WPs 2250-2251: "DOAS-BO: Towards a new FRM4DOAS-compliant site - Phase 2"

[D-3] Report on the inter-comparison results between ground-based and satellite measurements

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AMENDMENT RECORD SHEET

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1.0	12/05/2023	D-3 document of project "WPs-2250-2251 Phase 2: DOAS-BO: Towards a new FRM4DOAS-compliant site'".

Contents

1. List of Acronyms

AERONET	Aerosol Robotic Network
AOD	Aerosol Optical Depth
ALC	Automatic Lidar Ceilometer
ARPAE	Agenzia Regionale per la Prevenzione, l'Ambiente e l'Energia
CNR	Consiglio Nazionale delle Ricerche
DOAS	Differential Optical Absorption Spectroscopy
ECV	Essential Climate Variable
EE	Expected Error
FOV	Field Of View
FRM4DOAS	Fiducial Reference Measurements for DOAS
GCOS	Global Climate Observing System
ISAC	Istituto delle Scienze dell'Atmosfera e del Clima
MAIAC	Multi-Angle Implementation of Atmospheric Correction
MAX-DOAS	Multi-AXis DOAS

MODIS	Moderate Resolution Imaging Spectroradiometer
OLCI	Ocean and Land Colour Instrument
SCD	Slant Column Densities
SLSTR	Sea and Land Surface Temperature Radiometer
SPC	San Pietro Capofiume
STD	Standard Deviation
SZA	Solar Zenith Angle
TROPOMI	TROPOspheric Monitoring Instrument
UV	Ultra-Violet
VCD	Vertical Column Density
VIS	Visible

2. Introduction

In this document, we report the main outcomes of the inter-comparison between ground-based and satellite data obtained at San Pietro Capofiume (SPC) in the frame of the project “WPs-2250-2251: DOAS-BO: Towards a new FRM4DOAS-compliant site - Phase 2’’.

3. NO_2 and Aerosol extinctions profile retrievals from MAX-DOAS at “Giorgio Fea” observatory at San Pietro Capofiume

SkySpec-2D has been continuously acquiring MAX-DOAS measurements at the “Giorgio Fea” observatory in SPC since the 1st of October 2021. During all these months, the measurement strategy has remained unchanged except for the azimuth directions selected. Indeed, we decided to modify them because the telescope, on the 23rd of March 2022, was moved and installed in its permanent position (a few meters away from the previous one) and the previously chosen viewing directions were not free from obstacles anymore. The SkySpec-2D was permanently installed on the roof of the shelter containing the PC and spectrometers.
In [R1], we have reported the first results obtained by applying the DEAP retrieval code to the SPC SkySpec-2D MAX-DOAS measurements. In that case, we consider only 4 days of measurements and compare the obtained results with those from MAPA and MMF official retrieval codes as well as with in-situ data (Arpae) and TROPOMI for NO_2 and Ceilometer data to qualitatively evaluate the extinction retrievals.
In this document, we use the products obtained by applying the DEAP code to a complete year of MAX-DOAS measurements from October 2021 to October 2022.

Exploiting one year of data, we have the opportunity to study the seasonal behavior of NO2 and AOD tropospheric columns over SPC.

We briefly recall here the MAX-DOAS acquisition strategy used at SPC: the atmospheric spectra start to be acquired every morning when the SZA becomes lower than 94° (the sun is 4° below the horizon). In the beginning, the SkySpec-2D starts to acquire only zenith-sky spectra. When the SZA becomes lower than 85°, SkySpec-2D starts to perform MAX-DOAS measurements. During MAX-DOAS acquisitions, SkySpec-2D measures in three different azimuth directions: 120°, 225° and 300° from the 1st of October 2021 to the 23rd of March 2022, and 135°, 250° and 315° afterwards (Fig. 1). For each azimuth direction, spectra are acquired at the following elevation angles: 1°, 2°, 3°, 5°, 10°, 30° and 90°.

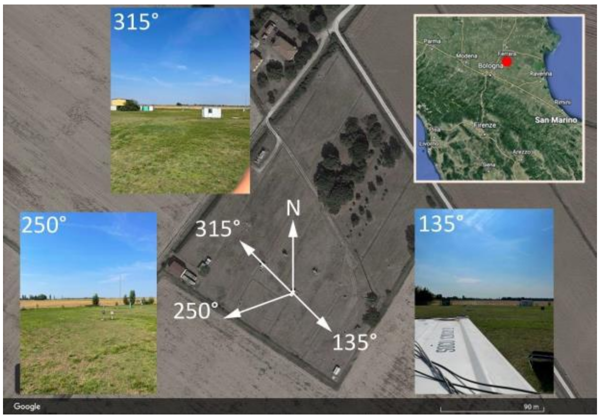


Figure 1: *Different views from SkySpec-2D in the three azimuth directions (135°, 250° and 315° after the 23rd of March 2022) adopted during MAX-DOAS measurements.*

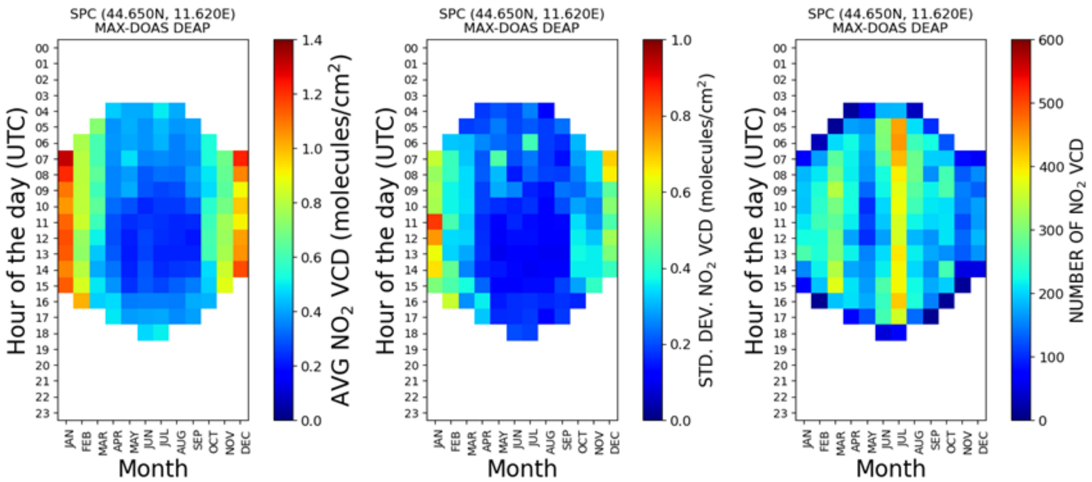


Figure 2: *Average NO_2 Tropospheric VCDs (1E16) retrieved from SkySpec-2D as a function of months and hours of the day, together with its standard deviation (1E16) and number of points. TROPOMI overpass time is around 13 UTC.*

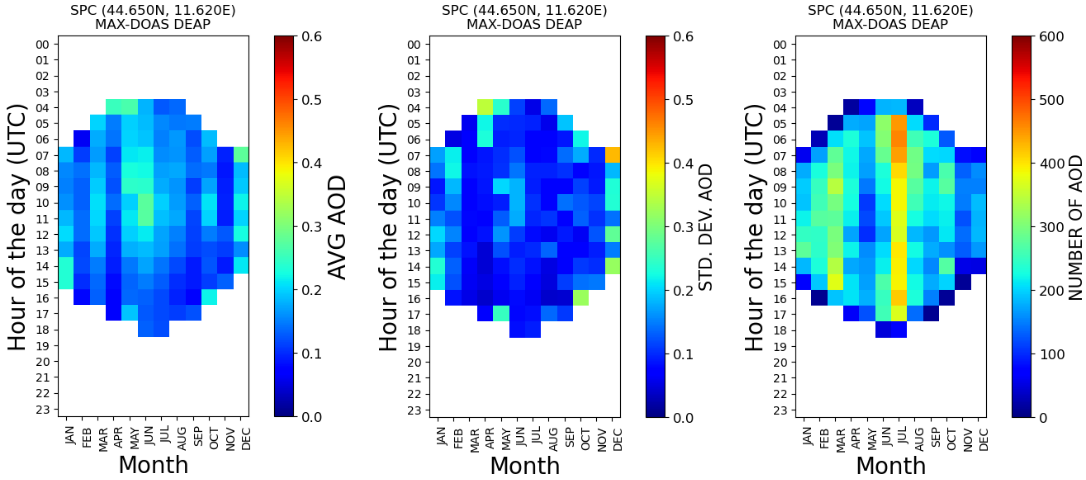


Figure 3: *Average Tropospheric AODs retrieved from SkySpec-2D as a function of moths and hours of the day, together with its standard deviation and number of points. In the computation of the statistics, AOD values higher than 2 were excluded.*

