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Atmospheric Measurement Techniques Discussions

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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We thank the reviewer for the 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 caused by the wind field and possibilities for their quantification. -we added more information on ad-

vantages 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.

GENERAL COMMENTS

This paper is an application of the method introduced by Johansson et al. (2008) to estimate area emissions of air pollutants by remote sensing measurements from a car driving around the area. An estimate is given for the NOx emissions from Mannheim and Ludwigshafen. This in itself is already worth publishing, although the method is not very innovative.

Author Reply: Many thanks for this positive comment!

The new aspect of this paper is that the measurements are performed under an angle of 45o, for which the authors claim they are more sensitive to tropospheric NO2 than the zenith sky measurements. However, the authors do not illustrate or argue that this increased sensitivity would indeed give a more accurate estimate of the area emission.

Author Reply: We agree that this aspect was not discussed in sufficient detail. Also it was not specifically confirmed by the presented measurements. In the revised version of our manuscript we added more information about this point. Besides an increase of the sensitivity (up to a factor of three compared to zenith observations), also 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. Both aspects are now explicitly mentioned in our manuscript.

Furthermore the systematic offset the zenith sky measurements would introduce are not relevant for this method since the difference between the in-flux and the out-flux over an area is not changed by a systematic offset in the vertical columns.

Author Reply: While this is in general true, there might also be cases where even for closed-loop observations the knowledge of the absolute tropospheric VCD is important (especially for encircling of extended areas). In cases when changing wind direction and speed have to be considered (e.g. if the wind speed is different for the influx region compared to the outflux region), it is essential that the absolute tropospheric VCDs are known. Otherwise the errors of the emission estimate will increase with increasing offset of the tropospheric VCD and increasing difference of the wind speed for the influx and outflux areas. We added this information to the revised version of our manuscript.

However, the authors briefly mention the importance of measuring absolute tropospheric columns when using the method for deriving absolute values of fluxes through transects. It is a pity that the method is not applied to such an example.

Author Reply: In the revised version of our manuscript we added examples of absolute flux calculations through transects (we determined the influx and outflux separately for the different loops). The comparison of the respective in- and outfluxes can provide additional confidence in the determined total emissions. For example, the variation of the influx is much smaller than that of the outflux, which indicates that the variations of the emissions inside the encircled area are the main reason for the variation of the outflux.

The innovative character of this paper should be enhanced by either concentrating on the benefits of multi-axis as compared to zenith looking, including a relevant application or example, or concentrating on the accurate estimation of emissions by improving the error assessment. Johansson et al. (2008) already tried to minimise the uncertainty in the wind speed and direction over the time period of a measurement loop by using a meteorological model. The authors should make an effort to improve this.

Author Reply: We added additional discussion of the advantages of MAX-DOAS compared to zenith sky observations (as discussed in more detail above and below). We also improved our error estimation and discussed in more detail the possibilities to de-

rive information (e.g. measurements versus model data) on the wind field and how to use this information for the flux calculations and error estimation (see completely new section 4.1.1).

SPECIFIC COMMENTS

Abstract, line 13-16: "In such cases, ... determined total emissions." The validity of this statement is not shown in the paper. With this method a systematic offset in the vertical columns would not lead to an offset in the determination of the area emission.

Author Reply: We modified the statement to: ‘Even if emission sources are completely surrounded, systematic offsets in the measured vertically integrated trace gas concentration can lead to errors in the determined total emissions, especially for observations around extended areas.’

We also added the following information to the introduction: ‘However, even if emission sources are completely surrounded, systematic offsets in the measured vertically integrated trace gas concentration can lead to errors in the determined total emissions: for example 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), it is essential that the absolute tropospheric VCDs are used for the flux calculations. A similar problem is related to the effects of chemical transformations (e.g. chemical destruction or deposition). Since the rate of chemical destruction depends (besides other dependencies) on the absolute trace gas concentration, the knowledge on the absolute tropospheric VCDs in the influx and outflux regions is essential for their correct quantification. Both aspects become especially important for observations around extended areas.’

Abstract, line 24: "... which is in surprisingly good agreement with existing emission estimates." This sentence seems to bring down the message in your paper. If your method is valid, why does it surprise you that it is consistent with other estimates? Or are you surprised that existing bottom-up estimates are ’correct’?

