Associate Editor Decision: Publish subject to minor revisions (review by editor) (16 Aug 2019) by Folkert Boersma
Comments to the Author:
Dear authors,

After carefully reading the review reports and your response and revision to the manuscript, I think the paper can be accepted for publication in AMT, but I would like you to make the following modifications. Congratulations on a nice and comprehensive piece of work.

In the abstract of the revised manuscript (L11-12) you write "OMI always misses the frequently much higher values of TCNO2 that occur after the OMI overpass time". This should be rephrased as OMI is designed such that -by definition- it cannot measure TCNO2 after its overpass.

The new abstract appears at the end of this reply

The next sentence should be nuanced or clarified. You write "OMI retrieved TCNO2 are not suitable for air quality assessments as related to human health, especially in polluted urban areas", but this statement is too sweeping. Please write exactly what you can justify based on your study, which is that OMI cannot resolve NO2 pollution within a city, which makes it less suitable for urban surface NO2 assesments (it can still provide some useful information if there is nothing else!).

Compared to local ground-based or aircraft measurements, OMI cannot resolve spatially variable $TCNO_2$ pollution within a city or urban areas, which makes it less suitable for air quality assessments related to human health.

L22: NO2 emissions --> NOx emissions Changed

L43-44: "First, the mid-day OMI observations do not see the large diurnal variation of TCNO2 that usually occur after the 13:30 overpass time". Please rephrase such to make clear that OMI cannot be expected to see diurnal variation in the first place (unless when combined with another instrument, or at high latitudes).

Because of OMI's selected polar orbit, it is not possible for the mid-day OMI observations to see the large diurnal variation of $TCNO_2$ that usually occur after the 13:30 overpass time,

L177: "In addition to missing the TCNO2 diurnal variation": again this should be reformulated. Readers should not get the impression that OMI was supposed to capture the TCNO2 diurnal variation.

In addition to not being designed to observe the $TCNO_2$ diurnal variation

L219-220: "The PANDORA values suggest upward airflow from the nearby circumferential ring road and resort areas".This statement comes a bit out of the blue. How do PANDORA values suggest this, why is it important? Please clarify.

Reply: There are no emission or combustion sources of NO2 at MLO at 3.4 km altitude. However, there is considerable production of NO2 arising from power plants and automobile traffic near sea level. This implies that somehow NO2 is getting to 3.4 km. Since the Pandora values are in excess of stratospheric values, to me this suggests upward airflow carrying NO2 from its sources. See the figure on pare 2 of this reply

The sentence has been changed to read:

OMI, which mainly measures values over the clean ocean, has an average value of about 0.1 DU (see appendix Fig. A2). Since there are no emission or combustion sources of NO_2 at high altitudes near MLO at 3.4 km, the PANDORA values suggest upward airflow from the near sea level circumferential ring road, Keahole oil Power plant, and resort areas.

Regarding the comments of Rev#2 and my earlier comments: I still think that Fig. 7 and 8 should be improved. They are not very clear, and require a lot of effort from a reader to see where the OMI time sits in the 3-D landscape. As suggested earlier, there are better ways to show the OMI 'underestimate' in the diurnal pattern. If you feel you really want to stick to Figure 7 and 8, please do so, but I think it hurts the clarity of the manuscript.

Last but not least, the thing still "hanging" with this work is the diurnal cycle in NO2 observed by the PANDORA, which often shows strong increases or maxima in the afternoon. Based on knowledge of the diurnal cycle in emissions, chemistry, and BL development this is quite surprising, and does not sit well with me. It would mean that we are totally overlooking an important process in the air pollution models, or that emissions are very, very different from what we think we know.

I suspect the sources are not well specified in urban areas. When I worked with the EPA models, the sources were very crude approximations to a very complex emission system.

But of course it could also mean that the PANDORA measurements have a weakness or not yet understood sensitivity. In the afternoon, the Sun starts to set, aerosols have been building up, and radiative transfer may not be as easy as in the morning or early afternoon, and this might affect the PANDORA retrieved values in the late afternoon.

