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Manuscript Name: Verification of the AIRS and MLS ozone algorithms based on retrieved daytime and nighttime ozone

Point-by-point response to the comments: For easier reading, our responses are written in **Blue Color** and the changes in the revised manuscript are marked yellow.

Referee #3

Review of "Verification of the AIRS and MLS ozone algorithm based on retrieved daytime and nighttime ozone" by Wang et al.

The authors have improved their paper and especially the clarity of their discussion and conclusions. An evaluation of the diurnal variability in AIRS and MLS ozone retrievals have scientific significance. It is important to understand the strengths and weaknesses of different satellite data products to correctly interpret their depiction of real atmospheric change. For this reason, I gave this paper a careful read. The authors are correct when they say that not much literature exists that adequately characterizes AIRS O3 diurnal variability and their paper could, therefore, add value to the broader scientific community. After careful assessment, however, my decision is that this paper, in its current form, is not ready for publication because the results presented here do not adequately support the authors' conclusions. The authors present an interesting problem, namely that the AIRS total column ozone (TCO) product sometimes has diurnal variability over some areas that cannot be explained by photochemical processes or O3 transportation. They conclude that these changes must be due to retrieval artefacts and specifically those that are caused by the mischaracterization of surface emissivity and cloud top pressure. Below I attempt to justify why I think this is an oversimplification.

We thank the reviewer for the suggestions and the valuable insights in the retrieval of AIRS ozone columns. After careful reading of the reviewers comments, we are still convinced about our conclusions, which we do not see as an oversimplification. However, we agree that we might clarify our conclusions with more detailed discussions. Below follows our response to the detailed remarks and a description about our adaptations in the manuscript if needed.

Comment 1: First, I will address specific statements in the Conclusion (Section 4, pages 9-10) followed by a discussion of the figures and technical issues.

(1) AIRS TCO diurnal variation due to surface emissivity (Lines 266–278).

- Figure 1 shows AIRS TCO diurnal variation over the Sahara desert for the months of Dec through May and over the Congo (tropical forest) for the months of Jun through Nov. If dry, hot surfaces were the primary reason for these variational biases then we would not see this seasonal latitudinal shift and would see similar TCO variations over Namibia, Australia and the USA Southwest, all dry hot regions. How do the authors explain the diurnal variability of TCO over the Congo, which is not a dry surface?

Response 1: Admittedly, the Figure is somewhat small to see all those details and therefore we increased the Figure size.

Figure 1 shows a superposition of two artefacts related to (1) dry hot surfaces over land and (2) cloudiness over both land and sea. Both play an important role.

The strong diurnal variability is actually south of Congo, the region bordering Angola. This region has a strong seasonal cycle in precipitation and corresponding change of vegetation over the year and therefore the surface emissivity and also humidity also show a strong seasonality. Due the alternation between a dry low cloud cover season and a cloudy wet season, day-night differences due to cloudiness, as evidenced by the day-night differences over oceans, may also play a role.

In the desert of Australia, a strong negative difference is visible. Both positive and negative differences are visible over the areas with dry hot surfaces.

It is beyond our scope to discuss every region in detail in relation with their typical seasonal vegetation, humidity (rain season) and climatology and the effect on the retrieval, but the main features of Figure 1 clearly show that over land the surface emissivity have a strong correlation with the day-night differences in the retrieval.

Comment 2: - The AIRS a-priori for O3 is a climatology without diurnal variation. Similarly, its a-priori for emissivity is a monthly average without diurnal variation. If the radiance information content for O3 is very low and the retrieval mostly sticks to the a-priori, then there will be no diurnal variability in the AIRS TCO product.

Response 2: We agree with this comment. We would like to add that if the information content is very low for the night observation and not for the day observation or vice versa, this will also show up in the difference Figure 1f. We added the following remark to the text at line 184-187:

"*Note that AIRS observations with low information content (especially around the poles) will be drawn to the AIRS a-priori value. This AIRS a-priori for O₃ is a climatology without diurnal variation. If either the day or night*

observation has a lower information content than the other, this too can result in a day-night difference. This is probably the reason for the differences in Figure 1 over pole ice."

Comment 3: - I do not doubt that retrieval artifacts indeed cause the observed TCO variability, but I argue that they cannot be explained by surface emissivity alone for a number of reasons, (i) not all surface types have diurnal variability in their emissivity and most of the patterns observed globally in Figure 1 cannot be explained by emissivity alone, (ii) using IASI measurements, Masiello et al., (2014) presented a very clear case for why and how the Sahara desert emissivity pose a problem to infrared O3 retrievals that the authors should consider here, (iii) apart from emissivity, AIRS O3 channels are also sensitive to surface temperature as well as boundary layer temperature and water vapor that have large diurnal variabilities that can affect O3 retrievals, and (iv) infrared O3 retrievals depend on an accurate representation of atmospheric temperature and water vapor; any uncertainty in their depiction at a given point in time and space will propagate into the O3 retrieval (Smith and Barnet, 2019).

Response 3: First of all, we conclude that we see two main patterns that determine the day-night differences: (1) surface type and (2) cloudiness. The both appear to play an important role in the day-night differences.

[i] Figure size was increased, see also response to comment (1).

[ii] Masiello et al. (2014) present an interesting study about the Sahara and emissivity retrieved in parallel with ozone profiles for AIRS. Their findings certainly contain clues on how to improve the retrievals over the Sahara, but improving the retrieval algorithms themselves is beyond the scope of our paper. We have added the reference of Masiello et al. (2014) when discussing the diurnal variation in the Sahara at line 160-162:

"*The presence of day-night differences apparently correlating with surface infrared emissivity properties of dry desert regions is consistent with Masiello et al. (2014), who discussed the variability of surface infrared emissivity in the Sahara desert and recommended to take the diurnal variation of surface emissivity into account in infrared retrieval algorithms.*"

[iii and iv] in summary: although it is beyond dispute that AIRS TCO retrievals are sensitive to temperature and humidity, this largely stems from comparing the effect of seasonal and regional temperature and humidity variations on retrievals.

The average day-night differences in both temperature and humidity are significantly smaller than their seasonal and regional variations/differences. In addition, day-night differences in temperature and humidity are confined to the lowermost troposphere (boundary layer), which constitutes only a small part of the atmosphere. Hence, it appears unlikely that temperature and humidity can be the main cause of the differences we report (see also the calculation we provided).

In addition, the day-night AIRS TCO difference patterns resemble global and regional cloud patterns and surface emissivity, not global and regional temperature and humidity patterns, provides strong support for cloud and emissivity as causes of the reported day-night differences, not temperature and humidity.

We modified the paragraph discussing figure 1 as follows, better emphasizing that difference patterns are associated with both surface emissivity and clouds, but that over land surface emissivity and cloud effects may overlap (like regions with strong seasonal variations in clouds and precipitation) at line 163-168 and at line 175:

"*Figure 1e shows for the annual mean large differences of AIRS TCO retrievals over deserts, difference patterns over the oceans associated with the Intertropical Convergence Zone (ITCZ) as well as regions with persistent seasonal subtropical stratocumulus fields. The spatial patterns over land mimic regions with low IR surface emissivity and/or regions where IR surface emissivity exhibits large seasonal variations (Feltz et al., 2018). Figure 1f shows absolute differences between all subsequent pixels in the longitude direction. The figure reveals significant non-physical TCO changes (discontinuities) for adjacent land-ocean pixels (visible at coast lines running in North-South direction).*"

"*Note that TCO day-night differences over land could also be (partly) related to clouds.*"

We added the following to the discussion of our manuscript in line 169-172:

"*The observed diurnal cycle in AIRS TCO is related to either the measurements or to the algorithm. If the diurnal cycles in AIRS TCO are related to the retrieval algorithm, it has to be caused by the representation of a process in the algorithm having a diurnal cycle, something Smith and Barnes (2019) argue is not in the algorithm but should be taken into account.*"

Comment 4: (2) AIRS TCO diurnal variation due to cloud top height variation (Lines 284–293).

- Line 284: "detection of cloud features in AIRS TCO day-night differences is difficult due to the presence of land surface emissivity related bias". How can this be true? Clouds present, by far, the largest source of uncertainty to atmospheric retrievals from space-based infrared instruments. AIRS observe the atmosphere from the top-down so clouds dominate the signal, not surface emissivity.

Response 4: We agree that clouds present a large contribution to the uncertainty of the TCO retrievals, but we are looking specifically at biases between day and night observations over land after averaging over at least 3 month periods. In these cases, the bias from surface emissivity is significant as can be seen in Figure 1. We clarified this by making the following modification at line 291-293:

"*The latter may also impact AIRS TCO retrievals over land, although detection of cloud features in AIRS TCO day-night differences over land is difficult due to the presence of the land surface emissivity related bias.*"

Comment 5: - The conclusion the authors draw here, that cloud top pressure cause diurnal TCO variation is not substantiated by their results; they do not provide quantitative information nor any figures in the main text. The only figure that they cite is Figure S2 in the supplement, which does not make a clear case.

- Again, I do not dispute the fact that diurnal variation in cloud uncertainty can affect the quality of O3 retrievals. I question whether the authors presented enough evidence to substantiate their claim.

Response 5: Our conclusion is mainly based on Figure 1, which clearly show patterns related to the ITCZ and other persistent cloud patterns. We modified the section describing Figure 1 and emphasizing that differences appear to be caused by both emissivity and clouds, while also noting that over land differences related to clouds may interfere with differences related to surface emissivity.

Figure S2 is of secondary importance and serves only to show that the cloud top pressure is more important than the cloud fraction. We add a references to Figure 1 at the lines 294-298 for clarification. In addition, we have adapted Figure S2 to show the evidence more clearly.

Comment 6: I think the authors will strengthen the value and significance of their results by improving their figure captions. For example, it helps a great deal if acronyms used in the figures are defined in the caption.

Response 6: It is common practice to define the acronyms only in the text but this depends on the rules of the journal. We are not sure about this and leave the decision with the editor on whether we should add acronyms to the figure captions.

Comment 7: Figure 1: - The text of the colorbars for panels (e) and (f) is too small to read comfortably.

Response 7: This has been adapted.

Comment 8: - I don't understand panel (f) which the authors describe as the "longitude gradient value using absolute difference between two pixels adjacent at the same latitude in (e)". It is unclear to me how the values were calculated and what they mean in the present context. In the main text the authors merely mention that "Figure 1f shows significant TCO changes at the land-ocean interface." Looking at Figure 1f, I do not distinguish a clear land-ocean interface everywhere and have no good sense if a value of ~2 (units?) can be deemed "significant". Can the authors explain how this figure contributes to the discussion and substatiates their conclusions?

Response 8: In Figure 1f, we calculate the longitudinal gradient, meaning the difference of two neighboring pixels at the same latitude. That is why only coast lines appear that run from North to South. We can also plot a similar Figure for the latitudinal differences, which would show the other coast lines running from West to East.

The unit is in % like the other plots. We have added this to the legend of the Figure.

The figure shows that ozone is not constant over coast region which cannot be geo-physically explained and is likely a retrieval artifact.