Author Reply: We changed the statement to:

'From our observations we derive a total NOx emission from the Mannheim/Ludwigshafen area of (7.4±1.8) ×1024 molec/sec, which if assumed to be 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. From our observations it is also possible to separately determine the average influx into the Mannheim/Ludwigshafen area (5.4±0.9 ×1024 molec/sec or 13010±2170 t/yr) and the average outflux (12.8±1.8 ×1024 molec/sec or 13010±4340 t/yr).'

I would suggest changing through the whole paper the vector ∼s to the scalar s, denoting the position along the driving route, and changing d∼s to ∼nds, where ∼n is a unity vector directed outward and normal to the driving route direction.

Author Reply: We thank the reviewer for the good suggestion which we adopted.

You do not need Eq. (1) if you have Eq. (2). Please compact page 472, line 18 to page 473, line 9.

In principle we agree with the reviewer. However, since especially from MAX-DOAS observations the absolute fluxes through planes above arbitrary driving routes can be retrieved, we prefer to keep equation 1.

The first part of Eq. (2) is wrong, should be

Author Reply: Many thanks for this hint! We corrected the equation.

page 473, line 13: The word 'averages' is used incorrect. The emission estimates are not averages of individual emission estimates, but they are based on instantaneous measurements of the NO2 column and an average wind field.

Author Reply: We changed the sentence to: 'Thus temporal variations on time scales below that period can not be resolved and the resulting emission estimates are only representative for the average conditions through that period.'

page 474, line 10: 'processes, which are slow ...': do you mean 'fast'? If not, please explain. Section, 2.2: Specify how you monitored the location (GPS?).

Author Reply: Many thanks for this hint. We exchanged 'slow' by 'fast'. We added information in section 2.2 on how we determined the position of the measurement.

page 478, line 1: '... typically below 15%.' This is not true for small relative azimuth angles. Add a sentence on this and quantify.

Author Reply: We changed the text as follows: 'The errors of the geometric approximation depend on the SZA and relative azimuth angle (in general they increase with increasing SZA and relative azimuth angle). For aerosol loads with optical depth <0.5 and for surface-near trace gases (<200m) the errors of the geometrical approximation are typically below 15%.'

We also added the following information: 'It is interesting to note here the for MAX-DOAS observations the uncertainties of the tropospheric AMF are usually smaller than for the observation of zenith scattered light. This aspect is not of great important for this study, because of the rather high elevation angle of 45° (leading to a reduction of the uncertainty by 10 – 30%). However, for elevation angles around 20° it can result in a reduction of the uncertainties by about 50% (elevation angles <20° might not be very useful for car MAX-DOAS observations, because of trees and buildings in the field of view).'

page 478, lines 8-9: The total error estimate should not be given as 'larger than', but rather as 'smaller than' or 'approximately'.

Author Reply: Many thanks for this hint! We replaced '>' by '<'.

page 480, line 23, and Table 1: how are the standard deviations of the wind speed and direction calculated, in time, or in both space and time? Does it make a difference?

Author Reply: The standard deviations in space and time are similar. We added this information to the text in section 4.1.1.

Section 4.1.1 and 4.1.2: These error estimates should be improved by using the individual measurements from the three wind stations to determine whether the average wind field is systematically changing during the measurement loop. I suggest that you exploit this information, and possibly additional information (other stations or a model) to improve your error estimates. This is already recognized by the authors in Section 4.1.3. Since you are circling the area almost four times you might want to consider taking only the measurements during the period for which the wind was most stable, or the total estimated error is smallest. After you have improved the error estimates the last sentence of section 4.1.1 will probably change. If not, there should at least be some explanation why the error can be estimated as 'half of the standard deviation'.

Author Reply: We completely rewrote the section on the influence of the wind field on the emission estimates (4.1.1). We added a detailed discussion about the advantages and disadvantages of measured wind data versus the use of model data. We discus the temporal and spatial scales of fluctuations of the wind field and their impact on the emission estimates. In principle we agree to use additional information (e.g. from model data or additional measurement stations). However, high resolution model data are unfortunately not available. Also, we found no additional measurement data within or close to the encircled area. Nevertheless, in our opinion observational data from three stations should already provide a reasonable estimate about the spatio-temporal fluctuations of the wind field.

Section 4.3 and Section 5. Since you know the Leighton ratio, you can calculate the mass of the NOx emission using both masses of NO and NO2. For a cL of 0.35 this would result in a NOx emission closer to 0.5 kg/s. You compare to existing emission estimates for Ludwigshafen and Mannheim. However, it is not clear if these emission estimates are comparable. What is the ratio of NO to NO2 assumed in these existing estimates?

