Reply to reviewer #3

First of all we want to thank this reviewer for the positive assessment of our manuscript and the many useful suggestions!
We followed most these suggestions as explained in detail below. In cases we disagree we give detailed explanations for the reasons.

General Comments:
This manuscript describes a simple, parameterizable, method for inversion of MAXDOAS observations to near-surface mixing ratios of three important gaseous pollutants. The method is described, as is the instrument used to make the observations. The results of the method are compared to long-path DOAS observations and visibility monitors and relatively good agreement is found. The manuscript contains valuable information, and particularly the comparison with in-situ observations is useful to the community. However, the manuscript, as written needs improvement before final publication. These general comments contain major issues to be resolved by the authors, and following that, some specific comments are given.

1) The manuscript is too long given its result and the language is difficult to read at times, making it confusing. This is a technique article that is describing a method that is similar to work others had done previously. Many of the later figures and text attempt to make a simple interpretation of the data on four days in terms of wind speed and direction, weekend effect, etc. While all this interpretation seems feasible, it is not relevant to the technique, which is the point of the manuscript. The manuscript would be a much more valuable contribution to the literature if the manuscript were more focused on the technique, and the comparison to LP-DOAS, which demonstrates the method's quality.

Author reply:
We agree that the focus of this paper is on technical aspects. Therefore we removed sections 4.3.1, 4.3.2 and 4.3.3 in the revised version of the paper.

2) Somewhere in the manuscript, possibly around the middle of page 8133, where light path properties are discussed, it would be useful to mention how topography can affect the effective altitude above ground level of the light path. Hills in the distance may block a 1 degree elevation angle light path, as well as valleys or simply placement of the instrument on a hill could cause the direct light path to be higher above the ground surface. It should be noted that the light path as calculated by this method is not the exact distance over which photons may have traversed. Some photons that end up being detected at the 1 degree elevation angle will have travelled shorter or longer distances along this final light travel direction. Therefore, hills at further distance than the "effective light path" can still affect the observation. Additionally, the concept of the "sensitive altitude range" is much more of an approximate concept than an exact range

over which the trace gas concentration is averaged. Therefore, Figure 14 is really not very useful. In fact, a secondary vertical axis could be placed on Figure 13 to give the same information. However, one might even eliminate both figures and simply indicate that effective pathlengths range from a few to _10km, just as was indicated by the modeling described in the first few figures. The actual path of photons is more complex, and thus the concept of "pathlength" is more qualitative than the term would suggest.

Author reply:
We agree that the topography in the field of view of the telescope has an influence the light path calculated by this method. As suggested by the reviewer we made additional radiative transfer simulations to investigate these effects in more detail. The results are added to the revised version (new section 2.2). We considered two cases, which might be important for many applications of our method:
a) the effect of operating an instrument at an elevated level (e.g. at the roof of a high building)
b) the effect of mountains in the field of view at different distances
While point a) is not critical for the interpretation of the MAX-DOAS measurements, point b) can have a strong influence (depending on the atmospheric conditions and the distance of the mountain. We added the following text (and also a new Figure) in the new section 2.2:

'So far we assumed that the path lengths are not affected by topography. However, for observations at low elevation angles, for which the light path is close to the surface, such effects might play a role. We investigate two possible effects of topography in more detail using radiative transfer simulations:
a) the effect of installing an instrument at an elevated level (e.g. at the roof of a high building). We performed radiative transfer simulations for an instrument located at 100 m height above the ground. The O_4 air mass factors for an elevation angle of 1 ° differ from the respective results for an instrument located at the ground by less than 1 percent (see Fig. 3). Thus we conclude that the effect of the height of the instrument can be neglected.
b) the effect of mountains in the field of view at different distances. Hills close to the observation site may block the view at low elevation angles. In such cases the effective light path length can become much shorter than without a mountain in the field of view. Moreover, the light path length derived from the O_4 absorption might not be representative anymore for the determination of the trace gas mixing ratios according to Eqs. 1, 2 and 3. To quantify the effects of mountains in the field of view we simulated O_4 AMFs at 320 nm, 360 nm and 440 nm for scenarios with mountains at 2 km, 5 km, 10 km, 15 km, 20 km, and 25 km distance. The results are shown in Fig. 3.