Fig. 2 shows the average NO_2 Tropospheric VCDs retrieved from SkySpec-2D as a function of months and hours of the day, together with its standard deviation and number of points. The most relevant result from Fig. 2 is the evident seasonal variation of the NO_2 peak value correlated to the Sun illumination over the year. NO_2 peak values are observed in the early morning during the summer, gradually moving towards the afternoon in spring and autumn. During the winter, the hourly distribution appears higher and more uniform, probably due to the slower photochemical reactions of NO_2, the stabile atmospheric conditions and the possible presence of a thermal inversion layer responsible for fog/low clouds and a reduced vertical mixing with consequent inhibition of the contaminants' dispersion. For this analysis, we used cloud-filtered products, but the effect of residual cloud presence can still be present, particularly in the case of fog or very low clouds. This aspect mainly affects the winter period, typical of fog in the Po Vally, and it is evident looking at the higher standard deviations of this period. The number of points is equally distributed except for May and September, when two major stops occurred. Fig. 3 shows the same plots as Fig. 2 but for AOD retrieved from the SkySpec-2D VIS channel. AOD values tend to be higher in winter and spring months. Except for the winter period, the mean values are slightly higher in the morning. Large standard deviations are observed especially in winter probably due to the less than perfect cloud filtering, especially in the case of fog and very low clouds.

3.1. Comparison of NO_2 Tropospheric VCDs from SkySpec-2D and TROPOMI data

In Fig. 4a, we report the results of the inter-comparison of NO_2 Tropospheric VCDs obtained from SkySpec-2D scans at 300 azimuth degrees and TROPOMI data in coincidence. For the inter-comparison, we considered TROPOMI data in a radius of 5 km around SPC and MAX-DOAS data within +/- 15 minutes from the TROPOMI overpass. Only TROPOMI data with quality above 0.75 are used. As already seen in Fig. 2, the NO_2 VCDs behavior changes with seasons with higher values during winter (very stable meteorological conditions) than in summer. This behavior is similar to those observed in the Total NO2 VCDs [R2], confirming that most of the contribution comes from the Troposphere. This result is also consistent with the TROPOMI overpass time (Fig. 2). The bias (TROPOMI - SkySpec-2D) is, on average, negative (about -0.45e+15 mol/cm2, as reported in Figs. 4 and 5 left panel). This is something expected from TROPOMI validation: TROPOMI tends to underestimate NO_2 Tropospheric VCDs in polluted regions due to the use of modelled TM5 NO_2 a-priori profiles [R-3]. As can be noticed from Fig.5 a good correlation between TROPOMI and SkySpec-2D is observed (about 0.85).

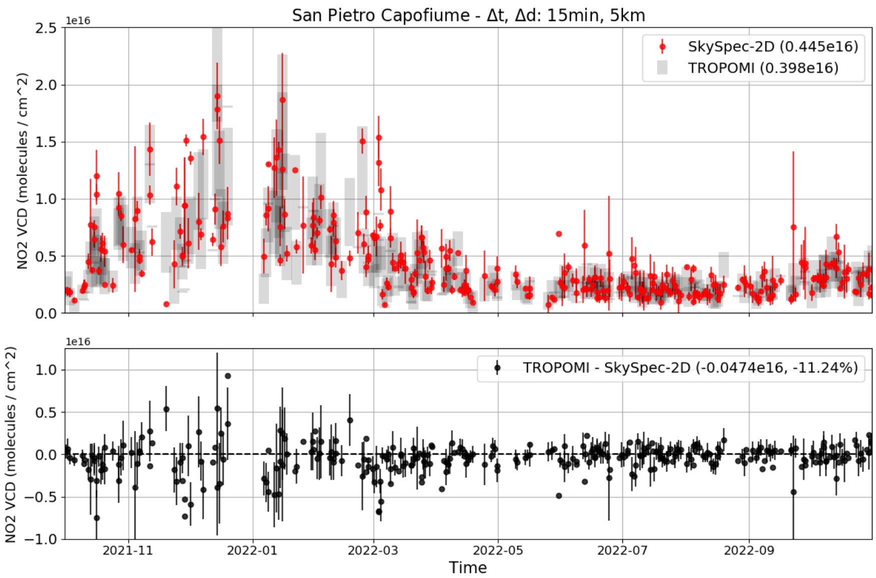


***Figure 4a**: Comparisons between NO_2 tropospheric VCDs retrieved from SkySpec-2D MAX-DOAS measurements and coincident (see text for details) TROPOMI data at "Giorgio Fea" observatory at San Pietro Capofiume (Bologna, Italy). Only 300/315 azimuth degree scans are used for this analysis.*

