

The paper presents a newly developed instrument (QCLAS) for the direct measurement of NO₂ using IR laser absorption spectroscopy. The technique is applied for mobile measurements on a tram in the city of Zurich in order to study the temporal and spatial distribution of NO₂ along selected roads. For quality control, measurements are compared with data from CLD instruments that are operated at fixed air-quality monitoring sites (AQMS). The measured data are then used as input for statistical models to predict spatial NO₂ concentration maps for the whole area of Zurich.

Major parts of the paper (the measurement technique, the instrumental comparisons and the model approach) are not satisfactorily described and discussed. Furthermore, the presented material does not sufficiently support results and conclusions. In the abstract, the authors state: "Thorough analysis of the obtained NO₂ data, for instance by comparison with data from fixed air quality monitoring (AQM) sites, revealed the instrument to be highly accurate ...". First of all, I am missing a presentation of an independent characterization of the QCLAS instrument, as well as a thorough discussion of its measurement errors (see detailed comments). Second, it is pointed out that QCLAS is a direct technique which relies on Beer's Lambert law, whereas NO₂ measurements by CLD (used at the monitoring stations) are indirect, need calibration and can have a positive bias from interferences especially in polluted urban air. My expectation would be that QCLAS serves as an absolute reference against which the CLDs can be tested. Contrary, the authors remove a systematic 20 % discrepancy observed between QCLAS and CLD data by scaling the QCLAS measurements to the CLD data. Not surprisingly, thereafter the data sets agree very well (Figure 4). This approach does not support the general claim of a 'high accuracy' of the QCLAS technique presented in this paper. It remains unexplained why the authors have more trust in the CLD data rather than in their new absorption spectrometer. They assume inlet losses in the QCLAS, but what about errors and possible interferences in the CLD? Another very important point that remains unexplained is the reported offset drift of the NO₂ data measured by the QCLAS instrument. How can a concentration measurement based on Beer's Lambert law exhibit an offset drift?

The second part of the paper describes how NO₂ measurements from the tram and from monitoring stations are used to predict NO₂ concentration maps by statistical models. Here, I am missing a more detailed introduction of the concept for those readers who are not familiar with statistical models and regression trees. Although I understand that the approach does not need a full understanding of all processes contributing to the distribution of NO₂, some reasonable parameters have to be chosen in the model which are expected to correlate with NO₂. It is intuitive to choose parameters (e.g. DTV030, DTV100) related to traffic intensity, since traffic emissions are the dominant source of NO_x in the city. However, what is the rationale for the "sky view factor" (SVF) and "elevation" (DTM)? An explanation or justification for the chosen input parameters (DTV_{nn}, SVF, DTM) should be given. With respect to the model results, I am missing a critical discussion of the possible role of ambient ozone and solar radiation, which play a role for the concentration of atmospheric NO₂ during daytime. As pointed out by Referee #1, most NO_x is emitted as NO and the resulting NO₂ concentration is dependent on ambient ozone. Furthermore, the partitioning of NO_x into NO and NO₂ is influenced by solar UV radiation (here: NO₂ photolysis frequency). The photostationary state of NO₂ can change on timescales of minutes, for example, with cloudiness or if an air mass passes

from a bright place into a dark street canyon or vice versa. How would such changes on a short time scale influence the model predictions of NO₂?

The paper in its current version is not suitable for publication in AMT and requires major revisions. The two main topics, the description of the measurement technique and the application for statistical modelling, are both not adequately presented and discussed. I recommend to extend the description of the measurement technique according to my suggestions below. I recommend to remove the part about statistical modelling. If the authors want to keep the statistical modelling part, major revisions would be needed here too which include a discussion of the influence of O₃ and solar radiation on NO_x and their relevance for the determination of maps of NO₂ concentrations in a city. Adequate presentation of both, the instrumental description and the statistical modelling, would certainly lead to a relatively long paper. Therefore, I recommend to leave out the model part here and consider to publish it as a revised version separately, for example, in ACP or a specialized journal on air pollution.

