Interactive comment on "Mobile MAX-DOAS observations of tropospheric NO_2 and HCHO during summer over the Three Rivers' Source region in China" _by_ Siyang Cheng et al.: Reply to Anonymous Referee #1

Referee comments are in black. Author responses are in blue.

This manuscript describes mobile MAX-DOAS measurements recorded on drives around the Tibetan Plateau. The measurements are used to quantify the column of NO_2 and HCHO along circular drive paths on the Plateau. The measurements are compared to TROPOMI satellite products. The manuscript represents a valuable contribution to the literature and reports ground truth around this relatively remote and high-altitude region. The manuscript uses the geometric method to retrieve tropospheric vertical column densities from differential slant column densities measured on the vehicle. This method, while lacking the refinement of one using radiative transfer calculations, is reasonable for this purpose. However there are some details on the method that should be discussed further and it would be valuable for other groups to understand how to optimize the measurements to get the most measurements from such studies. Concerns on the method are described below, followed by specific comments. If the concerns regarding the method can be addressed, this manuscript would be acceptable for publication in ACP.

Reply: First of all, we appreciate the reviewer's positive comments on our manuscript. In response to the reviewer's comments and suggestions, we have made relevant revisions to the manuscript. Listed below are our responses and the corresponding changes made to the manuscript according to the suggestions given by the reviewer. Note that the Sections 4.2 (Temporal variation) and 4.3 (Spatial distribution) in the original manuscript were reorganized into Section 4.2 (Spatio-temporal variation) in the revised manuscript. This change is not marked up using revision track in order to keep the manuscript clear to read.

Were the elevation angles recorded relative to the mobile vehicle or to gravity? If they were gravitationally referenced, was a gyroscope used? If they are relative to the road, how is the local horizon taken into consideration? I think lines 260-265 indicate that the angles are with respect to the vehicle, and that is a reason to use higher elevation angles, but the text is not very clear to this regard. Can the authors be more clear about how the view geometry is defined?

Reply: The elevation angles were recorded relative to the mobile vehicle. We didn't use a gyroscope. During our deployment strategies, we designed a partial system recording the attitude angles of the mobile vehicle to correct the elevation angle of MAX-DOAS measurements. However, it did not work well and couldn't be used for this study. To reduce the influences of local non-horizontal road on the un-corrected elevation angle, we used the DSCDs at larger elevation angles. Also, the VCDs were further filtered based on the absolute difference and the relative difference of VCDs between 15° and 20°. The definition of elevation angle has been added to the text in Section 2.1 of the revised manuscript.

As is pointed out by the authors, the higher altitude and lower aerosol extinction conditions of a sparsely populated plateau make the geometric approach more tenable. However, clouds or aerosol-particle-rich pollution plumes (which may accompany NO2) may affect this assumption. Therefore, it seems reasonable to check this assumption by using O4 observations. The authors could calculate the O4 VCD above the vehicle from the altitude (which they know) and pressures at meteorological stations (or better soundings if available). They can then use the mobile-measured geometrically calculated O4 VCD_15 to compare to the meteorologically calculated one. Due to radiative transfer effects, particularly the relative azimuth angle to the sun, these quantities won't be perfect, but times when there is a large amount of aerosol or clouds or the view azimuth happened to be close to the sun, one could tell that the NO2 and HCHO data are being affected by these confounding effects. This check should help to assure that the geometric method is working for NO2 and HCHO.

