

Interactive comment on “Auto MAX-DOAS measurements around entire cities: quantification of NO_x emissions from the cities of Mannheim and Ludwigshafen (Germany)” by O. Ibrahim et al.

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Anonymous Referee #2

Author Reply: We thank the reviewer for the critical assessment of our study. The comments and suggestions helped us to improve our manuscript (see details below), and we hope it is now acceptable for publication. The main changes compared to the previous version are: -we determined the absolute fluxes along parts of the encircled area. Thus it became possible to determine separately the influx and the outflux of the encircled area. This example clearly demonstrates the advantage of absolute determination of the tropospheric trace gas VCD. -we included a detailed discussion on errors

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caused by the wind field and possibilities for their quantification. -we added more information on advantages of MAX-DOAS observations over zenith sky observations. -we added a list of possible future improvements at the end of the conclusions. In addition we included many minor changes as suggested by both reviewers.

The paper is reporting an exercise of evaluation of the NO_x emission of the two cities by mobile DOAS measurements from a car travelling around the area, following an idea explored by Johansson et al. (2008) for the city of Beijing. General comments. Since the experiment is an application of the technique already proposed and discussed elsewhere, the question is to know what is the new information carried by this paper. In several aspects, one day of measurements in the summer between 10h45 and 15h compared to 2 campaigns of 2 and 3 weeks, average of surface wind measurements at three stations compared to the use of a meteorological model, the information provided by the new experiment is limited compared to the reference experiment. The only potential progress is the use of Max-DOAS observations at 45° and 90° SZA instead of Zenith sky observations at 90° only. Therefore, a new publication would be acceptable only if the advantage of the Max-DOAS technique compared to zenith-sky is demonstrated and adequately quantified, which is not the case for the moment. Since a potential offset in the zenith sky measurements would have little importance in the present application based on the evaluation of the NO_x enrichment between air masses entering and leaving the city, the advantage of the Max-DOAS is not obvious. In addition, even if the errors were small, I don't think that 4 hours of measurements on a single day in August, could allow a fair estimation of the average yearly NO_x emission of the cities of Mannheim and Ludwigshafen. Given the very limited useful information provided, I do not recommend publication of this paper as it stands today.

Author Reply: We think the reviewer is not right that in saying the only innovative aspect of our paper is the use of MAX-DOAS compared to zenith sky observation. We agree that this is the most important aspect (and we yield additional proof in the revised version, see below), but in our opinion the discussion and quantification of the

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effects of chemical partitioning and chemical transformation are also important aspects (at least for NO₂). They are neither discussed nor corrected in the reference experiment of Johansson et al. 2008. Nevertheless, the most important improvement is the application of MAX-DOAS, and we think that in the original version we missed to clearly demonstrate the full range of advantages compared to zenith sky observations. These advantages include the following aspects:

a) determination of absolute tropospheric VCDs. Absolute tropospheric VCDs are important for absolute flux calculations through arbitrary transects, e.g. parts on complete circles. In the revised manuscript we added examples of such absolute flux calculations: we determined separately the absolute influx and outflux for the Mannheim/Ludwigshafen area for the different circles. The comparison of the respective in- and outfluxes can provide additional confidence in the determined total emissions. Such a separation would not be possible with zenith sky observations.

There are two additional, more subtle, advantages of observations of the absolute tropospheric VCD. The general assumption that for determination of total emissions from measurements around complete circles does not depend on any additional offset in the tropospheric VCD is indeed not completely true. One complication arises if changing wind direction and speed have to be considered (e.g. wind speed is different for the influx region compared to the outflux region). Another problem is related to the effects of chemical transformations, e.g. chemical destruction are deposition. Since the rate of chemical destruction depends (besides other dependencies) on the absolute trace gas concentration, knowledge about the absolute tropospheric VCDs in the influx and outflux regions is essential for their quantification. Especially for encircling of extended areas both aspects can become important.

b) Because of the increased absorption paths through the troposphere, MAX-DOAS observations have higher sensitivity for tropospheric species. The increase of sensitivity depends on the elevation angle, and can be up to a factor 3 for an elevation angle about 20° (smaller elevation angles might not be useful for mobile MAX-DOAS obser-

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ervations). While for events of strong pollution, this increase of sensitivity is probably not very important, it will become an important aspect for cases with slightly enhanced pollution levels.

c) In addition to the increase of sensitivity, the uncertainty of the tropospheric AMF decreases for observations at low elevation angle. For example, for an elevation angle of about 20° the uncertainty of the tropospheric AMF is typically only half of that for zenith light observations.

Specific comments

I will not repeat the comments made by the first reviewer, which I share largely. However I will add a few, which might help the authors reconsidering eventually the paper

Title. What is the meaning of "auto"? The explanation comes far later in the text. I would suggest instead something like Mobile Max-DOAS measurements around the city of: :"

Author Reply: We changed the title to 'Car MAX-DOAS measurements around entire cities: Quantification of NO_x emissions from the Cities of Mannheim and Ludwigshafen (Germany)'

Abstract: - the larger source of error is 'probably' .. Why probably? I would suggest instead a list and if possible estimates of the respective contributions.