Aerosols without spectral structure have very little effect on direct-sun measurements and a DOAS style retrieval. The main effect of heavy aerosol loading is to decrease the signal to noise ratio for PANDORA. In a previous paper, I showed that even the presence of moderate cloud cover does little to degrade the retrieval.

From my AMT publication the retrieval with cloud cover is barely disturbed down to a reduction in signal of about 8. Herman et al., Atmos. Meas. Tech., 11, 4583–4603, 2018 https://doi.org/10.5194/amt-11-4583-2018

Added on page 8

Figure 6 also illustrates $TCNO_2$ diurnal behavior at two other sites, NASA HQ in Washington, DC and at City College of New York and compares the values to the OMI retrieved $TCNO_2$.

Both Figs. 6 and 2A show the PANDORA $TCNO_2$ retrieval with the values of the SZA plotted on the same graph showing that the direct-sun retrievals are good out to SZA = 70^O. Depending on atmospheric conditions, retrievals using BEER's law absorption attenuation and spectral fitting for SZA > 75^O begin to yield non-physical values ($TCNO_2$ too small). During mid-day measurements, the signal to noise ratio is very high since over 4000 clear-sky measurements are averaged together to produce one data point every 20 seconds. Even with aerosol loading or moderate cloud cover blocking the sun, the retrievals are still accurate (Herman et al., 2018).

4586 J. Herman et al.: NO_2 and HCHO measurements in Korea from 2012 to 2016

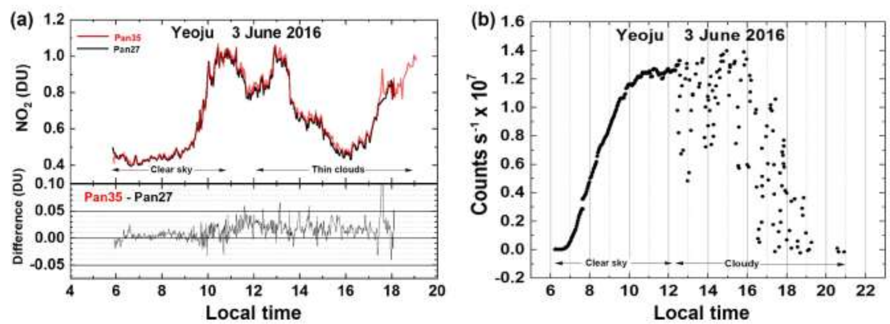

Figure 2. (a) $C(NO_2)$ amounts from Pandora 27 and 35 in Yeoju, Korea during 3 June 2016 and their difference |Pan35–Pan27| < 0.05 DU. **(b)** Pandora 35 estimate of cloud or aerosol reduced measured counts s^{-1} at approximately 500 nm.

The manuscript needs at least a short paragraph discussing strengths/weaknesses/unknowns of the PANDORA method, also in view of other publications addressing the issue of diurnal variation in NO2. One obvious question that comes to mind is whether PANDORA measurements in the late afternoon have been validated or evaluated themselves (against MAX-DOAS). The other one is the concern on whether PANDORA does not measure too high NO2 at Mauna Loa ("more than possible in the stratosphere") - a further indication that something may be amiss with late afternoon measurements.

I have added some text to the paper discussing accuracy and precision and references to two previous papers.

The accuracy and precision of PANDORA $TCNO_2$ measurements has been previously discussed (Herman et al., 2009; 2018).

Page 7 line 244 **An example of the diurnal behavior of $TCNO_2$ at Waterflow, New Mexico on 6 June 2012 is shown in Fig. 6 to illustrate the behavior of PANDORA $TCNO_2$ retrievals at a wide range of SZA. The terrain surrounding the Pandora site is flat with no obstructions (buildings) permitting observations to very high SZA. Almost every day the power plant briefly puts out very high emissions of NO_2 as part of its daily boiler cleaning cycle. This can be seen in the very high peak value of $TCNO_2$ of 3.4 DU compared to the nominal value of 0.5 DU occurring for most of the day. The value from the OMI**

retrieval at 21:01 GMT (14:01 local standard time) is about 0.2 DU compared to the PANDORA value of about 0.5DU. Figure 6 also illustrates $TCNO_2$ diurnal behavior at two other sites, NASA HQ in Washington, DC and at City College of New York and compares the values to the OMI retrieved $TCNO_2$.

