D-3 Report on measurements campaign within the ISAC-CNR (Bologna) site exploiting in-situ and the satellite-borne synergies

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

Document reference:	FRM4DOAS-BO_D3
Document Issue:	1.0
Document Issue date:	22/07/2021
Document authors and affiliations:	E. Castelli[1], P. Pettinari[1], E. Papandrea[1], P. Cristofanelli[1], M. Busetto[1], M. Valeri[2] [1] ISAC-CNR [2] Serco Italia

AMENDMENT RECORD SHEET

The Amendment Record Sheet below records the history and issue status of this document.

ISSUE	DATE	REASON
1.0	18/07/2021	D-3 document of project "WPs-2250-2251: DOAS-BO: Towards a new FRM4DOAS-compliant site'".

Table of contents

1 List of Acronyms

ACTRIS	Aerosol, Clouds and Trace gases Research InfraStructure
AKM	Averaging Kernel Matrix
AMF	Air Mass Factors
ARPAE - SIMC	Agenzia Regionale per la Protezione Ambientale Emilia - romagna - Servizio Idro - Meteo - Clima
BOX-AMF	Box - AMF
CCD	Charge - Coupled Device
CNR	Consiglio Nazionale delle Ricerche
DOAS	Differential Optical Absorption Spectroscopy
DOF	Degree of Freedom
FOV	Field Of View
FRM4DOAS	Fiducial Reference Measurements for DOAS
GAW	Global Atmosphere Watch
ISAC	Istituto di Scienze dell'Atmosfera e del Clima
LOS	Line of Sight
LUT	Look - Up Table
MAX-DOAS	Multi AXis – DOAS
MLE	Minimum - amount Langley Extrapolation
NDACC	Network for the Detection of Atmospheric Composition Change
SCD	Slant Column Density
SODCAL	Scanning Optical Device Collecting Atmospheric Light
TROPOGAS	TROPOspheric Gas Analyzer Spectrometer
TROPOMI	TROPOspheric Monitoring Instrument
UV	UltraViolet
VCD	Vertical Column Density
VCM	Variance Covariance Matrix
WMO	World Meteorological Organization

2 Introduction

This document reports the activities performed in the frame of the WPs 2250-2.1, 2250-2.2 and 2251-2.3 of the "WPs 2250-2251: DOAS-BO: Towards a new FRM4DOAS - compliant site" project.

3 Project tasks

The WPs 2250-2.1, 2250-2.2 and 2251-2.3 of the project are mainly centred on the measurement campaign performed in Bologna at the Istituto di Scienze dell'Atmosfera e del Clima - Consiglio Nazione delle Ricerche (ISAC-CNR) with the

TROPOspheric Gas Analyzer Spectrometer (TROPOGAS) instrument and reporting the obtained results in the light of the exploitation of synergies with in-situ (Sect. 3.2) and satellite (Sect. 3.3) measurements.

3.1 WP 2250-2.1: Measurement campaign within ISAC-CNR (Bologna) site

In the frame of the project, two measurement campaigns are foreseen with different applications. The first one took place in Bologna at ISAC-CNR premises in April-May 2021. The campaign was performed with the TROPOGAS updated measurement configuration that follows the Fiducial Reference Measurements for Differential Optical Absorption Spectroscopy (FRM4DOAS) guidelines (see [D - 1] and [R - 1]) as described in section 3.1.1.

3.1.1 TROPOGAS measurement configuration

As described in [D - 1], in WPs 2250-1.1 and 2250-1.2 of this project, we assessed the compliances of the TROPOGAS spectrometer to FRM4DOAS requirements regarding the measurement set-up. The outcome of those WPs were an updated measurement strategy and a different L1B file format.
The Bologna measurement campaign was performed using this final measurement set-up:

1) Zenith measurements in the spectral window centered at 486 nm for SZA larger than 85°, Multi AXis – DOAS (MAX-DOAS) scans (1°, 2°, 3°, 5°, 10°, 30°, 90° elevation degrees) measurements in between, in windows centered at 365, 461 and 486 nm.
   The time required for one full measurement scan depends on the integration times of the single acquired spectra that are related to the spectral window and the time.
   In the worst case (in the spectral window centered around 365 nm and during sunrise or sunset) one full measurement scan takes about 12 minutes, while in best conditions (spectral window around 486 nm and at noon) it takes about 4 minutes.
   Also, the acquisition frequency of zenith sky-spectra depends on the same variables. Zenith sky measurements are acquired every 8 minutes under best conditions and about every 20 minutes in the worst case.
2) Two Azimuthal viewing angles (at 5° and 190°), one looking towards Bologna city centre (190°), the other towards the Po Valley (5°). In this way, we can analyse possible differences due to air masses origins.
3) Every acquired spectrum is the average of 36 single spectra, in order to increase the SNR. One dark current measurement is performed at the end of the 36 single spectra acquisition.
   The averaging of 36 spectra allows to increase the SNR from a mean value of 500 to 3000. However, since this procedure increases the total acquisition time of one spectrum, the probability of introducing inhomogeneities in the field of

view (FOV) during the measurement also increases, mainly in the presence of clouds.

4) Saturation value=65535, minimum exposure time=0.4 s, maximum exposure time=3.0 s.
   At the end of March/beginning of April, we implemented the new measurement strategy. It required some time to get the correct trade-off for the automatic computation of the exposure time, with the purpose to provide high enough signals without reaching saturation. Actually, a too big integration time sometimes produces better SNR but with the possible introduction of inhomogeneity in the measurement conditions. On the other hand, low integration times lead to non-linear spectral behaviours. The choice of these integration time limits also has the purpose to avoid long times for one scan acquisition and between two consecutive zenith measurements.
   Since several days of this period were characterized by cloudy weather, it took some time to get the correct trade-off.
5) Measurements acquired in three spectral intervals centred on: 365 nm, 461 nm, 486 nm with about 60 nm bandwidth. Those bands are chosen to cover NO_2, O_3, O_4 and HCHO absorption features.

As reported in [D - 1], the TROPOGAS FOV is larger than FRM4DOAS requirements (3.5° versus 1.5°). Since this characteristic is intrinsically related to the instrument design, we have to cope with this limitation during data processing. The Field of view (FOV) aperture does not affect zenith or high elevation angle measurements. Instead lower angles (1°, 2° elevation) are affected. In order to estimate the impact of this instrumental limitation, we performed some simulations using the SCIATRAN code. Results and considerations are reported in Appendix A.

3.1.2 TROPOGAS Measurement campaign

The Bologna measurement campaign was performed from the 15th of April to the 3rd of June. Before the campaign, a testing phase from the 26th of March to the 10th of April was performed. As already said, this phase was necessary to make a trade-off analysis to tune automatic exposure time versus zenith sky measurement acquisition frequency and versus saturation of CCD counts.
Apart from two interruptions on 18th and 30th April due to technical problems, the instrument acquired the data continuously.
Typical Spring conditions characterized April and May 2021, with strongly variable weather and large temperature excursions. In the upper panel of Fig. 1, we report rain intensity and duration from measurements at ISAC premises. Instead, in the lower panel, we show the downward irradiance at the “Bologna Urbana” station (data from Agenzia Regionale per la Protezione Ambientale Emilia-romagna - Servizio Idro-Meteo-Clima, ARPAE - SIMC).

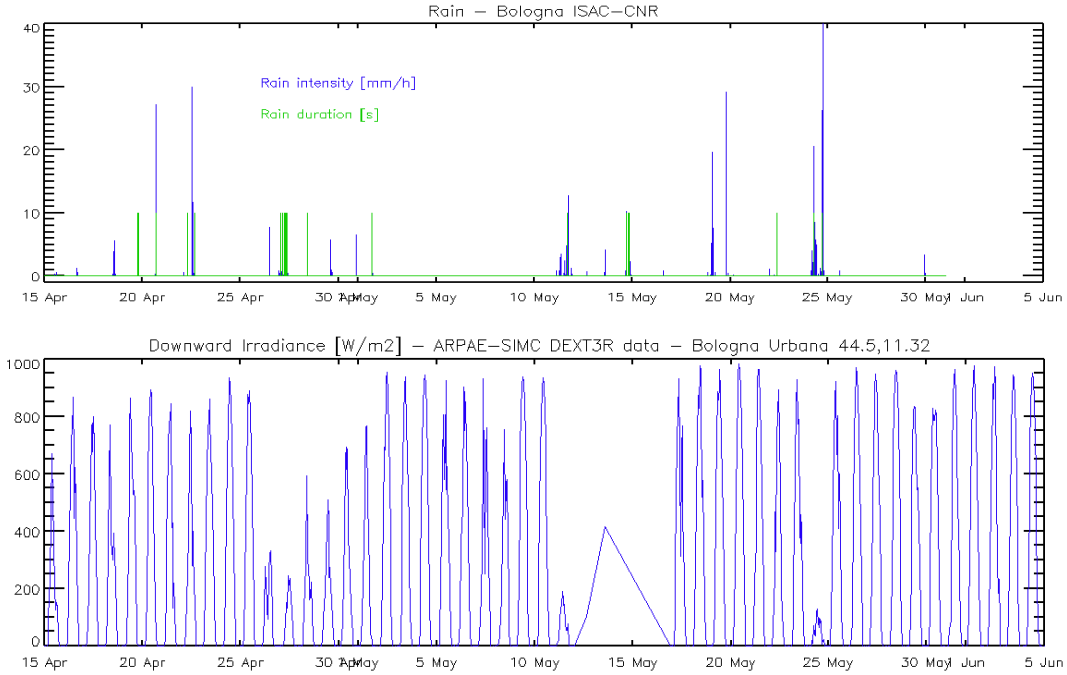

***Figure 1**: Upper panel: Rain data at ISAC-CNR as a function of time. Lower panel: Downward Irradiance at "Bologna Urbana" station as a function of time. Both data from ARPAE - SIMC DEXT3R dataset (https://simc.arpae.it/dext3r/).*