Detailed comments

Introduction

The overview of measurement techniques that are being used to measure atmospheric NO₂ is not complete. DOAS, LOPAP, LIF, luminol chemiluminescence should be mentioned. See for example, Villena et al., *Atmos. Meas. Tech.*, 4, 1663–1676, 2011; Sluis et al., *Atmos. Meas. Tech.*, 3, 1753–1762, 2010; Dari-Salisburgo et al., *Atmos. Env.* 43, 970–977, 2009; Dunlea et al., *ACP* 7, 2691, 2007; Thornton et al. *Anal. Chem.* 72, 528-539, 2000.

For the measurement of NO₂, the widely used CLD technique can have interferences in polluted air. This is not only the case for instruments with catalytic converters as mentioned in the introduction, but also for instruments with photolytic converters which can show interferences from PAN, HONO, VOCs (Reed et al., *Atmos. Chem. Phys.* 16, 4707, 2016 and Villena et al., *AMT* 5, 149, 2012).

Instrument

Some more technical details describing the instrument should be given, e.g. supplier and model of components (e.g. breadboard, etalon, mirrors, mirror holders, reflective coating of absorption cell), reflectivities of absorption cell walls and of turning mirrors, laser beam diameter, spectral bandwidth of laser, total optical transmission of absorption cell.

Evaluation of measured spectra

The NO₂ concentrations are calculated according to Beer's Lambert law and converted into mixing ratios. The values of all experimental parameters needed for the calculation should be specified together with their errors and uncertainties (absorption path lengths, absorption cross section, pressure and temperature in the absorption cell). How large is the accuracy of the resulting NO₂ mixing ratios?

Figure 1c displays a measured absorption spectrum with NO₂ and H₂O lines. Was the spectrum measured in synthetic air or in ambient air? Besides the intense absorption lines, there seem to be modulations like ripples in the spectrum. Are these caused by the instrument or by other weak absorbers? A spectrum of pure synthetic air should be shown for comparison.

How is the spectral baseline intensity (I_0 , without NO_2 absorber) at the central position of the NO_2 line determined? What is the smallest detectable absorbance of the instrument and what is the corresponding limit-of-detection for NO_2 ?

p. 6, line 4-5: "Moreover, data were omitted when the NO_2 spectrum was not clearly identified by the processing algorithm." Which criteria are used to decide, if a spectrum can be used or not? Normally, if the absorption of the analyte is smaller than the noise of the baseline, fitted spectra should yield concentrations scattering around zero within their fitting error.

p. 9, line 12-15: "Based on these results, the measurement strategy was designed such that it applies a drift correction to the concentration measurements by measuring NO_2 -free air for 2 min after 18 min of measuring. This offset-correction is achieved by subtracting the linear interpolation of the mean of the zero-air measurements before and after each 18 min measurement period." What is the cause for the offset drift and how large (ppbv?) were the corrections? How can a concentration measurement based on Beer's Lambert law have a drifting offset? Are there spectral interferences from other variable atmospheric compounds?

The processing of the measured atmospheric spectra, the determination of the NO_2 absorption cross section and the determination of the final NO_2 concentrations should be explained in detail. The QCLAS instrument should, in principle, allow absolute, calibration free measurements of NO_2 . Have the authors tested the instrument against an independent NO_2 standard (e.g. certified gas mixture)? How was the agreement?

The performance data of the new instrument should be mentioned in the abstract: upper and lower limit-of-detection, time resolution, precision and accuracy. In the text, a table with specifications and instrumental parameters would be useful.

Could the instrument be used for absolute water vapor measurements? Figure 1 shows an isolated H_2O absorption line that could probably be used?

Interferences

Possible limitations and interferences should be discussed in more detail.