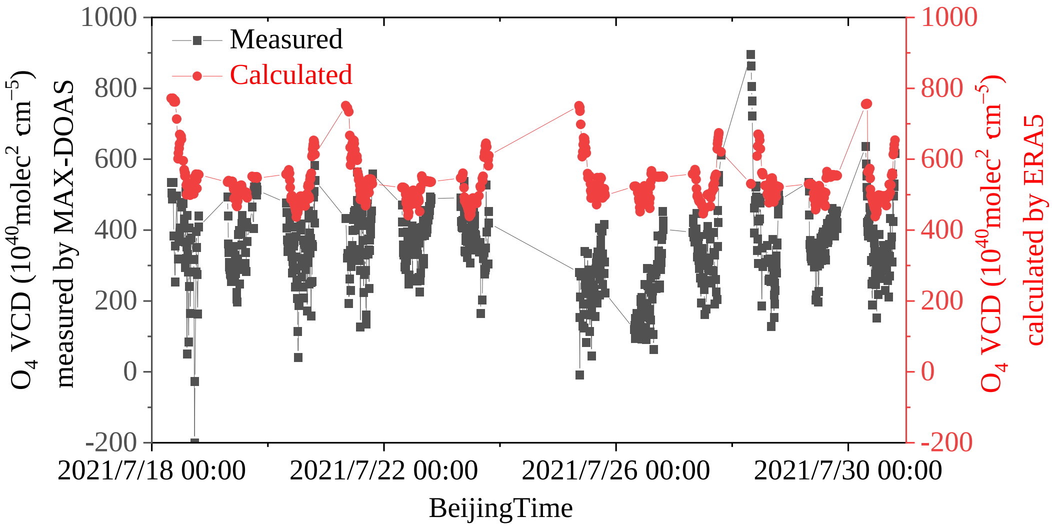
Reply: Many thanks for your suggestions. The procedures of O_4 VCDs derived from MAX-DOAS measurements and calculations are as the following.

(1) The O_4 DSCDs were retrieved from MAX-DOAS spectra in the wavelength interval of 351-390 nm using a sequential FRS and are then filtered by the conditions of SZA <80°, RMS < 0.005, offset (constant) between ±0.03. The O_4 VCDs obtained by the geometric approximation method at 15° elevation angle were further filtered by the differences of the O_4 VCDs between 15° and 20°. The O_4 VCDs were kept if the

absolute difference of VCDs between 15° and 20° is < 1×10^{42} molec^2 cm^{-5} or the relative difference is <10%.

(2) During the procedure of the O_4 VCD calculation, we used the air temperature and pressure profiles of hourly ERA5 with 0.25°×0.25° grid above the altitude of the driving route. Firstly, we extracted the profiles of temperature and pressure matched with each measurement at the same grid cell and the same hour. Then we calculated the O_2 concentrations from the surface to 30 km at each altitude with a vertical interval of 50m. The O_4 concentrations were assumed as the square of the O_2 concentrations at each vertical grid cell and integrated as O_4 VCDs from the surface to 30 km (Wagner et al., 2019).

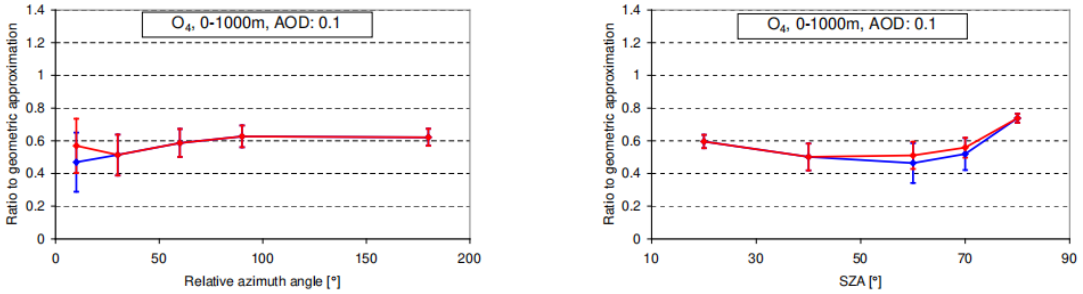
The results of O_4 VCDs derived from the MAX-DOAS measurements and calculated from ERA5 data are shown in the figure below. The main finding is that the measured O_4 VCDs are systematically lower than the calculated ones. Part of the underestimation is probably related to clouds, but a strong underestimation is also found for measurements for clear skies.