The description of figure 1f indeed is not completely clear, we change it to:

"*Figure 1: (a) AIRS TCO averaged day-to-night relative difference for Dec-Jan-Feb during 2003-2018. (b) Mar-Apr-May. (c) Jun-Jul-Aug. (d) Sep-Oct-Nov. (e) AIRS TCO 16-year averaged day-to-night relative difference during 2003-2018. (f) Absolute difference between two adjacent pixels at the same latitude in (e). Note: The relative difference is calculated as: 100 × (daytime - nighttime) / daytime (in percent, %).*"

Comment 9: Figure 5: Here the authors depict AIRS stratospheric column ozone (SCO), which they define as the vertical pressure range from 250 hPa to 1 hPa.

- While this range makes sense, given that MLS profiles (Figures 2 and 4) are defined within the same pressure bounds, it complicates interpretation of the AIRS SCO results. Here's why:

(1) Unlike MLS, AIRS channels in the 10 micron spectral region are sensitive to tropospheric and stratospheric O3. In the high latitudes, the tropopause occurs at higher pressure levels (~220 hPa) than in the Tropics (~100 hPa). When the authors define AIRS SCO using a fixed pressure range across all latitudes then their results will include upper tropospheric effects in the low latitudes, but not the high latitudes. Their results of SCO in the mid-latitudes and Tropics (panels a and b), therefore is not strictly stratospheric but includes O3 amounts from the upper troposphere. In contrast, the results depicted for high latitudes (panels a through f) represents information mostly about the stratosphere. A comparison between, say panels b and f, is therefore not as straightforward as the authors make it out to be. AIRS O3 sensitive channels are predominantly, not exclusively, sensitive to O3. In addition to O3, channels in the 10 micron AIRS band are also sensitive to temperature, lapse rate, water vapor gradients, surface temperature, emissivity and clouds, for example.

Olson et al. (2017, page 104 of the "AIRS Version 6 Release Level 2 Product User Guide", which the authors cite) explain the AIRS O3 product as such: "Errors in temperature profiles and water vapor mixing ratios will adversely affect the ozone retrieval. Significant biases (0 - 100%) may exist in the region between ~300 hPa and ~80 hPa; such biases currently being evaluated. Ozone mixing ratio data may not be reliable at pressures greater than 300 hPa or if the tropospheric mixing ratio is less 100 ppbv, however results may be qualitatively correct under

conditions of high upper tropospheric ozone (such as in a tropopause fold). Mixing ratios and columns should not be considered reliable under conditions of very low skin temperatures (< 240 K). V6 is a slight improvement over V5, but there are still problems when the surface skin temperature does not compare well to AMSR-E or the scene has a significant cloud amount."

Response 9: There appears to be a misunderstanding. Figure 2 and 4 were never meant to compare the SCO of MLS with those of AIRS. Although both satellites appear in the same Figure, we only want to show the difference between night and day observations of each instrument. We could have chosen to make separate figures for each instrument, but decided that this makes the manuscript unnecessary long.

We acknowledge those retrieval issues that are important for interpreting the SCO results, however this will only be relevant when we want to compare the values to those of MLS.

We added the following at line 228-230:

"*Note that figure 5 is not meant as a validation of AIRS SCO with MLS SCO, but to explore the seasonality of either AIRS or MLS SCO day-night differences, and explore whether the seasonality in day-night SCO varies in unison over the seasons*."

Comment 10: (2) When surface temperature is very low and atmospheric temperature lapse rate is close to zero (conditions often occurring in the Polar regions), AIRS channel sensitivity to O3 decreases significantly. This means the AIRS O3 retrieval will have a strong dependence on its climatological a-priori, which has no diurnal variation. This, at least, partly explains why AIRS SCO have low diurnal variability in the Polar regions. The authors oversimplify their interpretation of results by attributing the lack of SCO diurnal variability in the Polar regions to homogeneity in surface emissivity.

Response 10: We have added a remark about this issue. See the response to comment (1).

Comment 11: Figure 6: I would recommend that the authors enlarge panels e and f. This is an interesting result and its value will improve if the error bars can be distinguished and interpreted more readily.

Response 11: This has been adapted.

Comment 12: Figure S1: - I have studied both panels in this figure and their meaning remain unclear to me since they do not depict a correlation between diurnal variability and surface type. It is true that desert emissivity can have diurnal variation due to changes in soil moisture (Li et al., 2012; Masiello et al., 2014) but the same does not hold for forests. What do the authors wish to demonstrate here?

- In short, AIRS O3 verticality does not depend on surface emissivity, but predominantly on O3 amount, temperature, instrument spectral resolution, lapse rate, and so on. It is true that the AIRS O3 channels are sensitive to emissivity in the boundary layer and that errors in the representation of surface emissivity over deserts can introduce a small bias in stratospheric O3 retrievals (Masiello et al., 2014), but surface emissivity is not a dominant source of uncertainty in TCO.

- The definition the authors give here for verticality is not correct. Their definition, instead, applies to averaging kernels. Verticality is derived from the averaging kernels as a total column representation of the kernel functions and can therefore be greater than unity.

Response 12: On second thought, and considering the referee comments, we think Figure S1 is not adding much to our conclusions, and can be cause for confusion. Therefore, we think it is better to remove the entire Figure, which we did.

Instead, we provided a different representation of the same data by comparing the average day-night differences in cloud fraction and cloud pressure as a function of the differences in total ozone columns. This comparison clearly shows that there are relations between cloud fraction day-night differences and cloud pressure differences as a function of day-night total ozone columns differences. Thus providing additional support for our finding that the cloud representation in the AIRS retrievals results in total ozone column differences.

Comment 13: Figure S2: In addition to surface emissivity, the authors attribute diurnal variation in AIRS TCO to cloud top pressure. This is the only figure they have included in their paper that attempts to correlate cloud properties with TCO. I do not see a clear statistical correlation in this scatter plot and it is unclear to me how the authors reached their conclusion. The results will be more meaningful if the authors explain their figure more clearly and also include statistical values that quantify the correlations they wish to highlight.

Response 13: The Figure has been adapted to make clear that there is a dependence of the day-night differences on cloud-top height, which is much weaker for cloud fraction.

Comment 14: Data sources: The authors switch between AIRS total column ozone (TCO) and stratospheric column ozone (SCO) without adequately explaining why or how. Similarly, their use of AIRS Level 2 and Level 3 products creates confusion that obscures the relevance of their results. I recommend that the authors update Section 2.1 to clarify which products they used, where they sourced them from and why they switched between L2 and L3, SCO and TCO.

- In Section 2.1 the authors state that they employed AIRS V6 Level 3 products and list a weblink as source: https://disc.gsfc/nasa.gov/datasets/AIRS3STD_006/summary". When I follow this link, I see a tab at the bottom of the page called "Data Citation" that gives an example of how this data product should be cited. I recommend that the authors use the correct citation for AIRS V006 L3 with DOI number included. Here it is: AIRS Science Team/Joao Teixeira (2013), AIRS/Aqua L3 Daily Standard Physical Retrieval (AIRS-only) 1 degree x 1 degree V006, Greenbelt, MD, USA, Goddard Earth Sciences Data and Information Services Center (GES DISC), Accessed: [Data Access Date], doi:10.5067/Aqua/AIRS/DATA303

- On Page 11 in the "Data Availability" section, the authors list a different source for the AIRS TCO products as https://giovanni.gsfc.nasa.gov/giovanni. Giovanni is a GES DISC data tool, not data archive. Similarly, for MLS the authors list here a different source from the one they reported in Section 2.2. I recommend that the authors list a single source for their AIRS and MLS products to avoid confusion and promote confidence in their work.

Response 14: We agree with this comment. We removed the web links in Section 2 and updated "Data availability" section as following:

"*Satellite data sets used in this research can be requested from public sources. AIRS level 3 data are available online: AIRS Science Team/Joao Teixeira (2013), AIRS/Aqua L3 Daily Standard Physical Retrieval (AIRS-only) 1 degree x 1 degree V006, Greenbelt, MD, USA, Goddard Earth Sciences Data and Information Services Center (GES DISC), Accessed: [2020.04], doi:10.5067/Aqua/AIRS/DATA303.*

AIRS level 2 data are available from: AIRS Science Team/Joao Teixeira (2013), AIRS/Aqua L2 Standard Physical Retrieval (AIRS-only) V006, Greenbelt, MD, USA, Goddard Earth Sciences Data and Information Services Center (GES DISC), Accessed: [2020.04], 10.5067/Aqua/AIRS/DATA202.

MLS level 2 data can be obtained from: Schwartz, M., Froidevaux, L., Livesey, N. and Read, W. (2015), MLS/Aura Level 2 Ozone (O3) Mixing Ratio V004, Greenbelt, MD, USA, Goddard Earth Sciences Data and Information Services Center (GES DISC), Accessed: [2020.04], doi:10.5067/Aura/MLS/DATA2017."

Comment 15: - In Supplemental figures S1 and S2, the authors list "AIRS L2" as the product they depict yet they do not list a source for it or discuss why they used the Level 2 as opposed to the Level 3 product. Can the authors clarify this?

Response 15: We agree with the referee that it is necessary to introduce the usage of AIRS L3 and L2 data in our study.

The AIRS level 3 daily gridded data contains standard retrieval means, standard deviations and input counts. Each file covers a temporal period of 24 hours for either the descending or ascending orbit. The geophysical parameters

have been averaged and binned into 1 °×1 °(latitude × longitude) grid cells. It can be used to generate multi-day maps from the daily gridded products.

The AIRS level 2 data consists of retrieved estimates of cloud and surface properties, plus profiles of retrieved temperature, water vapor, ozone, carbon monoxide and methane. Estimates of the errors associated with these quantities is also part of the AIRS level 2 data. It is useful for further analysis of the details.

We added the following at line 122-127:

"*The AIRS V6 level 3 daily standard physical retrieval products (2003-2018) provide TCO and profiles of retrieved O_3. The daily level 3 products comprise daily averaged measurements on the ascending and descending branches of an orbit with the quality indicators 'best' and 'good' and binned into 1 °×1 °(latitude × longitude) grid cells. The O_3 profile is vertically resolved in 28 levels between 1100 hPa and 0.1 hPa. This makes it possible to compare SCO between AIRS and MLS. Besides, estimates of the errors associated with cloud and surface properties is part of the AIRS V6 level 2 standard physical retrieval product, which we used here to discuss further details.*"

Comment 16: The following statement on lines 9-11 gave me pause: "Based on knowledge of the chemistry and transport of O3, significant deviations between daytime and nighttime O3 are only expected either in the planetary boundary layer or high in the stratosphere or mesosphere, having little effect on the TCO." If O3 variation in the stratosphere or PBL is significant, then it would affect TCO, not so? The fact is that O3 concentrations vary with atmospheric pressure. I expect that variation in stratospheric O3, where concentrations are large relative to the free troposphere, will most definitely affect TCO.