We find that the effect of mountains depends on the wavelength and aerosol load. For high AOD (>0.5) only mountains at distances shorter than 10 km have a substantial effect on the O_4 AMF (deviation > 10% compared to the case without mountains). For low AOD (<0.1) also mountains at distances up to 20 km become important. Thus we recommend that the MAX-DOAS observations should be made at azimuth angles, at

which the field of view is free over about 20 km distance. In such cases the effects of mountains can be neglected.

If the distance of mountains in the field of view is smaller, the respective details of the topography should be included in the determination of the correction factors (section 2.3). If mountains are present at very short distances, the method of TOTAL-DOAS (Frins et al., 2006, 2008) might be applied in the data analysis.
For the interpretation of our measurements, topography effects can be fortunately neglected, because the surface around the observation site is flat and our MAX-DOAS instrument is only located on the 7th floor of the building, about 35 meters.'

3) The manuscript seems to go back and forth between considering the O4 measurement as a dSCD and as a dAMF. For example, on P8132, L 15, the O4 measurement is said to be a dSCD, which I would agree with – from the optical spectroscopy one gets a differential slant column between the 1 degree elevation path and the zenith path. However, on P8133, L2, the manuscript indicates that there is a measured O4 dAMF. One does not experimentally measure the O4 dAMF; the measurement is the dSCD. I presume that the authors are using the assumption that the VCD of O4 is effectively a constant, meaning that a dSCD can be converted to a dAMF, but it is confusing that the manuscript alternates between these two languages. Again, in P 8149, L3, the manuscript is back to having an O4 dSCD. I believe the more understandable language is to discuss only measured O4 dSCD. When the 1 degree referenced to 90 degree dSCD gets smaller, it is an indicator of less O4 differential absorption due to shorter light path near the surface, which makes logical sense.

Author reply:
We agree that the quantity derived from the measurements is the O_4 DSCD and not the O_4 DAMF. Nevertheless, we prefer to use the term O_4 dAMF also for the results of the O_4 measurements because this allows a direct comparison between measurements and model simulations. To avoid confusion, we made the following changes:

-the last sentence in point b) in the introduction was changed to:
'Using this parameterisation, appropriate correction factors for a given measurement can be directly determined according to the measured O_4 dSCDs (after conversion to O_4 dAMF, see section 2).'

-equation 1 was changed to $L = \frac{dSCD_{O4}}{c_{O4}} = \frac{dAMF_{O4} \cdot VCD_{O4}}{c_{O4}}$

The following text was added after equation 1:
'The O_4 dSCD can be also expressed as the product of the O4 $_4$dAMF and the O_4 VCD (last term in equation 1). In this study for the O_4 VCD a fixed value of 1.19 × 1043 molecules2 cm-5 was used calculated form standard pressure and temperature profiles in May at the northern latitude of 35 ° from the climatological database developed by

MPIC Mainz (Brühl and Crutzen, 1993). No temperature dependence of the O_4 absorption cross section (see e.g. Thalman and Volkamer, 2013) was considered. The surface elevation of the measurement site (approximately 50 m above sea level) was considered.
Here it should be noted that in the following the measured O_4 dSCDs are always expressed as O_4 dAMFs using the above mentioned value of the O_4 VCD. This procedure allows a direct comparison between the O_4 measurements and the results of the radiative transfer simulations.'

-equation 6 and some text before equation 6 was deleted.

-in the whole manuscript (after the beginning of sectiom 2) the term 'O_4 dSCD' was replaced by 'O_4 dAMF'

4) The question of the temperature dependence of the 2O2 <-> O4 equilibrium does not appear to be discussed. If there is a temperature dependence, it will affect the O4 VCD in addition to the "normal" pressure and temperature dependence of the O2 concentration (number density). Also on this topic, the manuscript, on P8135, L6, the wording of the way we express the O4 concentration is confusing and should be more clearly worded. I believe that there are more recent works on the temperature dependence of this reaction, which are relevant to these calculations. Is a single value of c_O4 used, or is a pressure and temperature varying value calculated from meteorological data. Similarly, on P8137, L12, a single value of the O4 VCD appears to be used. Please clarify if a time-varying or constant values are used for both of these parameters.