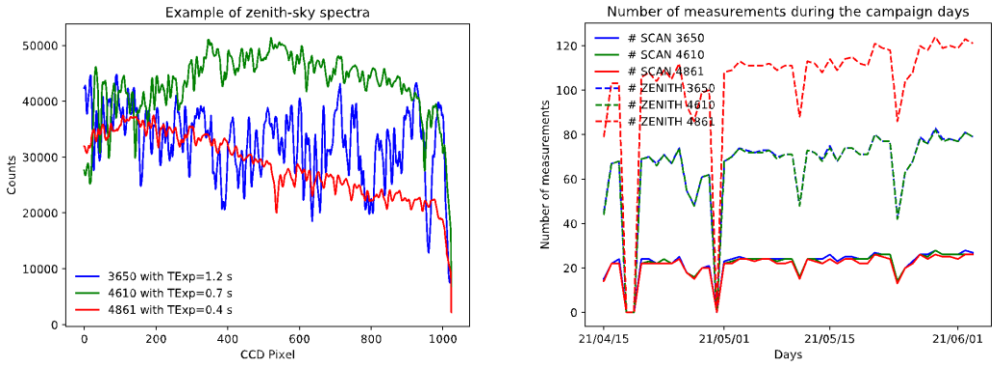

***Figure 2**: Left panel: example of zenith-sky spectra acquired in the three spectral windows with different exposure times. Spectra are neither spectrally nor radiometrically calibrated. Right panel: number of scans and zenith-sky spectra acquired every day in the three spectral windows.*

We acquired about 20 MAX-DOAS scans for each day and 60-100 (depending on spectral range) Zenith measurements per day (Fig. 2 right panel). All the measured spectra were written in netCDF format following the FRM4DOAS requirements, as reported in [D - 1], and delivered to ESA in the [D - 2A] (Dataset of Level 1 spectra in FRM4DOAS format acquired during the measurement campaign within the ISAC-CNR (Bologna) site).

Furthermore, an elevation calibration was performed on the 25th of May. The description of the used procedure is given in Appendix B.

3.1.3 TROPOGAS data analysis: from zenith sky spectra to VCD

The final products for FRM4DOAS network are the L1B spectra in netCDF format since centralized processing is foreseen for L2 production. However, to check the quality of produced measurements, a comparison of obtained Vertical Column Density (VCD) from zenith sky spectra with satellite data is highly desirable. For this reason, we analyse the TROPOGAS spectra with the QDOAS software to obtain NO_2 and O_3 Slant Column Densities (SCDs). Then, using the Network for the Detection of Atmospheric Composition Change (NDACC) Air Mass Factors (AMF), we retrieve NO_2 and O_3 VCDs from zenith sky measurements.

The TROPOGAS L1B spectral data analysis to obtain NO_2 and O_3 VCDs is described in this section.

Zenith sky and MAX-DOAS scan spectra acquired by TROPOGAS are analysed by the QDOAS software (http://uv-vis.aeronomie.be/software/QDOAS) in order to retrieve the O_3, NO_2 and O_4 SCDs.

The analysis reported here has been performed in the spectral interval between 460-490 nm, exploiting the spectra acquired in the spectral window centred at 486 nm. In this spectral region, features of NO_2, O_3 and O_4 are present. O_4 is used for the detection of aerosol and cloud presence that can bias NO_2 and O_3 SCDs.

The QDOAS settings (Tab. 1) used for the analysis follow as much as possible the FRM4DOAS community requirements. A detailed description of the used settings is given below.

We analysed all the spectra with respect to a fixed reference spectrum. We choose a noon spectrum recorded on the 24th April 2021 as a reference due to the particularly clear sky conditions on that day. A constant offset between the analysed and reference spectra and an order 3 polynomial are fitted simultaneously with NO_2, O_3, O_4, H_2O absorption cross sections. The ring effect is considered by means of a further one cross section (for more details see [R - 2]). Since NO_2 and O_3 cross sections depend on temperature, the absorption signature for each of both gases is fitted by two cross sections at different temperatures. Exploiting a new QDOAS option, available for versions higher or equal to 3.4, the higher temperature cross section is subtracted to the other one. In this way, their temperature dependence is linearized and the SCDs are fitted considering an effective atmospheric temperature. Moreover, NO_2 and O_3 theoretical cross sections are corrected through the convolution with I0 correction [R - 3].

Wavelength range	460-490 nm
Polynomial	Order 3
Offset	Constant
Cross sections:	
• NO_2 (220 K)	Vandaele et al 1996 with I0 correction (10E+17)
• NO_2 (298 K)	Subtracted Vandaele et al 1996 with I0 correction (10E+17)

• O_3 (223 K)	Bogumil et al 2003 with I0 correction (10E+20)
• O_3 (293 K)	Subtracted Bogumil et al 2003 with I0 correction (10E+20)
• O_4 (293 K)	Hermans et al 1999
• Ring	Generated according to Chance and Spurr 1997, using the solar atlas (Chance and Kuruck 2010)

***Table 1**: Main QDOAS settings used for NO_2 and O_3 SCDs analysis.*

An example of the differential optical paths, due to the NO_2, O_3 and O_4 absorption, fitted by QDOAS (https://uv-vis.aeronomie.be/software/QDOAS/) from a spectrum acquired after the adoption of the new measurement strategy is reported in Fig. 3. NO_2, O_3 and O_4 spectral signatures are well defined compared to the fit residuals. In Fig. 4, we show the same quantities fitted from a spectrum acquired with the old measurement strategy. The effect of the higher SNR, due to the new average strategy described in subsection 3.1.1, is evident in the fit residuals.

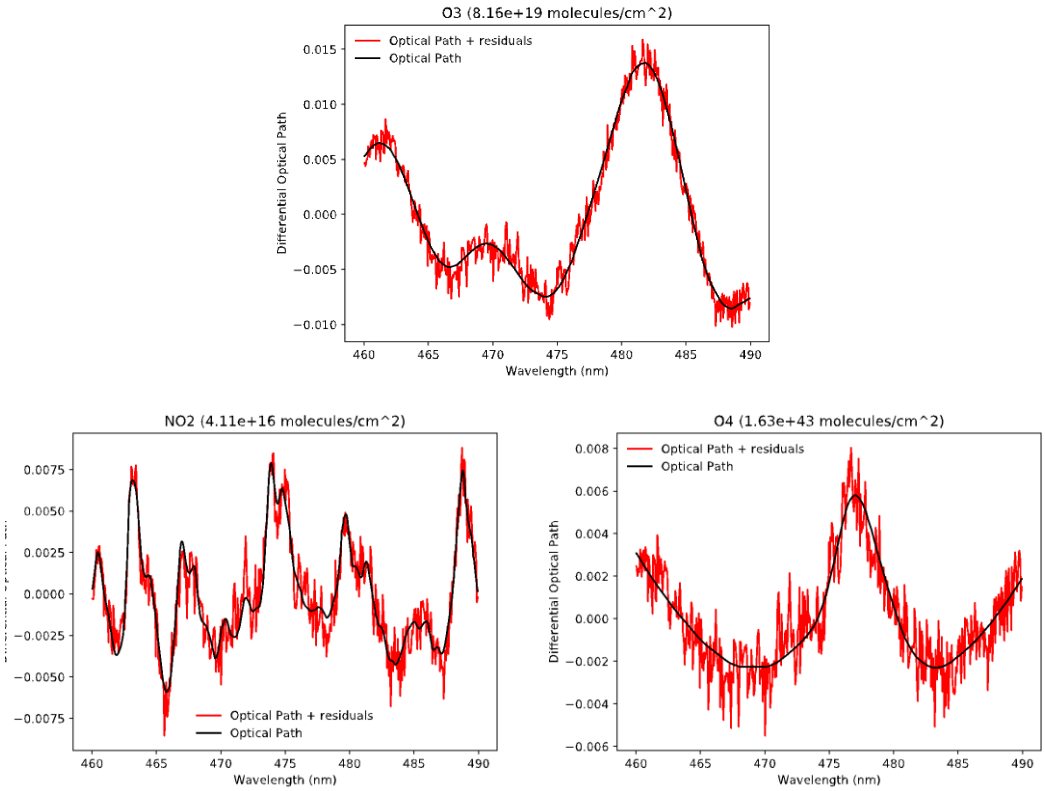

***Figure 3**: Examples of O_3, NO_2 and O_4 SCDs fitted by QDOAS after the adoption of the new measurement strategy. These fits refer to a spectrum acquired at 05:07 of 12/05/2021.*

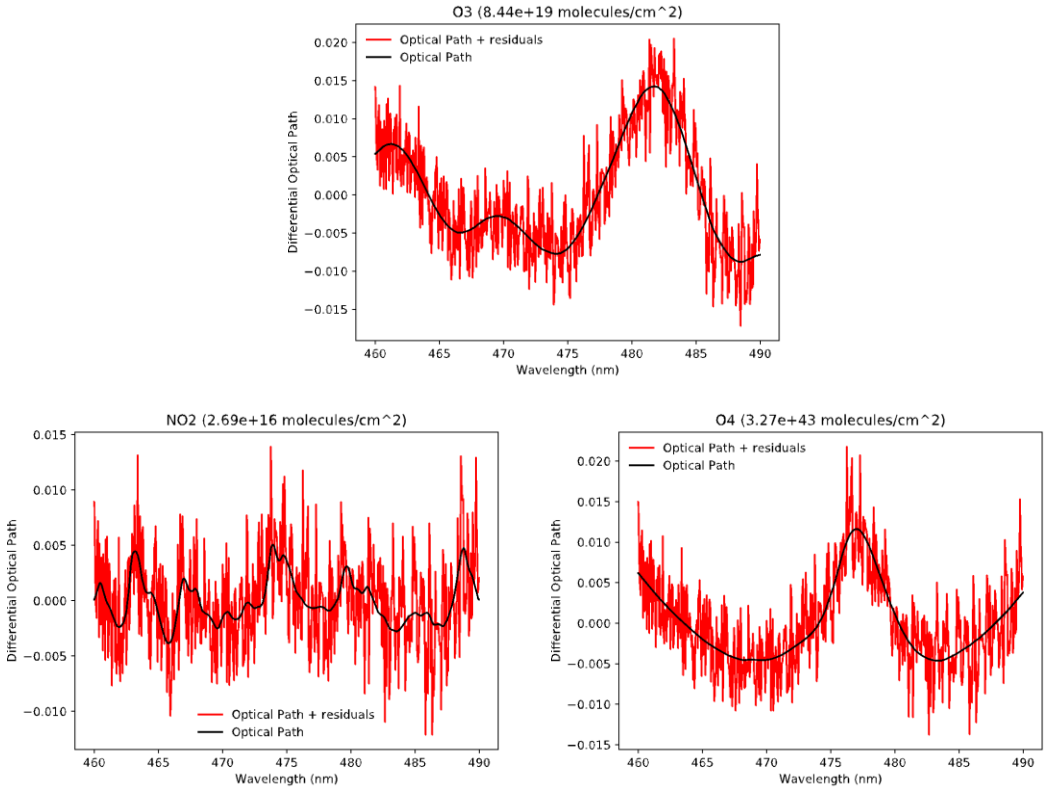

***Figure 4**: Examples of O_3, NO_2 and O_4 SCDs fitted by QDOAS before the adoption of the new measurement strategy. These fits refer to a spectrum acquired at 19:04 of 20/05/2020.*

