WPs-2250-2251: "DOAS-BO: Towards a new FRM4DOAS-compliant site"

D-4 Report on the inter-comparison campaign within the BAQUNIN supersite in Rome

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List of Acronyms

AMF	Air Mass Factor
BAQUNIN	Boundary-layer Air Quality-analysis Using Network of Instruments
CINDI	Cabauw Intercomparison of Nitrogen Dioxide Measuring Instruments
CNR	Consiglio Nazionale delle Ricerche
DOAS	Differential Optical Absorption Spectroscopy
ECMWF	European Centre for Medium-Range Weather Forecasts
EOS	Earth Observation System
FOV	Field Of View
FRM4DOAS	Fiducial Reference Measurements for DOAS
ISAC	Istituto di Scienze dell’Atmosfera e del Clima
LOS	Line of Sight
MAX-DOAS	Multi AXis – DOAS
NASA	National Aeronautics and Space Administration
NDACC	Network for the Detection of Atmospheric Composition Change
OMI	Ozone Monitoring Instrument
PGN	Pandonia Global Network
QA	Quality Assurance
QA4EO	Quality Assurance For Earth Observation
RTM	Radiative Transfer Model
S-5P	Sentinel-5 Precursor
SAP	Rome – La Sapienza
SCD	Slant Column Densities
SOW	Statement of Work
STD	Standard Deviation
SWIR	Short Wave Infra-Red
SZA	Solar Zenith Angle
SAA	Solar Azimuth Angle
TROPOGAS	Tropospheric Gas Analyzer Spectrometer
TROPOMI	TROPOspheric Monitoring Instrument
TVG	Rome – Tor Vergata
UV	UltraViolet
VIS	Visible
VCD	Vertical Column Density
XS	Cross Section

1 Introduction

This document is the report of the activities performed in the frame of WP 2251-3 of the IDEAS-QA4EO WPs-2250-2251 “DOAS-BO: Towards a new FRM4DOAS-compliant site’’. The WP 2251-3 is centered on the inter-comparison campaign performed at La Sapienza University in Rome, part of the BAQUNIN supersite. In May 2021, the ISAC-CNR institute acquired (in the frame of a national funded project “Programma biennale degli investimenti del CNR”) a new MAX-DOAS system, the SkySpec-2D. This system took part in several FRM4DOAS inter-comparison campaigns (e.g., CINDI) and full fills all the FRM4DOAS requirements. The SkySpec-2D final destination is the San Pietro Capofiume (BO) “Giorgio Fea” ISAC-CNR observatory in the Po Valley. Due to its full compliance with FRM4DOAS requirements and its more advanced technology, we decided to use the SkySpec-2D instrument instead of the TROPOGAS for the BAQUNIN campaign. However, before traveling to Rome, the SkySpec-2D was employed in an inter-comparison campaign with the TROPOGAS instrument in Bologna, in order to compare the performances of the two MAX-DOAS systems in the same conditions.

In this report, we briefly describe the SkySpec-2D system and report the results of the Bologna and BAQUNIN inter-comparison campaigns.

2 The SkySpec-2D system

The SkySpec-2D-210 (then named as SkySpec-2D) system is developed by Airyx GmbH. (https://airyx.de/wp-content/uploads/2021/03/SkySpec-all_2021-03-09.pdf). The SkySpec-2D instrument series allow to perform low- effort, efficient and reliable atmospheric observations with the Passive DOAS method (according to VDI standard 4212). The measurements provide information on the tropospheric and stratospheric concentration and distribution of various trace gases, e.g., NO_2, SO_2, formaldehyde, and aerosol optical depth in UV and VIS (from 300 nm to 550 nm approximately). The SkySpec-2D system, similarly to the TROPOGAS system, is composed of a measurement PC, a case containing the spectrometers, and a telescope. This kind of Airyx instrument represents a state-of-the-art system, and it took part in several FRM4DOAS inter-comparison campaigns, such as the CINDI ones.

3 TROPOGAS and SkySpec-2D inter-comparison campaign within ISAC-CNR (Bologna) site

The campaign was performed on the roof of the ISAC-CNR building in Bologna from 4th of August to 2nd September 2021. The period was characterized by generally stable and sunny weather.

Following the work done during the first part of the project (see [D-1] and [D-3]), the TROPOGAS system used the updated measurement configuration that follows the FRM4DOAS guidelines. The SkySpec-2D operated in a similar way. Both instruments look at two azimuthal angles (5° and 190°) and use the same MAX-DOAS scanning sequence (1°, 2°, 3°, 5°, 10°, 30°, 90° elevation angles), Fig. 1. To assess the quality of the observations of the two ground-based MAX-DOAS systems with respect to reference satellite data, we exploited S-5P TROPOMI and EOS-Aura OMI measurements. For more details about satellite data used for this exercise, see Sect. 5.2.1.

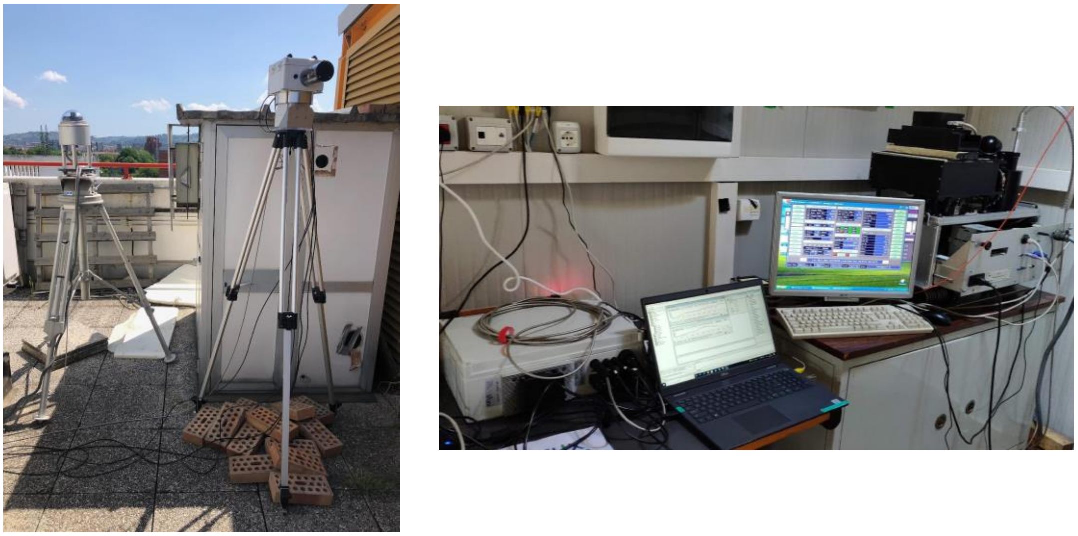

Figure 1: TROPOGAS and SkySpec-2D systems on the roof of ISAC building.

3.1 *TROPOGAS data analysis*

The TROPOGAS measurements are analyzed with the QDOAS software with the set -up reported in Table 1. Then, the obtained NO_2 and O_3 SCDs measured at zenith are converted into VCDs using AMF calculated with the SCIATRAN code.

The analysis is performed using a fixed reference spectrum (measured on the 11th of August 2021 at 29.10° SZA). The SCDs contained in the reference spectrum are inferred using the Langley plot analysis (Fig. 2 for NO_2). In this plot, all the measurements with SZA < 85° are considered (i.e., no O_4 filtering applied). This does not affect the determination of the amount of NO_2 in the reference spectrum. The main effect of O_4 filtering is removing high NO_2 SCDs values, while the Langley plot is based on the lower ones. For the Langley plot analysis, we bin (0.1° width) the data for different AMFs, then, for each bin we find the lowest value, black dots in Fig. 2 (we remove the outliers that fall outside 3*STD). The linear interpolation is then applied to all the points for which the number of elements in the bin is larger than a certain threshold. The value of the intercept is the SCD reference contribution.

In order to filter out the measurements heavily affected by clouds, we use O_4 SCDs in a similar way as reported in [D-3]. This type of filtering is applied to zenith SCDs only.

At the end of the filtering process, 83% of data are marked as not heavily contaminated by clouds (Fig. 3)

To evaluate TROPOGAS MAX-DOAS performances, SCDs obtained at elevation angles different from 90˚ are used for inter-comparison with the ones measured by the SkySpec-2D instrument. We must recall here that a pointing correction of about 1.1° should be applied to TROPOGAS measurement. Considerations about that are made when discussing the inter-comparison results.

	NO_2 Vis	NO_2 -O_3 UV	XS Files
Calibration	455-495 nm (6 points)	337-390 nm (5 points)	
Gases	460-490 nm	337-390 nm	
	NO_2 220K O_3 223 K O_4 Ring NO_2 298 K O_3 293 K Glyoxal NO_3 H_2O	NO_2 220K O_3 223 K O_4 Ring NO_2 298 K (orto) O_3 293 K (orto) BrO HCHO OClO	NO_2 220K Van Daele O_3 223K Bogumil O_4 Herman Ring NDSC 2003 NO_2 220K Van Daele O_3 293K Bogumil Glioxal Volkamer NO_3 298K HITRAN Orphal et al. H_2O HITRAN BrO 228K HITRAN Wilmouth HCHO 280K HITRAN Chance/Orphan OClO 273K HITRAN Kromminga et al.
Other fits	Polynomial order 5, linear offset order 1	Polynomial order 5, linear offset order 1	

Table 1: *QDOAS set-up settings for TROPOGAS data analysis.*

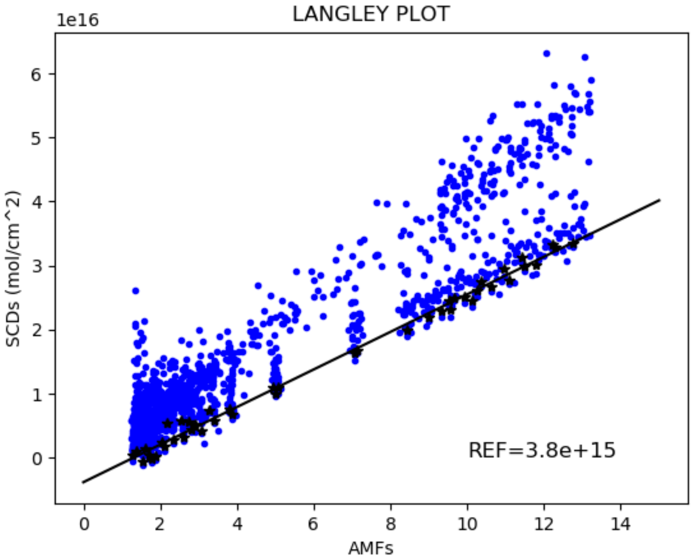

Figure 2: Langley plot for TROPOGAS system during the Bologna campaign.

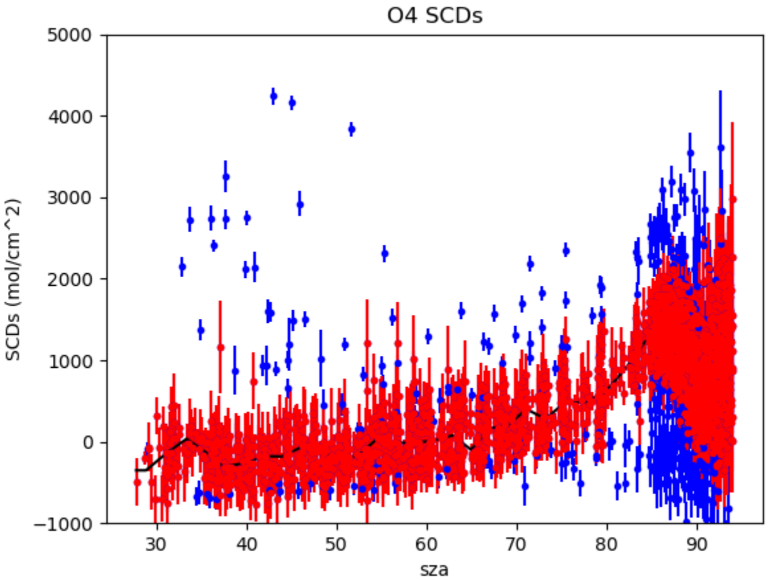

Figure 3: O_4 data filtering for TROPOGAS system during the Bologna campaign.

3.2 SkySpec-2D data analysis

The SkySpec-2D measurements are analyzed with the QDOAS software and the set-up is reported in Tab. 2. This set-up is almost the same used for TROPOGAS apart from the larger spectral interval used in the SkySpec-2D analysis. As for TROPOGAS, the obtained NO_2 and O_3 SCDs measured at zenith are converted into VCDs using AMF calculated with the SCIATRAN code.
For consistency reasons, the fixed reference spectrum used in the analysis is chosen as much as possible in close time coincidence with the one used for the TROPOGAS analysis (measured on 11 August 2021 at 29.38° SZA).

	NO_2 Vis	NO_2 - O_3 UV	XS Files
Calibration	420-500 nm (6 points)	335-400 nm (5 points)	
Gases	430-490 nm	330-390 nm	
	NO_2 220K O_3 223 K O_4 Ring NO_2 298 K O_3 293 K Glyoxal NO_3 H_2O	NO_2 220K O_3 223 K O_4 Ring NO_2 298 K (orto) O_3 293 K (orto) BrO HCHO OClO	NO_2 220K Van Daele O_3 223K Bogumil O_4 Herman Ring NDSC 2003 NO_2 220K Van Daele O_3 293K Bogumil Glioxal Volkamer NO_3 298K HITRAN Orphal et al. H_2O HITRAN BrO 228K HITRAN Wilmouth HCHO 280K HITRAN Chance/Orphan OClO 273K HITRAN Kromminga et al.
Other fits	Polynomial order 5, linear offset order 1	Polynomial order 5, linear offset order 1	

Table 2: *QDOAS settings for SkySpec-2D data analysis.*

The Langley plot (Fig. 4 for NO_2) is used to infer the value of SCD into the reference spectrum. As can be noticed the values differ from the one estimated for TROPOGAS. The zenith SCDs are further processed to remove the heavily cloud-contaminated measurements. Also, in this case the filtering is made using O_4 SCDs as a discriminator. 67% of the zenith sky VCDs are considered not too heavily contaminated by clouds (Fig. 5). Obtained VCDs are compared to the ones obtained by TROPOGAS and satellite instruments in the next section. As anticipated in the previous section, SCDs at different elevation angles obtained from the two instruments are inter-compared.