Response 16: We agree that ozone in the lower to middle stratosphere accounts for the majority of total column ozone. But diurnal ozone variations had generally been considered small enough to be inconsequential (1%) in the lower to middle stratosphere (Sakazaki et al., 2013). Diurnal ozone variations in the upper stratosphere and mesosphere have been extensively studied because of their large amplitude (>10% to the daily mean) (Huang et al., 2008; Dikty et al., 2010). Our Figure 2a also shows that the global (60 °S-60 °N) differences between day and night MLS O_3 profile occur in the mesosphere (10 hPa - 0.1 hPa).

Comment 17: Lines 50-51: "UV absorption spectroscopy with the sun or stars as sources of UV light is the most used method to derive O3" To substantiate this statement the authors cite a publication from 1978 and 2000, both well before the launch of modern-era instruments. What metric did the authors use to define "UV light" as the "most used method"?

Response 17: Ozone strongly absorbs ultraviolet light in the Hartley and Huggins bands from 200 - 360 nm, and has additional weak absorption bands in the visible (Chappius bands from 450 - 750 nm) and infrared (9.6 μm). Nowadays, remote sensing of ozone is done in different spectral regions (UV, visible, IR). Ozone strong absorption in the UV spectral range is easy to be detected by satellite instruments. In addition, regular and continuous ozone monitoring from space in the UV spectral range is performed since 1978 with the TOMS and SBUV instruments on the satellite Nimbus-7. Follow-up modern-era instruments include GOME, SCIAMACHY, OMI and GOME-2. To substantiate this statement, we added the following papers:

Fu, D., Worden, J. R., Liu, X., Kulawik, S. S., Bowman, K. W., and Natraj, V.: Characterization of ozone profiles derived from Aura TES and OMI radiances, Atmos. Chem. Phys., 13, 3445–3462, https://doi.org/10.5194/acp-13-3445-2013, 2013.

Koukouli, M. E., Lerot, C., Granville, J., Goutail, F., Lambert, J.-C., Pommereau, J.-P. Balis, D., Zyrichidou, I., Roozendael, M. Van., Coldewey-Egbers, M., Loyola, D., Labow, G., Frith, S., Spurr, R. Zehner, C.: Evaluating a new homogeneous total ozone climate data record from GOME/ERS-2, SCIAMACHY/Envisat, and GOME-2/MetOp-A, J. Geophys. Res. Atmos., 120, 12,296– 12,312, doi:10.1002/2015JD023699, 2015.

Comment 18: - Replace "long record" with "long term record" throughout the text to promote ease of reading (e.g., lines 13, 48).

- Line 21: Awkward sentence – "support for retrieval method origin of AIRS day-night TCO differences". Rephrase.

- Line 30: "has become as an important topic", remove "as".

- Line 73: "Further" should be "Furthermore".

- Line 152: Error in "over oceans differences".

- Line 158:" In Figure 1e shows" should be "Figure 1e shows".

- Line 159: Awkward sentence – "with persistent clouds and Arctic regions". Rephrase.

- Line 175: "cloud covers is another problem" should be "cloud cover".

- Line 192: "about 500 pixels". This fact will be more meaningful if the authors report it as a percentage.

- Line 249: "large areas at night besides in tropical western Pacific". Rephrase, awkward sentence.

- Line 269: "points to the emissivity rather than the averaging kernels dominating these differences"… Averaging kernels quantify the signal-to-noise and is a product of the retrieval system, not a cause for it.

- Line 303: Awkward sentence – "only in the mesosphere the loss timescale for O3". Rephrase.

Response 18: We agree with these grammatical changes. These had been adapted.

Comment 19: The Reference section needs work since there appears to be many inconsistencies in punctuation, journal abbreviations, doi numbers and so on.

Response 19: The Reference section has been updated according to the rules of the journal.

Comment 20: The font style of figure captions in the main text is different from those in the supplement.

Response 20: We have unified the font style in the main text and the supplement.

Comment 21: This paper lacks references to current and relevant research in the field of remote sounding and I provide here a list of papers for the authors to consider:

- AIRS instrument (Aumann et al., 2003, 2020; Chahine et al., 2006)

- AIRS retrieval algorithm (Susskind et al., 2003, 2011, 2014)

- IR ozone retrieval quality, uncertainty and evaluation (Li et al., 2012; Maddy et al., 2009; Maddy and Barnet, 2008; Nalli et al., 2018; Smith and Barnet, 2019, 2020; Tian et al., 2007; Wang et al., 2012; Wei et al., 2010)

Response 21: Results reported by listed papers are meaningful. We have added some of them in manuscript.

Reference

Dikty, S., Schmidt, H., Weber, M., Von Savigny, C., Mlynczak, M.: Daytime ozone and temperature variations in the mesosphere: A comparison between SABER observations and HAMMONIA model. Atmos. Chem. Phys., 10, 8331-8339. doi:10.5194/acp-10-8331-2010, 2010.

Huang, F. T., H. G.Mayr, J. M. Russell III,M. G. Mlynczak, and C. A. Reber.: Ozone diurnal variations and mean profiles in the mesosphere, lower thermosphere, and stratosphere, based on measurements from SABER on TIMED, J. Geophys. Res., 113, A04307, doi:10.1029/2007JA012739, 2008.

Sakazaki, T., Fujiwara, M., Mitsuda, C., Imai, K., Manago, N., Naito, Y., Nakamura, T., Akiyoshi, H., Kinnison, D., Sano, T., Suzuki, M., and Shiotani, M.: Diurnal ozone variations in the stratosphere revealed in observations from the Superconducting Submillimeter-Wave Limb-Emission Sounder (SMILES) on board the International Space Station (ISS), J. Geophys. Res. Atmos., 118, 2991– 3006, doi:10.1002/jgrd.50220, 2013.

Verification of the AIRS and MLS ozone algorithms based on retrieved daytime and nighttime ozone

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Abstract. Ozone (O_3) plays a significant role in weather and climate on regional to global spatial scales. Most studies on the variability in the total column of O_3 (TCO) are typically analysed using daytime data. Based on knowledge of the chemistry and transport of O_3, significant deviations between daytime and nighttime O_3 are only expected either in the planetary boundary layer (PBL) or high in the stratosphere or mesosphere, having little effect on the TCO. Hence, we expect the daytime and nighttime TCO to be very similar. However, a detailed evaluation of satellite measurements of daytime and nighttime TCO is still lacking, despite the existence of long term records of both. Comparing daytime and nighttime TCOs thus provides a novel approach to verify the retrieval algorithms of for example the Atmospheric InfraRed Sounder (AIRS) and the Microwave Limb Sounder (MLS). In addition, such a comparison also helps in assessing the value of nighttime TCO for scientific research. Applying this verification on the AIRS and the MLS data we identified inconsistencies in observations of O_3 from both satellite instruments. For AIRS, daytime-nighttime differences were found over oceans resembling cloud cover patterns, and over land, mostly over dry land areas, likely related to infrared surface emissivity. These differences point to issues with the representation of both processes in the AIRS retrieval algorithm. For MLS, a major issue was identified with the "ascending-descending" orbit flag, used to discriminate nighttime and daytime MLS measurements. Disregarding this issue, MLS day-night differences were significantly smaller than AIRS day-night differences, providing additional support for retrieval method origin of AIRS day-night TCO differences. MLS day-night differences are dominated by the upper stratospheric and mesospheric diurnal O_3 cycle. These results provide useful information for improving infrared O_3 products and at the same time will allow study the day-night differences of stratospheric and mesospheric O_3.

1 Introduction

Atmospheric ozone (O_3) is a key factor in the structure and dynamics of the Earth's atmosphere (London 1980). The 1987 Montreal Protocol on Substances that Deplete the O_3 Layer formally recognized the significant threat of chlorofluorocarbons and other O_3-depleting substances (ODCs) to the O_3 layer and marks the start of joint international efforts to reduce and ultimately phase-out the global production and consumption of ODCs (Velders et al., 2007). Indeed, concerns about changes in O_3 due to catalytic chemistry involving man-made chlorofluorocarbons has become an important topic for the scientific community, the general public and governments (Fioletov et al., 2002).

In response to this concern and associated environmental policies, during the last two decades a large number of studies have focused on estimating long-term variations and trends in stratospheric column of O_3 (SCO). A summary of the state of the science is frequently reported in the quadrennial O_3 Assessment Reports issued by the United Nations Environmental

35   Program (UNEP) and the World Meteorological Organization (WMO). These reports are written in response to the global treaties aiming at minimizing emissions of ODSs. The signatories of these treaties ask for regular updates on the state of the science and knowledge. The most recent O_3 Assessment reports extensively discuss long-term variations and trends in stratospheric O_3 in relation to expected recovery (WMO, 2011, 2014, 2018). According to WMO (2018), Antarctic stratospheric O_3 has started to recover, while outside of the polar regions, upper stratospheric O_3 has also increased. On the

40   other hand, no significant trend has been detected in global (60°S-60°N) total column O_3 over the 1997-2016 period with average values for the years since the last Assessment remaining roughly 2% below the 1964-1980 average. Moreover, recently a debate has emerged over the question as to whether lower stratospheric O_3 between 60°S-60°N has continued to decline despite decreasing O_3 depleting substances (Ball et al., 2018; Ball et al., 2019). In addition to the quadrennial O_3 Assessments, the Bulletin of the American Meteorological Society (BAMS) annually publishes its "State of the Climate", which since 2015

45   includes tropospheric O_3 trends and effects from El Nino-Southern Oscillation (ENSO) and a description of the relevant stratospheric events of the past year, the state of the Antarctic O_3 hole, as well as an annual update of global and zonal trends in stratospheric O_3. These regularly recurring reports and publications illustrate the continued attention and monitoring of the O_3 layer and its recovery, in which the long term records of satellite observations play a crucial role. Establishing and maintaining the quality of the satellite observations of stratospheric O_3 is therefore highly relevant.

50   A variety of techniques exist to measure the O_3 column and stratospheric O_3. UV absorption spectroscopy with the sun or stars as sources of UV light is the most used method to derive O_3 (Weeks et al., 1978; Fussen et al., 2000; Fu et al., 2013; Koukouli et al., 2015). In addition to the UV occultation method, the absorption of infrared radiation has also been used to detect O_3 profiles throughout the column (Gunson et al., 1990; Brühl et al., 1996). Another technique is the detection of the molecular oxygen dayglow emissions (Mlynczak and Drayson, 1990; Marsh et al., 2002). Some ground-based instruments use

55   O_3 emissions in the microwave region to infer the O_3 density in the mesosphere (Zommerfelds et al., 1989; Connor et al., 1994). Infrared emission measurements overcome the limitations in the local time coverage of solar occultation and dayglow technique and their altitude resolution is significantly higher compared with microwave measurements (Kaufmann et al., 2003). The strongest O_3 infrared absorption centres near 9.6 um.