The obtained NO_2 and O_3 SCDs are, then, filtered according to two criteria: the first one uses a QDOAS flag that certifies whether the fit was successful or not. Then, a second filter has been applied in order to exclude data heavily contaminated by clouds. Since SCDs are path-integrated quantities, variations in the light path due to scattering by particles produce biased SCDs and thus VCDs values.

As demonstrated by Wagner et al. [R - 12], O_4 SCDs can be used to infer information on particles' optical depths and vertical distribution. The O_4 SCDs behaviour with respect to the SZA can be modelled using a Radiative Transfer Model (RTM, e.g., SCIATRAN, [R - 4]). However, in several cases, as reported by [R - 5], the RTM modelled O_4 SCDs can differ (as a bias, so in absolute values not in the behaviour) from the measured ones. For this reason, to filter the data we decided to use the measured O_4 SCDs. The data are used to build histograms binning the SCDs every 2 SZA degrees. The maximum frequency for each SZA bin behaviour as a function of SZA follows the modelled one (not shown) in clear sky conditions. Data that fall outside 75% of the maximum frequency are filtered out (Fig. 5). We should mention that using this filtering procedure, particles contaminated spectra may still be present. Indeed, this method aims at filtering only spectra heavily contaminated by particles and to remove strong oscillations from the final dataset.

The O_3 and NO_2 SCDs measured from spectra identified as particles contaminated by the O_4 SCDs filtering are removed from the subsequent analysis. Finally, the 9% of measured SCDs has been filtered out.

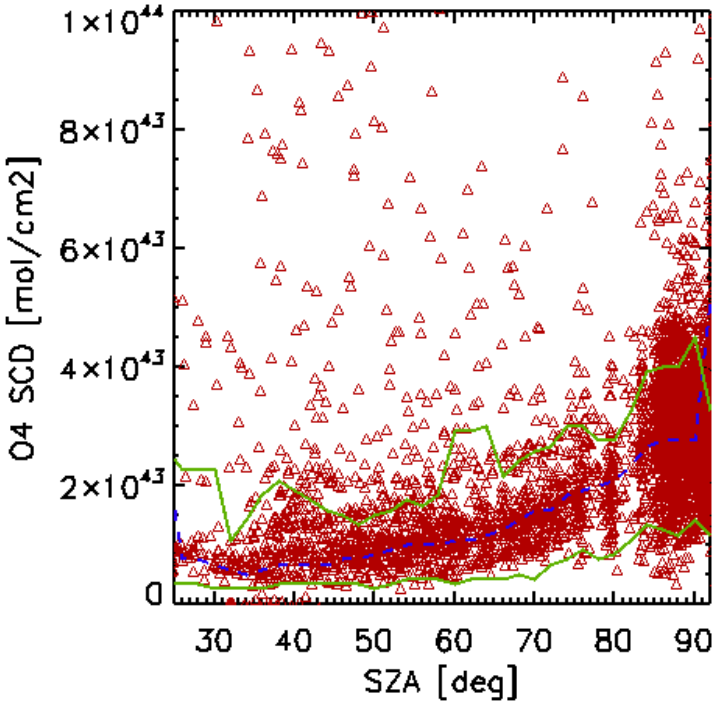

***Figure 5**: O_4 SCD as a function of SZA for May 2021 as measured by TROPOGAS. Blueline represents maximum frequency. The green line is the 75% limit (see text for details).*

The remaining SCDs are then processed in order to compute the VCDs. SCDs retrieved by the QDOAS represent the concentrations measured along the light path with respect to the spectra measured at low SZA, chosen to minimize the absorption along the shorter light path. However, also in the reference spectra, the absorber amount cannot be considered as completely negligible as it will be e.g., in spectra measured outside the atmosphere. For this reason, the correct calculation of VCD requires that the QDOAS SCDs are corrected by adding the SCD amount of the reference spectra. Here this is done using the Minimum-amount Langley Extrapolation (MLE) method as described in [R - 6]. The estimated NO_2 reference contribution is 1.3E+16 mol/cm^2, while for O_3 it is 3.05E+19 mol/cm^2.
The VCDs are then calculated by dividing the corrected SCDs by the corresponding AMF. We used the NDACC AMF to calculate the NO_2 and O_3 VCDs. The values of the AMF are obtained from NDACC look-up tables (LUTs) using the information on required wavelength, SZA day of the year and latitude/longitude position.

3.1.4 TROPOGAS data analysis: from MAX-DOAS spectra to ppb at the surface

MAX-DOAS measurements allow retrieval of tropospheric profiles of NO_2, aerosol extinction and HCHO. Even at lower altitude resolution with respect to the in-situ

measurements, the last retrieved point of MAX-DOAS profiles is directly comparable with in-situ surface measurements.
The development of a MAX-DOAS profile retrieval algorithm, although highly desirable to fully exploit the synergy of a measurement site with ground-based and in-situ instrumentation, is beyond the scope of this work.
However, since it is essential to understand the feasibility, synergies and limits of the direct comparison of in-situ and ground-based data, we developed a simple approach to estimate NO_2 at the surface from TROPOGAS MAX-DOAS measurements.
MAX-DOAS profile retrieval algorithms are composed of two steps [R - 7]. At first, the aerosol extinction profile is calculated following an iterative approach exploiting O_4 SCDs at MAX-DOAS elevation angles between 1° and 30°. Then, the retrieved extinction profile is used to calculate the NO_2 (or HCHO) Box - Air Mass Factors (BOX-AMF) and to retrieve the NO_2 (or HCHO) profile. Since this is a linear problem, no iteration is required. While both these two steps require the use of an RTM, the aerosol part requires iteratively calculate the derivative of O_4 SCD with respect to aerosol extinction, while the gaseous part requires only one calculation of BOX-AMF one time This can be done using the SCIATRAN code. Gas profiles are calculated via:

$$x_i = x_0 + \mathbf{S}_0\mathbf{K}^T(\mathbf{K}\mathbf{S}_0\mathbf{K}^T + g\mathbf{S}_y)^{-1}(y - \mathbf{K}x_0) \qquad [1]$$

Where x_I is the retrieved profile, x_0 is the initial guess profile used for BOX-AMF calculation, $\mathbf{K}$ is the BOX-AMF matrix, $\mathbf{S}_0$ is the a-priori variance-covariance matrix (VCM) matrix, g is a damping factor, $\mathbf{S}_y$ is the SCDs VCM matrix, y is the vector containing the measured NO_2 or HCHO SCDs at different elevation angles minus the corresponding SCD at 90°. The SCDs calculated at each elevation angle are obtained with the QDOAS software as reported in the previous section. No O_4 data filtering has been performed over MAX-DOAS SCDs.
In this project, we used this formula to estimate the NO_2 profiles retrieved from TROPOGAS MAX-DOAS SCDs. No aerosol retrieval is performed (since this requires complex and complete code development and validation). The aerosol profile used for NO_2 BOX-AMF calculation is consistent with low aerosol content. This will provide reliable results under clear sky scenarios while large deviations can be obtained in cloudy conditions or when the aerosol load is high.
One month of data was analysed using this strategy and the results at lower levels compared with the in-situ ones. Even if not conclusive, this analysis can give a hint on the possibility of exploiting the performed in-situ and remote sensing measurement synergies to study the air quality processes in Bologna. In case of positive results, a complete retrieval code development and validation, following the guidelines of the FRM4DOAS network, is recommended.
NO_2 profile retrieval for the Bologna campaign was performed using the following settings. For consistency with FRM4DOAS practices most of them come from [R - 8]:
Box-AMF calculated with fixed aerosol profile with AOT = 0.15 at 480 nm, asymmetry factor 0.68, NO_2 a-priori VCD of $2.4e^{+16}$ mol/cm^2, NO_2 at surface 1.75^{E+11} mol/cm^3 exponentially decreasing with altitude. For the Sa calculation, NO_2 a-priori error was set to 50% of the initial guess profile, with a vertical correlation length of 200m, the damping factor is 0.005. We retrieve one point every 200m from the surface up to 4

km. For this analysis we consider only scans looking towards Bologna city, pointing calibration as in Appendix B has been taken into account for this exercise.

