

Response to Reviewer #3, comments to “The CU 2-dimensional MAX-DOAS instrument - part 1: retrieval of NO₂ in 3 dimensions 1 and azimuth dependent OVOC ratios” by Ortega et al., 2014.

We thank the reviewer for the evaluation of our paper and for the several valuable comments. Please see below our replies. We use the following color code:

Black: Referee’s comments

Blue: Author’s reply

Green: sentence added/modified in the manuscript

The paper of Ortega et al. describes the University of Colorado (CU) two dimensional (2-D) Multi-Axis-Differential Optical Absorption Spectroscopy (CU-2D-MAX-DOAS) instrument which has been developed to probe the 3D distributions of aerosols and atmospheric trace gases that are relevant to air quality and tropospheric chemistry. This spectrometer was deployed as part of the Multi Axis DOAS Comparison campaign for Aerosols and Trace gases (MAD-CAT) in Mainz, Germany from 7 June to 6 July 2013. 2 modes of operation of the telescope (off-axis scans at a fixed azimuth angle and azimuthal scans at fixed elevation (almucantar scans)) as well as the light path variation with wavelength are exploited to retrieve aerosol and NO₂ vertical profiles and the horizontal distribution of the NO₂ near-surface concentration and OVOC slant column ratios (HCHO-to-NO₂, CHOCHO-to-NO₂ and CHOCHO-to-HCHO). A first attempt of OMI NO₂ data validation using these measurements is also presented.

Although investigating too many different topics to my opinion, this study is a valuable contribution on how to better exploit/characterize the horizontal extend of MAX-DOAS observations, which is a timely subject matter. Therefore I recommend the paper for publication in AMT after addressing the following comments:

Major comments:

1/Except for aerosols (comparison of retrieved AODs with AERONET), there is no attempt to validate/verify the retrieval results presented in this study, even if the challenges of validating 3-dimensional measurements are discussed in Sect. 4.6. To my opinion, this weakens the paper. In particular, what is the validity of approximating the PBL height as the altitude over which the NO₂ mixing ratio decreases to 1/(2e) of the near-surface value of the retrieved NO₂ vertical profiles ? Is this approximation also applicable to aerosol extinction profiles (Fig. 6 seems to indicate that the mixing layer height is quite different using aerosols or NO₂ profiles) ? During the MAD-CAT campaign, a ceilometer was also operated by MPIC to derive information on the vertical structure of the aerosol extinction. I recommend to compare the retrieved PBL height with those measured by the ceilometer. This is critical since the PBL height through the correction factor f_c is a crucial parameter in this study.

In the revised manuscript we adopted terminology consistent with that of Sinreich et al. (2013), however we refer to the NO₂ mixing layer height (MLH_{NO₂}) instead of planetary boundary layer (PBL) to avoid confusion with the meteorological term. We have modified section 4.6 to reflect similar comments also from other Reviewers, and present a sensitivity study that explores

sensitivity in the NO₂ VMR to the assumptions about the MLH_{NO2}. This independent approach assumes a NO_x box-profile, assigns the near surface VMR from an optimal estimation retrieval, and assigns an effective MLH height based on the measured NO₂ VCD using the following equation:

$$VCD_{NO_2} \approx VMR_{NO_2} \cdot MLH_{NO_2,eff} \cdot CF$$

where VCD_{NO_2} has units of molec·cm⁻², VMR_{NO_2} is in ppb, $MLH_{NO_2,eff}$ has units of cm, and CF is the conversion factor between mixing ratios and molec·cm⁻³. The retrieved $MLH_{NO_2,eff}$ was compared with the 1/2e decrease of the actual profile shape described in the manuscript. We found a good correlation ($R^2=0.81$) with a linear fit of $MLH_{NO_2,eff} = 0.93 \pm 0.06 \cdot MLH_{NO_2} + 0.10 \pm 0.04$ [$R^2 = 0.81$]. The resulting $MLH_{NO_2,eff}$ is within the error near the lower limit of the standard deviation calculated with the multi-wavelength retrieval of the MLH_{NO_2} , which is used to calculate the variability associated with the MLH_{NO_2} as mentioned in the revised manuscript. We have added a short description of this comparison exercise in section 4.1.2:

“For the calculation of f_c the time resolved average MLH_{NO_2} obtained with the three wavelengths is used and the standard deviation is used to estimate its variability. The sensitivity of the height distribution of NO₂ on f_c was tested with an independent method. This approach assumes a NO_x box profile shape, assigns the near surface NO₂ VMR from OE, and assigns an effective mixing height ($MLH_{NO_2,eff}$) based on the measured NO₂ VCD. The retrieved $MLH_{NO_2,eff}$ was compared with the MLH_{NO_2} calculated before. We found a good correlation ($R^2=0.81$) with a linear fit of $MLH_{NO_2,eff} = 0.93 \pm 0.06 \cdot MLH_{NO_2} + 0.10 \pm 0.04$ [$R^2 = 0.81$]. The resulting $MLH_{NO_2,eff}$ is within the error near the lower limit of the standard deviation, which is used to calculate the variability associated with the MLH_{NO_2} as mentioned before.”

Note that the MLH_{NO_2} derived with the NO₂ is the relevant quantity to calculate correction factors. This is an operationally defined quantity that is a characteristic height specific to the NO₂ vertical distribution (profile shape); it has nothing to do with the ceilometer measurement, which work on gradients in aerosol backscatter, or the PBL definition in meteorology textbooks, Aerosols have a very different lifetime than NO₂, and there is no reason why the ceilometer should present data that is suited for ‘validation’.

Also related to validation, why the retrieved NO₂ surface concentrations are not compared to values from the regional Rhineland Palatinate and Hesse air quality networks? An interesting verification exercise would be also to compare the NO₂ surface concentrations from the retrieved vertical profiles to those derived by using the Sinreich et al. (2013) approach. For instance, is the level of agreement between the two approaches depending on the considered ring/layer (L1/L2/L3) ?

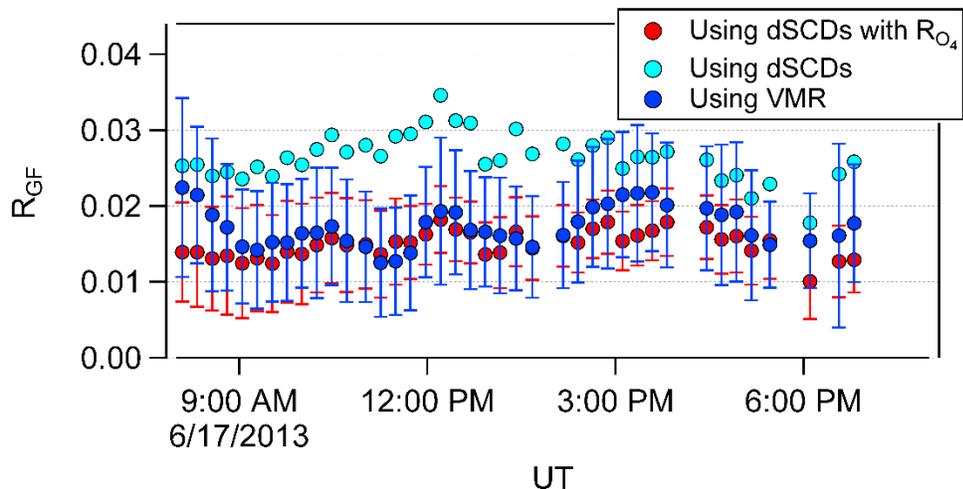
See our detailed response to Reviewers #1 and #2 regarding the comparison with in-situ sensors from the regional air quality network. We have added a new Figure S5 for the comparison suggested by the Reviewer, and refer to our response to Reviewer#2 for details. In the revised manuscript we modified section 4.6 where the multi-wavelength NO₂ near-surface mixing ratio retrieved with the parameterization approach are compared with those derived from optimal estimation for the standard azimuth view.