Based on knowledge of chemistry and transport of O_3, significant deviations between daytime and nighttime O_3 are only

60   expected either in the planetary boundary layer (PBL) and high in the stratosphere or mesosphere, having little effect on the total column of O_3 (TCO). Hence, we expect that the daytime and nighttime TCO to be very similar. This slight variation in diurnal TCO can serve as a natural test signal for remote sensing instruments and data retrieval techniques. We need to clarify how sensitive different space-based instruments are to TCO slight changes and to distinguish potential biases from retrieval artefacts. Day-night inter-comparisons present a unique opportunity to assess the internal consistency of infrared O_3

65   instruments (Brühl et al., 1996; Pommier et al., 2012; Parrish et al., 2014). Systematic differences could potentially arise, for

example, from temperature effects within the instrument, from differences in signal magnitude between daytime and nighttime or from the retrieval algorithms. The Stratosphere Aerosol and Gas Experiment (SAGE) applied day-night differences to validate O_3 profiles and found daytime values have a low bias due to errors in the retrieval method since the magnitude of the difference was much less in a photochemical model (Cunnold et al., 1989). There are satellite instruments, like Atmospheric

70 InfraRed Sounder (AIRS) and The Microwave Limb Sounder (MLS), that provide global daytime and nighttime TCO/SCO and O_3 profiles. Although their daytime O_3 retrievals have been validated (Livesey et al., 2008; Sitnov and Mokhov, 2016), day-night differences in TCO and SCO are still largely unexplored. Applying this day-night verification on the AIRS and the MLS data can assess their capacities to characterize atmospheric O_3. Furthermore, an accurate assessment of O_3 variation is needed for a reliable and homogeneous long-term trend detection in the global O_3 distribution.

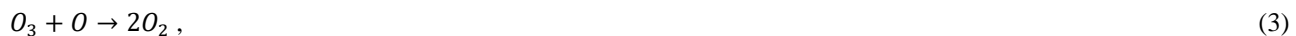
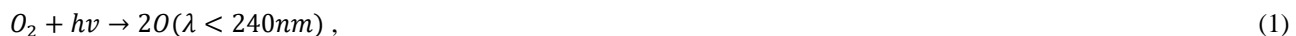
75   The O_3 diurnal cycle depends on latitude, altitude, weather and time. The variations of the diurnal cycle are less than 5% in the tropics and subtropics and increase to more than 15% in the upper stratosphere during the polar day near 70 °N (Frith et al., 2020). There exist diurnal variations in atmospheric O_3 at certain altitudes. There are two distinct O_3 maxima in the typical vertical profile of the O_3 volume mixing ratio, one in the lower stratosphere and one in the mesosphere. The secondary maximum in the mesosphere is present during both day and night (Evans and Llewellyn, 1972; Hays and Roble, 1973).

80 Chapman (1930) revealed the photochemical scheme in the mesosphere. The reactions of the Chapman cycle are important for us to understand diurnal O_3 variation.

$$O_2 + hv \rightarrow 2O\,(\lambda < 240nm)\;, \tag{1}$$

$$O + O_2 + M \rightarrow O_3 + M, \text{ (in which M stands for an air molecule)} \tag{2}$$

$$O_3 + O \rightarrow 2O_2\;, \tag{3}$$

85 $$O_3 + hv \rightarrow O_2 + O\,(\lambda < 1140nm)\;, \tag{4}$$

    In the daytime mesosphere, catalytic O_3 depletion by odd hydrogen has to be considered in addition to the Chapman cycle. The anti-correlation of O_3 and temperature is mainly due to the temperature dependence of the chemical rate coefficients (Craig and Ohring, 1958; Barnett et al., 1975). Huang et al. (2008) and Huang et al. (1997) found midnight O_3 increases in the mesosphere, based on SABER and MLS data, respectively. Zommerfelds et al. (1989) surmised that eddy transport may

90 explain this increase, while Connor et al. (1994) stated that atmospheric tides are expected to cause systematic day-night variations.

    During daytime, photolysis is the major loss process. The main nighttime O_3 source in the mesosphere is atomic oxygen, while its sinks are atomic hydrogen and atomic oxygen (Smith and Marsh, 2005). In addition to O_3 chemical reactions with active hydrogen and molecular, the turbulent mass transport also plays an important role in the explanation of the secondary

95 O_3 maximum (Sakazaki et al., 2013; Schanz et al., 2014).

    Tropospheric O_3 is mainly produced during chemical reactions when mixtures of organic precursors (CH_4 and non-methane volatile organic carbon, NMVOC), CO, and nitrogen oxides (or NO_x), are exposed to the UV radiation in the

troposphere (Simpson et al., 2014). At night, in the absence of the sunlight, there is no O_3 production, but surface O_3 deposition and dark reactions transform the NO_x-VOC mixture and remove O_3. The dark chemistry affects O_3 and its key ingredients mainly depend on the reactions of two nocturnal nitrogen oxides, NO_3 (the nitrate radical) and N_2O_5 (dinitrogen pentoxide). NO_3 oxidizes VOC at night, while reaction of N_2O_5 with aerosol particles containing water removes NOx. Both processes remove O_3 as well at night (Brown et al., 2006).

The diurnal cycle of O_3 in the middle stratosphere had generally been considered small enough to be inconsequential, with known larger variations in the upper stratosphere and mesosphere (Prather, 1981; Pallister and Tuck, 1983). Later studies have highlighted observed and modelled peak-to-peak variations of the order of 5% or more in the middle stratosphere between 30 and 1 hPa (Sakazaki et al., 2013; Parrish et al., 2014; Schanz et al., 2014).

In terms of dynamics, vertical transport due to atmospheric tides is expected to contribute to diurnal O_3 variations at altitudes where background O_3 levels have a sharp vertical gradient (Sakazaki et al., 2013). The Brewer/Dobson circulation transports air upwards in the tropics, polewards and downwards at high latitudes, with stronger transport towards the winter pole (Chipperfield et al., 2017).

The main objective of this paper is to analyse day-night differences in the AIRS TCO and the MLS SCO, as well as in MLS upper atmospheric O_3 profiles. Section 2 discusses the data used. Section 3 presents results for AIRS, MLS, the comparison of AIRS with MLS, and an application of AIRS TCO data over the Pacific low O_3 regions to highlight how day-night differences affect use and interpretation of TCO data. Finally, section 4 ends the paper with a brief summary and conclusions.

2 Data

2.1 AIRS total column of O_3 retrievals

The AIRS satellite instrument was the first in a new generation of high spectral resolution infrared sounder instruments flown aboard the National Aeronautics and Space Administration (NASA) Earth Observing System (EOS) Aqua satellite (Aumann et al., 2003, 2020; Chahine et al., 2006; Divakarla et al., 2008). The AIRS radiance data at 9.6 μm band are used to retrieve column O_3 and O_3 profiles during both day and night (including the polar night) (Pittman et al., 2009; Fu et al., 2018; Susskind et al., 2003, 2011, 2014). The AIRS V6 level 3 daily standard physical retrieval products (2003-2018) provide TCO and profiles of retrieved O_3. The daily level 3 products comprise daily averaged measurements on the ascending and descending branches of an orbit with the quality indicators 'best' and 'good' and binned into 1 °×1 °(latitude ×longitude) grid cells. The O_3 profile is vertically resolved in 28 levels between 1100 hPa and 0.1 hPa. This makes it possible to compare SCO between AIRS and MLS. Besides, estimates of the errors associated with cloud and surface properties is part of the AIRS V6 level 2 standard physical retrieval product, which we used here to discuss further details. Outside of the polar zones (60 °N-90 °N and 90 °S-60 °S), ascending and descending correspond respectively to daytime (13:30 in local solar time) and nighttime (01:30 in local solar time). Hereafter we refer to "day" and "night" rather than ascending and descending over 60°S-60 °N. In the polar

130   zones, it is inappropriate to use ascending/descending mode to define daytime/nighttime, therefore, we just compare
differences between ascending and descending mode. AIRS TCO measurements agree well with the global Brewer/Dobson
Network station measurements with a bias of less than 4% and a root mean squared error (RMSE) difference of approximately
8% (Divakarla et al., 2008; Nalli et al., 2018; Smith and Barnet, 2019). Analysis of AIRS TCO monthly maps revealed that its
retrievals depict seasonal trends and patterns in concurrence with OMI and SBUV/2 observations (Divakarla et al., 2008; Tian
135   et al., 2007).

2.2 MLS stratospheric column of O_3 and O_3 profile retrievals

The MLS instrument on-board Aura satellite, which was launched on 15 July 2004 and placed into a near-polar Earth
orbit at 705 km with an inclination of 98 °, uses the microwave limb sounding technique to measure vertical profiles of chemical
constituents and dynamical tracers between the upper troposphere and the lower mesosphere (Waters et al., 2006). Its orbital
140   ascending mode is at 13:42 (local solar time) and the orbital descending mode at 01:42 (local solar time) over 60 °S-60 °N. In
this study, we use the MLS v4.2x standard O_3 product during 2005-2018. Its retrieval is using 240-GHz radiance, providing
near-global spatial coverage (82 °S to 82 °N latitude), with each profile spaced 1.5 degrees or ~165 km along the orbit track.
This O_3 product includes the O_3 profile on 55 pressure surfaces and the recommended useful vertical range is from 261 to 0.02
hPa. In addition, it contains an O_3 column, which is the integrated stratospheric column down to the thermal tropopause
145   calculated from MLS measured temperature (Livesey et al., 2015). Jiang et al. (2007) found the MLS stratospheric O_3 data
between 120 and 3 hPa agreed well with ozonesonde measurements, within 8% for the global daily average. Froidevaux et al.
(2008) reported MLS stratospheric O_3 uncertainties of the order of 5%, with values closer to 10% (and occasionally 20%) at
the lowest stratospheric altitudes. Livesey et al. (2008) estimated the MLS O_3 accuracy as ~40 ppbv $\pm5\%$ (~20 ppbv $\pm20\%$
at 215 hPa). Expectations and comparisons with other observations show good agreements for the MLS O_3 product, generally
150   consistent with the systematic errors quoted above.

3 Results

3.1 AIRS O_3 retrievals day-night differences

Figure 1 shows spatial variations in the differences between the AIRS day and night measurements. Generally, 90% of
the world's AIRS TCO is smaller during nighttime compared to daytime. The reduction of AIRS TCO over land at night is
155   greater than over oceans depending on surface type. Seasonal averaged O_3 day-to-night relative difference shown in Figures
1a to 1d reveal that AIRS TCO day and night difference variations in Asia, Europe and North America during winter in the
Northern Hemisphere (DJF) are smaller than during summer-time (JJA), in line with the efficiency of photochemical
production between seasons in the Northern Hemisphere. The Sahara desert shows maximum difference value during winter-
time when there are large day-night temperature differences. The same phenomenon is observed in Western Australia during
160   summer-time. The presence of day-night differences apparently correlating with surface infrared emissivity properties of dry

desert regions is consistent with Masiello et al. (2014), who discussed the variability of surface infrared emissivity in the Sahara desert and recommended to take the diurnal variation of surface emissivity into account in infrared retrieval algorithms.