3.2 WP 2250-2.2: Exploitation of the in-situ synergies

3.2.1 In-situ instrumentation

In situ "near-surface" NO_2 measurements were performed using a NOx chemiluminescence analyser (http://www.teledyne-api.com/products/nitrogen-compound-instruments/t200up) equipped with a photolytic converter for NO_2 determination. Since the 9th of April, the instrument has been installed into the same shelter, on the top of the ISAC-CNR building roof in Bologna, where the TROPOGAS spectrometer is placed (Fig. 6 left panel). The instrument provided day and night near real-time online measurements of NO, NO_x, NO_2 (Fig. 6 right panel, time resolution 1 minute). The instrument used the chemiluminescence technique for detecting and quantifying NO and NO_2. The NO_2 present in the air sample must be converted to NO (by using the NO_2 photolysis) before detection. The instrument was calibrated at the Mt. Cimone World Meteorological Organization / Global Atmosphere Watch (WMO/GAW) station before the deployment at Bologna. The calibration factors (including the NO_2 to NO conversion efficiency) were assumed not to change during the Bologna experiment, however, the calibration was repeated at the end of the campaign. The instrumental detection limit was assessed to be 0.02 for NO and 0.05 for NO_2.

The in-situ near-surface NO_x observations were corrected for ozone and water vapor interferences. In particular, the corrections recommended in [R - 11] were implemented for NO (water vapor quenching in the reaction chamber and ozone titration in the inlet line) and NO_2 (ozone NO titration in the inlet line). Moreover, as said, after the experimental campaign, the instrument was tested at the Mt. Cimone WMO/GAW global station to evaluate the stability of calibration factors. To this aim, automated calibration following the Aerosol, Clouds and Trace gases Research InfraStructure (ACTRIS) guidelines [R - 11] was repeated over 7 days.

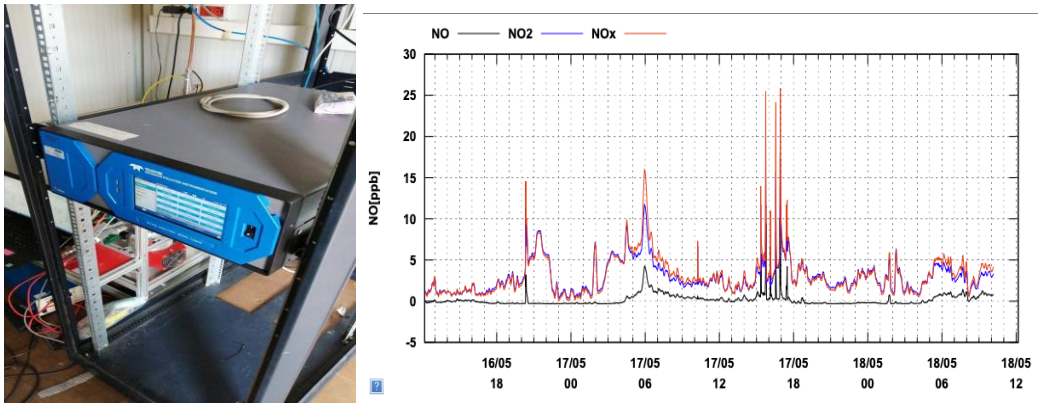

***Figure 6**: Left panel: NO_x chemiluminescence analyser inside the shelter. Right panel: example of measured NO_x, NO_2, NO data.*

3.2.2 In-situ vs remote sensing measurements

We report here the comparison between in-situ and TROPOGAS NO_2 focusing on the period from 1st May to 2nd June 2021.

The comparison between retrieved NO_2 VCDs and in-situ "near-surface" NO_2 is obviously not straightforward. However, aiming at understanding if the behaviour of surface data is similar to the one of VCDs total column, a comparison was made. Results are reported in Fig. 7 where we plot in blue the in-situ at surface NO_2 in ppb and in red the Total column NO_2 VCD retrieved from TROPOGAS zenith sky measurements as reported in section 3.1.3 scaled to be consistent with ppb values. As can be noticed, no correlation can be observed between total column and surface concentration. This result is not unexpected: the total column values are representative of both stratospheric and tropospheric behaviour, while "near-surface" observations are representative of the NO_2 variability within the PBL.

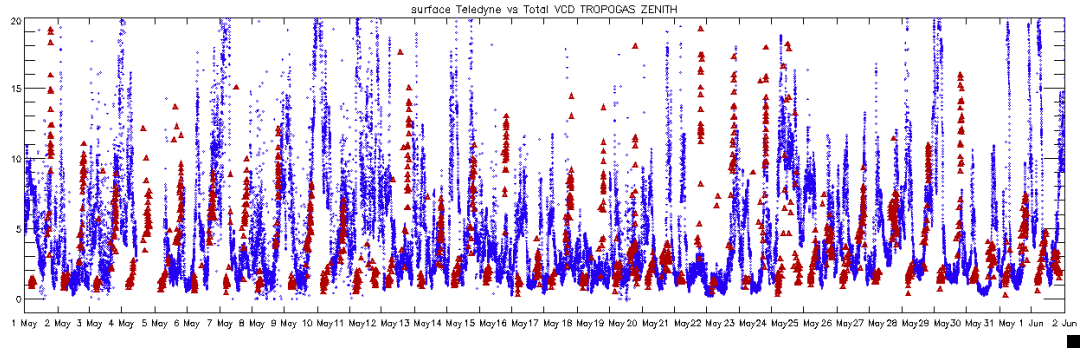

***Figure 7**: Comparison between NO_2 "near-surface" (blue) and TROPOGAS Total Column VCD (dark red) from zenith sky measurements.*

The algorithm developed as described in section 3.1.4 has been applied to the TROPOGAS MAX-DOAS measurements to retrieve NO_2 profiles from 0 to 4 km in the mentioned period. Results are reported in Fig. 8. The NO_2 was quite low in the first days of May (1-4 May), while higher values were reached on 5-7 and 11 May. On 11th May, the NO_2 values retrieved in the bottom part of the profile tends to be higher in the second part of the day in contrast with what happens in previous days.

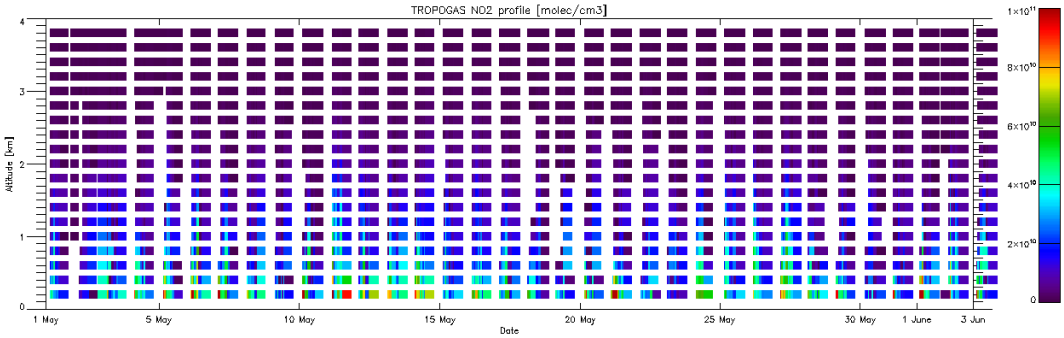

***Figure 8**: NO_2 profiles retrieved from TROPOGAS MAX-DOAS measurements.*

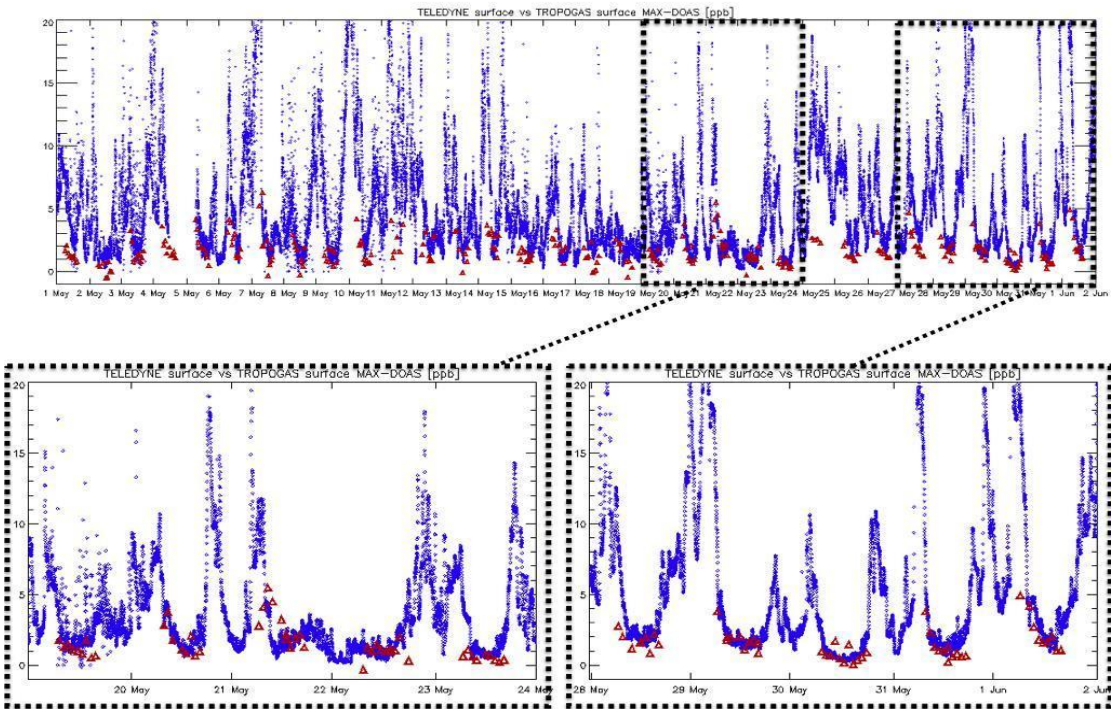

***Figure 9**: Comparison between NO_2 in situ (blue) and TROPOGAS at the last point of the retrieved profiles (dark red) obtained from MAX-DOAS measurements.*

The last point of the retrieved profiles can be used for a direct comparison with "near-surface" measurements. We recall here that due to the nature of remote sensing measurements and to the instrumental FOV, the values of the profile retrieved near the surface are somehow influenced by the NO_2 in the upper levels (as described by the Averaging Kernel Matrix (AKM) matrix, see Appendix A). In addition, the NO_2 retrieved profiles were obtained with a retrieval algorithm that does not retrieve the aerosol extinction but uses a fixed profile (see section 3.1.4). If the observed scenario deviates too much from these simulated conditions, biases on NO_2 profiles will be obtained.