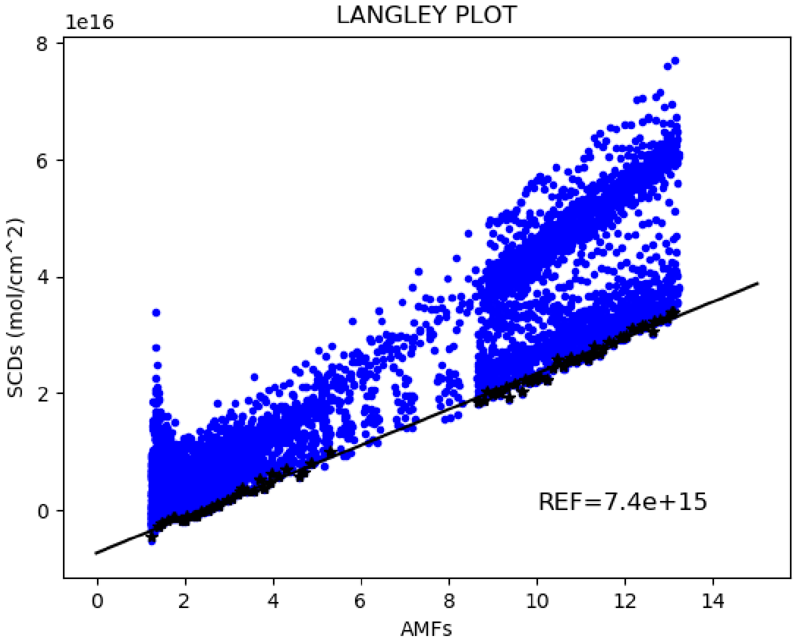

***Figure 4**: Langley plot for SkySpec-2D system during the Bologna campaign.*

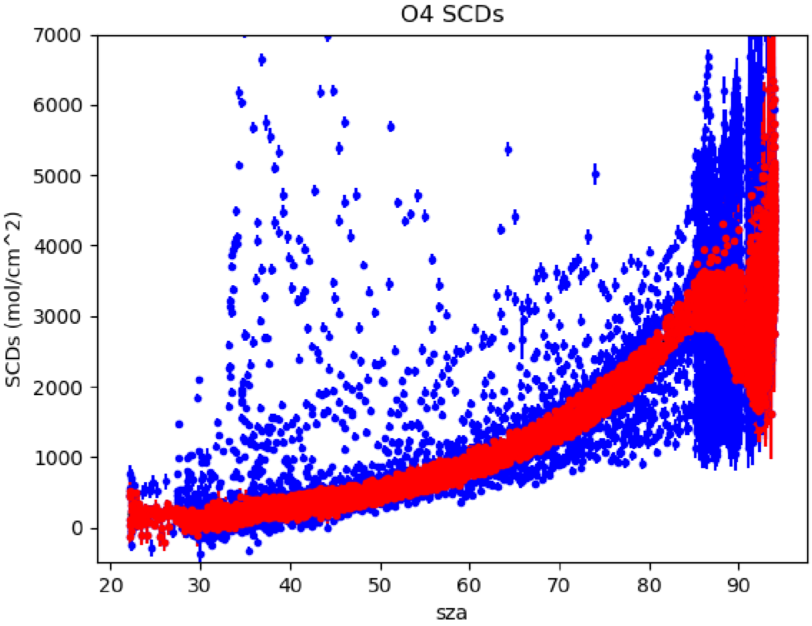

***Figure 5**: O_4 data filtering for SkySpec-2D system during the Bologna campaign.*

3.3 Results

In this section we show the results of the Bologna inter-comparison campaign. For clarity, we focus on NO_2 results only, even if similar considerations can be applied to O_3 results. Here we discuss the results of two types of inter-comparisons:

- Inter-comparison of total VCDs retrieved from the two ground-based instruments (zenith sky measurements only) and from satellites
- Inter-comparison of NO_2 SCDs retrieved from the two ground-based instruments at elevation angles different from 90˚.

Figs. 6a, 6b, and 6c show NO_2 un-filtered VCDs retrieved from 4 to 30 of August 2021 by SkySpec-2D, TROPOGAS, EOS-Aura OMI and S-5P TROPOMI. EOS- Aura OMI and S-5P TROPOMI spatial coincidence criteria are the same used in [D-3]. We observe a general good agreement between the two ground-based instruments considering both the absolute VCDs values and their behavior during the day.

The hourly average calculated using the entire un-filtered dataset is reported in Fig. 7a. Even in this case the agreement is generally very good. The major differences arise from data at the beginning and at the end of the day, corresponding to extremely high SZA. As can be seen from daily plots also, this is due to extremely low TROPOGAS values. Looking at the TROPOGAS spectra used for the analysis at those SZA, we notice that these spectra are extremely low and spectral features are hardly detectable. This results in strong NO_2 underestimation.

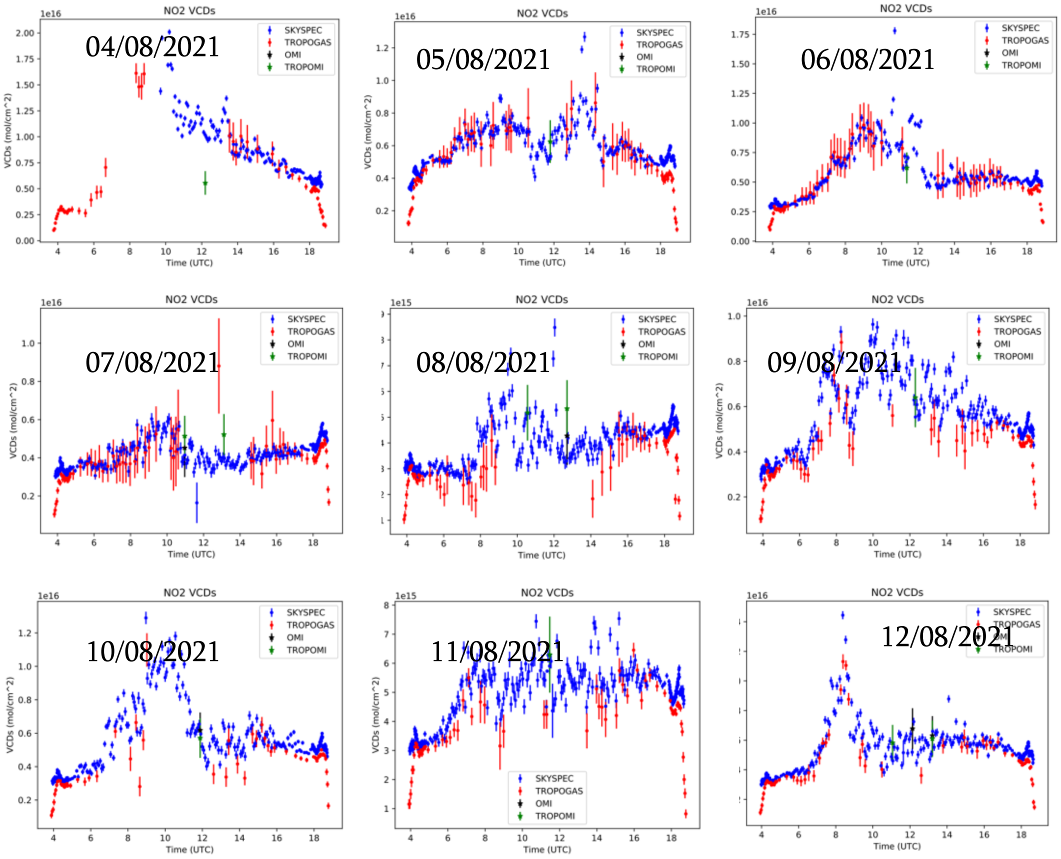

Figure 6a: *SkySpec-2D (blue), TROPOGAS (red), TROPOMI (green) and OMI (black) Total NO_2 VCD from 4th to 12th of August 2021.*

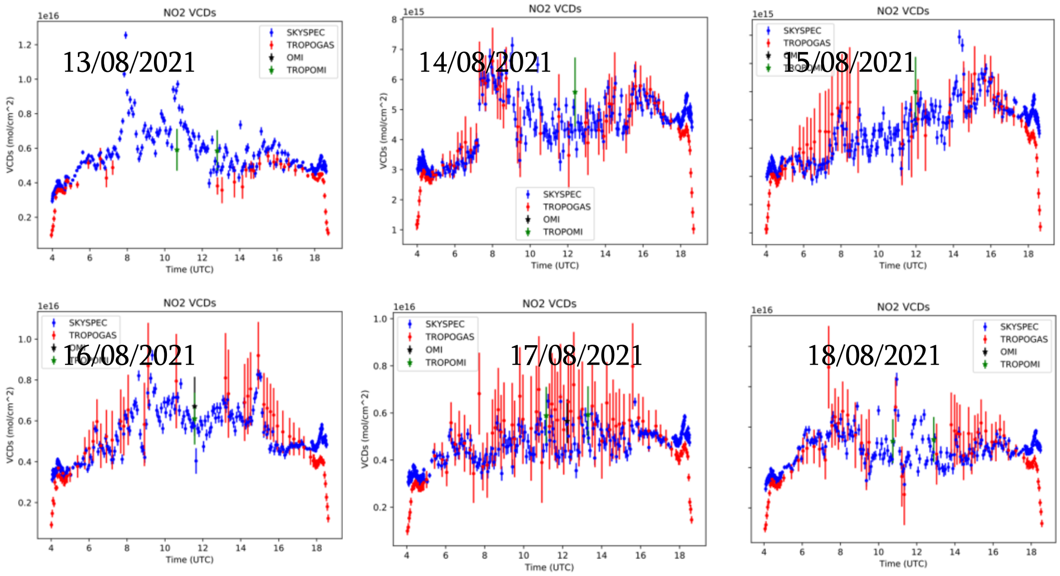

Figure 6b: *SkySpec-2D (blue), TROPOGAS (red), TROPOMI (green) and OMI (black) Total NO_2 VCD from 13th to 18th of August 2021.*

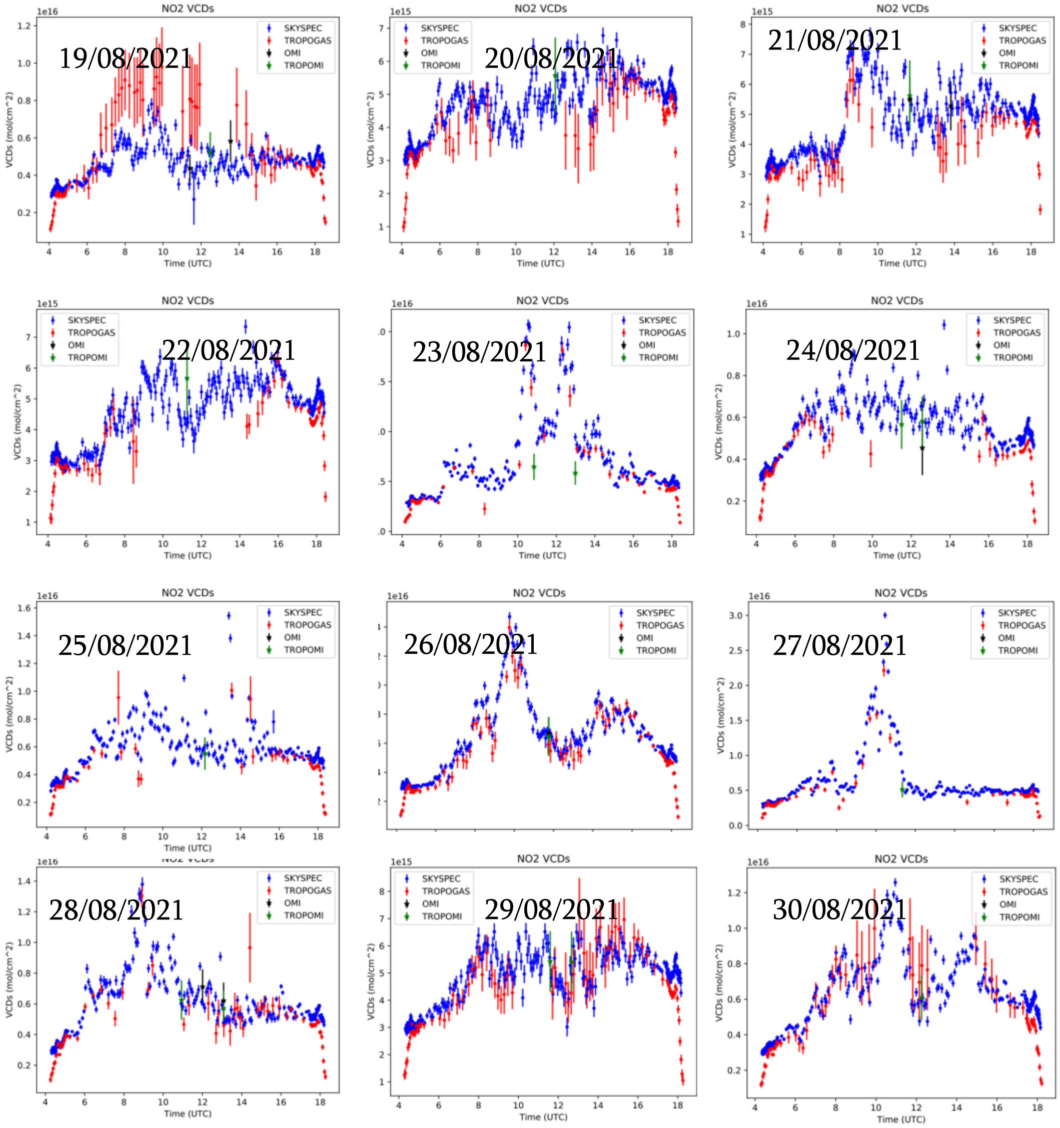

***Figure 6c**: SkySpec-2D (blue), TROPOGAS (red), TROPOMI (green) and OMI (black) Total NO_2 VCD from 19th to 30th of August 2021.*

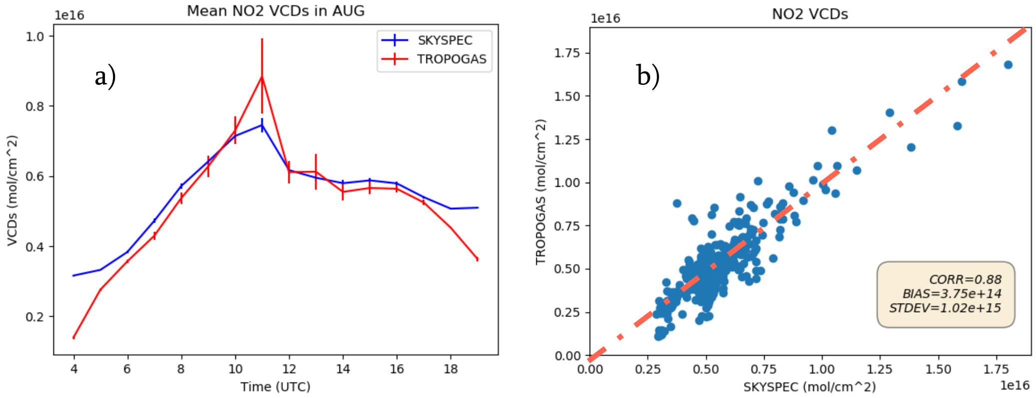

Figure 7:* a)** *Average day from SkySpec-2D and TROPOGAS.* ***b) *Scatterplot of NO_2 VCDs from SkySpec-2D against TROPOGAS.*

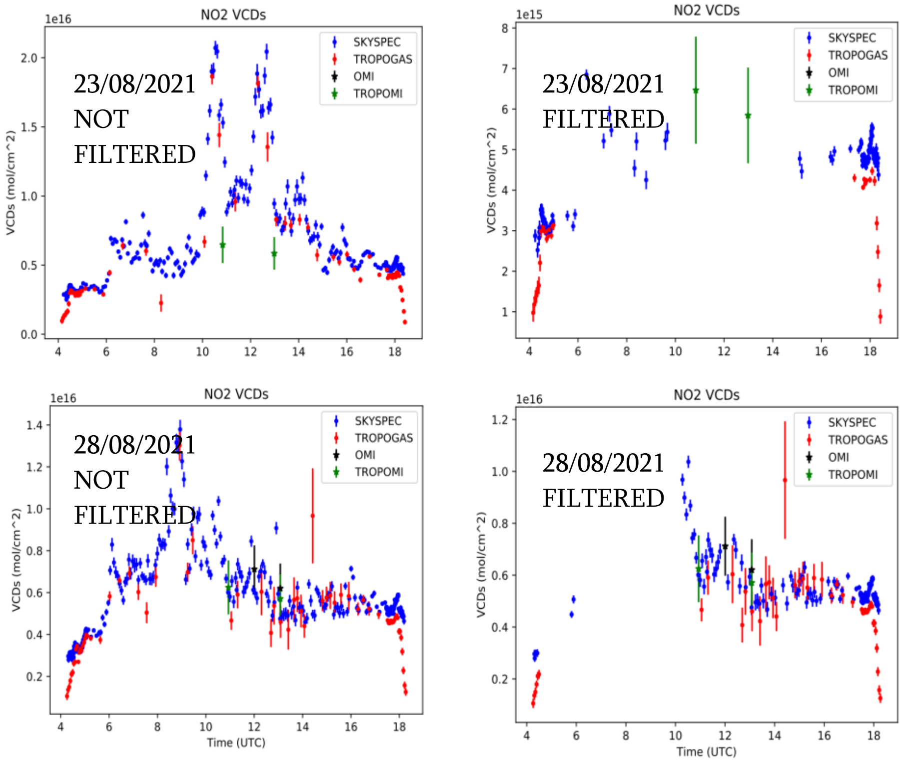

Figure 8*: As in Fig.4 but for 23rd and 28th of August, unfiltered data on the left.*

Fig. 7b reports the scatterplot of VCDs from the two ground-based DOAS instruments. The coincident observations have been computed averaging one hour of data to account for different measuring time and thus for different numbers of data in one hour. In general, the agreement is good with a bias of (3.8 ± 10.2) · 10^{14} (about 7 ± 19 %) and a high correlation (0.88). An example of the effect of the O_4 filtering procedure is given in Fig. 8. Here we report the results in cases of filtered and not filtered data for two days: the 23rd and 28th of August 2021. The filtering procedure removes the higher NO_2 values. In the case of the 23rd of August, the data filtering produces results that seem more in line with TROPOMI evaluations. It is worth noticing that on the 12th of August the O_4 filtering procedure does not remove the peak at around 8 UTC in both instruments. Then we look at the SkySpec-2D camera photos to understand if the filtering procedure was missing something. The photos reveal that on that day the sky was clear, no clouds were present. This means that the NO_2 peak is due to enhanced NO_2 values, not due to particles scattering effects, well observed by both ground-based DOAS systems.