Hence we further explored the applicability of the geometric approximation method by radiative transfer simulations. According to the AODs from the AERONET website (https://aeronet.gsfc.nasa.gov, last access: 2 December 2022) at three sites (Mt_WLG, NAM_CO, QOMS_CAS) over the Tibetan Plateau, we estimate the AODs around 0.1 during our field campaign. But similar results are also found for AODs of 0.05 and 0.2. The simulation scheme is as the following.

Parameters	O_4	NO_2	HCHO
Wavelength (nm)	340	440	340
Layer height (km)	US standard atmosphere	0-1; 0-2	0-1; 0-2
Aerosol height (km)	0-1	same as trace gases	
AOD	0; 0.05; 0.1; 0.2	0; 0.05; 0.1; 0.2	0; 0.05; 0.1; 0.2
SZA (°)	20, 40, 60, 70, 80		
RAA (°)	10, 30, 60, 90, 180		
Elevation angle (°)	15		
Terrain height (km)	2, 3, 4, 5		

The VCD ratios of the RTM simulations and the geometric approximation for 15° elevation angle under the condition of AOD=0.1 can be obtained for O_4, NO_2, and HCHO, respectively. The DAMF ratios' means and standard deviations for all geometries (blue symbols) and RAA=10°, SZA=60° and RAA=10°, SZA=70° excluded (red symbols, for these rare measurement scenarios the strongest errors occur) are shown below. The main findings are: (1) The typical errors of the geometric approximation are <20% for NO_2 and HCHO; (2) The errors of the geometric approximation are much larger for O_4 with a systematic underestimation between about 40% and 60%, which are in overall agreement with the comparison of the measured and calculated O_4 VCDs above; (3) The large underestimation of the O_4 VCDs indicates that O_4 can not be used for the test if the geometric approximation is justified or not for an individual measurement of NO_2 and HCHO.