The results of the comparison are reported in Fig. 9. In this plot, the red triangles are NO_2 concentration at the surface in ppbv retrieved from TROPOGAS. As can be seen, the comparison with "near-surface" NO_2, both in terms of absolute values and behaviour, is generally good. In particular, this is true at the end of the considered period when more clear sky conditions are found (see radiance enhancement in Fig. 1) as can be seen from the two zooms in Fig. 9.

This comparison is really promising and highlights the potential of MAX-DOAS measurements also for surface NO_2 determination.

3.3 WP 2251-2.3: Exploitation of the satellite-borne synergies

Due to its legacy, together with its high spectral and spatio-temporal resolution, the TROPOspheric Monitoring Instrument (TROPOMI) on Sentinel 5-P represents the best

choice for the inter-comparison of TROPOGAS products with respect to satellite-borne instruments.

The main objective of the Copernicus Sentinel-5P mission is to perform atmospheric measurements, to be used for air quality, ozone & UltraViolet (UV) radiation, and climate monitoring & forecasting. The Sentinel 5-P satellite was launched on the 13th of October 2017 with a local time of ascending node crossing of 13.30 h. For our inter-comparison purposes, we used the TROPOMI OFFL data product [http://doi.org/10.5270/S5P-s4ljg54], available in netCDF format. This task was performed using the Copernicus Data Hub, from https://s5phub.copernicus.eu/dhus, with the help of a bash script that exploits the capability of the 'open data protocol' interface for accessing the Earth Observation (EO) data stored on the archive. These products contain the NO_2 VCD, derived using the DOAS method applied to the measurements within the 405–465 nm wavelength range. Since earth radiance measurements are performed only on the dayside of the orbit, only one satellite overpass per day is available for comparison (at 13:30 local time).

We defined a specific criterion to select only the satellite pixels located within a certain radius around the position of the site. The threshold of 20 km has been defined to produce a robust analysis, considering the available satellite pixels/day in a homogeneous scene but at the same time include enough data.

This criterion leads to the selection of a maximum number of 52 pixels before the 6th of August 2019, as the ground pixel size was 7 km × 3.5 km, and 64 pixels afterwards, as the along-track pixel size has been reduced from 7 km to 5.5 km.

Furthermore, only NO_2 values with an associated quality assurance value higher than a certain threshold have been considered to select good quality retrievals and, at the same time, filter out errors and problematic retrievals.

Fig. 10 gives an example of TROPOMI NO_2 Total Column VCD data for the 24th of February 2020. The grey circle evidences the considered satellite measurements within a 20 km radius around the ISAC-CNR site in Bologna.

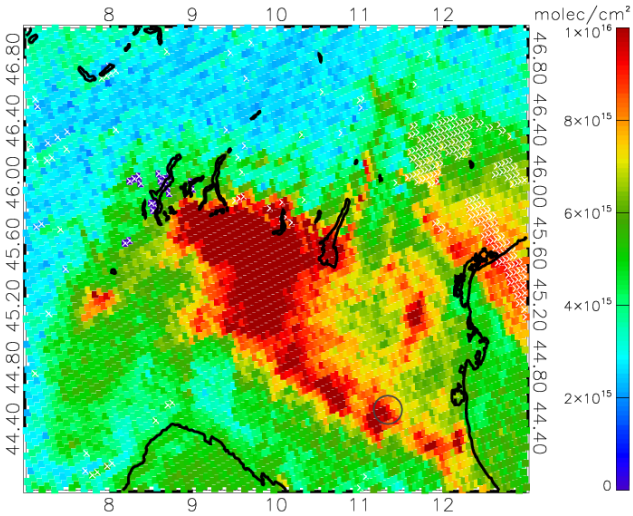

***Figure 10**: TROPOMI NO_2 Total column retrieval for the 24th of February 2020. Data inside the grey circle (20 km radius around the ISAC-CNR site in Bologna) are used for comparison with TROPOGAS data.*

The results of the comparison between the daily mean of the TROPOGAS NO_2 Total VCDs (acquired between 12 h and 16 h) and the daily mean of the coincident TROPOMI VCDs are reported in Fig. 11. For this exercise, we used the TROPOGAS data acquired during the daytime (SZA between 70° and 80° and the acquisition time between 11 and 15). Actually, for SZA angles higher than 80°, due to photochemistry, NO_2 VCDs start to increase. Since the TROPOMI overpass is around 13:30 h local time (full daytime), the comparison is meaningful if similar photochemical conditions are present. During the daytime, NO_2 concentration tends to be quite constant. In addition, due to measurement geometry, ground-based zenith sky measurements are more sensitive to NO_2 stratospheric concentrations. This consideration is particularly true for twilight measurements. Measurements for SZA < 80° enhance the tropospheric contribution and thus are more representative of the total column. For these reasons, we used only VCDs with SZA < 80°. To gain sensitivity, we used measurements with SZA > 70°. Measurements acquired with lower SZA have lower contrast with respect to the reference spectra, thus enhancing the noise contribution on retrieved VCDs. Analogous results are given in Fig. 13 for O_3. A general good agreement can be observed between the satellite and ground-based datasets for NO_2 with an average bias of -0.02 +/- 0.04 D.U. (-12 +/- 20%) for O_4 unfiltered VCDs and -0.01 +/- 0.04 D.U. (-6 +/- 20%) for filtered ones (Fig.s 12 and 14). These values are slightly lower than the -29% found at ISAC-ROME with Pandora instruments [R - 5].

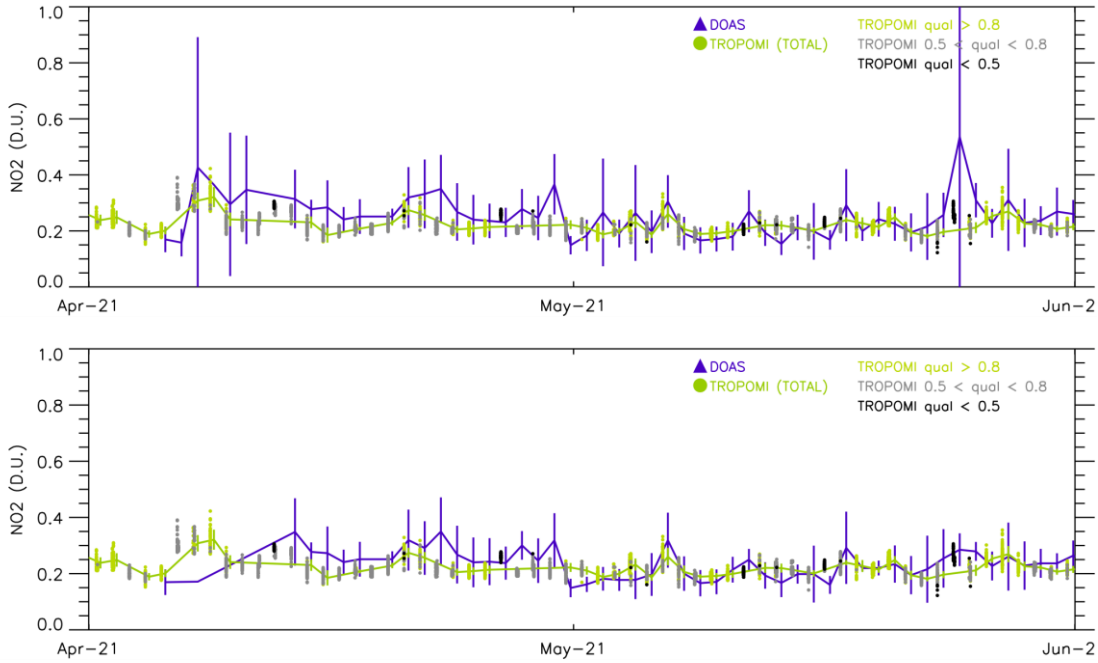

***Figure 11**: Upper panel: Daily mean of the TROPOGAS (blue) NO_2 Total column VCD and daily mean of the coincident TROPOMI (green) NO_2 Total Column VCD before O_4 filtering. Standard deviations are also reported. We also reported the observations with the quality flag within 0.5 and 0.8 (grey dots) and lower than 0.5 (black dots). Black dots are used as a proxy for cloud presence that could also affect TROPOGAS observations. Lower panel: As for the upper plot but after O_4 filtering. See text for details.*

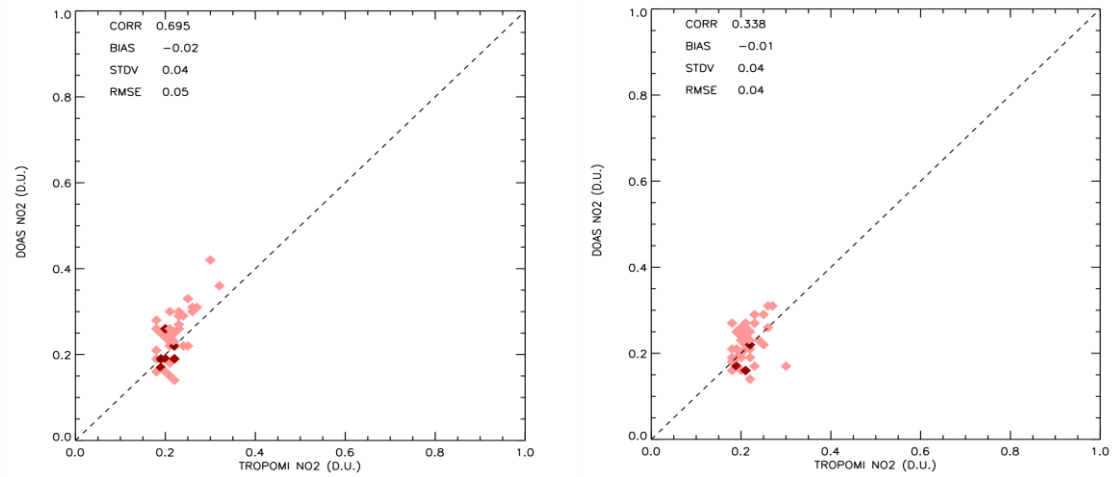

***Figure 12**: Left panel: TROPOGAS NO_2 Total column VCDs before O_4 filtering vs coincident TROPOMI NO_2 Total Column (quality flag > 0.8). Right panel: same results using TROPOGAS VCD after O_4 filtering. See text for details.*

As can be seen, the O_4 filtering procedure removes data with high standard deviations. For ozone, we obtain a bias of 2 +/- 31% for unfiltered data and 13 +/- 15% for filtered ones. These values are higher than those from the Brewer, Dobson and NDACC ZSL-DOAS/SAOZ TROPOMI O_3 validation. This is due to the fact that here we present only O_3 retrievals from the visible channel. Better results should be obtained by exploiting the UV channel.