Author Reply: We changed the sentence to 'In most cases, the largest error source is the variability and imperfect knowledge of the wind field.'

In principle we like the idea of giving a list of error sources. However, the importance of the different errors depends on the selected species, pollution level and actual measurement conditions. In our opinion, in the abstract a more general description is useful.

– surprising agreement. My understanding is that the estimated total NO_x emission

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of the cities for the 24 August is : : ., which if constant throughout the year would correspond to a total emission of X t/yr, consistent with: : :

Author Reply: Many thanks for this suggestion! We modified the sentence to:

'From our observations we derive a total NO_x emission from the Mannheim/Ludwigshafen area of $(7.4 \pm 1.8) \times 10^{24}$ molec/sec, which if constant throughout the year would correspond to a total emission of 17830 ± 4340 t/yr (calculated with the mass of NO₂) t/yr, consistent with existing emission estimates.'

Introduction - p 471 reference to GHG irrelevant. The DOAS technique do not allow measuring those.

Author Reply: There are several groups measuring greenhouse gases (CO₂ and CH₄) in the near IR from various platforms (ground, aircraft, satellite) based on the DOAS technique (e.g. so called WMF-DOAS, IMAP-DOAS). It is true that these methods do not apply the 'classical' DOAS technique, but include some modifications to account for the specialities in the near IR spectral range. Nevertheless, these techniques still utilise the basic principles of DOAS (measuring 'differential absorptions'). Thus we decided to keep the statement on GHG.

References Max-DOAS observations, p 475. No need for the long list of references of Max DOAS measurements of various species at fixed stations. Not relevant here. One or two references describing the Max-DOAS technique would be enough. Other references. I would recommend the authors to look carefully at which references are relevant to the subject. There are many not really needed.

Author Reply: We removed many of the references as suggested.

Errors The discussion of the impact of wind direction and speed variability is unclear to me. Not sure to understand the meaning of half standard deviation (see comments reviewer 1).

Author Reply: We agree that the original discussion was neither clear nor convincing.

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Therefore we completely rewrote the respective section (4.1.1). We also improved the error estimation by considering the respective variability of the wind direction for the individual loops.

Table 2 shows large differences in errors between the 4 loops, said largely caused by the average wind direction compared to the most polluted part of the loop. In that case, why using loop 2 in the average? Instead it would be better to discuss the case and conclude that this configuration is not convenient.

Author Reply: We now used the individual uncertainties of the different loops for the determination of the average emissions.

Discussion/ conclusions: Most useful, after a summary of sources of errors, would be a thorough discussion of optimum conditions for evaluating the NO_x emission of a city: minimum and maximum wind speed, wind direction variability and cloud cover, that is meteorological conditions; local time of measurements (chemistry, SZA, traffic); sampling and car speed; most pertinent ancillary data (wind measurements, altitude of boundary layer, in situ measurements from an air pollution network, meteorological model etc: : :), and finally, repetition of the measurements (week days, variety of meteorological situation, season..)

Author Reply: Many thanks for this suggestion! We included the following list of possible future improvements at the end of the conclusions: Emission estimates from car MAX-DOAS (or zenith sky) observations should be further improved, and especially the following aspects should be considered: a) The accuracy of the determination of the tropospheric VCD should be improved by the use of tropospheric air mass factors derived from radiative transfer simulations (instead of using simple geometric approximations). Especially for zenith sky observations multiple scattering effects can lead to large deviations (overestimations) of the geometric approximation compared to the true tropospheric air mass factor. For MAX-DOAS observations, the correct consideration of the relative azimuth angle between the viewing direction and the sun is especially

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important. b) More accurate wind data are needed, preferably for the exact times and locations of the measurements. For that purpose model simulations might be most useful. Another interesting option would be to measure the wind direction and speed directly on the car roof. c) For the determination of the effective wind speed relevant for the layer of the observed trace gas, more accurate information on the vertical trace gas profile is needed. Such information might be derived from regional model simulations. Alternatively, also simple transport calculations based on the atmospheric stability and turbulence might be used. Here it is important to note that in many cases the height of the boundary layer might not be a good estimate for the vertical extension of freshly emitted pollutants, because the vertical transport between the emission source and the location of the measurement might be too slow to fill the entire boundary layer close to the emission source. d) Clouds do not only affect the atmospheric absorption path lengths (see e.g. Johansson et al. [2008]) but also the partitioning of photochemical reactive species like e.g. NO/NO₂. Thus more detailed knowledge on cloud properties can improve the emission estimates. For example, besides the O₄ absorptions (see Johansson et al. [2008]), also the radiance measured by the DOAS instrument might be used. e) Also more detailed information on chemical species concentrations (e.g. O₃) would be helpful to characterise and quantify chemical transformations and partitioning. Such information might be derived from model simulations of regional chemistry and transport, but also from air pollution networks. Finally, car MAX-DOAS observations should be routinely be applied cover temporal variations of emissions on various time scales (from diurnal to seasonal variations).

Interactive comment on Atmos. Meas. Tech. Discuss., 3, 469, 2010.