Figure 1e shows for the annual mean large differences of AIRS TCO retrievals over deserts, difference patterns over the oceans associated with the Intertropical Convergence Zone (ITCZ) as well as regions with persistent seasonal subtropical stratocumulus fields. The spatial patterns over land mimic regions with low IR surface emissivity and/or regions where IR surface emissivity exhibits large seasonal variations (Feltz et al., 2018). Figure 1f shows absolute differences between all subsequent pixels in the longitude direction. The figure reveals significant non-physical TCO changes (discontinuities) for adjacent land-ocean pixels (visible at coast lines running in North-South direction). All these effects are important parameters for the retrieval algorithm but bear no physical relation with total O$_3$. The observed diurnal cycle in AIRS TCO is related to either the measurements or to the algorithm. If the diurnal cycles in AIRS TCO are related to the retrieval algorithm, it has to be caused by the representation of a process in the algorithm having a diurnal cycle, something Smith and Barnes (2019) argue is not in the algorithm but should be taken into account. Hence, the differences shown in Figure 1 provide strong indications that the largest AIRS day-night TCO differences are dominated by retrieval artefacts. As such changes are unphysical, it confirms the hypothesis that clouds and the surface type (land/desert/vegetation/snow or ice) affects the AIRS TCO retrievals. Note that TCO day-night differences over land could also be (partly) related to clouds.

The AIRS emissivity retrieval uses the NOAA regression emissivity product as a first guess over land. The NOAA approach is based on clear radiances simulated from the European Centre for Medium-Range Weather Forecasts (ECMWF) forecast and a surface emissivity training data set (Goldberg et al., 2003). The training data set used for the AIRS V4 algorithm has a limited number of soil, ice, and snow types and very little emissivity variability in the training ensemble. In the AIRS V5 version, the regression coefficient set has been upgraded using a number of published emissivity spectra (12 spectra for ice/snow, 14 for land) blended randomly for land and ice (Zhou et al., 2008). These improvements generated a better emissivity first guess for use with the AIRS V5, and improved retrievals over the desert regions (Divakarla et al., 2008). In AIRS V6, a surface climatology was constructed from the 2008 monthly MODIS MYD11C3 emissivity product, and extended to the AIRS IR frequency hinge points using the baseline-fit approach described by Seemann et al. (2008). Note that AIRS observations with low information content (especially around the poles) will be drawn to the AIRS a-priori value. This AIRS a-priori for O$_3$ is a climatology without diurnal variation. If either the day or night observation has a lower information content than the other, this too can result in a day-night difference. This is probably the reason for the differences in Figure 1 over pole ice. Nevertheless, using day-night differences for evaluation of the AIRS V6 O$_3$ product suggest that further refinements for better surface emissivity retrievals are required and that issues related to cloud cover need to be solved.

3.2 MLS O$_3$ retrievals day-night differences

3.2.1 MLS O$_3$ profile

In order to better understand day-night differences in TCO, we also study day-night changes in the vertical profile of O$_3$ using MLS O$_3$ profile measurements. Figure 2a shows that the global (60 °S-60 °N) differences between day and night MLS O$_3$ profile occur in the mesosphere (10 hPa - 0.1 hPa). The O$_3$ mixing ratios are about an order of magnitude larger during night in the mesosphere, which was revealed by Huang et al. (2008) previously. Different latitude bands (30 degree) between 60 °S and 60 °N all display similar results.

We also find an unexpected polar bias at high latitudes in Figure 2d and 2g. On the one hand, the larger differences between ascending ("daytime") and descending ("nighttime") MLS O$_3$ profile at high latitude extend from the stratosphere to the mesosphere. On the other hand, ascending O$_3$ is smaller than descending O$_3$ at 10 hPa over 60 °N-90 °N in Figure 2d, which is in contrast with the result of other latitude bands.

3.2.2 MLS O$_3$ retrievals in 90 °S-60 °S and 60 °N-90 °N

The MLS O$_3$ profile polar bias mentioned above turns out to be related to an inconsistency in the 'AscDescMode' flag of MLS v4.2x standard O$_3$ product in 90 °S-60 °S and 60 °N-90 °N. We counted the daily number of pixels at both poles when observation mode is ascending (AscDescMode = 1) and descending (AscDescMode = -1) respectively. Figures 3a and 3c show there is a clear change on 14 May 2015 in the daily number of ascending/descending pixels, consistent with the change of MLS SCO in Figure 3b and 3d. Before 14 May 2015, there are very large differences (about 500 pixels, 95% of total pixels) in the number of pixels between ascending and descending mode, as well as the differences in MLS SCO. After 14 May 2015, the ascending and descending MLS SCO are much closer with smaller differences (about 20 pixels, 2% of total pixels) of ascending and descending pixels.

For the MLS O$_3$ profile in Figure 4, differences between ascending and descending MLS O$_3$ profiles at high latitudes for 2016-2018 are much smaller and more realistic compared to the differences for 2005-2014. The large differences in the stratosphere disappear in polar regions with the correct 'AscDescMode' flag for 2016-2018. For 60 °N-90 °N, ascending mode O$_3$ also becomes larger than descending mode O$_3$ at 10 hPa in Figure 4b. This indicates that the MLS 'AscDescMode' flag is correct for 2016-2018.

The O$_3$ retrieval algorithm adopted by the MLS v2.2 products has been validated to be highly accurate using multiple correlative measurements and the data have been used widely (Jiang et al., 2007; Froidevaux et al., 2008). The MLS v3.3 and v3.4, O$_3$ profile was reported on a finer vertical grid and the bottom pressure level with scientifically reliable values (MLS O$_3$ accuracy was estimated at ~20 ppbv +10% at 261 hPa) increases from 215 to 261 hPa (Livesey et al., 2015). The latest MLS v4.2x O$_3$ profile used in this study, released in February 2015, were in general similar to the previous version. One of the major improvements of MLS v4.2x was the handling of contamination from cloud signals in trace gas retrievals that resulted in significant reduction in the number of spurious MLS profile in cloudy regions and a more efficient screening of cloud-

contaminated measurements. Furthermore, the MLS O₃ products have been improved through additional retrieval phases and reduction in interferences from other species (Livesey et al., 2015). We find no indications that changes in instrument or algorithm are responsible for this 'AscDescMode' flag inconsistency. This flag inconsistency is not present between 60°S and 60°N.

3.3 Comparison between AIRS and MLS O₃ retrievals

Figure 5 presents comparison of yearly and monthly averaged SCO for 2005-2018 observed by AIRS and MLS three latitude bands. ==Note that figure 5 is not meant as a validation of AIRS SCO with MLS SCO, but to explore the seasonality of either AIRS or MLS SCO day-night differences, and explore whether the seasonality in day-night SCO varies in unison over the seasons.== Figure 5a shows the 14-year average daytime AIRS SCO (250 hPa – 1 hPa) and MLS SCO (261 hPa – 0.02 hPa) in 60°S-60°N for 2005-2018. The time average MLS SCO column is 260.62 DU and AIRS SCO is 264.24 DU. The average MLS SCO day-night differences for 2005-2018 (0.88 DU) is smaller than the AIRS SCO day-night differences observed for the same time period (5.24 DU). The day-night difference of MLS SCO is 0.79 DU in the mesosphere (10 hPa - 0.1 hPa) and 0.03 DU in the stratosphere (100 hPa - 10 hPa). The day-night difference of AIRS SCO is 1.51 DU in the mesosphere (10 hPa - 1 hPa) and 3.85 DU in the stratosphere (100 hPa - 10 hPa). Compared to the AIRS SCO day-night differences, the magnitude of MLS SCO day-night differences in the stratosphere and in the mesosphere are much smaller. It has been pointed out that errors in temperature profiles and water vapour mixing ratios will adversely affect the AIRS O₃ retrieval. Significant biases (0 - 100%) may exist in the region between ~300 hPa and ~80 hPa (Wang et al., 2019; Olsen et al., 2017). AIRS O₃ retrievals do not distinguish portions of the O₃ profile as being of different qualities, because all AIRS O₃ channels sense the surface as well atmospheric O₃. Thus AIRS O₃ retrievals are compromised if the surface is not well characterized (Olsen et al., 2017). In addition, AIRS SCO retrievals show smaller day-night differences in the polar zones (1-2 DU) than in 60°S-60°N (4-5 DU). This is related to clouds and the surface type which affect the AIRS O₃ retrievals as mentioned above. Figure 5b shows the monthly 14-year average daytime AIRS SCO and MLS SCO in the 60°S-60°N for 2005-2018. Seasonal or random changes of clouds and the surface emissivity have more significant impact on each monthly AIRS SCO retrieval than on the MLS SCO retrieval. Compared with the 60°S-60°N region, surface types in polar zones are less diverse (snow or ice). Therefore, the monthly 14-year average daytime AIRS SCO and MLS SCO in Figure 5d and 5f show similar patterns. Figures 5c to 5f also confirm that MLS SCO has a polar bias when compared with AIRS SCO at high latitudes. In addition, for MLS SCO in Figure 5f, the biggest day-night differences (50-60 DU) occur in September and October during the Antarctic O₃ hole.

3.4 Day-night difference of equatorial Pacific low O₃ regions

Generally, the Pacific low O₃ region (TCO < 220 DU) exist all year round and its size is larger at night than during the day, unlike the seasonal O₃ hole which occurs over Antarctica during the Southern Hemisphere polar winter. On the one hand, there are limited direct NO_x emissions causing low O₃ over oceans compared to land. On the other hand, the low O₃ over the tropical western Pacific can be attributed to tropospheric O₃ loss in this area. Its presence is related to a pronounced minimum

in the tropospheric column of O_3 over the west Pacific, which loss is due to photochemical mechanism with higher air
255   temperatures and higher water concentrations for O_3. In addition, high sea surface temperatures also favour strong convective
activity in the tropical West Pacific, which can lead to low O_3 mixing ratios in the convective outflow regions in the upper
troposphere in spite of the increased lifetime of odd oxygen (Kley et al., 1996; Rex et al., 2014). A further reduction in the
tropospheric O_3 burden through bromine and iodine emitted from open-ocean marine sources has been postulated by numerical
models (Vogt et al., 1999; von Glasow et al., 2002; von Glasow et al., 2004; Yang et al., 2005) and observations (Read et al.,
260   2008).

Figure 6a and 6c show the low O_3 region is mainly located over the western Pacific by AIRS. Rajab et al. (2013)
investigated similar low TCO in Malaysia using AIRS data. They found the highest O_3 concentration occurred in April and
May and the lowest O_3 concentration occurred during November and December, which is consistent with our results in Figure
6f. They also found that O_3 concentrations exhibited an inverse relationship with rainfall, but was positively correlated with
265   temperature. Figure 6b shows that besides in the tropical Western Pacific, low O_3 regions for MLS appear all over the tropical
zone (30 °S-30 °N) at night. However, Figure 6d shows the occurrence frequency and intensity of daytime low O_3 regions by
MLS SCO retrievals drastically reduces and exists mainly in tropical western Pacific. In Figure 6e and 6f, yearly and monthly
averaged AIRS TCO and MLS SCO of the low O_3 regions show no consistency and regularity. The analysis of daytime MLS
SCO of the low O_3 regions is based on only a few observations. We cannot distinguish whether it is an algorithm problem or
270   a chemical mechanism that caused this phenomenon. For AIRS, clouds over oceans may have greater impact on the AIRS
TCO retrievals at night. For MLS, more active chemical reactions may occur in these low O_3 regions at night.