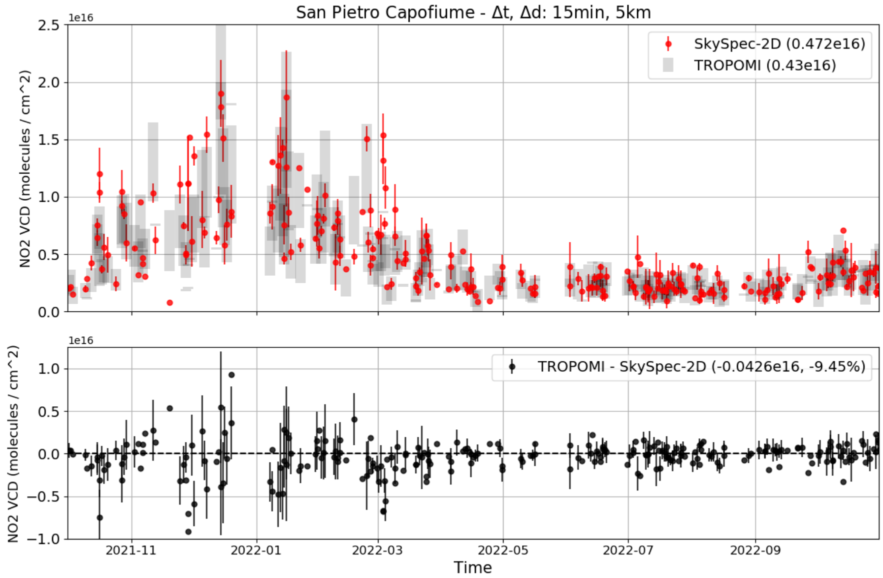


***Figure 4b**: Same as Figure 4 but with SkySpec-2D cloudy data filtered out.*

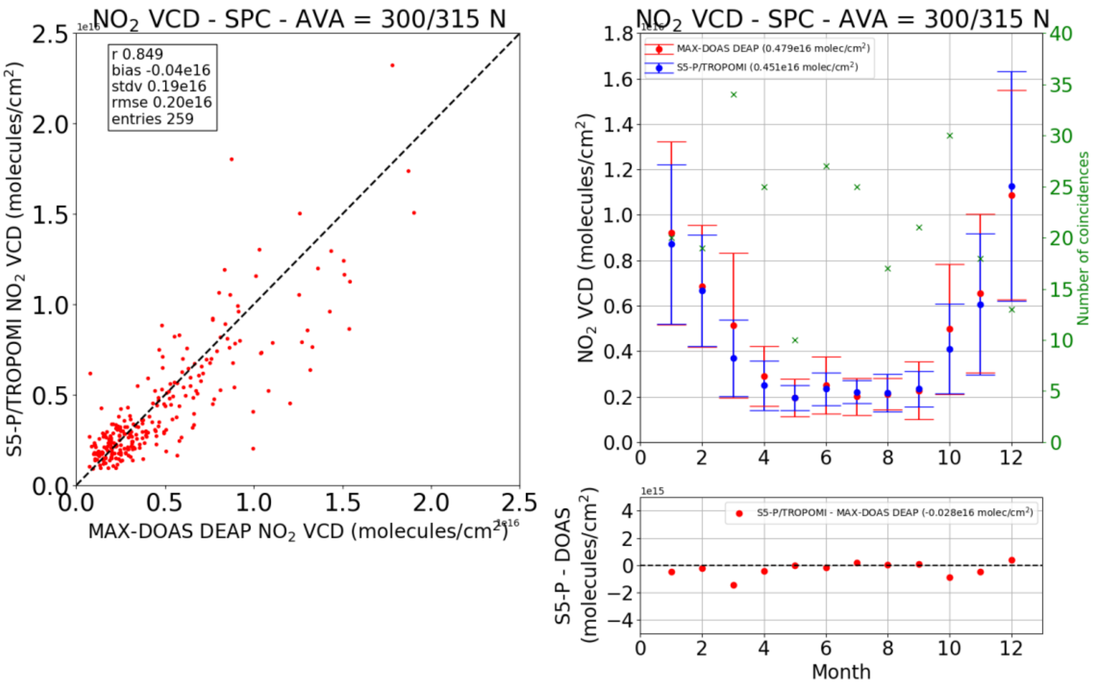


***Figure 5:** NO_2 VCDs from SkySpec-2D vs TROPOMI at SPC (left), NO2 from SkySpec-2D (red) and TROPOMI (blue) as a function of the months (right).*

Figure 4b reports the same results when the cloudy data are filtered out from SkySpec-2D dataset. The cloud filtering is based on a color index approach. In particular, a color index is estimated for each VIS spectrum as the ratio between the average radiance computed in the wavelength interval 410-415 nm and the one in the interval 545-550 nm. A retrieved vertical profile relative to a MAX-DOAS scan is flagged as cloudy if the zenith measurement, used as reference for the DOAS analysis, is cloudy or if clouds are present in the off-axis line of sights. The zenith reference spectrum is considered cloudy if the color index value is below 1.2. This threshold value has been estimated through the synergy between simulations and the color index distribution derived from real data (see Fig. 6).

In contrast with the zenith spectra, the simulations suggest that the estimate of a threshold color index for the off-axis spectra is a hard task. Indeed, they present complex dependences on the solar zenith and azimuth angles and on the aerosol load. For this reason, we decided to exploit a qualitative method inferred from the simulations. According to it, at least one of the off-axis spectra is considered cloudy and the scan is filtered out if the color indexes relative to the spectra measured at the elevation angles of 3°, 5°, 10°, 30° are not sorted in ascending order.

As can be noticed, the bias is slightly reduced due to the removal of outliers (e.g. in June 2021). However the SkySpec-2D cloud filtering did not has a significant effect on the comparison with satellite data, also due to the fact that part of the cloudy data are already filtered out considering only TROPOMI clear sky data.

The seasonal behaviour of NO_2 and of the bias is also evident from the right panel of Fig. 5, where the monthly average NO_2 VCDs are reported. As can be seen from the bottom plot (Fig. 5), winter values tend to be higher for the ground-based instrument than for the satellite ones.

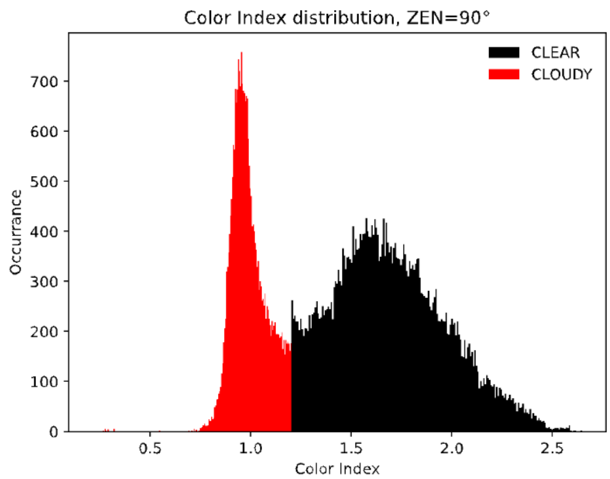


***Figure 6:** Color index distribution for the zenith-sky spectra measured from 01/10/2021 to 30/04/2023. The value 1.2 is used as threshold between clear and cloudy spectra.*

3.2. Comparison of AOD from SkySpec-2D and satellite data

In this section, we present the results of the inter-comparison of the AOD products retrieved from SkySpec-2D measurements and similar products retrieved from satellite observations. In particular, we focus on the Moderate Resolution Imaging Spectroradiometer (MODIS) Multi-Angle Implementation of Atmospheric Correction (MAIAC) and the Sentinel-3 Synergy AOD products.

3.2.1. Inter-comparison against MODIS MAIAC AOD products

The MODIS is a sensor onboard the NASA Terra and Aqua satellites flying respectively since 2000 and 2002. Terra MODIS (descending node, about 10:30 UTC) and Aqua MODIS (ascending node, about 13:30 UTC) are observing the entire Earth's surface every 1 to 2 days, acquiring data in 36 spectral bands ranging in wavelength from 0.4 µm to 14.4 µm, with a spatial resolution of 1 km at nadir (except for a few bands with higher spatial resolution).

The MAIAC algorithm ([R5] and references therein) is used to retrieve AOD over land exploiting MODIS observations. The algorithm uses time series to separate the contribution of aerosol, land reflection, and the effects of bidirectional surface reflectivity [R5]. Compared with other AOD MODIS products, such as Dark Target and Deep Blue, the MAIAC AOD product has higher spatial coverage and retrieval frequency. The high spatial resolution of MAIAC AOD retrievals (1 km) improves the ability to determine the characteristics of fine aerosols and distinguish aerosol sources [R6].

Here we used the MCD19A2 Version 6 data product of the MODIS MAIAC AOD gridded Level 2 product. The MCD19A2 AOD data product contains the following Science Dataset layers: blue band AOD at 0.47 µm, green band AOD at 0.55 µm, AOD uncertainty, fine mode fraction over water, column water vapour over land and clouds (in cm), smoke injection height (m above ground), AOD QA, AOD model at 1km, cosine of solar zenith angle, cosine of view zenith angle, relative azimuth angle, scattering angle, and glint angle at 5 km. As suggested in [R5], we consider as valid AOD products the pixels where QA_AOD = Best_Quality, which combines the best values of cloud and adjacency masks:

- QA.CloudMask = Clear
- QA.AdjacencyMask (±2 pixel vicinity) = Clear

First, we evaluated several spatial and temporal co-location criteria to evaluate the effects on the agreement between the SkySpec-2D DEAP and MODIS MAIAC AOD products. We performed the analysis considering regular grids of 1x1, 5x5, and 15x15 km centered on the SPC coordinates and maximum allowed time differences between MODIS and SkySpec-2D observations of ±15 and ±30 minutes. We used the MODIS MAIAC AOD at 470 nm for both MODIS satellites, and to prevent possible effects of outliers, we also consider only coincidences in which valid products populate at least 20% of the regular grid. The results are reported in Table 1.