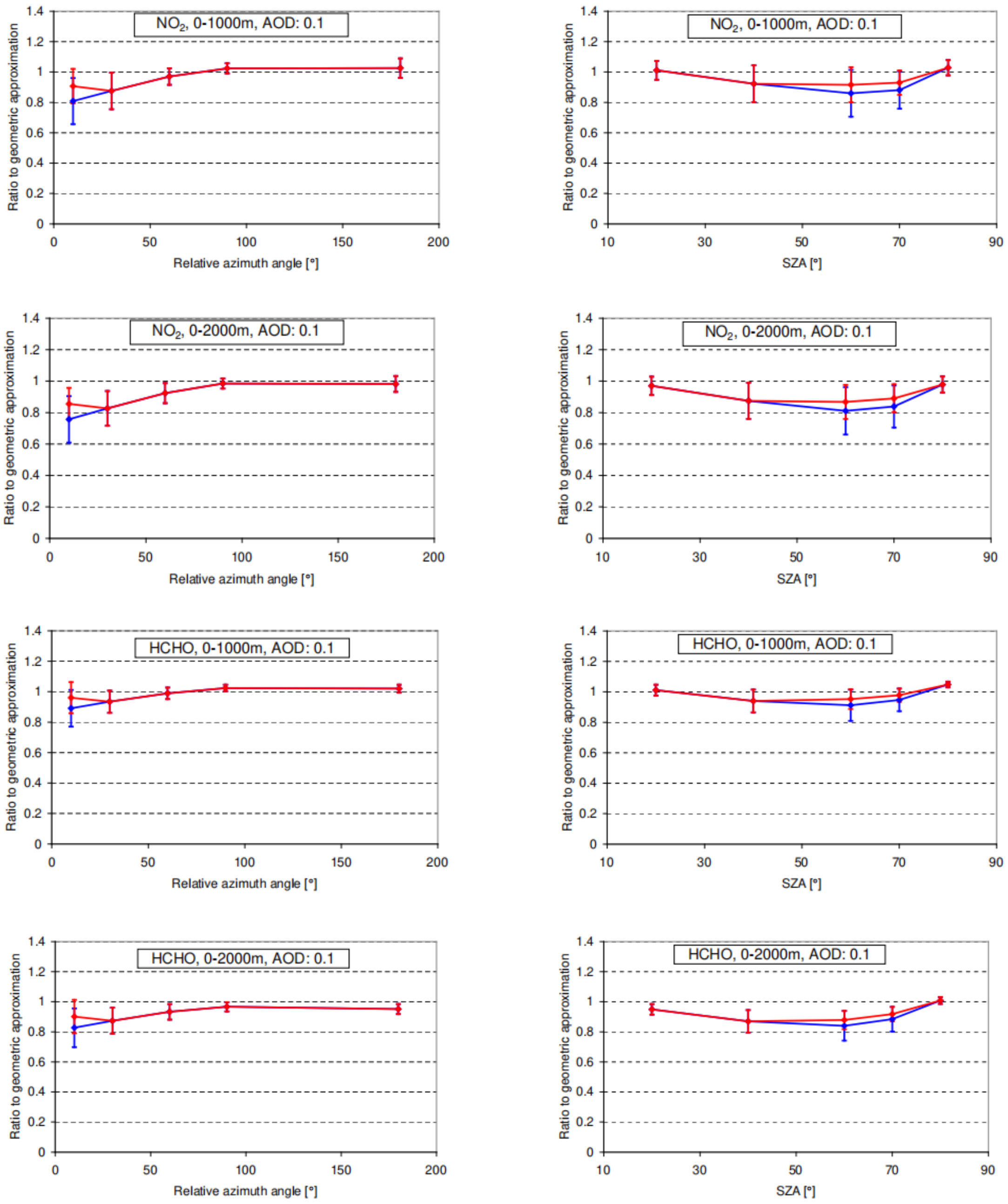


Figure S1 in the revised supplement

Reference:

Wagner, T., Beirle, S., Benavent, N., Bösch, T., Chan, K. L., Donner, S., Dörner, S., Fayt, C., Frieß, U., García-Nieto, D., Gielen, C., González-Bartolome, D., Gomez, L., Hendrick, F., Henzing, B., Jin, J. L., Lampel, J., Ma, J., Mies, K., Navarro, M., Peters, E., Pinardi, G., Puentedura, O., Puķīte, J., Remmers, J., Richter, A., Saiz-Lopez, A., Shaiganfar, R., Sihler, H., Van Roozendael, M., Wang, Y., and Yela, M.: Is a scaling factor required to obtain closure between measured and modelled atmospheric O_4 absorptions? An assessment of uncertainties of measurements and radiative transfer simulations for 2 selected days during the MAD-CAT campaign, Atmospheric Measurement Techniques, 12, 2745-2817, 10.5194/amt-12-2745-2019, 2019.

It seems like data were recorded at 7 elevation angles, but only four of them were used, and then the 15 degree angle was selected, so only two (15 and 90) were used for the final determination of tropospheric VCD. Therefore, the scan pattern seems inefficient. The authors should discuss good practices for mobile DOAS deriving from this experience. It seems like the upper elevation angles are useful to tell that 15 degrees is not biased compared to other angles, but the lower elevation angles are affected both by road tilt (if the geometry is based upon the vehicle -- see above) and obstructions (e.g. buildings, canyon walls, etc.). Can the authors discuss this issue and give advice for future studies?

Reply: Many thanks for your good comments and suggestions. Because this is the first practice of mobile MAX-DOAS observations over the Tibetan Plateau, we didn't know which elevation angle was the best for measuring the tropospheric VCDs of trace gases in the background atmosphere over mountain terrain before this campaign. Therefore, we made the telescope scanning at 7 elevation angles. In future studies on observing tropospheric NO_2 and HCHO VCDs by mobile DOAS, we suggest to measure at 15°, 20°, 90° elevation angles. There are at least two reasons: (1) The larger elevation angles were less influenced by the road tilt and obstructions; (2) The measurements at 15° and 20° elevation angles have an enhanced sensitivity to tropospheric trace gases (increase of sensitivity compared to 90° elevation is about a factor 3.8 and 2.9, respectively). The increased sensitivity is especially important for measurements of the rather low trace gas concentrations in the background atmosphere. We have added the suggestion to the text at the end of Section 3.2 in revised manuscript from our experiences in this study.