For past, current and future monitoring of atmospheric phenomena like the Pacific tropospheric low O_3 area, it is important
that observations are sufficient accurate. The evaluation of day-night differences in both MLS and AIRS has revealed the
existence of biases in the satellite data that are sufficiently large in comparison to expected variations and changes in
275   atmospheric O_3 that they may hamper the use of these satellite data studying them.

4 Conclusions

Comparison of daytime and nighttime AIRS TCO has revealed small but not insignificant biases in AIRS TCO. The
differences are likely related to surface type (land/desert/vegetation/snow or ice) and infrared surface emissivity, especially
over regions that exhibit smaller infrared emissivity or large seasonal variability in infrared emissivity. Differences typically
280   were of the order of a few percent, which is significant given that long term changes in TCOs related to anthropogenic
emissions of stratospheric O_3 depleting substances outside of polar regions are also of the order of a few percent.

Over land, patterns in day/night differences appear to be dominated by the dryness of the surface, suggesting that
emissivity may not be well represented or that reduced sensitivity to the lower troposphere during night compared to day over
hot surfaces results in a different AIRS TCO. The spatial inhomogeneity of day/night AIRS TCO differences over drier regions

285 points to emissivity dominating these differences. Infrared satellite retrieval artefacts due to land surface emissivity is well-known phenomenon (Zhou et al., 2013; George et al., 2015; Bauduin et al., 2017).

There were major changes to the surface emissivity retrieval in AIRS V6 compared to previous versions resulting in a very significant improvement in yield and accuracy for surface temperature and emissivity over land and ice surfaces compared to previous versions. Nevertheless, our results indicate that the AIRS V6 TCO still can be further improved with regard to the

290 representation of infrared emissivity. In addition, AIRS TCO differences over oceans bear a clear cloud cover signature which is likely related to uncertainties in the representation of clouds in the retrieval algorithm. The latter may also impact AIRS TCO retrievals over land, although detection of cloud features in AIRS TCO day-night differences over land is difficult due to the presence of the land surface emissivity related bias.

The strongest diurnal cycles in cloud fraction are found in the tropics over land, following strong daytime heating (Noel

295 et al., 2018). Over oceans, diurnal cycles in cloud fraction are weaker, but very broadly indicate reduced cloudiness during day compared to night, especially in the tropics and subtropics (Noel et al., 2018). In case of clouds, AIRS TCO appears to be larger during daytime compared to nighttime. This is consistent with the notion of increased cloudiness during the night, increasing the chance of shielding by undetected or unrecognized clouds in the AIRS retrieval. For ocean regions with persistent clouds during day and night (for example over ITCZ), Figure S1 in the supplement shows that variations of cloud

300 layer height have a greater impact on AIRS TCO day-night differences than of the cloud fraction.

Our results do not provide much evidence of another possible causes of day/night differences in AIRS TCO: the photochemical diurnal O_3 cycle in the lower troposphere and upper atmosphere. The strongest diurnal O_3 effects occur in the boundary layer over land due to nighttime surface deposition and daytime photochemical O_3 production in the presence of air pollution. In the marine boundary layer, the diurnal O_3 cycle is much weaker due to absence of air pollution and a general slow

305 O_3 destruction regime (~10%/day). Similarly, in the free troposphere, the diurnal O_3 cycle is also weak due to low O_3 production rates (generally low levels of pollution relevant for O_3 production). Hence, the diurnal O_3 cycle in the free troposphere above 750 hPa is negligible (Petetin et al., 2016). In summary, any tropospheric photochemical diurnal O_3 cycle effect should resemble some correspondence with air pollution. The day-night differences in AIRS TCO clearly do not resemble patterns of surface air pollution (Figure 1). MLS day/night differences are confined to the mesosphere (1 hPa and

310 higher). As shown in Smith et al. (2014) the lifetime of O_3 due to chemistry is strongly altitude dependent (< 20 min in the upper mesosphere above 0.01 hPa). Only in the mesosphere, the chemical lifetime of O_3 is long enough to see significant differences between average daytime and nighttime concentrations. However, the contribution of mesospheric O_3 to MLS SCO is negligible. The mesospheric diurnal O_3 cycle thus will also have a negligible effect on day/night AIRS TCO differences. In addition, Strode et al. (2019) simulated the global diurnal cycle in the tropospheric O_3 columns, their results indicated that the

315 mean peak-to-peak magnitude of the diurnal variability in tropospheric O_3 is approximately 1 DU. Figures S2 to S5 in the supplement also show that the AIRS TCO retrieval artefacts dominate the day/night variability of tropospheric O_3 residuals (TOR = AIRS TCO – MLS SCO).

In summary, our analysis has identified evidence and indications that clouds, land surface infrared emissivity, and sensitivity of satellite measurements to the lower troposphere, influence AIRS satellite TCO observations, pinpointing to areas and processes for algorithm improvement.

The MLS v4.2x was very useful for verification of daytime and nighttime SCO and O_3 profile between 60 °S-60 °N. MLS day-night differences in SCO and O_3 profiles show that day-night differences are only small (< 1 DU) and likely to be in the upper stratosphere and mesosphere. However, an inconsistency was found in the 'AscDescMode' flag in 60°N-90 °N and in 90 °S-60 °S, resulting in inconsistent profiles in these regions before 14 May 2015. In processor version v4.22 and later versions this issue has been fixed, but since it is a relatively small issue, the MLS data set before 2016 has not been reprocessed.

A case study of day-night differences O_3 over equatorial Pacific revealed that both AIRS and MLS O_3 retrievals have biases in comparison to expected variations and changes. Our results show that maintaining the quality of the satellite observations of stratospheric O_3 is therefore highly relevant.

Data availability

Satellite data sets used in this research can be requested from public sources. AIRS level 3 data are available online: AIRS Science Team/Joao Teixeira (2013), AIRS/Aqua L3 Daily Standard Physical Retrieval (AIRS-only) 1 degree x 1 degree V006, Greenbelt, MD, USA, Goddard Earth Sciences Data and Information Services Center (GES DISC), Accessed: [*2020.04*], doi:10.5067/Aqua/AIRS/DATA303.

AIRS level 2 data are available from: AIRS Science Team/Joao Teixeira (2013), AIRS/Aqua L2 Standard Physical Retrieval (AIRS-only) V006, Greenbelt, MD, USA, Goddard Earth Sciences Data and Information Services Center (GES DISC), Accessed: [*2020.04*], 10.5067/Aqua/AIRS/DATA202.

MLS level 2 data can be obtained from: Schwartz, M., Froidevaux, L., Livesey, N. and Read, W. (2015), MLS/Aura Level 2 Ozone (O3) Mixing Ratio V004, Greenbelt, MD, USA, Goddard Earth Sciences Data and Information Services Center (GES DISC), Accessed: [*2020.04*], doi:10.5067/Aura/MLS/DATA2017.

Author contributions

WNW and JL provided satellite data, tools, and analysis. RA, JL and THC undertook the conceptualization and investigation. WNW prepared original draft. RA and JL carried out review and editing. JW checked the English language. All authors discussed the results and commented on the paper.

Competing interests

The authors declare that they have no conflict of interest.

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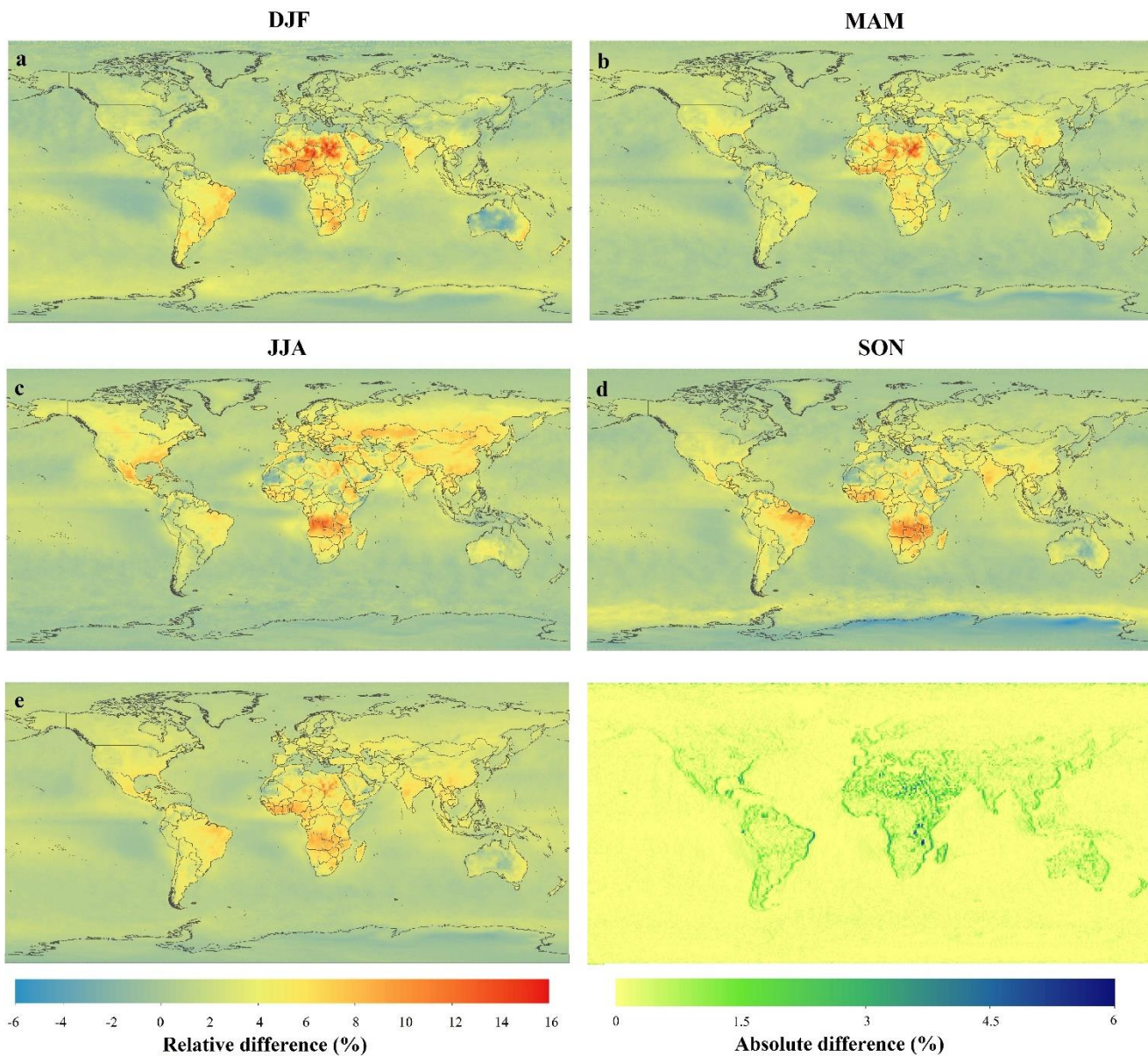
Figure 1: (a) AIRS TCO averaged day-to-night relative difference for Dec-Jan-Feb during 2003-2018. (b) Mar-Apr-May. (c) Jun-Jul-Aug. (d) Sep-Oct-Nov. (e) AIRS TCO 16-year averaged day-to-night relative difference during 2003-2018. (f) Absolute difference between two adjacent pixels at the same latitude in (e). Note: The relative difference is calculated as: 100 × (daytime - nighttime) / daytime (in percent, %).