		MODIS/Aqua				MODIS/Terra				MODIS/Aqua+Terra			
Δt (min)	**Grid (km)**	**N**	**MODIS-DOAS**	**Std. Dev.**	**r**	**N**	**MODIS-DOAS**	**Std. Dev.**	**r**	**N**	**MODIS-DOAS**	**Std. Dev.**	**r**
± 15	**1x1**	120	0.034	0.097	0.655	151	-0.005	0.133	0.584	271	0.013	0.12	0.561
	5x5	137	0.027	0.093	0.665	169	0.003	0.133	0.569	306	0.014	0.117	0.574
	15x15	150	0.022	0.089	0.672	178	0.001	0.131	0.574	328	0.01	0.114	0.585
± 30	**1x1**	120	0.035	0.096	0.67	151	0.001	0.1	0.703	271	0.016	0.1	0.655
	5x5	137	0.028	0.091	0.689	169	0.007	0.104	0.677	306	0.017	0.099	0.659
	15x15	150	0.022	0.088	0.685	178	0.006	0.102	0.677	328	0.013	0.096	0.665

***Table 1**: Results of the inter-comparison of MODIS MAIAC (Aqua + Terra) and SkySpec-2D AOD products at SPC for the period 1/10/2021 – 30/09/2022 considering different co-location criteria.*

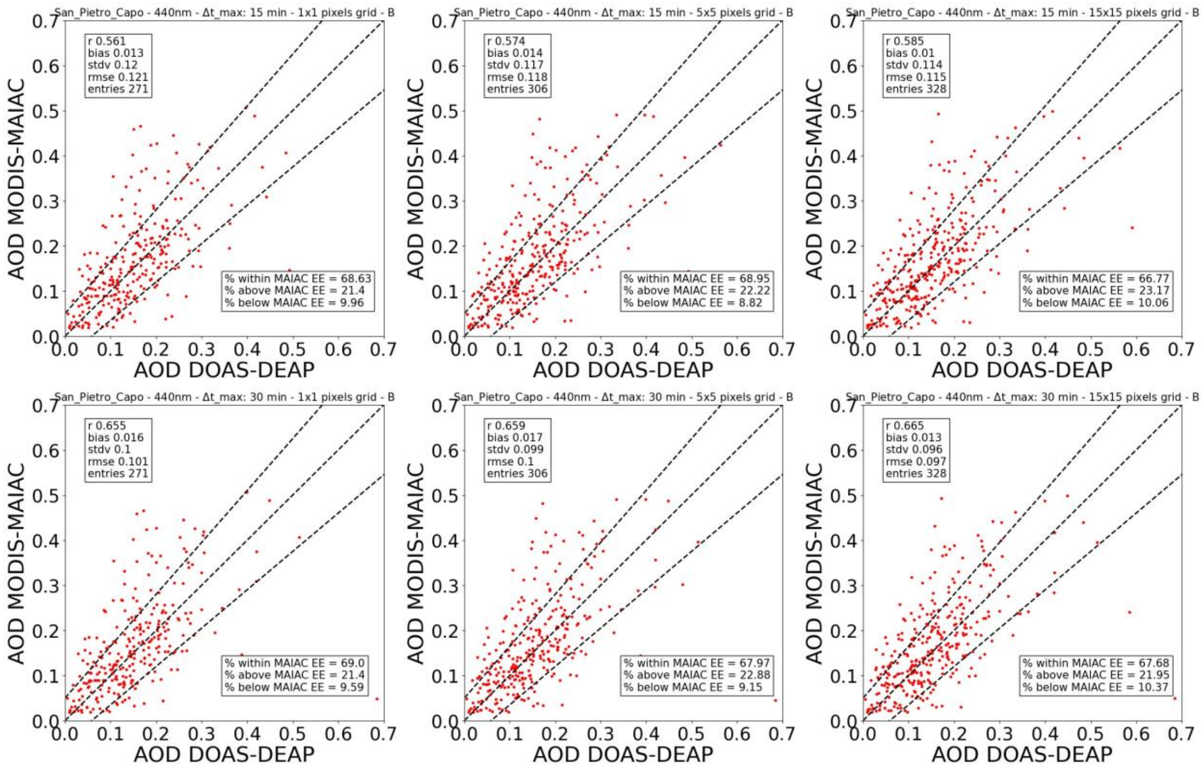


***Figure 7**: Results of the inter-comparison of MODIS MAIAC (Aqua + Terra) and SkySpec-2D AOD products considering different temporal (±15 minutes in the upper*

row and ±30 minutes in the lower row) and spatial (1 km in the left column, 5 km in the central column and 15 km in the right column) co-location criteria. The y=x lines and MODIS MAIAC EE envelopes ± (0.05 + 15% AOD) are plotted as dashed lines.

MODIS/Aqua MAIAC AOD products generally overestimate SkySpec-2D products by about 0.03 (0.035 - 0.022), with a better agreement considering higher spatial co-location criterium (15 km). Generally, the differences and standard deviations computed with respect to MODIS/Aqua satellite seem to be less sensitive to the changes in the temporal co-location criterium. The agreement against MODIS/Terra MAIAC AOD products is better than that observed against MODIS/Aqua products. MODIS/Terra MAIAC AOD products slightly underestimate SkySpec-2D AOD products (-0.005) considering 1 km and Δt_max = ±15 minutes co-location criteria and overestimate ground-based products (0.001/0.007) considering higher distances (5 and 15 km). As expected, by increasing the spatial co-location criterium, the standard deviation increases and the correlation decreases, highlighting that we are considering more heterogeneous portions of the atmosphere. This typical behavior is not present considering MODIS/Aqua MAIAC AOD products.

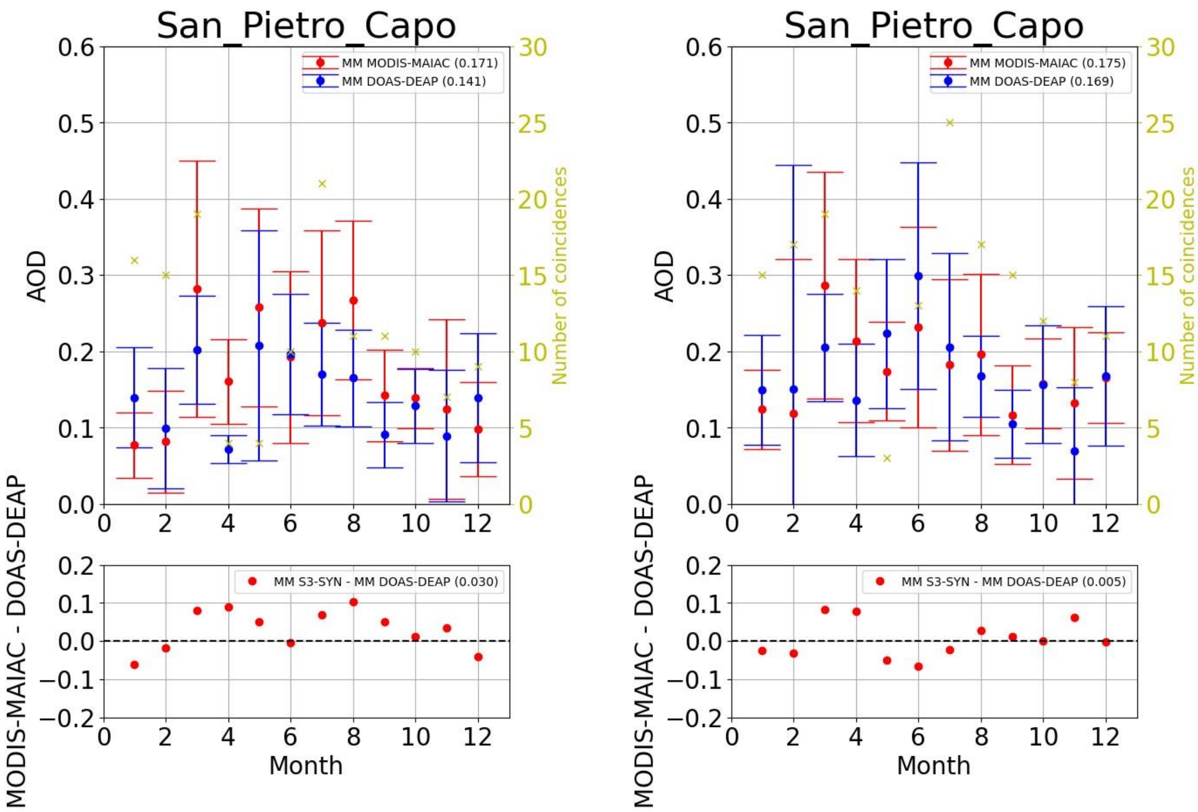


Figure 8: *Results of the analysis of the monthly behavior of the differences between SkySpec-2D and MODIS/Aqua (left plot) and MODIS/Terra (right plot) MAIAC AOD*