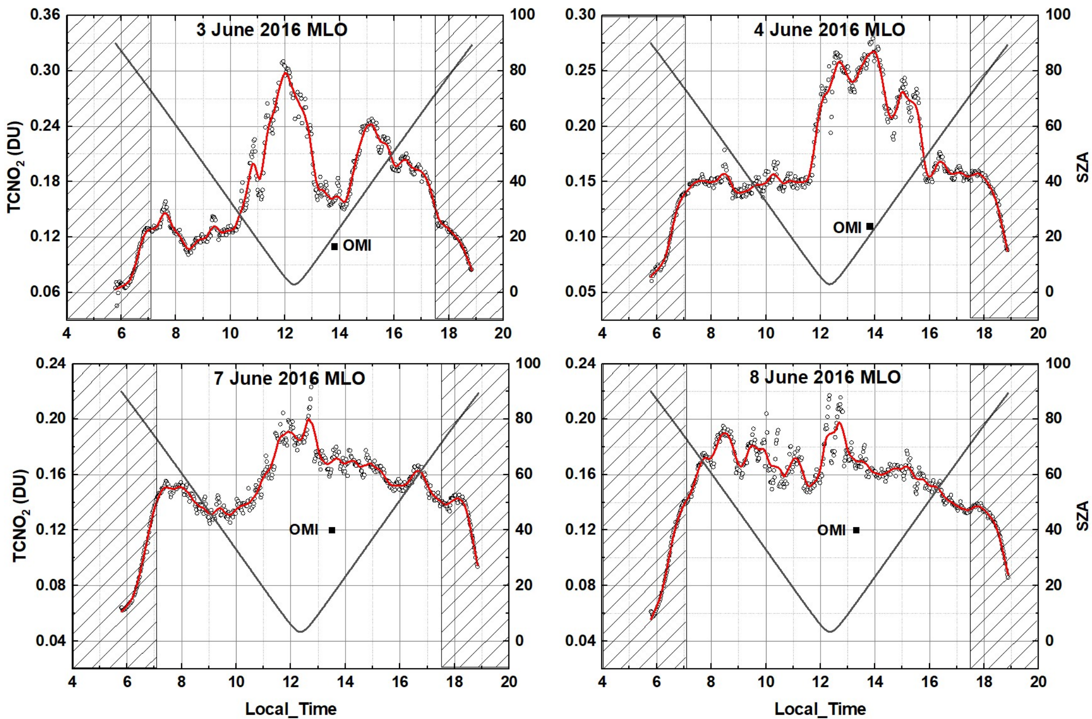

Fig. A2 The diurnal variation of $TCNO_2$ at MLO on 4 days during June 2016 compared to OMI $TCNO_2$

Reply: If the "late afternoon" measurements were made at very high SZA, I would agree with you. However, the SZA's of these measurements are less than 70^{O}. Almost always, the Pandora retrievals show a decrease at SZA's greater than 80^{O}, not an increase. On many days, the diurnal variation observed by Pandora is nearly flat. Because this is a direct sun observation, the radiative transfer is simply a slightly modified Beer's law absorption. Most of the solar photons for wavelengths between 420 and 500 nm that reach the collimated Pandora CCD are not scattered in the atmosphere but show absorption by NO2. The absorption clearly shows up in a DOAS type retrieval.

