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Interactive comment on "Near-surface and path-averaged mixing ratios of NO_2 derived from car DOAS zenith-sky and tower DOAS off-axis measurements in Vienna: a case study" *by* Stefan F. Schreier et al.

Stefan F. Schreier et al.

stefan.schreier@boku.ac.at

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We would like to thank the reviewer for his / her useful comments.

General comments: The paper presents approaches to derive near-surface and path-averaged mixing ratios from zenith-sky car DOAS and azimuth tower DOAS observations as well as a comparison with mixing ratios derived from in situ monitoring stations. Based on 9 days of car DOAS measurements and 5 days of tower measurements, acquired in 2015 and 2016, the paper provides an insight on the NO2 spatiotemporal distribution in Vienna, Austria. The paper is well written and generally well-structured and provides interesting approaches to study the urban spatiotemporal NO2 distribution. The paper has improved compared to the initial submission and most comments provided in the quick review are addressed well. However, some critical issues remain and therefore my opinion has not changed that the paper would better fit in the scope of AMT than ACP. The work has a stronger focus on the performed measurement techniques and applied retrievals approaches than on geophysical interpretation of the data, chemical/physical processes and new findings on the urban spatiotemporal NO2 distribution. I would support publication in ACP when more data and better statistics would be available in order to thoroughly assess the novel approaches and to substantiate the findings, e.g. based on long-term, routine tower DOAS and car DOAS measurements. The authors recognize the limited data set several times in the paper and foresee routine measurements based on tower DOAS off-axis and MAX-DOAS in the future.

We agree that our manuscript might also fit in the scope of AMT. We do not fully agree with the argument that more data are needed to publish such a study in ACP. On the one hand, we have clearly defined our study as a “case study”. On the other hand, there are other studies in ACP which evaluate data from only few days. “Estimation of NOx emissions from Delhi using Car MAX-DOAS observations and comparison with OMI satellite data” by Shaignafar et al. (2011), a well cited ACP study, is only one example.

A new, and indeed interesting, approach to convert DOAS columns to near-surface VMR (a very relevant but complex problem!) based on a linear regression analysis is introduced but not developed well in the paper. This is something that the authors recognize and attribute to the limited data/statistics available. Most of the analysis in 4.3 (comparison of car-DOAS with in-situ measurements) is not based on the new approach but on a simple assumption, assuming a constant mixing ratio in the BLH. The authors discuss that this is not necessarily valid in an urban area. I fully agree with

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this and I highly doubt the validity of this approach in a city, where you rather expect an exponential NO2 profile and also a strong variability over city, industry and highways. The data set is too small to fully evaluate the approach and some correlations are bad which is most likely related to the wrong assumptions in the NO2 vertical distribution. If the authors keep this approach in the paper they should at least assess the impact of other, more realistic, NO2 profiles on the statistical comparison with in situ stations and perform a sensitivity study. Eventually typical urban NO2 profiles could be derived from a high resolution CTM.

We agree that the newly introduced linear regression analysis is not yet developed well, which mainly depends on the availability of data for only few days. Nevertheless, we argue that it is meaningful to present a new method to convert VCDtropo into near-surface mixing ratios, even if only limited data is available. The collection of data, which is available for testing this new method, was well thought out and a lot of effort and time was spent to get this unique data set. There is no comparable study, which collected data for one and the same car route for many times as well as for many different meteorological conditions. We argue that our data, collected in an urban environment, in combination with a relatively large number of air quality monitoring stations, is exactly what we need for introducing and testing such a new method. We agree that most of the analysis in Sect. 4.3 is based on the method of Knepp et al. (2013). From this analysis we found that for some days (mostly when air masses came from southeastern directions and when wind speeds were rather low) the correlation was high but slope and intercept were not satisfying enough, most probably because of the fact that the assumption of a constant mixing ratio within the PBL does not work for urban environments having different meteorological conditions. Again, our intention was to perform such car DOAS zenith-sky measurements on days with different meteorological conditions to see how these changing conditions affect the assumption of a constant mixing ratio within the PBL. The findings of this analysis raised the motivation to go one step further and test a new method – a method that seems to reduce the complexity of the problem of converting DOAS columns to near-surface mixing ratios, without deriving

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typical NO2 profiles from highly resolved CTM, which also have well known problems in representing the vertical distribution of NO2 in complex urban environments. Our aim was not to fully evaluate this method but rather introduce it and test it on a unique data set. We agree that deriving typical urban profiles from high resolution CTMs and perform sensitivity analysis to assess the impact of more realistic NO2 profiles is an interesting and worthwhile suggestion. However, the main motivation of this work was to evaluate a new method, and as shown in Fig. 17, this method appears to perform very well for at least for our data set.

Specific comments: P3, L9: The background signal in the reference could also be obtained by measuring one additional spectrum at 30° at the reference area and by application of the geometric approximation approach.

We agree that additional measurements at EA = 30° would help in this case. Unfortunately, such measurements were not performed and are thus not available. Nevertheless, we will consider such measurements for future car DOAS measurements.