products. In the upper panels, the monthly averages of MODIS MAIAC (red dots) and SkySpec-2D (blue dots) are reported. The number of coincidences for each month is also reported (yellow dots). In the lower panels, the monthly differences are reported (red dots). The results reported here refer to the analysis performed considering a regular grid of 5x5 km centered on the SPC coordinates and Δt_max (time between MODIS and SkySpec-2D observations) of ±30 minutes.

Generally, considering both MODIS satellites (Aqua + Terra, Fig. 7), the agreement between the two datasets is extremely good, with a percentage of AOD data falling within the MODIS MAIAC Expected Error (EE) of ± (0.05 + 15% AOD) (Levy et al., 2013) higher than 67% and an overall bias that varies from 0.01 to 0.017 depending on the co-location criteria adopted. To better understand the possible temporal dependency of the differences, we computed the monthly averages of the retrieved AOD values and the corresponding differences (Fig. 8). MODIS/Aqua MAIAC AOD products generally overestimate SkySpec-2D products except for winter. By contrast, MODIS/Terra MAIAC products overestimate SkySpec-2D products in spring and autumn and underestimate them in summer and winter.

3.2.2. Preliminary exploitation of AERONET AOD products at SPC for inter-comparison purposes

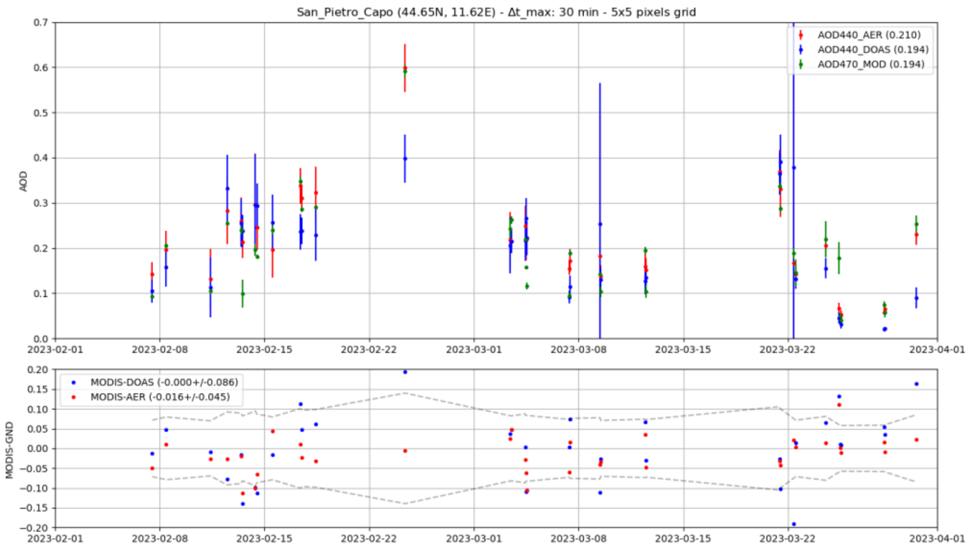


***Figure 9:** Upper panel: Co-located MODIS MAIAC (green dots), SkySpec-2D (blue dots) and AERONET (red dots) AOD products at SPC. The results reported here refer to the analysis performed considering a regular grid of 5x5 km centered on the SPC coordinates and Δt_max (time between MODIS and SkySpec-2D observations) of ±30 minutes. Lower Panel: Absolute differences between MODIS MAIAC and SkySpec-2D*

(blue dots) and between MODIS MAIAC and AERONET (red dots) co-located AOD products at SPC.

Both SkySpec-2D and AERONET AOD products slightly overestimate MODIS MAIAC products. This result is consistent with the distribution of the monthly differences observed in the previous section (Fig. 8). This part of the analysis is performed considering only February and March 2023, and from the previous results (Fig. 8), we observed negative differences in this part of the year. Generally, also considering the other spatial co-location criteria, the differences between MODIS MAIAC and SkySpec-2D are lower. However, the differences between MODIS MAIAC and AERONET AOD products have a lower standard deviation. More generally, the agreement between MODIS MAIAC and both ground-based instruments products are good: considering the MODIS MAIAC EE (grey dashed lines in Fig. 9), most of the matchups are within it.

3.2.3. Inter-comparison against Sentinel-3 SYN AOD products

We also exploit version 1.06 of the Sentinel 3 SYN AOD products. This product has been operated since January 2020 and delivered by ESA in Non-Time Critical timeliness based on SYN product, a synergy of both Ocean and Land Colour Instrument (OLCI, https://sentinels.copernicus.eu/web/sentinel/technical-guides/sentinel-3-olci/olci-instrument) and Sea and Land Surface Temperature Radiometer (SLSTR, https://sentinels.copernicus.eu/web/sentinel/technical-guides/sentinel-3-slstr/instrument). Since the SLSTR retrieval has a variable quality, with higher uncertainty in retrievals in the oblique backscattering direction, the combination with OLCI aims to improve the SLSTR retrieval exploiting additional spectral information from OLCI observations [R7]. The algorithm exploits the L1c co-registered OLCI and SLSTR data product as input, projected on the OLCI grid and it provides several aerosol characteristics, including AOD at different wavelengths, SSA, and Fine-Mode Fraction for both S – 3A and – 3B satellites. The co-registered pixels are grouped into *super-pixels,* formed by blocks of 15 x 15 pixels of the L1c SYN pixels at 300m spatial resolution. The result is a super-pixel of about 4.5 x 4.5 km spatial resolution with aggregated cloud-free TOA radiance for the nadir and oblique view (if present) of the same surface location. The inversion is carried out for land and ocean super-pixels which are at least 50% free of cloud, ice, and snow. Over land, both nadir and oblique must be valid for dual-view retrieval or nadir only for single view (spectral) retrieval, while over-ocean retrieval proceeds if either nadir or oblique super-pixels are valid. Over ocean, AOD is returned using the full swath of the L1c product (1400 km), while over land, the region covered by both nadir and oblique view (750 km) is used for the best-quality retrieval, and aerosol retrieval is also made outside this region where both nadir-only SLSTR and OLCI are available (about 1200 km). Beginning with the L1c product, pixels are flagged to screen cloud, snow ice, or sun glint areas.