The writing of this manuscript is readable, but in places it could be condensed regarding details that don't seem relevant to the study. For instance, description of the study region seems to include details not really related to the purpose of the study. In places some phrases may also need minor English language editing to read more clearly.

Reply: Many thanks for your kind suggestions. The paragraph about the study region has been refined. We also improved the English language in the revised manuscript.

Specific comments:

Units -- ACP uses SI units, which indicate that ppb and ppt are language dependent, so they prefer mixing ratios in nmol mol^-1 or pmol mol^-1.

Reply: Agreed. We have checked the units in this paper and revisions have been made.

Line 117: Maybe a transition here to say that although there are challenges, it is useful for reasons...

Reply: Agreed. The description has been modified as "Although there are challenges in measuring NO_2 and HCHO concentrations by mobile MAX-DOAS over the Tibetan Plateau, they are useful for studies on the spatio-temporal evolution of the atmospheric composition in the background atmosphere, validation and improvement of satellite products over mountain terrain, and evaluation of the simulation results of atmospheric chemistry models over the Tibetan Plateau.".

Line 150: Were the angles with respect to gravity or with respect to the mobile platform? How where they corrected to be with respect to gravity?

Reply: The angles were with respect to the mobile platform. We use the uncorrected elevation angles in this study. Originally we planned to use the platform attitude angle to correct the elevation angles. It is a pity that the partial system of the attitude angles of the mobile vehicle did not work well during the field campaign. Nevertheless, we estimated the uncertainties for measurements on tilted roads and found them very small (~1%) for the average of several measurements (for more details see below).

Line 152: What company manufactured the spectrometer?

Reply: AVANTES. This information and model number (AvaSpec-ULS2048x64-USB2) have been added to the revised manuscript.

Lines 162 to 174: Some of this repeats information in the introduction, and some are a bit challenging to read (e.g. what does "four indistinct seasons" mean?). I'd suggest making this section more directly relevant to the mobile campaigns.

Reply: Many thanks for your kind suggestions. This paragraph has been refined.

Line 202: I found this sentence confusing. You could possibly reword or add the word "respectively" after "... can be neglected or cancels out". I think you mean that if a species has no stratospheric part, you can neglect the SCD_stra, or in the other case, if a species has a stratospheric part and there is no light scattering in the stratosphere (thus the light path in the stratosphere is the same independent of alpha) that SCD_stra appears in both SCDs and will then cancel out.

Reply: Per your suggestion, we have added the word “respectively”. You understood this sentence correctly.

Line 209: I presume the interpolation is in time at which the off-zenith spectrum occurs weighting the two neighboring zenith spectra. Can you clarify?

Reply: Yes, the “sequential FRS” are defined as the time interpolated spectra between two zenith spectra measured before and after the measurement time of the current off-zenith elevation angle. We have amended the description in the revised manuscript.

Line 266: I think that the authors should estimate the effect of the elevation angle error. Presuming that the view is relative to the car, one could use an estimate of road grade angle to calculate the magnitude of this error. In the US, interstate highways are allowed to be up to 6% grade (angle = arctan(0.06) = 3.4°). It would be good to quantify the magnitude of this error, and while I expect it to be small compared to others, the authors should show that it "can be neglected".

Reply: Many thanks for your kind suggestion. we estimate the error of the elevation angle to be about 2.3°, based on the median of the mobile platform attitude angle during the effective MAX-DOAS measurement period. The corresponding error of an individual measurement will be up to about 21%. However, it should be noted that on average the positive and negative deviations of the elevation angle will almost cancel each other. Thus the errors of individual measurements will be usually much smaller (except for measurements on continuous strong slopes). For averages of several measurements the errors of the elevation angles lead to much smaller VCD errors with a magnitude smaller than 1% when using geometric approximation method (equation 6):

$\alpha = 15° - 2.3° = 12.7°$, VCD=0.2818×DSCD;