2/Investigating the HCHO-to-NO₂, CHOCHO-to-NO₂, and CHOCHO/HCHO dSCD ratios is an interesting study on its own but is for me a bit out of scope here, especially given the fact that dSCDs are used to investigate these OVOCs ratios and not near surface concentrations. The reason invoked is that the use of dSCDs does not require ‘complex and laborious RT calculations, resulting in a fast retrieval for near-real time monitoring of air pollution/chemistry’. Does it mean that the surface concentration retrieval methods presented here are not applicable for near real time analysis (let’s say within 24h delay) due to a too high computing time ? If yes, how this could be improved? Is it related to the type of RT model (full spherical Monte Carlo) used in this study ? May be this should be discussed in a revised Sect. 4.6 on the challenges of 3 dimensional MAX-DOAS measurements/retrievals themselves and not only their validation. This point is important for future satellite validation campaigns involving MAX-DOAS measurements.

We agree with the referee, and have modified section 4.6 to discuss the challenges of 3D retrievals themselves. In the revised manuscript we have expanded the Section 4.6 to compare our parameterization approach with optimal estimation for the standard view.

As mentioned in the manuscript, the ratios calculated with the dSCD are straightforward to derive (within seconds apart from the measurements), hence for future 3D application they can be used quasi real time to inform air mass chemistry around the measurement site. Measurements of 3D retrievals are still in its infancy. Ours is the first retrieval strategy to interpret 2D-MAX-DOAS data, and our retrieval strategy has not been optimized for ‘speed’. There is significant development need, and different strategies are yet to emerge, and will then need to be compared before the emphasis should be on ‘speed’ in our opinion.

As mentioned also in the manuscript, ratios calculated with the same window (R_{FN} , R_{GN}) do not carry high uncertainty. However, for the R_{GF} (CHOCHO-to-HCHO) the difference in wavelength needs to be accounted for, as is demonstrated in the below Figure. We have retrieved vertical profiles of CHOCHO and HCHO for the standard azimuth view using OE. The near surface VMR of CHOCHO and HCHO are used to calculate R_{GF-OE} and compared with the R_{GF} based on dSCD, and R_{GF} as described in the paper (using the R_{O4} factor). If the R_{O4} factor is not used R_{GF} is overestimated by up to 45% based on the ratio of dSCD.



For trace gas ratios profiles in the boundary layer a complete retrieval approach, e.g., optimal estimation, should be used. In addition, the error in the ratios, especially for HCHO-to-NO₂ and CHOCHO-to-NO₂, is lower since the error propagation carries only dSCD fit errors. We have modified part of the description of the ratio calculation (section 3.4) to make it more explicit:

“With the intention of evaluate the azimuthal distribution of the trace gas ratios in the PBL we use dSCD. R_{FN} and R_{GN} are calculated with the dSCD obtained in the same wavelength window, hence the optical path lengths are very similar and they are not expected to carry a high uncertainty due to differences in scattering events along the light path. However, R_{GF} needs special attention since HCHO and CHOCHO retrievals employ different wavelengths during the DOAS analysis (Table 3), and thus reflect different optical paths.... Another important advantage which arises from using dSCD in the azimuth scan is that no complex and laborious RTM is necessary, resulting in a fast retrieval to determine near-real time air mass chemistry.”

We also have added a short description at the end of section 4.4 to describe the error of the trace gas ratios:

“The error on the ratios, calculated with the DOAS fit error propagation of the dSCDs, show errors lower than 5%, 10%, and 20% for R_{FN} , R_{GN} , and R_{GF} respectively.”