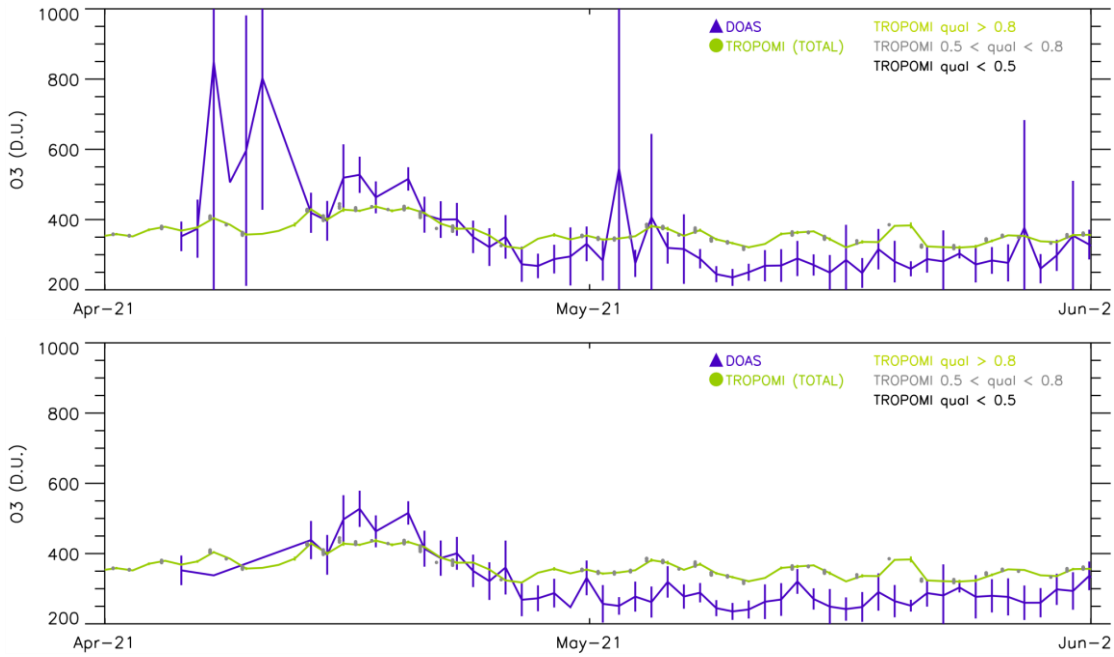

***Figure 13**: As in Fig. 11 but for O_3.*

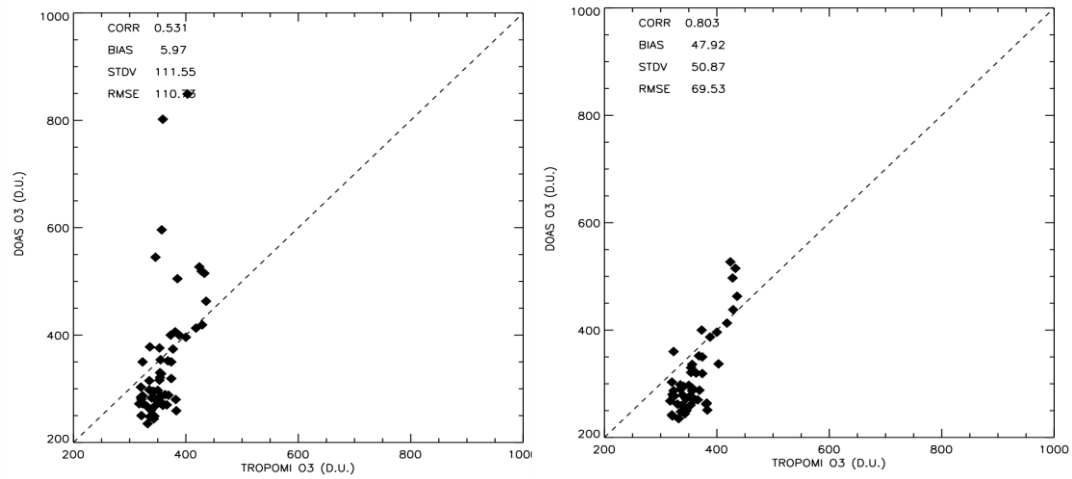

***Figure 14**: As in Fig. 12 but for O_3.*

TROPOMI provides not only the Total Column VCD but also the stratospheric and tropospheric VCDs. In particular, the tropospheric VCD is a widely used product (e.g. it has been used to investigate NO_2 reduction in the lockdown period due to Covid-19).

The validation of TROPOMI tropospheric VCD is routinely made using MAX-DOAS measurements from the FRM4DOAS network. In our case, we can compare the tropospheric TROPOMI NO_2 VCDs with the tropospheric VCDs by TROPOGAS calculated by integrating the profiles on the altitude range from 0 to 4 km.

An excerpt of this routine validation is shown in Fig.s 15 and 16. In Fig. 15, we plotted the TROPOGAS NO_2 tropospheric column VCDs and the coincident TROPOMI NO_2 tropospheric column VCDs retrieved in the period from 1st May to 2nd June 2021. In Fig. 16, we reported the same analysis considering the daily means of the tropospheric columns. We observed a generally good agreement. As noticed in other validation activities [R - 9], TROPOMI Tropospheric VCDs are lower than ground-based VCDs, -33% in our case.

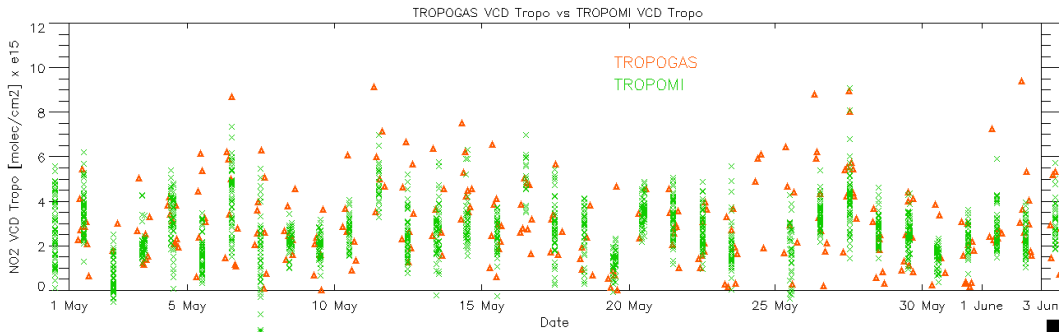

***Figure 15**: TROPOGAS NO_2 tropospheric column VCDs (orange triangles) and coincident TROPOMI NO_2 tropospheric column VCDs (green crosses).*

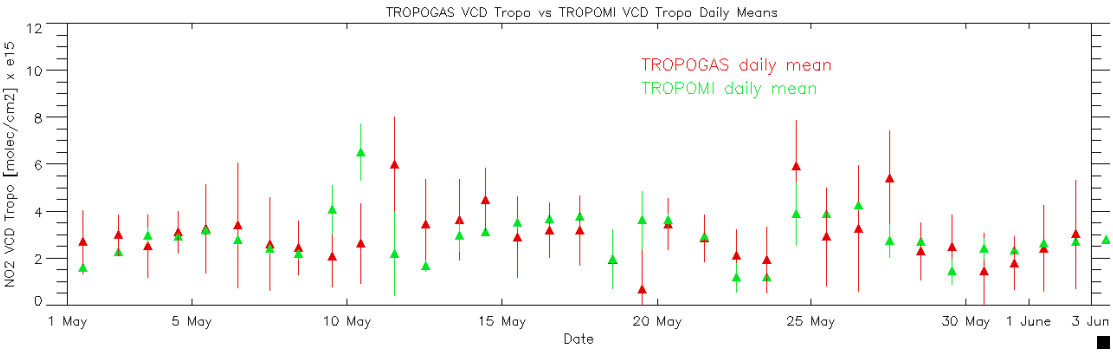

***Figure 16**: Daily mean of the TROPOGAS NO_2 tropospheric column VCDs (red triangles) and daily mean of the coincident TROPOMI NO_2 tropospheric column VCDs (green triangles). The standard deviations are also reported.*

4 Conclusions

We reported the results obtained from the TROPOGAS spectrometer during the measurement campaign held in Bologna at ISAC premises in Spring 2021.

In the frame of this campaign, we updated the TROPOGAS measurement configuration in order to follow the FRM4DOAS requirements. Furthermore, according to these requirements, the measured spectra will be delivered in netCDF FRM4DOAS format [D - 2A].

The zenith sky spectra were analysed with the QDOAS software to retrieve NO_2, O_3 and O_4 SCDs. Then, after a cloud filtering based on the O_4 SCDs, we calculated the VCDs exploiting the NDACC AMF.

MAX-DOAS spectra recorded at different elevation angles between 1° and 30° have been processed in the same way with the QDOAS software to obtain SCDs. Then, a roughly approximated algorithm for the NO_2 profile retrieval only has been developed, exploiting SCIATRAN for BOX-AMF calculations.