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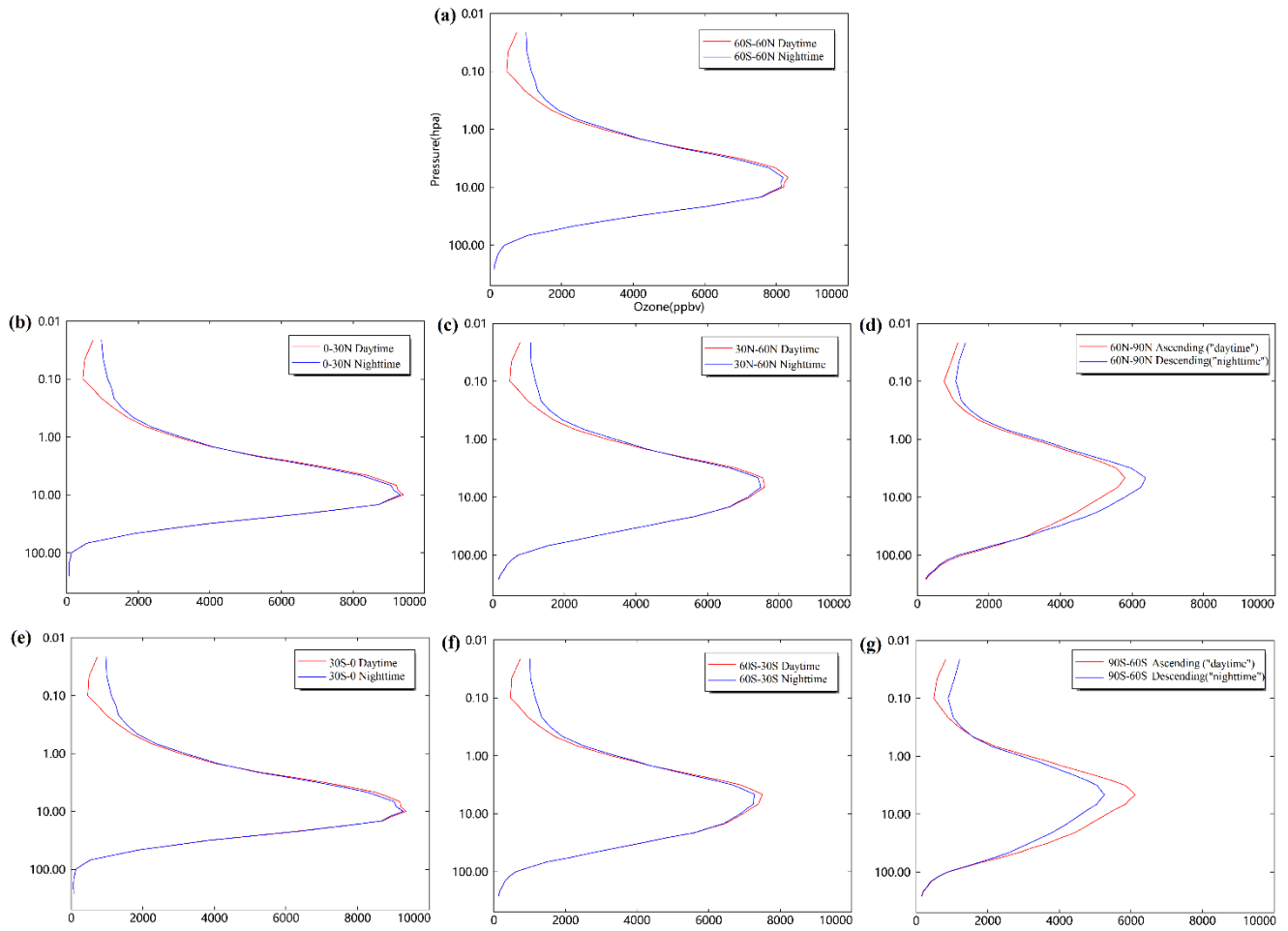
Figure 2: Averaged MLS ozone profile between 261 hPa and 0.02 hPa per latitude band (30 degree) for 2005-2018. (a) 60˚S-60˚N. (b) 0-30˚N. (c) 30˚N-60˚N. (d) 60˚N-90˚N. (e) 30˚S-0. (f) 60˚S-30˚S. (g) 90˚S-60˚S.

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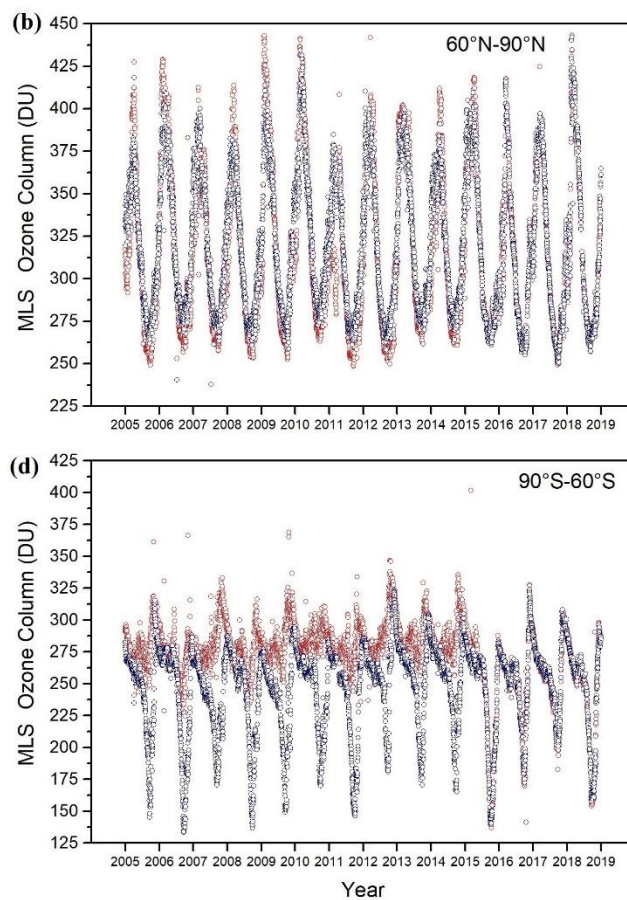
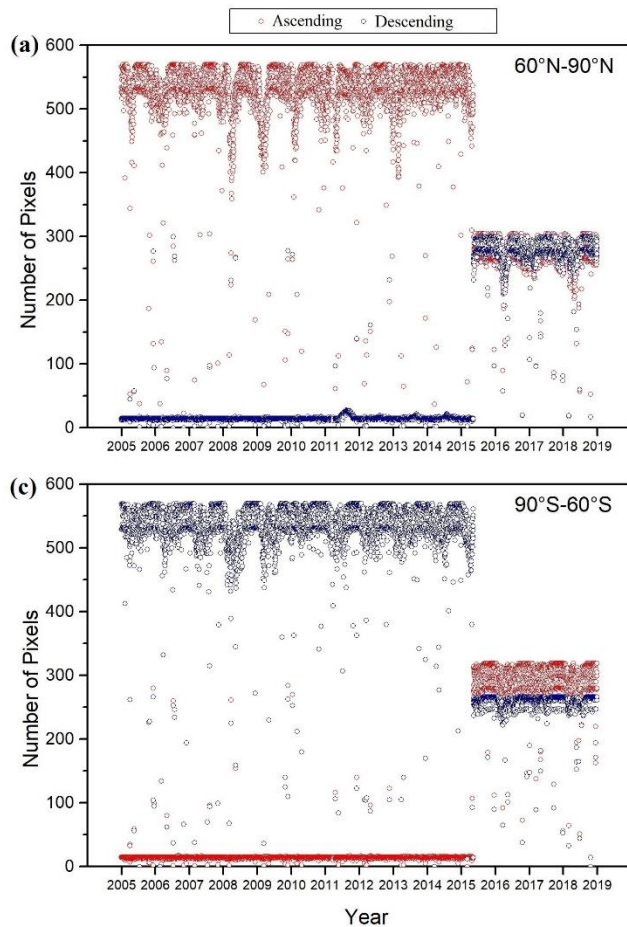
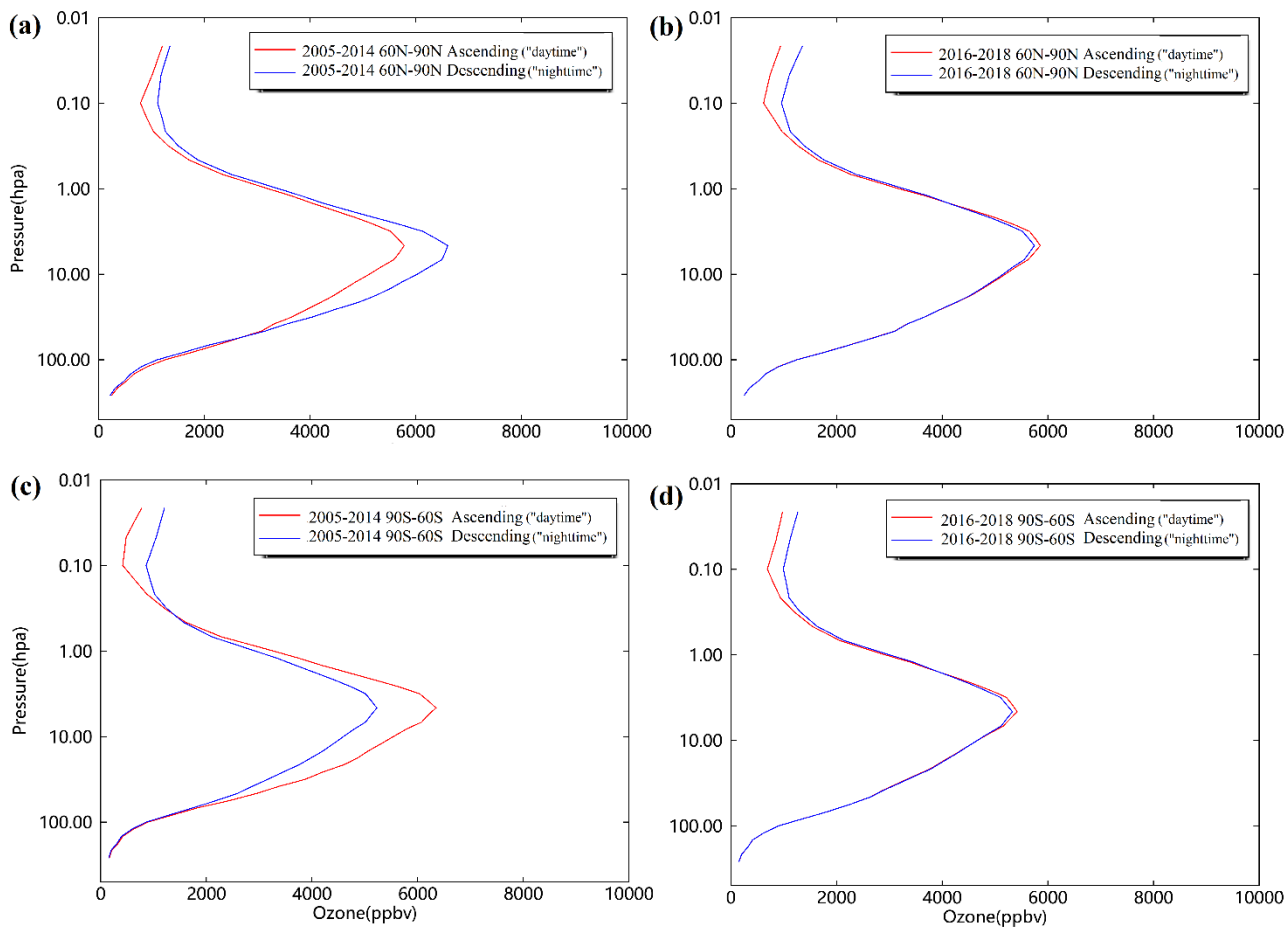


Figure 3: (a) Time series of daily number of Ascending ("daytime") and Descending ("nighttime") pixels in 60 °N-90 °N. (b) Time series of daily average Ascending and Descending MLS SCO in 60 °N-90 °N. (c) Same as (a), but in 90 °S-60 °S. (d) Same as (b), but in 90 °S-60 °S.