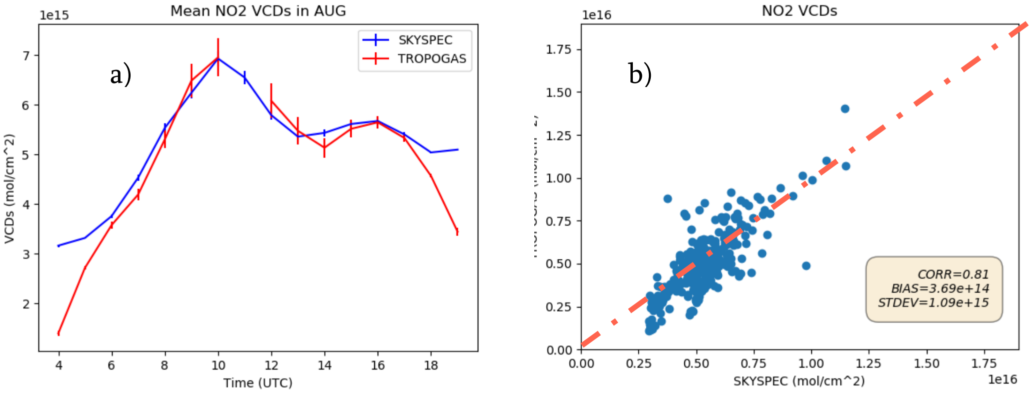

Figure 9*: As for Fig. 7 but considering filtered data only.*

Fig. 9 is analogous to Fig. 7 but for filtered data. As can be seen, the hourly behavior of SkySpec-2D and TROPOGAS has a very good agreement apart from very large SZA as discussed before. Finally, we performed a test removing TROPOGAS data with SZA > 91.5°. The agreement between the two instruments clearly improves and the bias moves from 7 ± 19 % to 4.5 ± 17 % for unfiltered data and from 7 ± 20% to 3.8 ± 18% for VCDs where the O_4 filtering is applied. The effect of retrieving VCDs from TROPOGAS spectra measured at high SZA has a larger impact on bias with respect to the one due to the cloud filtering.

Apart from the total VCDs behavior from the zenith sky measurements, it is interesting to inter-compare MAX-DOAS measurements from the two instruments. The comparison is made on NO_2 SCDs at elevation angles different from zenith, computing the average NO_2 SCDs in 15 minutes time bins. The comparison was performed for both the measurement azimuth directions: one in the north direction, looking at the Po Valley (azimuth 5°, then named as "countryside") and the other in the south direction towards Bologna (azimuth 190°, then named as "city").
The comparison results for elevation angles of 1°, 2°, 3°, 5°, 10°, 30° are summarized in the scatter plots of Fig. 10 and Tab. 3. In general, the agreement between SkySpec-2D and TROPOGAS tends to improve increasing the measurement elevation angle. It is also evident that the bias, defined as SkySpec-2D minus TROPOGAS, is negative in the countryside direction and positive, with worse

agreement, in the city direction. A different behavior occurs at 1° elevation angle because those measurements are partially contaminated by the fact that both instruments FOV crosses the ground. In all cases, the correlation between TROPOGAS and SkySpec-2D SCDs is really high ranging from 0.88 to 0.98.

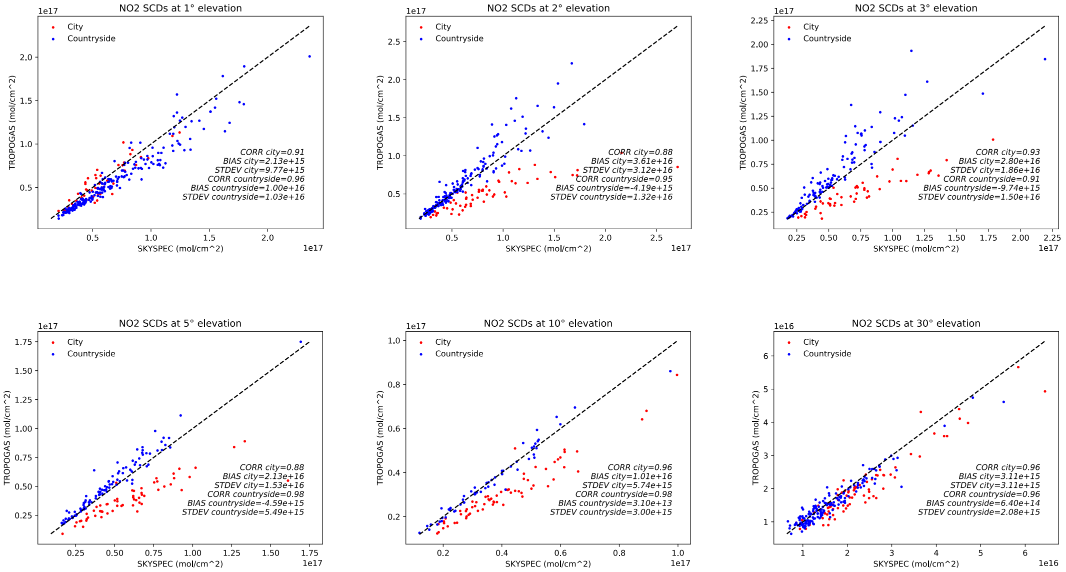

Figure 10: *Comparison between NO2 SCDs measured by SKYSPEC and TROPOGAS in the two different viewing direction.*

	1°		*2°*		*3°*		*5°*		*10°*		*30°*	
	city	*country*	*city*	*country*	*city*	*country*	*city*	*country*	*city*	*country*	*city*	*country*
SCDs results (Figure 10)												
CORR	0.91	0.96	0.88	0.95	0.93	0.91	0.88	0.98	0.96	0.98	0.96	0.96
BIAS	2.10E+15	1.00E+16	3.60E+16	-4.20E+15	2.80E+16	-9.70E+15	2.10E+16	-4.60E+15	1.00E+16	3.10E+13	3.10E+15	6.40E+14
DISPERSION	9.80E+15	1.00E+16	3.10E+16	1.30E+16	1.90E+16	1.50E+16	1.50E+16	5.50E+15	5.70E+15	3.00E+15	3.10E+15	2.10E+15
SCDs results with corrected angles (Figure 11)												
CORR	/	0.98	0.92	0.97	0.91	/	/	/	/	/	/	/
BIAS	/	6.70E+15	3.20E+16	-7.10E+14	2.70E+16	/	/	/	/	/	/	/
DISPERSION	/	9.50E+15	2.80E+16	9.50E+15	2.40E+16	/	/	/	/	/	/	/

Table 3: *Results of the inter-comparison of SkySpec-2D and TROPOGAS NO_2 SCDs without any corrections (upper part of the table) and accounting for the elevation angle mismatch (lower part of the table).*

As reported in Sect. 3.1, the pointing of the TROPOGAS system is affected by a mismatch of about 1°. In particular, we estimated the elevation angle to be 1.1° lower than the indicated one for the countryside direction and 1.1° higher in the city direction, as reported in the appendix B of [D-3] document.

To account for this correction, we performed a further test comparing TROPOGAS NO_2 SCDs at the “corrected” angle with the SkySpec-2D corresponding ones. Results are reported in Fig. 11 and Tab. 3.

In the countryside direction, the SkySpec-2D SCDs at 2° elevation angle are compared with the TROPOGAS SCDs acquired at the “nominal” elevation angle of 3° (corresponding to a “corrected” elevation angle of 2°). On the contrary, in the city direction the SkySpec-2D SCDs at 2° are compared with the TROPOGAS SCDs at the “nominal” elevation angle of 1°.

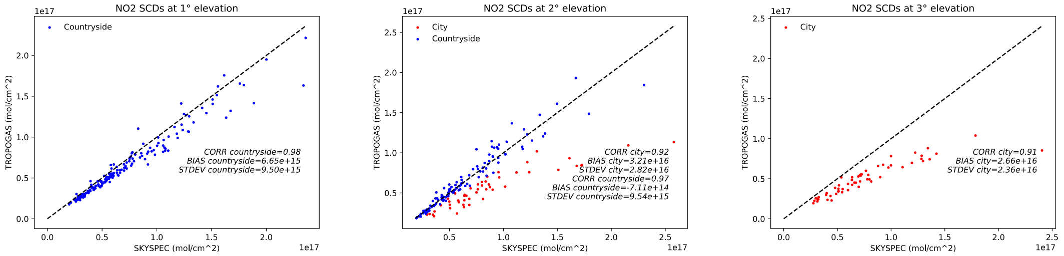

Figure 11: *Comparison between NO_2 SCDs measured by SKYSPEC and TROPOGAS with the correction of the TROPOGAS elevation angle mismatch.*

The plots in Fig. 11 show a good agreement in the countryside direction, especially at the 2° elevation angle. All the statistical parameters relative to SCDs acquired in the countryside direction improve when the TROPOGAS elevation angle mismatch is corrected. This is evidence that the estimated correction is not far from the truth for low elevation angles in the countryside direction. Indeed, in this direction, the bias decreases but partially remains in the SCDs at 1° and is quite completely removed at 2°. One of the reasons why the bias is not completely removed at the elevation angle of 1° is that the TROPOGAS FOV is partially contaminated by the ground signal (TROPOGAS has a 3° FOV).

On the other hand, the bias in the city direction still remains, presenting high values of the order of magnitude of 10^{16} mol/cm^2.

It is important to mention that, for practical reasons, we performed the TROPOGAS elevation calibration measurements only for one specific elevation angle in the countryside direction [D-3], thinking to treat this mismatch as a constant offset along the telescope movement.

However, these comparisons show us that the elevation angle mismatch is not probably a constant offset and depends on the elevation angle and viewing direction. This is the most realistic explanation of the high biases found in the city direction, even though further tests are needed.

Further evidence for our considerations come from simulations. We simulated the NO_2 SCDs with the SCIATRAN RTM for realistic combinations of SZA and SAA positions.

For each combination of solar positions, we simulated the NO_2 SCDs in the countryside and city direction, measured by SkySpec-2D (having a FOV of 0.3°) and TROPOGAS (FOV of 3°). While SKYSPEC-2D simulations are performed only at the measurement elevation angles (1°, 2°, 3°, 5°, 10°, 30°), TROPOGAS SCDs are simulated also for elevation angles perturbed at 1° step from the right ones.

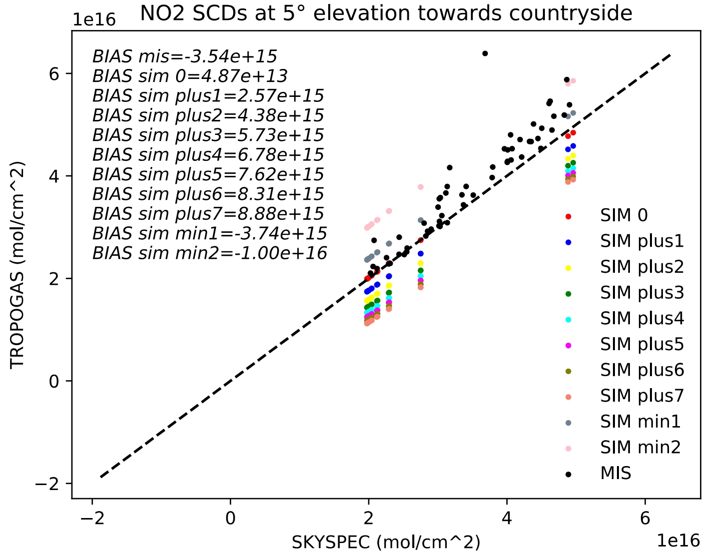

Figure 12: *Measured ("MIS") and simulated ("SIM")* NO_2 *SCDs for SkySpec-2D and TROPOGAS in both viewing directions. All the simulations except "SIM 0" are performed perturbing the TROPOGAS elevation angle. For example, data labelled as "SIM plus2" represent* NO_2 *SCDs simulated at the right 5° elevation angle for SkySpec-2D and at 7° (5 plus 2) elevation angles for TROPOGAS.*

Fig. 12 shows the impact of an elevation angle mismatch in the TROPOGAS instrument at the elevation angle of 5° in the countryside direction.

As we can see, the bias between measurements ("BIAS mis") in the countryside direction is very similar to the bias computed from the simulations in the case of a bias of minus 1° (named "SIM min1"). This is a further suggestion that the SCDs comparison results in the countryside direction and for low elevation angles are in agreement with an overestimation of the TROPOGAS elevation angle of about 1°. On the city side, the results are less clear. There is a hint to angular correction higher than 1° and further tests to understand the behavior on this side will be performed in the future. In conclusion, The MAX-DOAS spectra acquired by TROPOGAS on the countryside, with the pointing corrected by -1° and acquired at low elevation angles are consistent with the one measured by the SkySpec-2D. The spectra acquired at higher elevation angles and on the cityside require a thought analysis and further tests to be corrected for mis-pointing. This point will be addressed in the future. As said, the correlation between NO_2 SCDs from TROPOGAS (in both azimuth directions) and the corresponding SkySpec-2D ones is always high suggesting that the differences are mainly due only to pointing differences.

However, in any case, the zenith sky measurements (due to their nature) are totally unaffected by this problem as also shown by the quality of the comparison of NO_2 VCDs between the two MAX-DOAS instruments and with satellite data.

4 BAQUNIN inter-comparison campaign

In this section we describe the results of the inter-comparison of the MAX-DOAS SkySpec-2D NO_2 and O_3 VCDs with the Pandora #117 VCDs during the measurement campaign performed from 7th to 21st September 2021. In this frame, the SkySpec-2D instrument was temporarily installed on the roof of the Fermi building at La Sapienza University (part of the BAQUNIN super site, https://www.baqunin.eu/). To evaluate the quality of the products of the two ground-based instruments, we compared the SkySpec-2D and Pandora #117 NO_2 and O_3 VCDs with respect to similar products retrieved from the S-5P TROPOMI and the EOS-Aura OMI observations. Furthermore, during the same period, a second MAX-DOAS SkySpec-2D (acquired under the same Italian funded program) was installed in Rome Tor Vergata (about 13 km from the Rome La Sapienza site) and a preliminary inter-comparison was performed.