The graphs above are from measurements made at the Mauna Loa Observatory MLO on 4 days during June 2016. The measurements appear to be valid up to an SZA of about 75^{O}. For SZA > 75^{O}, there appears to be a non-physical decrease in TCNO2 having to do with the Beer's Law DOAS retrieval algorithm. The mid-day retrievals of TCNO2 are valid (07:00 – 17:00) and show a value of TCNO2 that is systematically higher than the stratospheric value of approximately 0.1 DU.

Figure A2 shows the diurnal variation of TCNO2 at MLO on specific days 3,4,7,and 8 of June 2016 along with the variation in SZA. This shows that the MLO is polluted by NO_2 with column amounts in excess of stratospheric amounts (approximately 0.1 DU) even though there are no local sources. OMI retrievals of TCNO2 on each day are much lower because of the averaging over OMI's large FOV that includes very clean ocean areas.

The new Fig. 6 graph (below) may convince you of the validity of the Pandora measurements. The measurement at Waterflow New Mexico is very unusual in that the terrain surrounding the Pandora is flat with no obstructions (buildings) permitting observations to very high SZA. There is very little automobile traffic, but there is a nearby (2 km) power plant. Once per day, the power plant puts out a very high rate of emission as part of its boiler cleaning cycle. The peak TCNO2 measurement also corresponded to very high levels of CO2 from a co-located FTIR. The OMI measurement is averaging the surrounding very clean area. Unlike most urban areas, this location has very well-defined sources of NO2. The other panels of Fig.6 show examples of OMI TCNO2 compared to diurnal variation at NASA HQ and in NYC. These explicitly show the OMI sampling problem.

I will add the graph below and some short paragraphs to the paper. I prefer to keep the 3-D images, since it is the only way to show a year's worth of minute by minute daily Pandora data. The 3D images give a qualitative view of the frequency of occurrence on high values of TCNO2.