Author reply:
We added the following information to the text (after equation 1):
'No temperature dependence of the O_4 absorption cross section (see e.g. Thalman and Volkamer, 2013) was considered.'
The Thalman and Volkamer reference was added to the reference list.
We also added the information that 'In this study for the O_4 VCD a fixed value of 1.19×10^{43} molecules^2 cm^{-5} was used…'

5) Much of this manuscript describes "error analysis", or explores variability in the correction factors calculated for different aerosol amount and profile assumption, different gas profile assumption, etc. While it is good to see that the authors are considering ranges of correction factors, these ranges are not actually an "error analysis". These ranges depend completely on the ranges of assumed optical parameters or trace gas profiles. Therefore, the authors should choose an appropriate term for the results sensitivity to assumed (but in fact unknown) parameters. The ranges chosen by the authors does appear reasonable, so I think the authors have done a

reasonable job here, but it is not actually an error analysis. One must also remember that the RTM is 1-D, so does not allow for horizontal variability in trace gas concentration (which is shown by the results to exist), nor does it allow for horizontal structures in aerosol or clouds. Therefore, actual errors could be larger than calculated by this method.

Author reply:
We agree and added the following text in section 2.3 (old section 2.2):
'Here it should be noted that these uncertainties are only valid for the assumed trace gas and aerosol profiles. Although these assumptions might be representative for most situations, in individual cases the actual profiles might be very different. Thus the uncertainties provided by the maximum and minimum values do not represent the true error for a given measurement, but can only provide a lower limit of the measurement error under the assumption that the true aerosol and trace gas profiles are within the range assumed for the radiative transfer simulations.'

We also clarified this aspect in section 6.

6) Section 6 – Error discussion, is confusing. As was discussed in the earlier point, some of these calculations (ones from the RTM) are not actually errors, but simply sensitivity to ranges of assumptions made by the authors. Additionally, many of the statistics in this section describe relative errors as percentages. These percentages are not at all clear, and often don't make sense. For example, on P8150, L14, the NO2 "error" is said to be 0.14 ppb (or 15%). The NO2 mixing ratio can vary from ppt levels to _50 ppb, so it doesn't make sense to say that 0.14 ppb is 15% of the NO2 mixing ratio. I think that the authors wish for a percent error so they can combine that with other errors to get a total error. However, it makes this section difficult to follow so as to be assured that the authors have made the calculation correctly. Please rework this section to be simpler and clearer.

Author reply:
We completely rewrote this section as suggested.

7) The comparison of the data between the rapid method and the LP DOAS is a good point of this manuscript. However, the abstract, P8130, L24, indicates different Rsquared values from the later discussion, on P8145, L27. These results appear to be different by rounding, but should be the same. The point that the slopes of the correlation plots are not unity is made in the middle of the manuscript, but not discussed in the abstract. It would be valuable to add to this discussion a zero-intercept-constrained fit to the data. I would expect that the slope of that line would be close to unity in each case, which may indicate that the slope difference in the unconstrained fit is possibly due to the positive intercept. I believe that the RA value discussed will be the slope of the zero-intercept-constrained fit, so this line's addition could help the discussion of AR and RA, which I found somewhat confusing. I am not

sure if I would believe the argument about the lifetime of NO2 affecting these observations. Typically NO2 is lived for on the order of a day, which is long compared to vertical and horizontal transport on these length scales. Source variability appears more likely.

Author reply:
Many thanks for this hint! We corrected the values in the abstract.
In addition we added the information to the text that '….that RA is similar to the slope of the regression lines if they are forced to the origin.'