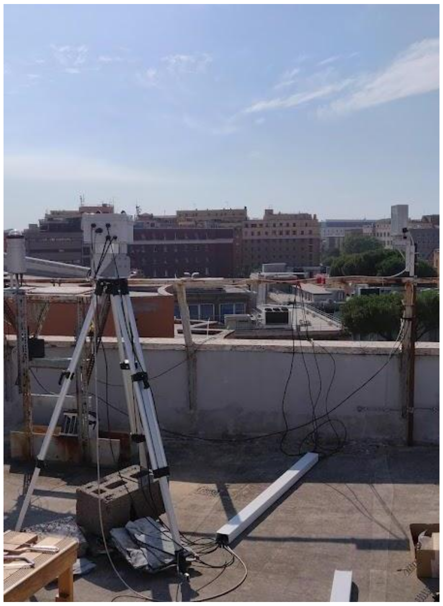

Figure 13: *The SkySpec-2D system located at the physics department of the La Sapienza University in Rome (part of the BAQUNIN super-site).*

4.1 SkySpec-2D measurements and data analysis

The SkySpec-2D was installed at BAQUNIN in the afternoon of 6 September 2021. We decided to look at three different azimuth angles: 90°, 180° and 270° in order to cover as much as possible the area around La Sapienza.

The SkySpec-2D measurements are analyzed with the QDOAS software and the set -up reported in Table 2. The obtained NO_2 and O_3 SCDs measured at zenith are converted into VCDs using the AMFs calculated with the SCIATRAN code. The fixed reference spectrum used in the analysis is chosen on clear-sky days according to the pictures recorded by the SkySpec-2D cameras (spectrum measured on 12 September 2021 at 37.89˚ SZA). The Langley plot, reported in Fig. 14 for NO_2, is used to infer the value of SCD into the reference spectrum. The zenith SCDs are further processed to remove the heavily cloud-contaminated measurements. As made in the previous cases, the filtering based on using O_4 SCDs as a discriminator has been applied. The filtering excluded 37% of the observations (Fig. 15).

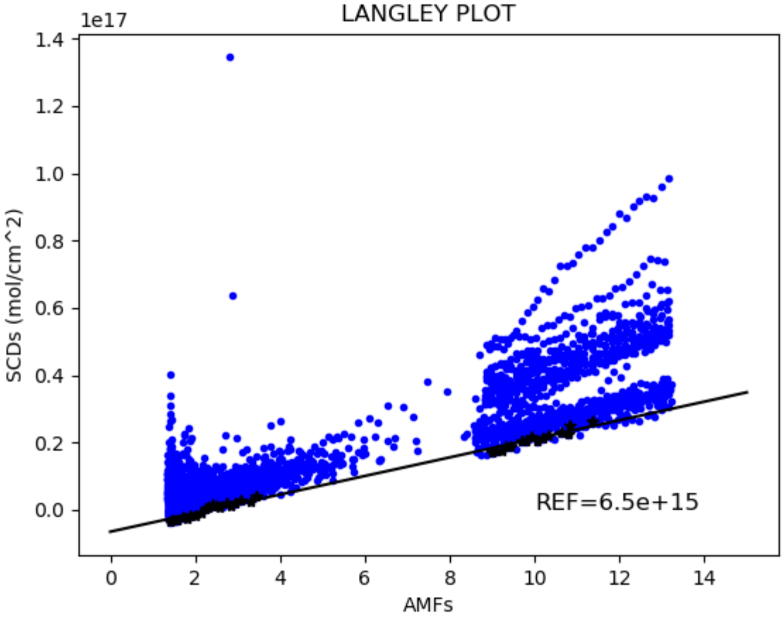

***Figure 14**: Langley plot for SkySpec-2D system during the BAQUNIN campaign.*

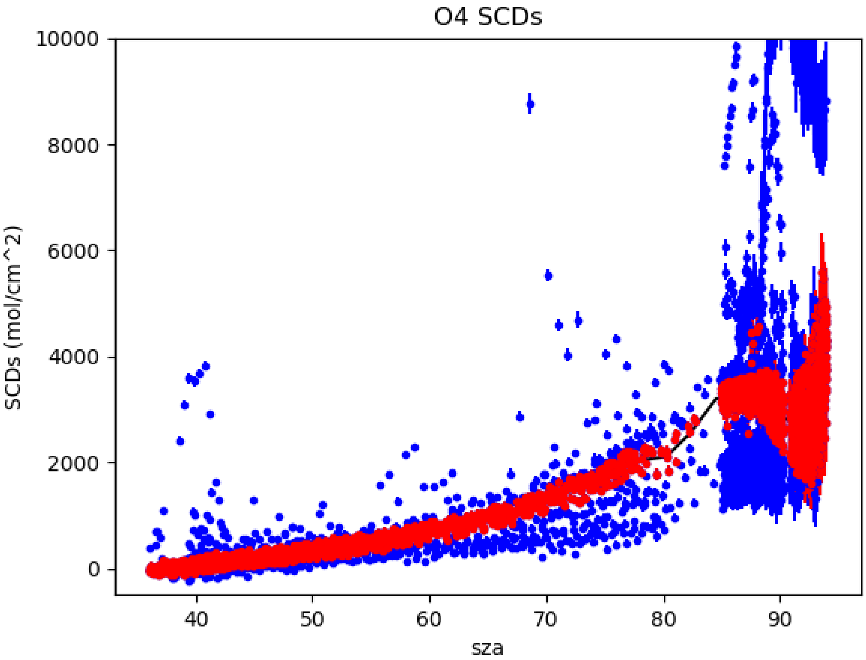

Figure 15*: O_4 data filtering for SkySpec-2D system during the BAQUNIN campaign.*

4.2 Data description

4.2.1 Satellite products

TROPOMI is a passive-sensing hyperspectral nadir-viewing imager aboard the S-5P satellite. It was launched in October 2017. S-5P is a near-polar Sun-synchronous orbit satellite flying at an altitude of 817 km, with an overpass local time at ascending node of 13:30 and a repeat cycle of 17 days. TROPOMI has a swath width of approx. 2600 km, and a spatial resolution of 3.5 x 7 (5.5) km at the beginning of the mission (since 6 August 2019). TROPOMI has four separate spectrometers that measure from UV to SWIR, in order to retrieve the concentrations of several atmospheric constituents including O_3, NO_2, SO_2, CO, CH_4, CH_2O and aerosol properties, as well as surface UV radiation. The instrument and the data product have been described in detail by [R-12], [R-13], and [R-17].

OMI is a UV–Vis nadir-viewing spectrometer developed by the Netherland's Agency for Aerospace Programs and the Finnish Meteorological Institute. It is on-board NASA's EOS-Aura satellite platform. EOS-Aura has a Sun-synchronous polar orbit with an ascending node overpass local time of 13:30. The nominal footprint of the OMI ground pixels is 24 x 13 km (across x along track) at nadir to 165 x 13 km at the edges of the 2600 km swath. For more details on the instrument, see [R-14] and [R-15].

For S-5P TROPOMI, we used the OFFL v2.2.0 NO_2 and O_3 products. For EOS-Aura OMI, we used the V4.0 Aura OMI NO_2 Standard Product, also called OMNO2, and the version 3 of the O_3 OMDOAO3 products. During this exercise, for both satellites, we used the NO_2 summed total column, which is the sum of the tropospheric and stratospheric VCDs. It was chosen over the total column product since the latter’s sensitivity to the ratio between the stratospheric and tropospheric a priori columns may lead to substantial systematic retrieval errors. The intermediate step of using data assimilation to first estimate the stratospheric column does remove part of this error. The summed total column product is described by the data provider as the best physical estimate of the NO_2 vertical column and recommended for comparison to ground-based total column observations [R-18]. For O_3 VCDs, we used the total vertical column. For both satellites, we used only products with a combined quality assurance value (qa_value) higher than 0.75. The satellite products were averaged over a circle centered on the La Sapienza site. For this exercise, we tried 3 different radiuses (5, 10, and 20 km). For EOS-Aura OMI, due to the lower spatial resolution of the instrument, we adopted only 10 and 20 km radiuses.

4.2.2 PGN products

For this exercise, we used the NO_2 and O_3 total columns measured by the ground-based Pandora instrument #117 located at the physics department of the La Sapienza University in Rome (Lat: 41.901695, Lon: 12.515773, Altitude: 75 m). Pandora instrument performs direct-sun measurements in the UV–VIS spectral range (280–525 nm) and provides NO_2 and O_3 total VCDs, among other products. The full description of the Pandora instrument and the algorithm for the inversion methodology has been presented by Herman et al. [R-11]. Pandora #117 is part of the PGN that provides homogeneous calibration, central data processing and formatting, and quick delivery of final data products. The PGN data have been used to routinely validate EOS-Aura OMI and S-5P TROPOMI products. The Pandora #117 date were directly downloaded from the PGN website (https://www.pandonia-global-network.org/). We used the most updated version of the data for both NO_2 (rnvs1p1-7) and O_3 (rout0p1-7). We considered only Pandora retrievals with a data quality flag value of 0 and 10, corresponding to the so-called assured high-quality data [R-9]. The Pandora #117 VCDs were averaged in a time interval centered on the satellite (S-5P or EOS-Aura) overpass time. We used 3 different time intervals (±15, ±30, and ±60 minutes).

4.2.3 MAX-DOAS SkySpec-2D

More details about the new SkySpec-2D MAX-DOAS system are reported in Sect. 3. For this phase, we used only the zenith sky observations. The cloud filtering based on measured O_4 SCDs (see

[D-3] for more details about the filtering procedure) was applied. For this exercise, we adopted the NO_2 XS at 254.4K (more details are in Sect. 5.3.1). A few tests were performed in order to evaluate the consistency of our results and the uncertainty introduced not reliable XSs. As for Pandora products, the DOAS VCDs were averaged considering a time interval centered on the satellite (S-5P or EOS-Aura) overpass time. We consider 3 different time intervals (±15, ±30, and ±60 minutes).

4.3 NO_2 inter-comparison results

We started our analysis evaluating the agreement between the ground-based instruments and the satellite datasets, exploiting the S-5P or EOS-Aura overpasses occurred during the measurement campaign. In Figs. 16, 17, 18 (S-5P TROPOMI) and Fig. 19 (EOS-Aura OMI), we reported the distributions of the ground-based observations and the differences (absolute and relative) between these and the satellite observations. The results are also summarized in Tab. 4.

Generally, we observed that both Pandora #117 and SkySpec-2D NO_2 VCDs overestimated the satellite NO_2 VCDs. Pandora #117 overestimates TROPOMI VCDs of about 30/40 % and EOS-Aura OMI of about 30/50 %. At the same time, even SkySpec-2D VCDs overestimate TROPOMI data of about 15/25 % and EOS-Aura OMI of 10/35 %. Since the agreement get worse increasing the radius of the area considered, we obtain the best agreement considering the most strictly time and space co-location criteria. Considering Δt_max = ± 15 minutes and Δd_max = 5 km, we observed a bias of -16 % for SkySpec-2D and -29 % for Pandora#117 with respect to S-5P TROPOMI and of -11 % for SkySpec-2D and -27 % for Pandora#117 with respect to EOS-Aura OMI.

	Δt_max (min)	Δd_max (km)	SAT-DOAS	(SAT-DOAS)/DOAS	SAT-PGN	(SAT-PGN)/PGN
			(*e16, molecules/cm2)	(%)	(*e16, molecules/cm2)	(%)
Sentinel-5P TROPOMI	±15	5	-0.206	-15.8	-0.336	-28.9
		10	-0.227	-18.1	-0.357	-30.9
		20	-0.273	-24.2	-0.407	-37
	±30	5	-0.199	-16.1	-0.356	-29.9
		10	-0.215	-17.9	-0.379	-31.7
		20	-0.265	-24.2	-0.429	-37.6
	±60	5	-0.265	-18.6	-0.429	-32
		10	-0.25	-21	-0.417	-34
		20	-0.295	-26.7	-0.461	-39.4
EOS-Aura OMI	±15	10	-0.078	-11.5	-0.221	-27
		20	-0.497	-37.8	-0.673	-48.5
	±30	10	-0.105	-16.5	-0.266	-32.7
		20	-0.397	-32.5	-0.625	-46.3
	±60	10	-0.114	-17.6	-0.269	-32.9
		20	-0.425	-36	-0.659	-48.4

Table 4: *Results of the inter-comparison exercise of SkySpec-2D and Pandora #117 NO_2 VCDs with respect to S-5P TROPOMI and EOS-Aura OMI similar NO_2 products. The results are reported as a function of the different co-location criteria adopted.*

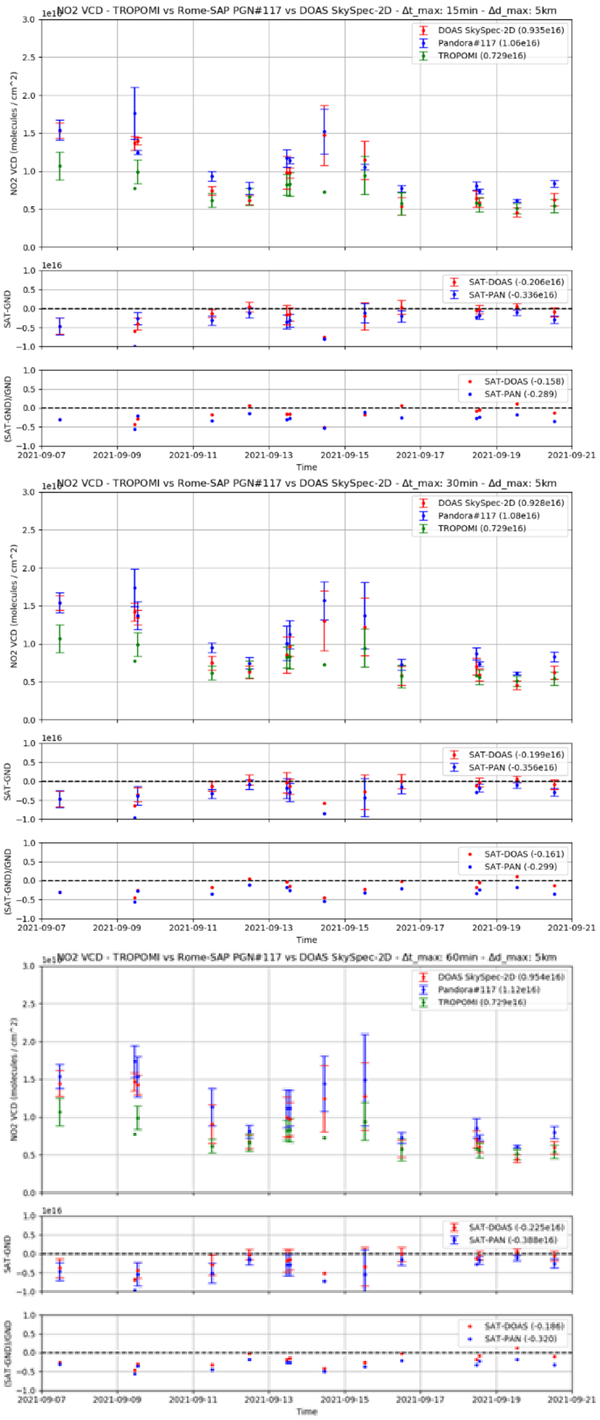

Figure 16: *Analysis of SkySpec-2D (red dots) and Pandora#117 (blue dots) NO_2 VCDs with respect to the S-5P TROPOMI NO_2 products (green dots). The co-location criteria are reported in the upper right part of each plot. In this case Δd_max= 5 km and Δt_max = ±15 (upper plot), ±30 (mid plot), ±60 (lower plot) minutes. For each plot, the absolute (mid panel) and the percentage relative (lower panel) differences between the ground-based instrument and satellite are reported.*