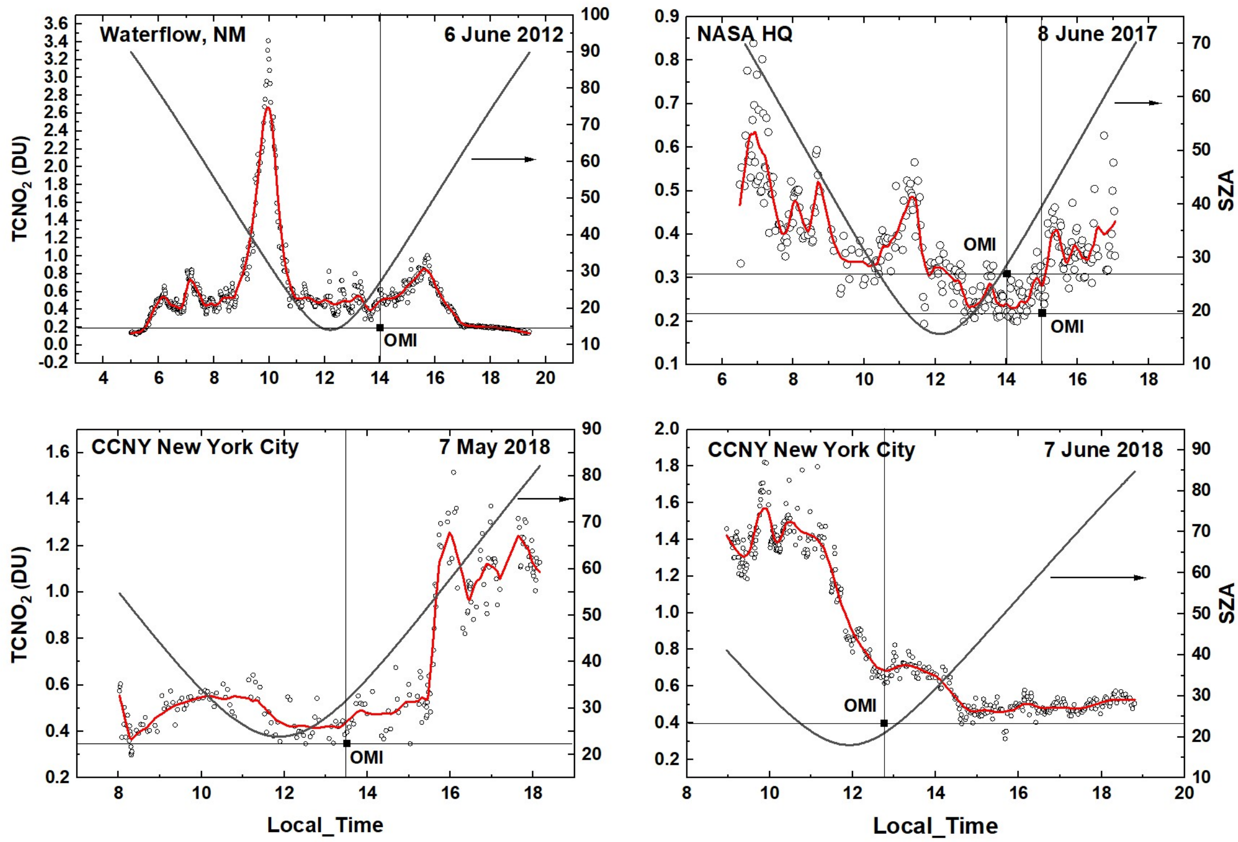

Fig.6 Diurnal variation of $TCNO_2$ on a single day 1) Two km north of Waterflow, NM near a power plant, 2) On the roof of NASA Headquarters Washington, DC and 3) On the roof or a building at CCNY City College of New York, New York City

Added to text

Both Figs. 6 and 2A show the PANDORA $TCNO_2$ retrieval with the values of the SZA plotted on the same graph showing that the direct-sun retrievals are good out to SZA = 70^O. Depending on atmospheric conditions, retrievals using BEER's law absorption attenuation and spectral fitting for SZA > 75^O begin to yield non-physical values ($TCNO_2$ too small). During mid-day measurements, the signal to noise ratio is very high since over 4000 clear-sky measurements are averaged together to produce one data point every 20 seconds. Even with aerosol loading or moderate cloud cover blocking the sun, the retrievals are still accurate (Herman et al., 2018).

The abstract now reads

Retrievals of Total Column NO_2 ($TCNO_2$) are compared for 14 sites from the Ozone Measuring Instrument (OMI using OMNO2-NASA v3.1) on the AURA satellite and from multiple ground-based PANDORA spectrometer instruments making direct-sun measurements. **While OMI accurately provides the daily global distribution of retrieved $TCNO_2$, OMI almost always underestimates the amount $TCNO_2$ by 50 to 100% in polluted areas, while occasionally the daily OMI value exceeds that measured by PANDORA at very clean sites. Compared to local ground-based or aircraft measurements, OMI cannot resolve spatially variable $TCNO_2$ pollution within a city or urban areas**, which makes it less suitable for air quality assessments related to human health. In addition to systematic underestimates in polluted areas, **OMI's selected 13:30 equator crossing time** orbit causes it to miss the frequently much higher values of $TCNO_2$ that occur **before or** after the OMI overpass time. Six discussed Northern Hemisphere PANDORA sites have multi-year data records (Busan, Seoul, Washington DC, Waterflow New Mexico, Boulder Colorado, and Mauna Loa) and one site in the Southern Hemisphere (Buenos Aires Argentina). The first four of these sites and Buenos Aires frequently have high $TCNO_2$ ($TCNO_2 > 0.5$ DU). Eight additional sites have shorter term data records in the US and South Korea. One of these is a one-year data record from a highly polluted site at City College in New York City with pollution levels comparable to Seoul, South Korea. OMI estimated air mass factor, surface reflectivity, and the OMI 24x13 km^2 FOV (field of view) are three factors that can cause OMI to underestimate $TCNO_2$. Because of the local inhomogeneity of NO_x emissions, the large OMI FOV is the most likely factor for consistent underestimates when comparing OMI $TCNO_2$ to retrievals from the small PANDORA effective FOV (measured in m^2) calculated from the solar diameter of 0.5^O.