# **Reply to Referee #1**

First of all we want to thank this reviewer for the positive assessment and constructive comments.

We addressed these comments as explained in detail below.

This manuscript addresses an inconsistency persistently reported in several past studies (some of them by the same authors) between observations of the O4 absorption in atmospheric spectra and radiative transport simulations attempting to reproduce these observations. This inconsistency represents a major issue for the interpretation of MAX-DOAS measurements of aerosol properties, which are based on O4 slant column measurements. Results from past studies indicated that, to reconcile observations with simulations, it is often (but not always) necessary to apply a scaling factor of typically -20% to observations. The reason why this correction is needed remains unknown, but some authors suggested that it might be related to uncertainties in the knowledge of aerosol properties in the atmosphere, which can possibly affect the light path of the solar radiation in a complex way. In the present study, the authors try to overcome this difficulty by concentrating their analysis on observations performed under very low AOD conditions, therefore minimizing uncertainties due to aerosols. Even in such particular conditions, they find that simulations underestimate measurements by about 20%, which confirms that a fundamental inconsistency - not related to aerosols - exists between observations and simulations. Although the study is limited in coverage (only one day of measurements is presented), the proposed case is fully pertinent as it suggests that at least for the conditions of the study inconsistencies cannot be resolved by uncertainties in aerosol properties. The mystery remains however unresolved, since no valid explanation can be proposed. The suggestion that systematic errors on the O4 spectroscopy could be an explanation is on the one hand in contradiction with known uncertainties on laboratory measurements, and on the other hand also in contradiction with published results indicating that a scaling factor is not always required to bring measurements and simulations in good agreement. It would of course be interesting to multiply measurements in similarly low AOD conditions but this is clearly beyond the scope of the paper. From an editorial point of view, the manuscript is concise, well written and well organized. I therefore recommend its publication in AMT, after attention to the few comments listed below.

## Many thanks for this positive assessment.

## Specific comments

Pg. 5, l. 3: please justify the use of 0.05 as appropriate value for the albedo of the sea at UV wavelengths. A reference would be enough here. Also indicate at which wavelength the radiative transfer calculations have been computed.

We chose the value of 5% to be consistent with the MAPA inversions, and because it is appropriate for many parts of the global ocean. However, by having a closer look at maps of albedo (Kleipool et al., 2008) and chlorophyll content (e.g. from the NASA Earth Observatory: https://earthobservatory.nasa.gov/globalmaps/MY1DMM\_CHLORA), we found that at the specific location of the measurements, very clear waters exist, for which the surface albedo is typically higher (about 7 to 8%). The presence of very clear waters is also supported by the in situ chlorophyll measurements made aboard the ship.

We therefore made additional radiative transfer simulations using a surface albedo of 8%. We found that the obtained  $O_4$  dAMFs were almost identical with those obtained for 5% surface albedo (differences <1%). The reason for the good agreement is that the effect of the surface albedo is similar for the  $O_4$  AMFs for different elevation angles. Thus the effect of varying surface albedo almost cancels out. We added this information to section 6.

Pg. 5, l. 205: I have the impression that the use of lidar backscatter ratio profiles as a proxy for aerosol extinction profiles involves more assumptions than stated here. E.g., one also has to assume that the aerosol phase function does not vary much with altitude, and maybe more important that the backscatter profile shape measured at 1000 nm is also valid at 360nm. But despite all uncertainties, I agree that using ceilometer profiles makes sense in the absence of real extinction values. Maybe the system could be improved by adding a device to measure aerosol surface extinctions (if possible).

Unfortunately, no measurements of aerosol surface extinction are available.

With respect to the representativeness of the measurements at 1064 nm for the MAX-DOAS measurements, we agree with the reviewer that the aerosol properties can change with altitude, and thus the relative profile shape of aerosol extinction at 360 nm might differ from that at 1064 nm.

In order to estimate the effect of the varying aerosol profiles at both wavelengths, we performed additional radiative transfer simulations using modified tropospheric aerosol profiles. The aerosol extinction in the lowest 1000 m of the extracted profiles was changed by +/-20% and the free tropospheric part above was adjusted to keep the total AOD unchanged. The resulting O<sub>4</sub> dAMFs were almost unchanged for elevation angles >4°. For lower elevation angles, the changes were found to be +/-2%. We added this information to section 6.1.

Pg. 5, l. 221: add a reference to justify the Angström exponent of 2 used for the conversion of the stratospheric AOD (unless this would be documented in Thomason et al., 2018)

We took the value of 2 from existing publications (e.g. Malinina et al., 2019). However, most provided values are representative for larger wavelengths (typically 525 nm or larger). To estimate the uncertainties of the simulated O<sub>4</sub> dSCDs related to the uncertainty of the Angström exponent, we performed additional radiative transfer simulations assuming a stratospheric AOD of 0.008 (corresponding to an Angström exponent of 1). We found that the O<sub>4</sub> dSCDs differ from those for a stratospheric AOD of 0.012 by less than 1%. We added this information to section 6.1.