- Are there any known spectral interferences?
- The production of NO_2 from the reaction of NO and O_3 in the inlet line and absorption cell is mentioned. Can you quantify the expected percentage range of perturbation for low O_3 (10 ppbv) and high O_3 (100 ppbv) conditions?
- The absorption cell is operated at reduced pressure favouring the thermal decomposition of labile components like PAN. Could this effect play a role in the instrument on a hot summer day in a polluted urban environment?
- Page 10: "... a correction to the normally calibration free QCLAS method was necessary because of loss of NO_2 during the sampling and in the long path cell... The contact of NO_2 with metal or plastic surfaces leads to dissociation." Is there direct, independent experimental evidence for such a wall loss in the instrument, or is this just an assumption? Which kind of materials were used? How long was the inlet line? Has the loss been checked by using different lengths of inlet lines or by variation of the volume flow rate of the sampled air? If the NO_2 wall loss is high, it could change over time with surface conditions (adsorbed H_2O , trace gases, particles). Are there any indications for such a behaviour?

Measurement comparisons

On page 10, the NO₂ measurements obtained by the QCLAS instrument and a CLD instrument are directly compared side-by-side at one AQMS station. The comparison and the conclusions drawn from it must be examined more critically.

The authors have apparently more confidence in the CLD measurements than in the QCLAS measurements and correct (calibrate) the QCLAS data to match the CLD measurements. This is somewhat surprising because the QCLAS is in principle an absolute technique, while the CLD needs calibration. Since the QCLAS measurements were scaled to the CLD data, Figure 4 cannot be said to demonstrate "excellent agreement". Rather, the scatter plot demonstrates a high linear correlation of the two techniques and a negligible offset. I suggest to plot the uncorrected QCLAS data against the CLD measurements and discuss linearity, slope and offset. The deviation of the slope (1.2) from unity should be discussed more critically with respect to known measurement errors of the QCLAS (see comments above) and CLD instruments (see comments below). Only if these cannot explain the 20% difference, it is meaningful to speculate about other possible reasons.

The CLD technique is known to have several sources of measurement errors which are not discussed in the paper, but could contribute to the observed discrepancy. How was the CLD calibrated (against which standard?) and what was the accuracy of the calibration? The detection sensitivity of CLD instruments have a water vapor dependence. Was this corrected? CLD measurements of NO₂ rely on chemical conversion of NO₂ to NO. For catalytical and photolytic converters, interferences have been reported which can be quite significant in polluted urban air. To my knowledge, the Horiba APNA-370 instruments are equipped with catalytic converters which have a significant sensitivity to other nitrogen species (e.g. PAN, HONO etc.) yielding too high NO_x readings. Have these interferences been characterized for the CLD used in this study and could these interferences explain the difference of 20 % between the QCLAS and CLD measurements?

Possible NO₂ losses in the inlet line of the QCLAS instrument are mentioned (s. above). What about possible losses in the inlet line of the CLD? Were other materials used than for the QCLAS instrument?

How far apart were the inlets of the two instruments? Were both inlets exposed to the same amount of direct and diffuse solar UV? If the jNO₂ values are different, the NO₂/NO ratio may be different even if NO_x is the same.

Statistical model

In addition to the report of Referee #1, I have the following question.

Has the "statistical model approach" ever been tested with simulated NO₂ concentrations from a regional atmospheric-chemistry model? One could simulate stationary or mobile measurements taking modelled NO₂ values or at fixed locations or along selected trajectories (roads), respectively, and superimpose artificially measurement noise. The statistical model could then be fed with simulated measurements and its output could be compared with the complete spatial NO₂ distributions from the atmospheric-chemistry model. The whole test could be done for variable ozone background and varying solar radiation.

Technical comments

- p. 2, line 14: give reference for electrochemical sensors.
- p.7, definitions of DTV: do you mean "at a distance of..." or "within a distance of..."?
- p. 9, Figure 3: the explanations of the colors in the legend and in the figure caption disagree.
- Figure 4: are the errors of the fitted parameters 1sigma values?
- Figure 7: errors of the fit parameters should be given.
- p. 13, line 11: one of the reasons for the large scatter in Figure 7b is explained to be due to "a larger distance" than in Figure 7a. However, for both panels, a radius of 30 m is specified.
- NABEL 2016: where is the report available? The source, publisher, authors, ISSN etc. should be given in the reference.