Total column VCDs retrieved from zenith sky spectra were compared with collocated TROPOMI data for NO_2 and O_3. We observed a good agreement for NO_2, with a negative bias (TROPOMI minus TROPOGAS) of -6+/-20% for the whole period. This value is slightly higher than the -29% found at ISAC-Rome with Pandora instruments [R - 9].

A similar comparison was performed considering the tropospheric VCDs. In this case, the NO_2 TROPOGAS tropospheric VCDs are calculated from NO_2 profiles retrieved exploiting MAX-DOAS measurements. These VCDs agree pretty well with collocated TROPOMI data for NO_2. We found a negative bias for TROPOMI of the order of -33%, relatively consistent with validation studies from the FRM4DOAS network [R - 9].

The TROPOGAS total NO_2 VCDs and last point of the NO_2 retrieved profiles were compared with in-situ data measured by an ACTRIS compliant NO_X chemiluminescence analyser. While the behaviour of total column VCDs, as expected, do not show any correlations with in-situ data, good agreement is found with the values retrieved at the surface. This result is auspicious.

Ground-based remote sensing measurements act as a trade union between in-situ surface measurements and satellite measurements. Satellite measurements have a high spatial resolution and low temporal resolution. On the contrary, in situ measurements have low spatial resolution and high temporal resolutions. Ground-based MAX - DOAS measurements have spatial resolutions of a few km around the stations and a medium temporal resolution. Due to their characteristics, these measurements can be used in regional-scale air quality models, as shown in [R - 10]. Up to now, no TROPOMI NO_2 profiles are available. Thus, a direct validation of satellite products with in-situ measurements is not possible. Nevertheless, in-situ data can be used as ancillary data, e.g. constraining the at surface values, e.g. for profile a-priori initial guess of remote sensing data, improving the knowledge on diurnal variability. At the same time, even if the FRM4DOAS network foresees a centralized processing of MAX - DOAS spectra, it would be highly desirable to have a fully developed and validated (using FRM4DOAS requirements) profile retrieval code. This tool could be developed starting from the code used in this work.
Moreover, this code will allow the full exploitation of a unique set of continuous MAX-DOAS measurements in the Po Valley (more than two years, from 2019 onwards), opening up to the possibility of validating TROPOMI products in the pre-and Covid-19 periods.

5 References

[D-1] D-1 Report on TROPOGAS compliance/difference with FRM4DOAS requirements, Version 1.0, 18/02/2021

[R-1] FRM4DOAS Instrument Operation and Calibration Guidelines, Date: 16/03/2018 Version: 1.1, ESA Contract No. 4000118181/16/I-EF

[R-2] Chance K.V., Spurr R.J.D., "Ring effect studies: Rayleigh scattering, including molecular parameters for Rotational Raman scattering and the Fraunhofer spectrum"

[R-3] Aliwell, S., Van Roozendael, M., Johnston, P., Richter, A., Wagner, T., Arlander, D. W., Burrows, J. P., Fish, D. J., Jones, R. L., Tørnkvist, K. K., Lambert, J.-C., Pfeilsticker, K., and Pundt, I. (2002). Analysis for BrO in zenith-sky spectra: An intercomparison exercise for analysis improvement. Journal of Geophysical Research, 107(D14).

[R-4] Rozanov, V.V, Buchwitz, M., Eichmann, K., U., R. de Beek, Burrows, J.P., Sciatran - a new radiative transfer model for geophysical applications in the 240–2400 nm spectral region: the pseudo-spherical version, Advances in Space Research, Volume 29, Issue 11, 2002, Pages 1831-1835, ISSN 0273-1177,https://doi.org/10.1016/S0273-1177(02)00095-9.

[R-5] Spinei, E., Cede, A., Herman, J., Mount, G. H., Eloranta, E., Morley, B., Baidar, S., Dix, B., Ortega, I., Koenig, T., and Volkamer, R.: Ground-based direct-sun DOAS and airborne MAX-DOAS measurements of the collision-induced oxygen complex, O_2O_2, absorption with significant pressure and temperature differences, Atmos. Meas. Tech., 8, 793–809, https://doi.org/10.5194/amt-8-793-2015, 2015.

[R-6] Herman J., Cede A., Spinei E., Mount G., Tzortziou M., Abuhassan N.: NO2 column amounts from ground-based Pandora and MFDOAS spectrometers using the direct-sun DOAS technique: Intercomparisons and application to OMI validation, Date: 15/07/2009, Journal of Geophysical Research: Atmospheres, Volume 114, https://doi.org/10.1029/2009JD011848.

[R-7] Bösch, T., Rozanov, V., Richter, A., Peters, E., Rozanov, A., Wittrock, F., Merlaud, A., Lampel, J., Schmitt, S., de Haij, M., Berkhout, S., Henzing, B., Apituley, A., den Hoed, M., Vonk, J., Tiefengraber, M., Müller, M., and Burrows, J. P.: BOREAS – a new MAX-DOAS profile retrieval algorithm for aerosols and trace gases, Atmos. Meas. Tech., 11, 6833–6859, https://doi.org/10.5194/amt-11-6833-2018, 2018.

[R-8] Frieß, U., Beirle, S., Alvarado Bonilla, L., Bösch, T., Friedrich, M. M., Hendrick, F., Piters, A., Richter, A., van Roozendael, M., Rozanov, V. V., Spinei, E., Tirpitz, J.-L., Vlemmix, T., Wagner, T., and Wang, Y.: Intercomparison of MAX-DOAS vertical profile retrieval algorithms: studies using synthetic data, Atmos. Meas. Tech., 12, 2155–2181, https://doi.org/10.5194/amt-12-2155-2019, 2019.

[R-9] Verhoelst, T., Compernolle, S., Pinardi, G., Lambert, J.-C., Eskes, H. J., Eichmann, K.-U., Fjæraa, A. M., Granville, J., Niemeijer, S., Cede, A., Tiefengraber, M., Hendrick, F., Pazmiño, A., Bais, A., Bazureau, A., Boersma, K. F., Bognar, K., Dehn, A., Donner, S., Elokhov, A., Gebetsberger, M., Goutail, F., Grutter de la Mora, M., Gruzdev, A., Gratsea, M., Hansen, G. H., Irie, H., Jepsen, N., Kanaya, Y., Karagkiozidis, D., Kivi, R., Kreher, K., Levelt, P. F., Liu, C., Müller, M., Navarro Comas, M., Piters, A. J. M., Pommereau, J.-P., Portafaix, T., Prados-Roman, C., Puentedura, O., Querel, R., Remmers, J., Richter, A., Rimmer, J., Rivera Cárdenas, C., Saavedra de Miguel, L., Sinyakov, V. P., Stremme, W., Strong, K., Van Roozendael, M., Veefkind, J. P., Wagner, T., Wittrock, F., Yela González, M., and Zehner, C.: Ground-based validation of the Copernicus Sentinel-5P TROPOMI NO_2 measurements with the NDACC ZSL-DOAS, MAX-DOAS and Pandonia global networks, Atmos. Meas. Tech., 14, 481–510, https://doi.org/10.5194/amt-14-481-2021, 2021.

[R-10] Blechschmidt, A.-M., Arteta, J., Coman, A., Curier, L., Eskes, H., Foret, G., Gielen, C., Hendrick, F., Marécal, V., Meleux, F., Parmentier, J., Peters, E., Pinardi, G., Piters, A. J. M., Plu, M., Richter, A., Segers, A., Sofiev, M., Valdebenito, Á. M., Van Roozendael, M., Vira, J., Vlemmix, T., and Burrows, J. P.: Comparison of tropospheric NO2 columns from MAX-DOAS retrievals and regional air quality model simulations, Atmos. Chem. Phys., 20, 2795–2823, https://doi.org/10.5194/acp-20-2795-2020, 2020.

[R-11] Gilge et al. (2014). Deliverable WP4 / D4.10 (M42) Version: 2014/09/19 WP4-NA4: Trace gases networking: Volatile organic carbon and nitrogen oxides Deliverable D4.10: Standardized operating procedures (SOPs) for NO_{xy} measurements.

[R-12] Wagner, T., B. Dix, C. v. Friedeburg, U. Frieß, S. Sanghavi, R. Sinreich, and U. Platt (2004), MAX-DOAS O_4 measurements: A new technique to derive information on atmospheric aerosols—Principles and information content, J. Geophys. Res.,109, D22205, doi:10.1029/2004JD004904.

[RA-1] MAX-DOAS Calibration and Operations Best Practices, Date: 10/01/2018 Version: 1.0, ESA Contract No. 4000118181/16/I-EF

[RB-1] Donner, S., Kuhn, J., Van Roozendael, M., Bais, A., Beirle, S., Bösch, T., Bognar, K., Bruchkouski, I., Chan, K. L., Dörner, S., Drosoglou, T., Fayt, C., Frieß, U., Hendrick, F., Hermans, C., Jin, J., Li, A., Ma, J., Peters, E., Pinardi, G., Richter, A., Schreier, S. F., Seyler, A., Strong, K., Tirpitz, J.-L., Wang, Y., Xie, P., Xu, J., Zhao, X., and Wagner, T.: Evaluating different methods for elevation calibration of MAX-DOAS (Multi AXis Differential Optical Absorption Spectroscopy) instruments during the CINDI-2 campaign, Atmos. Meas. Tech., 13, 685–712, https://doi.org/10.5194/amt-13-685-2020, 2020.