Concerning the possible effect of the atmospheric lifetime we still believe that this could be a plausible explanation for the different findings for the different trace gases. We disagree with the reviewer that the lifetime of NO2 is typically of the order of a day. Especially during summer the NO2 lifetime can be expected to be much shorter, typically in the order of a few hours.
Nevertheless, we modified the sentence to:
'These findings probably indicate that the NO2 profile probably has a steeper vertical gradient close to the surface than SO2 and HCHO. For measurements close to strong emission sources such differences in the vertical profiles might be expected due to the different atmospheric lifetimes (usually with the shortest lifetime for NO2).'

8) In a few places, the manuscript indicates good agreement between MODIS AOD and aerosol extinction as observed by the rapid inversion method. I do not believe that the manuscript ever shows anything more than vague qualitative consistency between MODIS AOD and surface-layer extinction. Therefore, language about agreement with MODIS should be eliminated or somehow more accurately stated. The point of agreement with visibility monitors is a good one, however. The authors seem to understand the reason for lack of relationship with MODIS, and described on P 8144, L 16 - 17. Additionally, if you examine Fig. 15, the AOD varies between 0.4 and 0.5 over these four days, which is shown on an expanded vertical axis (starting at 0.3). This is roughly 20% variation. The light path, however, is shown on an axis starting at 0, and varies more than the AOD. Overall, I think that comparison to MODIS over this short period of time and without any consideration of possible aerosol particles aloft is not useful.

Author reply:
We agree and we removed Fig. 15 and the related discussion.

9) One should not use references in the abstract of an article – because some services publish the abstract without the full paper. Therefore, on P 8130, L 4, references in the abstract need to be full references so that one can find them if the abstract is published without the article. Write out the reference here (e.g. say Sinreich, et al., Atmos. Meas.

Tech., 6, 1521-1532, doi: 10.5194/amt-6-1521-2013, 2013). Later reference to this paper in the abstract should be clearly referring to the Sinreich et al., 2013 work.

Author reply:
In our opinion, it is not appropriate to include this extended reference in the abstract because of two reasons:
-it makes the reading of the text more difficult and increases the length of the abstract.
-since AMT is an open access journal, it will be not problem for the interested reader to find the full Sinreich et al. 2013 reference and get access to the paper.
If the editor has a different opinion on this, it will of course not be a problem to include the extended reference.

10) The extrapolation of the effective light path to other wavelengths is probably not the largest source of error to these calculations. However, it is important to note that while the wavelength dependence of Rayleigh scattering is well known, the wavelength dependence of aerosol particle scattering is not well known and varies significantly with particle size. That complexity of aerosol particle properties gives me concern. Specifically, it seems that the calculation assumes an "urban" aerosol particle type in the boundary layer and "continental" above. It doesn't seem to consider any variability in aerosol particle optical properties, so this treatment seems incomplete. Therefore, a more complete treatment of aerosol light scattering might be warranted for use of this method under other conditions, or for coastal cities.

Author reply:
We agree that for different aerosol properties (slightly) different relationships between the path lengths at different wavelengths should be found.
We added the following text to section 2.1:
'Note that these aerosol particle properties are well suited for polluted sites. If this method is used in other conditions, also different aerosol properties should be used. However, since the differences in wavelength considered here are rather small, the resulting deviations from the relationships determined in this study are also expected to be small.'

11) The authors make a point of selecting data with SZA < 60 degrees. They also indicate at times that certain RAA values are problematic. Can the authors make suggestions as to the appropriate cutoff values for SZA and RAA that give "good" data. Additionally, could the authors indicate what "good" is and suggest the increase in uncertainty associated with exceeding these limits?

Author reply:
We added a new Figure (Fig. 7) to our paper which shows the dependency of the relative uncertainty of the correction factor as function of the correction factor itself.

Also shown (colour coded) are the dependencies on SZA and RAA. It follows from this figure that the uncertainties are especially large for specific observation geometries, especially for SZA > 70 ° and for RAA < 50 °. Such measurement conditions should be avoided when applying the method proposed in this study.