Minor comments:

Page 11663, lines 4-6: the zenith spectrum measured at the end of each EA sequence is used as reference for removing the stratospheric contribution for all trace gases and for a complete modes 1+2 cycle. By proceeding this way, you don't take into account the possible variation of the stratospheric contribution during a complete cycle. A better approach would be to interpolate

the zenith SCD at the time of each single measurement using the zenith SCDs of two consecutive cycles.

Thanks for the suggestion. Actually we had a mistake in the description of this paragraph. The paragraph has been modified because the actual zenith spectra measured at the beginning of mode 1 is used to analyze mode 1. At the end of mode 1 another zenith spectra is also measured and used as a reference spectrum for mode 2. The paragraph reads as follow:

“The zenith spectrum measured at the beginning of mode 1 is used as a reference spectrum in the analysis of all trace gases in mode 1. At the end of mode 1 another zenith spectrum is measured and used to analyzed trace gases in mode 2. Thereby we minimize stratospheric contributions and possible variation of stratospheric contribution during a complete cycle.”

We have also modified table 2 accordingly.

Page 11666, lines 8-11 and Eq. (4): It is not clear to me how the S_a matrix is constructed, in particular, what are the variance and correlation length which have been used ? Please mention these information in the revised manuscript.

The paragraph was modified accordingly to make it clear:

“The S_a matrix was treated as a tuned parameter in order to avoid non-real oscillations in the retrieved profiles (Clémer et al., 2010; Baidar et al., 2013; Hendrick et al., 2013.). The diagonal elements of the S_a were set to account for large variations, up to 100%, of the initial a priori profiles. The non-diagonal in the S_a matrix were correlated through the altitudes (z) with a well-used exponential Gaussian decay function (Barret et al., 2003; Clémer et al., 2010):”

“In this equation z_i and z_j are the altitudes of the i -th and j -th grid layers respectively and γ is the correlation parameter, which was set to 0.3 km, similar to the inversion grid height. The wavelengths used to retrieve NO_2 vertical profiles are the same as for the aerosol extinction profiles (350 nm, 450 nm, and 560 nm).”

Page 11671, lines 10-11: it is stated that, according to the averaging kernels, the first two kilometers are well constrained by the measurements. This would be more convincing if you show these averaging kernels.

An averaging kernel example is now shown on the modified Fig. 6.

Sect. 4.2.2, page 11674: It would be useful for the reader to include a table summarizing the error budget on the retrieved NO_2 vertical profiles and surface VMRs.

In the revised manuscript we have included Table 6 (see below), which summarizes the error budget in both the vertical profiles and near surface averaged NO₂ VMR. We also noticed that description of the error in the profiles is missing. Hence, we have introduced a short description at the beginning of section 4.2.2.:

“Table 6 shows a summary of the errors for both OE and parameterization. In the following, the errors of the vertical profile retrievals by OE are discussed briefly. For a detailed and more formal description of the error associated in the retrieval of vertical profile using OE we refer to the excellent studies by Rodgers, 1990; Rodgers, 2000; and Steck, 2002. We have considered three main errors: (1) retrieval noise error associated with the uncertainty in the dSCD, 2) the smoothing error, which represents how in average the constrained retrieval differs from the true state due to the vertical smoothing, and (3) systematic errors from the forward model parameters. The retrieval noise is so far the easiest error to be determined since it is retrieved directly from the gain matrix (G_y) and the S_ϵ covariance matrix error as: $S_n = G_y S_\epsilon G_y^T$. As mentioned before S_ϵ is built using the square of the DOAS fit error which represents a final error of less than 1%, however the final noise error should have uncertainties in the NO₂ absorption cross section (~5%). The error due to smoothing and the forward model covariance matrixes listed in Table 6 were taken from sensitivity studies. The smoothing error is determined based on the inversion with simulated NO₂ dSCD. First, simulated NO₂ dSCD under pre-defined scenarios were used to retrieve the NO₂ vertical profiles under known conditions. The difference between the ‘real’ and the retrieved NO₂ profiles was taken as an estimate of this error. On the other hand the forward model parameters are estimated by changing the most important input parameters such as aerosol optical properties in an expected range.”