		S-3A / Single View (Nadir)				S-3B / Single View (Nadir)				S-3A / Dual View				S-3B / Dual View			
Δt (min)	Grid (km)	N	S3-DOAS	Std. Dev.	r	N	S3-DOAS	Std. Dev.	r	N	S3-DOAS	Std. Dev.	r	N	S3-DOAS	Std. Dev.	r
± 15	5x5	12	0.504	0.233	0.812	7	0.424	0.209	0.329	53	0.057	0.159	0.373	53	0.037	0.119	0.424
	15x15	16	0.446	0.239	0.75	12	0.314	0.189	0.435	62	0.066	0.142	0.465	68	0.055	0.132	0.514
± 30	5x5	12	0.557	0.223	0.863	7	0.432	0.192	0.453	54	0.06	0.157	0.372	53	0.035	0.121	0.398
	15x15	16	0.486	0.214	0.814	14	0.363	0.21	0.603	65	0.059	0.228	0.237	71	0.061	0.147	0.464

***Table 2**: Results of the inter-comparison of S-3 (A and B) SYN and SkySpec-2D AOD products at SPC for the period 1/10/2021 – 30/09/2022 considering different co-location criteria.*

As made for MODIS MAIAC, we evaluated several spatial and temporal co-location criteria to evaluate the effects on the agreement between the SkySpec-2D DEAP and S-3S SYN AOD products. We performed the analysis considering a maximum distance between S-3 SYN products and the SPC site of 5 and 15 km and a maximum time difference between S-3 SYN products and SkySpec-2D observations of ±15 and ±30 minutes. We used the S-3S SYN AOD at 440 nm for both S-3 satellites, and we evaluated the agreement considering the S-3 SYN products retrieved exploiting SLSTR dual view or single view (only nadir for retrieval performed over land). The results are reported in Table 2.

Since the single-view products are quite a few and the sample appears inadequate for statistical analysis, here we mainly focus on the results of the analysis considering the S-3 SYN AOD products retrieved exploiting the SLSTR dual view. We note that the agreement between S-3 SYN and SkySpec-2D AOD products is more sensitive to spatial criterium than the temporal one. As expected, the bias and the standard deviation (except for S-3A with Δt_max = ±15 minutes) increase by moving from 5 to 15 km of the maximum allowed distance. The correlation between the two datasets is quite poor, and relatively low compared with the one observed against MODIS MAIAC and those reported in [R7]. By contrast, with respect to the results reported in [R7], the differences between S-3 SYN and SkySpec-2D AOD products are lower in the case of dual view retrieval. We also highlight a better agreement considering S-3B, and the percentage of coincidences within the GCOS Requirement Measurements Uncertainty is reasonably in line with those observed in [R7].

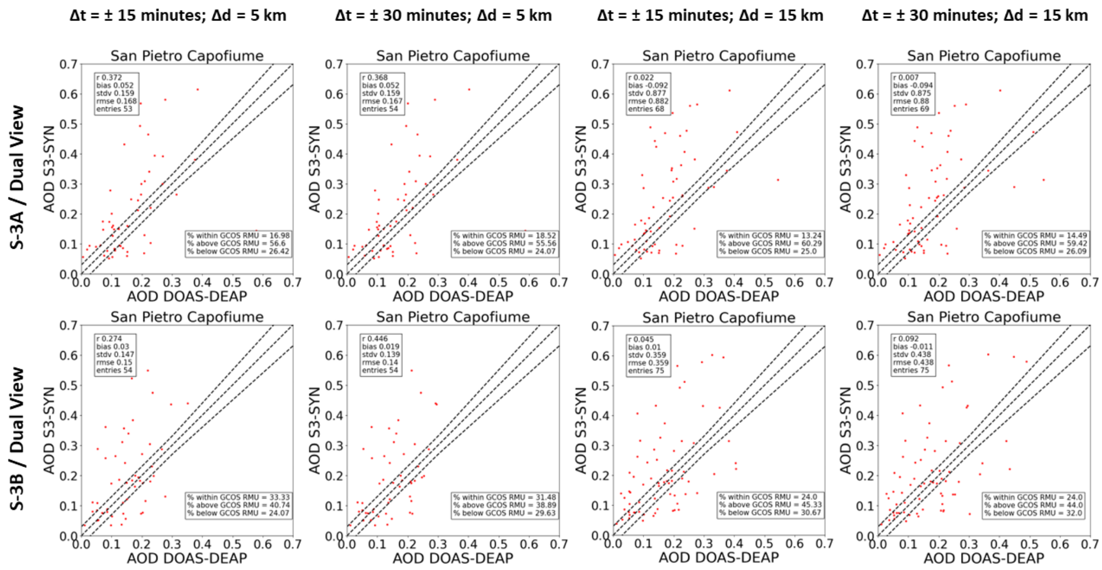


***Figure 10**: Results of the inter-comparison of SkySpec-2D and S-3A (upper row) and S-3B (lower row) SYN AOD products considering different spatial-temporal co-location criteria as reported in the upper part of the plot. The y=x lines and GCOS AOD Required Measurement Uncertainty (Max(0.03;10%)) are plotted as dashed lines.*

The analysis of the differences between the two datasets as a function of the month highlights a similar behavior independent of the co-location criteria adopted. The main discrepancies are in spring, where S-3 SYN AOD products overestimate SkySpec-2D ones. The agreement in summer and autumn improves, with slightly negative differences (S-3 SYN < SkySpec-2D) in summer and positive differences (S-3 SYN > SkySpec-2D) in autumn. In winter, we observe the main difference between the two S-3 satellites, with S-3A showing slightly positive differences and S-3B significant negative differences. This analysis also highlights a bias between the S-3 satellites of 0.05, independent of the co-location criteria.

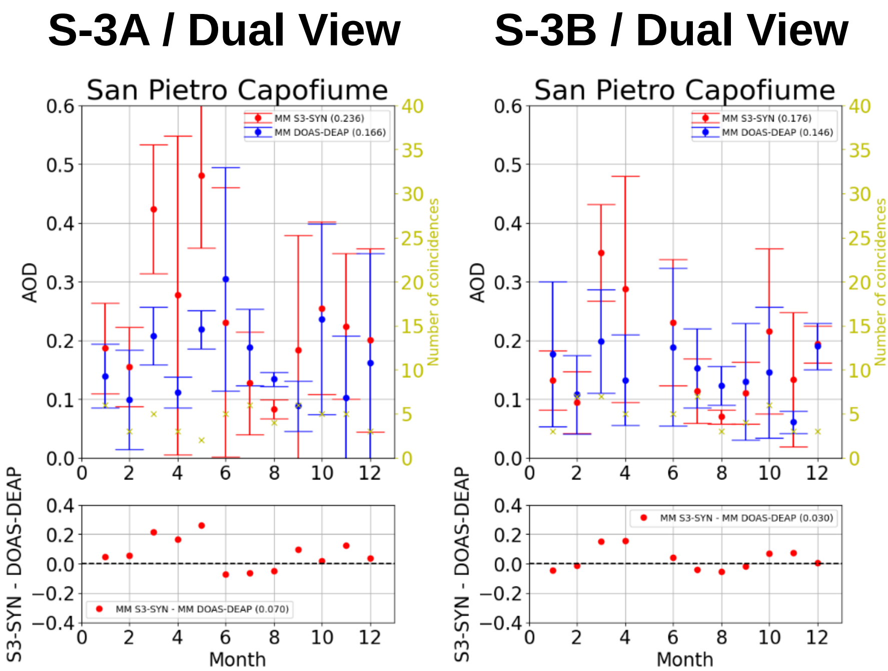


Figure 11: *Results of the analysis of the monthly behavior of the differences between SkySpec-2D and S-3A SYN (left plot) and S-3B SYN (right plot) AOD products. In the upper panels, the monthly averages of and S-3(A/B) SYN (red dots) and SkySpec-2D (blue dots) are reported. The number of coincidences for each month is also reported (yellow dots). In the lower panels, the monthly differences are reported (red dots). The results reported here refer to the analysis performed considering a maximum distance of 5 km and maximum time difference between S-3 SYN and SkySpec-2D observations of ±15 minutes.*

Generally, we observed that the results of the statistics are affected by several outliers. The main cause could be the less than perfect cloud screening. Further investigation fully excluding any pixels containing clouds or removing of cloud edge pixels might be considered.

3.3. Comparison of NO_2 Tropospheric VCDs from SkySpec-2D retrieved using ALC and CIMEL profiles as aerosol extinction initial guess and TROPOMI data

As stated in [R4], the SPC “Giorgio Fea” observatory is equipped with an LD40 Vaisala Automatic Lidar Ceilometer (ALC). Those data have been used in [R1] for a qualitative inter-comparison with DEAP retrievals and to detect cloudy days. For DEAP retrievals, we used a smooth and constant aerosol extinction profile. The use of a more realistic profile should improve the convergence and produce better results, also in terms of NO_2 retrievals.