We added the following text in section 2.3:
'In Fig. 7 the relative uncertainties of the correction factors are plotted against the corresponding correction factors. The smallest uncertainties are found for correction factors close to unity. In addition, it is found that the uncertainties are especially large for specific observation geometries, especially for SZA > 70 ° and for RAA < 50 °. Such measurement conditions should be avoided when applying the proposed method.'

We modified the text at the end of section 6 to:
'It should be noted that for specific observation geometries (SZA > 70 °, RAA < 50 °) the uncertainties of the correction factors becomes especially large. Thus we recommend that the rapid method should be applied for SZA < 70 ° and RAA > 50 ° to ensure that the uncertainties are mainly <20%. In this study, the SZA was always < 60 °, but we excluded measurements with RAA < 50°.'

12) The radiative transfer modeling must have assumed some surface albedo. Please list that value. Additionally, the parameters listed in the table are presumably a function of this assumed albedo, and if they vary strongly with albedo, they would not be appropriate to other situations. Please include discussion of albedo in this work.

Author reply:
Many thanks for this important hint!
To determine the sensitivity of the correction factors on the surface albedo we performed additional radiative transfer simulations. We found that the correction factors are almost insensitive to variations of the surface albedo. We added this information at the end of section 2.3 (old section 2.2):
'We also investigated the influence of the surface albedo on the correction factors.
In addition to the value of 0.05, which was used as a standard value in this study, we also calculated correction factors for surface albedos of 0.03 and 0.1. We found that over the entire range of parameters used in this study, the differences to the correction factors for an albedo of 0.05 are <2%. So we conclude that the correction factors are almost insensitive to surface albedo. Here it should be noted that this conclusion is probably not valid for exceptionally high values of the surface albedo like e.g. over snow and ice.'

Terminology problems:

The language of the article needs to be improved. Some examples of words that are used poorly or are the incorrect words are below. These words should be found and

replaced or made consistent throughout the text. Some sections say measurements were made in the "outskirt", while others use the correct term, outskirts. The phrase "surface near" should probably be near-surface. The phrase "circularly measuring" is confusing. The use of the phrase "divergences" is strange and should probably be differences. I think that divergence seems to indicate the vector operator, and that is not what is being discussed. The phrase "sensitive altitude range" is poorly worded, and probably not necessary. The article has a large number of very similar acronymns that make things confusing – RAA, RA, AR, and AA, are all used – The article could become more clear through decreased use of acronyms. Figures indicate measurement in the term "maxing ratio", which should be "mixing ratio". Many prepositions chosen are not correct. Please assure that all co-authors read the text for grammar.

Author reply:
Many thanks for the identification of these errors and the respective suggestions!
-The term outskirt was replaced by outskirts
-"surface near" was replaced by ‘near-surface’
-‘circularly measuring’ and ‘circularly pointed’ was replaced by more adequate wording
-divergence(s) was replaced by ‘difference(s)’
-‘sensitive altitude range’ was replaced by ‘probed altitude range’
-‘AA(s)’ is replaced by ‘azimuth angle(s)’
-maxing ratio’ is replaced by ‘mixing ratio’

We also carefully read the manuscript and corrected many parts of the text. Please also note that the manuscript will be proof-read by a language expert after final publication.

Specific comments:

Note that terminology and grammar problems are described above, and many instances of these exist in the text but are specifically called out below. Only some of these instances are listed below, as well as other specific comments.

P 8130, L14: The abstract says "the uncertainties are especially small". It is not clear what uncertainties are being discussed here.

Author reply:
We replaced ‘uncertainties’ by ‘uncertainties of the retrieved values of the mixing ratios and surface extinction’

P 8130, L15-20: This section should be reworded for clarity. The section seems to imply that the correction factors are a function of modeled O4 absorption, when they actually appear to be a function of relative azimuth angle. Possibly this section of the abstract could be cut, retaining only the result of typical uncertainty?

Author reply:
We replaced the sentences:
‘We apply correction factors (and their uncertainties) as function of the simultaneously modelled O4 absorption. In this way the correction factors can be directly determined according to the measured O4 dAMF.’

with

‘We determine (and apply) correction factors (and their uncertainties) directly as function of the measured O_4 absorption.’