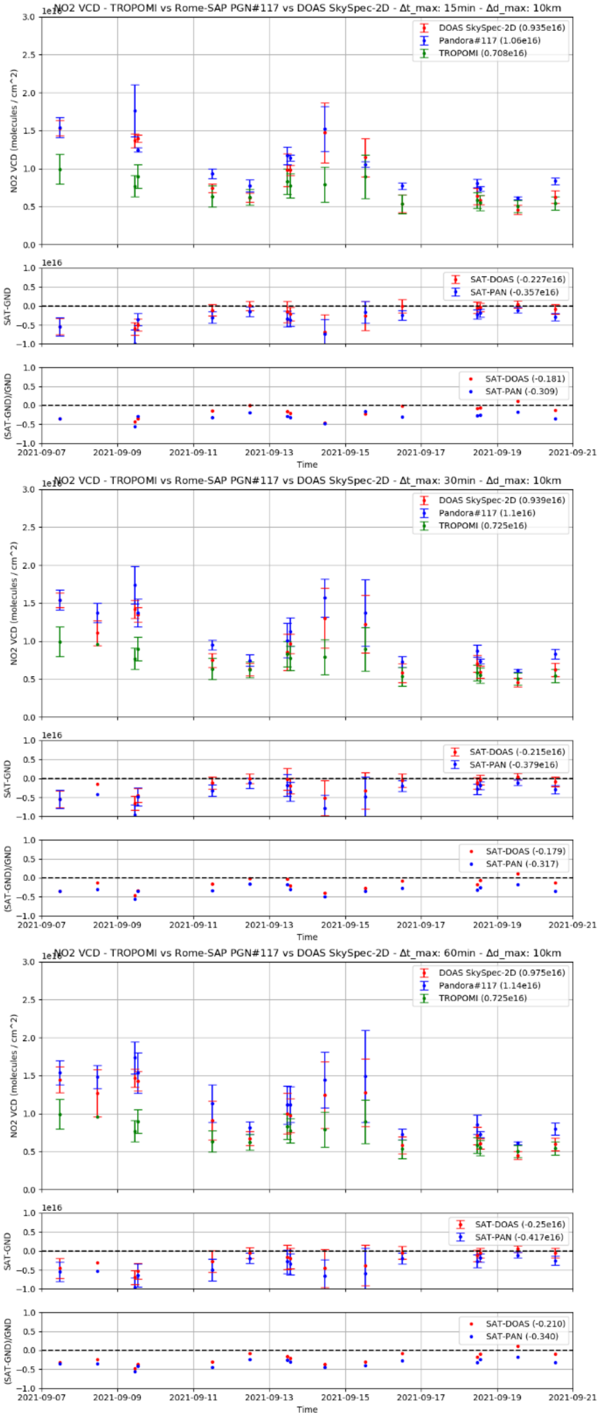

Figure 17: *As in Fig. 16 but for Δd_max= 10 km*

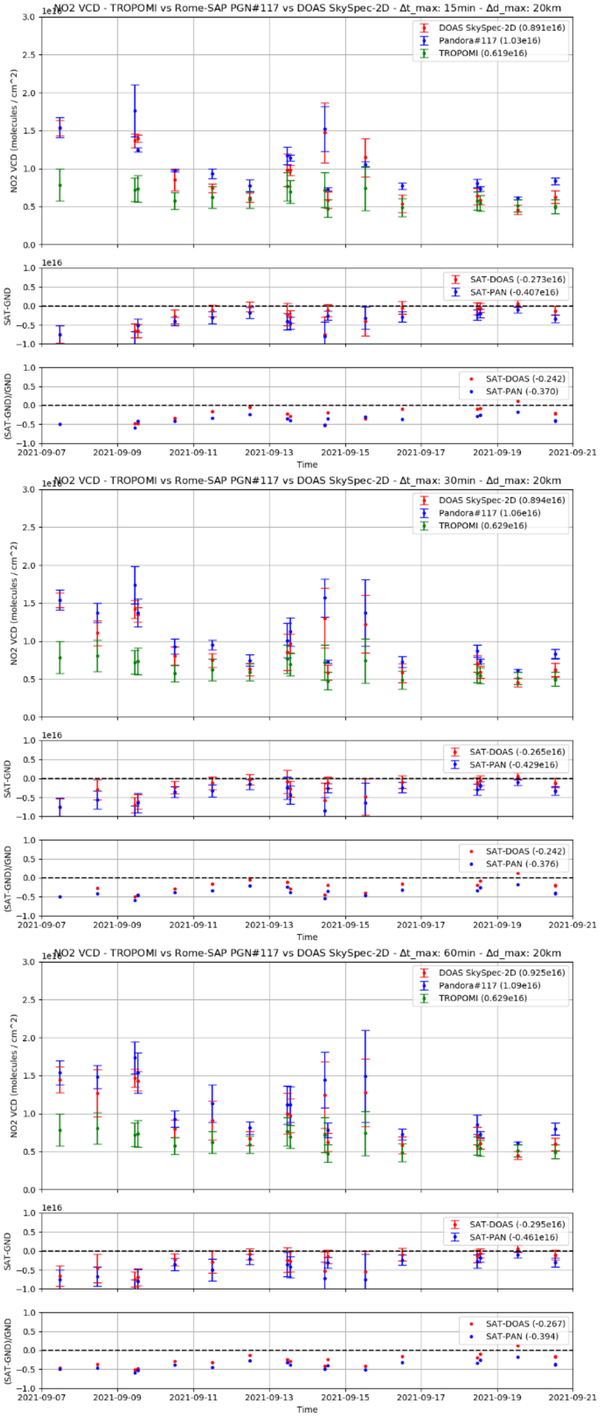

Figure 18: *As in Fig. 16 but for Δd_max= 20 km*

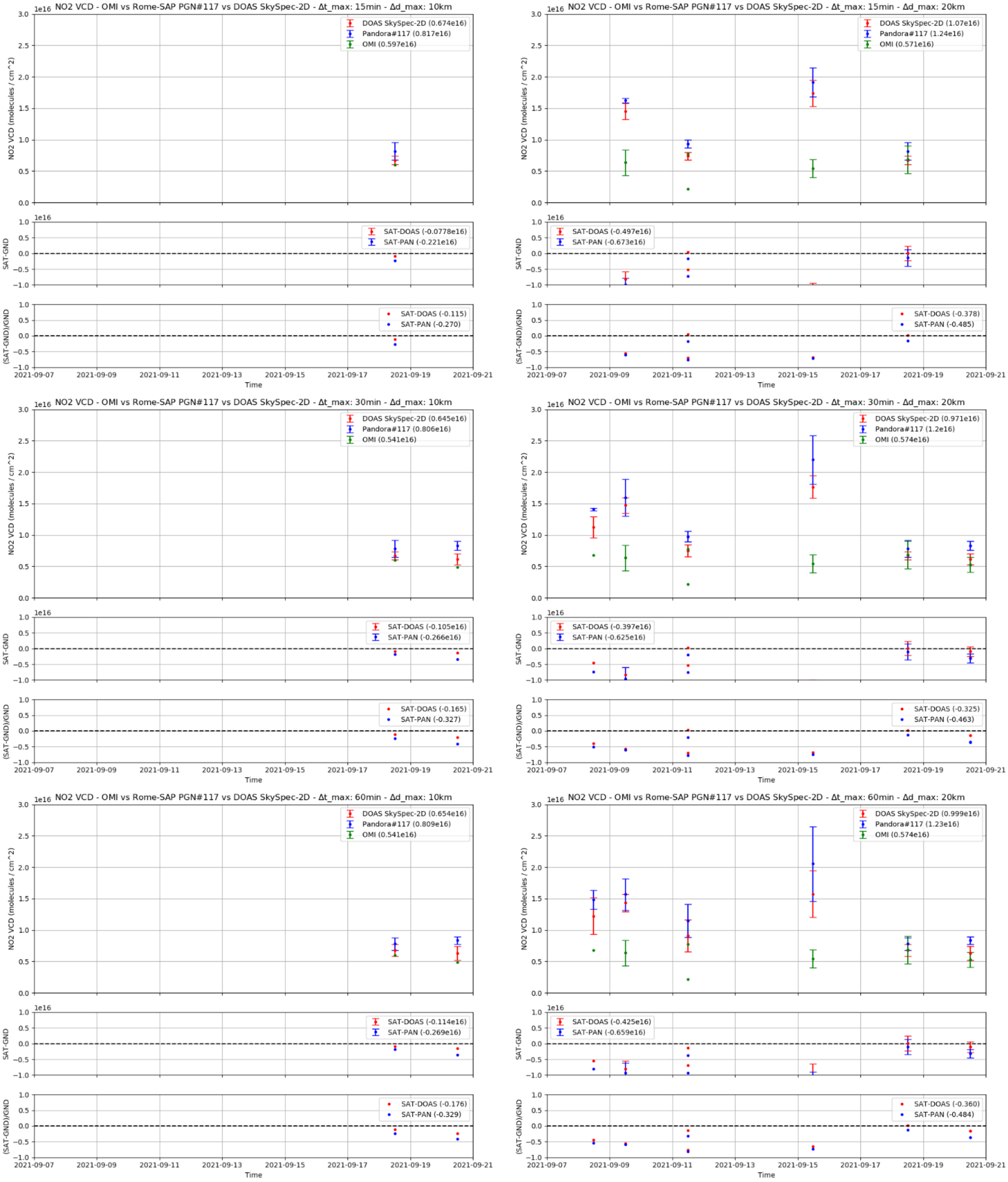

Figure 19: *Analysis of SkySpec-2D (red dots) and Pandora#117 (blue dots) NO_2 VCDs with respect to the EOS-Aura OMI NO_2 products (green dots). The co-location criteria, also are reported in the upper right part of each plot, are Δd_max= 10 km (left column), 20 km (right column) and Δt_max = ±15 (upper row), ±30 (mid row), ±60 (lower row) minutes. For each plot, the absolute (mid panel) and the percentage relative (lower panel) differences between the ground-based instrument and satellite are reported.*

The differences between the two ground-based datasets were evaluated even considering the entire period of the measurement campaign (not only in correspondence of the satellite overpasses). The two datasets were averaged on 10 minutes interval. The plot in Fig. 20 shows the distribution of NO_2 VCDs retrieved by the 2 instruments and the differences between the two products. In Fig. 21, we also reported the scatterplot of the coincident observations. We observed an extremely high correlation between the 2 datasets (0.916). SkySpec-2D correctly reproduce all the features of the NO_2 distributions observed by the Pandora #117. The bias between the 2 ground-based datasets is about $-0.232 \cdot 10^{16}$ molecules/cm^2 (-22 %).

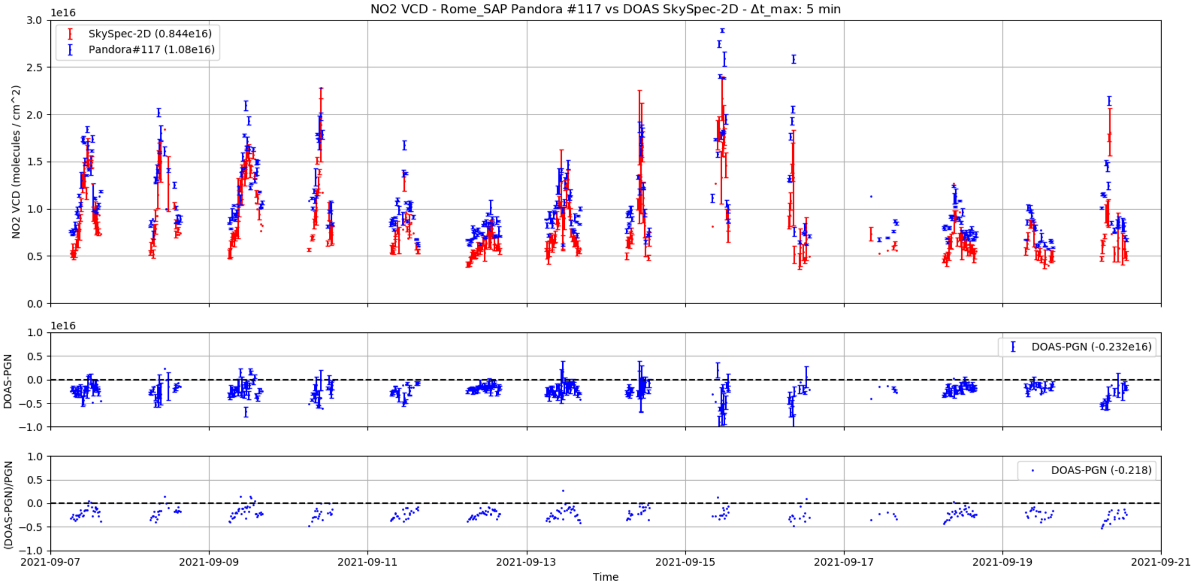

Figure 20: *Inter-comparison of SkySpec-2D (red dots) and Pandora #117 (blue dots) NO_2 VCDs. Each dot represents the mean of SkySpec-2D and Pandora #117 NO_2 VCDs over an interval of 10 minutes. The absolute (mid panel) and the percentage relative (lower panel) differences are reported.*

We analyzed the differences between SkySpec-2D and Pandora NO_2 VCDS as a function of the hour of the day, the solar zenith angle and solar azimuthal angle (Fig. 22 panel a, b, and c). Please keep in mind that, since we are using only the SkySpec-2D zenith-sky observation, the only instrument that changes its observation geometry (directly pointing the Sun) is the Pandora. We did not observe any evident dependency by these three quantities.

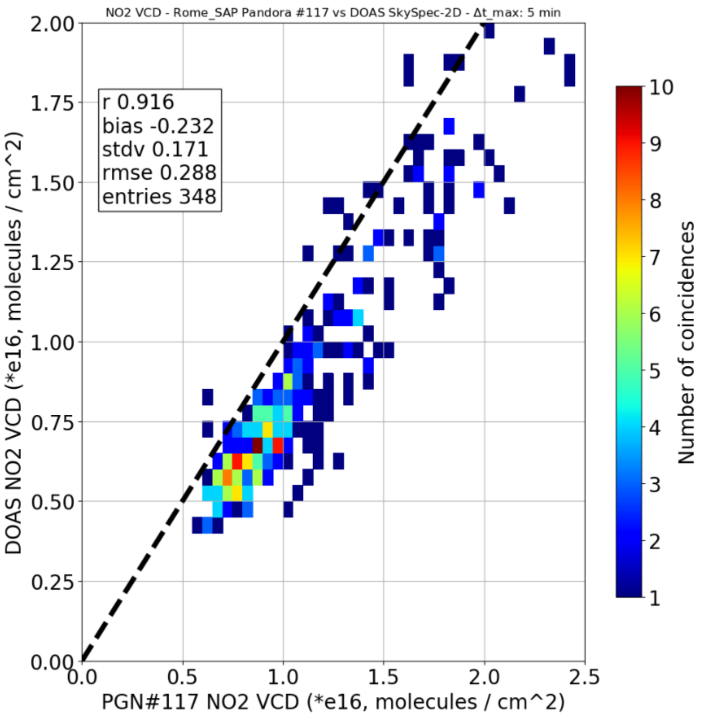

***Figure 21:** Scatterplot of the time coincident (10 minutes mean, same data used in Fig. 20) SkySpec-2D and Pandora #117 NO_2 VCDs.*

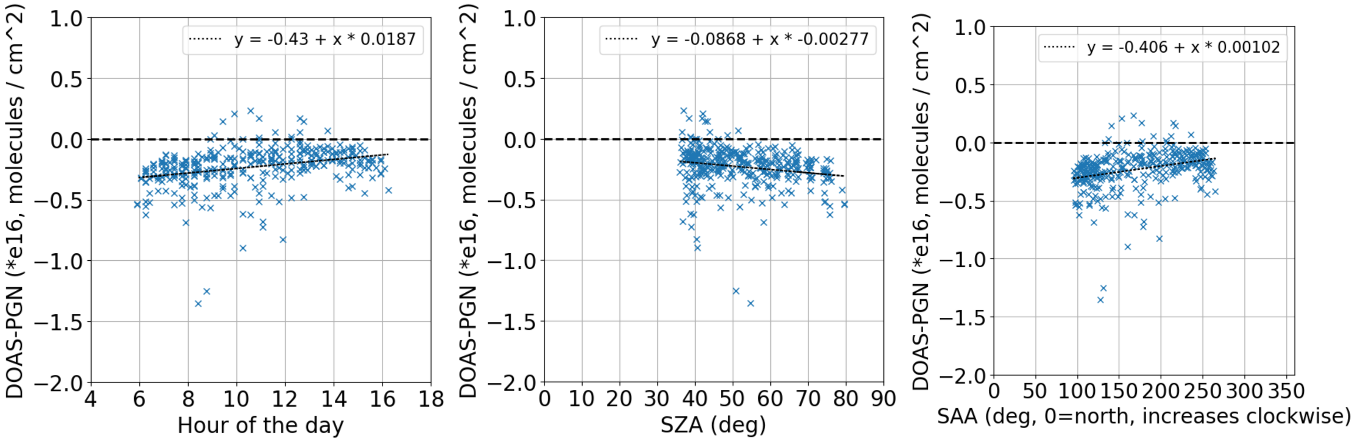

***Figure 22:** Analysis of SkySpec-2D and Pandora #117 NO_2 VCDs absolute differences as a function of the hour of the day (left plot), the SZA (mid plot), and the SAA (right plot).*

4.3.1 NO_2 cross sections at different temperatures

As reported in Section 6.5.1 of the S-5P Routine Operations Consolidated Validation Report [R-16], *“a potential source of inconsistences between the different data products lies in the NO_2 absorption cross sections that are used in the DOAS retrieval of the SCD. An overview of the different NO_2 cross sections choices made for each instrument is provided … by Verhoelst et al. (2021). For a detailed discussion we refer to this work. The main conclusions are:*

- *A small (few percent) seasonal cycle in the stratospheric column comparisons can be expected, due to the seasonal variation in stratospheric temperature not being accounted for in the ZSLDOAS data processing.*
- *PGN columns may either overestimate by up to 10% when the column is mostly stratospheric or underestimate by a similar order of magnitude when large tropospheric amounts are present, due to the use of a fixed effective temperature of 254.4 K.*
- *The MAX-DOAS data may be biased in either direction by a few percent when tropospheric and/or stratospheric temperatures differ strongly from the 298 K and 220 K default temperatures. “*

In order to evaluate the consistency of our results and the uncertainty introduced by non-representative XSs, we computed the SkySpec-2D VCDs considering the NO_2 XSs at 220 K, 254.4 K, and 298 K, and we compared the different products with respect to the Pandora #117 VCDs (Fig. 23).