Pg. 7, sect. 7.2: considering the very low aerosol content, and the comparatively large uncertainty of the assumed stratospheric AOD (basically a climatological value at 525 nm converted to 360 nm using a not well established Angstrom exponent), I think that the AOD values retrieved by MAPA are highly uncertain. The fact that the retrieved scaling factor matches the values empirically derived in the previous section is not really surprising, since this scaling is already necessary to bring clear-sky simulations

in agreement with observations. Inspecting more closely Fig. A13, it seems that the retrieved AOD values are very unstable. Comparing e.g. results derived using SF=0.8 and SF=0.85, we see that AOD values differ quite substantially although RMS values are similar. I am not really convinced that MAPA inversions add a lot of information in the study. At least they are not inconsistent. Something that would be very interesting would be to test whether the discrepancy depends on the O4 wavelength used for the retrieval. Unfortunately, this is not possible using the current setup due to the limited spectral range of the spectrometer, but it should be considered for future studies. Finally, one may also wonder whether this particular day was really the only clean day (during the ship cruise) allowing for a comparison of measured and simulated O4 slant columns. If other similarly clean days were encountered, it would be nice to know whether similar inconsistencies were found.

We fully agree with the reviewer that the aerosol results from MAPA have large uncertainties.

In the original manuscript, we already wrote: ,However, here it should be noted that for these low aerosol extinctions, the information content of the measurements is probably too low to constrain the aerosol extinction profiles, especially for high altitudes.'

In the revised version we modified this sentence to: ,However, here it should be noted that for these low aerosol extinctions, the information content of the measurements is probably too low to constrain the aerosol extinction profiles, especially for high altitudes. Thus also the retrieved AOD values are very unstable (see Fig. A15). Nevertheless, rather clear results for the scaling factor are found:'

For the other two points, we made the following changes:

### -other wavelengths:

We added the following sentence at the end of the conclusions: ,We recommend that similar studies under extremely low aerosol load should be made at different locations and seasons. Also  $O_4$  absorptions at different wavelengths should be investigated.'

#### -other measurement days:

The extremely low AODs only occurred on the selected day. Only at the beginning of the following day, still low AODs were measured (< 0.05 at 360 nm). However, during this period, the measurements at low elevation angles were strongly affected by clouds. Nevertheless, we compared the MAX-DOAS  $O_4$  measurements retrieved during that period with radiative transfer simulations. Here, we only made simulations for an aerosol-free atmosphere to limit the effort (and also because of the rapid temporal variation of the AOD). The comparison results are shown below:



Fig. A13 Comparison of the measured and simulated  $O_4$  dAMFs for two elevation sequences on 05 March 2019. For the first elevation sequence, the AOD was <0.05 at 360 nm. During the second elevation sequence it already increased to 0.06. Note that the radiative transfer simulations were made for an aerosol-free atmosphere.

Like on 02 May 2019, the simulated  $O_4$  dAMFs (for aerosol-free atmosphere) are smaller than the measurements (for cloud-free observations).

We added the following information to section 7.1.:

,It should be noted that during the entire ship cruise, only during the beginning of 3 May 2019, similarly low (but still larger) AOD were measured as on 2 May 2019. We compared the measured  $O_4$  dAMFs for the first two elevation sequences on 3 May with radiative transfer simulations. For that comparison we only made simulations for an aerosol-free atmosphere in order to to limit the effort (and also because of the rapid temporal variation of the AOD during that time period). The results (see Fig. A13) are similar to those on 2 May 2019: Except for the cloud contaminated measurements, the simulations are smaller than the measurements.'

Spelling, typos:

Pg. 1, l. 21: remove 'variation' Corrected

Pg. 1, l. 33: remove 'mainly' Corrected

Pg. 3, l. 101: add 'at' between 'are not' and 'the identical location' Corrected

Pg. 4, l. 151: add 'dry air' between 'For the' and 'mixing ratio of O2' Corrected

## References

Kleipool, Q., Dobber, M., de Haan, J., and Levelt, P., Earth surface reflectance climatology from 3 years of OMI data, J. Geophys. Res.-Atmos., 113, D18308, https://doi.org/10.1029/2008JD010290, 2008.

Malinina, E., Rozanov, A., Rieger, L., Bourassa, A., Bovensmann, H., Burrows, J. P., and Degenstein, D.: Stratospheric aerosol characteristics from space-borne observations: extinction coefficient and Ångström exponent, Atmos. Meas. Tech., 12, 3485–3502, https://doi.org/10.5194/amt-12-3485-2019, 2019.