For this reason, we tested the use of ALC profiles as an initial guess. Since the output of ALC is not converted into a physical quantity but is only given in terms of arbitrary units, we can only exploit the extinction profile shape from ALC (no quantitative information). We then decided to use as a-priori an extinction profile with the shape given by the ALC measurement collocated (in time) with each MAX-DOAS scan and whose AOD is normalized at the same values used as a-priori in the processing reported in Sect. 3. The ALC profile is interpolated on the MAX-DOAS retrieval altitude grid. An example of this procedure is shown in the left panel of Fig. 12. We repeated the retrieval using these new profiles and the same setup reported in Sect. 3 (the measurements collected on the 10th of October 2021 at 300 degrees azimuth). In the right panel of Fig. 12, we report the Chi-square obtained with the original and the modified (with ALC) a-priori profiles. As can be seen, the Chi-square decreases significantly when the ALC data are used as a-priori.

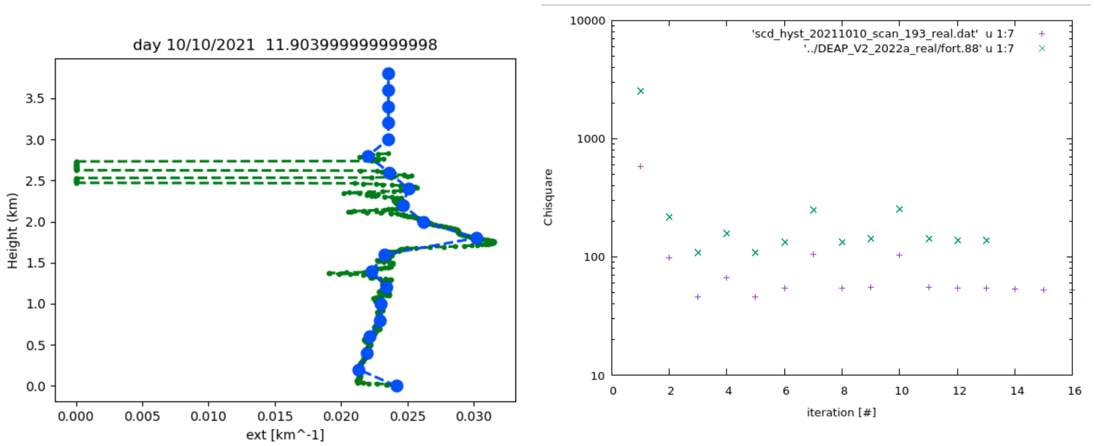
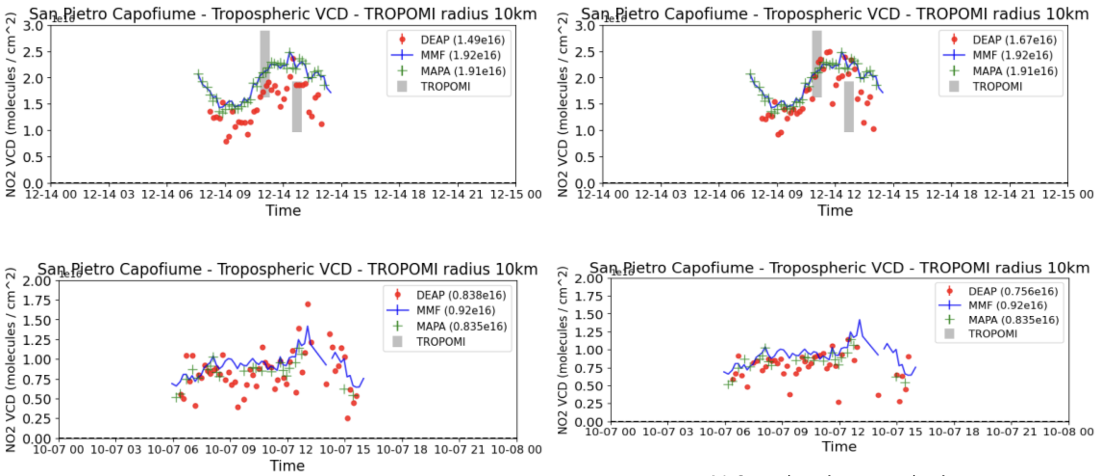


Figure 12: *Aerosol extinction profile for a-priori as extracted from ALC (left, see text for details) on 10 October 2021, Chi-square for scan #183 on the 10 October 2021 using standard and ALC a-priori extinction profile.*

The impact of the quality of retrieved aerosol extinction profiles on the subsequent NO_2 retrieved profiles is a well-known issue. Thus, an estimate of the impact of using different aerosol a-priori can be inferred from NO_2 retrievals. Fig. 13 shows the values of Tropospheric VCDs retrieved with SkySpec-2D and the DEAP code using standard and ALC a-priori initial guess profiles for 14 December 2021 (top) and 7 October 2021 (bottom, extremely cloudy day). Since February 2023, the SPC observatory has been equipped with a CIMEL sun photometer. The CIMEL is part of the AERONET network (https://aeronet.gsfc.nasa.gov). The AOD Level 1.5 files retrieved from SPC have been available from the website since 6 February 2023. We exploit these data for two different applications: 1) to compare them with AOD retrieved from MAX-DOAS measurements, and 2) to constrain the AOD of the profile used as a-priori. In this last case, we repeat the procedure above and extract the shape of initial guess extinction profiles from ALC coincident data and their AOD from CIMEL collocated measurements (AOD at 440 nm is used here).



Standard extinction a-priori

ALC extinction a-priori

Figure 13: *NO_2 Tropospheric VCDs from SkySpec-2D on 12 December (top) and 10 October 2021 (bottom) retrieved using standard a-priori exaction profile (left) and a-priori as extracted from ALC (right).*

As an example, we use the data retrieved on the 12th of February 2023. The extinction profiles retrieved from MAX-DOAS measurements (visible channel from 430 nm to 490 nm used for the analysis) at 315 azimuth degrees when no a-priori information on aerosols from SPC data are used are reported in Fig. 14 (left panel) in comparison with the ones from the ALC (Fig. 13, right panel). As can be seen, the MAX-DOAS instrument well captured the larger extinction between 0.6 km and the ground between 11 and 16 UTC.

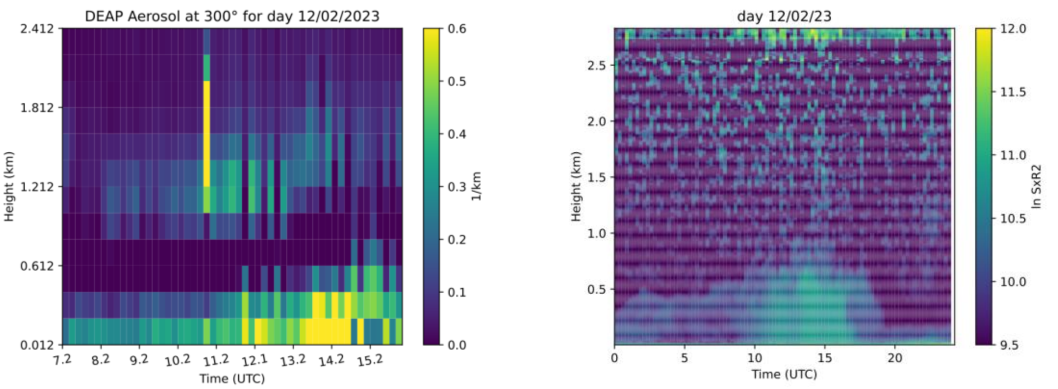


***Figure 14:** Aerosol extinction profiles from the SkySpec -2D on 12 February 2023 (left, the altitude range of the plot is reduced to match the one from ALC) and aerosol information from ALC data (right) for the same day.*

The AOD products obtained from the integration on altitude domains of the above-mentioned MAX-DOAS measurements in comparison to those from AERONET at 440 nm are reported in Fig. 15. The results show good agreement in both the shape and values of AOD, especially in the first part of the day. The MAX-DOAS AOD show more oscillations. Both the extinction profile shape and the AOD retrieved from the MAX-DOAS measurements agree well with coincident remote sensing aerosol measurements from ALC and CIMEL, demonstrating the sensitivity of MAX-DOAS measurements to aerosol extinction.