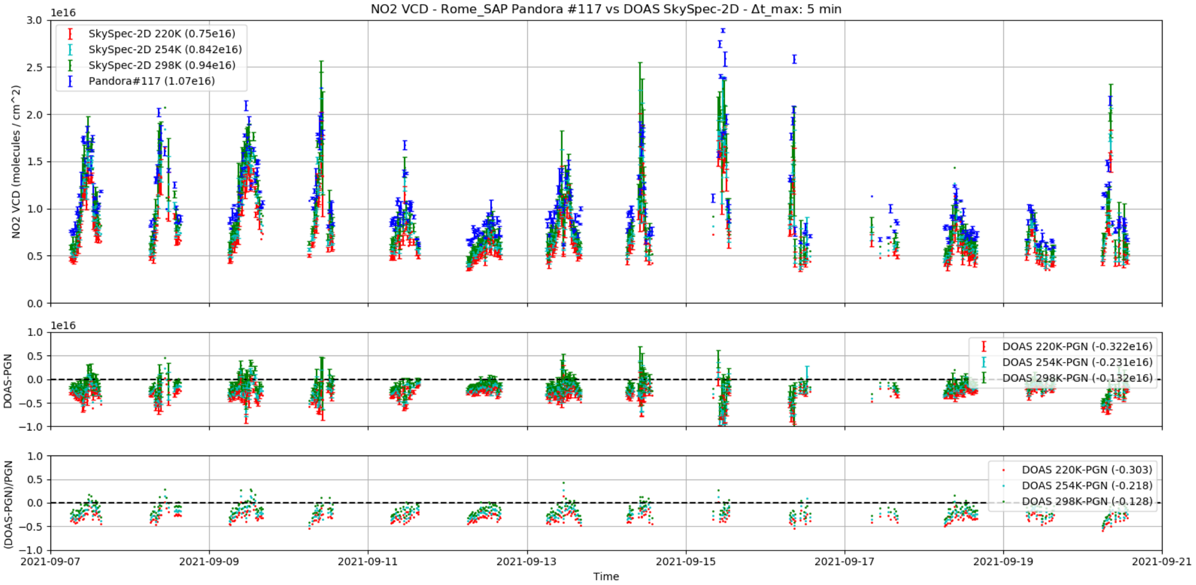

Figure 23: *Analysis of SkySpec-2D VCDs computed considering the NO_2 XSs at 220 K (red dots), 254.4 K (cyan dots), and 298 K (green dots), and Pandora #117 (blue dots) NO_2 VCDs. The absolute (mid panel) and the percentage relative (lower panel) differences between the different SkySpec-2D VCDs and Pandora #117 VCDs are reported.*

We observed a better agreement with respect to Pandora #117 using the NO_2 XS at 298K. This result can be explained considering that most of the NO_2 signal comes from the boundary layer. On the other hand, we preferred to use the NO_2 XS at 254.4K in order to consider both contributions from troposphere and stratosphere and to be consistent with the XS used for the Pandora processing. Generally, we observed that different NO_2 XSs work as an offset, and they do not introduce any evident dependency from the SZA. Through this exercise, we also observed, as reported in Section 6.5.1 of the [R-16] about PGN, the uncertainty introduced using a non-representative NO_2 XS is at least 10%.

4.3.2 Rome La Sapienza versus Rome Tor Vergata inter-comparison

During the period in which the SkySpec-2D was located in the Rome La Sapienza site (SAP hereafter), another equivalent ISAC MAX-DOAS system was installed at ISAC-CNR in Rome Tor Vergata (TVG hereafter) site. This activity represented an almost unique opportunity of having two equivalent MAX-DOAS systems so close. This activity was not initially planned in the frame of these IDEAS-QA4EO WPs, and it was possible thanks to the contributions of ISAC-CNR colleagues Francesco Cairo (PI of the TVG MAX-DOAS instrument) and Luca Di Liberto. The two instruments worked with the same observations strategies and the measurements were processed with the same procedure. Here we analyzed the NO_2 VCDs observed by the two instruments.

In Figs. 24, 25, 26, we observe the NO_2 VCDs of the two MAX-DOAS systems and the S-5P TROPOMI VCDs. Note that the distance between the two sites is about 13 km. The satellite products were averaged using the same approach used in the previous sections. Considering the distance between the two sites (about 13 km), the averages over a circle with radius higher than 5 km are observing a portion of the same area. For this reason, considering the coincidences with a radius of 20 km, we noted that TROPOMI VCDs are almost equal for the two sites. For the other spatial criteria (5 and 10 km), SAP NO_2 VCDs are higher than TVG ones by 20/30 % [R-5]. We also observed a better agreement (SkySpec-2D vs TROPOMI) at the TVG site.

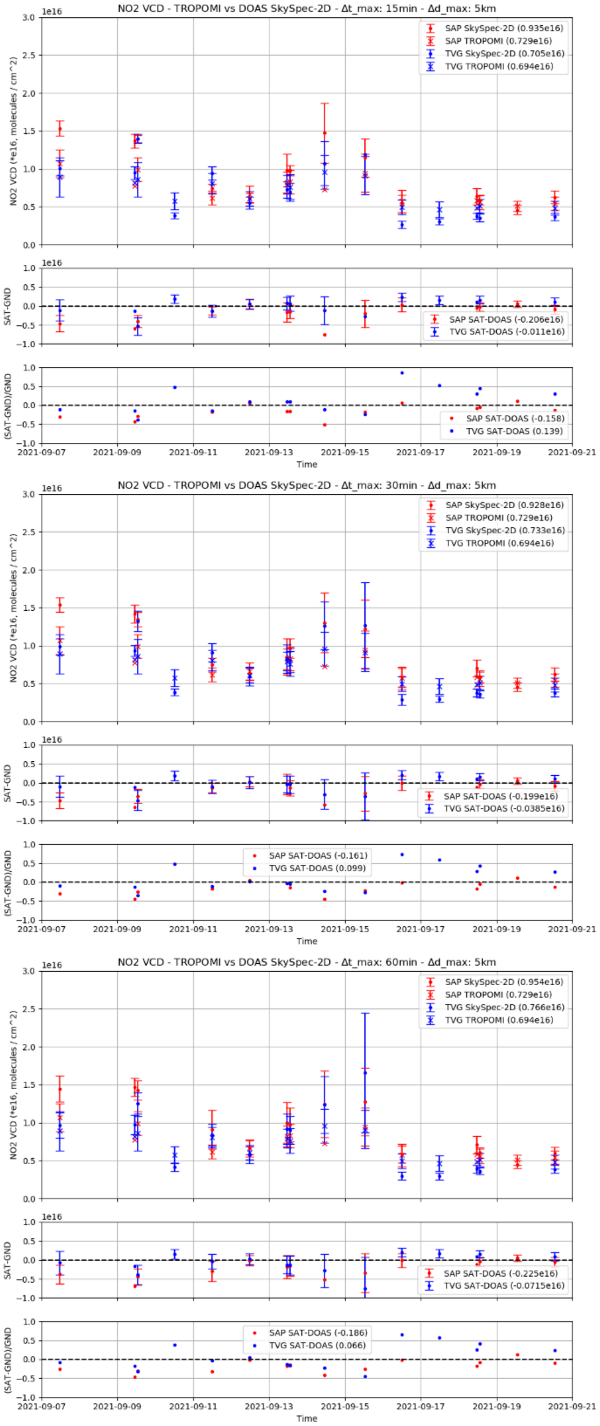

***Figure 24**: Analysis of Rome-La Sapienza (red symbols) and Rome-Tor Vergata (blue symbols) SkySpec-2D (dots) NO_2 VCDs with respect to the S-5P TROPOMI NO_2 products (crosses). The co-location criteria are reported in the upper right part of each plot. In this case Δd_max= 5 km and Δt_max = ±15 (upper plot), ±30 (mid plot), ±60 (lower plot) minutes. For each plot, the absolute (mid panel) and the percentage relative (lower panel) differences between the ground-based instrument and satellite are reported.*

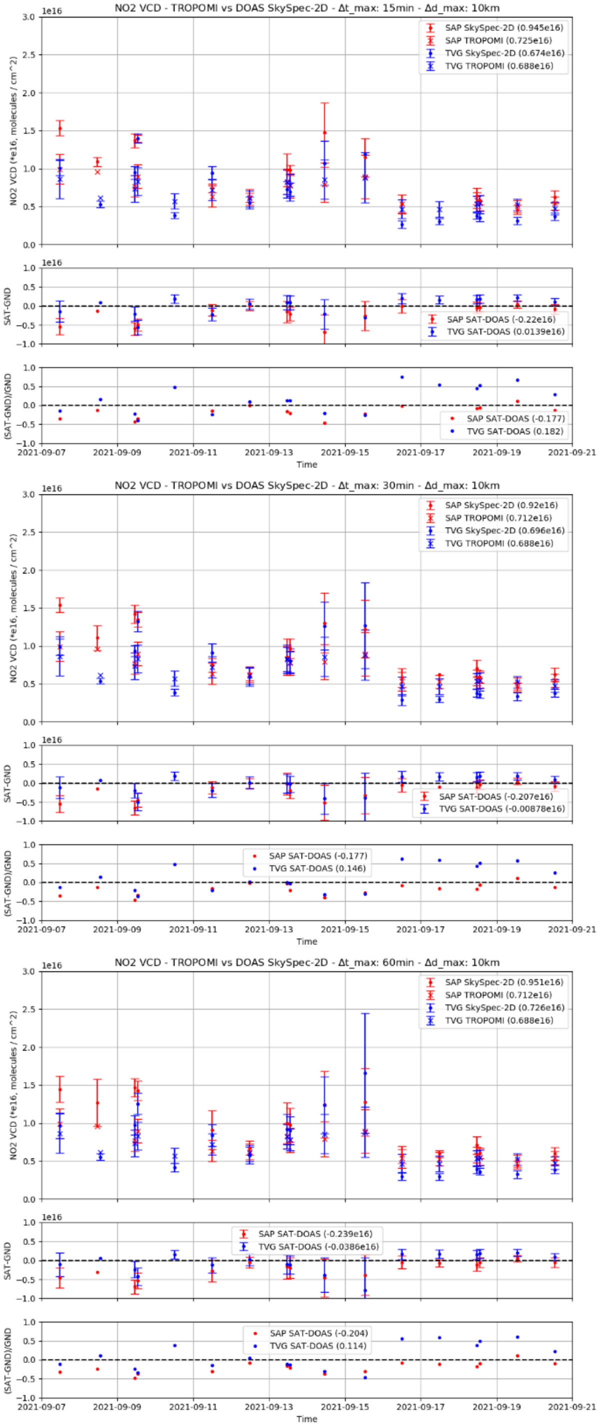

Figure 25: *As in Fig. 24 but for Δd_max= 10 km.*

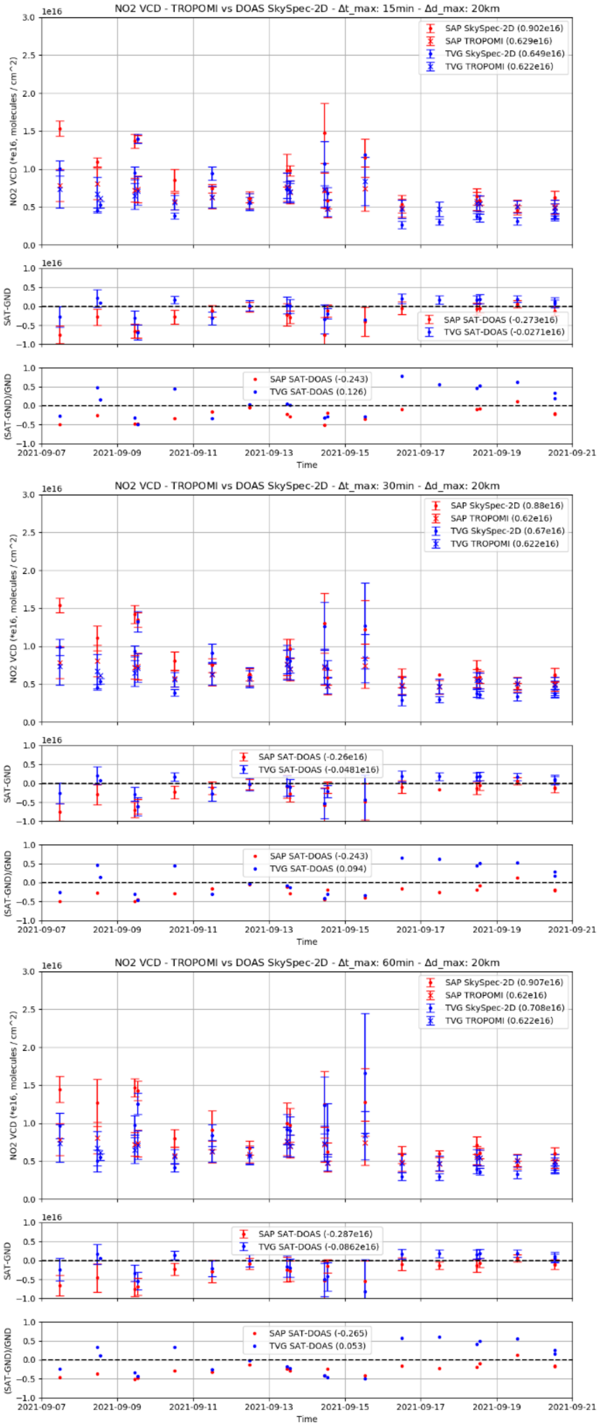

Figure 26: *As in Fig. 24 but for Δd_max= 20 km.*

We also analyzed the differences between the NO_2 VCDs retrieved by the two MAX-DOAS systems for the entire measurement campaign (Fig. 27). Generally, SAP NO_2 VCDs are higher than TVG values by 30% (as observed in [R-5]). Looking at the differences as a function of the SZA (Fig. 28), we observed a better agreement between the two sites for high SZA, when major part of the NO_2 signal comes from stratospheric NO_2.