$\alpha = 15°$, VCD=0.3492×DSCD;

$\alpha = 15° + 2.3° = 17.7°$, VCD=0.4232×DSCD;

[(0.2818×DSCD+0.4232×DSCD)÷2-0.3492DSCD] ÷(0.3492×DSCD)×100 =1%

Line 270: I think that this implies that "the geometric approximation method is self consistent", but not that it "has high accuracy". The test done by the authors is only a test of how consistent their data at one elevation angle is compared to another of their elevation angles. If there were aerosol light extinction that reduced pathlengths on each view, the results would still be correlated, but would be affected and not be accurate.

Reply: Agreed. The description has been amended as “the geometric approximation method is self-consistent”.

Line 320: I think the wording "This implies that..." is a bit too strong. The HCHO data are consistent with increasing temperature leading to more BVOC emissions, but they could also be affected by the temperature of the photochemical sources and sinks of HCHO.

Reply: Many thanks for your suggestion. The description of “This implies that” has been amended to “Probably” in the revised manuscript.

Around line 341: Could the U-shape for NO2 also be affected by the city at the start and end of each daily journey?

Reply: Yes. The U-shape of NO_2 VCD diurnal variation was affected by several factors. From our findings we conclude that the NO_2 diurnal variations were primarily caused by enhanced pollution in the morning and evening when the mobile observation vehicle was located in or close to the cities or county town. An additional effect on the diurnal variation is probably caused by the enhanced NO_2 photolysis around noon.

Line 394: Are these figure numbers right? I'm not sure how I can tell about the telescope direction from these maps. Possibly some better annotation on the maps (e.g. an arrow or special marker) would help. I'm not sure what "vehicle flowrate was less" means.

Reply: We checked the figure numbers again and they are correct. According to the explanations of the driving routes in Table 1, we added the marks ('XD', 'DY', 'YX') of the driving routes in figure 11 and figure 12 (of the original manuscript) to indicate the driving direction. The telescope pointed backwards of the driving direction, which was illustrated in Section 2.1. We have amended the description of "vehicle flowrate was less" to "traffic flow was lower" in the revised manuscript.

Line 465: It is of note that there is a large positive offset on the TROPOMI HCHO. It appears that this offset is larger than the MAX-DOAS observed typical column. Discussion of the offset in addition to the correlation would be appropriate.

Reply: Many thanks for your comments. Previous studies found that the offsets of the TROPOMI HCHO were dependent on the HCHO concentration levels and presented to be positive at remote sites (Vigouroux et al., 2020). The larger positive offsets of the TROPOMI HCHO in this study were probably related to the HCHO horizontal inhomogeneity, caused by mountain terrains and varying local microclimates over the Tibetan Plateau. This discussion has been added in revised manuscript.

Reference:

Vigouroux, C., Langerock, B., Aquino, C. A. B., Blumenstock, T., Cheng, Z., Mazière, M. D., Smedt, I. D., Grutter, M., Hannigan, J. W., Jones, N., Kivi, R., Loyola, D., Lutsch, E., Mahieu, E., Makarova, M., Metzger, J.-M., Morino, I., Murata, I., Nagahama, T., Notholt, J., Ortega, I., Palm, M., Pinardi, G., Röhling, A., Smale, D., Stremme, W., Strong, K., Sussmann, R., Té, Y., Roozendael, M. v., Wang, P., and Winkler, H.: TROPOMI–Sentinel-5 Precursor formaldehyde validation using an extensive network of ground-based Fourier-transform infrared stations, Atmos. Meas. Tech., 13, 3751–3767, 10.5194/amt-13-3751-2020, 2020.

Figures 9 and 10: It would be useful for Figure 9 vertical axes to say that NO2 VCD is plotted, and for Figure 10 to say HCHO VCD on the axis.

Reply: Per your suggestion, the title of the vertical axes in Figure 9 and Figure 10 (of the original manuscript) has been amended as "NO_2 VCD" and "HCHO VCD", respectively.