590   **Figure 4: (a) Averaged MLS ozone profile between 261 hPa and 0.02 hPa for 2005-2014 in 60 ̊N-90 ̊N. (b) Averaged MLS ozone profile between 261 hPa and 0.02 hPa for 2016-2018 in 60 ̊N-90 ̊N. (c) Same as (a), but in 90 ̊S-60 ̊S. (d) Same as (b), but in 90 ̊S-60 ̊S.**

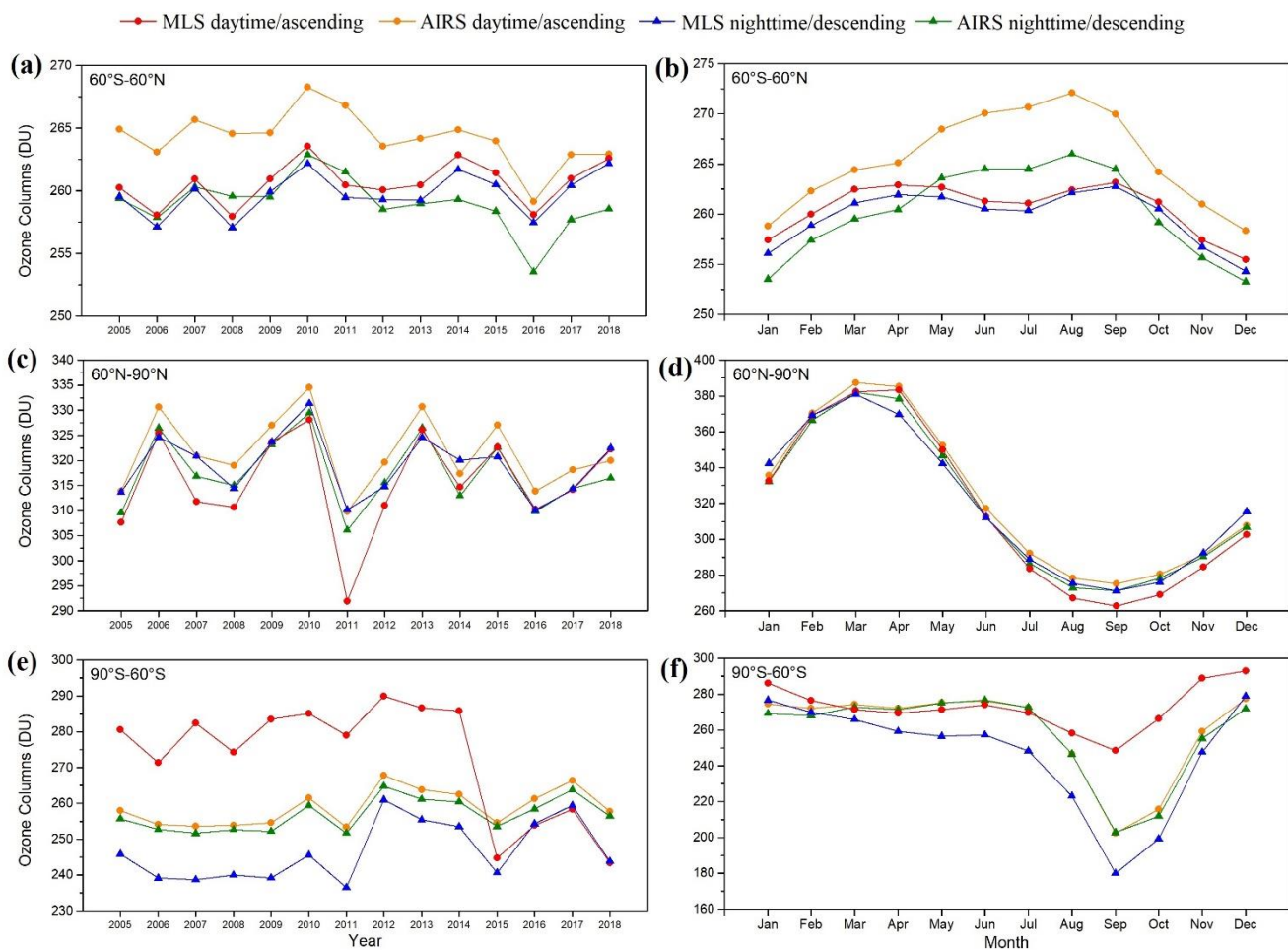



Figure 5: Yearly and monthly averaged AIRS SCO and MLS SCO for 2005-2018. AIRS SCOs are calculated from 250 hPa to 1 hPa.

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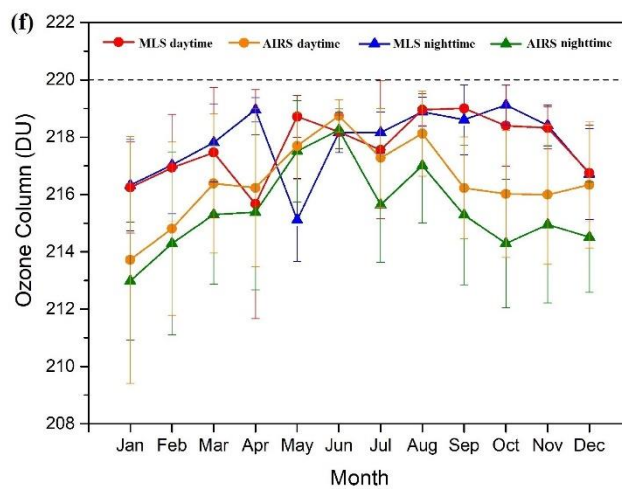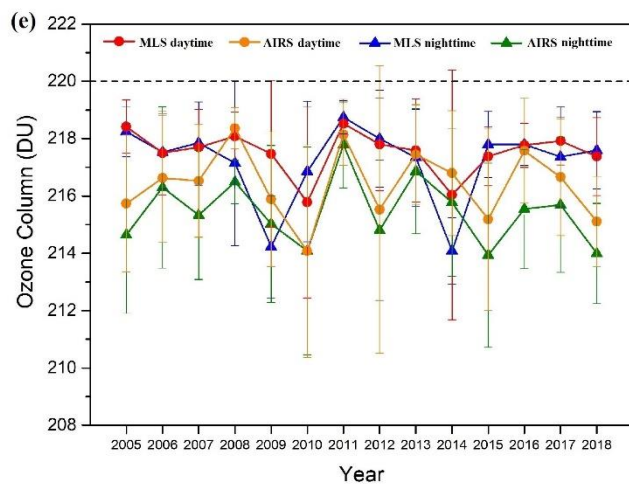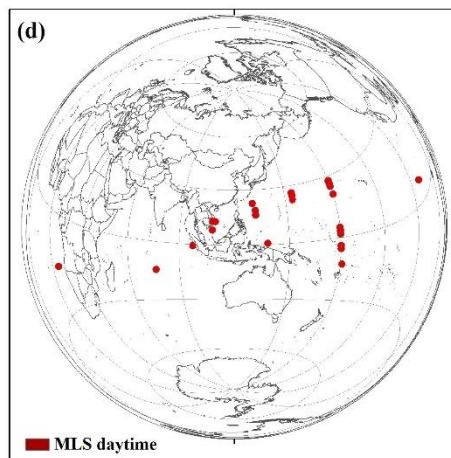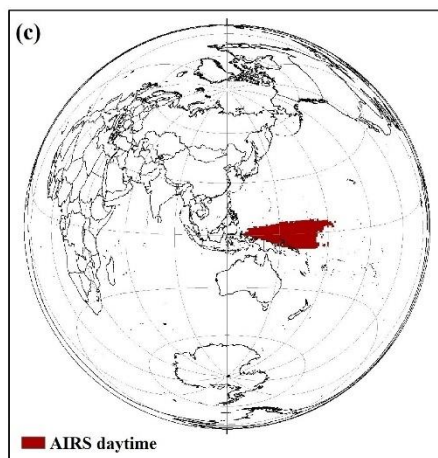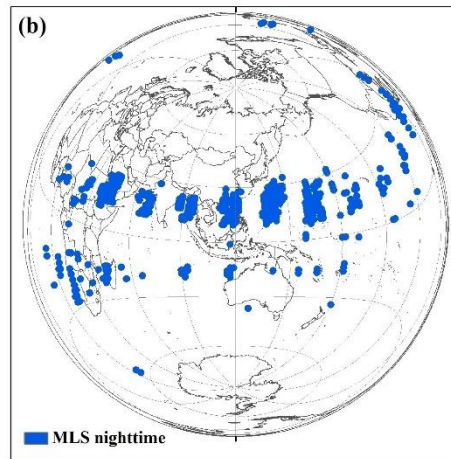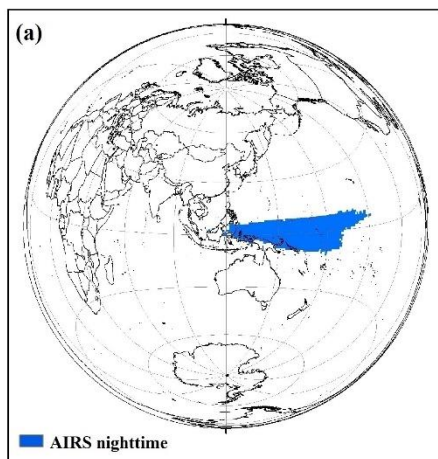
Figure 6: Spatial and temporal distribution of the low ozone. (a) Location (composite pixel) of the yearly nighttime low ozone from 2005 to 2018 for AIRS TCO. (b) Same as a but for MLS SCO. (c) Location (composite pixel) of the yearly daytime low ozone from 2005 to 2018 for AIRS TCO. (d) Same as c but for MLS SCO. (e) Yearly averaged AIRS TCO and MLS SCO of the low ozone regions for 2005-2018. (f) Monthly averaged AIRS TCO and MLS SCO of the low ozone regions for 2005-2018. Uncertainties represent the standard deviation of the measured values.

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