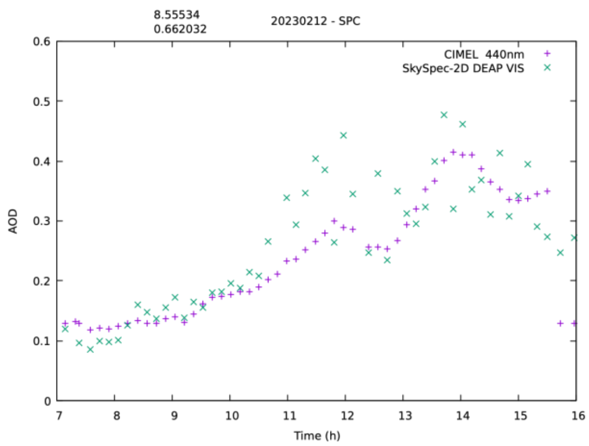


***Figure 15:** AOD from SkySpec -2D on 12 February 2023 (green) and from co-located CIMEL measurements at 440 nm.*

As already highlighted, the quality of the aerosol extinction retrieval significantly impacts on the subsequent NO_2 retrievals from MAX-DOAS measurements. The NO_2 Tropospheric vertical columns retrieved for this day from SkySpec-2D are reported in Fig. 16 (left panel) in coincidence with TROPOMI data. In Fig. 17 (left panel), we show the results of NO_2 retrieved at the surface against in-situ ARPAE data. Despite some oscillations, the Tropospheric VCD and the surface values retrieved from SkySpec-2D agree quite well with satellite and in-situ measurements.

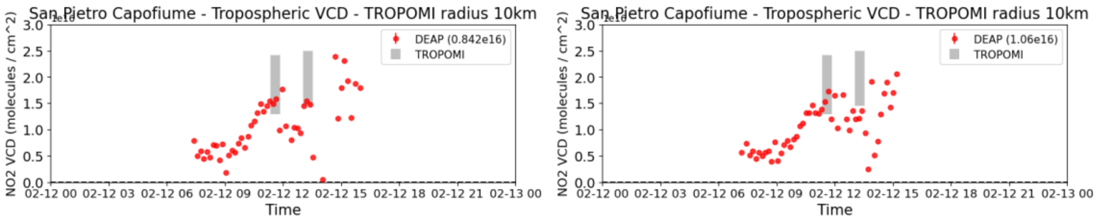


***Figure 16:** NO_2 Tropospheric VCD from SkySpec -2D on 12 February 2023 (red) and from collocated TROPOMI data (grey). Left: no a-priori information on aerosol extinction from SPC instruments used for the retrievals. Right: use of a-priori information on aerosols from ALC and CIMEL*

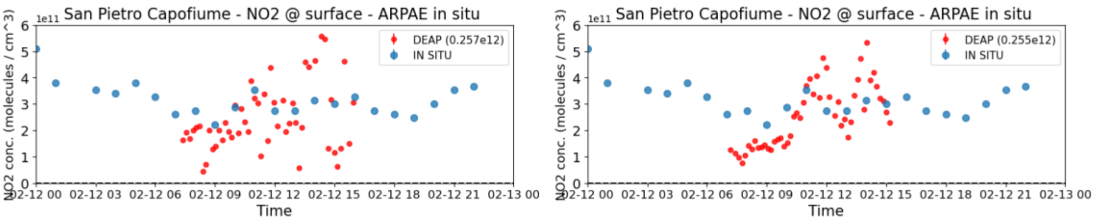


***Figure 17:** NO_2 at the surface from SkySpec-2D on 12 February 2023 (red) and from collocated ARPAE data (blue). Left panel: no a-priori information on aerosol extinction from SPC instruments used for the retrievals. Right panel: use of a-priori information on aerosols from ALC and CIMEL.*

Then we repeat the retrieval from MAX-DOAS measurements for this day using as a-priori extinction profile the one obtained from the combination of ALC and AERONET data as explained above. The results of this test are reported in the right panels of Figs. 14 and 15. As can be noticed, the results are quite similar to those obtained with the standard a-priori extinction profile. However, they show a smoother behavior on both the VCDs and the surface values and agree slightly better with comparative data. This result shows, on one side, the added value of correlative aerosol information (from ALC and CIMEL) and, on the other side, still assesses the quality of MAX-DOAS measurements also when used without the use of any additional information.

4. Conclusions

In this report, we analyse the results obtained from the analysis of one year (from October 2021 to October 2022) of MAX-DOAS measurements in the Po Valley. NO_2 Tropospheric columns show higher values in winter than in summer. The comparison of SkySpec-2D Tropospheric VCDs with the TROPOMI ones shows a positive bias of

0.4*10^{15} mol/cm^2, in agreement with the observed TROPOMI tendency in underestimating NO_2 Tropospheric VCDs in polluted regions. MAX-DOAS retrievals are considered as reference measurements for DOAS and NO_2 satellite validations. The GCOS ECVs requirements 2022 [R8] for NO_2 Tropospheric columns are: Goal max 20% (1*10^{15} mol/cm^2), Breakthrough max 40% (2*10^{15} mol/cm^2), Threshold max 100% (5*10^{15} mol/cm^2). In the light of these values, the bias of +0.4*10^{15} mol/cm^2 we found with respect to TROPOMI data is really good (within the goal value).
The retrieval of aerosol extinction profiles is crucial in MAX-DOAS analysis: a wrong aerosol estimation can lead to significant NO_2 biases. Despite the comparison of AOD retrieved with SkySpec-2D and Sentinel 3 SYN AOD shows poor agreement, the comparison with MODIS MAIAC and AERONET AOD shows significantly better results with a really good agreement (bias below 0.02 against MODIS MAIAC). Keeping in mind the GCOS ECVs requirements 2022 [R8] for Multi-wavelength Aerosol Optical Depth (Goal 4%, or 0.02; Breakthrough 10%, or 0.03; Threshold max 20%, or 0.06), the biases we observed are on average lower than 0.07 against S3-A/B considering the dual view approach (0.6 for the nadir view only) and below 0.02 against MODIS (Terra/Aqua) MAIAC. Even if only for a brief period (February/March 2023), MODIS MAIAC values agree very well with coincident AERONET data, suggesting that the quality of MAX-DOAS retrieved AOD is quite close to the one retrieved from state-of-the-art measurements. This result is very encouraging mainly because MAX-DOAS data are not considered the reference for AOD retrievals.
Due to the impact of aerosol extinction on the subsequent NO_2 retrievals, we also test the use of correlative information from ALC and AERONET data as a-priori for aerosol determination. The results of NO_2 retrievals for some test cases are promising. However: 1) the difference with respect to the retrieval with blind a-priori extinction is not so relevant, and 2) the AOD retrieval with blind a-priori well compares with AERONET retrieval. Using the correlative information from AERONET will result in losing independence from these networks for comparisons. For these reasons, the NO_2 retrievals using as a-priori the information from coincident ALC and AERONET data are only performed for a few cases, while an extensive analysis is performed using blind a-priori for both aerosols extinction and NO_2.

5. Acknowledgment

AOD AERONET data is downloaded from AERONET website. We thank the Project PI Luca di Liberto and Co-PI Angelo Lupi for their effort in establishing and maintaining San Pietro Capofiume sites. ARPAE NO_2 in-situ data are downloaded from https://sdati-test.datamb.it/arex/.

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