Author Reply: Maybe there is a misunderstanding here. As already stated in the text we calculated the mass of NOx assuming the mass of NO2. In this way the mass becomes

independent of the assumed Leighton ratio and can be directly compared to similar quantities from the bottom-up emission estimates. To avoid further misunderstandings, modified the information in the brackets to '(the mass is calculated assuming that all NOx was NO2)' In addition, we added the information that the emissions from the bottom-up estimates were also given assuming the mass of NO2 in section 5.

Section 4.4 title: only one additional error source is dealt with in this subsection, so maybe you want to change the title accordingly, e.g. 'Effect of ozone depletion'.

Author Reply: Many thanks for this suggestion which we adopted.

page 483, line 17-18: ' ... is found to be higher than the NOx concentration'. This is not true before 11:00.

Author Reply: The reviewer is right and we changed the text to: '. . .is found to be higher than the NOx concentration for most of the time (after 11:00).'

Section 5 contains statements that are not dealt with in the rest of the paper. These statements should go to e.g. the introduction. These are lines 7-16: 'Moreover, MAX-DOAS observations ... for satellite validation.'

Author Reply: We partly agree and we removed the sentence: 'This makes the method especially well suited for observations of emissions from extended areas, for which the emission plumes might not be characterised by well defined and sharp gradients.' For the other sentences we feel that they contain important information which should be presented in the conclusion section. In particular, in the revised version of our paper we added examples of absolute flux calculations for parts of the circles which is possible from MAX-DOAS observations.

Figure 1 should be removed. It does not give much additional information. Alternatively, Figures 1 and 2 could be merged to a (3D) sketch of the area over which the integration is performed.

Author Reply: We thought about the suggestions from the reviewer. However, we feel that: a) Fig. 1 is important to show that car MAX-DOAS observations allow the integration of the absolute flux along arbitrary driving routes. b) merging of both figures is difficult from a graphical point of view; also the aspect mentioned above makes both figures basically independent.

Thus we suggest to keep both figures in the paper. Alternatively, we would rather remove Fig. 2 instead of Fig. 1. However, Fig. 2 is a rather small figure which is illustrative and does not need much space.

TECHNICAL CORRECTIONS

Abstract, line 6: change 'based on of zenith' to 'based on zenith'

corrected

Abstract, line 23: change '17350_4100t' to '17350_4100 t/yr'

corrected

page 476, line 11: change 'light weighted' to 'light-weight'

corrected

page 476, line 24: change 'via one USB cable' to 'via a USB cable'

corrected

page 477, Eq. (3): specify a

done

page 479, line 2: change 'typically expressed as Leighton ratio (L=[NO]/[NO2]).' to 'a function of the Leighton ratio (L=[NO]/[NO2]; cL = 1 + L).'

done

page 479, line 5: change 'terms' to 'factors'

corrected

page 480, line 14: change 'south-west' to 'South-East'

corrected

page 480, line 23: change 'time of the measurements' to 'time period of each measurement loop'

corrected

page 482, line 12: change 'the time the air' to 'the time for the air'

corrected

page 482, line 12-13: change 'Because most NOx ... area, we assume an effective transport time of 1 h.' to 'Assuming most NOx ... area, the effectice transport time would be 1 h.'

corrected

page 482, line 23: change '... of 1.35 to obtain to determine' to '... of 1.35 to obtain'

Author Reply: We changed the sentence to: 'Thus we use a correction factor cL of 1.35 to determine the total NOx emissions.'

page 484, line 4: change 'but instead measuring scattered' to 'but instead of measuring scattered'

corrected

page 484, line 5: change ' sun light under zenith sky' to 'sun light from zenith-sky'

corrected

page 484, line 5: change '... we use a MAX-DOAS instrument mounted on a car.' to '... we measure under a slant angle with a MAX-DOAS instrument mounted on a car.'

Author Reply: We changed the sentence to: ‘we measure under a different angles with a MAX-DOAS instrument mounted on a car’

Figure 5. The letters and numbers along the axes and within the plots should be enhanced with at least a factor two.

corrected

Figure 6, caption: change ’the driving distance during one observation’ to ’the driving distance between two consecutive observations’

corrected

Figure 7, caption: change ’The vertical lines indicate ...’ to ’The dashed vertical lines indicate ...’

corrected

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