P10, L13: Please quantify improvement in SNR after averaging + same for averaging tower measurement on P16, L17. I t is not clear to us what the reviewer would like to see here. Averaging reduces the variability in NO2 signal as expected, and this is illustrated in Figure 4 in the manuscript. Raw data (0.05 seconds) appear to have a random scatter of the order of 8 x 1015 molec cm-2 peak-to-peak, which is reduced to less than 1 x 1015 molec cm-2 in the averaged data (5 seconds). Thus one could say that the signal to nose ratio has improved by a factor of 8. However, as also seen in Fig. 4, it is not trivial to distinguish between measurement related noise and real atmospheric variability, and thus it is in our opinion not clear what the real improvement in SNR is.

P26, L3: I would elaborate a bit more on the comparison between tower VMR (at 160 m) and in-situ station VMR as this is indicated as novel in the introduction, e.g. by quantifying both instead of only giving an overall factor.

Due to the fact that data is only available for a couple of days, and reasonable comparison between tower and in situ NO2 mixing ratios can only be made for the two rotations of 29 April and 9 May 2016, quantification is challenging. Nevertheless, we have now added a new figure (Fig. 21) to compare the NO2 mixing ratios derived from tower DOAS off-axis measurements with the one calculated from surface NO2 concentrations. The comparison is based on round 4 and round 6 of 29 April and 9 May 2016, respectively (e.g. the same two rounds as presented in Fig. 18, Fig. 19, and Fig. 20). We have computed the mean and standard deviation of tower DOAS off-axis NO2 mixing ratios of the full tower rotation and the mean and standard deviation of in situ NO2 mixing ratios from those stations which are within the circle as determined by hOPL. The results are described in Sect. 4.5 (Page 29, Line 1-18) and Sect. 5 (Page 31, Line 23-24) and highlighted in the abstract.

P20, L18: Please give a number on how far the air masses moved based on wind speed and time difference between the measurements. This allows to cross-check if indeed the same air masses are observed.

When considering round-averaged wind directions, wind speeds and 1.5 hours for the time difference between the measurements at one and the same location, air masses on 10 April 2015 moved about 5.85 km (from the first to the second round) and 8.1 km (from the second to the third round). Consequently, in total those air masses moved about 14 km, which is in good agreement with the position of the NO2 peak of round 1 (red) at about 20 km and the position of the second of the two NO2 peaks of round 3 (blue) at about 6 km (see Fig. 11). We note that the 3-rounds averaged wind direction of that day (125.3 deg) slightly differs from the position of the A22 highway ($\sim$150 deg), which was considered for this case study.

P24, L4: As indicated earlier, weak correlations are probably related due to wrong assumptions in the NO2 profile.

We agree that weak correlations are probably related due to wrong assumptions in

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the NO2 profile, in addition to changing air masses with sometimes only low pollution levels. As argued above, we conclude that using the method of Knepp et al. (2013) assuming constant mixing of NO2 within the PBL does not work as good for all days of our study performed in the urban environment of Vienna. This fact was basically the motivation to test a new method, e.g. the linear regression analysis, which also accounts for other meteorological parameters that could have an effect on NO2 profiles, e.g. wind speed. Due to the good correlation between modeled and measured NO2 surface mixing ratios (R = 0.94) achieved with this new introduced and tested method we can argue that NO2 profiles are not essentially needed for the conversion of VCDtropo into mixing ratios as wind speed, na, MH seem to strongly affect NO2 profiles, at least over the urban area of Vienna, and at least for the data we have analyzed. This is generally the main message of our introduced and tested method. In the future, we will apply this method to zenith-sky measurements from operating MAX-DOAS instruments in Vienna, where better statistics are available. While weak correlation is found when using the method of Knepp et al. (2013), a very high correlation is found with our new method. This makes it worthwhile enough to publish this method and to motivate other research group to work on this complex problem of converting DOAS columns to surface mixing ratios.

Technical corrections: P3, L9: great advantage < added-value P4, L9: add “for example” after estimated P8, L12: rotations < rotation P10, L10: drives < route P10, L11: lines < box P11, L26: the < an P15, L4: In situ < in situ P19, L5: move “are” behind “magnitude”

We have considered all the “technical corrections” in the new version of the manuscript.

P19, L16: Is “temporal evolution” appropriate in the title, as you also measure spatial distribution with the moving measurement platform? Maybe split as well the car and tower measurements in different (sub)sections as they are not directly linked.

We agree that “temporal evolution” is not meaningful enough in this case and thus,

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changed it into “spatio-temporal patterns” (see Page 21, Line 22-23). We also agree that for a better overview, splitting car and tower DOAS (Sect. 4.2) is the right way. We have now added a new (sub)section (Sect. 4.3) (see Page 23, Line 21-22). We have now also added “obtained from tower DOAS off-axis” in the title of Sect. 4.5 (see Page 27, Line 12).

P26, L22: “unique” is not appropriate

We have now removed “unique” in the first sentence of the summary and outlook sections.

P46 – Figure3: Please put residuals on another scale. It is not possible to check potential residual structures at this scale

We have now put residuals on a different scale to make them more readable (see Page 51).

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