At the end of the section we added:

“Table 6 shows a summary of the errors for both optimal estimation and parameterization.”

Method	Error overview (%)	Total error (%)
OE	Noise: ~5; Smoothing: ~7; Forward model: ~10	~13-16
Parameterization	Fit error: ~ 5; correction factor: ~10	~12-15

Table 6. Overview of the most important errors in the determination of NO₂ vertical profiles.

Sect. 4.4, page 11676: what are the uncertainties on the three OVOC ratios ?

We have added a short description at the end of section 4.4 to describe the error of the trace gas ratios:

“The uncertainty on the ratios is calculated with the error propagation of the 2-sigma fit error obtained for the dSCD. The final error are lower than 5%, 10%, and 20% for R_{FN} , R_{GN} , and R_{GF} respectively.”

Sect. 4.5, pages 11677-11678 + Figure 11, page 11709: nothing is said about the uncertainty on the OMI NO₂ VCDs presented here and there is no error bar on OMI observations in Figure 11. They are probably quite large given the fact that only two pixels are used. So, is the overestimation of OMI by MAX-DOAS still significant if you put error bars on OMI data in Fig. 11 ?

This is a very good point. We have introduced the error bars on OMI observations in Fig 11, and added two sentences near the end of the second paragraph on section 4.5 that discuss the error in the tropospheric NO₂ VCD derived with OMI:

“The error bars in the NO₂ wavelength dependence represent the NO₂ VCD standard deviation calculated based on the azimuth distribution and the OMI error bars are the errors in the NO₂ VCD reported during the overpass.”

“Note that even though the error of the OMI based NO₂ are quite large due to the single overpass the overestimation of the MAX-DOAS obtained in the UV is still significant. Further research should be done to investigate the azimuth distribution and wavelength dependence with long time series. It is interesting to note that the assumption made to calculate the azimuth NO₂ VCD using the azimuthal NO₂ VMR would be overestimated based on the NO₂ vertical profiles (Fig.6), which are not box profile type. To establish the possible overestimation we performed a sensitivity study where the NO₂ VCD in the standard azimuth view was calculated integrating the NO₂ vertical profiles and compare them with the assumption of using the MLH_{NO₂} estimated previously. As expected, the NO₂ VCD is overestimated by a factor of 15-20% if we use the assumption of the MLH_{NO₂}. In this context, the agreement of the NO₂ VCD at 560 nm would be even better and the overestimation of the 350, and 450 nm NO₂ VCD would be in the order of 35% and 25% respectively”

Table 1, page 11693: the spatial resolution of the measurements is estimated to 5-30 km. Maybe you should mention how these values are derived ?

The description of the spatial resolution is presented in section 4.2. Hence, in Table 1 we have directed the Reader to section 4.2.

Figure 3, page 11701: Examples of DOAS fits are shown for the different trace gases. Why the date of these example fits (June 6th, 2013) is not corresponding to the date of all the retrieval results presented in this study (June 17th, 2013) ?

Thanks for the suggestion. We have changed the fit examples from 17 June, 2013.

Technical corrections

Table 4, page 11696: CHOCHO cross sections (No. 6) is missing in the list of cross sections fitted for CHOCHO/NO₂.

Corrected.

Sect. 3.2.2, pages 11665-11666: The title of this section ‘NO₂ vertical profile and boundary layer height’ is a bit misleading since there is no discussion about the boundary layer height in it. I think renaming this section ‘NO₂ vertical profile retrieval’ would be more appropriate.

Thanks for the suggestion. We agree and modified accordingly.

Reference added:

Steck, T.: Methods for determining regularization for atmospheric retrieval problems, *ao*, 41, 973–1788–1797, doi:10.1364/AO.41.001788, 2002.