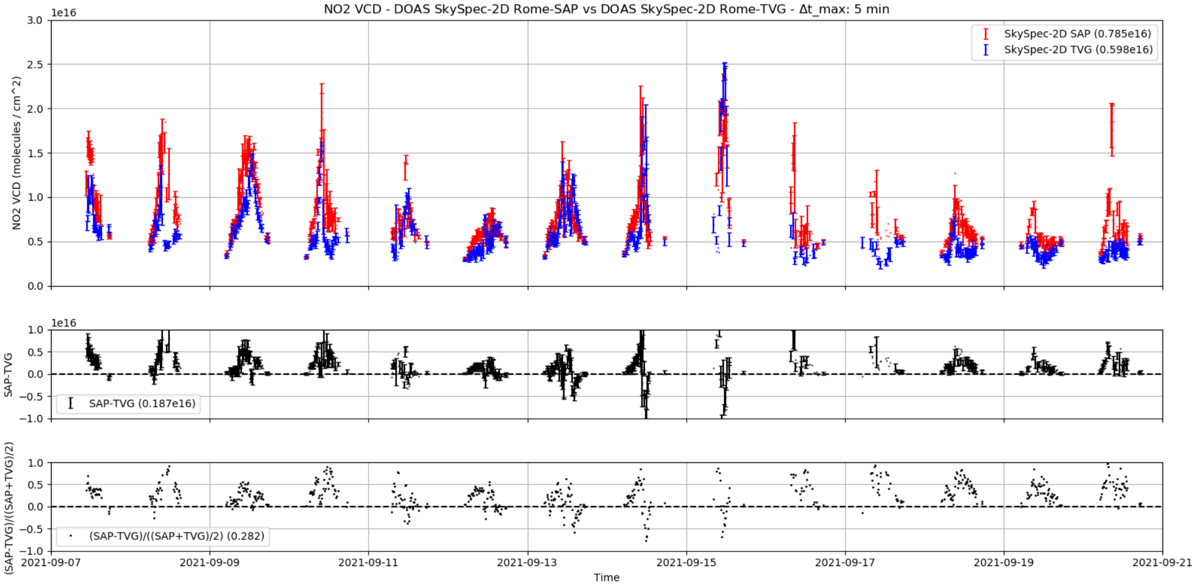

Figure 27: *Inter-comparison of Rome-La Sapienza (red dots) and Rome-Tor Vergata (blue dots) SkySpec-2D NO_2 VCDs. The absolute (mid panel) and the percentage relative (lower panel) differences are reported.*

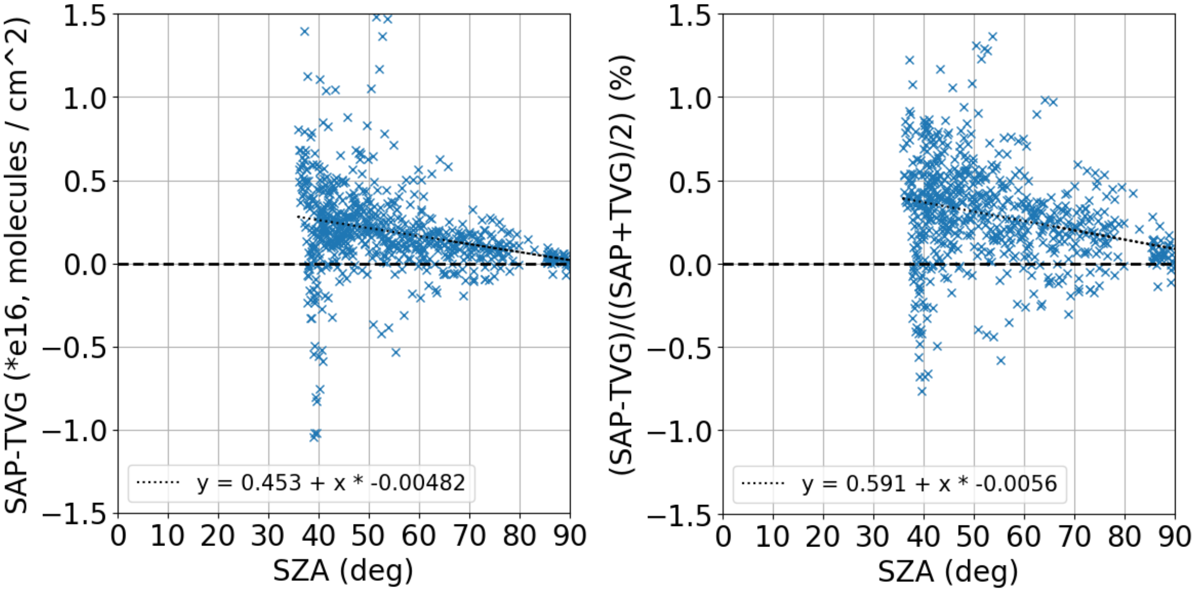

Figure 28: *Analysis of Rome-La Sapienza and Rome-Tor Vergata SkySpec-2D NO_2 VCDs absolute (left plot) and percentage relative (right plot) differences as a function of the SZA.*

4.4 O_3 inter-comparison results

As made for NO_2, we exploited the S-5P or EOS-Aura overpasses occurred during the measurement campaign, to evaluate the agreement between the ground-based instruments and the satellite O_3 VCDs datasets. In Figs. 29, 30, 31 (S-5P TROPOMI) and Fig. 32 (EOS-Aura OMI), we reported the distributions of the ground-based observations and the differences (absolute and relative) between these and the satellite observations. The results are also summarized in Table 5. We observed that both Pandora #117 and SkySpec-2D O_3 VCDs underestimated the TROPOMI O_3 VCDs, respectively of 3.6/3.8 % and 0.9/1.3 %. The results of the inter-comparison with respect to TROPOMI are less dependent by the co-location criteria with respect to what we observed for NO_2. This is not true considering the inter-comparison with respect to OMI. Due to the reduced number of coincidences the results are more variable as a function of the spatial co- location criteria. SkySpec-2D overestimate OMI O_3 VCDs of -0.4/-0.7 % considering Δd_max = 10 km and -3.9/-4.1 % considering Δd_max = 20. At the same time, Pandora#117 bias passes from 2.8 % for Δd_max = 10 km to -0.9 % for Δd_max = 20.

	Δt_max (min)	Δd_max (km)	SAT-DOAS (*e19, molecules/cm2)	(SAT-DOAS)/DOAS (%)	SAT-PGN (*e19, molecules/cm2)	(SAT-PGN)/PGN (%)
Sentinel-5P TROPOMI	±15	5	0.011	1.3	0.0319	3.8
		10	0.0097	1.1	0.0305	3.7
		20	0.00973	1.1	0.0316	3.8
	±30	5	0.01	1.2	0.0312	3.7
		10	0.0084	1	0.0301	3.6
		20	0.0091	1.1	0.0314	3.8
	±60	5	0.00957	1.1	0.0311	3.7
		10	0.00777	0.9	0.0299	3.6
		20	0.00841	1	0.0313	3.8
EOS-Aura OMI	±15	10	-0.00342	-0.4	0.0217	2.8
		20	-0.0365	-4.1	-0.00837	-0.9
	±30	10	-0.00437	-0.5	0.0214	2.8
		20	-0.0348	-4	-0.00815	-0.9
	±60	10	-0.0057	-0.7	0.0219	2.8
		20	-0.0343	-3.9	-0.00784	-0.9

Table 5: *As in Table 4 but for O_3.*

As reported in Section 4.4 of [R-16], the systematic difference between S-5P L2_O3 OFFL and reference ground-based data at individual stations (40 Brewer and Dobson sites, and 12 ZSL-DOAS SAOZ sites) rarely exceeds 2 %. The median bias calculated over the entire ground-based networks is of the order of +0.3 %. This median bias value falls well within the mission requirements (max. bias 5 %). Even the bias observed for the SkySpec-2D falls within the mission requirements and it is perfectly in line with the biases observed in the routinely validation of TROPOMI O_3 products.

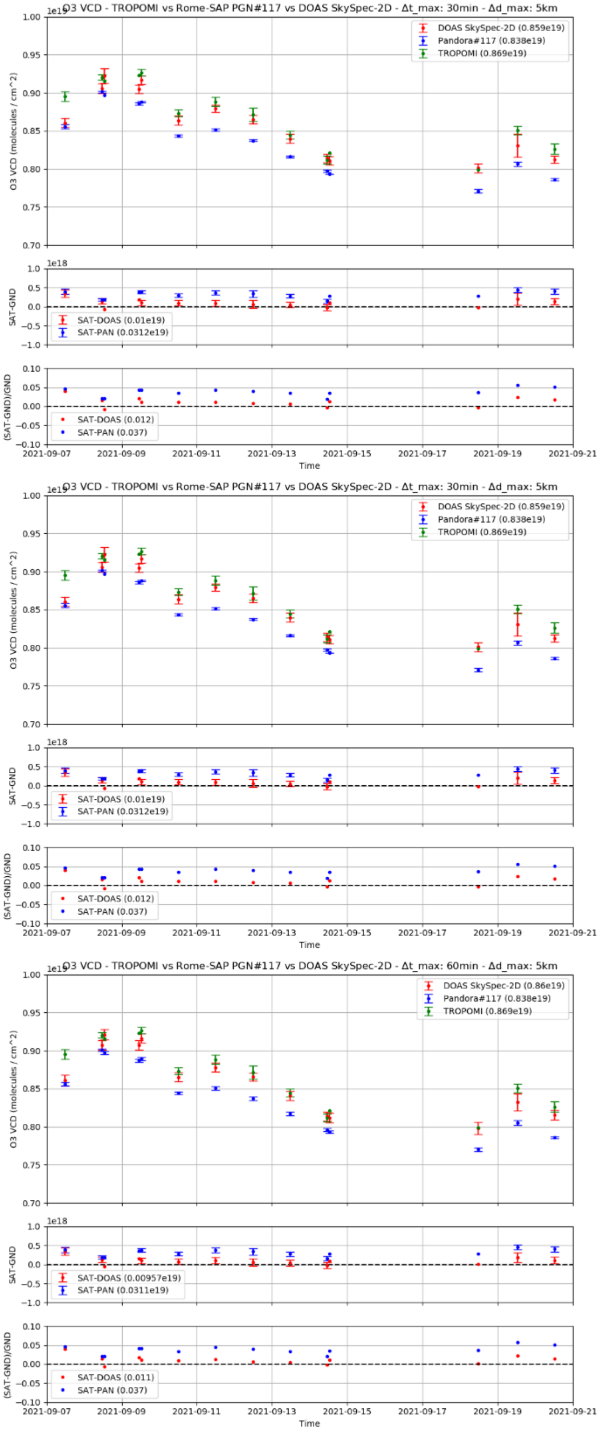

Figure 29: *As in Fig. 16 but for O_3.*

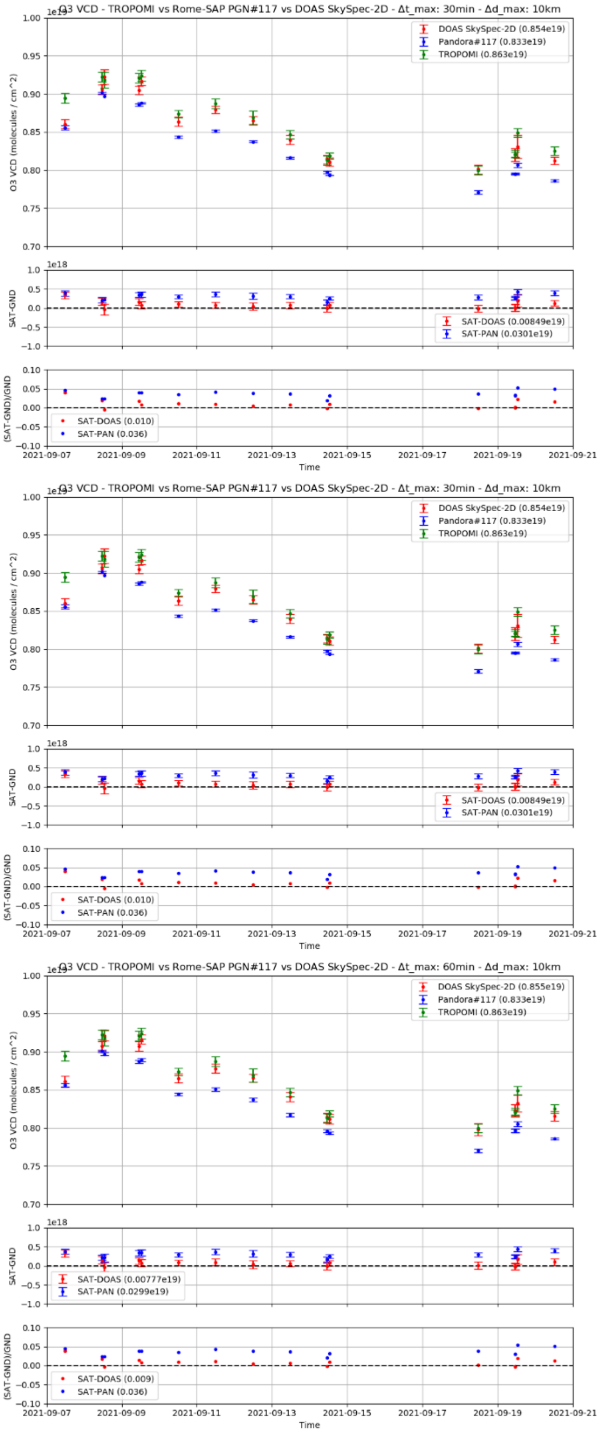

Figure 30: *As in Fig. 17 but for* O_3.