P8130, L23: I think you want "outskirts"
corrected

P8132, L10: I think you mean "optimal estimation"
corrected

P8132, L14: There is a colon that should probably be a period.

Author reply:
We think that the colon is appropriate here.

P8133, L13: Measurement at "90 degrees" is indicated. How often is this measurement made? Later, in the fitting section, do you measure 1 degree, then 90 degrees, then next azimuth 1 degree....? Overall, this is not clear as to how the reference is dealt with.

Author reply:
The sentence was replaced by:
‘For each azimuth angle, after each spectrum measured at 1 ° elevation angle, an observation at 90° was made to get a Fraunhofer reference spectrum.’

P8134, whole page: This description of MAX-DOAS is not very clear. Please try to reword it more clearly. For example, the Frauenhofer reference does remove solar absorption features, but in this application of MAXDOAS, it also removes all stratospheric absorptions from the dSCDs observed because the stratospheric paths are similar between light detected at 1 degree elevation and 90 degree elevation angle.

Author reply:
We completely rewrote this part after ‘compared to the near surface layer.’:
‘For MAX-DOAS observation, a Fraunhofer reference spectrum is needed to remove the strong Fraunhofer lines of the measured spectrum at low elevation angle. For trace gases with a substantial stratospheric partial column also the stratospheric aborption cancles out, because the stratospheric light paths are almost independent on elevation

angle. The application of the Fraunhofer reference spectrum further enhances the weighting of the measurement sensitivity towards the surface, because the absorptions from the atmosphere above the surface-near layers mainly cancel.

P8138, L4 and below: The units are missing from these equations.

Author reply:
We added the units

P8138, end of page: the use of "real" in strange here. I would suggest using "assumed"

Author reply:
We changed “real” to “assumed”.

P8141, L11: The anti-reflection is a coating. A 2-D motor is probably two motors. What is the manufacturer of the compass and inclinometer? Is the accuracy of the inclinometer actually 0.01 degrees?

Author reply:
This text is replaced by:
‘The instrument includes a quartz telescope (field of view angle of 0.2 °) with an ultraviolet-anti-reflection coating. The telescope is carried by two motors , which are located outdoors on an elevated platform to collect scattered sunlight. The motors allow a two dimensional pointing of the telescope to any direction with a precision of 0.05 ° based on the feedback of the electronic inclinometer with a precision of 0.01°.’

We checked that the information about the accuracy of the inclinometer is correct.

P8143, L7: The window contains two O4 absorption bands.

Author reply:
‘O_4’ was added.

P8144, L26: Some RAA values are edited out of the data for comparison. As mentioned above, can the authors suggest values to use?

Author reply:
We clarified this aspect (see point 11 above)

P8145, L27: R-squared values differ from abstract.
corrected

P8147, L9: U-shaped concentration profiles are commonly also affected by increased vertical convective mixing during midday causing dilution by entrainment of air above.

Author reply:
Many thanks! We agree with this additional explanation. However, we removed the whole section 4.3.1 from the revised version of the paper (see point 1 of the major comments).

P8152, L25: Again, here the "maximum and minimum" values of correction factors are really just the range of assumptions made, not true maximum and minima.

Author reply:
We replaced ‘uncertainty’ with ‘and the respective differences between minima and maxima’

P8154, L15: No quantitative relationship between AOD from MODIS and MAXDOAS has been shown in this manuscript, so this conclusion should be eliminated.

Author reply:
We removed the figure and the related text.

P8161, Table 1: The unit on the height of the BL is missing. I presume all combinations of these values were explored. Make that clearer.

Author reply:
The unit was added and the sentence “All combinations of these values were explored” was added to the paper.

P8162, Table 2: Units are missing from this table.

Author reply:
We added the units “ppb” for the “intercept”.

P8176, Fig 14: If this figure is not eliminated, its vertical axis should have the same label as the final term used for this parameter. The current figure’s title disagrees with the text.

Author reply:
This figure was eliminated

P8180-P8182, Figures 18-20 say "maxing ratio" but should say "mixing ratio"
corrected