6 Appendix A: Evaluation of FOV aperture impact on profiles retrievals

As reported in the [D - 1] document, the FOV aperture is the only FRM4DOAS requirement [R - 1], [RA - 1] not reached by the TROPOGAS spectrometer. The required value is 1.5 °, while the TROPOGAS FOV aperture is estimated at 3.5 °.
To assess the impact of this aperture on retrieved profiles, we used the SCIATRAN Forward Model simulations. The FOV amplitude impacts off-axis measurements used for profile retrievals, while a negligible effect is present on zenith sky simulations.
For this test, we evaluated the impact on NO_2 retrievals only. Similar considerations should apply to HCHO retrieval.
We simulated NO_2 BOX-AMF measured at 1°, 2°, 3°, 5° 10° and 30 ° elevations (minimal required FOV elevations from FRM4DOAS requirements [R - 1], [RA - 1]).
For these simulations, we used 60m as an instrument elevation a.s.l. and NO_2 profiles for summer at 45 N latitude degrees. The SZA was 40° while the azimuth was 0°.
We used two different BOX-Car FOV for this test (simulated with 5 line of sight, LOS), one with a 1.5 ° aperture and one with 3.5 °. The results of these simulations are reported in Fig. A1.

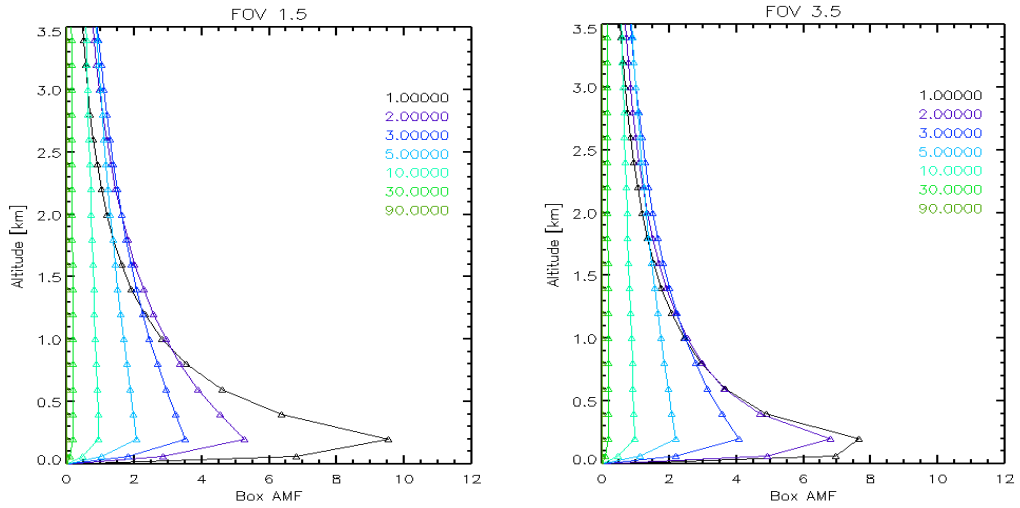

***Figure A1**: NO_2 BOX AMF for 1, 2, 3, 5, 10, 30 and 90° elevation with 1.5°, 3.5 ° FOV aperture.*

As can be seen, increasing the FOV aperture results in different contributions of SCDs measured at low elevations (1° and 2° elevation mainly, 3° in a minor way) while it has almost no effect on higher elevation angles from 5° to 90°.
In order to directly evaluate the impact on NO_2 profile retrievals, we calculate the AKM for NO_2. As a-priori NO_2 profiles and errors we used the one given in the retrieval algorithm intercomparison exercise performed in the frame of FRM4DOAS activities [R - 3].
We used 50% a priori error and a NO_2 a priori profile that has a value of $2e^{+11}$ mol/cm^2 at the surface and that decreases exponentially with eight. The correlation length of the a-priori matrix is 0.2 km. The dSCDs noise value is $5e^{+14}$ mol/cm^2 for NO_2. The used retrieval grid is composed of one point every 0.2 km from 0 to 3.5 km.
Then we applied the formula (as in [R - 4]):

$$AKM = S_a K^T (K S_a K^T + S_y)^{-1} K \qquad [A1]$$

Where S_a is the a-priori covariance matrix, K is the BOX-AMF matrix, S_y is the DSCD covariance matrix. The resulting AKM for the two cases mentioned above are reported in Fig. A2.

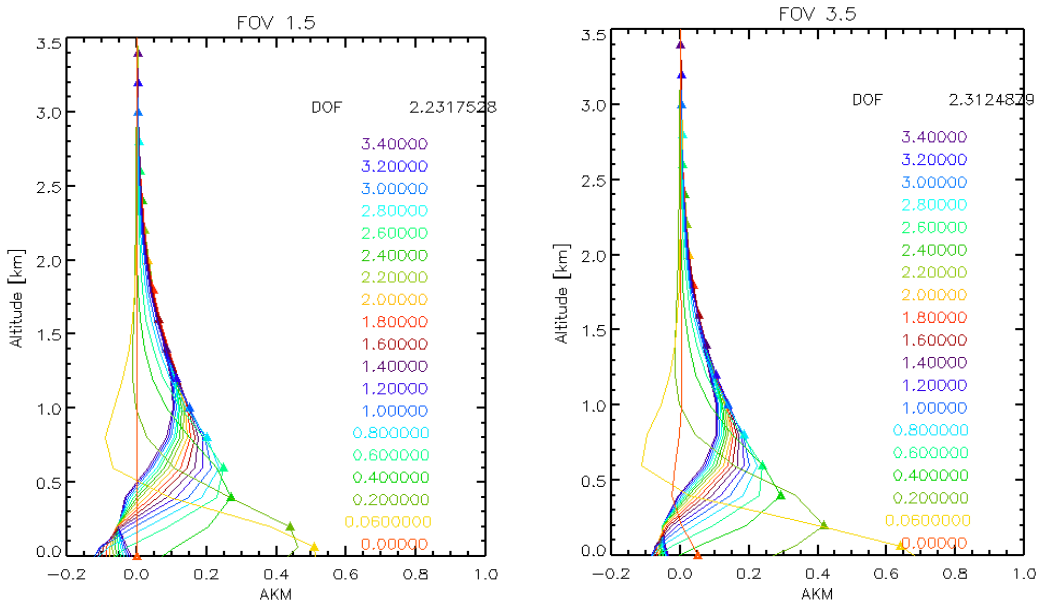

***Figure A2**: AKM matrix for NO_2 retrievals calculated with 1. 5°, 3.5 ° FOV aperture. Degree of freedom (DOF) calculated as TRACE of AKM matrix.*

As can be seen from these Fig.s the highest impact is obtained for retrieval altitudes below 0.6 km, in particular at 0.2 and 0.4 km retrieval altitudes. However, the difference between 1.5° and 3.5° FOV is not critical and will possibly just result in a slightly larger FWHM at these levels for 3.5° FOV. Only a few differences in the computed AKM are present below 0.6km, possibly just resulting in a slightly different vertical resolution of the obtained profiles. Possibly this test can be repeated for aerosol extinction retrievals, if a complete profile retrieval code is developed.

7 Appendix B: TROPOGAS elevation calibration

Elevation calibration is an important source of error in MAX-DOAS profile retrieval. For this reason, different techniques to accurately evaluate the pointing of MAX-DOAS instruments have been developed [RB - 1]. Among these methods we can find the horizon scan methods (used in [D - 1]), the near- and far-lamp measurements or the white stripe scan. On the 24th of May, we performed an elevation scan calibration exploiting this last method. The white-stripe method can also be applied under daylight conditions and a white or at least bright stripe in front of a black or dark background is used as a reference target. In order to perform the pointing calibration, the true elevation angle corresponding to the centre of the white stripe, measured by the instrument, has to be known. From trigonometric considerations, exploiting length measurements, we estimated that the true elevation angle is 2.9°. These measurements were performed over the roof of the ISAC institute. As black plate we use an Ikea blackboard designed for children (MALA product https://www.ikea.com/it/it/p/mala-cavalletto-da-pittore-legno-dolce-bianco-50021076/) elevated at the right altitude through the use of bricks (see Fig. B1).

Figure B1*: Left: Mala blackboard used for the white stripe elevation test (front view). Right: Mala blackboard used for the white stripe elevation test (back view) the Scanning Optical Device Collecting Atmospheric Light (SODCAL) platform can be seen in the background.*

Fig. B2 shows the signal intensity (blue dots) measured at different elevation angles. The behavior is similar to a Gaussian curve because the signal is low at the beginning, when the blackboard is in the instrument FOV, it increases when TROPOGAS measures the white stripe and it decreases again when the instrument starts to detect the blackboard again. Data are fitted by a Gaussian curve (red curve) with the center located around 4°. This value represents the elevation angle of the white stripe according to the TROPOGAS measurements. It means that the zenith angles relative

to the scans acquired in the same direction of this calibration (towards the Po Valley) must be reduced to 1.1°, while zenith angles in the opposite direction (towards the city) must be increased to 1.1°.

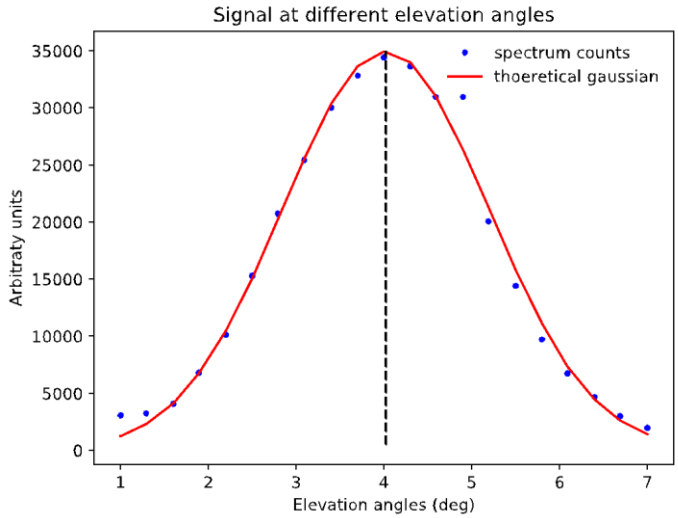

***Figure B2**: Intensity of the spectra, measured in arbitrary units, with respect to different elevation angles (blue dots). The red line is the Gaussian curve used to fit the data. The center of the curve represents the elevation angle relative to the white stripe, according to TROPOGAS.*