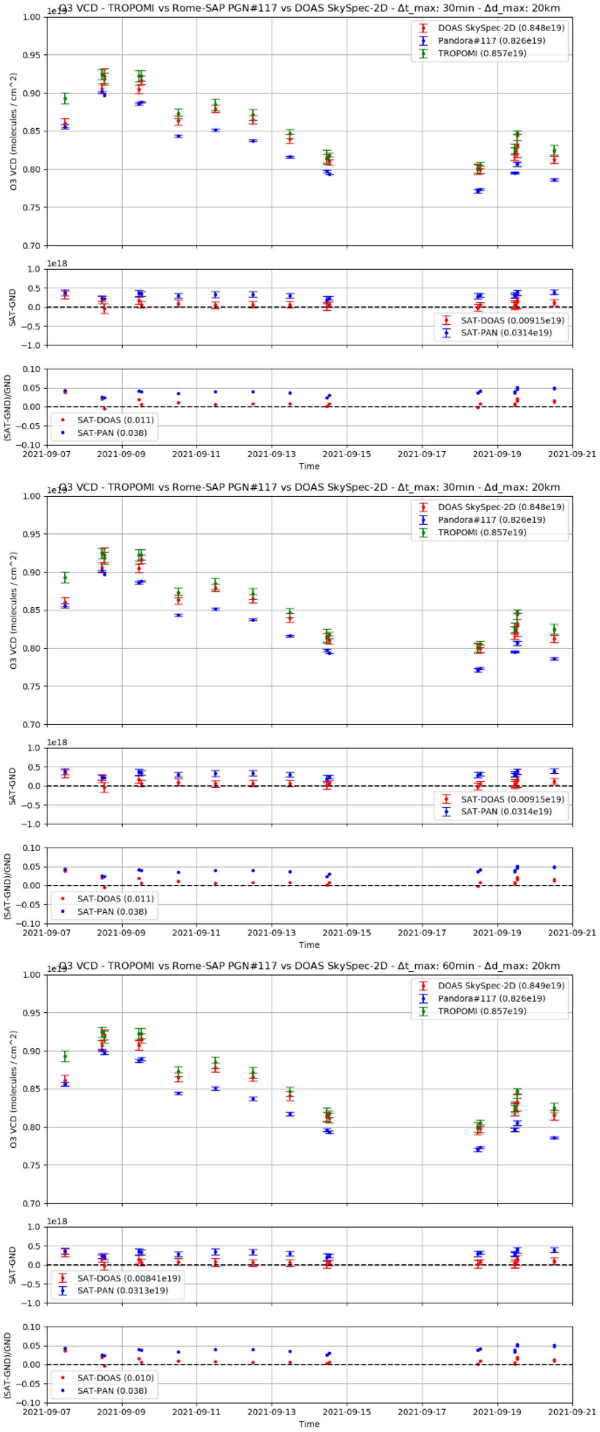

Figure 31: *As in Fig. 18 but for O_3.*

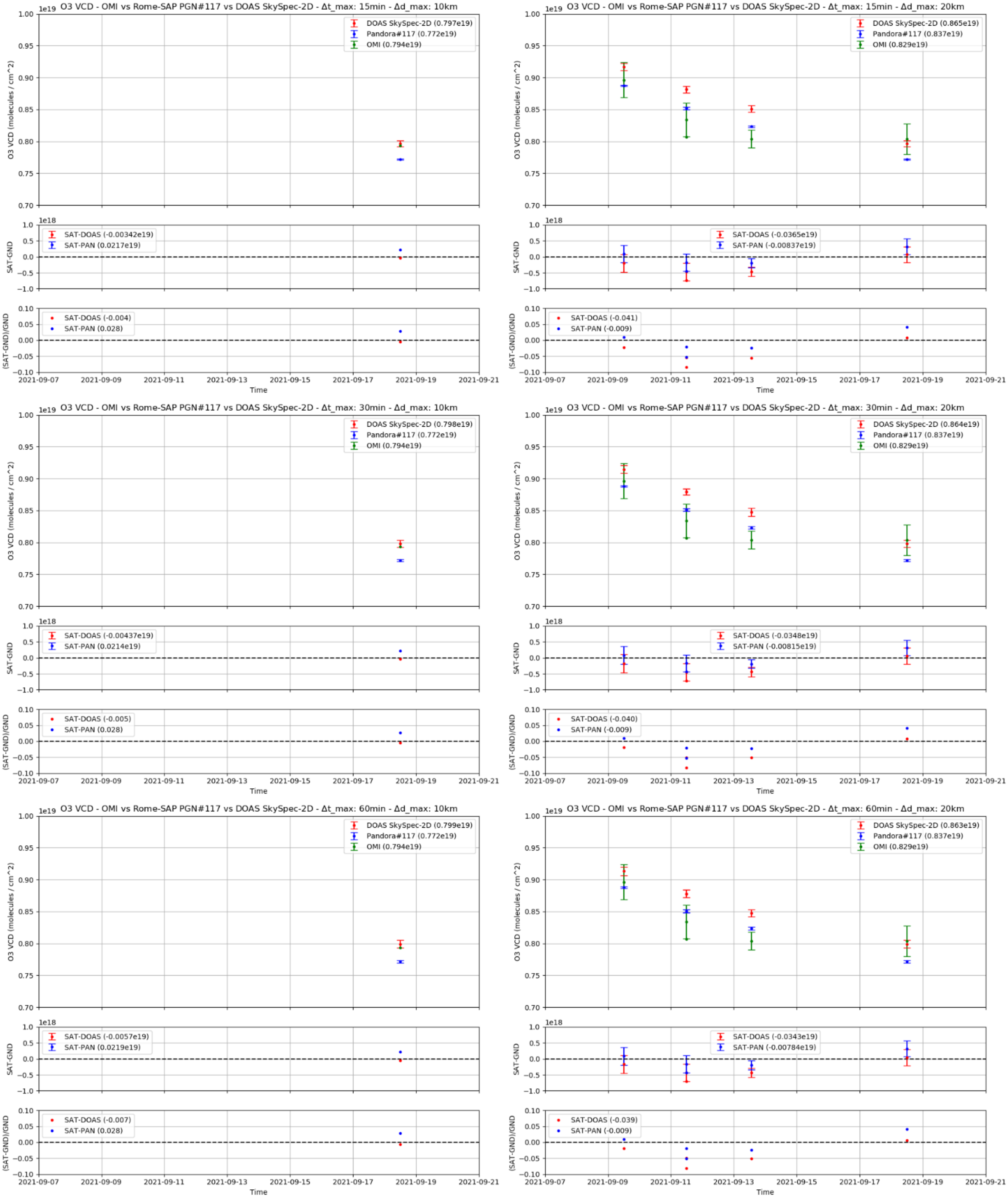

Figure 32: *As in Fig. 19 but for O$_3$.*

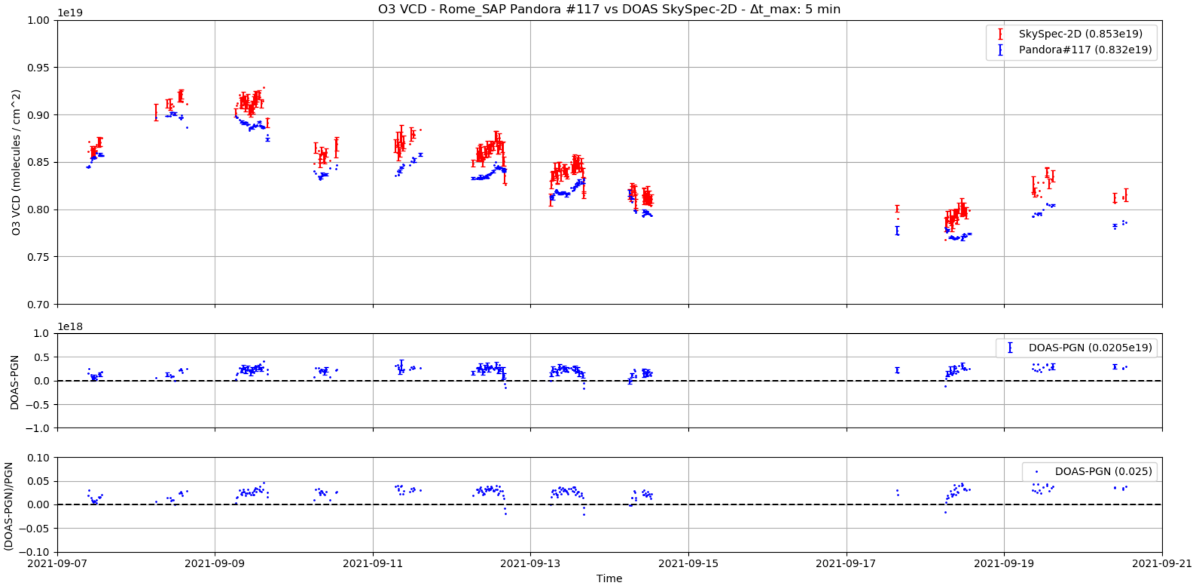

Figure 33: *As in Fig. 20 but for O*$_3$*.*

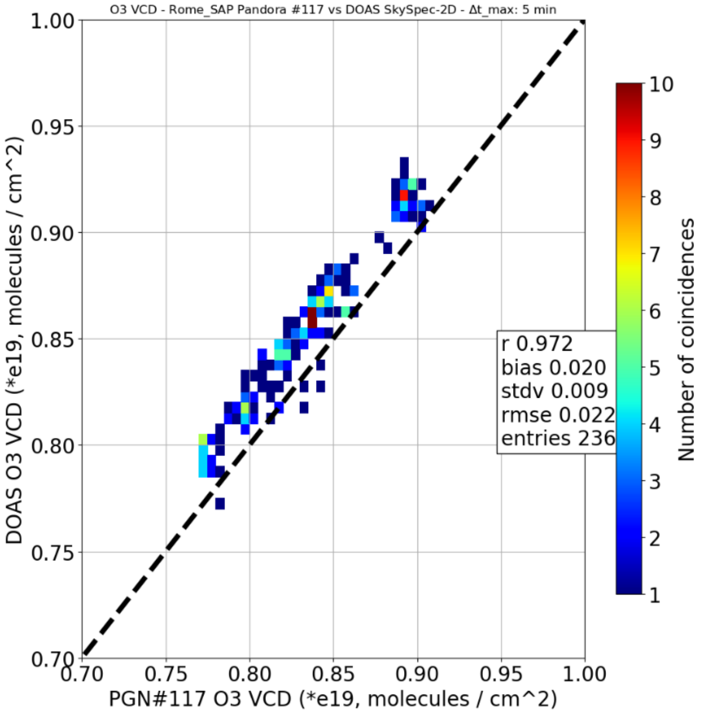

Figure 34: *As in Fig. 21 but for O*$_3$*.*

We evaluated the differences between the two ground-based datasets even considering the entire period of the measurement campaign. As made for NO_2, we averaged the two datasets on 10 minutes interval. The plot in Fig. 33 shows the distribution of O_3 VCDs retrieved by the SkySpec-2D and Pandora #117, and the differences between the two products. In Fig. 34, we also reported the scatterplot of the coincident observations. The correlation between the two datasets is extremely high (0.972) and the mean bias is $0.02 \cdot 10^{19}$ molecules/cm^2 (-2.5 %). We also analyzed possible relation of the bias by the hour of the day, the SZA and the SAA (Fig. 35). We did not observe any evident dependency of the bias. It is worth noticing that for the SkySpec-2D VCDs calculations we used an O_3 profile extracted from ECMWF in coincidence with Rome, due to the impact of O_3 profile on AMFs.

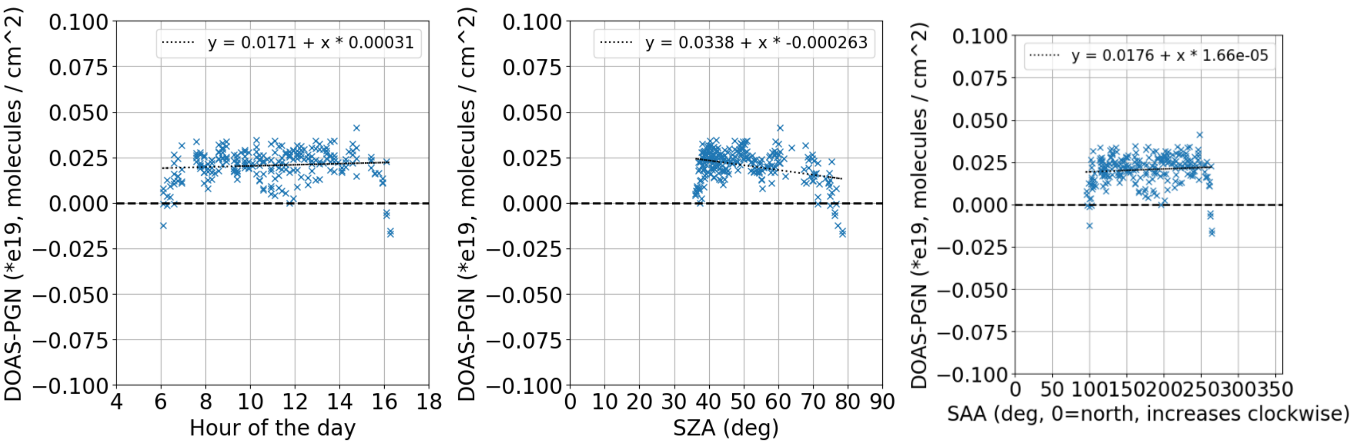

Figure 35: *As in Fig. 22 but for O_3.*

5 Conclusions

Since ISAC-CNR acquired the SkySpec-2D system, we clearly understood the necessity to assess the performances of an old-fashion MAX-DOAS system, like the TROPOGAS, with respect to a new state-of-the-art system. For this purpose, we performed an inter-comparison campaign in Bologna at ISAC-CNR premises during August 2021. We observed a generally good agreement (r = 0.81 considering filtered data) between the two ground-based MAX-DOAS instruments considering both the absolute VCDs values and their behavior during the day. At the same time, this exercise highlighted a problem in the pointing system of the TROPOGAS. The mismatch affects only the observations toward the city side and seems to not work as a constant bias, it varies as a function of the elevation angle. This problem needs further investigation, and it will be solved as soon as possible. Nevertheless, despite the old design and the ageing of a few components, the analysis has shown that the TROPOGAS is still a remarkable instrument. It represents the MAX-DOAS know-how still present in Italy, and there is the intention to maintain it operative on the roof of the ISAC-CNR in Bologna as far as possible.

However, SkySpec-2D represents the evolution of the MAX-DOAS instrument design, more reliable, easier to transport, and refurbish in case of inconveniences.
Even for these reasons, from 7th to 21st of September, the SkySpec-2D took part in the inter-comparison campaign at La Sapienza in Rome. This campaign allowed us to perform measurements in another extremely polluted area such as Rome and exploit other instruments' observations in BAQUNIN. For our purposes, we focused on Pandora #117, part of the PGN, which provides valuable information on the total column of NO_2 and O_3.
We performed an inter-comparison of the MAX-DOAS SkySpec-2D NO_2 and O_3 VCDs with the Pandora #117 VCDs during the entire measurement campaign. For NO_2 VCDs, SkySpec-2D correctly reproduce all the features of the distributions observed by Pandora #117, the correlation between two ground-based instruments (0.916). The bias between the two ground-based datasets is about $-0.232 \cdot 10^{16}$ molecules/cm^2 (-22%). At the same time, for O_3, we observed an even higher correlation (0.972), and the mean bias is $0.02 \cdot 10^{19}$ molecules/cm^2 (-2.5 %).

Moreover, to evaluate the quality of the two ground-based products, we compared the SkySpec-2D and Pandora #117 NO_2 and O_3 VCDs with respect to similar products retrieved from S-5P TROPOMI and EOS-Aura OMI observations. We observed that both ground-based instruments overestimated the satellite NO_2 VCDs. Pandora #117 overestimates S-5P TROPOMI and EOS-Aura OMI VCDs of about 30/50 %. At the same time, even SkySpec-2D VCDs overestimate TROPOMI data by about 15/25 % and EOS-Aura OMI by 10/35 %. In the most reliable co-location criteria, (Δt_max = ± 15 minutes and Δd_max = 5 km), the bias is -16 % for SkySpec-2D and -29 % for Pandora#117 with respect to S-5P TROPOMI and -11 % for SkySpec-2D and -27 % for Pandora#117 with respect to EOS-Aura OMI. About O_3, we observed that both Pandora #117 and SkySpec-2D O_3 VCDs underestimated the TROPOMI O_3 VCDs, respectively, of 3.7 % and 1.1 %. At the same time, SkySpec-2D overestimate OMI O_3 VCDs of -0.4/-0.7 % (Δd_max = 10 km, -3.9/-4.1 % considering Δd_max = 20).

During the period in which the SkySpec-2D was located in the Rome La Sapienza site, an equivalent MAX-DOAS system was installed at ISAC-CNR in the Rome Tor Vergata site. The two instruments worked with the same observation strategies, and the measurements were processed with the same procedure. Regarding the satellite coincidence criteria, for Δd_max of +/-5 and +/-10 km, Rome La Sapienza NO_2 VCDs are higher than Rome Tor Vergata ones by about 20/30 %. Considering S-5P TROPOMI VCDs as a reference, we observed a better agreement between ground-based and satellite NO_2 VCDs at Rome Tor Vergata. This exercise represented the first step towards a new Italian MAX-DOAS network that aims to cover some of the most significant polluted areas in Italy with fully FRM4DOAS compliant MAX-DOAS systems. The measurement campaign in the BAQUNIN supersite remarked the importance of having analogous systems close to each other, such as La Sapienza and Tor Vergata, to deeply investigate the production/destruction processes and the dynamics of the pollutants. Even on this basis, ISAC-CNR decided to pursue the opportunity to position the SkySpec-2D in the meteorological station "Giorgio Fea", located at the rural site of St. Pietro Capofiume (Bologna, Italy) and to maintain the TROPOGAS at the ISAC-CNR premises in Bologna. This experience has also shown the crucial importance of synergies between different instruments to better exploit a single instrument's potential. In this respect, the CNR – ISAC has planned to acquire a sunphotometer and a LIDAR (Q2/Q3 2022) that, together with the development of a code for routinely retrieving NO_2, O_3, and AOD vertical profiles through MAX-DOAS observations, will guarantee the full exploitation of the MAX-DOAS system.

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